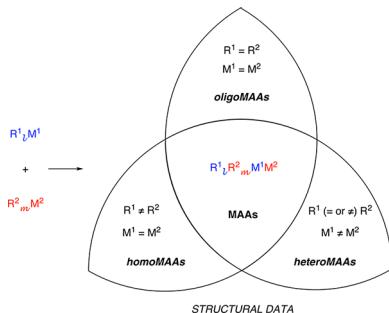


Mixed AggregAte (MAA): A Single Concept for All Dipolar Organometallic Aggregates. 1. Structural Data

Anne Harrison-Marchand*,† and Florence Mongin*,‡

†Laboratoire COBRA de l'Université de Rouen, INSA de Rouen, CNRS, UMR 6014 & FR 3038, IRCOF, Rue Tesnière, 76821 Mont St Aignan Cedex, France

‡Équipe Chimie et Photonique Moléculaires, Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Bâtiment 10A, case 1003, Avenue du Général Leclerc, 35042 Rennes Cedex, France



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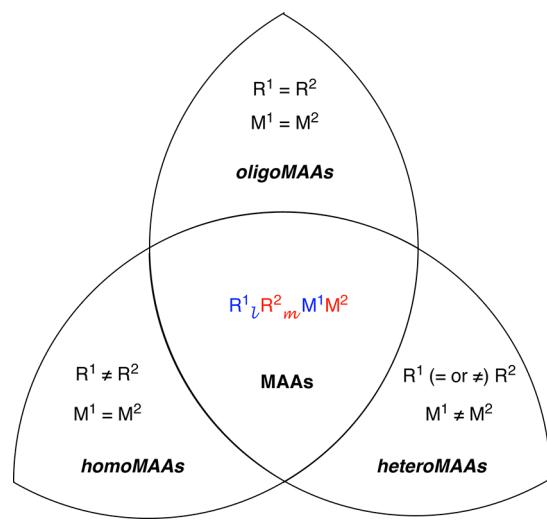
1. INTRODUCTION

Organometallic chemistry is one of the key assets to successfully achieve complex organic transformations. Numerous tools have been conceived and developed to address problems related to the chemo-, regio-, and stereoselectivities of general reactions such as the deprotonation of prochiral species (epoxides, aziridines, cyclic ketones) or the creation of C–C bonds. Mixing two organometallic reagents (R^1M^1 and $R^2_mM^2$) can lead to a new species ($R^1R^2_mM^1M^2$, Scheme 1) that benefits from a synergy with properties distinct from those of each component. The “ate complexes¹”, the “mixed aggregates²” or complexes³”, and the uni- and heterobimetallic superbases (USB⁴ and Schlosser–Lochmann superbases,⁵ respectively) figure among the most representative of such mixed entities, which all result from dipolar interactions between single organometallic parent-partners from the “top” of the Mendeleev classification (periods 2–4). Actually, the capacity for the latter to establish dipolar links is observed even when considered by themselves, aggregating as oligomers instead of staying in a monomeric form ($[R^1M^1]_x$ and $[R^2_mM^2]_y$).⁶ Such a dipole–dipole aggregation phenomenon, common to single and mixed organometallic reactants and that led to the establishment, by Snaith and co-workers, of the “ring stacking” and “ring laddering” general principles,⁷ prompted us to examine those species as a sole class of reagents, which we suggest naming “Mixed AggregAteS” or MAAs. Note that this

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Scheme 1. The Three Categories of MAA Obtained Mixing Two Organometallics ($R^1 \mu M^1$ and $R^2 \mu M^2$)



acronym aims to gather the three key terms in the field—*aggregation*, *mixed*, and *ate*—meeting the principle of dipole–dipole interaction, without seeking to form a neologism that would suggest wrongly that the oligomers, the mixed aggregates, the superbases, and the ate complexes have similar physical and chemical properties.

In the proposed concept, three categories of MAA emerge: (i) the “oligoMAAs” made of a sole type of metal and a sole type of anion (the case of single dipolar organometallic oligomers), (ii) the “homoMAAs” made of a sole type of metal also but combining distinct anionic appendages (the case of mixed aggregates, USBs), and (iii) the “heteroMAAs”, for which at least two dissimilar metals are involved (the case of ate complexes, Schlosser–Lochmann superbases). Although oligoMAAs are different in term of composition from the homo- or heteroMAAs, since they engage only one organometallic species (they are not fundamentally “mixed” species), their ability to homoaggregate and the difference of reactivity observed when changing the size of the related oligomers make them fully part of the notion of MAA.

By way of announcement of the concept, it was decided to dedicate this preliminary review (part 1) on the structural knowledge, in the solid state and/or in solution, of oligo-, homo-, and heteroMAAs that are made of lithium, sodium, and potassium species, as well as magnesium, aluminum, and zinc derivatives. With the latter selection covering still a large panel of organo(bi)metallic combinations depicted in the literature, only systems that are the most encountered and discussed by organic chemists and that are either obtained directly by mixing two commercial organometallics routinely used in organic chemistry or very frequently synthesized and easy to access will be depicted. As an ultimate limitation, this review will focus on structures of organo(bi)metallic species for which the ligands mainly realize nucleophilic transfers for addition or deprotonation purposes. Such reactivities are actually detailed in the companion review, “Mixed Aggregate (MAA): A Single Concept for All Dipolar Organometallic Aggregates. 2. Syntheses and Reactivities of Homo/HeteroMAAs” (doi: 10.1021/cr3002966; the following paper in this issue), which deals with nucleophilic and basic reactivity of homo- and heteroMAAs. The main goal of part 1 being to help the organic chemist to quickly respond to the basic question, *what is the*

state of aggregation of this MAA in the solid state and/or in solution in a selected solvent?, structural data will be collected in tables as much as possible. Note that, in spite of the fact that structure/reactivity relationships will be rather revealed in part 2, general conclusions have been drawn at the level of this paper, however, without discussing in detail the features of the possible evolutions of the depicted arrangements (i.e., fluxional, inter- and intrametallic exchanges, etc.). The sheer number of compounds that the paper gets through implied that neither structure nor bonding/reactivity issues could be considered in any great depth in a sole paper. Note at last that theoretical considerations (static and dynamic calculations) will be little mentioned. However, the authors want to underline the numerous studies devoted to this domain that are helpful and essential for a complementary understanding of the chemical reactivity of the organometallics. They invite the readers to consult reviews by Schleyer and co-workers,⁸ Pratt and Khan,⁹ Rayez and co-workers,¹⁰ and Jemmis and Gopakumar.¹¹

2. OligoMAAs

Dipolar organometallic species tend to form oligomers $[R_xM]_x$ in which “ x ” represents the degree of oligomerization and is dependent on the solvent, the concentration, the anionic moiety, and the temperature. According to the size of the arrangements, the reactivity can fluctuate and, thus, orientate the chemists in the choice of their reaction conditions. Having a good knowledge of the structures of the oligoMAAs is thus fundamental to better anticipate and understand their behavior when reacting by themselves or mixing them with other organometallics. This aggregation phenomenon has been the object of several reviews.^{8,7} The objective here is to gather and actualize structural knowledge about the oligomerization states known for the most commonly encountered organolithium, -sodium, -potassium, -magnesium, -aluminum, and -zinc compounds that are actually also the most often engaged in the homo- and heteroMAAs depicted afterward.

2.1. Lithium Compounds

Lithium compounds are certainly the most used reactants in organic synthesis, and this explains why they have been the object of the most numerous physical studies. The following itemizes the crystallographic structures (PXRD data and single-crystal X-ray determinations) and those in solution known for the most encountered lithio reactants.

2.1.1. Organolithiums (C–Li). **2.1.1.1. Alkylolithiums ($C^{sp^3}-Li$).** Results are presented for MeLi, EtLi, PrLi, i-PrLi, BuLi, i-BuLi, s-BuLi, t-BuLi, c-HexLi, Me_3SiCH_2Li , $(Me_3Si)_2CHLi$, and $(Me_3Si)_3CLi$.

2.1.1.1.1. Crystallographic Structures (Table 1). The earliest significant X-ray diagrams of alkylolithiums were obtained in the sixties¹² from ethyllithium¹³ and methylolithium¹⁴ samples isolated in the solid state from benzene solution or after pyrolysis. Both alkylolithiums presented a cubic tetrameric unit, part of an unsolvated three-dimensional polymeric structure. In the two lattices of general formula $\{[MeLi]_4\}_\infty$ (Table 1, entry 1a) and $\{[EtLi]_4\}_\infty$ (Table 1, entry 2), respectively, the cubes were found to be linked to each other thanks to R–Li interactions (R = Me or Et) between vertices. Note that there is a significant distortion of the $[EtLi]_4$ cube assigned to the lower symmetry of the ethyl groups. By contrast, the X-ray structure obtained from crystals of methylolithium grown in cumene/THF solution highlighted a nonpolymeric but tetrasolvated cubic tetrameric arrangement $[MeLi]_4 \cdot 4THF$ (Table 1, entry 1b).^{14d}

Table 1. Crystallographic Structures of $C_mH_{2m+1}Li$ ($m = 1-4$) Alkyllithium Derivatives, *c*-HexLi, and Trimethylsilylmethylolithium Species

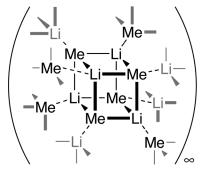
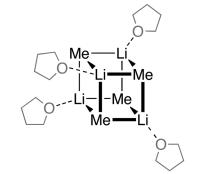
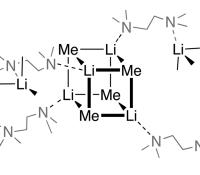
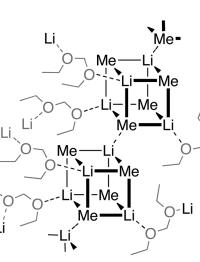
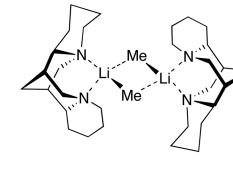
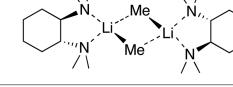
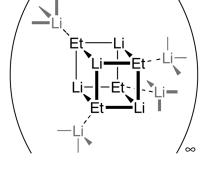
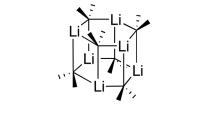
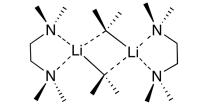
Entry	AlkLi	Solvation	Structure	Ref
1a	MeLi	none (after pyrolysis)	$\{[MeLi]_4\}_\infty$: 	14a,b
1b		THF (grown in cumene/THF)	$[MeLi]_4 \cdot 4\text{THF}$: 	14d
1c		TMEDA 1 equivalent (grown in Et ₂ O)	$\{[MeLi]_4 \cdot 2\text{TMEDA}\}_\infty$: 	14c
1d		DEM (grown in cyclopentane/ DEM)	$\{[MeLi]_4 \cdot 1.5\text{DEM}\}_\infty$: 	14e
1e		sparteine (grown in pentane/Et ₂ O)	$[MeLi]_2 \cdot 2(-)\text{-sparteine}$: (idem with (+)-surrogate) 	15a
1f		TMCDA (grown in pentane/Et ₂ O)	$[MeLi]_2 \cdot 2(R,R)\text{-TMCDA}$: 	15c
2	EtLi	none (grown in benzene)	$\{[EtLi]_4\}_\infty$: 	13c
3a	<i>i</i> -PrLi	none (grown in hexane)	$[i\text{-PrLi}]_6$: 	17a
3b		TMEDA 1 equivalent (grown in pentane)	$[i\text{-PrLi}]_2 \cdot 2\text{TMEDA}$: 	17b

Table 1. continued

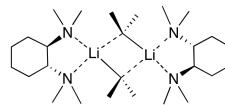
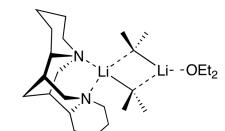
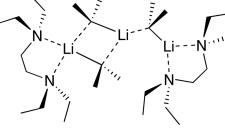
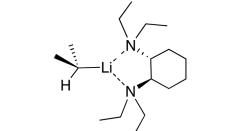
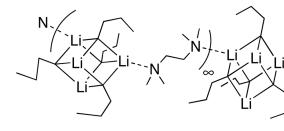
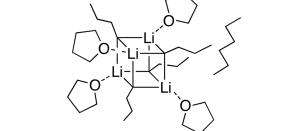
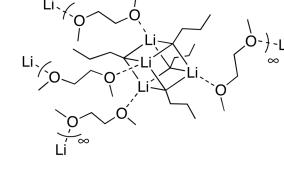
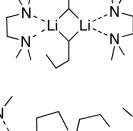
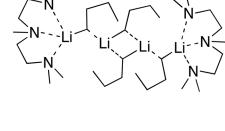
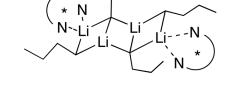
Entry	AlkLi	Solvation	Structure	Ref
3c	<i>i</i> -PrLi	(<i>R,R</i>)-TMCD A (grown in pentane)	[<i>i</i> -PrLi] ₂ ·2(<i>R,R</i>)-TMCD A: 	15c
3d		(-)sparteine and Et ₂ O (grown in pentane/Et ₂ O)	Et ₂ O·[<i>i</i> -PrLi] ₂ ·sparteine : 	18a
3e		TEEDA (grown in pentane)	[<i>i</i> -PrLi] ₃ ·2TEEDA : 	17b
3f		(<i>R,R</i>)-TECDA (grown in pentane)	[<i>i</i> -PrLi]·(<i>R,R</i>)-TECDA : 	17b
4	BuLi	none (grown in hexane or pentane)	[BuLi] ₆ : 	20
4b		TMEDA (grown in hexane + 0.25 equiv TMEDA)	{[BuLi] ₄ ·TMEDA} _∞ : 	19
4c		THF (grown in hexane + 1 equiv THF)	{[BuLi] ₄ ·4THF}.Hex : 	19
4d		DME (grown in hexane + 1.2 equiv DME)	{[BuLi] ₄ ·4DME} _∞ : 	19
4e		TMEDA (grown in hexane + 1.5 equiv TMEDA)	[BuLi] ₂ ·2TMEDA : 	19
4f		PMDTA 0.5 equivalent (grown in pentane/ hexane)	{[BuLi] ₂ ·PMDTA} ₂ : 	18b
4g		(<i>R,R</i>)-TMCD A (grown in pentane/hexane + 0.5 equiv TMCD A)	{[BuLi] ₂ ·TMCD A} ₂ : 	18c

Table 1. continued

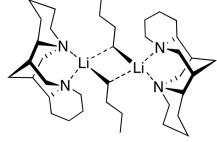
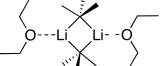
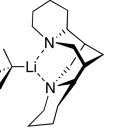
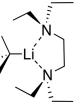
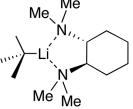
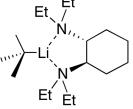
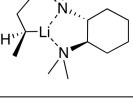
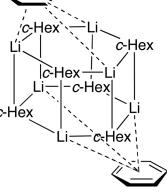
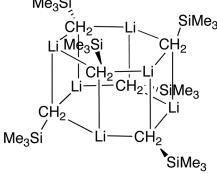
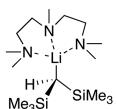
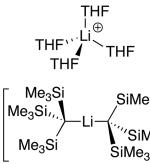
Entry	AlkLi	Solvation	Structure	Ref
4h		(-)-sparteine (grown in pentane/Et ₂ O + 1 equiv (-)-sparteine)	[BuLi] ₂ ·2(-)-sparteine : 	18a
5a		none (grown in pentane)	[t-BuLi] ₄ : 	20
5b		Et ₂ O (grown in pentane + 3.4 equiv Et ₂ O)	[t-BuLi] ₂ ·2Et ₂ O : 	20
5c	t-BuLi	sparteine (grown in pentane)	[t-BuLi]·(-)-sparteine : 	21a
5d		TEEDA (grown in pentane)	[t-BuLi]·TEEDA : 	21c
5e		(R,R)-TMCDA (grown in pentane)	[t-BuLi]·TMCDA : 	21b
5f		(R,R)-TECDA (grown in pentane)	[t-BuLi]·TECDA : 	21d
6	s-BuLi	(R,R)-TMCDA (grown in pentane/cyclohexane)	[s-BuLi]·TMCDA : 	15c
7	c-HexLi	benzene (grown in benzene)	[c-HexLi] ₆ ·2C ₆ H ₆ : 	16
8a	TMSCH ₂ Li	none (grown from sublimation)	[Me ₃ SiCH ₂ Li] ₆ : 	22c
8b	TMS ₂ CHLi	PMDTA (grown in benzene + 1 equiv PMDTA)	[(Me ₃ Si) ₂ CHLi]·PMDTA : 	22a

Table 1. continued

Entry	AlkLi*	Solvation	Structure	Ref
8c	TMS ₃ CLI	THF (grown in toluene)	$\left[\left(\text{Me}_3\text{Si} \right)_3\text{C} \right]_2\text{Li}^+ \cdot [\text{Li}^+] \cdot 4\text{THF}$:	 22b

*TMS = Me₃Si.

In the presence of an equimolar amount of TMEDA (*N,N,N',N'*-tetramethylethylenediamine), a tetrameric organization of MeLi was also observed, part of a three-dimensional polymeric sequence. In the $\{[\text{MeLi}]_4 \cdot 2\text{TMEDA}\}_{\infty}$ structure thus evidenced (Table 1, entry 1c), the MeLi cubes were found to be linked through Li–TMEDA–Li bridges in all directions.^{14c} A similar arrangement, $\{[\text{MeLi}]_4 \cdot 1.5\text{DEM}\}_{\infty}$ (Table 1, entry 1d), was reported for the polymeric aggregate of methylolithium formed in DEM (diethoxymethane).^{14e} In this example, the [MeLi]₄ cubes are linked through one intermolecular C–Li interaction, while the three additional Li cations of each tetramer are connected to one oxygen of a DEM molecule. The strong tendency for MeLi to preferably arrange as a cubic tetramer was contradicted by growing the crystals in the presence of (−)-sparteine^{15a} and its (+)-surrogates^{15a} or with (R,R)-TMCDA (*N,N,N',N'*-tetramethylcyclohexane-1,2-diamine).^{15c} Disolved dimeric structures, $[\text{MeLi}]_2 \cdot 2(-)\text{-sparteine}$, $[\text{MeLi}]_2 \cdot 2(+)\text{-sparteine}$ surrogate, and $[\text{MeLi}]_2 \cdot 2(R,R)\text{-TMCDA}$, respectively, were reported (Table 1, entries 1e,f).

The first prismatic hexameric arrangements were described in the mid-1970s from crystals of cyclohexyllithium grown in benzene.¹⁶ Benzene adduct $[\text{c-HexLi}]_6 \cdot 2\text{C}_6\text{H}_6$, in which the two benzene molecules were seen as facing the two transoidal equilateral triangles of the lithium octahedron (Table 1, entry 7), was emphasized. Comparable oligomeric arrangement, but this time unsolvated, was observed from crystals of isopropylolithium grown in hexane ($[\text{i-PrLi}]_6$, Table 1, entry 3a).^{17a} In the presence of diamines TMEDA^{17b} and (R,R)-TMCDA,^{15c} isopropylolithium oligomerized as symmetrical dissolved dimers, $[\text{i-PrLi}]_2 \cdot 2\text{TMEDA}$ and $[\text{i-PrLi}]_2 \cdot 2(R,R)\text{-TMCDA}$ (Table 1, entries 3b,c), respectively. With (−)-sparteine in diethyl ether (Table 1, entry 3d), the *i*-PrLi dimeric core was also dissolved but not symmetrically since one lithium was coordinated to one molecule of Et₂O and the other lithium was coordinated by the two nitrogens of a molecule of sparteine.^{18a} A monosolvated monomer, $[\text{i-PrLi}] \cdot (\text{R},\text{R})\text{-TECDA}$ (*N,N,N',N'*-tetraethylcyclohexane-1,2-diamine), was characterized for isopropylolithium crystallized in the presence of the (R,R)-TECDA diamine (Table 1, entry 3f).^{17b} One can note also the description of the dissolved intermediary nonsymmetrical aggregate $[\text{i-PrLi}]_3 \cdot 2\text{TEEDA}$ (*N,N,N',N'*-tetraethylmethylenediamine) combining a dimeric core and a pseudomonomer (Table 1, entry 3e).^{17b}

The crystallographic structures for aggregates of butyllithium isomers such as *n*-butyllithium (afterward, simply written as butyllithium and abbreviated as BuLi for brevity sake; this also applies to *n*-Pr, *n*-Pent, *n*-Hex, which are written as Pr, Pent, and Hex, respectively),^{18–20} *sec*-butyllithium,^{15c} and *tert*-butyllithium^{20,21} were depicted later, from the 1990s. It was shown that crystals of butyllithium grown in hexane or pentane

corresponded to unsolvated prismatic hexameric units $[\text{BuLi}]_6$ ²⁰ free of interactions between oligomers (Table 1, entry 4a).²⁰ Adding a substoichiometric amount of TMEDA (0.25 equiv/BuLi) to the hydrocarbon solution afforded the long-chain oligomeric arrangement $\{[\text{BuLi}]_4 \cdot \text{TMEDA}\}_{\infty}$, in which the butyllithium units corresponding to cubic tetramers were linked to each other through Li–TMEDA–Li bridges setting up with two of the four lithium cations of the cubes (Table 1, entry 4b).¹⁹ The presence of an excess of TMEDA favored the $[\text{BuLi}]_2 \cdot 2\text{TMEDA}$ dimeric arrangement (Table 1, entry 4e).¹⁹ The other cubic tetrameric complex $\{[\text{BuLi}]_4 \cdot 4\text{THF}\}\text{-Hex}$ was obtained from an almost equimolar mixture of BuLi in hexane and THF (1.2 equiv of THF for 1 equiv of BuLi, Table 1, entry 4c).¹⁹ In the latter, each lithium atom of the cube was found to be solvated by one molecule of THF. Switching from THF to DME (dimethoxyethane) under the same conditions for the preparation of the crystals led to the $\{[\text{BuLi}]_4 \cdot 4\text{DME}\}_{\infty}$ polymer in which cubic tetrameric units of BuLi were linked to each other through DME bridges between all Li vertices of the cubes (Table 1, entry 4d).¹⁹ It appears that bidentate ligands (TMEDA, DME) would favor polymeric arrangements if introduced in stoichiometric or substoichiometric amounts. Concerning now tridentate PMDTA (*N,N,N',N'',N''*-pentamethyldiethylenetriamine),^{18b} $\{[\text{BuLi}]_2 \cdot \text{PMDTA}\}_2$ complex was identified (Table 1, entry 4f) in which two open dimers of BuLi were linked to each other (this can also be seen as the combination of a central closed dimer, surrounded by two monomers). In a recent example, a ladder-type oligomer also involving four molecules of BuLi was obtained in the presence of the (R,R)-TMCDA chiral diamine ($\{[\text{BuLi}]_2 \cdot (\text{R},\text{R})\text{-TMCDA}\}_2$, Table 1, entry 4g).^{18c} A dissolved dimeric system formed with (−)-sparteine ($[\text{BuLi}]_2 \cdot 2(-)\text{-sparteine}$, Table 1, entry 4h).^{18a} The successive results above present the following trend: donor solvating media advantage the crystallization of oligomers smaller than those grown in hydrocarbons (tetramer versus hexamer for butyllithium). More hindered *tert*-butyllithium follows this rule, since the tetrameric structure $[\text{t-BuLi}]_4$ is grown in pentane (Table 1, entry 5a)²⁰ and a dissolved dimeric complex, $[\text{t-BuLi}]_2 \cdot 2\text{Et}_2\text{O}$, is formed upon addition of Et₂O to the pentane solution (Table 1, entry 5b).²⁰ Due to the steric hindrance of the *tert*-butyl appendage, using diamines easily avoided oligomerization, leading to monosolvated monomers such as the $[\text{t-BuLi}] \cdot (-)\text{-sparteine}$,^{21a} $[\text{t-BuLi}] \cdot \text{TEEDA}$,^{21c} $[\text{t-BuLi}] \cdot (\text{R},\text{R})\text{-TMCDA}$,^{21b} and $[\text{t-BuLi}] \cdot (\text{R},\text{R})\text{-TECDA}$ ^{21d} chelates (Table 1, entries 5c–f). As far as *sec*-butyllithium is concerned, one crystalline structure is known to date, which corresponds to the $[\text{s-BuLi}] \cdot (\text{R},\text{R})\text{-TMCDA}$ monomer (Table 1, entry 6).^{15c} In ending this section, one can mention the crystallographic results obtained for the silylmethylolithium derivatives $\text{Me}_3\text{SiCH}_2\text{Li}$,^{22a,c} $(\text{Me}_3\text{Si})_2\text{CHLi}$,^{22a} and $(\text{Me}_3\text{Si})_3\text{CLI}$.^{22b} Crystals of $\text{Me}_3\text{SiCH}_2\text{Li}$

Table 2. Oligomeric Degree of $C_mH_{2m+1}Li$ ($m = 1–4$) Alkyllithium Derivatives in Solution with $[AlkLi]_6$ for Prismatic Hexamers; $[AlkLi]_4$ for Cubic Tetramers; $[AlkLi]_2$ for Planar Quadrilaterals; and $[AlkLi]$, $[AlkLi]_8$, and $[AlkLi]_9$ for Monomers, Octamers, and Nonamers, Respectively

entry	AlkLi	solvent	$[AlkLi]_x$	ref
1	MeLi	hydrocarbon ^a ether/amine ^b	— ^c $[MeLi]_4 \cdot nS^d$ (S = THF, Et ₂ O, Et ₃ N)	— 14d, 24b, 25, 28, 31b, 36
2	EtLi	hydrocarbon ^a ether/amine ^b	$[EtLi]_6^e + [EtLi]_8 + [EtLi]_9$ $[EtLi]_4 \cdot nEt_2O^d$	24a, 26, 27, 31a 24b, 36b
3	PrLi	hydrocarbon ^a ether/amine ^b	$[PrLi]_6^e + [PrLi]_8 + [PrLi]_9$ —	26, 27 —
4	i-PrLi	hydrocarbon ^a ether/amine ^b	$[i\text{-}PrLi]_4^{e,f} + [i\text{-}PrLi]_6$ Et ₂ O-[i-PrLi] ₂ (-)sparteine (in Et ₂ O) [i-PrLi] ₂ 2(+)-sparteine surrogate (in Et ₂ O) THF-[i-PrLi](+)-sparteine surrogate (in THF)	17a, 27 27c, d
5	BuLi	hydrocarbon ^a ether/amine ^b	$[BuLi]_6^e + [BuLi]_8 + [BuLi]_9$ $[BuLi]_4 \cdot nS^d$ (S = DMM, DME, Et ₂ O) $[BuLi]_2 \cdot 4S + [BuLi]_4 \cdot 4S^f$ (S = Me ₂ O, THF)	27 30, 36a, 37, 38 39–41
6	i-BuLi	hydrocarbon ^a ether/amine ^b	$[i\text{-}BuLi]_6$ —	27 —
7	s-BuLi	hydrocarbon ^a ether/amine ^b	$[s\text{-}BuLi]_2 + [s\text{-}BuLi]_4 + [s\text{-}BuLi]_6$ $[s\text{-}BuLi] \cdot nTHF + [s\text{-}BuLi]_2 \cdot nTHF^d$ [s-BuLi]-PMDTA	27, 44 47 47
8	t-BuLi	hydrocarbon ^a ether/amine ^b	$[t\text{-}BuLi]_4$ $[t\text{-}BuLi]_2 \cdot 4Et_2O$ $[t\text{-}BuLi] \cdot nTHF^d$ [t-BuLi]-PMDTA	27, 32, 45, 46 48 47 47

^aHydrocarbon = benzene, cyclopentane. ^bEther = diethyl ether (Et₂O), dimethyl ether (Me₂O), dimethoxymethane (DMM), diethoxymethane (DEM), tetrahydrofuran (THF); amine = triethylamine (Et₃N). ^cMeLi not soluble in hydrocarbon solvents. ^dn undetermined ^eMain species at higher temperature (from –20 °C to room temperature). ^fMain species at low concentration

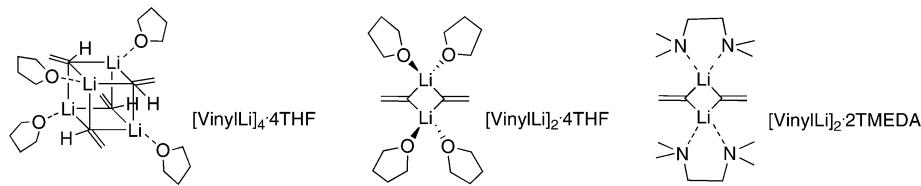
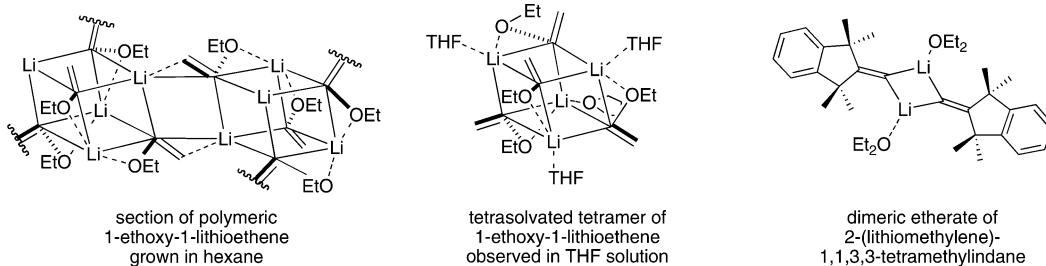
were prepared by sublimation, and the crystallographic data evidenced an unsolvated prismatic hexameric arrangement ($[Me_3SiCH_2Li]_6$, Table 1, entry 8a).^{22c} Analyzing by ebullioscopy the structure of the same species in the presence of PMDTA suggested the formation of a monomeric solvate.^{22a} Crystals of the $(Me_3Si)_2CHLi$ congener were obtained in the presence of the same triamine (PMDTA), and a monomeric solvate was characterized by X-ray crystallography ($[(Me_3Si)_2CHLi] \cdot PMDTA$, Table 1, entry 8b).^{22a} Crystals of the more hindered analogue tris(trimethylsilyl)methylolithium, synthesized in THF and then grown in a toluene solution, were found to correspond to a separated ion pair system in which a lithium cation was solvated by four molecules of THF ($[Li^+] \cdot 4THF$) next to an unsolvated $[(Me_3Si)_3C)_2Li^-$ anionic moiety (Table 1, entry 8c).^{22b}

2.1.1.2. Structures in Solution (Table 2). Main efforts in this field, initiated in the 1960s, consisted of registering ¹H, ¹³C, ⁷Li,^{12,23–25} and then later on ⁶Li^{26–29} magnetic resonance spectra of organolithium reactants in deuterated solvents. Compared with the crystallographic approach, the NMR technique is supposed to afford a more representative picture of the lithio reactant structure when engaged in a reaction, since the analyses are made in solution. Nevertheless, note that results obtained from solid-state structures often correspond to a part of the information brought by NMR analyses. In other respects, data acquired from cryoscopic measurements;³⁰ vapor pressure lowering quantifications;³¹ and Raman,³² infrared,^{12a,24a,33} electronic,³⁴ and mass³⁵ spectroscopies are also of high significance, even if they refer to more ancient work, and deserve to be taken into account.

Starting with methylolithium, a cubic tetrameric organization was evidenced in the late 1960s when working in donor

solvents ($[MeLi]_4 \cdot nS$, S = THF, Et₂O, or Et₃N; Table 2, entry 1).^{14d,24b,25,28,31b,36} Such a result was among others based on the observation of multiplets arising from scalar ¹³C–⁶Li spin–spin couplings.²⁵ It then relied on isotope effects (deuterium) on the ⁶Li chemical shifts.²⁸ Note that the solvation remains a topic of discussion, although the THF-aggregate isolated in the solid state suggests a tetrasolvated structure,^{14d,36} and structures are unknown for MeLi in hydrocarbons, most likely due to its insolubility in this medium.

Studies carried out on organolithiums of longer alkyl chains (≥ 2 carbons) distinguish the case of straight-chain alkyllithium derivatives (ethyl, propyl, butyl = series 1; Table 2, entries 2, 3, and 5) from the branched-chain ones (isopropyl, isobutyl, sec-butyl, *tert*-butyl = series 2; Table 2, entries 4 and 6–8).²⁷ All species of series 1 were found to behave identically in hydrocarbon solvents (benzene,^{24a} cyclopentane^{26,27}), forming three types of oligomers: a hexamer, an octamer, and a nonamer ($[AlkLi]_6 + [AlkLi]_8 + [AlkLi]_9$, Alk = Et, Pr, or Bu; Table 2, entries 2, 3, 5). The hexamer, described as being prismatic,^{26b} was observed as the major oligomer at higher temperature.^{26,30,31a} The same straight-chain alkyllithiums formed smaller oligomers in basic solvents (ethers, amines) or when adding basic additives (amines, diamines) to the hydrocarbon solutions. This tendency was justified by the capacity for the basic environment to coordinate (solvate) the lithium atoms of the reactants. Thus, ethyllithium was identified as a single cubic tetramer in diethyl ether ($[EtLi]_4 \cdot nEt_2O$, n undetermined; Table 2, entry 2).^{24b} Similar cubic tetrameric units were depicted for butyllithium in DMM (dimethoxymethane),³⁷ DEM (diethoxymethane),³⁷ and diethyl ether ($[BuLi]_4 \cdot nS$, S = DMM, DEM or Et₂O, and n undetermined; Table 2, entry 5).^{30,37,38} In tetrahydrofuran (THF) or dimethyl

Scheme 2. Tetrasolvated (THF, TMEDA) Tetramer and Dimers of Vinylolithium⁴⁹Scheme 3. Crystalline 1-Ethoxy-1-lithioethene⁵⁰ and 2-(Lithiomethylene)-1,1,3,3-tetramethylindane⁵¹

ether (Me_2O), the presence of dimer ($[\text{BuLi}]_2 \cdot n\text{S}$, $\text{S} = \text{THF}$, Me_2O) was reported for this alkylolithium, in addition to tetramers.^{39–41} This smaller oligomer became predominant when diamine additives were introduced to the analyzed solution.^{27d,39,42b} Upon cooling, the equilibrium $[\text{(BuLi)}_4 \cdot 4\text{THF}] + 4\text{THF} \rightleftharpoons 2[\text{(BuLi)}_2 \cdot 4\text{THF}]$ shifted to the right.^{39,40}

For the branched alkylolithiums (series 2), a new distinction is made depending on the distance of the branching ($\text{C}^\beta-\text{C}^\alpha-\text{Li}$) from the $\text{C}-\text{Li}$ bond.^{27,30} Branching β (and γ) to lithium substitution had the effect of avoiding the formation of octamers and nonamers in hydrocarbon solution. Thus, isobutyllithium organized as a single prismatic hexamer in cyclopentane ($[\text{i-BuLi}]_6$, Table 2, entry 6).^{27b} Identical oligomerization was adopted for 2-methylbutyllithium (β -substitution)^{27b,43} and isopentyllithium (γ -substitution)²⁷ in the same solvent. Still working in hydrocarbon, but branching α to lithium substitution, introduced a bulkiness at the origin of a new reduction of the size of the oligomers, as observed for isopropyllithium (Table 2, entry 4),²⁷ sec-butyllithium (Table 2, entry 7),⁴⁴ and sec-pentyllithium,²⁷ which formed tetramers, even dimers (Alk = *s*-Bu),⁴⁴ in addition to the hexamers ($[\text{AlkLi}]_6 + [\text{AlkLi}]_4 + [\text{AlkLi}]_2$, Alk = *i*-Pr or *s*-Bu). Note that a concentration effect was also observed with isopropyllithium, the tetrameric form becoming predominant at low lithio derivative molarity.²⁷ Increasing the number of substituents on this α -position reduced once again the size of the aggregates examined in nonbasic solvents, as illustrated with *tert*-butyllithium now present as a single tetramer in cyclopentane ($[\text{t-BuLi}]_4$, Table 2, entry 8).^{27,32,45,46} The role played by basic solvents or additives to advantage small-sized aggregates is corroborated with the branched alkylolithium series. Thus, the unsymmetrically solvated dimeric complex formed in Et_2O and characterized in the solid state after adding (−)-sparteine to *i*-PrLi ($\text{Et}_2\text{O} \cdot [\text{i-PrLi}]_2 \cdot (−)\text{-sparteine}$, Table 1, entry 3d) was confirmed in solution (Table 2, entry 4).^{27c,d} Switching to the (+)-sparteine surrogate led to the symmetrically solvated dimeric complex $[\text{i-PrLi}]_2 \cdot 2(+)\text{-sparteine surrogate}$ in Et_2O , whereas monomer $\text{THF} \cdot [\text{i-PrLi}] \cdot (+)\text{-sparteine surrogate}$ was characterized in THF.^{27d} *s*-BuLi showed a monomer–dimer equilibrium in THF, although the solvation was not considered ($[\text{s-BuLi}] \cdot n\text{THF} + [\text{s-BuLi}]_2 \cdot n\text{THF}$, Table 2, entry 7), and

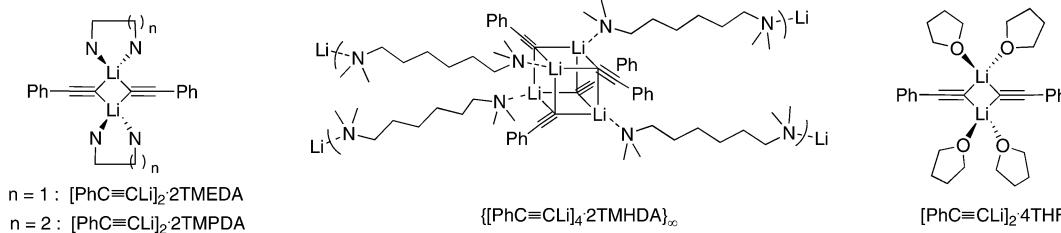
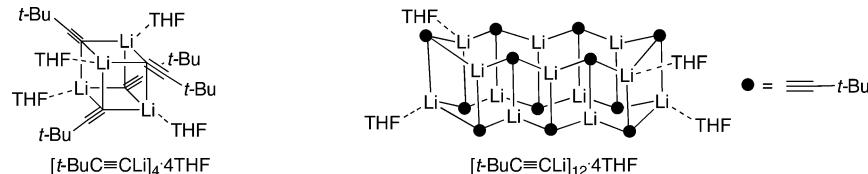
addition of the PMDTA triamine transformed all dimer to almost certainly monosolvated monomer ($[\text{s-BuLi}] \cdot \text{PMDTA}$, Table 2, entry 7).⁴⁷ In the same way, addition of Et_2O to a hydrocarbon solution of *tert*-butyllithium transformed the tetrameric oligomer into a tetrasolvated dimeric complex ($[\text{t-BuLi}]_2 \cdot 4\text{Et}_2\text{O}$, Table 2, entry 8).⁴⁸ The same hindered alkylolithium was characterized in pure Et_2O and THF solutions:⁴⁷ the single formation of dimeric complex was mentioned in Et_2O ($[\text{t-BuLi}]_2 \cdot n\text{Et}_2\text{O}$) and a monomer was realized in THF ($[\text{t-BuLi}] \cdot n\text{THF}$), without indication about the solvation this time. A monomer was also described in the presence of PMDTA, probably monosolvated ($[\text{t-BuLi}] \cdot \text{PMDTA}$).⁴⁷

2.1.1.2. Alkenyllithiums ($\text{C}^{\text{sp}2}-\text{Li}$).

Results are presented for $\text{H}_2\text{C}^{(\beta)}=\text{C}^{(\alpha)}\text{HLi}$, $\text{H}_2\text{C}=\text{C}^{(\alpha\text{-substituted})}\text{Li}$, and $\text{C}^{(\beta\text{-substituted})}=\text{CHLi}$.

Although alkenyllithiums were the object of observations from the early 1960s,^{23,34a} a clear and precise description of their homoaggregation only began in the mid-1980s.^{6c} Thus, vinylolithium⁴⁹ crystallized with 1 equiv of tetrahydrofuran as a single tetrasolvated cubic tetramer of formula $[\text{VinylLi}]_4 \cdot 4\text{THF}$ (Scheme 2, left). If characterized in a THF solution through $^6\text{Li} \cdot ^1\text{H}$ NMR spectroscopy, equilibrium was observed at -90°C with an approximate tetramer–dimer ratio of 8:1 (Scheme 2, middle), both forms being solvated by four molecules of THF ($[\text{VinylLi}]_4 \cdot 4\text{THF} \rightleftharpoons [\text{VinylLi}]_2 \cdot 4\text{THF}$). The dimeric oligomer became predominant upon addition of TMEDA.^{49b} In this context, each lithium cation was found to establish two dative bonds with the two nitrogens of a diamine molecule, which resulted in a disolvated complex of formula $[\text{VinylLi}]_2 \cdot 2\text{TMEDA}$ (Scheme 2, right).

Introduction of α ⁵⁰ or β -substitution(s)^{50b,51} to the $\text{C}^{\text{sp}2}-\text{Li}$ bond modifies the degree of aggregation shown above for vinylolithium. Thus, crystalline α -ethoxy-substituted vinylolithium (1-ethoxy-1-lithioethene) grown in hexane showed an unsolvated polymeric arrangement that can actually be seen as an edge-to-edge connection of cubic tetramers (Scheme 3, left).⁵⁰ Noteworthy are the coordinations established by the lithium cation with both ethoxy and vinylic moieties. When examined in THF solution, a single tetrasolvated cubic tetramer was notified, in which the intramolecular coordination of each lithium with the ethoxy group persisted (Scheme 3, middle).⁵⁰

Scheme 4. Structures of $\text{PhC}\equiv\text{CLi}$ in the Presence of Diamines (solid state)^{54a,b} and THF (solution)⁵⁷**Scheme 5.** NMR^{55,58} and Crystallographic⁵⁵ Structures Obtained for $t\text{-BuC}\equiv\text{CLi}$ in the Presence of THF

Crystalline β,β -disubstituted vinylolithiums [2-(lithiomethylene)-1,1,3,3-tetramethylindane] isolated from a diethyl ether solution were defined as a disolvated centrosymmetric dimer with a Li–C–Li–C four-membered quadrilateral unit (Scheme 3, right).⁵¹ The NMR analysis made in THF solution showed that the latter reactant was rather predominant as a monomer at low temperature and dimerized endothermically.⁵¹ From these observations, no generalities can be established, however, about the role and the influence of an α - and/or β -substitution on the aggregation of the corresponding vinylolithium derivatives, since the number of examples structurally studied still remains poor.

The reason why no NMR description of vinylolithium derivatives in hydrocarbons could be found is probably the consequence of the low solubility of these species in such media. Indeed, vinylolithium itself precipitates in pentane⁵² and α -ethoxyvinyllithium is crystalline in hexane.^{50a}

2.1.1.3. Alkynyllithiums ($C^p\text{-Li}$). Results are presented for $\text{PhC}\equiv\text{CLi}$, $t\text{-BuC}\equiv\text{CLi}$, and $c\text{-PrC}\equiv\text{CLi}$.

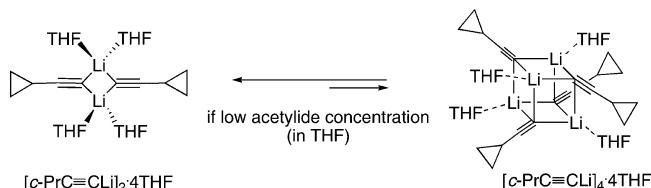
X-ray diffraction^{6,53–55} and cryoscopic measurements,⁵⁶ as well as NMR spectroscopy investigations,^{39,57–59} have been carried out to identify the degree of oligomerization of alkynyllithiums. The most representative results were obtained for lithium phenylacetylide ($\text{PhC}\equiv\text{CLi}$),^{54,56} lithium *tert*-butylacetylide ($t\text{-BuC}\equiv\text{CLi}$),^{55,56,18,59b,c} and lithium cyclopropylacetylide ($c\text{-PrC}\equiv\text{CLi}$).^{59a}

Crystals of lithium phenylacetylide were prepared in the presence of variable length tetramethylalkanediamine ligands (ethane, TMEDA; propane, TMPDA; and hexane, TMHDA). Diamines with short-sized alkyl chains (TMEDA and TMPDA) favored dimeric oligomers in which each lithium was chelated ($[\text{PhC}\equiv\text{CLi}]_2 \cdot 2\text{TMEDA}$ and $[\text{PhC}\equiv\text{CLi}]_2 \cdot 2\text{TMPDA}$, Scheme 4, left).^{54b} Diamine with an alkyl chain of longer size (TMHDA) let the acetylene arrange in a cubic tetramer in which the four lithiums established a coordination with only one nitrogen of the base. The second nitrogen was found to be linked to another cubic tetramer of acetylene, leading in this way to a three-dimensional polymeric arrangement ($\{[\text{PhC}\equiv\text{CLi}]_4 \cdot 2\text{TMHDA}\}_\infty$, Scheme 4, middle).^{54a} A tetrasolvated dimeric oligomer was preferentially obtained for the same acetylide when analyzed in pure THF solution ($[\text{PhC}\equiv\text{CLi}]_2 \cdot 4\text{THF}$, Scheme 4, right).⁵⁷

NMR studies conducted with lithium *tert*-butylacetylide showed that this compound existed at low temperature as a

tetrasolvated cubic tetramer in THF solution ($[\text{t-BuC}\equiv\text{CLi}]_4 \cdot 4\text{THF}$, Scheme 5, left).¹⁸ Crystals of such entities were isolated afterward⁵⁵ in addition to a less common tetrasolvated dodecamer ($[\text{t-BuC}\equiv\text{CLi}]_{12} \cdot 4\text{THF}$, Scheme 5, right).

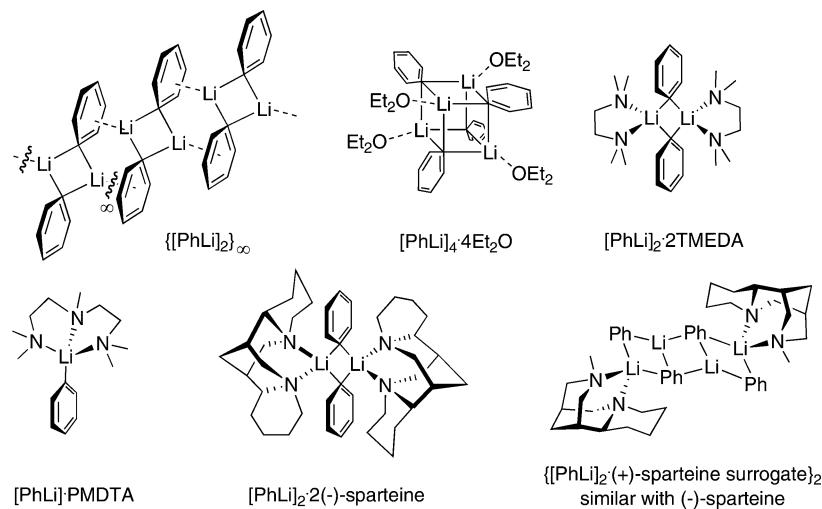
Lithium cyclopropylacetylide ($c\text{-PrC}\equiv\text{CLi}$) turned into an intermediate skeleton of particular interest when synthesizing Efavirenz, a molecule now prescribed for the treatment of HIV infection.⁵⁹ In order to better understand the stereochemical outcome of this lithio reactant when engaged in the Efavirenz enantioselective synthesis, its structural elucidation was undertaken. The NMR spectroscopic data obtained in THF evidenced a mixture of a dimer and a tetramer, both including four molecules of THF ($[\text{c-PrC}\equiv\text{CLi}]_2 \cdot 4\text{THF}$ and $[\text{c-PrC}\equiv\text{CLi}]_4 \cdot 4\text{THF}$, Scheme 6).^{59a} The dimeric unit became predominant at high solvent concentration (low acetylide concentration).

Scheme 6. Structures of $c\text{-PrC}\equiv\text{CLi}$ in THF Solution^{59a}

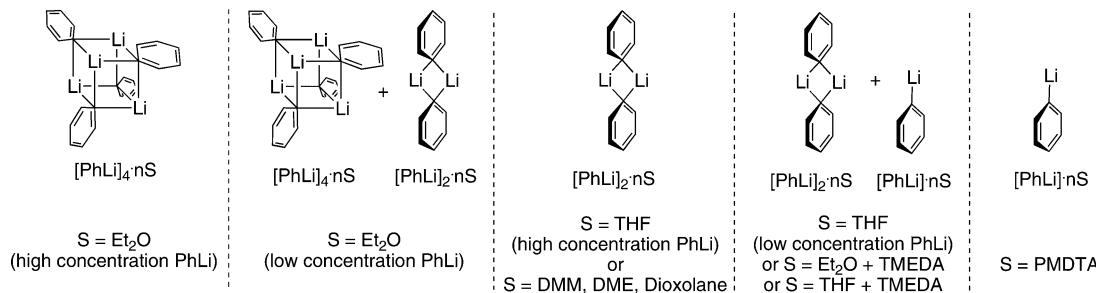
2.1.1.4. Aryllithiums ($Ar\text{-Li}$). Results are presented for PhLi .

The degree of aggregation for phenyllithium has been the object of a long debate, probably because of its structurally high sensitivity to its environment. Preliminary crystallographic data^{6b,c} announced the formation of a tetrasolvated tetramer when isolating crystals from a diethyl ether solution ($[\text{PhLi}]_4 \cdot 4\text{Et}_2\text{O}$, Scheme 7, top middle),⁶⁰ a disolvated dimeric complex when crystallized in the presence of TMEDA ($[\text{PhLi}]_2 \cdot 2\text{TMEDA}$, Scheme 7, top right),⁶¹ and a monomeric complex when grown with the PMDTA triamine ($[\text{PhLi}] \cdot \text{PMDTA}$, Scheme 7, bottom left).⁶² Phenyllithium/(-)-sparteine^{15b} and phenyllithium/(+)-sparteine surrogate^{15a} complexes were also characterized in the solid state. With the first chiral diamine, two arrangements were evidenced that corresponded to a 4:2 ladder-type oligomer ($\{[\text{PhLi}]_2 \cdot (-)\text{-sparteine}\}_2$, Scheme 7, bottom right) and a less stable dimeric phenyllithium core in which both lithium cations were capped

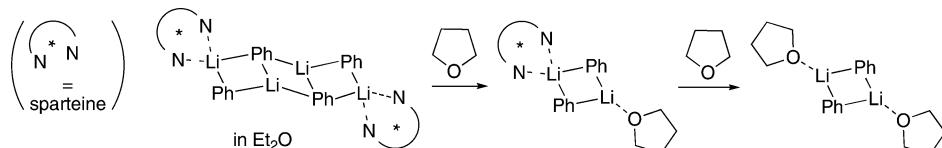
Scheme 7. Crystallographic Structures of Phenyllithium, either Solvent-Free⁶³ or in the Presence of Et₂O,⁶⁰ TMEDA,⁶¹ PMDTA,⁶² (−)-Sparteine,^{15b} and (+)-Sparteine Surrogate^{15a}



Scheme 8. Phenyllithium Oligomers in Solution (S)^{37,65–67}



Scheme 9. Phenyllithium–(−)-Sparteine Affinities in Et₂O and THF Solution⁶⁹

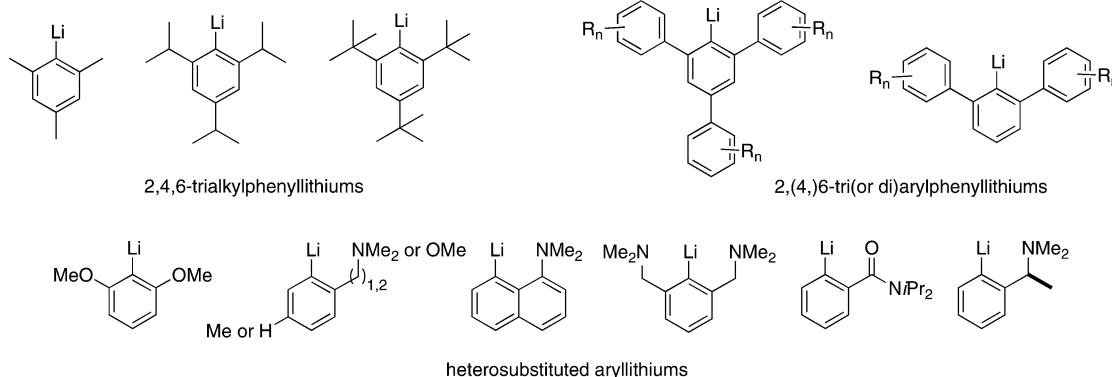


by a (−)-sparteine ligand ($[\text{PhLi}]_2 \cdot 2(-)\text{-sparteine}$, Scheme 7, bottom middle). Working with (+)-sparteine surrogate, only the 4:2 ladder structure of formula $\{[\text{PhLi}]_2 \cdot (+)\text{-sparteine surrogate}\}_2$ was depicted (Scheme 7, bottom right). The solid-state structure of unsolvated Lewis base-free PhLi was also reported, and a polymeric arrangement made of quadrilateral dimeric C^{ipso}–Li–C^{ipso}–Li units interacting between each other was depicted ($\{[\text{PhLi}]_2\}_\infty$, Scheme 7, top left).⁶³ In such an arrangement, the π -electrons of the phenyl rings interact with the Li cations of neighboring $[\text{PhLi}]_2$ units.

Concerning the structure of phenyllithium in solution, note that controversial results were first published^{1a,31b,36b,64} until it was surely established (Scheme 8) that PhLi was mostly tetrameric if highly concentrated in diethyl ether ($[\text{PhLi}]_4 \cdot n\text{Et}_2\text{O}$),^{65,66} while both dimeric and tetrameric arrangements were present in dilute diethyl ether solution ($[\text{PhLi}]_2 \cdot n\text{Et}_2\text{O} + [\text{PhLi}]_4 \cdot n\text{Et}_2\text{O}$).^{65–67} Switching to more solvating tetrahydrofuran (THF), phenyllithium was determined as being mainly dimeric ($[\text{PhLi}]_2 \cdot n\text{THF}$),^{55,66} with a tendency to also exist as a monomer at low lithio derivative concentration ($[\text{PhLi}] \cdot n\text{THF} + [\text{PhLi}]_2 \cdot n\text{THF}$).^{66,67} Working in dimethoxymethane (DMM),³⁷ dimethoxyethane (DME),⁶⁷

and dioxolane⁶⁷ was found to favor the exclusive formation of dimeric oligomers ($\{[\text{PhLi}]_2 \cdot n\text{S}\}$, S = DMM, DME, dioxolane). Addition of TMEDA to highly concentrated PhLi–Et₂O or PhLi–THF solutions led to dimer–monomer mixtures ($[\text{PhLi}]_2 \cdot n\text{S} + [\text{PhLi}] \cdot n\text{S}$).^{66,67} For its part, the presence of the PMDTA triamine in Et₂O or THF solutions of PhLi provoked the formation of a significant amount of monomeric species ($[\text{PhLi}] \cdot \text{PMDTA}$).^{47,67} Note that for all of these studies run in coordinating media, the solvation was not fully established (n undetermined). A polymeric network could account for the insolubility of phenyllithium in hydrocarbons.⁶⁸

A recent NMR and DFT calculation study reported the coordination of phenyllithium by chiral (−)-sparteine in ethereal solutions.⁶⁹ It referred to a ladder-type structural organization including four RLi members in Et₂O ($\{[\text{PhLi}]_2 \cdot (-)\text{-sparteine}\}_2$, Scheme 9, left). Upon progressive addition of THF to the diethyl ether solution, the ladder complex evolved into the $[\text{PhLi}]_2 \cdot 2\text{THF}$ disolvated dimeric aggregate next to free sparteine (Scheme 9, right). In this sequence, an intermediate aggregate was attained, which was made of a phenyllithium dimer solvated by one molecule of sparteine on one lithium cation and one molecule of THF on

Scheme 10. Substituted ArLi Examined by X-ray Crystallography and/or NMR Spectroscopy^{70–72}

the other lithium atom ($\text{THF}\cdot[\text{PhLi}]_2\cdot(-)$ -sparteine, Scheme 9, middle).

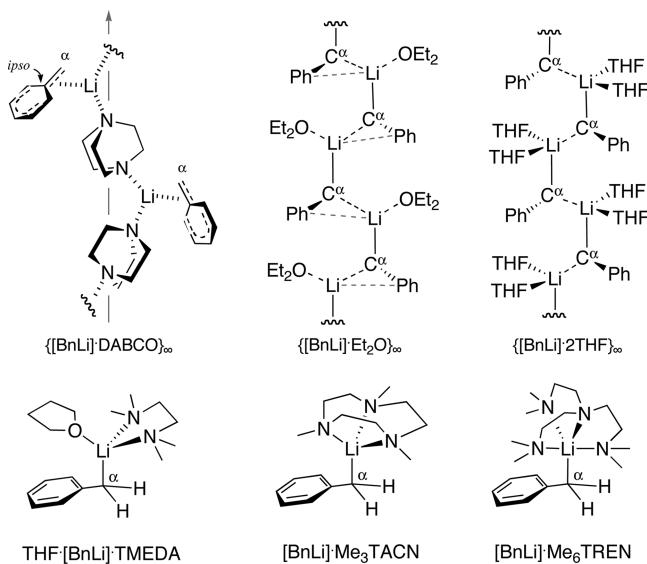
Substituted aryllithiums such as 2,4,6-trialkyl⁷⁰ and 2,(4,)6-tri(or di)arylphenyllithiums^{70c,71} (Scheme 10, top) have of course been the object of crystallographic and NMR observations: tetramers to monomers were described. The presence of heteroatom on the substituents⁷² (Scheme 10, bottom) was found to compete with the solvent, establishing intramolecular coordinations.

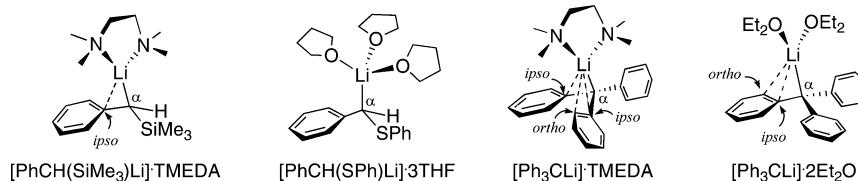
2.1.1.5. Benzyllithiums and Allyllithiums. A common feature between benzyllithium and allyllithium is the possibility for the negative charge on the benzylic or allylic position (C^α) to delocalize through the conjugated anionic part, which brings about an sp^2 hybridization of the C^α .⁷³

2.1.1.5.1. Benzyllithiums. First, concerning unsubstituted benzyllithium $C_6H_5\text{CH}_2\text{Li}$ (BnLi), X-ray structures were obtained from crystals grown using successively 1,4-diazabicyclo[2.2.2]octane (DABCO),⁷⁴ diethyl ether,^{70b} and tetrahydrofuran⁷⁵ as coordinating solvents. With the diamine,⁷⁴ the structural arrangement consisted in an infinite $[\cdots\text{Li}\cdots\text{DABCO}\cdots\text{Li}\cdots\text{DABCO}]_\infty$ polymeric chain linked by one benzylic unit on each lithium cation ($\{[\text{BnLi}]\cdot\text{DABCO}\}_\infty$, Scheme 11, top left). Note that the lithium cation interaction

was observed as being mainly located at the $C^\alpha\text{---}C^{\text{ipso}}$ level. Also a polymeric system showed up using diethyl ether,^{70b} but this time the sequence alternates benzyl and lithium ions with an additional external coordination of one molecule of Et_2O on the cation ($\{[\text{BnLi}]\cdot\text{Et}_2\text{O}\}_\infty$, Scheme 11, top middle). The geometry of the lithium was determined as being mainly trigonal planar if considering a main close contact to the C^α carbons. However, apparent weaker interactions with the adjacent ring carbons could not be fully ignored. In THF/toluene,⁷⁵ a similar backbone was observed, except for the solvation that corresponded to two THF per lithium ($\{[\text{BnLi}]\cdot2\text{THF}\}_\infty$, Scheme 11, top right). An X-ray monomeric structure was fully described after growing the crystals of benzyllithium in a TMEDA/THF mixture ($\text{THF}\cdot[\text{BnLi}]\cdot\text{TMEDA}$, Scheme 11, bottom left).⁷⁶ In this case, the lithium established four coordinations: a single one with the benzylic appendage, through the C^α atom for which a quasipyramidal configuration could be determined, a second with THF, and two with a TMEDA molecule. Also solvated monomers were depicted for crystals of BnLi grown in the presence of either tridentate Me_3TACN (N,N',N' -trimethyl-1,4,7-triazaacyclonanone) ($[\text{BnLi}]\cdot\text{Me}_3\text{TACN}$, Scheme 11, bottom middle)^{77a} or tetradentate Me_6TREN (tris(N,N -dimethyl-2-aminoethyl)-amine) ($[\text{BnLi}]\cdot\text{Me}_6\text{TREN}$, Scheme 11, bottom right).^{77b}

Crystallographic structures of C^α silyl- and sulfur-substituted benzylic derivatives were obtained from TMEDA and THF solutions, respectively. They were identified as monomeric solvates with a pyramidal C^α .⁷⁸ Thus, the $[\text{PhCH}(\text{SiMe}_3)\text{Li}]\cdot\text{TMEDA}$ complex presented a tetracoordinated lithium cation, on one hand η^2 -bonded to both C^α and C^{ipso} of the benzylic part and on the other hand dicoordinated to one TMEDA (Scheme 12, left). In the $[\text{PhCH}(\text{SPh})\text{Li}]\cdot3\text{THF}$ example (Scheme 12, middle left), also evidencing a tetracoordinated lithium, only a $C^\alpha\text{---Li}$ bond was observed while three additional molecules of THF surrounded the metal. Branching aromatic units to the C^α also favored monomeric complexes as observed for triphenylmethylolithium crystallized in TMEDA and then Et_2O .^{79,80} The $[\text{Ph}_3\text{CLi}]\cdot\text{TMEDA}$ complex was characterized by a lithium cation chelated by TMEDA in addition to four close contacts with the benzylic appendage (Scheme 12, middle right).⁷⁹ One corresponded to the $C^\alpha\text{---Li}$ bond, while two $C^{\text{ipso}}\text{---Li}$ interactions were taking place. The fourth interaction involved a C^{ortho} carbon of one of the phenyl group already approached by the metal through the C^{ipso} interaction. In the Et_2O complex (Scheme 12, right), monomer $[\text{Ph}_3\text{CLi}]\cdot2\text{Et}_2\text{O}$ was depicted with the lithium atom coordinated by two molecules of solvent and three carbons of

Scheme 11. Solid-State Structures of Benzyllithium in the Presence of DABCO,⁷⁴ Et_2O ,^{70b} THF,⁷⁵ THF/TMEDA,⁷⁶ Me_3TACN ,^{77a} and Me_6TREN ^{77b}

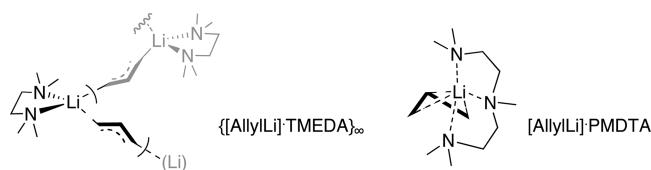
Scheme 12. X-ray Monomeric Structures of Benzylic Derivatives^{78–80}

the $\text{Ph}_3\text{C}^\alpha$ moiety: the benzylic C^α plus the C^{ipso} and C^{ortho} of one of the three phenyl moieties.⁸⁰

The determination of the degree of oligomerization of benzyl lithium in solution has actually been the object of rare studies. The single information on hand is a monomeric description in THF made from colligative property measurements on oxygen- and moisture-sensitive organolithium derivatives.³¹ The multinuclear NMR studies that have been conducted to examine the structure of BnLi in solution mainly focused on the nature of the $\text{C}^\alpha\text{—Li}$ bonding. As already mentioned earlier, the electrons on C^α have the possibility to delocalize throughout the aromatic ring. Such a phenomenon was evidenced from a long-wavelength electronic absorption^{34a,73} as well as high-field displacements of the aromatic protons from those of toluene in the ^1H NMR spectra.⁸¹ Thus, the C^α -electrons are automatically part of a global π -system giving an sp^2 hybridized character, whose importance depends on the solvent, to the benzylic carbon:⁷³ a higher level of sp^2 hybridization was observed in electron-donating solvents [ethers, (poly)amines as polar solvents] than in hydrocarbons (apolar solvents). As a rational interpretation, one can say that donating solvents doubtless coordinate the lithium cation, which thus partly find an electronic compensation. The negative charge on the benzylic carbon is then less retained by the metal and turns out to be free to move through the mesomeric appendage. In contrast, with hydrocarbons, the single source of electrons found by the lithium atom is the benzylic charge, maintaining in this way the electrons on the C^α . In conclusion to this study, and as a consequence of these spectroscopic observations, the $\text{C}^\alpha\text{—Li}$ bond of benzyl lithium would be more ionic in coordinating solvents than in apolar ones. In any cases, a non-negligible degree of covalency is also to be taken into account, even if being not always detectable [low or nonexistent ${}^1\text{J}({}^{13}\text{C}\text{—}{}^6\text{Li})$].^{39,73,82}

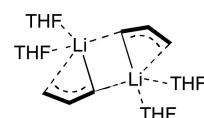
The α -substituted benzyl lithium derivatives $\text{PhCH}(\text{X})\text{Li}$, with $\text{X} = \text{Me}$, SiR_3 , SPh , and SePh , have been the object of particular synthetic attention.⁸³ A sulfur species has even been structurally characterized with the NMR technique and was found to correspond to a monomer in THF.⁸⁴ The spectra showed that the lithium cation was bonded to the benzylic carbon and solvated by three molecules of THF, a result similar to the X-ray structure. Note that polyamines added to the THF solution converted the CIP (contacted ion pair) into an SIP (separated ion pair).

2.1.1.5.2. Allyllithium. Crystal structures of the non-substituted allyllithium $\text{H}_2\text{C=CH—CH}_2\text{Li}$ (AllyLLi) were obtained by growing the lithiated species either in TMEDA⁸⁵ or in PMDTA.⁸⁶ With the diamine, a polymeric chain formed, which alternated one allyl moiety and one solvated lithium ($\{[\text{AllyLLi}]\cdot\text{TMEDA}\}_\infty$, Scheme 13, left). In such an organization, each terminal carbon of the allylic appendages was found to link with one lithium cation. Complementarily, the latter was characterized as establishing four coordinations: two with two allylic anions and two with the nitrogens of the ligand.

Scheme 13. X-ray Structures of Allyllithium Complexes with TMEDA⁸⁵ and PMDTA⁸⁶

The triamine ligand led to a crystalline monomeric complex in which the lithium cation was asymmetrically bonded to the three nitrogen atoms of the PMDTA and both terminal carbons of the allyl skeleton ($[\text{AllyLLi}] \cdot \text{PMDTA}$, Scheme 13, right). The allylic unit was not planar and the central H^2 atom was slightly bent toward the lithium.

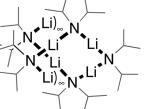
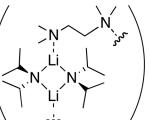
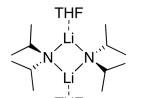
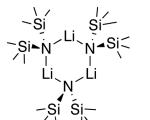
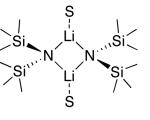
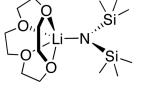
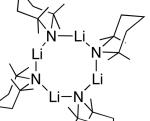
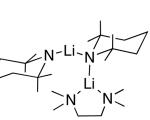
From the various spectroscopic investigations (IR, NMR) devoted to the structural description of allyllithium in ethereal solution (allyllithium is actually sparingly soluble in hydrocarbon), one can say that the ionic pair character was seen as predominant,⁸⁷ even if either as intimate ion pair or cluster, and the lithium cation was found to bridge the two terminal carbons of the allylic moiety, forming in this way a distorted π -complex (Scheme 14).^{87,88} About the degree of oligomerization and the solvation, only a centrosymmetric tetrasolvated (two molecules of solvent per lithium) dimer in THF has been evidenced to date.⁸⁹

Scheme 14. Tetrasolvated Allyllithium Dimer in THF Solution⁸⁹

It should be noted that variously substituted allyllithiums have been the object of structural considerations.⁹⁰ Most parameters examined in those studies were (i) the cis/trans isomerization,^{90a,c,f,n} (ii) the ion pair strength,^{90b,d,o} (iii) the bridged topology,^{90d-g,j,m,o,r} (iv) the solvation and/or intramolecular complexation effects,^{90g,h,p,s-u} and (v) rotation properties.^{90e,f,i,k-m,q}

To conclude with the oligomerization state of the highly dipolar organolithium derivatives, the general tendency is that hydrocarbon solvents advantage large-sized oligomers (tetramers to nonamers), while a basic environment [ethers, (poly)amines] favors small-sized ones (tetramers to monomers). Steric hindrance at the proximity of the C—Li bond has the effect of reducing the aggregation. Temperature and concentration also act on the oligomerization phenomenon. Such information is relevant for the structure/reactivity relationship postulating faster reactivity with smaller aggregates,^{6f,15b,17b,50a,59b,67,91} even if this should be taken with caution.^{14e,42d,91a} Although a widely held notion consists of

Table 3. Crystallographic Structures of DALi, HMDSLi, and TMPLi

Entry	Lithium Amide	Solvation (S)	Structure	Ref
1a		none (grown in hexane)	Helical polymer : 	92
1b	<i>i</i> -Pr ₂ NLi (DALi)	TMEDA (grown in hexane + excess TMEDA)	{[DALi] ₂ ·TMEDA} _∞ : 	93
1c		THF (grown in THF)	[DALi] ₂ ·2THF : 	94
2a		none (grown in petroleum ether)	[HMDSLi] ₃ : 	95
2b	(Me ₃ Si) ₂ NLi (HMDSLi)	Et ₂ O or THF or pyridine (grown in hexane + S)	[HMDSLi] ₂ ·2S : 	96 97
2c		12-crown-4 (1 equivalent) (grown in hexane)	[HMDSLi]·12-crown-4 : 	98
3a		none (grown in pentane)	Planar [TMPLi] ₄ : 	96b
3b	(TMPLi)	TMEDA	[TMPLi] ₂ ·TMEDA : 	99

saying that monomers are the reactive species and, thus, organolithium aggregates should first dissociate before reacting,^{6f} aggregate-based reaction mechanisms have also been proved.^{6f}

2.1.2. Lithium Amides (N–Li). Results are presented for DALi, HMDSLi, TMPLi, *c*-C₆H₁₂NLi, Bn₂NLi, BnN(H)Li, *t*-BuNH₂Li, *c*-C₄H₈NLi, Ph(Me)NLi, Ph(naphthyl)NLi, Ph₂NLi, PhCH=C=NLi, ICALi, *c*-Hex₂NLi, (2-adamantyl)₂NLi, Et₂NLi, CLAs (Chiral Lithium Amides).

Among a large variety of structurally studied lithium amide reactants, lithium diisopropylamide (DALi), lithium hexamethyldisilazide (HMDSLi), and lithium 2,2,6,6-tetramethylpiperidide (TMPLi) have been the object of particular interest and are well-documented as regards crystallographic and solution structure descriptions (in particular based on ¹H, ¹³C, ⁶Li, and ¹⁵N NMR spectroscopy). The following, which distinguishes the solid-state arrangements from those known in solution, is mainly referring to these three lithium amides, although results obtained for close analogues are mentioned afterward. The case of CLAs is considered separately at the end of this section.

2.1.2.1. Crystallographic Structures.^{7,56} Solid-state structures were obtained for the three DALi, HMDSLi, and TMPLi amides (Table 3). X-ray analyses run on crystals of DALi grown in hexane highlighted a helical polymer, with a sequence based on N–Li–N connections (Table 3, entry 1a).⁹² After addition of TMEDA in excess to the hexane solution, crystals corresponding to an infinite array of dimers linked by bridging TMEDA ligands were recovered ({[DALi]₂·TMEDA}_∞, Table 3, entry 1b).⁹³ In other respects, DALi crystallized from THF solution as a dissolved dimer ([DALi]₂·2THF, Table 3, entry 1c).⁹⁴ Working with HMDSLi revealed that a trimeric solid-state oligomer was isolated from a petroleum ether solution ([HMDSLi]₃, Table 3, entry 2a),⁹⁵ dissolved dimers grew up from ethereal or amino media ([HMDSLi]₂·2S, S = Et₂O,^{96a,b} THF,^{96c} pyridine,⁹⁷ Table 3, entry 2b), and a monomeric structure was evidenced in the presence of 12-crown-4 ([HMDSLi]·12-crown-4, Table 3, entry 2c).⁹⁸ TMPLi behaved in still another way in view of the fact that it organized in the solid state as a planar tetrameric core if grown in pentane

Table 4. Crystallographic Structures of *c*-C₆H₁₂NLi, Bn₂NLi, BnN(H)Li, *t*-BuNHLi, *c*-C₄H₈NLi, Ph(Me)NLI, Ph(naphthyl)NLI, Ph₂NLI, and PhCH=C=NLI

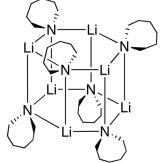
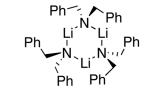
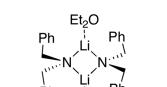
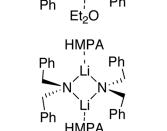
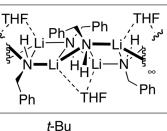
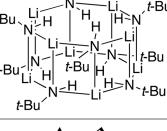
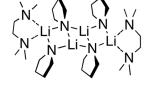
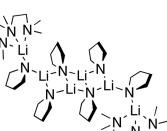
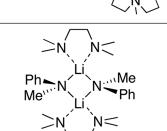
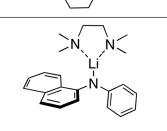
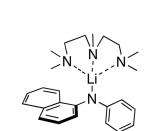
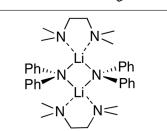
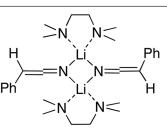
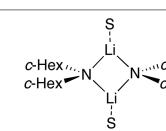
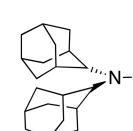
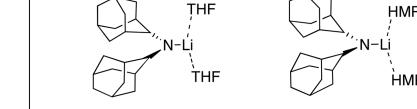
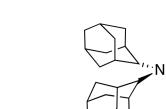
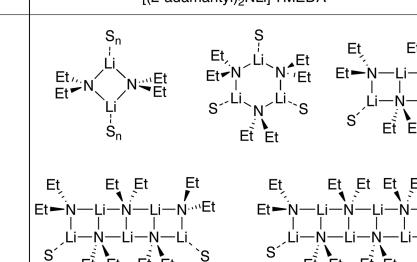
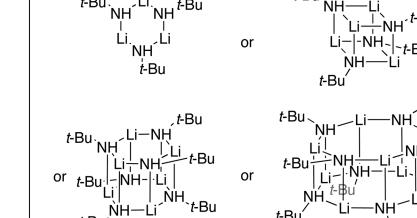
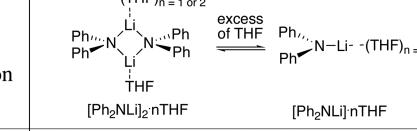
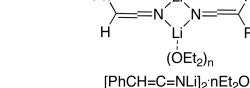
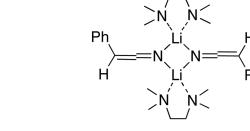
Entry	Lithium Amide	Solvation	Structure	Ref
1	<i>c</i> -C ₆ H ₁₂ NLi	none (grown in hexane/ toluene)	[<i>c</i> -C ₆ H ₁₂ NLi] ₆	
2a		none (grown in hexane)	[Bn ₂ NLi] ₃	
2b	Bn ₂ NLi	Et ₂ O	[Bn ₂ NLi] ₂ ·2Et ₂ O	
2c		HMPA	[Bn ₂ NLi] ₂ ·2HMPA	
3	BnN(H)Li	THF	{[BnN(H)Li] ₂ ·THF} _∞	
4	<i>t</i> -BuNHLi	none (grown in hexane)	{[<i>t</i> -BuNHLi] ₂ } ₄ (or also [<i>t</i> -BuNHLi] ₈)	
5a		TMEDA (grown in hydrocarbon)	{[<i>c</i> -C ₄ H ₈ NLi] ₂ ·TMEDA} ₂	
5b	<i>c</i> -C ₄ H ₈ NLi	PMDTA (grown in hydrocarbon)	{[<i>c</i> -C ₄ H ₈ NLi] ₃ ·PMDTA} ₂	
6	Ph(Me)NLI	TMEDA grown in (hexane/ toluene)	[Ph(Me)NLI] ₂ ·2TMEDA	
7a		TMEDA (grown in hexane/ toluene)	[Ph(naphthyl)NLI]·TMEDA:	
7b	Ph(naphthyl)NLI	PMDTA grown in (hexane/ toluene)	[Ph(naphthyl)NLI]·PMDTA:	
8		TMEDA (grown in hexane/ toluene)	[Ph ₂ NLI] ₂ ·2TMEDA	
9	PhCH=C=NLI	TMEDA (grown in hexane)	[PhCH=C=NLI] ₂ ·2TMEDA :	

Table 5. Structures in Solution of Lithium Amides DALi, HMDSLi, TMPLi, ICALi, *c*-Hex₂NLi, (2-adamantyl)₂NLi, Et₂NLi, *t*-BuNHLi, Ph₂NLi, PhCH=C=NLi

Entry	Lithium amide	Solvent (S)	Structure	Ref
1a		pentane hexane toluene		109
1b	<i>i</i> -Pr ₂ NLi (DALi)	THF, Et ₂ O DMM, DME BuOMe <i>t</i> -BuOMe THP TMEDA HMPA		37 93 94 110 111 113
1c		(<i>R,R</i>)- TMCDAs		111
2a		pentane toluene		114 115
2b		THF, Et ₂ O <i>i</i> -PrOMe BuOMe <i>t</i> -BuOMe THP		114 116
2c	(Me ₃ Si) ₂ NLi (HMDSLi)	TMEDA		118
2d		PMDTA		118
2e		HMPA		115
3a	(TMPLi)	pentane		120 122
3b		THF		118a 119 120
4	<i>i</i> -Pr(<i>c</i> -Hex)NLi (ICALi)	THF		124

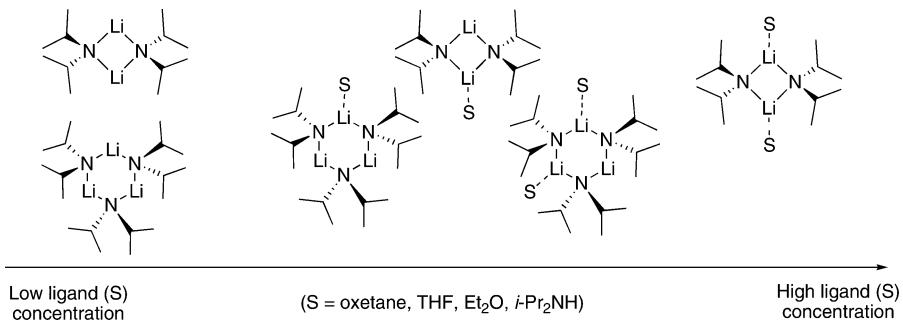
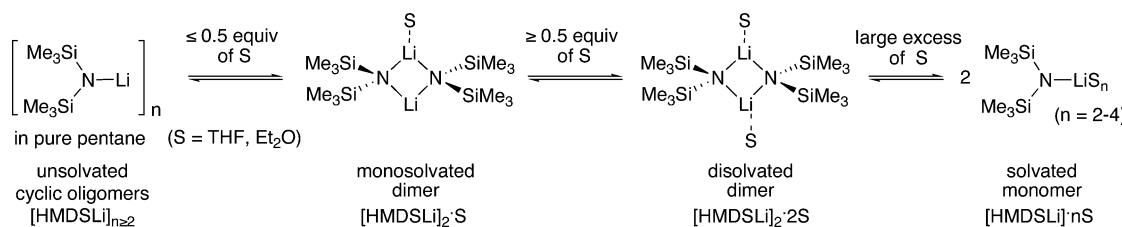
Table 5. continued

Entry	Lithium amide	Solvent (S)	Structure	Ref
5	$c\text{-Hex}_2\text{NLi}$	THF HMPA		125
6a		THF HMPA		126
6b	$(2\text{-adamantyl})_2\text{NLi}$	TMEDA		126
7	Et_2NLi	oxetane THF Et_2O		127
8	$t\text{-BuNHLi}$	toluene		128
9	Ph_2NLi	THF/ hydrocarbon		2b
10a	$\text{PhCH}=\text{C=NLi}$	EtO		129
10b	$\text{PhCH}=\text{C=NLi}$	TMEDA		129

($[\text{TMPLi}]_4$, Table 3, entry 3a),^{96b} while an open dimer incorporating one molecule of TMEDA was characterized when the crystals grew in the presence of this diamine ($[\text{TMPLi}]_2\text{-TMEDA}$, Table 3, entry 3b).⁹⁹

Among other “simple” lithium amides being the object of crystallographic examinations (Table 4), one can retain the case of lithium azepan-1-ide, which organized as a prismatic hexamer when grown in a hexane/toluene medium ($[\text{c-C}_6\text{H}_{12}\text{NLi}]_6$,

Table 4, entry 1).¹⁰⁰ Lithium dibenzylamide was observed, in the solid state, as a planar trimeric oligomer ($[\text{Bn}_2\text{NLi}]_3$, Table 4, entry 2a) after being grown in hexane, whereas dissolved dimeric arrangements were adopted for this amide in the presence of either Et_2O ($[\text{Bn}_2\text{NLi}]_2\text{-2Et}_2\text{O}$, Table 4, entry 2b) or HMPA (HexaMethylPhosphorAmide) ($[\text{Bn}_2\text{NLi}]_2\text{-2HMPA}$, Table 4, entry 2c).¹⁰¹ Crystals of the monobenzyl analogue BnN(H)Li grown in THF highlighted a polymeric ladder

Scheme 15. Unsolvated, Monosolvated or Disolvated Oligomers of DALi as a Function of the Ligand (S) Concentration¹¹²**Scheme 16.** Oligomeric Evolution of HMDSLi through Incremental Addition of Ethereal (S = THF, Et₂O) Ligands^{114–116}

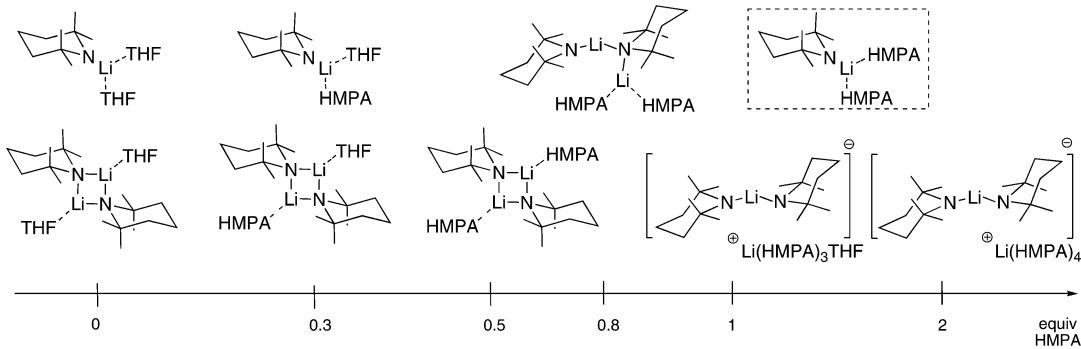
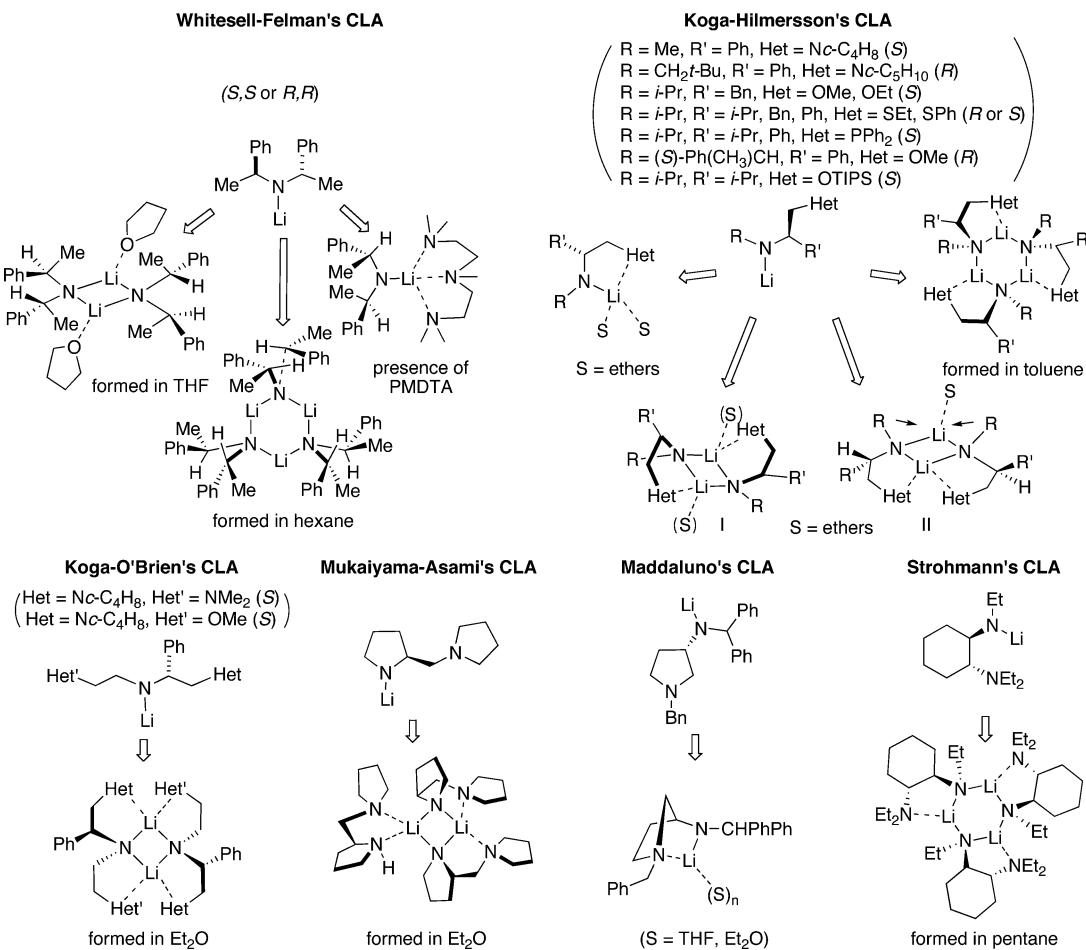
structure complexed by molecules of THF ($\{[\text{BnN(H)}\text{Li}]_2\cdot\text{THF}\}_\infty$, Table 4, entry 3).¹⁰² Crystals of *t*-BuNHLi grown in hexane also evidenced a ladder sequence, this time placed within a cyclic octamer ($\{[\text{t-BuNHLi}]_2\}_4$, Table 4, entry 4).¹⁰³ Lithium pyrrolidide led to solid-state aggregates, when grown in the presence of TMEDA or PMDTA in hydrocarbon solution, that corresponded to a disolvated ladder tetramer with the diamine ($\{[\text{c-C}_4\text{H}_8\text{NLi}]_2\cdot\text{TMEDA}\}_2$, Table 4, entry 5a) and a semiladder organization with PMDTA. The latter consisted in two attached N–Li–N–Li rings with two terminal NLi units complexed by the triamine ($\{[\text{c-C}_4\text{H}_8\text{NLi}]_3\cdot\text{PMDTA}\}_2$, Table 4, entry 5b).¹⁰⁴ Amides Ph(Me)NLi and Ph(naphthyl)NLi, mixed with TMEDA and PMDTA, also led to crystals examined by X-ray diffraction.¹⁰⁵ With the diamine, the formation of a disolvated cyclic dimeric complex was observed for Ph(Me)NLi ([Ph(Me)NLi]₂·2TMEDA, Table 4, entry 6), while a monosolvated monomeric arrangement was found for Ph(naphthyl)NLi ([Ph(naphthyl)NLi]·TMEDA, Table 4, entry 7a). Note the unusual tricoordinated Li atom encountered in this case. A monosolvated monomeric complex was also depicted for the latter amide with the triamine, this time placing the Li cation in a normal tetrahedral sphere of coordination ([Ph(naphthyl)NLi]·PMDTA, Table 4, entry 7b). The solid-state structure obtained for Ph₂NLi and PhCH=C=NLi in the presence of TMEDA matched with the disolvated cyclic dimers [Ph₂NLi]₂·2TMEDA (Table 4, entry 8)¹⁰⁶ and [PhCH=C=NLi]₂·2TMEDA (Table 4, entry 9), respectively.¹⁰⁷ With regard to lithium amides with possible intramolecular complexations with the lithium atom, few X-ray structures have been recorded, and they clearly showed the participation of intermolecular heteroatoms.¹⁰⁸

2.1.2.2. Structures in Solution (Table 5). NMR analyses of DALi conducted in pure hexane, pentane, or toluene showed the coexistence of dimeric and trimeric cyclic oligomers ($[\text{DALi}]_2$ and $[\text{DALi}]_3$, Table 5, entry 1a), in addition to unclarified higher-size oligomers ($[\text{DALi}]_{n>3}$).¹⁰⁹ Investigating the solution structure of the same amide in THF revealed multiplicities in accordance with the presence of a cyclic aggregate assigned to a disolvated dimer ($[\text{DALi}]_2\cdot2\text{THF}$,

Table 5, entry 1b), identical with its corresponding crystallographic structure (Table 3, entry 1c).^{94,109,110} Disolvated dimeric arrangements were also observed in S = dimethoxy- and diethoxyethane,³⁷ as well as in the presence of Et₂O, BuOMe, *t*-BuOMe, (substituted) THF, THP, TMEDA, and MeOCH₂CH₂NR₂ ($[\text{DALi}]_2\cdot2\text{S}$, Table 5, entry 1b).¹¹¹ Note, however, that, depending on the “ligand/solvent concentration”, partially solvated trimeric oligomers, in addition to dimers, were detected (Scheme 15).¹¹² Indeed, increasing amounts of ethereal ligands such as oxetane, THF, diethyl ether, or again diisopropylamine were added to a solution of DALi in hydrocarbon (pentane, toluene), in which the unsolvated dimeric and trimeric arrangements were coexisting. The progressive formation of mono and disolvated dimers and trimers were observed, the proportions for each species depending on the ligand type and concentration. In all cases, a large excess of base (S) was in favor of the single presence of the disolvated dimer.

Spectroscopic studies made on DALi in neat TMEDA also evidenced a cyclic dimer with a η^1 -coordinated diamine ligand on each lithium cation (Table 5, entry 1b).⁹³ With THF easily and rapidly replacing TMEDA, this diamine proved to be a poor ligand for DALi. This is in contrast with the observation made upon adding HMPA, which was found to be able to displace the THF of solvation and afforded preferentially the disolvated HMPA–dimeric complex ($[\text{DALi}]_2\cdot2\text{HMPA}$, Table 5, entry 1b).¹¹³ Treatment of DALi with (R,R)-TMCDA in hydrocarbon afforded exclusively a monosolvated monomer ($[\text{DALi}]\cdot\text{TMCDA}$, Table 5, entry 1c).¹¹¹

Examining next the structure of HMDSLi in solution, the addition of ethers (S) such as THF derivatives (THF, 2-MeTHF, 2,2-Me₂THF), Et₂O, *i*-PrOMe, BuOMe, *t*-BuOMe, or THP to a hydrocarbon solution of this amide (pentane,¹¹⁴ toluene¹¹⁵) respected the following evolution (Scheme 16): (i) pure HMDSLi in pentane corresponded to a mixture of two or more unsolvated cyclic oligomers ($[\text{HMDSLi}]_{n>2}$, Table 5, entry 2a); (ii) progressive addition of ethereal ligand led to the presence of first monosolvated dimers ($[\text{HMDSLi}]_2\cdot\text{S}$) and then disolvated ($[\text{HMDSLi}]_2\cdot2\text{S}$), while the initial unsolvated

Scheme 17. TMPLi·HMPA Solvates Formed upon Addition of HMPA onto a THF Solution of TMPLi¹²³Scheme 18. CLAs Being the Object of Structural Characterizations (X-ray, NMR): Whitesell–Felman’s,^{3b,134–136} Koga–Hilmersson’s,^{137,138} Koga–O’Brien’s,¹³⁹ Mukaiyama–Asami’s,¹⁴⁰ Maddaluno’s,¹⁴¹ and Strohmann’s CLAs^{21d}

species decreased; (iii) the stoichiometric [ligand/HMDSLi] ratio turned out to be in favor of the main formation of disolvated dimer ($[HMDSLi]_2 \cdot 2S$, Table 5, entry 2b); and (iv) forms of monomeric solvates started to be observed once a large excess of ligand was introduced ($[HMDSLi] \cdot nS$, $n = 2–4$, Table 5, entry 2b).^{114–116} Solvation by monoamine ligands has then been examined and went more or less along the same evolution.¹¹⁷ A crystalline sample of the $[HMDSLi]_2 \cdot 2\text{pyr}$ dimer was even characterized (Table 5, entry 2b).

A study made on the influence of polydentate amines and ether solvates brought the following information about the affinity in solution for HMDSLi of the TMEDA diamine and the PMDTA triamine:¹¹⁸ (i) addition of TMEDA to pure

HMDSLi in pentane afforded a monomeric structure of the amide in which the lithium was chelated by TMEDA ($[HMDSLi] \cdot \text{TMEDA}$, Table 5, entry 2c), (ii) TMEDA could not displace the THF coordination on preformed $[HMDSLi]_2 \cdot 2\text{THF}$ complex, and (iii) treatment by the PMDTA triamine gave a tricoordinated monomer ($[HMDSLi] \cdot \text{PMDTA}$, Table 5, entry 2d). Progressive addition of HMPA to the monomer–dimer mixture of HMDSLi in THF provided a complex evolution of the species.¹¹⁵ Excess of this chelating agent (>2 equiv/Li) led to a disolvated monomer ($[HMDSLi] \cdot 2\text{HMPA}$) and a tetrasolvated separated ion pair (Table 5, entry 2e).

The TMPLi lithium amide was found to correspond to a monomer/dimer mixture in THF, the dimeric oligomer being predominant and both forms being disolvated ($[{\text{TMPLi}}]_2 \cdot 2\text{THF}$ and $[{\text{TMPLi}}]_2 \cdot 2\text{THF}$, Table 5, entry 3b),^{118a,119–121} while organized as higher-size oligomers (planar trimer $[{\text{TMPLi}}]_3$ and tetramer $[{\text{TMPLi}}]_4$) in hydrocarbon solvents (Table 5, entry 3a).^{120–122} Addition of TMEDA to a hydrocarbon solution of TMPLi afforded a mixture of unsolvated oligomers with monosolvated monomer and open dimer consistent with the one already observed through the crystallographic studies.¹²² Addition of HMPA, performed from the monomer/dimer mixture of this reactant in THF, was revealed to be more tedious.^{113a,123} Seven new HMPA solvates formed progressively with the incremental addition of the phosphoramido (Scheme 17), and a large excess of the latter was found to favor the main presence of the TMPLi monomer disolvated by HMPA (Scheme 17, framed structure).

Results obtained for other lithium amides that have been the object of solution structure studies are also gathered in Table 5. Thus, lithium isopropylcyclohexylamide (ICALi) was depicted as a 1:1 mixture of stereoisomeric dimers in THF, without precise information about the solvation ($[{\text{ICALi}}]_2 \cdot n\text{THF}$, n undetermined; Table 5, entry 4).¹²⁴ Lithium dicyclohexylamide was found to behave identically to DALi in THF or in the presence of HMPA, organizing as a disolvated dimeric complex ($[{\text{c-Hex}_2\text{NLi}}]_2 \cdot 2\text{S}$, $\text{S} = \text{THF, HMPA}$; Table 5, entry 5).¹²⁵ Crowded lithium bis(2-adamantyl) amide was characterized as a disolvated monomer, whatever the basic THF or HMPA solvation ($[{\text{(2-adamantyl)}_2\text{NLi}}] \cdot 2\text{THF}$ and $[{\text{(2-adamantyl)}_2\text{NLi}}] \cdot 2\text{HMPA}$, Table 5, entry 6a),¹²⁶ and a monomer, this time monosolvated, was highlighted in the presence of TMEDA ($[{\text{(2-adamantyl)}_2\text{NLi}}] \cdot \text{TMEDA}$, Table 5, entry 6b).¹²⁶ Lithium diethylamide was examined in oxetane, THF, or Et_2O , and cyclic dimers ($[{\text{Et}_2\text{NLi}}]_2 \cdot n\text{S}$) and trimers ($[{\text{Et}_2\text{NLi}}]_3 \cdot n\text{S}$), in addition to four-, five-, and six-runged ladders, were detected, without precision about their solvation (Table 5, entry 7).¹²⁷ The solution structure of the lithium monoalkylamide *t*-BuNHLi has also been investigated (Table 5, entry 8),¹²⁸ but the exact oligomerization level could not be precisely determined. The authors suggested a cyclic trimer or prismatic tetra-, hexa-, or octamers. NMR studies run on a low THF concentration lithium diphenylamide solution highlighted the single presence of a di- or tri-THF-solvated cyclic dimer ($[{\text{Ph}_2\text{NLi}}]_2 \cdot n\text{THF}$, $n = 2$ or 3; Table 5, entry 9).^{2b} A di- or tri-THF-solvated monomer showed up upon addition of THF until becoming the main species at high THF concentration ($[{\text{Ph}_2\text{NLi}}] \cdot n\text{THF}$, $n = 2$ or 3; Table 5, entry 9). Structural determination of Et_2O - and TMEDA-solvated lithium (2-phenylvinylidene)amide $\text{PhCH}=\text{C}=\text{NLi}$ complexes in solution were in favor of $n\text{S}$ -solvated cyclic dimers, with n undetermined when $\text{S} = \text{Et}_2\text{O}$ ($[{\text{PhCH}=\text{C}=\text{NLi}}]_2 \cdot n\text{S}$, Table 5, entry 10a) and $n = 2$ if $\text{S} = \text{TMEDA}$ ($[{\text{PhCH}=\text{C}=\text{NLi}}]_2 \cdot 2\text{TMEDA}$, Table 5, entry 10b).¹²⁹ At last, experimental structural data were obtained for the simplest lithium amide LiNH_2 using a combination of gas-phase synthesis and wave spectroscopy. A monomeric planar structure was pointed out.¹³⁰

Examining the case of CLAs reveals particularly relevant information, since a good knowledge of their conformation in solution allows us to better understand the stereochemical outcomes of the reaction processes in which they are involved. CLAs indeed proved their efficiency as chiral bases in enantioselective deprotonations¹³¹ and as chiral ligands in

enantioselective nucleophilic 1,2-¹³² and 1,4-additions.¹³³ Mainly six categories of CLA—Whitesell–Felman’s, Koga–Hilmersson’s, Koga–O’Brien’s, Mukaiyama–Asami’s, Maddaluno’s, and Strohmann’s CLAs (Scheme 18)—have been the object of structural (crystallography and NMR spectroscopy analyses) characterizations. Thus, Whitesell–Felman’s CLA crystallized as a disolvated dimeric complex in THF,¹³⁴ while an unsolvated cyclic trimer formed in hexane.¹³⁵ In the presence of PMDTA, a monomer complex was isolated in which the lithium cation was coordinated to the three nitrogen atoms of the ligand.¹³⁶ From Koga–Hilmersson’s CLAs, which derive from the previous ones considering an additional intramolecular chelating heteroatom,^{3b,137,138} two dimeric structures I and II, organized around $\text{N}-\text{Li}-\text{N}-\text{Li}$ quadrilaterals, were observed in ethers, as crystals and in solution. In arrangement I, both lithiums were seen to be similarly tricoordinated by the two lithium amide nitrogens of the quadrilateral and the intramolecular heteroatom. An additional solvation (one THF per lithium) could be observed as was the case for sulfur derivatives.^{138h} In dimeric structure II, the two lithiums were not found to be equally coordinated. One lithium would be tetracoordinated, being surrounded by a double intramolecular coordination in addition to the two lithium amide nitrogens. The second one would be tricoordinated by the two lithium amide nitrogens of the quadrilateral and one molecule of THF. The presence of disolvated monomer was also notified and its importance would depend on the structure itself, the concentration, and the solvent.^{138c} A study run in toluene evidenced an unsolvated trimer in which each lithium was establishing a coordination with the intramolecular atom.^{138f} Note also the recent observation of a cyclic dimer in toluene with the very hindered lithium amide analogue derived from (*S*)-*N*-isopropyl-*O*-triisopropylsilylvalinol.^{138j} Examining next by NMR in Et_2O or THF solution Koga–O’Brien’s CLAs, for which the nitrogen of the lithium amide bears two substituents with each containing a chelating heteroatom, evidenced a nonsolvated dimer intramolecularly and symmetrically coordinated.¹³⁹ The Mukaiyama–Asami’s CLAs series also showed a dimeric structure with intramolecular coordinations between the lithium cations and the heteroatoms in the γ -position ($\text{LiN}-\text{C}-\text{C}-\text{Het}$ sequence). NMR studies¹⁴⁰ first conducted in THF indicated the intramolecular coordination but did not exhibit well-resolved signals required for a full structure determination. When formed in diethyl ether, an immediate precipitation occurred. The addition of the amine precursor provoked the dissolution of the solid formed, and the NMR experiments finally proved the presence of an $[\text{amide}]_2$ -amine chelate. Similar results were observed when introducing TMEDA to the amide precipitate solution. Maddaluno’s CLAs correspond to 3-aminopyrrolidine lithium amides, and a disolvated azanorbornyl-like conformation, due to an intramolecular coordination between the lithium cation and the pyrrolidine nitrogen, was described in one case, however, without indications about the aggregation degree (monomer or dimer) and the solvation.¹⁴¹ Finally, an unsolvated cyclic trimer was observed by Strohmann, from a (*R,R*)-TECDA lithium amide derivative isolated in the solid state from pentane solution.^{21d}

To conclude with lithium amide structural aspects, one can note that the main tendency is that mono and bidentate ethereal or amino solvents favor the formation of homoaggregates containing a dimeric core (either as a sole dimer or engaged in a ladder or a polymeric sequence), both in the solid

state and in solution, while higher-size oligomers, such as trimers, cubic and planar tetramers, and hexamers, rather form in hydrocarbon solutions. The observation of monomeric solvates requires being in the presence of amide substituents presenting a big steric hindrance or using hindered diamines or, again, being in the presence of polyethers or triamine additives. It actually remains difficult to date to propose immutable arguments for a relationship between the observed ground-state structures and reactivity for this class of lithio derivatives, in spite of the numerous efforts dedicated to such a purpose, in particular by Collum^{109–119,122–129} or Williard.^{94,99,110b,c} Part of the explanation is due to the fact that aggregation is highly sensitive to solvent or basic additive concentrations: in a single solution, a lithium amide can be monomeric to trimeric, while mono- to di- and trisolvated. Analyses by NMR of the structures in solution often evidence a complex mixture containing several of these solvates, with one becoming the main species at high solvent concentration. As an illustration of the structure/reactivity relationship that emerged, one can evoke observations made when studying enolization reactions in the presence of lithium amides: (i) enolization of pinacolone with disolvated $[DALi]_2 \cdot 2THF$ in hydrocarbon solution led to a tetrameric THF-solvated enolate, while carrying out the same transformation from unsolvated DALi (mixture of dimer, trimer, and higher-size homoaggregates) under the same conditions afforded the enolate as an unsolvated hexameric aggregate;⁹⁴ (ii) using solvent-free DALi for the enolization reaction of 3-pentanone led to a 1:1.5 mixture of *E* and *Z* isomers, while a 3:1 ratio could be reached when engaging $[DALi]_2 \cdot 2THF$;¹⁰⁹ (iii) reacting the same 3-pentanone with the monomeric hindered bis(2-adamantyl) lithium amide THF, TMEDA, or HMPA solvates allowed the obtention of very high *E/Z* selectivities (in the 25:1 to 80:1 range).¹²⁶ We are well aware that the chosen applications above are not representative of the whole set of studies dedicated to the structure/reactivity correlations made on lithium amide species. Referring to all of the examples quoted in the literature would require the writing of an entire paper, which is not the aim in this review. Note especially that (i) lithium amides cover a wide spectrum of reactivity, since they can act either as bases, nucleophiles, or ligands, which explains why these derivatives are also the object of numerous studies, and (ii) a particular effort has been dedicated to the understanding of structure/reactivity correlations when the lithium amides are chiral, in order to interpret the inductions.^{131–133}

2.1.3. Lithium Alkoxides, Phenoxides, and Enolates ($O-Li$).

2.1.3.1. Lithium Alkoxides.

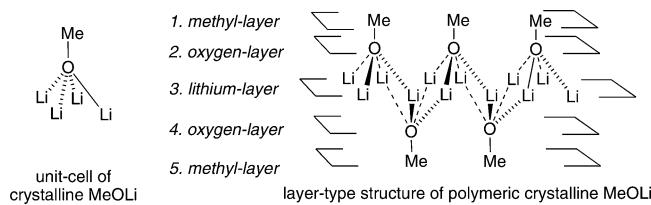
Results are presented for MeOLi, *t*-BuOLi, Ph(Me)₂COLi, Me(*c*-Pr)₂COLi, (HC≡C)(Me)₂COLi, *t*-Bu₃COLi, and chiral lithium alkoxides.

Although alkali metal alkoxides present numerous and useful synthetic applications, both as single reactants or associated with another organometallic species (superbases), their structural description in the solid state or in solution has been relatively little studied. Regarding lithium alkoxides, the covalent character of the O–Li bond was underlined,^{142a} and the question of their solubility in organic solvents was often evoked.¹⁴² About the latter point, the following tendency seems to be retained: straight-chain ROLi (R = Pr, Bu) present a low solubility in hydrocarbon and dissolve pretty well in hydroxyllic solvents, while, in contrast, branched-chain ROLi have a good solubility in hydrocarbons or ethers but precipitate in their corresponding alcohol.^{142b,c} Increasing the number of carbons in the alkyl chain favors the solubility. The low capacity for

“small” lithium alkoxides (MeOLi, EtOLi) to dissolve either in hydrocarbons, ethers, or alcohol may justify the difficulties encountered to get accurate structural data.

Analyses have been, however, conducted on crystalline powders of lithium methoxide isolated from a methanol solution. An unsolvated polymer was mentioned with a “layer-type structure”.^{6b,143} The unit cell was found to correspond to a square-based pyramid, the methoxy anion being bounded to four lithium cations (Scheme 19, left). The

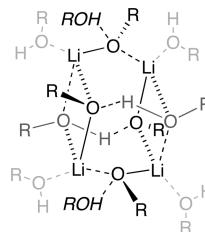
Scheme 19. Layer-type Crystallographic Structure of Lithium Methoxide¹⁴³



polymer could be described as a five-layer system (Scheme 19, right) with a central layer made of lithium atoms, surrounded on each side by an oxygen layer, and the two external layers would be made of the methyl appendages.

A solvate with a 1:2 MeOLi/MeOH ratio has also been described.¹⁴⁴ The unit would include four lithium atoms engaged in the $[Li_4(\mu-OR)_4(\mu-ROH)_2(ROH)_4] \cdot 2ROH$ general structure depicted Scheme 20. Note that the solvate alcohol (2ROH) was depicted as falling off easily to afford polymeric MeOLi.

Scheme 20. Crystalline Solvate $[Li_4(\mu-OR)_4(\mu-ROH)_2(ROH)_4] \cdot 2ROH$ ¹⁴⁴



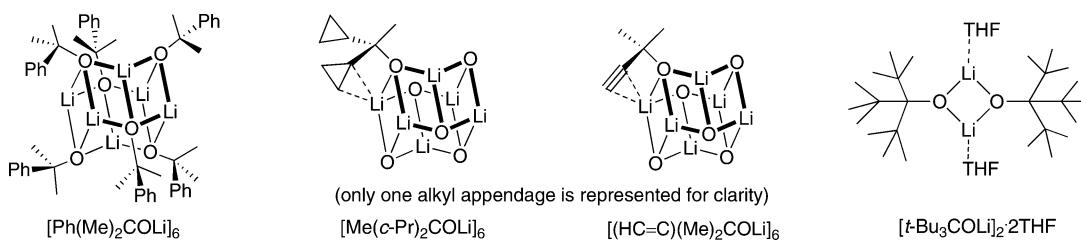
The fact remains that most of the known structures that have been established for alkoxides account at least four carbon atoms. Thus, BuOLi would correspond to a cubic tetramer in THF, however, without certainty.^{40a} Its isomer *tert*-butoxide was studied more precisely. First, *t*-BuOLi crystals grown in hexane evidenced a prismatic hexameric unit ($[t\text{-}BuOLi]_6$, Scheme 21, left).¹⁴⁵ An unusual prismatic octamer was also characterized for crystals isolated from a cooled solution of

Scheme 21. Prismatic Hexameric¹⁴⁵ (left) and Octameric¹⁴⁶ (right) Crystallographic Arrangements of *t*-BuOLi Grown in Hydrocarbon Solvents^a

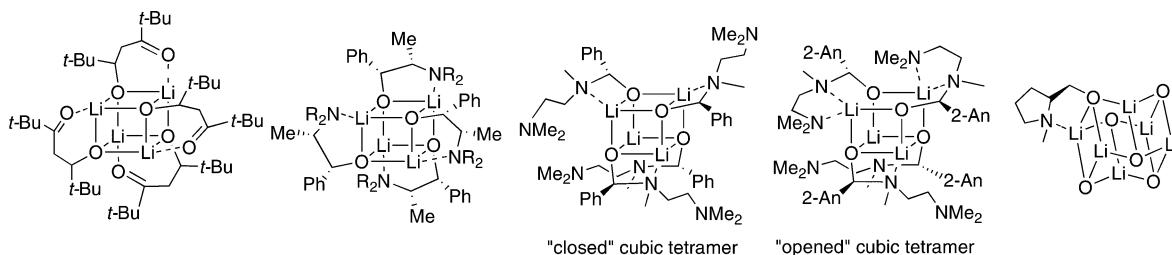


^a *t*-Bu appendages have been omitted for clarity.

Scheme 22. Crystallographic Structures of $[\text{Ph}(\text{Me})_2\text{COLi}]_6$,^{145a} $[\text{Me}(c\text{-Pr})_2\text{COLi}]_6$,¹⁴⁸ $[(\text{HC}\equiv\text{C})(\text{Me})_2\text{COLi}]_6$,⁵³ and $[\text{t-Bu}_3\text{COLi}]_2 \cdot 2\text{THF}$ ¹⁴⁹



Scheme 23. Structure (solid state and solution) of Chiral Lithium Alkoxides Derived from (i) an Aldol Condensation (left),^{150a} (ii) Ephedrine (middle left),^{59a,150b,c} (iii) Aminoarylmetoxides (middle, middle right),¹⁵² and (iv) N-Methylprolinol (right)¹⁵¹



^aOnly one N-methylpyrrolidinomethyl group is presented for clarity.

commercial $t\text{-BuOLi}$ in hexane/pentane ($[\text{t-BuOLi}]_8$, Scheme 21, right).¹⁴⁶ In the few attempts to clarify the structure of $t\text{-BuOLi}$ in THF solution (NMR, IR), a cubic tetrameric organization was additionally proposed, but without formal proof.¹⁴⁷

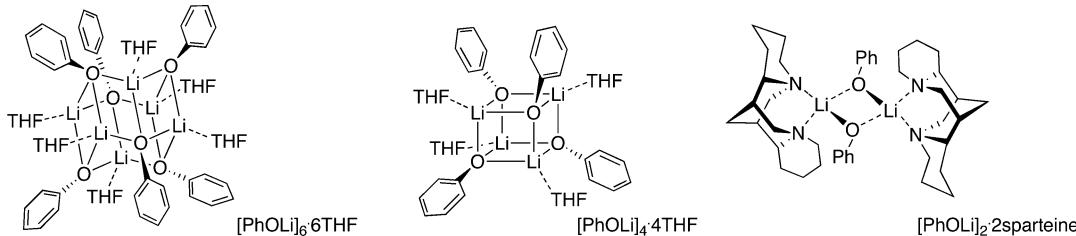
Among other ROLi alkoxides from which structural information was obtained, one can retain the 1-methyl-1-phenylethoxide $[\text{Ph}(\text{Me})_2\text{COLi}]$,^{145a} 1,1-dicyclopropylethoxide $[\text{Me}(c\text{-Pr})_2\text{COLi}]$,¹⁴⁸ and 2-methylbut-3-yne 2-oxide $[(\text{HC}\equiv\text{C})(\text{Me})_2\text{COLi}]$ ⁵³ samples, for which crystals, grown in hydrocarbon solvents, corresponded to prismatic hexameric structures. In some cases, the lithium cations were found to also interact with the R appendage thanks to electrostatic ($\text{Li}\cdots\text{C}$) or π -cation interactions (Scheme 22, middle). Interestingly, studying the structure of $\text{Ph}(\text{Me})_2\text{COLi}$ in solution showed that the hexameric form depicted at the solid state remained in hydrocarbon solution, and an equilibrium between this hexamer and a tetrameric form would settle in the presence of THF.^{145a} X-ray analyses carried out on crystals of the very hindered tri-*tert*-butylmethoxide $t\text{-Bu}_3\text{COLi}$, grown in either THF or hexane, evidenced a dimer, dissolved in the presence of the THF solvent (Scheme 22, right).¹⁴⁹

Adding a heteroatom onto the R appendage of ROLi alkoxides led to intramolecular coordinations between this heteroatom and the lithium cations.^{59a,150} Mostly cubic tetramers (Scheme 23) were described with these derivatives, either from X-ray crystallographic data or in solution thanks to the NMR spectroscopy technique. An unsolvated prismatic hexamer was however observed for the chiral alkoxide derived from N-methylprolinol (Scheme 23, right).¹⁵¹ Note among all the very special case of chiral aminoarylmetoxides for which the amino substituent derives from *N,N,N'*-trimethylethylenediamine. A cubic tetrameric arrangement was observed that could “close” when the aryl moiety corresponded to a phenyl group and “open” when working with a 2-anisyl group (Scheme 23, middle and middle right).¹⁵²

2.1.3.2. Lithium Phenoxides.

Results are presented for PhOLi .

The structures of lithium phenoxides ArOLi , obtained by deprotonation of the ArOH related precursors with butyllithium, have been examined widely in solution and, in particular, in weakly polar aprotic solvents such as 1,3-dioxolane, 1,2-dimethoxyethane, pyridine, tetrahydrofuran, diethyl ether, 2,6-lutidine, or triethylamine.^{153,154} The degree of oligomerization could be established from various methods such as vapor pressure barometry and ^{13}C (chemical shifts and spin–lattice relaxation time) and ^7Li (nuclear quadrupole coupling constants) NMR spectroscopy. X-Ray data were also obtained from crystals grown in these solvents.^{153f,155,156} Monomers, as well as dimeric, trimeric, tetrameric, and/or hexameric oligomers, formed, depending on one hand on steric and electronic effects related to the substitution on the aromatic ring and on the other hand on the Lewis basicity of the solvent. Thus, the general trends were found: (i) phenoxides with no ortho substituents would mainly organize as cubic tetramers as the single oligomer or in addition to hexamer when the solvent is dioxolane or THF and dimer in the presence of pyridine at low temperature and concentration; (ii) ortho substitution(s) would advantage smaller sized aggregates, presumably for steric reasons, as observed for 2,6-dimethylphenoxide, which corresponded to a dimer in all conditions, and 2,6-di-*tert*-butylphenoxide, which showed monomeric form; (iii) increasing the basicity of the oxygen anion, which means examining phenoxides bearing electron donating substituents, would be in favor of bigger oligomers and vice versa, while (iv) increasing the basicity of the solvent would promote deaggregation phenomenon (the same phenoxide can be hexamer in dioxolane, either tetramer in THF, and predominantly dimer in pyridine). In the same context, addition of TMEDA provoked the dissociation of hexa- and tetramers to exclusively dimers.¹⁵⁷ Note that running the deprotonation of the ArOH with HMDSLi^{155b,156} (in THF or pyridine) before crystal-

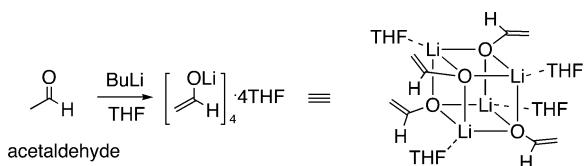
Scheme 24. Crystalline Hexameric, Tetrameric, and Dimeric Oligomers of Solvated PhOLi^{15b,153f,155g}

lization of the aggregates to carry out X-ray analyses allowed the observation of an unusual trisolvated trimeric arrangement.

The simplest lithium phenoxide PhOLi was found to coexist as a 1:1 mixture of a tetramer and a hexamer in dioxolane solution.^{153f} In THF, the tetrameric arrangement was predominant,^{153f} and analyzing the sample in pyridine at low temperature and low concentration led to the additional observation of dimer.^{153b} Both hexa- and tetrameric oligomers crystallized in THF.^{153f} A hexasolvated hexamer was recovered using butyllithium to deprotonate the phenol ([PhOLi]₆·6THF, Scheme 24, left),^{153f} while a tetrasolvated tetramer formed using the HMDSLi base ([PhOLi]₄·4THF, Scheme 24, middle).^{155g} A crystal structure of lithium phenoxide complexed by (−)-sparteine was also analyzed and revealed a disolvated cyclic dimer ([PhOLi]₂·2(−)-sparteine, Scheme 24, right).^{15b}

2.1.3.3. Lithium Enolates.^{6c,56,153a,158} Results are presented for enolates derived from aldehyde (acetaldehyde), ketone (pinacolone, cyclopentanone, isobutyrophenone), ester (*tert*-butyl propionate, *tert*-butyl 2-methylpropionate, methyl 3,3-dimethylbutanoate, ethyl *N,N*-diethylglycinate, pyrrolidine vinylogous urethane, and *tert*-butyl α-cyanoacetate), and amide (*N,N*-dimethylpropionamide, *N,N*-dimethylcycloheptatrienecarboxamide).

Regarding the structure of the simplest enolate, lithium enolate of acetaldehyde was described in THF solution, thanks to the NMR technique, as a tetrasolvated tetramer ([CH₂=C(H)OLi]₄·4THF, Scheme 25).¹⁵⁹

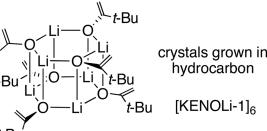
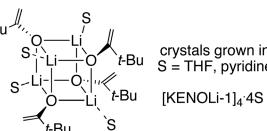
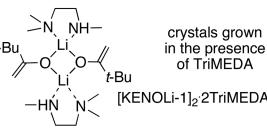
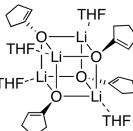
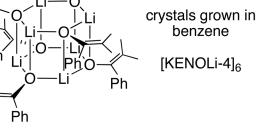
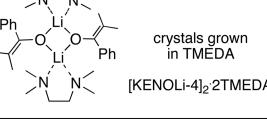
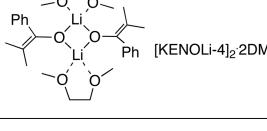
Scheme 25. Structure in THF Solution of Lithium Enolate of Acetaldehyde¹⁵⁹

With regard to lithium ketone enolates (Table 6), one can note that those derived from pinacolone (KENOLi-1, Table 6, entry 1),^{157,160} cyclopentanone (KENOLi-2, Table 6, entry 2), cyclohexanone (KENOLi-3, Table 6, entry 2),^{157,160a,161} and isobutyrophenone (KENOLi-4, Table 6, entry 3)^{157,162,163} were the most studied. The first structural data of the lithium enolate of pinacolone was obtained from an X-ray analysis of crystals isolated from a THF solution. It evidenced a THF-tetrasolvated cubic tetramer ([KENOLi-1]₄·4THF, Table 6, entry 1b).^{160a} A similar arrangement was reported from a pyridine medium ([KENOLi-1]₄·4pyridine, Table 6, entry 1b).^{160e} When grown in an apolar solvent (hydrocarbon), an unsolvated prismatic hexameric arrangement was rather supported ([KENOLi-1]₆, Table 6, entry 1a).^{160b,d} In the presence of the TriMEDA

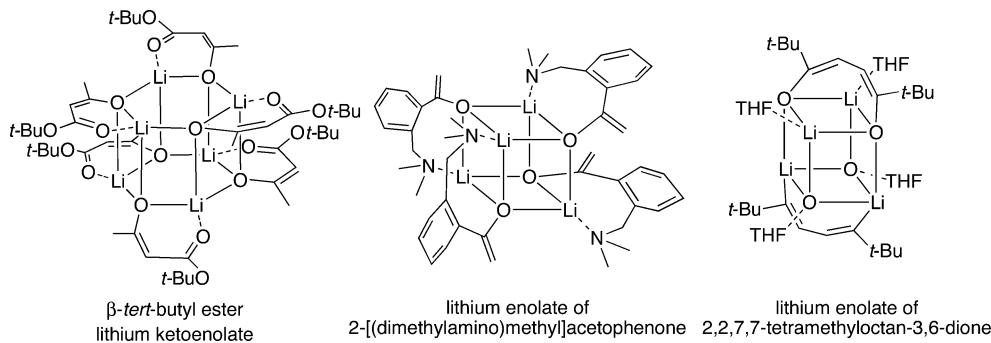
diamine (*N,N,N'*-trimethylethylenediamine), a disolvated dimer (still crystallographic data) was described in which each lithium cation was found to be chelated by one diamine molecule ([KENOLi-1]₂·2TriMEDA, entry 1c).^{160c} Examining next the structure of the lithium enolate of cyclopentanone¹⁶¹ led to comparable descriptions if considering the crystals isolated from a THF solution, with the highlighting of a tetrasolvated cubic tetramer ([KENOLi-2]₄·4THF, Table 6, entry 2, X-ray data).^{160a} Such an arrangement was found to remain in ethereal solutions (S = DME, THF, and THF/Et₂O media) for the same cyclopentanone enolate as for the cyclohexanone enolate congener ([KENOLi-2]₄·4S and [KENOLi-3]₄·4S, Table 6, entry 2, NMR data, top).^{161c,e} Dimers would form in the presence of TMEDA in the solutions ([KENOLi-2]₂·2TMEDA and [KENOLi-3]₂·2TMEDA, Table 6, entry 2, NMR data, bottom).^{161c} The latter result, obtained by using the method of continuous variation in which ensembles of homo- and heteroaggregates were monitored by ⁶Li NMR spectroscopy, was not observed when performing NMR–HMPA titrations.^{161e} Concerning now the structural information obtained for lithio-enolates of isobutyrophenone, recent crystallographic data brought out two unsolvated prismatic hexameric conformers (grown in benzene and that differ slightly in the conformations of the enolate moieties, ([KENOLi-4]₆, Table 6, entry 3, X-ray data) and a TMEDA-disolvated dimer ([KENOLi-4]₂·2TMEDA, Table 6, entry 3, X-ray data).¹⁶² Structural studies carried out in solution¹⁶³ led to the conclusion that a cubic tetrameric complex was present in S = THF and dioxolane, while in DME, the major oligomer corresponded to a disolvated dimer, in equilibrium with some tetramer (in a ≈ 85:15 ratio) ([KENOLi-4]₂·2DME ⇌ [KENOLi-4]₄·nS, Table 6, entry 3, NMR data).¹⁶³ Note that the solvation of the cubic tetramer was found to vary with the temperature, the less highly solvated species being favored at higher temperature. Interestingly, substituting the para-position of the phenyl group of isobutyrophenone by a phenyl appendage had the effect of showing the presence of monomer.¹⁶⁴ The latter became the main entity upon addition of HMPA.^{164e} Also a monomer was evidenced, in the presence of a dimer, when examining the lithium enolate of α-tetralone derivatives in dilute THF solution.^{165b}

Among other ketone enolates, one can evoke the data obtained from crystals grown in toluene of a lithium *β*-*tert*-butyl ester keto-enolate (Scheme 26, left).¹⁶⁶ An unsolvated prismatic hexamer, in which the lithium cations were seen to interfere with the carbonyl group of the ester moieties, was depicted. Crystals of the lithium enolate of 2-[dimethylamino)methyl]-acetophenone, grown in a diethyl ether solution, afforded another example of solvent-free oligomer, corresponding to a cubic tetramer in which all lithiums were coordinated by the amino appendage of the enolate itself (Scheme 26, middle).¹⁶⁷ Thus, a common point of the latter derivatives would be the

Table 6. Lithium Enolates of Ketones That Have Been the Object of Structural Studies (solid state and solution), from Pinacolone, from Cycloalkanones, and from Isobutyrophenone

Entry	Lithium enolate of	Solid-state structures (X-ray data)	Structures in solution (NMR data)	Ref
1a	pinacolone 	 crystals grown in hydrocarbon		160b,d
1b		 crystals grown in S = THF, pyridine	None	160a,e
1c	KENOLi-1	 crystals grown in the presence of TriMEDA		160c
2	cycloalkanones ($x = 1, 2$) 	 crystals grown in THF	 [KENOL-2]4·4S ($x = 1$) [KENOL-3]4·4S ($x = 2$) (S = THF, Et2O, HMPA, DME)	160a 161
3	iso-butyrophenone 	 crystals grown in benzene	 [KENOLi-4]4·nS (S = THF, dioxolane) (n = f(T))	162
	KENOLi-4	 crystals grown in TMEDA		163

Scheme 26. Unsolvated Structures (X-ray) of Lithium Ketone Enolates Bearing a Heteroelement on the Enolate Appendage^{166,167} and THF-Tetrasolvated Dimeric Complex of a Lithium Dienolate (X-ray, NMR)¹⁶⁸

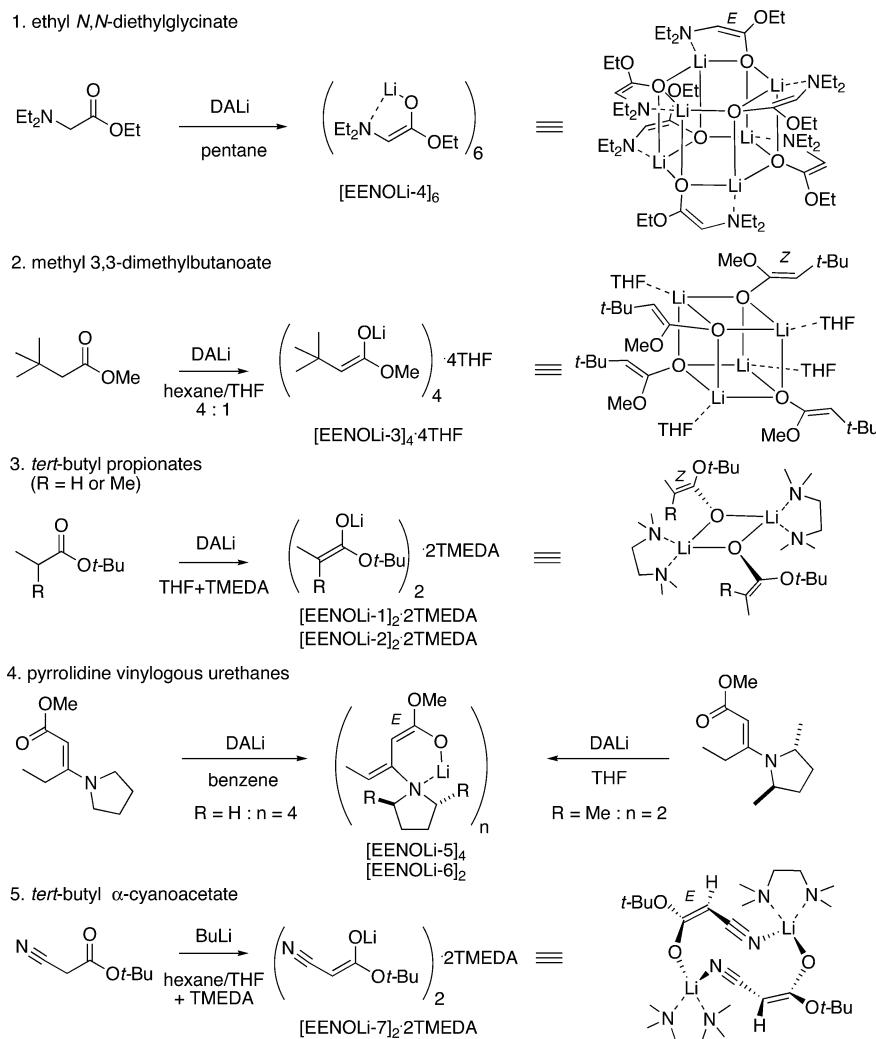


absence of solvation, replaced by intramolecular interactions between the lithium atom and heteroelements placed on the enolate appendage. Finally, one can evoke the THF-tetrasolvated cubic dimeric structure observed for the lithium dienolate derived from 2,2,7,7-tetramethyloctan-3,6-dione, both

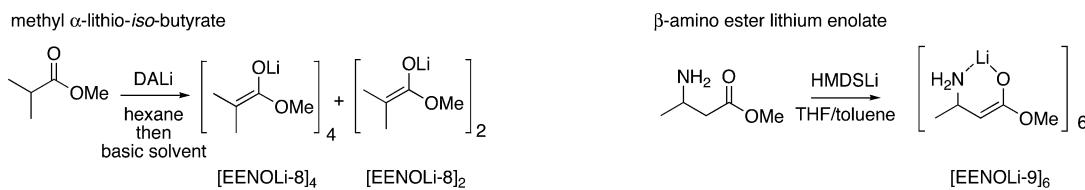
in the solid state by X-ray diffraction and in solution by diffusion NMR (Scheme 26, right).¹⁶⁸

About lithium ester enolates, X-ray structural information was obtained for those derived from *tert*-butyl propionate (EENOLi-1),¹⁶⁹ *tert*-butyl 2-methylpropionate (EENOLi-2),¹⁶⁹ methyl 3,3-dimethylbutanoate (EENOLi-3),¹⁶⁹ ethyl *N*-

Scheme 27. Crystallographic Structures of Lithium Ester Enolates Derived from Ethyl *N,N*-Diethylglycinate,¹⁷⁰ Methyl 3,3-Dimethylbutanoate,¹⁶⁹ *tert*-Butyl Propionates,¹⁶⁹ Pyrrolidine Vinylogous Urethane,¹⁷¹ and *tert*-Butyl α -Cyanoacetate¹⁷²



Scheme 28. Known Structures in Solution of Lithium Ester Enolates Methyl α -Lithioisobutyrate¹⁷³ and β -Amino Ester Lithium Enolate¹⁷⁴

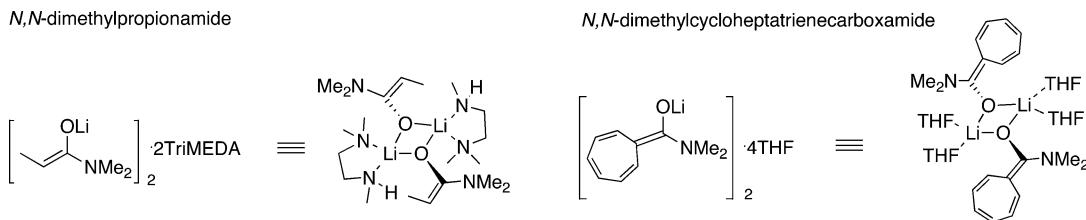


diethylglycinate (EENOLi-4),¹⁷⁰ pyrrolidine vinylogous urethanes (EENOLi-5 and EENOLi-6),¹⁷¹ and *tert*-butyl α -cyanoacetate (EENOLi-7)¹⁷² (Scheme 27).

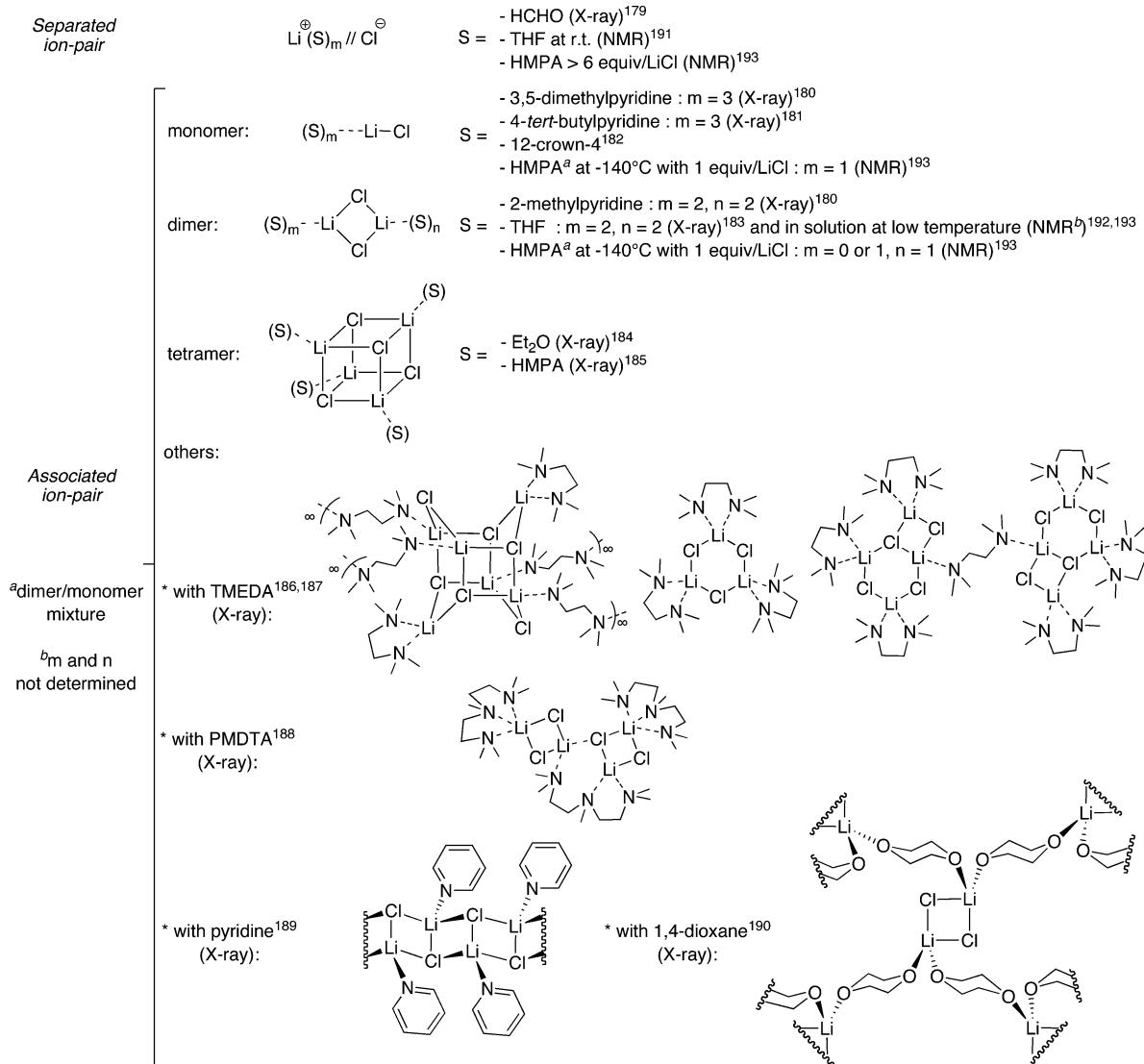
The general rule that postulates bigger oligomers when crystals are isolated from nonbasic solvents (hydrocarbons) and, by contrast, smaller oligomers when increasing the coordinative ability of the solvent is here corroborated. Thus, an unsolvated prismatic hexameric aggregate was depicted for the crystals of the enolate of ethyl *N,N*-diethylglycinate grown in pentane ($[EENOLi-4]_6$, Scheme 27, line 1).¹⁷⁰ Note, however, the intramolecular coordinations between the lithium cations and the diethylamino appendages. Tetrasolvated cubic tetramers rather formed in THF, as observed for the enolate of methyl 3,3-dimethylbutanoate ($[EENOLi-3]_4 \cdot 4\text{THF}$, Scheme

27, line 2).¹⁶⁹ Addition of TMEDA when preparing the crystals of the enolates of *tert*-butyl propionate and *tert*-butyl 2-methylpropionate provided dimeric oligomers with one TMEDA per Li cation ($[EENOLi-1]_2 \cdot 2\text{TMEDA}$ and $[EENOLi-2]_2 \cdot 2\text{TMEDA}$, Scheme 27, line 3).¹⁶⁹ The degree of oligomerization of the enolate of unsubstituted-pyrrolidine vinylogous urethane corresponded to an unsolvated tetramer for crystals isolated from benzene ($[EENOLi-5]_4$, Scheme 27, line 4, left), while its substituted-pyrrolidinic analogue grown in THF arranged in an unsolvated dimeric core ($[EENOLi-6]_2$, line 4 right).¹⁷¹ Note that, for the latter example, the steric hindrance added onto the heterocycle was also responsible for the smaller aggregation. Examining the structure of the enolate of *tert*-butyl α -cyanoacetate in the presence of TMEDA became

Scheme 29. Lithium Amide Enolates of Which Structural Data (X-ray) Are Known^{160c,175,176}



Scheme 30. Structures (X-ray and solution) of Anhydrous LiCl in Various Organic Solvents (S)



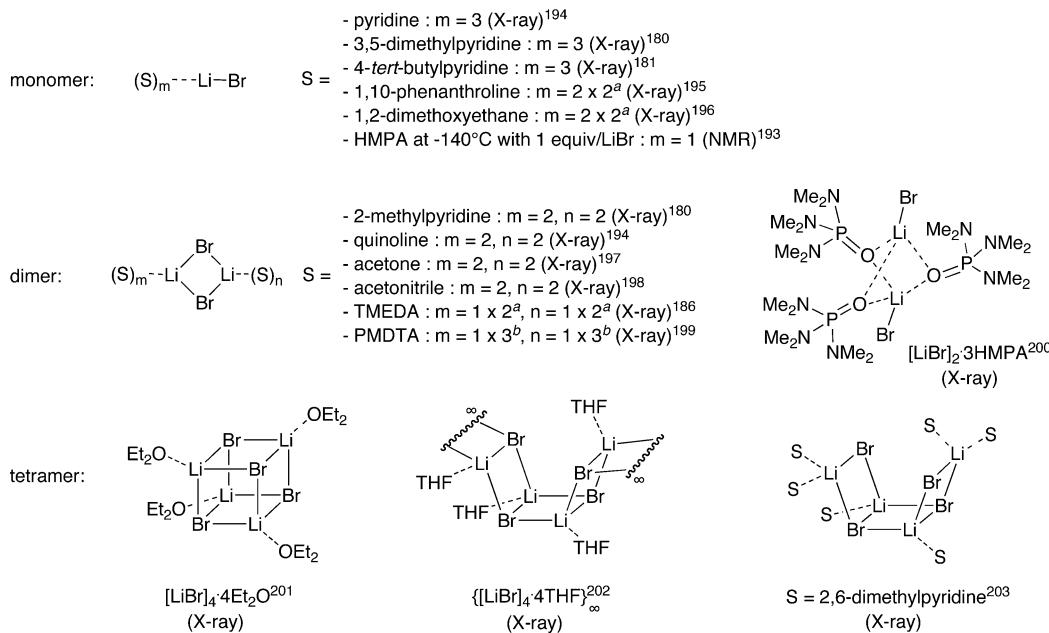
puzzling, with an unusual disolvated dimer organized in a 12-chain-ring core ($[\text{EENOLi-7}]_2\text{TMEDA}$, Scheme 27, line 5). The geometry of the enol double bond was seen to correspond to a *Z*-configuration when no intramolecular interactions with the lithium were involved and a *E*-configuration in the opposite case.

Few studies were devoted to finding structural data about lithium ester enolates in solution. Methyl α -lithioisobutyrate (EENOLi-8) was probably the first one for which the question of the degree of oligomerization in a solvent medium was raised.¹⁷³ It showed a tetramer/dimer mixture in THF ($[EENOLi-8]_4 + [EENOLi-8]_2$, Scheme 28, left), the smaller

oligomer becoming more abundant by a decrease of temperature or concentration.^{173a} Adding ligands able to bind lithium cation also promoted the formation of the dimer in the order DME < glyme-3 < 12-crown-4 ether < HMPA. Recently, the characterization of a β -amino ester lithium enolate (EENOLi-9) was carried out, and both crystallographic and NMR analyses, conducted from or in a 9.0 M THF/toluene solution, showed unsolvated prismatic hexameric arrangements in which the amino group coordinates lithium ($[EENOLi-9]_6$, Scheme 28, right).¹⁷⁴

Lithium amide enolates, in spite of showing a higher stability than ester enolates, proved to be the least depicted enolate

Scheme 31. Structures (X-ray and solution) of LiBr (associated ion pairs) with Organic Solvents



^aS establishes two coordinations with one Li. ^bS establishes three coordinations with one Li.

derivatives. Crystallographic descriptions are accessible for the lithium enolate of *N,N*-dimethylpropionamide, which was found to organize as a dimer in the presence of TriMEDA (Scheme 29, left)^{160c} and *N,N*-dimethylcycloheptatrienecarboxamide, also as a dimeric oligomer solvated by four molecules of THF (Scheme 29, right).^{175,176} Interestingly, when nonsymmetrical, the geometry of the double bond was determined as being opposite to that observed for the ester enolate.

To conclude with the class of lithium–oxygen species such as lithium alkoxides, phenoxides, and enolates, one can remark that, compared with lithium amides above, higher-sized homoaggregates tend to subsist in the presence of basic solvents. The formation of hexamers and tetramers is often observed, either unsolvated or solvated by monodentate additives, while dimers form with bidentate solvating entities. Monomers may exist, but for particularly hindered substrates that are not presented here or in polar aprotic solvents (HMPT, DMSO, DMF). As regards the structure/reactivity relationship, in spite of the fact that it is still not easy to provide details about the exact participation of the aggregates in the reaction mechanisms, more has been elucidated for enolate compounds.^{158b} Similarly with the previous lithiated derivatives, the nature of the solvent and, thus, the degree of aggregation are expected to influence the rate, regiochemistry, and stereochemical outcome of the reactions in which those species are involved. Among fundamental observations that have been made upon running lithium enolates alkylations, one can mention that a higher degree of aggregation, as observed in ethers (Et_2O , THF, DME) or amines (aliphatic tertiary amine, pyridine), would advantage C-alkylation reactions, while the O-alkylation would be rather favored from smaller aggregates existing in polar aprotic solvents.^{153a,163c} Otherwise, a faster reactivity is observed when reducing the size of the aggregates. For example, lithium enolate derived from heptan-2-one, known to be tetramer in weakly polar solvents, does not react with benzyl bromide in these media, while the alkylation becomes feasible after addition of HMPA, an additive

dissociating the tetramers into monomers.^{164e} A similar effect was noticed for HMPA assisting the methylation of cyclopentanone or, again, the proton abstraction from 2-methylcyclopentanone.^{161f} As another case illustrating the rate acceleration, one can evoke the rate enhancement by adding either 1,1,4,7,10,10-hexamethyltriethylenetetramine or ureas, as substitutes for HMPA, when running the alkylation of a tetralone lithium salt in DME.^{165a} As for the lithium amides, a pretty massive amount of studies relate to structure/reactivity correlations. Only few representative examples are mentioned in this paper.

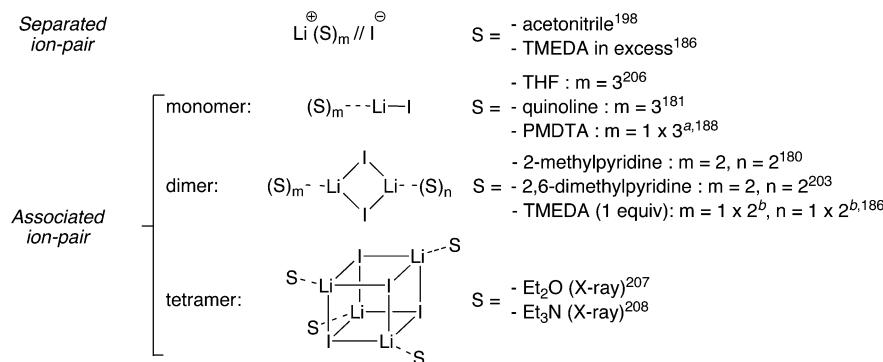
2.1.4. Lithium Halides (Li–X).

Results are presented for LiCl, LiBr, and LiI.

Because they easily form mixed aggregates, lithium halides are known to exert a significant influence on the behavior of organometallic reagents, affecting both the reactivity and the selectivity.^{177b} Note that working in organometallic chemistry with salt-free conditions can reveal difficulties when salts form during the reaction process and are soluble in the medium. In such cases, it is impossible to ignore the role played by these salts, and having a good knowledge of their structure in solution becomes an essential item to understand the related reaction mechanisms. The numerous studies dedicated to their oligomeric structural properties mainly focused on the lithium chloride, bromide, and iodide species and exhibited a remarkable diversity.^{177a} Thus, separated ion pairs to differently aggregated associated ion pairs (monomers, dimers, tetramers, polymers, ...) can form. Note that only anhydrous LiX and nonacidic solvent are here taken into consideration.

2.1.4.1. Lithium Chloride. Preliminary investigations (vapor phase osmometric studies) run with anhydrous lithium chloride reported strongly associated ion pair systems that would be monomeric in acetone and higher aggregated in THF: a dimeric arrangement was proposed in the latter case.¹⁷⁸ X-ray diffraction analyses conducted afterward on still water-free LiCl crystals confirmed that variable arrangements could be observed depending on the organic solvent used (Scheme

Scheme 32. X-ray Structures of LiI Solvates



^aS establishes three coordinations with one Li. ^bS establishes two coordinations with one Li.

30). Thus, growing the crystals in a formamide solution favored the formation of highly separated ion pairs.¹⁷⁹ By contrast, crystalline associated ion pairs corresponded to (i) trisolvated monomers formed in the presence of 3,5-dimethylpyridine,¹⁸⁰ 4-*tert*-butylpyridine,¹⁸¹ or 12-crown-4;¹⁸² (ii) tetrasolvated dimers for crystals grown in 2-methylpyridine¹⁸⁰ or THF,¹⁸³ and (iii) tetrasolvated cubic tetramers using diethyl ether¹⁸⁴ or HMPA.¹⁸⁵ Interestingly, three different TMEDA-solvated LiCl aggregates were depicted in the solid state, depending on the reaction conditions used to isolate them, and they corresponded to (i) a polymeric association in which a double cubane Li_8Cl_6 unit solvated by chelating and bridging TMEDA molecules were involved,¹⁸⁶ (ii) a trisolvated trimer,¹⁸⁷ and (iii) a bicyclic structure made of fused six- and four-membered rings.¹⁸⁷ Note also that crystallization of LiCl with an excess of PMDTA led to a trisolvated “double dimer”,¹⁸⁸ and crystalline polymeric structures made of dimeric units were described with pyridine¹⁸⁹ and 1,4-dioxane.¹⁹⁰ When examined in solution by the NMR technique, lithium chloride was described as a separated ion pair in THF at room temperature,¹⁹¹ while it would rather arrange as a dimeric associated ion pair in the same solvent at low temperature ($-140^\circ\text{C} < T < -78^\circ\text{C}$).^{192,193} Addition of HMPA to the latter solution had the effect of breaking down the dimer to monomer, and the formation of separated ion pairs was even noticed beyond 6 equiv of the phosphoramide.¹⁹³

2.1.4.2. Lithium Bromide. While the already mentioned precursory vapor-phase osmometric studies, run in dry acetone and THF, predicted structures for nonaqueous LiBr corresponding to mainly associated ion pairs,¹⁷⁸ X-ray data and structural analyses in solution (NMR), obtained later on from various organic solvents, came to support this observation (Scheme 31).

Similarly to lithium chloride, more or less high degrees of aggregation were observed, depending on the nature of the solvent from which the LiBr structure was studied. Thus, X-ray data highlighted trisolvated monomeric arrangements for crystals of LiBr grown in the presence of pyridine,¹⁹⁴ 3,5-dimethylpyridine,¹⁸⁰ and 4-*tert*-butylpyridine,¹⁸¹ as well as disolvated monomeric adducts, in which the lithium cation was pentacoordinated, when grown in the presence of 1,10-phenanthroline¹⁹⁵ and 1,2-dimethoxyethane.¹⁹⁶ Tetrasolvated cyclic dimers formed with 2-methylpyridine,¹⁸⁰ quinoline,¹⁹⁴ acetone,¹⁹⁷ and acetonitrile¹⁹⁸ in the solid state, while a disolvated dimer was depicted in the presence of TMEDA¹⁸⁶ and PMDTA.¹⁹⁹ Working with HMPA led to an unusual

crystallographic dimer presenting the bromines on the outside of a Li–O–Li–O rings core.²⁰⁰ Tetrasolvated cubic tetrameric units were described from crystals grown in Et_2O .²⁰¹ When isolated from a THF solution, the crystals corresponded to a polymeric structure in which the unit can be seen as an open-cubic tetramer (also named “broken cube”), solvated on each lithium atom by one THF molecule.²⁰² Switching to 2,6-dimethylpyridine also gave an open-cubic tetramer (or three-member ring ladder), this time as a single hexasolvated oligomer with all lithiums in a tetrahedral environment.²⁰³ Examination of the structure of LiBr in solution, thanks to the NMR technique, suggested the observation of a cubic tetramer at low temperature in toluene/ Et_2O (no precision about the solvation)²⁰⁴ and a monomer (mostly monosolvated) in the presence of 1 equiv of HMPA.¹⁹³

2.1.4.3. Lithium Iodide. Anhydrous LiI was early announced as an ion pair in THF at room temperature^{178,193} and then postulated as corresponding to an aggregate smaller than LiBr in ethereal solvents.²⁰⁵ X-ray studies on crystals of LiI obtained from ethereal to amino media confirmed roughly these assumptions (Scheme 32).

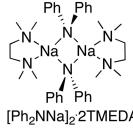
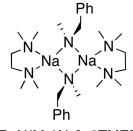
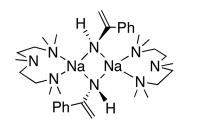
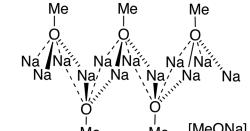
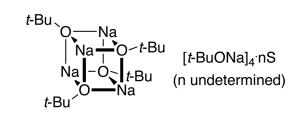
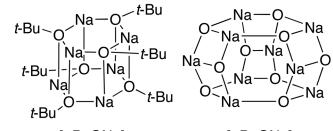
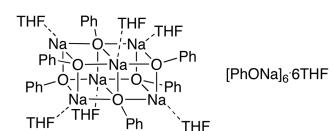
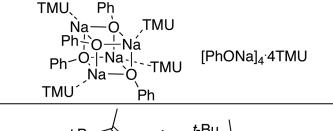
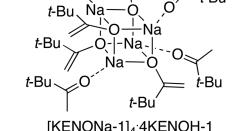
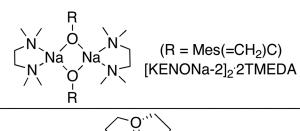
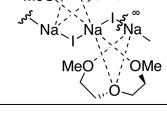
Cases of separated ion pairs were in fact highlighted from crystals grown in acetonitrile¹⁹⁸ and an excess of TMEDA.¹⁸⁶ With regard to the possibility to exist as associated ion pairs, monomers were reported in the presence of THF²⁰⁶ or quinoline¹⁸¹ (Li trisolvated) and PMDTA (Li tricoordinated by one molecule of triamine).¹⁸⁸ Dimers formed with 2-methylpyridine (Li disolvated),¹⁸⁰ 2,6-dimethylpyridine (Li disolvated),²⁰³ and an equimolar amount of TMEDA (Li dicoordinated by one molecule of diamine),¹⁸⁶ while Et_2O ²⁰⁷ and Et_3N ²⁰⁸ led to tetrasolvated cubic tetramers.

As conclusive remarks on the structure of lithium halides, one can say that LiCl, LiBr, and LiI can exist as very different oligomers, depending on the organic solvent used. There are two things that these three lithium amides have in common: they all exist as tetramers in Et_2O , and pyridinic additives favor dimeric or monomeric oligomers. Regarding now structure/reactivity correlations, although the interactions between lithium chloride, bromide, or iodide and other lithiated derivatives have been the object of intensive studies on chemical, spectroscopic, or theoretical grounds, precise phenomena triggered by the salts remain difficult to interpret at the molecular level.^{177b} Depending on the reactions studied, these salts may have a negative effect³¹¹ or, conversely, a beneficial effect^{158b,339} on the yields and/or (stereo)-selectivities. A recent highlight by Mulvey concludes in

Table 7. Structural Data of Sodium Derivatives

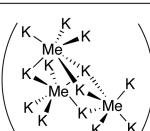
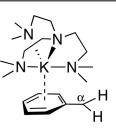
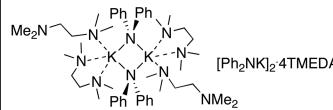
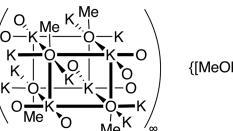
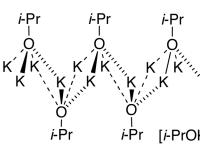
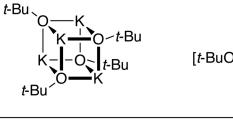
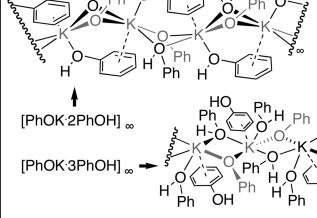
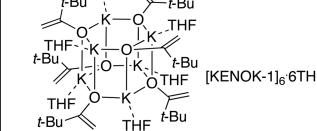
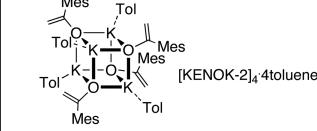
Entry	Organosodium	Analytical technique	Structure	Ref
1	MeNa	X-ray, unsolvated (grown in ether/hexane)		209
2	EtNa	X-ray, unsolvated (grown in pentane)		210
3a	PhNa	X-ray, solvated by PMDTA (grown in hexane + 2.3 equiv PMDTA)		212a
3b		X-ray, unsolvated (grown in hexane)		212b
4a	BnNa	X-ray, solvated by TMEDA (grown in hexane + 1 equiv TMEDA)		213
4b		X-ray, solvated by Me6TREN (grown in toluene + 1 equiv Me6TREN)		77b
5a	H ₂ NNa	X-ray, unsolvated		214
5b	Me ₂ NNa	X-ray, solvated by TMEDA (grown in hexane + excess of TMEDA)		215

Table 7. continued

Entry	Organosodium	Analytical technique	Structure	Ref
5c	Ph ₂ NNa	X-ray, solvated by TMEDA (grown in hexane + 1 equiv TMEDA)		106
5d	BnN(Me)Na	X-ray, solvated by TMEDA (grown in hexane + 1 equiv TMEDA)		216
5e	PhC(=CH ₂)NHNa	X-ray, solvated by PMDTA (grown in hexane + 1 equiv PMDTA)		136
6a	MeONa	X-ray, unsolvated (grown in MeOH)		217
6b-1	t-BuONa	IR, in THF		218
6b-2	t-BuONa	X-ray, unsolvated (grown from sublimation)		145b
6c-1	PhONa	X-ray, solvated by THF (grown in THF)		219
6c-2	PhONa	X-ray, solvated by TMU (grown in THF)		219
7a	t-Bu(H ₂ C=)CONa (KENONa-1)	X-ray, solvated by pinacolone (grown in heptane)		160d
7b	Mes(H ₂ C=)CONa (KENONa-2)	X-ray, solvated by TMEDA (grown in hexane)		220b
8	INa	X-ray, solvated by diglyme (grown in ether/cyclohexane)		221

^aThe t-Bu groups are not presented for clarity.

Table 8. Structures (X-ray and solution) of Potassium Derivatives

Entry	Organopotassium	Analytical technique	Structure	Ref
1	MeK	X-ray, unsolvated (grown in pentane)		222
2	BuK	NMR in THF + TMEDA	Monomer	211b
3	BnK	X-ray, solvated by Me ₆ TREN (grown in toluene + 1 equiv Me ₆ TREN)		77b
4	Ph ₂ NK	X-ray, solvated by TMEDA (grown in hexane)		106
5	MeOK	X-ray, unsolvated (grown in MeOH)		223
6	<i>i</i> -PrOK	X-ray, unsolvated (grown in hexane)		224
7	<i>t</i> -BuOK	X-ray, unsolvated (grown from sublimation)		218 225
8	PhOK	X-ray, solvated by PhOH (grown in pentane)		219 226
9	<i>t</i> -Bu(H ₂ C=)COK (KENOK-1)	X-ray, solvated by THF (grown in heptane + 1.1 equiv THF)		160d
10	Mes(H ₂ C=)COK	X-ray, solvated by toluene (grown in toluene)		227

considering that “Molecular salt chemistry is certain to be a hot topic for many years to come.”^{177b}

2.2. Sodium Compounds

Results are presented for MeNa; EtNa; PhNa; BnNa; some sodium amides, such as H₂NNa, Me₂NNa, Ph₂NNa, Bn-N(Me)Na, and PhC(=CH₂)NHNa; sodium alkoxides, like

MeONa and *t*-BuONa; PhONa; enolates derived from pinacolone and 2,4,6-trimethylacetophenone; and NaI.

Structural data obtained for sodium derivatives are mainly related to X-ray analyses, being done only a few times in solution. The related arrangements going from dimeric to polymeric systems are itemized in Table 7. The crystal structure of methylsodium was determined from a powder diagram

carried out on a solid reached by reaction between methylolithium and sodium *tert*-butoxide in diethyl ether. It highlighted a three-dimensional polymeric arrangement combining cubic tetramers linked through Na–Me interactions ($\{[\text{MeNa}]_4\}_\infty$, Table 7, entry 1).²⁰⁹ A polymeric system, composed of double-layered vicinal Et–Na–Et–Na quadrilaterals, was also shown on the X-ray powder diagram of ethylsodium synthesized in pentane, the ethyl groups being oriented perpendicularly to the layers ($2\{[\text{EtNa}]_2\}_\infty$, Table 7, entry 2).²¹⁰ Investigations run on the structure of BuNa in hexane solution and in the presence of TMEDA were considered as not reporting the degree of association of this alkylsodium clearly enough.²¹¹ Concerning phenylsodium in the presence of PMDTA, X-ray analyses pointed out a disolvated dimeric structure in which each sodium cation was pentacoordinated ($[\text{PhNa}]_2 \cdot 2\text{PMDTA}$, Table 7, entry 3a).^{212a} Crystals of disubstituted analogue 2,6-bis[(dimethylamino)methyl]phenylsodium were also isolated from a hexane solution, and a trimeric arrangement, totally intramolecularly solvated, was reported ($[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Na}]_3$, Table 7, entry 3b).^{212b} Synthesizing benzylsodium by metalation of toluene in hexane and in the presence of TMEDA led to crystals corresponding to a tetrameric structure organized into a planar eight-membered ring, each sodium atom being chelated by one molecule of TMEDA ($[\text{BnNa}]_4 \cdot 4\text{TMEDA}$, Table 7, entry 4a).²¹³ The same sodium derivative was put in the presence of Me₆TREN in toluene solution, and the crystals grown showed a monomeric solvate in which the ligand was mainly in interaction with the lithium cation through four coordinations with the four nitrogens of the tetramine ($[\text{BnNa}] \cdot \text{Me}_6\text{TREN}$, Table 7, entry 4b).^{77b} Note that, compared to its lithium congener, the metal cation slipped slightly toward the delocalized π -electrons while maintaining a partial σ -interaction with the CH₂ group. Now concerning the information obtained with sodium amides, one can retain the solid-state structural data related to H₂NNa that showed an unsolvated three-dimensional polymeric system incorporating cubic tetramer units linked to each other thanks to H₂N···Na intercubic interactions ($\{[\text{H}_2\text{NNa}]_4\}_\infty$, Table 7, entry 5a),²¹⁴ an organization similar to that already depicted for MeNa. Next, concerning Me₂NNa, two fully described crystal structures corresponding to tetrasolvated large-size oligomers (10–12 Me₂NNa units) were obtained by combining the amide with TMEDA ($[\text{Me}_2\text{NNa}]_{10} \cdot 4\text{TMEDA}$ and $[\text{Me}_2\text{NNa}]_{12} \cdot 4\text{TMEDA}$, Table 7, entry 5b).²¹⁵ Crystals of sodium diphenylamide grown in a hexane solution containing TMEDA were found to correspond to a disolvated dimeric oligomer ($[\text{Ph}_2\text{NNa}]_2 \cdot 2\text{TMEDA}$, Table 7, entry 5c).¹⁰⁶ Comparable arrangements were observed from N-benzyl-N-methyl sodium amide in the presence of the same diamine ($[\text{BnN}(\text{Me})\text{Na}]_2 \cdot 2\text{TMEDA}$, Table 7, entry 5d),²¹⁶ as well as with sodium enamide PhC(=CH₂)N(H)Na mixed with PMDTA ($[\text{PhC}(=\text{CH}_2)\text{N}(\text{H})\text{Na}]_2 \cdot 2\text{PMDTA}$, Table 7, entry 5e).¹³⁶ Examining now the case of sodium alkoxides, it was observed from an X-ray powder diagram that the solid-state structure of sodium methoxide obtained in the parent alcohol was isostructural to its lithium analogue, being organized in a five-layer polymeric structure:²¹⁷ a central layer made of sodium atoms is surrounded on each side by oxygen layers that are connected to the methyl appendages directed on the outside of the entire system ($[\text{MeONa}]_\infty$, Table 7, entry 6a). The structure of sodium *tert*-butoxide was examined in THF solution (from vibrational spectra)²¹⁸ and the presence of

cubic tetramers was suggested without discussing further the solvation ($[\text{t-BuONa}]_4 \cdot n\text{S}$, *n* undetermined; Table 7, entry 6b-1). Other kinds of oligomers would form in nonpolar solvents, however, without precise structural information. Crystallographic data obtained by sublimation of this alkoxide showed two nonsolvated prismatic organizations that corresponded to hexameric and nonameric arrangements ($[\text{t-BuONa}]_6$ and $[\text{t-BuONa}]_9$, Table 7, entry 6b-2).¹⁴⁵ X-ray analyses, conducted this time on sodium phenoxide crystals isolated from THF, evidenced a hexasolvated oligomer corresponding to two hexasolvated face-fused cubic tetramers ($[\text{PhONa}]_6 \cdot 6\text{THF}$, Table 7, entry 6c-1).^{154b,155e,219} A PhONa solid-state arrangement was also isolated and studied in the presence of *N,N,N',N'*-tetramethylurea (TMU), and a tetrasolvated single cubic tetramer ($[\text{PhONa}]_4 \cdot 4\text{TMU}$, Table 7, entry 6c-2) was evidenced.²¹⁹ Next referring to data obtained for crystals of sodium enolate, one can mention those derived from pinacolone (KENONA-1). A cubic tetramer, tetrasolvated by molecules of unenolized ketone (KENO-1), was shown ($[\text{KENONA-1}]_4 \cdot 4\text{KENO-1}$, Table 7, entry 7a).^{160d,220a} Crystals of Mes(=CH₂)CONa (Mes = mesityl) enolate (KENONA-2) obtained in the presence of TMEDA showed the formation of a disolvated cyclic dimer ($[\text{KENONA-2}]_2 \cdot 2\text{TMEDA}$, Table 7, entry 7b).^{220b} Finally, the solid-state structural data obtained from a diglyme complex of sodium iodide was described as infinite zigzag chains surrounded by diglyme molecules that bridge the Na atoms through four crossed oxygen coordinations (Table 7, entry 8).²²¹

2.3. Potassium Compounds

Results are presented for MeK, BuK, BnK, Ph₂NK, MeOK, *i*-PrOK, *t*-BuOK, PhOK, and a few potassium enolates.

The X-ray analyses conducted on crystals of methylpotassium, grown in either hydrocarbon solvents or Et₂O, highlighted an unsolvated polymeric arrangement, in which the methyl groups were found to be surrounded by six K atoms in a trigonal prismatic arrangement (Table 8, entry 1).²²² Studies, conducted in solution (NMR technique), with initially precipitated BuK, led to the conclusion that this reactant could be monomeric in a THF/TMEDA mixture at low temperature (Table 8, entry 2).^{211b} Coming back to X-ray analyses, this time run on crystals of benzylpotassium grown in a toluene solution containing the Me₆TREN tetramine, the smallest molecular weight molecular organopotassium solvate was characterized. In the solvated monomer depicted, the anion binds to the tetracoordinated potassium exclusively through its delocalized π -system resulting in a planar CH₂ group ($[\text{BnK}] \cdot \text{Me}_6\text{TREN}$, Table 8, entry 3).^{77b} From crystals of potassium diphenylamide obtained in the presence of TMEDA, a tetrasolvated dimeric structure was depicted, in which the potassium cations were pentacoordinated ($[\text{Ph}_2\text{NK}]_2 \cdot 4\text{TMEDA}$, Table 8, entry 4).¹⁰⁶ Crystals of potassium methoxide isolated from a methanol solution underscored an unsolvated three-dimensional polymeric system made of cubic tetrameric units connected to each other through O···K interactions ($\{[\text{MeOK}]_4\}_\infty$, Table 8, entry 5).²²³ Potassium isopropoxide was found to be isostructural to lithium or sodium methoxides in the solid state, being organized in the five-layer system already mentioned twice in the present paper that incorporates a central metallic layer (here potassium) besieged by two oxygen bands, themselves overlapped by the isopropyl appendages ($[\text{i-PrOK}]_\infty$, Table 8, entry 6).²²⁴ X-ray diffraction studies conducted on single

Table 9. Structures (X-ray) of Homoleptic Magnesium Derivatives

Entry	Magnesium derivative	Solvation	Structure	Ref
1a	Me_2Mg	none (grown from sublimation)		230a,c
1b		by TMEDA (grown in diethylether/hexane + 1 equiv TMEDA)		230d
1c		by PMDTA (grown in diethylether + 1 equiv PMDTA)		230e,f
1d		by quinuclidine (grown in benzene/hexane + 2 equiv quinuclidine)		230b
2a	Et_2Mg	none (grown from sublimation)		231a,b
2b		by TMEDA (grown in diethylether + 1 equiv TMEDA)		230e
2c		by PMDTA (grown in diethylether + 1 equiv PMDTA)		230e
2d		by 18-crown-6 (grown in toluene + 1 equiv 18-crown-6)		231c
3	$s\text{-Bu}_2\text{Mg}$	by TMEDA (grown in heptane + 1 equiv TMEDA)		232
4	$t\text{-Bu}_2\text{Mg}$	none (grown from sublimation)		233
5	$(t\text{-BuC}\equiv\text{C})_2\text{Mg}$	TMEDA		234
6a	Ph_2Mg	by Et_2O or THF (grown in diethylether or THF)		64a, 235a,c
6b		by TMEDA (grown in diethylether/hexane + 1 equiv TMEDA)		235b
7a	Bn_2Mg	by TMEDA (grown in Et_2O + hexane)		236a
7b		by THF (grown in THF + pentane)		236b
8a	HMDS_2Mg	none (prepared in toluene)		237b
8b		$\text{S} = \text{THF}$ or pyridine		237a 97

Table 9. continued

Entry	Magnesium derivative	Solvation	Structure	Ref
9	(<i>c</i> -Hex ₂ N) ₂ Mg	none (grown in toluene)		238
10	(Ph ₂ N) ₂ Mg	by HMPA (grown in 2:3 HMPA/THF)		239
11a	$(Bn_2N)_2Mg$	none (prepared in hydrocarbon)		240a
11b		S = THF or HMPA		240b
12a	$MgBr_2$	HMPA (prepared in THF/Et ₂ O + 1 equiv HMPA)		241d
12b		PMDTA (prepared in THF + 1 equiv PMDTA)		230f
12c		Et ₂ O		241a
12d		THF		241b
13	$MgCl_2$	pyridine		242

crystals of *t*-BuOK isolated after sublimation revealed for this more hindered alkoxide an unsolvated cubic tetramer ($[t\text{-BuOK}]_4$, Table 8, entry 7).²²⁵ The exclusive presence of such a tetramer was also revealed by analysis of vibrational spectra, whether in hydrocarbon or THF solution.²¹⁸ In the presence of *t*-BuOH, a one-dimensional ribbonlike chain was reported in the solid state.²²⁵ Examining potassium phenoxide in the solid state evidenced entangled arrangements related to polymeric zigzag chains solvated by phenol molecules (Table 8, entry 8).^{219b,226} Finally, among potassium enolates from which structural information was given,^{160d,220,227,228} one can retain the case of potassium enolate of pinacolone (KENOK-1) that was crystallized in a heptane/THF mixture. A THF-hexasolvated prismatic hexamer was characterized ($[KENOK-1]_6 \cdot 6\text{THF}$, Table 8, entry 9).^{160d} Replacing the *tert*-butyl group by a mesityl appendage (KENOK-2) had the effect of reducing the size of the aggregate, a cubic tetramer being observed in this case ($[KENOK-2]_4 \cdot 4\text{toluene}$, Table 8, entry 10).²²⁷ Note the unusual solvation of this latter oligomer by toluene thanks to π -cation interactions.

As an overview on the structural data of sodium and potassium compounds, one can say that with both alkaline metals being larger than the other alkaline lithium ($K > Na > Li$), they legitimately tolerate surrounding steric hindrance better than lithium, and thus, the sodium and postpotassium species easily lead to high-size aggregates, even in the presence of polydentate basic additives. As regards their reactivity in classical weakly polar aprotic solvents [(poly)ethers, (poly)-

amines], potassium reactants use to be more reactive than sodium ones, themselves more reactive than lithium congeners. Note however that sodium derivatives, in many cases, adopt a chemistry that resembles more those of lithium than those of potassium.^{6e} The greater reactivity of sodium and potassium compounds can be a disadvantage, as it can make them difficult to handle and, thus, explains the slow developments dedicated to these categories of reactants.

2.4. Magnesium Compounds

2.4.1. Homoleptic Magnesium Compounds. Results are presented for Me_2Mg , Et_2Mg , $s\text{-}Bu_2Mg$, $t\text{-}Bu_2Mg$, $(t\text{-}BuC\equiv C)_2Mg$, Ph_2Mg , Bn_2Mg , $HMDS_2Mg$, $(c\text{-}Hex}_2N)_2Mg$, $(Ph_2N)_2Mg$, $(Bn_2N)_2Mg$, $MgBr_2$, and $MgCl_2$.

Homoleptic magnesium derivatives have been the object of several X-ray characterizations^{229–242} among which those listed above and for which the arrangements are shown in Table 9. A nonsolvated monodirectional polymeric structure in which the magnesium units are staggered, and thus the Mg cations are tetrahedral, was depicted for crystals of dimethylmagnesium obtained after sublimation (Table 9, entry 1a).^{230a,c} Addition of basic additives such as TMEDA,^{230d} PMDTA,^{230e,f} and quinuclidine^{230b} to this dialkylmagnesium reactant led to crystals for which monomeric complexes were recorded (Table 9, entries 1b–d). The magnesium atom of the Me_2Mg unit was found to be chelated by TMEDA, leading to 1:1 $[Me_2Mg]\cdot\text{TMEDA}$, for which the Mg atom was tetrahedral (Table 9, entry 1b).^{230d} Switching to the triamine

led to the 1:1 $[\text{Me}_2\text{Mg}] \cdot \text{PMDTA}$ structure with a pentacoordinated Mg (Table 9, entry 1c).^{230e,f} With quinuclidine, two molecules of amine were involved to afford the Mg-tetrahedral $[\text{Me}_2\text{Mg}] \cdot 2\text{quinuclidine}$ complex (Table 9, entry 1d).^{230b} Diethylmagnesium was found to behave like its methyl analogue showing a comparable polymeric staggered sequence for crystals also isolated by sublimation (Table 9, entry 2a).^{230e,231a,b} Similar monomeric complexes were also evidenced in the presence of TMEDA ($[\text{Et}_2\text{Mg}] \cdot \text{TMEDA}$, Table 9, entry 2b) and PMDTA ($[\text{Et}_2\text{Mg}] \cdot \text{PMDTA}$, Table 9, entry 2c).^{230e} A centrosymmetric structure was depicted for the $[\text{Et}_2\text{Mg}] \cdot 18\text{-crown-6}$ complex, in which the magnesium was hexacoordinated by 18-crown-6, with long, nearly equal Mg—O distances and the Mg—Et bonds perpendicular to the plane (Table 9, entry 2d).^{231c} Selective crystallization was conducted with di(*sec*-butyl)magnesium in the presence of bidentate TMEDA, and the tetracoordinated-Mg (tetrahedral) monomeric complex $[\text{sec-Bu}_2\text{Mg}] \cdot \text{TMEDA}$ was pointed out (Table 9, entry 3).²³² Crystals were also obtained after sublimation of di(*tert*-butyl)magnesium. The X-ray structure showed an unsolvated dimeric arrangement in which intramolecular Me—Mg agostic interactions were setting up ($[(t\text{-Bu}_2\text{Mg})_2]$, Table 9, entry 4).²³³ Magnesium diacetylide ($t\text{-BuC}\equiv\text{C}_2\text{Mg}$) crystallized in the presence of TMEDA as a disolvated linear monomer ($[(t\text{-BuC}\equiv\text{C}_2\text{Mg})_2 \cdot 2\text{TMEDA}$, Table 9, entry 5).²³⁴ As regards diarylmagnesium derivatives,^{235d,e} Mg-tetrahedral di- to monosolvated monomeric complexes were formed from diphenylmagnesium when put in the presence of Et_2O ($[\text{Ph}_2\text{Mg}] \cdot 2\text{Et}_2\text{O}$, Table 9, entry 6a),^{64a} THF^{235c} ($[\text{Ph}_2\text{Mg}] \cdot 2\text{THF}$, Table 9, entry 6a), and TMEDA^{236b} ($[\text{Ph}_2\text{Mg}] \cdot \text{TMEDA}$, Table 9, entry 6b). Note that a polymeric arrangement $[\text{Ph}_2\text{Mg}]_\infty$ also accounted for this compound when crystallized in a nonbasic solvent.^{235c} By examining the dibenzyl magnesium derivative, crystals were obtained in the presence of TMEDA, and a monomeric solvate was highlighted ($[\text{Bn}_2\text{Mg}] \cdot \text{TMEDA}$, Table 9, entry 7a).^{236a} The same species was depicted as a disolvated monomer in THF ($[\text{Bn}_2\text{Mg}] \cdot 2\text{THF}$, Table 9, entry 7b).^{236b} Among homoleptic magnesium diamides, one can consider the case of HMDS₂Mg isolated in the solid state from a saturated toluene solution: an unsolvated Mg-trigonal cyclic dimer showed up ($[\text{HMDS}_2\text{Mg}]_2$, Table 9, entry 8a).^{237b,c} Growing the crystals of this same magnesium bis-amide in THF^{237a} or pyridine⁹⁶ led to the observation of disolvated Mg-tetrahedral monomers ($[\text{HMDS}_2\text{Mg}] \cdot 2\text{THF}$ and $[\text{HMDS}_2\text{Mg}] \cdot 2\text{pyr}$, Table 9, entry 8b). Crystallographic data acquired from crystals of $(c\text{-Hex}_2\text{N})_2\text{Mg}$ grown in toluene pointed out an unsolvated cyclic dimer ($[(c\text{-Hex}_2\text{N})_2\text{Mg}]_2$, Table 9, entry 9).²³⁸ In such an arrangement, the geometry of the magnesium was trigonal, being connected to three ligands. With regard to crystals of $(\text{Ph}_2\text{N})_2\text{Mg}$ grown in the presence of HMPA, another Mg-tetrahedral disolvated monomeric complex was described ($[(\text{Ph}_2\text{N})_2\text{Mg}] \cdot 2\text{HMPA}$, Table 9, entry 10).²³⁹ Solid-state structures obtained for $(\text{Bn}_2\text{N})_2\text{Mg}$ pointed out an unsolvated Mg-trigonal quadrilateral dimer in hydrocarbon media ($[(\text{Bn}_2\text{N})_2\text{Mg}]_2$, Table 9, entry 11a)^{240a} and disolvated Mg-tetrahedral dimers when grown in the presence of THF or HMPA ($[(\text{Bn}_2\text{N})_2\text{Mg}]_2 \cdot 2\text{S}$, S = THF, HMPA; Table 9, entry 11b).^{240b} Finally, this section will focus on magnesium bis-halide compounds. MgBr_2 crystallized in the presence of HMPA as a disolvated monomeric species ($[\text{MgBr}_2] \cdot 2\text{HMPA}$, Table 9, entry 12a)^{241d} and a monosolvated monomeric arrangement in which the magnesium atom was found to be

pentacoordinated with PMDTA ($[\text{MgBr}_2] \cdot \text{PMDTA}$, Table 9, entry 12b).^{230f} Also, di-, tetra-, and hexasolvated monomers were highlighted for crystals grown in the presence of diethyl ether ($[\text{MgBr}_2] \cdot 2\text{Et}_2\text{O}$, Table 9, entry 12c),^{241a} THF ($[\text{MgBr}_2] \cdot 4\text{THF}$, Table 9, entry 12d),^{241b} and pyridine ($[\text{MgBr}_2] \cdot 6\text{pyr}$).^{241c} Switching to the chlorinated analogue, a complex of MgCl_2 with pyridine was isolated in the solid state, and its crystallographic data showed a tetrasolvated monomer ($[\text{MgCl}_2] \cdot 4\text{pyr}$, Table 9, entry 13).²⁴²

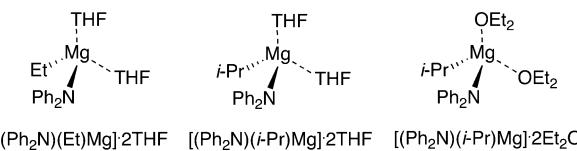
2.4.2. Heteroleptic Magnesium Compounds. Because many heteroleptic magnesium derivatives exist, for which a sizable number has actually already been characterized from a structural point of view, mostly by crystallography,^{6e,229,238} the authors underline that hydrated complexes are not included in this review. Their selection focused on species with “simple” solvation (Et_2O , THF, HMPA, Et_3N) and substitutions (i.e., a low number of C, N, O, Si, and halogen atoms), which were the first considered systems in routine organic chemistry.

2.4.2.1. Heteroleptic Magnesium Amides ($R^1R^2N(R^3)Mg$) ($R^3 \neq R^1R^2N$). Results are presented for $(Ph_2N)(Et)Mg$, $(Ph_2N)(i-Pr)Mg$, $(DA)(i-Pr)Mg$, $(DA)(t-Bu)Mg$, $(HMDS)(s-Bu)Mg$, $(HMDS)(t-Bu)Mg$, $(TMP)(Et)Mg$, $(TMP)(Bu)Mg$, $(TMP)(t-Bu)Mg$, $(c-Hex_2N)(t-Bu)Mg$, $(Bn_2N)(t-Bu)Mg$, $(t-BuNH)(t-Bu)Mg$, $(DA)(PhC\equiv C)Mg$, $(DA)(Me_3SiC\equiv C)Mg$, $(i-Pr_3SiNH)(Me)Mg$, $(PhNH)(HMDS)Mg$, Et_2NMgBr , $((MeOCH_2CH_2)_2N)(Et)Mg$, $((Me_2NCH_2CH_2)(Me)N)(Me)Mg$, $(Ph_2N)(Ph(2-pyr)N)Mg$, $(HMDS)(Ph_2C(H)O)Mg$, $HMDSMgBr$, $HMDSMgCl$, and $TMPMgCl$.

The name of heteroleptic magnesium amides has been given to heteroleptic magnesium compounds bearing an amide substitution $[(R^1R^2N)(R^3)Mg]$. For its part, the R^3 group can be an alkyl, alkenyl, alkynyl, aryl, alkoxy, another amino, or a halo appendage. The arrangements observed for such selected species proved to correspond to monomers in few cases but to dimers for most examples.

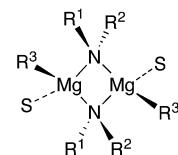
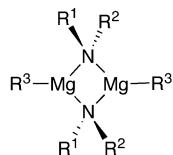
Thus, dissolved monomeric complexes, in which the magnesium atom was found to be tetrahedral, were depicted for $(\text{Ph}_2\text{N})(\text{Et})\text{Mg}$ and $(\text{Ph}_2\text{N})(i\text{-Pr})\text{Mg}$ when crystallized in tetrahydrofuran and diethyl ether ($[(\text{Ph}_2\text{N})(\text{Et})\text{Mg}] \cdot 2\text{THF}$,^{239,243} $[(\text{Ph}_2\text{N})(i\text{-Pr})\text{Mg}] \cdot 2\text{THF}$,²³⁹ and $[(\text{Ph}_2\text{N})(i\text{-Pr})\text{Mg}] \cdot 2\text{Et}_2\text{O}$,²⁴³ Scheme 33). Note that in hexane both magnesium amides showed polymeric structures.²⁴³

Scheme 33. X-ray Structures of THF and Et₂O Solvates



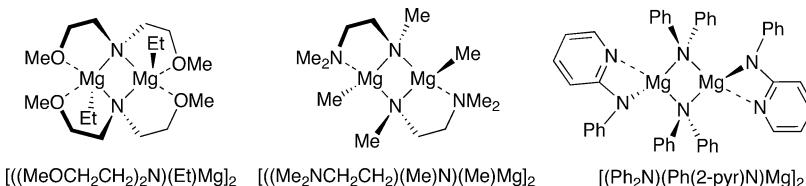
Concerning $(DA)(i\text{-Pr})\text{Mg}$, $(DA)(t\text{-Bu})\text{Mg}$, $(\text{HMDS})(s\text{-Bu})\text{Mg}$, $(\text{HMDS})(t\text{-Bu})\text{Mg}$, $(\text{TMP})(\text{Et})\text{Mg}$, $(\text{TMP})(\text{Bu})\text{Mg}$, $(\text{TMP})(t\text{-Bu})\text{Mg}$, $(c\text{-Hex}_2\text{N})(t\text{-Bu})\text{Mg}$, $(\text{Bn}_2\text{N})(t\text{-Bu})\text{Mg}$, $(t\text{-BuNH})(t\text{-Bu})\text{Mg}$, $(DA)(\text{PhC}\equiv\text{C})\text{Mg}$, $(DA)(\text{Me}_3\text{SiC}\equiv\text{C})\text{Mg}$, $(i\text{-Pr}_3\text{SiNH})(\text{Me})\text{Mg}$, $(\text{PhNH})(\text{HMDS})\text{Mg}$, and Et_2NMgBr , those heteroleptic magnesium amides preferably arranged as cyclic dimers organized around a $\text{N}-\text{Mg}-\text{N}-\text{Mg}$ quadrilateral, in which the magnesium atom was trigonal if unsolvated $\{[(DA)(i\text{-Pr})\text{Mg}]_2\}^{243}$ $[(DA)(t\text{-Bu})\text{Mg}]_2$ ²⁴⁴ $[(\text{HMDS})(s\text{-Bu})\text{Mg}]_2$ ²⁴⁴ $[(\text{HMDS})(t\text{-Bu})\text{Mg}]_2$ ²⁴⁴ $[(\text{TMP})(\text{Et})\text{Mg}]_2$ ²⁴³ $[(\text{TMP})(\text{Bu})\text{Mg}]_2$ ²⁴⁵ $[(\text{TMP})(t\text{-Bu})\text{Mg}]_2$ ²⁴⁴ $[(c\text{-Hex}_2\text{N})(t\text{-Bu})\text{Mg}]_2$ ²⁴⁴.

Scheme 34. Dimeric X-ray Structures of (DA)(*i*-Pr)Mg,²⁴³ (DA)(*t*-Bu)Mg,²⁴⁴ (HMDS)(*s*-Bu)Mg,²⁴⁴ (HMDS)(*t*-Bu)Mg,²⁴⁴ (*TMP*)(Et)Mg,²⁴³ (*TMP*)(Bu)Mg,²⁴⁵ (*TMP*)(*t*-Bu)Mg,²⁴⁴ (*c*-Hex₂N)(*t*-Bu)Mg,²⁴⁴ (*Bn*₂N)(*t*-Bu)Mg,²⁴⁴ (*t*-BuNH)(*t*-Bu)Mg,²³⁸ (DA)(PhC≡C)Mg,²³⁹ (DA)(Me₃SiC≡C)Mg,²³⁹ (*i*-Pr₃SiNH)(Me)Mg,^{229g} (PhNH)(HMDS)Mg,²⁴⁶ and Et₂NMgBr²³⁹

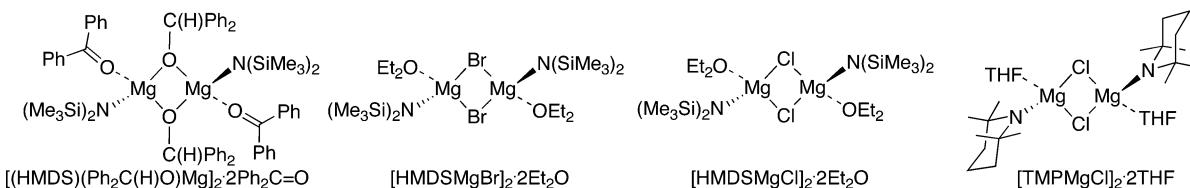


R ¹ = R ² = <i>i</i> -Pr, R ³ = <i>i</i> -Pr	: [(DA)(<i>i</i> -Pr)Mg] ₂
R ¹ = R ² = <i>i</i> -Pr, R ³ = <i>t</i> -Bu	: [(DA)(<i>t</i> -Bu)Mg] ₂
R ¹ = R ² = SiMe ₃ , R ³ = <i>s</i> -Bu	: [(HMDS)(<i>s</i> -Bu)Mg] ₂
R ² = R ³ = SiMe ₃ , R ¹ = <i>t</i> -Bu	: [(HMDS)(<i>t</i> -Bu)Mg] ₂
R ¹ R ² N = TMP, R ³ = Et	: [(<i>TMP</i>)(Et)Mg] ₂
R ¹ R ² N = TMP, R ³ = Bu	: [(<i>TMP</i>)(Bu)Mg] ₂
R ¹ R ² N = TMP, R ³ = <i>t</i> -Bu	: [(<i>TMP</i>)(<i>t</i> -Bu)Mg] ₂
R ¹ = R ² = <i>c</i> -Hex, R ³ = <i>t</i> -Bu	: [(<i>c</i> -Hex ₂ N)(<i>t</i> -Bu)Mg] ₂
R ¹ = R ² = Bn, R ³ = <i>t</i> -Bu	: [(<i>Bn</i> ₂ N)(<i>t</i> -Bu)Mg] ₂

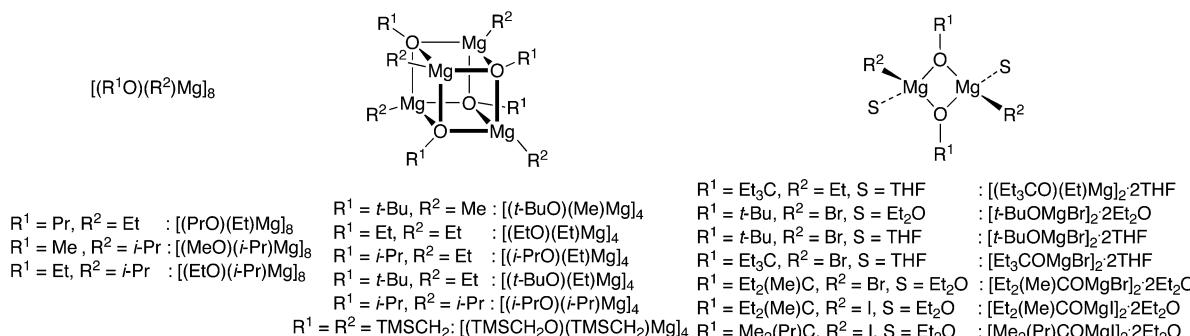
Scheme 35. Solid-State Structures of ((MeOCH₂CH₂)₂N)(Et)Mg,²²⁹ⁱ ((Me₂NCH₂CH₂)(Me)N)(Me)Mg,²⁴⁷ and (Ph₂N)(Ph(2-pyr)N)Mg²⁴⁸



Scheme 36. Crystallographic Structures of (HMDS)(Ph₂C(H)O)Mg,²⁴⁹ HMDSMgBr,²³⁹ HMDSMgCl,²⁵⁰ and TMPMgCl²⁵¹



Scheme 37. Crystallographic Data of Heteroleptic Magnesium Alkoxides (PrO)(Et)Mg, (MeO)(*i*-Pr)Mg, (EtO)(*i*-Pr)Mg, (*t*-BuO)(Me)Mg, (EtO)(Et)Mg, (*i*-PrO)(Et)Mg, (*t*-BuO)(Et)Mg, (*i*-PrO)(*i*-Pr)Mg, (TMSCH₂O)(TMSCH₂)Mg, (Et₃CO)(Et)Mg, *t*-BuOMgBr, Et₂COMgBr and Et₂(Me)COMgBr, Et₂(Me)COMgI, and Me₂(Pr)COMgI²⁵²



Bu)Mg]₂²⁴⁴ [(Bn₂N)(*t*-Bu)Mg]₂²⁴⁴ Scheme 34 left} while tetrahedral when solvated by THF or HMPA {[*(t*-BuNH)(*t*-Bu)Mg]₂·2THF,²³⁸ [(DA)(PhC≡C)Mg]₂·2THF,²³⁹ [(DA)(Me₃SiC≡C)Mg]₂·2THF,²³⁹ [(*i*-Pr₃SiNH)(Me)Mg]₂·2THF,^{229g} [(PhNH)(HMDS)Mg]₂·2THF,²⁴⁶ [*Et*₂NMgBr]₂·2HMPA,²³⁹ Scheme 34 right].

Note the possibility for the magnesium atom of the cyclic dimeric oligomer to be intramolecularly solvated, and thus tetrahedral or even pentacoordinated, when the nitrogen substitution includes supplementary heteroatoms as observed

for alkylmagnesium amide ((MeOCH₂CH₂)₂N)(Et)Mg {[((MeOCH₂CH₂)₂N)(Et)Mg]₂, Scheme 35, left}²²⁹ⁱ and aminomagnesium amides ((Me₂NCH₂CH₂)(Me)N)(Me)Mg {[((Me₂NCH₂CH₂)(Me)N)(Me)Mg]₂, Scheme 35, middle}²⁴⁷ and (Ph₂N)(Ph(2-pyr)N)Mg {[[(Ph₂N)(Ph(2-pyr)N)Mg]₂, Scheme 35, right]²⁴⁸.

All the cyclic dimers of heteroleptic magnesium amides did not necessarily organize around an N—Mg—N—Mg quadrilateral. When R³ corresponded to an alkoxo or a halo substitution, moieties likely to be also coordinated by the

magnesium metal, the dimeric oligomers could organize through O–Mg–O–Mg or X–Mg–X–Mg ($X = \text{halide}$) four-membered rings, respectively. Such an observation was illustrated with alkoxo magnesium amide ($\text{HMDS}(\text{Ph}_2\text{C}(\text{H})\text{O})\text{Mg}$) disolvated by benzophenone $\{[(\text{HMDS})(\text{Ph}_2\text{C}(\text{H})\text{O})\text{Mg}]_2\cdot 2\text{Ph}_2\text{C}=\text{O}$, Scheme 36 left),²⁴⁹ halo magnesium amides HMDSMgBr disolvated by diethyl ether $\{[\text{HMDSMgBr}]_2\cdot 2\text{Et}_2\text{O}$, Scheme 36 middle left),²³⁹ HMDSMgCl disolvated by diethyl ether $\{[\text{HMDSMgCl}]_2\cdot 2\text{Et}_2\text{O}$, Scheme 36 middle right),²⁵⁰ and TMMPMgCl disolvated by THF ($[\text{TMMPMgCl}]_2\cdot 2\text{THF}$, Scheme 36 right).²⁵¹

2.4.2.2. Heteroleptic Magnesium Alkoxides ($(R^1\text{O})(R^2)\text{Mg}$ ($R^2 \neq R^1\text{O}$)). Results are presented for $(\text{PrO})(\text{Et})\text{Mg}$, $(\text{MeO})(i\text{-Pr})\text{Mg}$, $(\text{EtO})(i\text{-Pr})\text{Mg}$, $(t\text{-BuO})(\text{Me})\text{Mg}$, $(\text{EtO})(\text{Et})\text{Mg}$, $(i\text{-PrO})(\text{Et})\text{Mg}$, $(t\text{-BuO})(\text{Et})\text{Mg}$, $(i\text{-PrO})(i\text{-Pr})\text{Mg}$, $(\text{TMSCH}_2\text{O})(\text{TMSCH}_2)\text{Mg}$, $(\text{Et}_3\text{CO})(\text{Et})\text{Mg}$, $t\text{-BuOMgBr}$, Et_3COMgBr , $\text{Et}_2(\text{Me})\text{COMgBr}$, $\text{Et}_2(\text{Me})\text{COMgI}$, $\text{Me}_2(\text{Pr})\text{COMgI}$, $(\text{PrO})(\text{Me})\text{Mg}$, and $(i\text{-PrO})(\text{Me})\text{Mg}$.

The name of heteroleptic magnesium alkoxides ($(R^1\text{O})(R^2)\text{Mg}$) has been given to heteroleptic magnesium compounds consisting of an alkoxo substitution ($R^1\text{O}$) to the magnesium cation, the R^2 group being mainly an alkyl or a halide. The case of R^2 corresponding to an amide is not reconsidered in this section since it was already discussed in section 2.4.2.1.

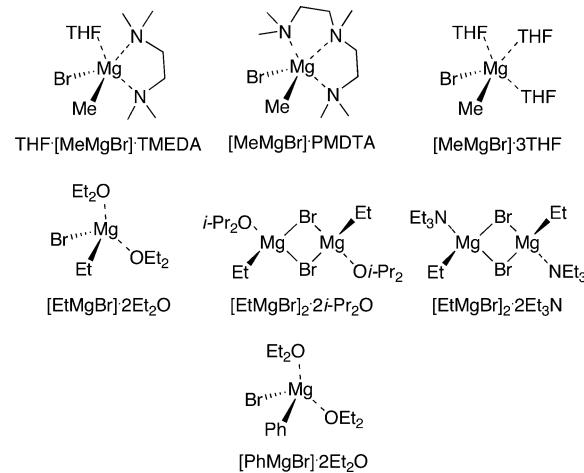
A series of “simple” alkylmagnesium alkoxides was prepared and crystallized.²⁵² When examining $(\text{PrO})(\text{Et})\text{Mg}$, $(\text{MeO})(i\text{-Pr})\text{Mg}$, and $(\text{EtO})(i\text{-Pr})\text{Mg}$, solid-state structures were isolated from benzene/ Et_2O media, and arrangements free from ether were highlighted, corresponding to octamers $\{[(\text{PrO})(\text{Et})\text{Mg}]_8$, $[(\text{MeO})(i\text{-Pr})\text{Mg}]_8$, and $[(\text{EtO})(i\text{-Pr})\text{Mg}]_8$, Scheme 37, left). Unsolvated cubic tetramers were identified from crystals of $(t\text{-BuO})(\text{Me})\text{Mg}$, $(\text{EtO})(\text{Et})\text{Mg}$, $(i\text{-PrO})(\text{Et})\text{Mg}$, $(t\text{-BuO})(\text{Et})\text{Mg}$, and $(i\text{-PrO})(i\text{-Pr})\text{Mg}$ derivatives also grown in benzene/ Et_2O mixture $\{[(t\text{-BuO})(\text{Me})\text{Mg}]_4$, $[(\text{EtO})(\text{Et})\text{Mg}]_4$, $[(i\text{-PrO})(\text{Et})\text{Mg}]_4$, $[(t\text{-BuO})(\text{Et})\text{Mg}]_4$, and $[(i\text{-PrO})(i\text{-Pr})\text{Mg}]_4$, Scheme 37, middle).^{252a} A similar arrangement was depicted for crystals of $(\text{TMSCH}_2\text{O})(\text{TMSCH}_2)\text{Mg}$ grown in light petroleum/ Et_2O solution $\{[(\text{TMSCH}_2\text{O})(\text{TMSCH}_2)\text{Mg}]_4$, Scheme 37, middle).^{252b} Among crystallographic data reporting solvated oligomeric structures (solvent = Et_2O or THF), one can mention those of $(\text{Et}_3\text{CO})(\text{Et})\text{Mg}$, $t\text{-BuOMgBr}$, Et_3COMgBr , $\text{Et}_2(\text{Me})\text{COMgBr}$, $\text{Et}_2(\text{Me})\text{COMgI}$, and $\text{Me}_2(\text{Pr})\text{COMgI}$ that were depicted as Mg-tetrahedral disolvated cyclic dimers organized around a O–Mg–O–Mg core $\{[(\text{Et}_3\text{CO})(\text{Et})\text{Mg}]_2\cdot 2\text{THF}$, $[(t\text{-BuOMgBr})_2\cdot 2\text{Et}_2\text{O}$, $[(t\text{-BuOMgBr})_2\cdot 2\text{THF}$, $[(\text{Et}_3\text{COMgBr})_2\cdot 2\text{THF}$, $[(\text{Et}_2(\text{Me})\text{COMgBr})_2\cdot 2\text{Et}_2\text{O}$, $[(\text{Et}_2(\text{Me})\text{COMgI})_2\cdot 2\text{Et}_2\text{O}$, and $[(\text{Me}_2(\text{Pr})\text{COMgI})_2\cdot 2\text{Et}_2\text{O}$, Scheme 37, right).

The structures in solution of methyl magnesium alkoxides $(\text{PrO})(\text{Me})\text{Mg}$, $(i\text{-PrO})(\text{Me})\text{Mg}$, and $(t\text{-BuO})(\text{Me})\text{Mg}$ were also studied in benzene, Et_2O , and THF solution using the NMR and IR techniques.²⁵³ In the hydrocarbon solvent, cubic tetramers were announced for $(i\text{-PrO})(\text{Me})\text{Mg}$ and $(t\text{-BuO})(\text{Me})\text{Mg}$, while higher-sized oligomers (hepta to nonamers) were detected for $(\text{PrO})(\text{Me})\text{Mg}$. Working in Et_2O was different since linear oligomers and cubic tetramers were pointed out for the three compounds. Cyclic dimers were preferred in THF.

2.4.2.3. Heteroleptic Magnesium Halides RMgX ($R = \text{C}_x\text{H}_y$) or Grignard Reagents. Results are presented for MeMgBr , EtMgBr , PhMgBr , MeMgCl , $t\text{-BuMgCl}$, PhMgCl , and BnMgCl .

Heteroleptic magnesium halides (RMgX) correspond in fact to Grignard reagents for which R is a hydrocarbon moiety. Although those reactive species have shown a wide range of chemical applications for more than 100 years, details about their structure still remain relatively vague, probably because of the confusion that persisted about the precise nature of these reagents in solution. However, it seems accepted that the composition of these species would obey the Schlenk equilibrium $2\text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2$.²⁵⁴ Crystallographic studies have been performed on RMgX species (Scheme 38).^{230f,255,256} Thus, crystals of MeMgBr obtained from a

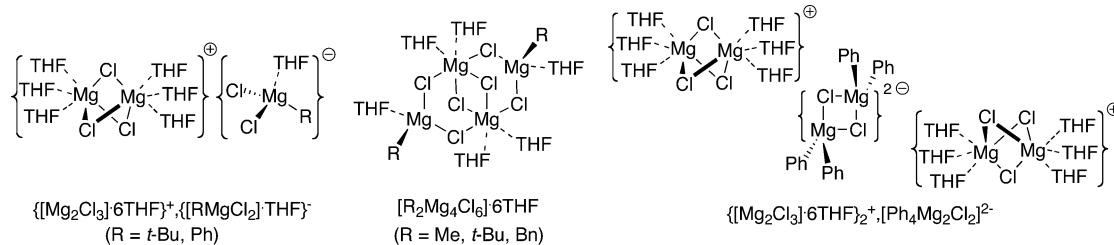
Scheme 38. X-ray Structures Obtained for MeMgBr (top),^{230f,255e,g} EtMgBr (middle),^{255b-d,f} and PhMgBr (bottom)^{235a,255a}



THF/TMEDA solution showed a monomeric structure solvated by both the ether and the diamine ($\text{THF}\cdot[\text{MeMgBr}]\cdot\text{TMEDA}$).^{230f} The addition of PMDTA to a THF solution of MeMgBr yielded a monosolvated monomeric complex ($[\text{MeMgBr}]\cdot\text{PMDTA}$),^{230f} while a trisolvated monomeric adduct formed in pure THF ($[\text{MeMgBr}]\cdot 3\text{THF}$).^{255e,g} In these three arrangements, the magnesium cation was found to be pentacoordinated. The case of EtMgBr was explored in the presence of diethyl ether,^{255b,d,g} diisopropyl ether,^{255e,g} and triethylamine.^{255c,g} A disolvated monomeric complex was highlighted with Et_2O ($[\text{EtMgBr}]\cdot 2\text{Et}_2\text{O}$),^{255b,d} whereas disolvated cyclic dimers, with Mg tetrahedral, were described in the presence of $i\text{-Pr}_2\text{O}$ ($[\text{EtMgBr}]_2\cdot 2i\text{-Pr}_2\text{O}$) or Et_3N ($[\text{EtMgBr}]_2\cdot 2\text{Et}_3\text{N}$). For its part, the crystalline sample of PhMgBr grown in the presence of Et_2O was depicted as a disolvated monomer ($[\text{PhMgBr}]\cdot 2\text{Et}_2\text{O}$).^{235a,255a}

The constitution of the chlorinated Grignard reagents MeMgCl , $t\text{-BuMgCl}$, PhMgCl , and BnMgCl proved more intricate.²⁵⁶ Crystals of these species isolated from THF solutions underscored the three types of solid-state structures $\{[\text{Mg}_2\text{Cl}_3]\cdot 6\text{THF}\}^+$, $\{[\text{RMgCl}_2]\cdot\text{THF}\}^-$ when $\text{R} = t\text{-Bu}$ and Ph (Scheme 39, left), $[\text{R}_2\text{Mg}_4\text{Cl}_6]\cdot 6\text{THF}$ for $\text{R} = \text{Me}$, $t\text{-Bu}$, Bn (Scheme 39, middle), and $\{[\text{Mg}_2\text{Cl}_3]\cdot 6\text{THF}\}_2^+$, $[\text{Ph}_4\text{Mg}_2\text{Cl}_2]^{2-}$ (Scheme 39, right).

Regarding conclusions about the structures of magnesium derivatives here depicted, one can see that those mainly exist in the solid state, or in solution, as monomers or dimers, with a tetragonal, sometimes trigonal, geometry for the magnesium atom. Note that they show a lower tendency to form aggregates than lithium compounds. Such a difference is attributed to the

Scheme 39. X-ray Data Obtained for MeMgCl , $t\text{-BuMgCl}$, PhMgCl , and PhCH_2MgCl ²⁵⁶

fact that magnesium species are less polar than lithium ones. The chemistry of organomagnesium compounds, among which an important subset is the Grignard reagent category, constitutes an active field of research for a long time. Their convenient synthesis, reasonable stability, and high reactivity make those species essential intermediates in academic and industrial research. Efforts dedicated to structural elucidations, and thus the establishment of structure/reactivity correlations, constitute an active complementary research topic.^{229j,k} The most spectacular observation made in this field is probably the one about Grignard reagents. Indeed, it is important to know that the simple “ RMgX ” representation adopted for such species is in fact far beyond the reality. In fact, in coordinating solvents, the most used for these derivatives, it exists as mixtures of several aggregates, among which are R_2Mg and MgX_2 , and proportions depend on the nature of R and X, the solvent itself, concentration, and temperature.

2.5. Aluminum Compounds

2.5.1. Homoleptic Aluminum Compounds. Results are presented for Me_3Al , Et_3Al , Pr_3Al , $i\text{-Pr}_3\text{Al}$, $t\text{-Bu}_3\text{Al}$, Ph_3Al , Bn_3Al , $(\text{Me}_2\text{N})_3\text{Al}$, $(c\text{-C}_4\text{H}_8\text{N})_3\text{Al}$, $(c\text{-C}_5\text{H}_{10}\text{N})_3\text{Al}$, and $(t\text{-BuO})_3\text{Al}$.

First, concerning the simplest trialkylaluminum, Me_3Al , an unsolvated cyclic dimer was characterized either in the solid state^{257f} or in nonbasic solution ($[\text{Me}_3\text{Al}]_2$, Table 10, entry 1a).^{257a-e,g} In contact with basic chelates, this oligomerization collapsed, as seen with dioxane, which afforded the $\{[\text{Me}_3\text{Al}] \cdot c\text{-}(\text{O}(\text{CH}_2\text{CH}_2)_2\text{O}) \cdot [\text{AlMe}_3]\}$ complex (Table 10, entry 1b),²⁵⁸ TMMDA (N,N,N',N' -tetramethylmethylenediamine), which provided the $\{[\text{Me}_3\text{Al}] \cdot \text{Me}_2\text{NCH}_2\text{NMe}_2 \cdot [\text{AlMe}_3]\}$ arrangement (Table 10, entry 1c),²⁵⁹ and diglyme, for which the $\{[\text{Me}_3\text{Al}] \cdot \text{O}(\text{CH}_2\text{CH}_2\text{OMe}_2 \cdot [\text{AlMe}_3])_2\}$ structure was evidenced (Table 10, entry 1d).²⁶⁰ In these three cases, all the oxygen or nitrogen atoms of the basic additives were coordinated to a Me_3Al unit. Working with crown-ethers (Table 10, entry 1e),^{261a-c} aza-crown, or sulfur-crown proved to be slightly different as all heteroatoms could not fix the aluminum entity for reasons of conformational steric availability. Thus, 12-crown-4 fastened two molecules of Me_3Al ,^{261c} and 15-crown-5^{261a} and 18-crown-6^{261b} connected to four Me_3Al , while dibenzo-8-crown-6 fixed only two.^{261a,b} Interestingly, N_4 -aza crown 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, with a size intermediate between those of 12-crown-4 and 15-crown-5, coordinated one molecule of Me_3Al on each nitrogen atom.^{261d} The sulfur [12]aneS₄ congener led to both “saturated” (one AlMe_3 per sulfur atom) and “unsaturated” (one AlMe_3 on one sulfur atom of the four available) solvates.^{261e,f} By examining Et_3Al , early NMR studies conducted in hydrocarbon solution were in favor of an unsolvated cyclic dimeric structure ($[\text{Et}_3\text{Al}]_2$, Table 10, entry 2),^{257a,262} as well as for the Pr_3Al reactant ($[\text{Pr}_3\text{Al}]_2$, Table 10,

entry 3a).^{257a} In contrast, $i\text{-Pr}_3\text{Al}$ was found to be essentially monomeric ($[i\text{-Pr}_3\text{Al}]$, Table 10, entry 3b).^{257a} More hindered $t\text{-Bu}_3\text{Al}$ ²⁶³ crystallized in the presence of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OH}$ or $\text{Me}_2\text{NCH}_2(\text{CH}_2)_n\text{N}(\text{Me})\text{H}$ ($n = 1$ or 2) and monomeric complexes in which the H-heteroatom connected to the aluminum metal established an intramolecular hydrogen bond with the NMe_2 group were described (Table 10, entry 4a).^{263c} Also monomers were depicted for crystals of $t\text{-Bu}_3\text{Al}$ grown in the presence of hydrazines ($[t\text{-Bu}_3\text{Al}] \cdot \text{H}_2\text{NNHR}$, Table 10, entry 4b).^{263d} Structural data on triarylaluminum species have been obtained as well.²⁶⁴ X-ray analyses made on crystals of Ph_3Al grown in hydrocarbon solvent evidenced a dimeric arrangement organized around a $\text{C}^{\text{ipso}}\text{-Al-C}^{\text{ipso}}\text{-Al}$ quadrilateral ($[\text{Ph}_3\text{Al}]_2$, Table 10, entry 5a).^{264a,b} Introducing a basic additive (Et_2O , $\text{O}=\text{PPh}_3$, 4-DMAP) had the effect of reducing the aggregation since monomeric solvates were then depicted ($[\text{Ph}_3\text{Al}] \cdot \text{OEt}_2$, $[\text{Ph}_3\text{Al}] \cdot \text{O}=\text{PPh}_3$, and $[\text{Ph}_3\text{Al}] \cdot 4\text{-DMAP}$; Table 10, entries 5b-d).^{264c} Crystal structures of tribenzylaluminum were reported both in the absence of solvation and solvated by diethyl ether.²⁶⁵ In the unsolvated batch, a polymeric η^1 -arene coordinated structure made of Bn_3Al units linking thanks to aryl–metal interactions was reported ($[\text{Bn}_3\text{Al}]_\infty$, Table 10, entry 6a).^{265a} The tribenzylaluminum diethyl etherate was found to correspond to a disolvated monomer in which the geometry of the aluminum metal was tetrahedral ($[\text{Bn}_3\text{Al}] \cdot 2\text{Et}_2\text{O}$, Table 10, entry 6b).^{265b} The structure of aluminum trisamide $(\text{Me}_2\text{N})_3\text{Al}$ was studied in hydrocarbon solution, thanks to both the NMR technique and X-ray diffraction,^{266a,b} and an unsolvated N–Al–N–Al cyclic dimer showed up ($([\text{Me}_2\text{N})_3\text{Al}]_2$, Table 10, entry 7a). Comparable structures were highlighted for (pyrrolidino)₃Al and (piperidino)₃Al [$(c\text{-C}_4\text{H}_8\text{N})_3\text{Al}]_2$ and $(c\text{-C}_5\text{H}_{10}\text{N})_3\text{Al}]_2$, Table 10, entries 7b,c).^{266c} Finally, with aluminum alkoxide ($t\text{-BuO})_3\text{Al}$, also an unsolvated cyclic dimer was identified in nonbasic solvent ($((t\text{-BuO})_3\text{Al})_2$, Table 10, entry 8).²⁶⁷

2.5.2. Heteroleptic Aluminum Compounds. Results are presented for $(\text{H})(t\text{-Bu})_2\text{Al}$, $(\text{EtO})(\text{Me})_2\text{Al}$, $(\text{MeO})(\text{Et})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_2\text{O})(\text{Me})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_2\text{O})(\text{Et})_2\text{Al}$, $(\text{EtO}(\text{CH}_2)_2\text{O})(\text{Et})_2\text{Al}$, $(\text{Et}_2\text{N}(\text{CH}_2)_2\text{O})(\text{Et})_2\text{Al}$, $(\text{EtO}(\text{CH}_2)_3\text{O})(\text{Et})_2\text{Al}$, $(\text{Et}_2\text{N}(\text{CH}_2)_3\text{O})(\text{Et})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_2\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_2\text{O})(i\text{-Bu})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_3\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_3\text{O})(\text{Me})_2\text{Al}$, $(\text{MeS}(\text{CH}_2)_2\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{MeS}(\text{CH}_2)_2\text{O})(i\text{-Bu})_2\text{Al}$, $(\text{MeS}(\text{CH}_2)_3\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{Me}_2\text{N}(\text{CH}_2)_2\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{Me}_2\text{N}(\text{CH}_2)_2\text{O})(i\text{-Bu})_2\text{Al}$, $(\text{Me}_2\text{N}(\text{CH}_2)_3\text{O})(\text{Me})_2\text{Al}$, $(\text{EtO})(\text{Me})\text{AlCl}$, $(\text{EtO})(\text{Et})\text{AlCl}$, $(\text{naphthylNH})(\text{Me})_2\text{Al}$, $(\text{mesityl}_2\text{N})(t\text{-Bu})_2\text{Al}$, and $((\text{Ph}_3\text{Si})_2\text{N})(t\text{-Bu})_2\text{Al}$.

Aluminum compounds being trisubstituted $((\text{R}^1)(\text{R}^2)(\text{R}^3)\text{-Al})$, the heteroleptic ones can correspond to either those with $\text{R}^1 = \text{R}^2 \neq \text{R}^3$ or $\text{R}^1 \neq \text{R}^2 \neq \text{R}^3$. Among the structural studies devoted to this class of species, a series was found to implicate aluminum alkoxides $(\text{R}^1\text{O})(\text{R}^2)(\text{R}^3)\text{-Al}$.²⁶⁸ In this work, cyclic

Table 10. Structures of Homoleptic Aluminum Derivatives

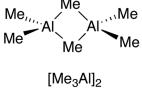
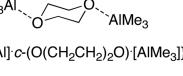
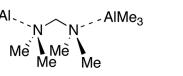
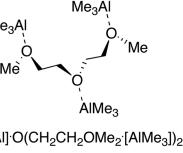
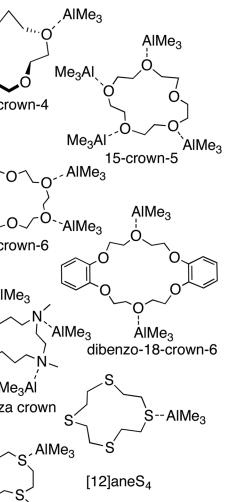
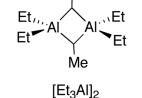
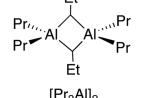
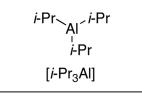
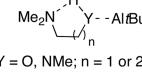
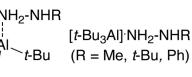
Entry	Aluminum derivative	Analytical technique	Solvation	Structure	Ref
1a	Me_3Al	X-Ray or Raman, NMR	none (grown freezing pure Me_3Al or analyzed in hydrocarbon)		257
1b			1,4-dioxane (grown in dioxane)		258
1c			TMMDA (grown/analyzed in toluene + 1 equiv TMMDA)		259
1d			diglyme (grown/analyzed in hydrocarbon + 1/3 equiv diglyme)		260
1e			crown ethers, amine and sulfur		261c 261a 261b 261a,b 261d 261e 261f
2	Et_3Al	NMR	none (in hydrocarbon)		257a 262
3a	Pr_3Al	NMR	none (in hydrocarbon)		257a
3b	$i\text{-Pr}_3\text{Al}$				257a
4a	$t\text{-Bu}_3\text{Al}$	X-Ray	$\text{Me}_2\text{N}(\text{CH}_2)_{n+1}\text{YH}$ (grown in hexane + 1 equiv amino-chelate)		263c
4b			$\text{H}_2\text{N}-\text{NHR}$ (grown in pentane)		263d

Table 10. continued

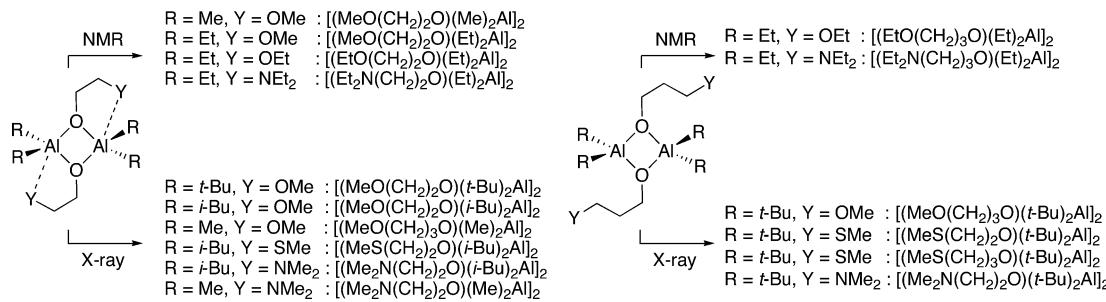
Entry	Aluminum derivative	Analytical technique	Solvation	Structure	Ref
5a			none (in hydrocarbon)		264a,b
5b	Ph ₃ Al	X-Ray	Et ₂ O		264c
5c			O=PPh ₃		264c
5d			4-DMAP		264c
6a	Bn ₃ Al	X-Ray	none (grown in benzene)		265a
6b			Et ₂ O		265b
7a	(Me ₂ N) ₃ Al	NMR X-ray	none (in benzene) (grown in hexane)		266a,b
7b	(c-C ₄ H ₈ N) ₃ Al	NMR X-Ray	none (grown in THF)		266c
7c	(c-C ₅ H ₁₀ N) ₃ Al	X-Ray	none (grown in THF)		266c
8	(t-BuO) ₃ Al	Raman	none (in toluene)		267

dimers organized around an O–Al–O–Al core were highlighted in toluene solution thanks to the NMR technique, as observed for $(\text{MeO}(\text{CH}_2)_2\text{O})(\text{Me})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_2\text{O})-(\text{Et})_2\text{Al}$, $(\text{EtO}(\text{CH}_2)_2\text{O})(\text{Et})_2\text{Al}$, $(\text{Et}_2\text{N}(\text{CH}_2)_2\text{O})(\text{Et})_2\text{Al}$, $(\text{EtO}(\text{CH}_2)_3\text{O})(\text{Et})_2\text{Al}$, and $(\text{Et}_2\text{N}(\text{CH}_2)_3\text{O})(\text{Et})_2\text{Al}$, with a possible intramolecular coordination between the aluminum atom and the OEt or NEt₂ group for the two-carbon chain derivatives (Scheme 40, top).^{268a} Crystallographic data were also obtained for the $(\text{MeO}(\text{CH}_2)_2\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{MeO}-(\text{CH}_2)_2\text{O})(i\text{-Bu})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_3\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{MeO}-(\text{CH}_2)_3\text{O})(\text{Me})_2\text{Al}$, $(\text{MeS}(\text{CH}_2)_2\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{MeS}-$

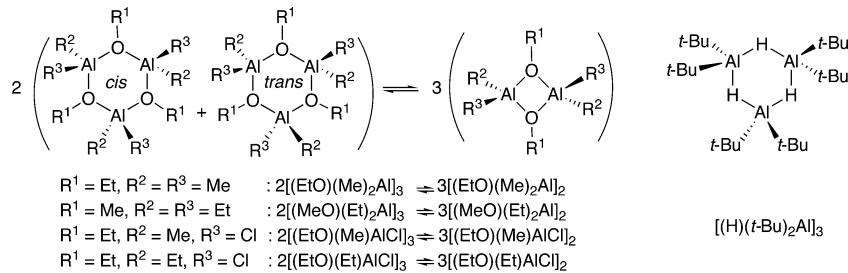
$(\text{CH}_2)_2\text{O})(i\text{-Bu})_2\text{Al}$, $(\text{MeS}(\text{CH}_2)_3\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{Me}_2\text{N}-(\text{CH}_2)_2\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{Me}_2\text{N}(\text{CH}_2)_2\text{O})(i\text{-Bu})_2\text{Al}$, and $(\text{Me}_2\text{N}(\text{CH}_2)_2\text{O})(\text{Me})_2\text{Al}$ congeners.^{268c} All the solid-state structures were found to be dimeric with O–Al–O–Al central quadrilateral and intramolecular coordinations taking place for those being less hindered in the Al surroundings (Scheme 40, bottom).

The structures of $(\text{EtO})(\text{Me})_2\text{Al}$ and $(\text{MeO})(\text{Et})_2\text{Al}$, as well as $(\text{EtO})(\text{Me})\text{AlCl}$ and $(\text{EtO})(\text{Et})\text{AlCl}$, have been investigated in 2-dichlorobenzene by ¹H NMR spectroscopy.^{268b} The major presence of trimeric $(\text{O}-\text{Al})_3$ oligomers was detected at room

Scheme 40. Dimeric Structures in Toluene Solution of $(\text{MeO}(\text{CH}_2)_2\text{O})(\text{Me})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_2\text{O})(\text{Et})_2\text{Al}$, $(\text{EtO}(\text{CH}_2)_2\text{O})(\text{Et})_2\text{Al}$, $(\text{Et}_2\text{N}(\text{CH}_2)_2\text{O})(\text{Et})_2\text{Al}$, $(\text{EtO}(\text{CH}_2)_3\text{O})(\text{Et})_2\text{Al}$, and $(\text{Et}_2\text{N}(\text{CH}_2)_3\text{O})(\text{Et})_2\text{Al}$ (top)^{268a} and Crystallographic Dimeric Structures of $(\text{MeO}(\text{CH}_2)_2\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_2\text{O})(i\text{-Bu})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_3\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{MeO}(\text{CH}_2)_3\text{O})(\text{Me})_2\text{Al}$, $(\text{MeS}(\text{CH}_2)_2\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{MeS}(\text{CH}_2)_2\text{O})(i\text{-Bu})_2\text{Al}$, $(\text{MeS}(\text{CH}_2)_3\text{O})(t\text{-Bu})_2\text{Al}$, $(\text{Me}_2\text{N}(\text{CH}_2)_2\text{O})(i\text{-Bu})_2\text{Al}$, and $(\text{Me}_2\text{N}(\text{CH}_2)_2\text{O})(\text{Me})_2\text{Al}$ ^{268c}



Scheme 41. Structures in 2-Dichlorobenzene Solution of $(\text{EtO})(\text{Me})_2\text{Al}$, $(\text{MeO})(\text{Et})_2\text{Al}$, $(\text{EtO})(\text{Me})\text{AlCl}$, and $(\text{EtO})(\text{Et})\text{AlCl}$ ^{268b} and X-ray Structure of $(\text{H})(t\text{-Bu})_2\text{Al}$ ^{263b}



temperature, while the dimeric $(\text{O}-\text{Al})_2$ form was found to become more abundant upon increasing the temperature (Scheme 41, left). Note that the crystallographic structure obtained in hydrocarbon solvents for di-*tert*-butylalane was found to correspond to a planar six-membered $\text{Al}-\text{H}$ heterotrimer $\{[(\text{H})(t\text{-Bu})_2\text{Al}]_3$, Scheme 41, right^{263b}.

Although a non-negligible number of aluminum amide structures have been determined, only a few are evoked in this review: those corresponding to the lowest molecular weight species. Thus, an unsolvated dimeric arrangement organized around an $\text{N}-\text{Al}-\text{N}-\text{Al}$ quadrilateral was found from crystals of the $(\text{naphthylNH})(\text{Me})_2\text{Al}$ entity grown in ether solvents.^{269a} Otherwise, crystallographic data related to $(\text{mesityl}_2\text{N})(t\text{-Bu})_2\text{Al}$ and $((\text{Ph}_3\text{Si})_2\text{N})(t\text{-Bu})_2\text{Al}$ evidenced unsolvated monomers.^{269b} Note at last the preliminary investigation carried out with dialkyaluminum acetylacetones.^{270b}

As said earlier, this review is limited to the depiction of only a few aluminum Al(III) derivatives chosen for their simplicity and those are precursors of aluminate species acting as bases or nucleophiles. Anyone interested in obtaining a more complete set of structural, bonding, and reactivity information is strongly invited to consult the very recent paper by Lewinski and Wheatley.^{270a} Note that, from the few data reported here, one can see that mostly unsolvated dimers form in hydrocarbon media, while rather solvated monomers form in basic solvents or in the presence of additives. Concerning now structure/reactivity correlations, organoaluminum compounds are highly reactive with a wide range of substrates, a behavior attributed to the important charge separation between the metal and the carbon chains. One can also justify the high reactivity by the fact that aluminum species maintain a low level of aggregation, whatever the solvent (mainly monomers or dimers). The most popular property known for such derivatives is probably their

Lewis acid character.^{270c} In the Lewis acid–base complexes that are formed, the aluminum is monomeric, tetracoordinated, and generally adopts a tetragonal geometry. Note that the chemistry of aluminum compounds has boomed considerably over the past decade. Among all the new developments, one can evoke (i) applications in the field of frustrated Lewis pairs;^{270d–f} (ii) a positive use of the originally undesired organoaluminum– O_2 interaction, to attain aluminum alkylperoxides and alkoxides, promising tools for monoelectronic transfer reactions;^{270g,h} (iii) a challenging work for reaching, understanding the mechanism of formation, and using as original reactants aluminum amides and imides,^{270i–n} and (iv) a continuous interest for getting new ligands adapted for this class of organometallic.^{270o,p} Such an evolution in the field justifies that more and more structural depictions are found in the bibliography, with the objective of interpreting the chemical results with a full understanding of the reaction mechanisms, which is possible thanks to the characterization of the reaction intermediates.

2.6. Zinc Compounds

2.6.1. Homoleptic Zinc Compounds. Results are presented for Me_2Zn , Et_2Zn , $s\text{-Bu}_2\text{Zn}$, $t\text{-Bu}_2\text{Zn}$, $(\text{H}_2\text{C}=\text{C}(\text{Me}))_2\text{Zn}$, $(\text{Me}_2\text{C}=\text{CH})_2\text{Zn}$, $(\text{PhC}\equiv\text{C})_2\text{Zn}$, Ph_2Zn and related Ar_2Zn (Ar = mesityl, $4\text{-CF}_3\text{C}_6\text{H}_4$, C_6F_5), Bn_2Zn , TMP_2Zn , $((t\text{-Bu})(\text{Me}_3\text{Si})\text{N})_2\text{Zn}$, $(\text{Bn}_2\text{N})_2\text{Zn}$, and $((\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{N})_2\text{Zn}$.

Crystals of dimethylzinc²⁷¹ have been obtained without²⁷¹ⁱ and with^{271a–h} basic additives. In the first case, an unsolvated linear monomer was pointed out ($[\text{Me}_2\text{Zn}]$, Table 11, entry 1a). In solvating media, complexed monomers in which the zinc metal was found to establish one or two dative bonds with the base, thus presenting a tetrahedral geometry, were characterized. Thus, DME, NMe_3 , NEt_3 , pyridine, 1,4-dioxane, 4-DMAP, 2,2-bipyridine (BIPY), hexahydro-1,3,5-trimethyl-1,3,5-

Table 11. Structures (X-ray) of Homoleptic Zinc Derivatives

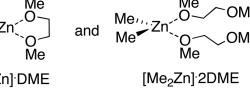
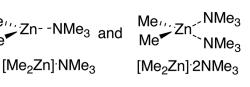
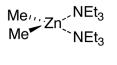
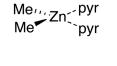
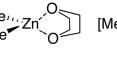
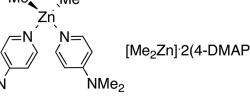
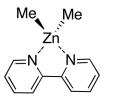
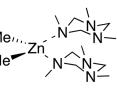
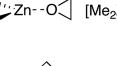
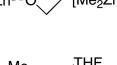
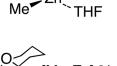
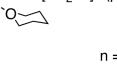
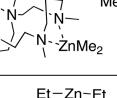
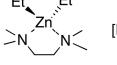
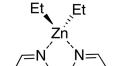
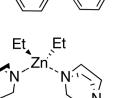
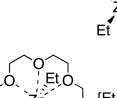
Entry	Zinc derivative	Solvation	Structure	Ref
1a		none	 [Me ₂ Zn]	271i
1b		DME (grown in DME)	 [Me ₂ Zn]DME and [Me ₂ Zn]2DME	271c
1c		NMe ₃ (grown in NMe ₃)	 [Me ₂ Zn]NMe ₃ and [Me ₂ Zn]2NMe ₃	271d
1d		NEt ₃ (grown in NEt ₃)	 [Me ₂ Zn]2NEt ₃	271d
1e		pyridine (grown in pyridine)	 [Me ₂ Zn]2pyr	271d
1f		1,4-dioxane (grown in 1,4-dioxane)	 [Me ₂ Zn](1,4-dioxane)	271c
1g	Me ₂ Zn	4-DMAP (grown in hexane + 2 equiv 4-DMAP)	 [Me ₂ Zn]2(4-DMAP)	271h
1h	Me ₂ Zn	BIPY (grown in hexane + 1 equiv 2,2'-bipyridine)	 [Me ₂ Zn]BIPY	271e
1i	Me ₂ Zn	HHTT (grown from sublimation)	 [Me ₂ Zn]2HHTT	271f
1j	Me ₂ Zn	ethylene oxide (grown in <i>c</i> -O(CH ₂) ₂)	 [Me ₂ Zn](ethylene oxide)	271b
1k	Me ₂ Zn	trimethylene oxide (grown in <i>c</i> -O(CH ₂) ₃)	 [Me ₂ Zn](trimethylene oxide)	271b
1l	Me ₂ Zn	THF (grown in THF)	 [Me ₂ Zn]2THF	271b
1m	Me ₂ Zn	pentamethylene oxide (grown in <i>c</i> -O(CH ₂) ₅)	 [Me ₂ Zn]2(pentamethylene oxide)	271b
1n	Me ₂ Zn	N _n -aza crowns (grown in toluene + 0.5 equiv aza crown)	 n = 4 and n = 6 [Me ₂ Zn]4aza crown and [Me ₂ Zn]6aza crown	271g
2a		none	 [Et ₂ Zn]	271i
2b		TMEDA (grown in hexane/THF + 0.5 equiv TMEDA)	 [Et ₂ Zn]TMEDA	272b
2c	Et ₂ Zn	BIPY (grown in hexane + 1 equiv 2,2'-bipyridine)	 [Et ₂ Zn]BIPY	272c
2d	Et ₂ Zn	DABCO (grown in Et ₂ O + 1 equiv DABCO)	 {[Et ₂ Zn]DABCO} _∞	272a
2e		18-crown-6 (grown in benzene + 1 equiv 18-crown-6)	 [Et ₂ Zn]18-crown-6	231c

Table 11. continued

Entry	Zinc derivative	Solvation	Structure	Ref
3a	$s\text{-Bu}_2\text{Zn}$	pyridines (grown in hexane + 2 equiv pyridine)	 (R = H : pyridine R = Me : 2-picoline and 3-picoline) [$s\text{-Bu}_2\text{Zn}$]2pyr	273b
3b	$s\text{-Bu}_2\text{Zn}$	TxEDA ($x = \text{M or E}$) (grown in hexane + 1 equiv TxEDA)	 (R = Me or Et) [$s\text{-Bu}_2\text{Zn}$]TxEDA	273b
3c	$t\text{-Bu}_2\text{Zn}$	none (from sublimation)	$t\text{-Bu}-\text{Zn}-t\text{-Bu}$ [$t\text{-Bu}_2\text{Zn}$]	273a
4a	$(\text{H}_2\text{C}=\text{C}(\text{Me}))_2\text{Zn}$	none (grown in hexane then from sublimation)		274a
4b	$(\text{H}_2\text{C}=\text{C}(\text{Me}))_2\text{Zn}$	BIPY (grown in hexane + 1 equiv 2,2'-bipyridine)		274a
5a	$(\text{Me}_2\text{C}=\text{CH})_2\text{Zn}$	none (grown in hexanes then from sublimation)		274a
5b	$(\text{Me}_2\text{C}=\text{CH})_2\text{Zn}$	TMEDA (grown in hexane + 1 equiv TMEDA)		274a
5c	$(\text{Me}_2\text{C}=\text{CH})_2\text{Zn}$	BIPY (grown in hexane + 1 equiv 2,2'-bipyridine)		274a
6	$(\text{PhC}\equiv\text{C})_2\text{Zn}$	TMEDA (grown in hexane + 0.5 equiv TMEDA)		274b
7a	Ph_2Zn	none (grown in hexane)		275a
7b	Ph_2Zn	polymethylene sulfides (grown in <i>n</i> -hexane + 1 equiv sulfide)		275b
8a	$(2,4,6\text{-CF}_3\text{C}_6\text{H}_2)_2\text{Zn}$	none (grown in hexane)		276a,b
8b	$(4\text{-CF}_3\text{C}_6\text{H}_4)_2\text{Zn}$	none (grown in benzene)		276c
9a	$(\text{C}_6\text{F}_5)_2\text{Zn}$	none (grown in benzene)		277b
9b	$(\text{C}_6\text{F}_5)_2\text{Zn}$	THF		277a
10	Bn_2Zn	TMEDA (grown in Et_2O + 1 equiv TMEDA)		278
11a	TMP_2Zn	none (grown from sublimation)		279
11b	$((t\text{-Bu})(\text{SiMe}_3\text{N})_2\text{Zn}$	none (grown in THF)		280

Table 11. continued

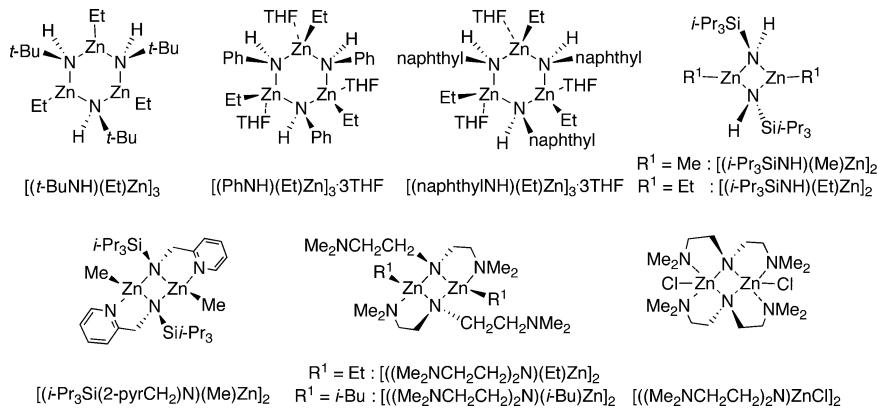
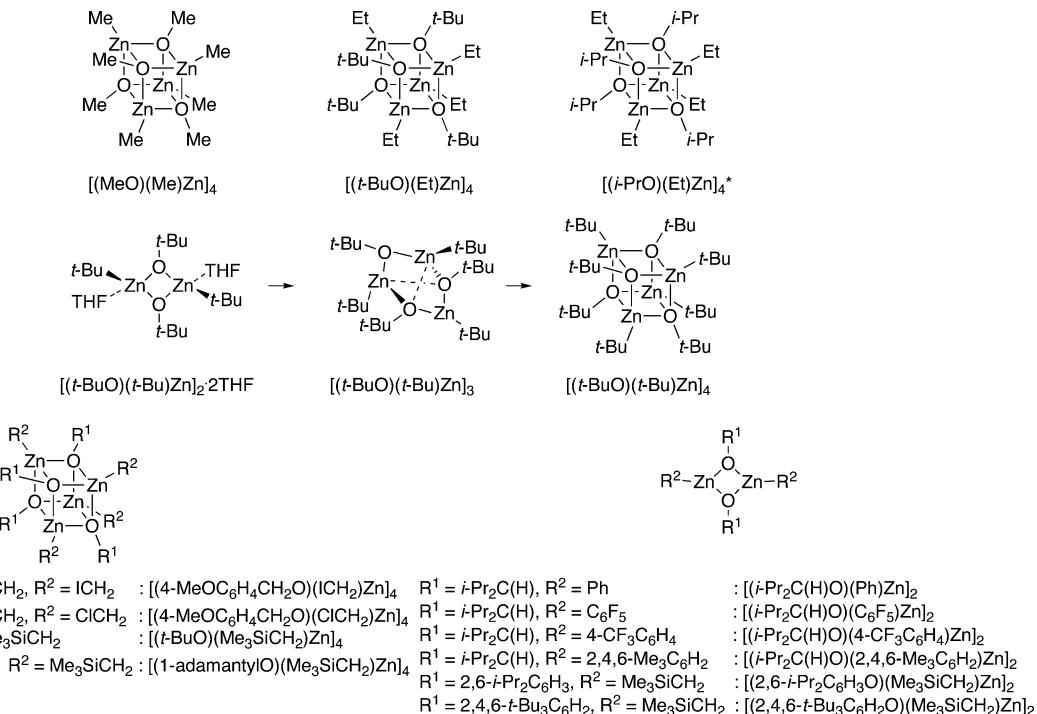
Entry	Zinc derivative	Solvation	Structure	Ref
11c	(Bn ₂ N) ₂ Zn	benzene		281
11d	((Me ₂ NC ₂ H ₄) ₂ N) ₂ Zn	none (grown in Et ₂ O)		282

triazine (HHTT), and (poly)ethylene oxides afforded with Me₂Zn the consecutive [Me₂Zn]·DME and [Me₂Zn]·2DME (Table 11, entry 1b),^{271c} [Me₂Zn]·NMe₃ and [Me₂Zn]·2NMe₃ (Table 11, entry 1c),^{271d} [Me₂Zn]·2NEt₃ (Table 11, entry 1d),^{271d} [Me₂Zn]·2pyr (Table 11, entry 1e),^{271d} [Me₂Zn]·1,4-dioxane (Table 11, entry 1f),^{271c} [Me₂Zn]·2(4-DMAP) (Table 11, entry 1g),^{271h} [Me₂Zn]·BIPY (Table 11, entry 1h),^{271e} [Me₂Zn]·2HHTT (Table 11, entry 1i),^{271f} [Me₂Zn]·(ethylene oxide) (Table 11, entry 1j),^{271b} [Me₂Zn]·(trimethylene oxide) (Table 11, entry 1k),^{271b} [Me₂Zn]·2(tetramethylene oxide or THF) (Table 11, entry 1l)^{271b} and [Me₂Zn]·2(pentamethylene oxide) (Table 11, entry 1m)^{271b} mono- or disolvated monomers. Engaging N₄ and N₆ aza-crown additives led to crystal units incorporating two Me₂Zn for one molecule of aza-crown and in which each zinc was coordinated by two nitrogen atoms separated by two or three atoms of carbon (Table 11, entry 1n).^{271g} A linear monomer was also shown for crystalline samples of unsolvated Et₂Zn ([Et₂Zn], Table 11, entry 2a).²⁷¹ⁱ Mixing diethylzinc with TMEDA^{272b} or BIPY^{272c} favored the formation of monosolvated Zn-tetrahedral monomeric crystals ([Et₂Zn]·TMEDA and [Et₂Zn]·BIPY, Table 11, entries 2b and 2c, respectively), while in the presence of DABCO, a linear polymeric structure intercalating one Et₂Zn molecule and one DABCO unit was identified ({[Et₂Zn]·DABCO}_∞, Table 11, entry 2d).^{272a} A centrosymmetric structure was evidenced with 18-crown-6, zinc being hexacoordinated and the Zn—Et bonds being perpendicular to the plane ([Et₂Zn]·18-crown-6, Table 11, entry 2e).^{231c} Zn-tetrahedral di- or monosolvated monomers were still characterized for s-Bu₂Zn in the presence of pyridines {[s-Bu₂Zn]·2C₅H₅N, [s-Bu₂Zn]·2(2-MeC₅H₄N), and [s-Bu₂Zn]·2(3-MeC₅H₄N), Table 11, entry 3a}^{273b} or ethylenediamines {[s-Bu₂Zn]·TMEDA and [s-Bu₂Zn]·TEEDA, Table 11, entry 3b),^{273b} respectively. The t-Bu₂Zn isomer showed a crystalline linear monomeric form when unsolvated ([t-Bu₂Zn], Table 11, entry 3c), while a Zn-tetrahedral polymer settled in the presence of 1,2-bis(4-pyridyl)ethane.^{273a} Unsaturated disubstituted species,²⁷⁴ such as divinylzinc (H₂C=C(Me))₂Zn and (Me₂C=CH)₂Zn, showed polymeric arrangements in the absence of solvation (Table 11, entries 4a and 5a), while the addition of 2,2'-bipyridine or TMEDA led to dicoordinated monosolvated monomers, zinc having a tetrahedral geometry {[H₂C=C(Me)]₂Zn}·BIPY, [(Me₂C=CH)₂Zn]·TMEDA, and [(Me₂C=CH)₂Zn]·BIPY; Table 11, entries 4b, 5b, and 5c, respectively).^{274a} In the same way, the acetylenic derivative (PhC≡C)₂Zn crystallized in the presence of TMEDA as a Zn-tetrahedral monosolvated monomer {[PhC≡C]₂Zn}·TMEDA, Table 11, entry 6).^{274b} Dimeric structures were observed with diarylzinc compounds. Thus,

crystals of diphenylzinc obtained in hexane evidenced an unsolvated quadrilateral dimer in which zinc was found to be planar-trigonal ([Ph₂Zn]₂, Table 11, entry 7a).^{64a,275a} Adding cyclic thioethers did not alter the dimerization phenomenon, but increased by one (Zn tetrahedral) the number of coordination of the metal since one molecule of thioether was fixed on each Zn ([Ph₂Zn]₂thioether, Table 11, entry 7b).^{275b} Substitutions on the phenyl appendage had the consequence of affording monomeric linear structures for crystals isolated from hydrocarbon solutions (hexane, toluene) ([2,4,6-CF₃C₆H₂)₂Zn] and [(4-CF₃C₆H₄)₂Zn], Table 11, entries 8a,b).²⁷⁶ Similar observation was made from crystals of (C₆F₅)₂Zn grown in benzene ([C₆F₅)₂Zn], Table 11, entry 9a),^{277b} while in the presence of THF, the monomer observed presented a tetrahedral geometry around zinc, the latter being disolvated ([C₆F₅)₂Zn]·2THF, Table 11, entry 9b).^{277a} Diphenylzinc behaved as its dialkyl analogues in the presence of TMEDA, affording a crystalline structure corresponding to a Zn-tetrahedral monosolvated monomer ([Bn₂Zn]·TMEDA, Table 11, entry 10).²⁷⁸ Crystals of bisamides TMP₂Zn²⁷⁹ and ((t-Bu)(SiMe₃)N)₂Zn²⁸⁰ were characterized in the solid state, and linear unsolvated monomers were depicted ([TMP₂Zn] and [(t-Bu)(SiMe₃)N]₂Zn], Table 11, entries 11a,b). Concerning ((Bn₂N)₂Zn synthesized in benzene solution, characterization performed by single X-ray diffraction, as well as NMR spectroscopy, pointed out the formation of a benzene-monosolvated dimer ([Bn₂N]₂·C₆H₆, Table 11, entry 11c).²⁸¹ Zinc bisamides incorporating chelating heteroatoms on the amino substituents have also been synthesized and structurally analyzed. Thus, ((Me₂NCH₂CH₂)₂N)₂Zn was crystallized, and the X-ray data were consistent with a cyclic dimer composed of a N—Zn—N—Zn core in which each zinc atom was intramolecularly coordinated by one NMe₂ group {[((Me₂NCH₂CH₂)₂N)₂Zn], Table 11, entry 11d}.²⁸²

2.6.2. Heteroleptic Zinc Compounds. Heteroleptic zinc amides (R¹R²N)(R³)Zn and alkoxides (R¹O)(R²)Zn figure among the main heteroleptic zinc compounds from which structural data were obtained. One example of heteroleptic zinc halide will be discussed at the end of this section, in addition to a heteroleptic diorganozinc (R¹R²Zn, R¹ ≠ R²).

2.6.2.1. Heteroleptic Zinc Amides (R¹R²N)(R³)Zn (R³ ≠ R¹R²N). Results are presented for (t-BuNH)(Et)Zn, (PhNH)(Et)Zn, (naphthylNH)(Et)Zn, (i-Pr₃SiNH)(Me)Zn, (i-Pr₃SiNH)(Et)Zn, (i-Pr₃Si(2-pyrCH₂)N)(Me)Zn, ((Me₂NCH₂CH₂)₂N)(Et)Zn, ((Me₂NCH₂CH₂)₂N)(i-Bu₂N)Zn, (i-Pr₃SiNH)((Me₃Si)₃C)Zn, and ((Me₂NCH₂CH₂)₂N)ZnCl.

Scheme 42. Crystallographic Structures of Heteroleptic Zinc Amides^{238,282–285}Scheme 43. Crystallographic Structures of Heteroleptic Zinc Alkoxides^{276c,286–290}

*The structure of $(i\text{-PrO})(\text{Et})\text{Zn}$ was determined from a cryoscopy study.

With regard to zinc amides, $(t\text{-BuNH})(\text{Et})\text{Zn}$, synthesized from Et_2Zn and $t\text{-BuNH}_2$ in the absence of solvent, was described in the solid state as an unsolvated cyclic trimeric oligomer $[(t\text{-BuNH})(\text{Et})\text{Zn}]_3$, Scheme 42, top left).²³⁸ Crystals of its phenyl amide analogue, $(\text{PhNH})(\text{Et})\text{Zn}$, were isolated from a THF solution, which did not change the size of the oligomer, still a cyclic trimer, but introduced a trisolvation by THF $[(\text{PhNH})(\text{Et})\text{Zn}]_3 \cdot 3\text{THF}$, Scheme 42, top middle left).²³⁸ X-ray analyses run on the $(\text{naphthylNH})(\text{Et})\text{Zn}$ derivative also showed a THF-trisolvated trimer $[(\text{naphthylNH})(\text{Et})\text{Zn}]_3 \cdot 3\text{THF}$, Scheme 42, top middle right).^{269a} For their part, methyl- and ethylzinc triisopropylsilylamides $(i\text{-Pr}_3\text{SiNH})(\text{Me})\text{Zn}$ and $(i\text{-Pr}_3\text{SiNH})(\text{Et})\text{Zn}$, respectively, were presented as unsolvated cyclic dimers after being isolated in the solid state from a toluene solution $[(i\text{-Pr}_3\text{SiNH})(\text{Me})\text{Zn}]_2$ and $[(i\text{-Pr}_3\text{SiNH})(\text{Et})\text{Zn}]_2$, Scheme 42, top right).²⁸³ Cyclic dimers were highlighted as well, this time intramolecularly solvated, from crystallographic data obtained

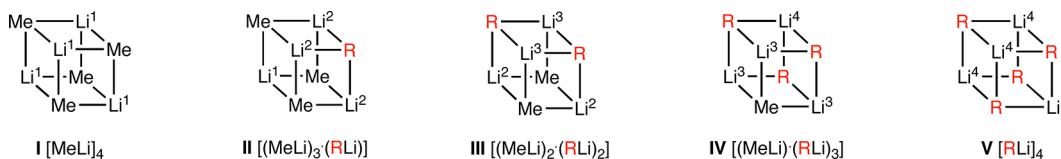
on $(i\text{-Pr}_3\text{Si}(2\text{-pyrCH}_2)\text{N})(\text{Me})\text{Zn}$,²⁸⁴ $((\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{N})(\text{Et})\text{Zn}$,²⁸² $((\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{N})(i\text{-Bu}_2\text{N})\text{Zn}$,²⁸² and $((\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{N})\text{ZnCl}$ ²⁸² $\{[(i\text{-Pr}_3\text{Si}(2\text{-pyrCH}_2)\text{N})(\text{Me})\text{Zn}]_2, [((\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{N})(\text{Et})\text{Zn}]_2, [((\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{N})(i\text{-Bu}_2\text{N})\text{Zn}]_2, [((\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{N})\text{ZnCl}]_2$, Scheme 42, bottom}. Note that a monomeric form would prevail with the very bulky $(i\text{-Pr}_3\text{SiNH})((\text{Me}_3\text{Si})_3\text{C})\text{Zn}$.²⁸⁵

2.6.2.2. *Heteroleptic Zinc Alkoxides $(R^1\text{O})(R^2\text{Zn})$ ($R^2 \neq R^1\text{O}$)*. Results are presented for $(\text{MeO})(\text{Me})\text{Zn}$, $(t\text{-BuO})(\text{Et})\text{Zn}$, $(i\text{-PrO})(\text{Et})\text{Zn}$, $(\text{PhCH}_2\text{CH}_2\text{O})(\text{Et})\text{Zn}$, $(t\text{-BuO})(t\text{-Bu})\text{Zn}$, $(i\text{-PrO})(\text{ICH}_2)\text{Zn}$, $(\text{BuO})(\text{ICH}_2)\text{Zn}$, $(\text{PhCH}_2\text{CH}_2\text{O})(\text{ICH}_2)\text{Zn}$, $(i\text{-PrO})(\text{ClCH}_2)\text{Zn}$, $(\text{PhCH}_2\text{CH}_2\text{O})(\text{ClCH}_2)\text{Zn}$, $(4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{O})(\text{ICH}_2)\text{Zn}$, $(4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{O})(\text{ClCH}_2)\text{Zn}$, $(t\text{-BuO})(\text{Me}_3\text{SiCH}_2)\text{Zn}$, $(1\text{-adamantylO})(\text{Me}_3\text{SiCH}_2)\text{Zn}$, $(i\text{-Pr}_2\text{C}(\text{H})\text{O})(\text{Ph})\text{Zn}$, $(i\text{-Pr}_2\text{C}(\text{H})\text{O})(\text{C}_6\text{F}_5)\text{Zn}$, $(i\text{-Pr}_2\text{C}(\text{H})\text{O})(4\text{-CF}_3\text{C}_6\text{H}_4)\text{Zn}$, $(2,6\text{-i-Pr}_2\text{C}_6\text{H}_3\text{O})(\text{Me}_3\text{SiCH}_2)\text{Zn}$, and $(2,4,6\text{-t-Bu}_3\text{C}_6\text{H}_2\text{O})(\text{Me}_3\text{SiCH}_2)\text{Zn}$.

Scheme 44. Crystallographic Structure of $\text{Me}_3\text{Si}(\text{Ph})\text{C}(\text{H})\text{ZnCl}$ ²⁹¹ and $(\text{PhC}\equiv\text{C})(t\text{-Bu})\text{Zn}$ ^{274b} with TMEDA



Scheme 45. The Five Tetrameric HomoMAAs Formed between MeLi and RLi ($\text{R} = \text{Et}$ or Bu) in Ethereal Solvents (Et_2O , THF)^{24b,292,293}



Among heteroleptic zinc alkoxides for which structural information was reported, one can cite studies carried out on the very simple methylzinc methoxide $(\text{MeO})(\text{Me})\text{Zn}$.²⁸⁶ X-ray examination performed on crystals grown in hexane pointed out an unsolvated cubic tetrameric oligomer made of $\text{Zn}-\text{O}$ edges $\{[(\text{MeO})(\text{Me})\text{Zn}]_4$, Scheme 43, top left). A similar oligomeric shape was reported for crystalline ethylzinc *tert*-butoxide $(t\text{-BuO})(\text{Et})\text{Zn}$ $\{[(t\text{-BuO})(\text{Et})\text{Zn}]_4$, Scheme 43, top middle).²⁸⁷ Cryoscopy measurements realized in benzene solution estimated the degree of association of $(i\text{-PrO})(\text{Et})\text{Zn}$ $\{[(i\text{-PrO})(\text{Et})\text{Zn}]_4$, Scheme 43, top right) as being four (tetramer),²⁸⁸ while it is one (monomer) for $(\text{PhCH}_2\text{CH}_2\text{O})(\text{Et})\text{Zn}$ $\{[(\text{PhCH}_2\text{CH}_2\text{O})(\text{Et})\text{Zn}]_1$.²⁸⁸ A crystalline THF-disolvated dimeric arrangement was observed for $(t\text{-BuO})(t\text{-Bu})\text{Zn}$, a dimer that evolved by solid-state conversions to give the unsolvated trimeric and then tetrameric oligomers $\{[(t\text{-BuO})(t\text{-Bu})\text{Zn}]_2, 2\text{THF} \rightarrow [(t\text{-BuO})(t\text{-Bu})\text{Zn}]_3 \rightarrow [(t\text{-BuO})(t\text{-Bu})\text{Zn}]_4$, Scheme 43, middle).²⁸⁹ (Halomethyl)zinc alkoxides such as $(i\text{-PrO})(\text{ICH}_2)\text{Zn}$, $(\text{BuO})(\text{ICH}_2)\text{Zn}$, $(\text{PhCH}_2\text{CH}_2\text{O})(\text{ICH}_2)\text{Zn}$, $(i\text{-PrO})(\text{ClCH}_2)\text{Zn}$, and $(\text{PhCH}_2\text{CH}_2\text{O})(\text{ClCH}_2)\text{Zn}$ were all announced as monomers in benzene solution according to a cryoscopy study $\{[(i\text{-PrO})(\text{ICH}_2)\text{Zn}], [(\text{BuO})(\text{ICH}_2)\text{Zn}], [(\text{PhCH}_2\text{CH}_2\text{O})(\text{ICH}_2)\text{Zn}], [(\text{i-PrO})(\text{ClCH}_2)\text{Zn}],$ and $[(\text{PhCH}_2\text{CH}_2\text{O})(\text{ClCH}_2)\text{Zn}]\}$.²⁸⁸ By contrast, crystals obtained from hexane/ CH_2Cl_2 solution with parent species $(4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{O})(\text{ICH}_2)\text{Zn}$ and $(4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{O})(\text{ClCH}_2)\text{Zn}$ showed cubic tetrameric arrangements $\{[(4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{O})(\text{ICH}_2)\text{Zn}]_4$ and $[(4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{O})(\text{ClCH}_2)\text{Zn}]_4$, Scheme 43, bottom left).²⁸⁸ Cubic tetramers were also depicted from crystallographic investigations run on $(t\text{-BuO})(\text{Me}_3\text{SiCH}_2)\text{Zn}$ and $(1\text{-adamantylO})(\text{Me}_3\text{SiCH}_2)\text{Zn}$ derivatives obtained in the solid state in hexane solution $\{[(t\text{-BuO})(\text{Me}_3\text{SiCH}_2)\text{Zn}]_4$ and $[(1\text{-adamantylO})(\text{Me}_3\text{SiCH}_2)\text{Zn}]_4$, Scheme 43, bottom left).²⁹⁰ Unsolvated dimeric oligomeric shapes were obtained from crystals grown in hexane of the more hindered $(i\text{-Pr}_2\text{C}(\text{H})\text{O})(\text{Ph})\text{Zn}$,^{276c} $(i\text{-Pr}_2\text{C}(\text{H})\text{O})(\text{C}_6\text{F}_5)\text{Zn}$,^{276c} $(i\text{-Pr}_2\text{C}(\text{H})\text{O})(4\text{-CF}_3\text{C}_6\text{H}_4)\text{Zn}$,^{276c} $(i\text{-Pr}_2\text{C}(\text{H})\text{O})(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Zn}$,^{276c} as well as $(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{O})(\text{Me}_3\text{SiCH}_2)\text{Zn}$,²⁹⁰ and $(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{O})(\text{Me}_3\text{SiCH}_2)\text{Zn}$,²⁹⁰ species $\{[(i\text{-Pr}_2\text{C}(\text{H})\text{O})(\text{Ph})\text{Zn}]_2, [(i\text{-Pr}_2\text{C}(\text{H})\text{O})(\text{C}_6\text{F}_5)\text{Zn}]_2, [(i\text{-Pr}_2\text{C}(\text{H})\text{O})(4\text{-CF}_3\text{C}_6\text{H}_4)\text{Zn}]_2, [(i\text{-Pr}_2\text{C}(\text{H})\text{O})(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Zn}]_2, [(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{O})(\text{Me}_3\text{SiCH}_2)\text{Zn}]_2,$ and $[(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{O})(\text{Me}_3\text{SiCH}_2)\text{Zn}]_2$, Scheme 43, bottom right).

2.6.2.3. Heteroleptic Zinc Halides $R^1\text{ZnX}$ ($R^1 \neq X$) and Diorganozincs ($R^1R^2\text{Zn}$, $R^1 \neq R^2$). Results are presented for $\text{Me}_3\text{Si}(\text{Ph})\text{C}(\text{H})\text{ZnCl}$ and $(\text{PhC}\equiv\text{C})(t\text{-Bu})\text{Zn}$.

“Simple” zinc halide $\text{Me}_3\text{Si}(\text{Ph})\text{C}(\text{H})\text{ZnCl}$ crystallized in the presence of TMEDA as a monosolvated Zn -tetrahedral monomer $\{[\text{Me}_3\text{Si}(\text{Ph})\text{C}(\text{H})\text{ZnCl}]\cdot\text{TMEDA}$, Scheme 44, left).²⁹¹ Diorganozinc $(\text{PhC}\equiv\text{C})(t\text{-Bu})\text{Zn}$ behaved identically in comparable medium (crystals grown in hexane in the presence of 1 equiv of TMEDA, $\{[(\text{PhC}\equiv\text{C})(t\text{-Bu})\text{Zn}]\cdot\text{TMEDA}$, Scheme 44, right).^{274b}

To conclude with structural data about zinc compounds, one can see that homoleptic zinc species are mainly monomers, with a tetragonal geometry for the zinc atom, when derived from a coordinant medium. Unsolvated linear monomers are rather identified in hydrocarbons. Heteroleptic zinc compounds show a higher aptitude to arrange as dimers and trimers. Concerning structure/reactivity correlations, zinc species are good Lewis acids, with two coordination sites. As regards nucleophilic or basic properties, the linear structures used to be inert, while affording a tetragonal geometry to the zinc atom increases the reactivity of the corresponding zinc reactants. This observation explains why zinc derivatives are good candidates for the elaboration of new chiral ligands in asymmetric synthesis. Indeed, obtaining good chemical yields and high stereoselectivities when engaging organometallic species in enantioselective transformations requires a firm control all along the trajectory of the organometallic reactant. For highly reactive species, such as lithium or magnesium derivatives, reaching both objectives at the same time is tricky, since generally the reaction itself goes faster than the stereochemical process, which limits the overall chemical potential of these reactants. A general solution to this conundrum consists of resorting to a dimmed reagent that becomes simultaneously chiral and active when interacted with an activator: organozinc reagents constitute a remarkable illustration. A wide range of chiral ligands have been elaborated to transform these sluggish nucleophiles into “magic bullets” able to differentiate between the enantiofaces of aldehydes, even when employed in substoichiometric amounts. The interaction of zinc species with O_2 is also the subject of constant interest,^{271j-m} with a considerable effort being spent to better understand the composition of the products and the associated mechanisms. In these recent years, there has been an increased interest in various organic reactions initiated by metal alkyls/ O_2 systems.

3. HomoMAAs

As already specified in the main introduction, all the organo(bi)metallic species mixing at least two single organometallics bearing the same metal but having different anionic moieties are called “homoMAAs”. This definition gathers the

mixed aggregates (also named mixed complexes) and the unimetal superbases (USB). Note that most of these reactants correspond to Li_xLi-homoMAAs, compounds for which structural data are reported in the present review.

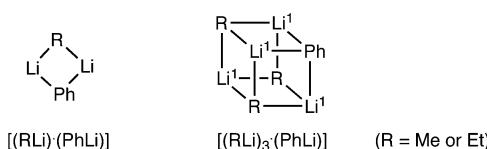
3.1. C–Li/C’–Li-HomoMAAs

Results are presented for [(MeLi)_x·(EtLi)_y], [(MeLi)_x·(BuLi)_y], [(EtLi)_x·(t-BuLi)_y], [(MeLi)_x·(PhLi)_y], [(EtLi)_x·(PhLi)_y], [(t-BuLi)_x·(Me₃SiCH₂Li)_y], and [(BuLi)_x·(PhC≡CLi)_y].

As regards the first results obtained for an equimolar methylolithium–ethylolithium aggregate studied in Et₂O,^{24b,292} pieces of structural information were deduced from ¹H and ⁷Li NMR spectra registered at low temperature (−80 °C). After considering two models (trimeric and tetrameric arrangements), the authors supported the possibility of observing, as a mixture, five cubic tetrameric species of composition [MeLi]₄, [(MeLi)₃·(EtLi)], [(MeLi)₂·(EtLi)₂], [(MeLi)·(EtLi)₃], and [EtLi]₄ (Scheme 45). They also considered that no intramolecular exchange would proceed at the applied temperature and that they would observe four distinct types of lithium environment in the medium in this case. Such a hypothesis was verified by the identification of four distinct signals on the ⁷Li spectra (Li¹–Li⁴). A random distribution of both methyl and ethyl groups was assumed in the tetramers. Switching from EtLi to BuLi and Et₂O to THF led to comparable conclusions.²⁹³ The NMR study highlighted five cubic tetramers, [(MeLi)_x·(BuLi)_{y=4-x}] (Scheme 45), for which abundance was found to be dependent on the proportion of each alkylolithium involved, and this also followed a random distribution. This time, the formation of tetrameric units was unambiguously demonstrated, mainly due to the fact that this second study resorted to ⁶Li labeling of the partners. Note though that the solvation was not discussed in any of those studies. The mixture EtLi/t-BuLi was also examined in a precursory study, carried out on a [(EtLi)_x·(t-BuLi)_y] complex, however, without leading to a full description of the structures of the aggregates.^{294a}

With regard to the couples of reactants MeLi/PhLi and EtLi/PhLi in diethyl ether,²⁹⁵ ¹H and ⁷Li NMR data together indicated that two mixed species were identified. They would correspond to a 1:1 cyclic dimer and a 3:1 cubic tetramer, however, without certainty and indication of the solvation [(RLi)·(PhLi)] and [(RLi)₃·(PhLi)], R = Me or Et, Scheme 46).

Scheme 46. Presumed HomoMAAs Emerging from Mixtures of MeLi or EtLi with PhLi²⁹⁵

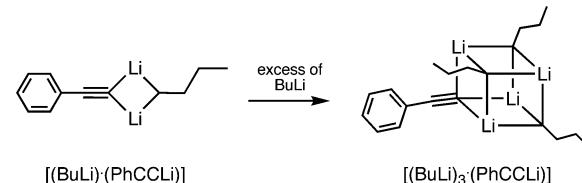


Mixtures of *tert*-butyllithium and trimethylsilylmethylolithium [(t-BuLi)_x·(Me₃SiCH₂Li)_y]] were examined in hydrocarbon solvents (cyclopentane, toluene).^{45a,292} The ¹H and ⁷Li NMR spectra showed a random distribution of the two lithio species among cubic tetrameric arrangements, as above.

Finally, addition of butyllithium to a THF solution of lithium phenylacetylide led to the initial observation of mixed dimer [(BuLi)·(PhC≡CLi)], which was found to evolve upon addition of a large excess of alkylolithium to a mixed cubic tetramer incorporating one acetylidyne unit for three alkyl

moieties [(BuLi)₃·(PhC≡CLi)], Scheme 47).⁵⁷ Nor was the solvation discussed in this example.

Scheme 47. Dimeric and Tetrameric Structures of [(BuLi)_x·(PhC≡CLi)_y] Mixed Aggregates⁵⁷



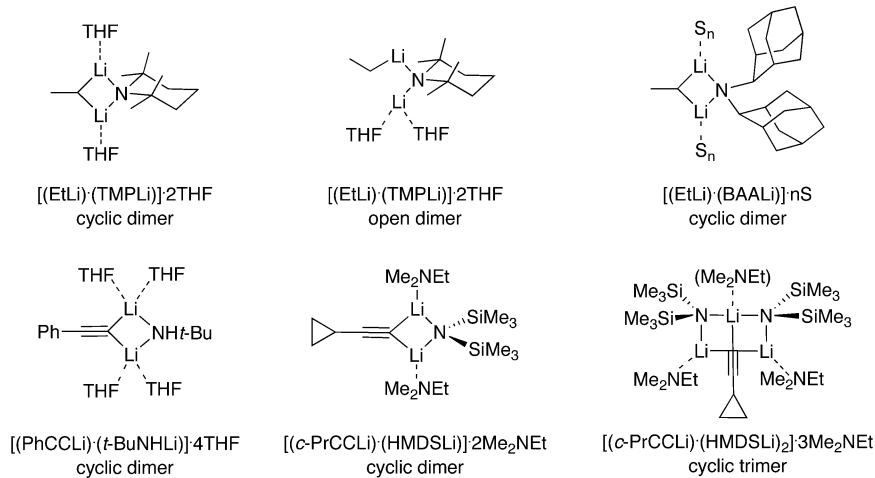
3.2. C–Li/N–Li-HomoMAAs

Results are presented for [(EtLi)_x·(TMPLi)_y], [(EtLi)_x·(BAALi)_y] (BAALi = bis(2-adamantylamide)), [(PhC≡CLi)_x·(t-BuNHLi)_y], [(c-PrC≡CLi)_x·(HMDSLi)_y], and [(alkyllithium)_x·(CLA)_y].

First, as regards [(EtLi)_x·(TMPLi)_y], dissolved 1:1 heterodimers ($x = y = 1$) were pointed out in THF by analyzing the sample by NMR.²⁹⁶ With two nonequivalent lithium nuclei being observed, assumptions for the presence of a mixed cyclic dimer (Scheme 48, top left), in which the lithium atoms exchange very slowly on the NMR time scale, and a mixed open dimer (Scheme 48, top middle) were made. Switching from the TMPLi amide to BAALi [lithium bis(2-adamantylamide)], the quantitative formation of a cyclic dimer was reported in THF solution, without referring, however, to the solvation [(EtLi)·(BAALi)]·nS, Scheme 48, top right).¹²⁶ A cyclic dimer was also characterized, still by NMR, as solvated by four molecules of THF, when mixing PhC≡CLi and t-BuNHLi in an equimolar ratio [(PhC≡CLi)·(t-BuNHLi)]·4THF, Scheme 48, bottom left).¹²⁸ (⁶Li, ¹⁵N) NMR investigation run on [(c-PrC≡CLi)_x·(HMDSLi)_y] homoMAA led to the conclusion that no aggregation took place between these two partners in THF. By contrast, in the less-coordinating Me₂NEt solvent, a mixed dimer/trimer equilibrium was seen. Both species were found to be di- or trisolvated, corresponding to [(c-PrC≡CLi)·(HMDSLi)]·2Me₂NEt and [(c-PrC≡CLi)·(HMDSLi)₂]·3Me₂NEt, respectively, with a HMDSLi–acetylidyne–HMDSLi ladder shape for the trimeric structure (Scheme 48, bottom middle and right).²⁹⁷

Most structural studies about (C–Li/N–Li)-homoMAAs inserted a chiral lithium amide.^{3,132b,d,138a,f,139,141a,298–300} Structures of such mixed complexes obtained from NMR investigations run on Koga–Hilmersson’s CLAs (Scheme 18, Table 12) led to the conclusion that, in the presence of an alkylolithium (BuLi, s-BuLi) at low temperature (in the −80 to −116 °C range) in ethereal solvents (Et₂O, THF, DMM), 1:1 solvated cyclic mixed dimers formed (Table 12, entries 1–11). The latter were described as being organized around a N–Li–C–Li quadrilateral in which the two lithium atoms were inequivalent, since an intramolecular coordination would take place with the Het moiety of the CLA unit.^{138a,298b} Such aggregates were found to coexist in solution with the CLA and alkylolithium oligoMAAs. With high enantioselectivities being attained anyway in the enantioselective transformations in which these mixtures were involved, it was established that the reactivity of the alkylolithium was increased once complexed.^{298b} Depending on the nature of the substituents constitutive of the CLA partner (R, R', and Het), the ability of the lithium amide to aggregate with the alkylolithium was observed as being

Scheme 48. Structures in Solution (NMR analyses) of Two Possible $[(\text{EtLi}) \cdot (\text{TMPLi})]$ Mixed Dimers Formed in THF,²⁹⁶ $[(\text{EtLi}) \cdot (\text{BAALi})]$ ¹²⁶ and $[(\text{PhC}\equiv\text{CLi}) \cdot (\text{t-BuNHLi})]$ ¹²⁸ Cyclic Dimers Observed in THF, and $[(c\text{-PrC}\equiv\text{CLi}) \cdot (\text{HMDSLi})]$ and $[(c\text{-PrC}\equiv\text{CLi}) \cdot (\text{HMDS}_2\text{Li})]$ Dimer and Trimer Obtained with Me_2NEt



variable. Among justifications brought to explain this phenomenon, steric hindrance parameters and/or a weak tendency for heteroatom units (Het = pyrrolidinic nitrogen for example) to intramolecularly coordinate were advanced.^{298b} Note the unexpected result obtained with Het corresponding to a sulfide appendage: the internal sulfide coordination with one of the lithium cation was found to persist in the mixed dimeric complex in both Et_2O and THF, while, according to the HSAB principle, this interaction was expected to be much weaker than the O–Li one.^{138f} Otherwise, the solvation could be apprehended from a competitive exchange between Et_2O and the more basic THF.^{3c,298b} Here again, the intramolecular coordination between one of the lithium cation and the Het moiety was found to be preserved whatever the basic solvent used. Moreover, a correlation could be established between the $^6\text{Li}, ^{15}\text{N}$ coupling constant and the coordination number at lithium.^{3c} Indeed, the $^1\text{J} (^6\text{Li}, ^{15}\text{N})$ was found to decrease as the solvation at the lithium would increase. Finally, with the induction being improved in the nucleophilic 1,2-addition of these homoMAAs onto aldehydes when adding DMM to the Et_2O solutions, the effect of this additive on the general structure of the mixed complex was investigated, however, without observation of structural change.^{298b} In hydrocarbon solvents (hexane, toluene), mixed trimers incorporating two Koga–Hilmersson’s CLA units for one alkylolithium were identified with the NMR technique (Table 12, entry 12).^{298c,299b,c} This arrangement was confirmed from crystallographic data on a solid-state structure grown in hexane.^{299a}

Structures in solution of two $[(\text{BuLi})_x \cdot (\text{Koga–O'Brien's CLA})_y]$ homoMAAs have been studied by NMR (Schemes 18 and 49) and were found to arrange as 1:1 cyclic mixed dimers in Et_2O .¹³⁹ In these arrangements, two intramolecular coordinations were found to take place on each lithium atom, as a consequence of the presence of a coordinative heteroelement on both nitrogen amide substituents. The possibility for Et_2O to interact with the metallic cations was not discussed.

The structure of the (C–Li/O–Li)-homoMAA incorporating both Mukaiyama–Asami’s CLA (Scheme 18) and BuLi (Scheme 50) was also examined by the NMR technique, and the cubic tetrameric $[(\text{BuLi})_3 \cdot (\text{Mukaiyama–Asami's CLA})]$ mixed aggregate, in which an intramolecular coordination took

place, was evidenced in Et_2O , however, without precise information about the ethereal solvation.^{298a}

The last set of data concerning (C–Li/N–Li)-homoMAAs structures was found to combine MeLi or BuLi with a chiral lithium amide derived from 3-aminopyrrolidines (3APLi), earlier named Maddaluno’s MAA (Scheme 18). Robust 1:1 noncovalent mixed cyclic dimers organizing around a quadrilateral C–Li–N–Li core were observed at -78°C in Et_2O ^{141b} as well as THF^{141a,300} (Scheme 51). An azanorbornyl-like conformation was adopted by the pyrrolidinic ring, establishing an intramolecular coordination between the pyrrolidinic nitrogen and one of the two lithium cations. Depending on the lateral amino chain composition, two arrangements were highlighted: an exo topology, in which the alkylolithium unit faced the CH_2 -bridge of the norbornyl folding (Scheme 51, left), and an endo topology, which placed the alkylolithium next to the CH_2 – CH_2 bridge of the norbornyl structure (Scheme 51, right). Density functional theory calculations showed that the two topologies should be isoenergetic and thus coexist in a 1:1 ratio, a result never observed before. Such a contradiction led to the conclusion that the formation of these aggregates would obey kinetic control.

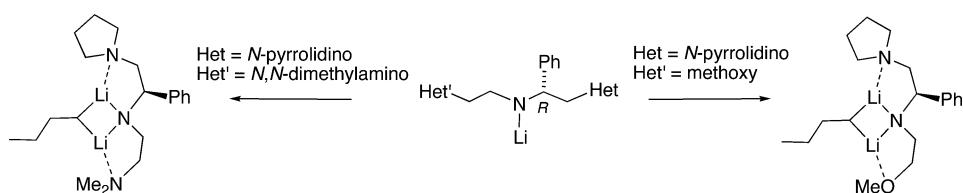
3.3. C–Li/O–Li-HomoMAAs

Results are presented for $[(\text{AlkLi})_x \cdot (\text{MeOLi})_y]$ ($\text{Alk} = \text{Me, Et, } s\text{-Bu, } t\text{-Bu}$), $[(\text{EtLi})_x \cdot (\text{EtOLi})_y]$, $[(\text{PrLi})_x \cdot (\text{PrOLi})_y]$, $[(\text{BuLi})_x \cdot (\text{BuOLi})_y]$, $[(t\text{-BuLi})_x \cdot (t\text{-BuOLi})_y]$, $[(\text{PhLi})_x \cdot (\text{PhOLi})_y]$, $[(\text{BuLi})_x \cdot (\text{t-BuOLi})_y]$, $[(\text{BuLi})_x \cdot (1\text{-naphthylOLi})_y]$, $[(\text{BuLi})_x \cdot (\text{R}^1\text{R}^2\text{NCH}(\text{R})\text{CH}_2\text{OLi})_y]$, $[(t\text{-BuLi})_x \cdot (\text{EtOLi})_y]$, $[(\text{BuLi})_x \cdot (\text{R}^*\text{OLi})_y]$, and $[(\text{RC}\equiv\text{CLi})_x \cdot (\text{R}^*\text{OLi})_y]$ ($\text{R}^*\text{OLi} = \text{chiral alkoxide}$).

Studies about structural data on (C–Li/O–Li)-homoMAAs refer to computational investigations, as well as NMR spectroscopy and solid-state analyses. The structures related to (C–Li/O–Li)-homoMAAs incorporating identical carbon chain moieties will be discussed first [(RLi/ROLi)-homoMAAs, Table 13]. The formation of $[(\text{MeLi})_x \cdot (\text{MeOLi})_y]$ mixed dimers, trimers, and tetramers was first postulated from a theoretical approach. After taking into account a solvation effect ($S = \text{THF}$), the calculations postulated that mixed tetramers $[(\text{MeLi})_x \cdot (\text{MeOLi})_y]$ ($x + y = 4$), solvated by one THF per lithium cation, should be favored, with a preference for the

Table 12. Structures in Solution of $[(\text{Alkyllithium})_x \cdot (\text{Koga-Hilmersson's CLA})]$ HomoMAAs

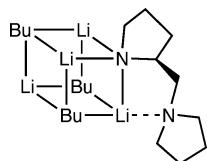
Entry	C-Li	Koga-Hilmersson's CLA	Solvent	(C-Li/N-Li)-homoMAAs structure	Ref
1	BuLi s-BuLi		Et ₂ O THF		138a 298b
2	BuLi		Et ₂ O		298b
3	BuLi		Et ₂ O		298b
4	BuLi		Et ₂ O		298b
5	BuLi		Et ₂ O	[AlkLi·Koga-Hilmersson's-CLA]	298b
6	BuLi		Et ₂ O		298b
7	BuLi		Et ₂ O		298b
8	BuLi		Et ₂ O		138f
9	BuLi		Et ₂ O		138f
10	BuLi		Et ₂ O		138f
11	BuLi		Et ₂ O		138f
12	BuLi s-BuLi t-BuLi		none (X-ray) or toluene (NMR)	$[(\text{AlkLi}) \cdot (\text{Koga-Hilmersson's-CLA})_2]$ 	298c 299

Scheme 49. Structures of Two 1:1 Dimeric $[(\text{BuLi}) \cdot (\text{Koga-O'Brien's CLA})]$ HomoMAAs in Et₂O¹³⁹

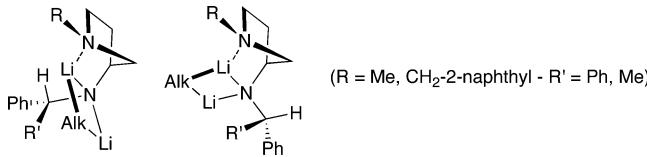
$[(\text{MeLi})_3 \cdot (\text{MeOLi})]$ combination (Table 13, entry 1).³⁰¹ Switching to ethyl groups, an NMR pioneering work conducted in the mid-1960s was carried out on the EtLi/EtOLi system and postulated that, in hydrocarbon solution, (i) a mixed complex $[(\text{EtLi})_x \cdot (\text{EtOLi})_y]$ was formed, however, without precision about the x/y ratio and (ii) the inclusion of EtOLi molecules in the initial prismatic hexamer $[\text{EtLi}]_6$ oligoMAA did not seem to promote the dissociation of the hexameric aggregate (Table 13, entry 2).^{24b,302} More precise data were

collected 20 years later with the examination of the $[(\text{BuLi})_x \cdot (\text{BuOLi})_y]$ homoMAA in THF through a RINMR (rapid injection NMR) study.⁴⁰ Adding dioxygen to the BuLi tetramer/dimer equilibrium observed in this solvent had the effect of detecting the rising presence of cubic tetrameric $[(\text{BuLi})_x \cdot (\text{BuOLi})_y]$ aggregates with x/y evolving from 3:1 to 1:3 as the concentration of lithium butoxide was increasing (Table 13, entry 4). Note that the homoMAA incorporating three alkoxy groups would tend to be less stable and the

Scheme 50. Structure in Et_2O Solution of 3:1 Cubic Tetrameric $[(\text{BuLi})_3 \cdot (\text{Mukaiyama-Asami's CLA})]$ HomoMAA^{298a}



Scheme 51. Structures of 1:1 Mixed Dimer $[(\text{AlkLi}) \cdot (\text{Maddaluno's CLA})]$ HomoMAA in Ethereal Solvents (Alk = Me, Bu)^{141,300}



possibility to form a mixed dimer was excluded. The solvation was not detailed in this study. Pieces of structural information on the $[(t\text{-BuLi})_x \cdot (t\text{-BuOLi})_y]$ homoMAA isomer were also

acquired, this time in a hydrocarbon medium (cyclopentane).^{46,303} Prismatic hexamers $[(t\text{-BuLi}) \cdot (t\text{-BuOLi})_5]$ and $[(t\text{-BuLi})_2 \cdot (t\text{-BuOLi})_4]$ were identified in cyclopentane,^{303a} in addition to $[(t\text{-BuLi})_3 \cdot (t\text{-BuOLi})]$ tetramer (Table 13, entry 5).⁴⁶ The observation done in cyclopentane at -25°C for the $[(\text{PrLi})_x \cdot (\text{PrOLi})_y]$ homoMAA was less common, since the latter was seen as a dodecameric mixed aggregate with $x/y = 8/4$, the lithium atoms showing a cuboctahedral arrangement (Table 13, entry 3).³⁰⁴ In this unusual structure, six square and eight triangular faces delimitated by the 12 lithium atoms bounded the alkoxy and alkyl moieties, respectively. The structure of a $[(\text{PhLi})_x \cdot (\text{PhOLi})_y]$ homoMAA was also stated, but this time from a crystallographic study (Table 13, entry 6).^{15b} In the presence of sparteine, this homoMAA revealed a mixed dimer ($x = y = 1$) organized around a C-Li-O-Li quadrilateral, each lithium cation being doubly coordinated by one sparteine ligand.

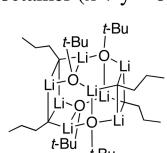
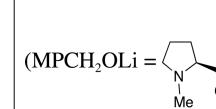
Regarding structural knowledge about (C-Li/O-Li)-homoMAAs consisting of two different carbon chain appendages $[(\text{RLi}/\text{R}'\text{OLi})\text{-homoMAAs}]$, one can first return to the theoretical study earlier mentioned for MeOLi, this time associated with EtLi. The formation of tetrasolvated mixed tetramers, preferentially versus dimeric or trimeric aggregates, was once again predicted when solvated by THF molecules, the

Table 13. Structures Related to (C-Li/O-Li)-HomoMAAs Incorporating Identical Carbon Chain Moieties $[(\text{RLi}/\text{ROLi})\text{-HomoMAAs}]$

Entry	(RLi/ROLi)-homoMAA	Analytical method	Solvent (S)	$[(\text{RLi})_x \cdot (\text{ROLi})_y] \cdot nS$	Ref
1	MeLi/MeOLi	computation	THF	tetramer ^a ($x + y = 4$) $[(\text{MeLi})_3 \cdot (\text{MeOLi})] \cdot 4\text{THF}$	³⁰¹
2	EtLi/EtOLi	NMR	cyclohexane	$[(\text{EtLi})_x \cdot (\text{EtOLi})_y]^c$	³⁰²
3	PrLi/PrOLi	NMR	cyclopentane	dodecamer ^d ($x + y = 12$) $[(\text{PrLi})_8 \cdot (\text{PrOLi})_4]$	³⁰⁴
4	BuLi/BuOLi	NMR	THF	tetramers ^a ($x + y = 4$) $[(\text{BuLi})_3 \cdot (\text{BuOLi})]$ $[(\text{BuLi})_2 \cdot (\text{BuOLi})_2]$ $[(\text{BuLi}) \cdot (\text{BuOLi})_3]^e$	⁴⁰
5	<i>t</i> -BuLi/ <i>t</i> -BuOLi	NMR	cyclopentane	hexamers ^b ($x + y = 6$) $[(t\text{-BuLi}) \cdot (t\text{-BuOLi})_5]$ $[(t\text{-BuLi})_2 \cdot (t\text{-BuOLi})_4]$ & tetramer ^a ($x + y = 4$) $[(t\text{-BuLi})_3 \cdot (t\text{-BuOLi})]$	^{303a}
6	PhLi/PhOLi	X-ray	pentane/ Et_2O + sparteine	dimer ($x + y = 2$) $[\text{PhLi} \cdot \text{PhOLi}] \cdot 2\text{sparteine}$	^{15b}

^aLikely cubic. ^bLikely prismatic. ^c x/y not determined. ^dCuboctahedral arrangement of the lithium atoms. ^eLess stable.

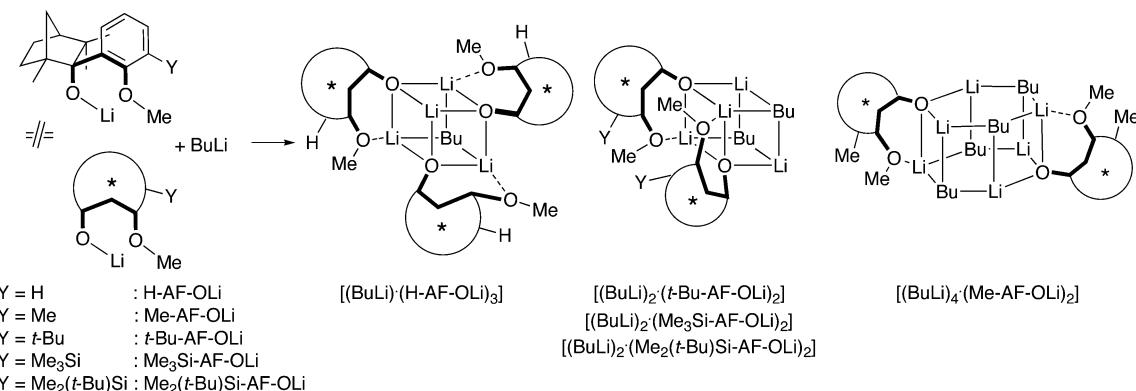
Table 14. Structures Related to (C–Li/O–Li)-HomoMAAs Incorporating Two Different Carbon Chain Moieties [(RLi/R'OLi)-HomoMAAs]

Entry	(RLi/R'OLi)-homoMAA	Analytical method	Solvent (S)	$[(\text{RLi})_x \cdot (\text{R}'\text{OLi})_y] \cdot n\text{S}$	Ref
1	EtLi/MeOLi	computation	THF	tetramer ($x + y = 4$) [(EtLi) ₂ ·(MeOLi) ₂]·4THF	301
2	BuLi/ <i>t</i> -BuOLi	NMR	benzene	tetramer ^a ($x + y = 4$) [(BuLi)·(<i>t</i> -BuOLi) ₃]	305a
			THF	tetramers ^a ($x + y = 4$) [(BuLi) ₃ ·(<i>t</i> -BuOLi)] [(BuLi) ₂ ·(<i>t</i> -BuOLi) ₂]	40
		X-Ray	hexane	octamer ($x + y = 8$)  [(BuLi) ₄ ·(<i>t</i> -BuOLi) ₄]	305b
3	BuLi/1-naphthylOLi ^b	NMR	TMEDA	dimer ($x + y = 2$) [(BuLi)·(1-naphthylOLi)]·2TMEDA	42a
4	BuLi/MPCH ₂ OLi ^c (MPCH ₂ OLi =  <td data-kind="parent" data-rs="2">computation</td> <td>hexane</td> <td>hexamer^d ($x + y = 6$) [(BuLi)₃·(MPCH₂OLi)₃]^e</td> <td>306</td>	computation	hexane	hexamer ^d ($x + y = 6$) [(BuLi) ₃ ·(MPCH ₂ OLi) ₃] ^e	306
		THF	tetramer ^a ($x + y = 4$) [(BuLi) ₂ ·(MPCH ₂ OLi) ₂]·2THF ^e		
5	<i>t</i> -BuLi/EtOLi	NMR	Et ₂ O	tetramer ^a ($x + y = 4$) [(<i>t</i> -BuLi) ₃ ·(EtOLi)]	48

^aLikely cubic. ^bNaphth = naphthyl. ^cMPCH₂OLi = lithium (1-methylpyrrolidin-2-yl)methanolate). ^dLikely prismatic. ^eMajor species.

Scheme 52. X-ray Structures for $[(\text{BuLi})_x \cdot (\text{Y}-\text{AF}-\text{OLi})_y]$ (C–Li/O–Li)-HomoMAAs³⁰⁷

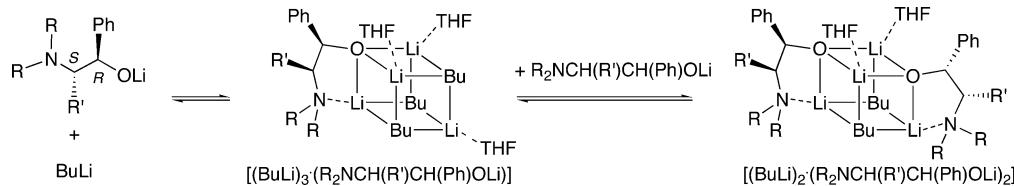
lithium anisyl fencholates : Y-AF-OLi



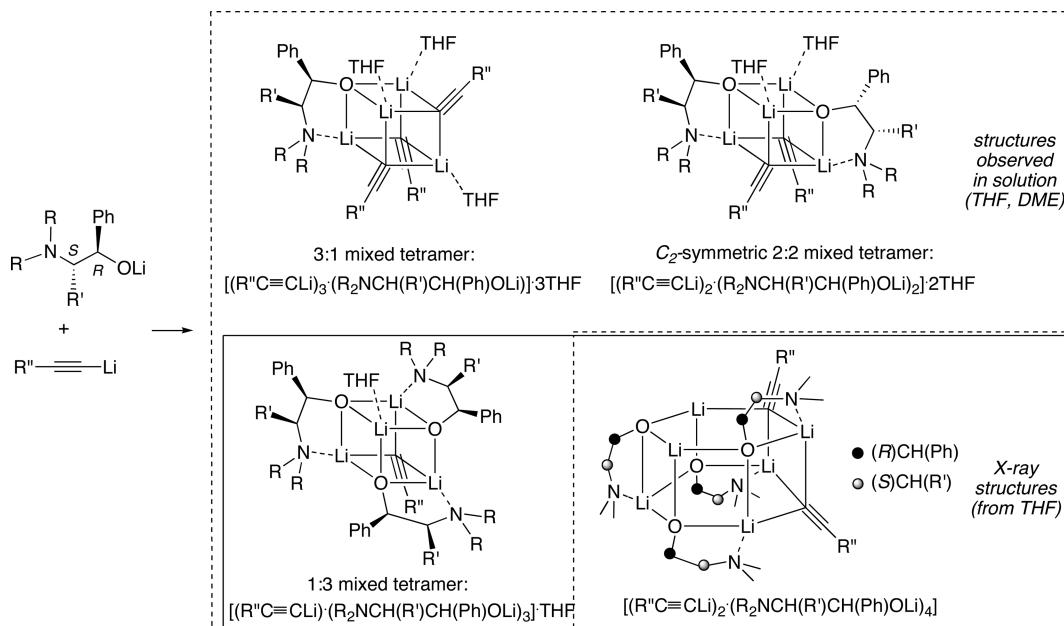
$[(\text{EtLi})_2 \cdot (\text{MeOLi})_2] \cdot 4\text{THF}$ complex tending to be this time the major species (Table 14, entry 1).³⁰¹ The situation showed to be less clear when associating MeOLi to the bulkier *s*-BuLi or *t*-

BuLi. Tetramers might form but were probably surrounded by less than four THF ligands. NMR and crystallographic studies were carried out to determine the structure of the $[(\text{BuLi})_x \cdot (\text{t$

Scheme 53. Structures in THF/Pentane Solution of $[(BuLi)_x \cdot (R_2NCH(R')CH(Ph)OLi)_y]$ ($C-Li/O-Li$ -HomoMAAs)³⁰⁸



Scheme 54. Structures in THF/Pentane Solution and in the Solid State of $[(R''C\equiv CLi)_x \cdot (R_2NCH(R')CH(Ph)OLi)_y] \cdot nTHF$ ($C-Li/O-Li$ -HomoMAAs)³⁰⁹



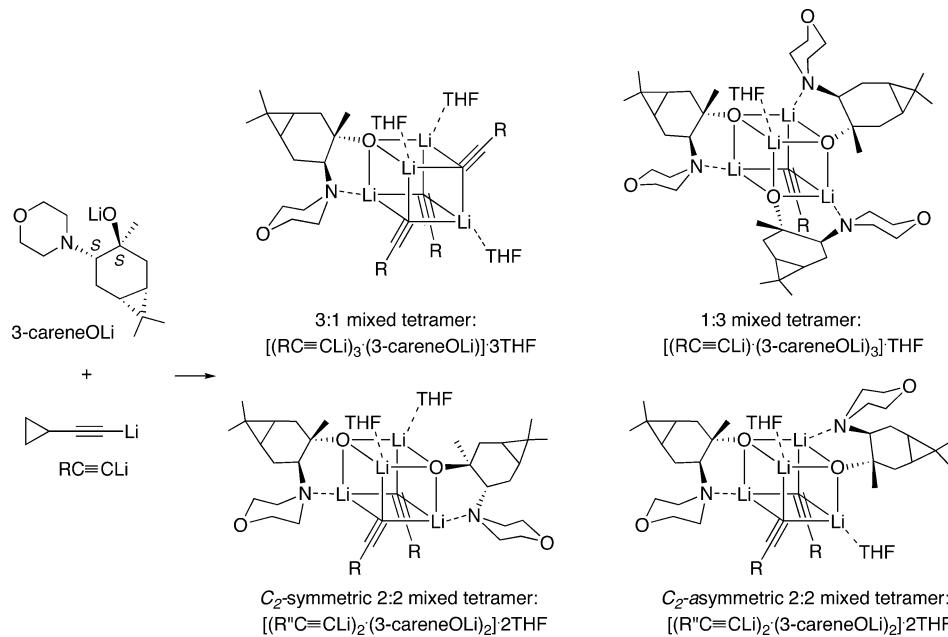
$BuOLi_y]$ homoMAA (Table 14, entry 2). Two mixed cubic tetramers $[(BuLi)_3 \cdot (t-BuOLi)]$ and $[(BuLi)_2 \cdot (t-BuOLi)_2]$ were mainly observed in THF solution.⁴⁰ Complementarily, crystals isolated from a hexane solution evidenced a $[(BuLi)_4 \cdot (t-BuOLi)_4]$ polyhedron.³⁰⁵ When butyllithium was associated with the lithium aryl oxide 1-naphthylOLi, the NMR spectra recorded at $-20^\circ C$ in TMEDA highlighted the disolvated mixed dimer $[(BuLi) \cdot (1-naphthylOLi)] \cdot 2TMEDA$ (Table 14, entry 3).^{42a} Still concerning this alkylolithium, a theoretical investigation was achieved to evaluate its ability to aggregate lithium aminoalkoxide MPC_2OLi [lithium (1-methylpyrrolidin-2-yl)methanolate] in hexane and in THF (Table 14, entry 4).³⁰⁶ Using an equal concentration of each starting material to afford the corresponding $[(BuLi)_x \cdot (MPC_2OLi)_y]$ homoMAAs, heterohexameric arrangements were announced to be favored in the hydrocarbon media, while disolvated heterotetramers would predominate in the ethereal solvent. Otherwise, mixed tetramer $[(t-BuLi)_3 \cdot (EtOLi)]$ was assigned in Et_2O on the basis of 6Li and ^{13}C NMR data (Table 14, entry 5).⁴⁸ Among other ($C-Li/O-Li$)-homoMAAs for which structures have been reported in the literature, one can mention the case of lithium phenylacetylide with lithiated quinazolinones,^{59b} as well as adducts combining benzyllithium and an aminoalkoxide cluster.¹⁵¹

The ($C-Li/O-Li$)-homoMAAs involving chiral alkoxides (R^*OLi) contain members that proved their efficiency as good chiral ligands for alkylolithiums in enantioselective transformations.^{59,151,307-309} First, concerning lithium anisyl fen-cholate derivatives $Y-AF-OLi$ (Scheme 52), variously

substituted on the ortho-position of the anisyl moiety [$Y = H, Me, t-Bu, Me_3Si, Me_2(t-Bu)Si$],³⁰⁷ treatment of $H-AF-OLi$ with butyllithium in hexane at $0^\circ C$ and then recrystallization from toluene/hexane led to crystals of structure corresponding to a cubic tetramer incorporating three $H-AF-OLi$ entities for one alkylolithium unit $[(BuLi) \cdot (H-AF-OLi)_3]$.^{307a} Changing the nature of the Y substitution had the effect of varying the size of the solid-state aggregates formed and/or the x/y ratio in the $[(BuLi)_x \cdot (Y-AF-OLi)_y]$ general formula. Thus, cubic tetrameric arrangements were still adopted from $Y-AF-OLi$ containing $Y = t-Bu, Me_3Si$, and $Me_2(t-Bu)Si$, but this time with a 2:2 x/y ratio.^{307b,c} In contrast, $Me-AF-OLi$ combined with the alkylolithium around a hexameric structure, including two alkoxide items and four $BuLi$ appendages $[(BuLi)_4 \cdot (Me-AF-OLi)_2]$).^{307b}

Further investigations about $[(BuLi)_x \cdot (R^*OLi)_y]$ complexes were dedicated to structural depictions in solution using 6Li , ^{13}C , and ^{15}N NMR spectroscopy. The chiral lithium alkoxide series involved was in this case α,β -aminoalkoxides of general structure $R_2NCH(R')CH(Ph)OLi$ ($R_2N = Me_2N$ or pyrrolidino, $R' = Me$ or Ph), also called lithium ephedrates.³⁰⁸ Data obtained in THF/pentane medium highlighted the formation of the $[(BuLi)_3 \cdot (R_2NCH(R')CH(Ph)OLi)]$ and $[(BuLi)_2 \cdot (R_2NCH(R')CH(Ph)OLi)_2]$ mixed tetramers (Scheme 53). Note that the solvation was advertised as corresponding to three and two THF, respectively.

The same class of aminoalkoxides was widely used as a chiral partner for lithium acetylides (lithium cyclopropylacetylide $R''C\equiv CLi$ with $R'' = c-Pr$) involved in the synthesis of the HIV

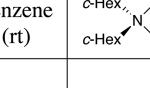
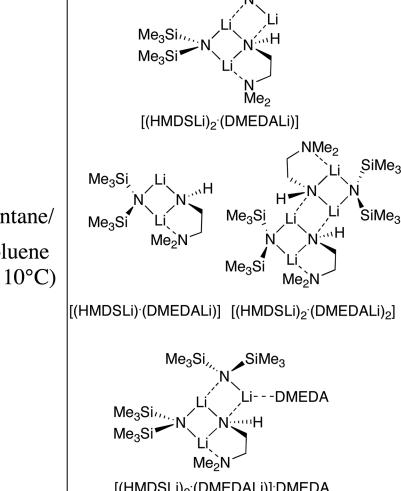
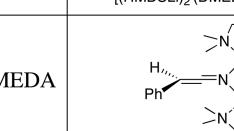
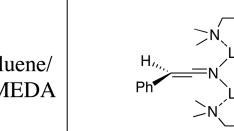
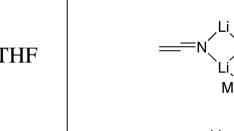
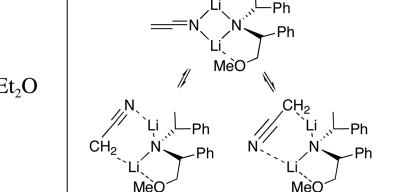
Scheme 55. Structures in Solution of $[(\text{RC}\equiv\text{CLi})_x \cdot (\text{3-careneOLi})_y] \cdot n\text{THF}$ (C-Li/O-Li -HomoMAAs)²⁹⁷Table 15. Structures in Solution of (C-Li/Li-X)-HomoMAAs

Entry	(C-Li/Li-X)-homoMAA	Solvent (S)	$[(\text{C-Li})_x \cdot (\text{Li-X})_y] \cdot n\text{S}$	Ref
1	MeLi/LiCl	THF (170 K)	$\begin{array}{c} \text{Li}-\text{Me} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Me} \end{array} + \begin{array}{c} \text{Li} \\ \\ \text{Cl}-\text{Li} \\ \\ \text{Cl} \end{array} \rightleftharpoons 2 \begin{array}{c} \text{Li} \\ \\ \text{Li}-\text{Cl} \\ \\ \text{Li} \end{array}$ [(MeLi)(LiCl)] · 3THF	192
2a	MeLi/LiBr	Et ₂ O (195 K)	$\begin{array}{c} \text{Li}-\text{Me} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Me} \end{array} + \begin{array}{c} \text{Li}-\text{Me} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Br} \end{array} \rightleftharpoons \begin{array}{c} \text{Li}-\text{Me} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Br} \end{array}$ [(MeLi) ₃ (LiBr)] $\begin{array}{c} \text{Li}-\text{Br} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Br} \end{array}$ [(MeLi)(LiBr) ₃] [(MeLi) ₂ (LiBr) ₂] [LiBr] ₄	28b, 204, 205, 310
2b		THF (183 K)	$\begin{array}{c} \text{Li}-\text{Me} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Me} \end{array} + \begin{array}{c} \text{Li}-\text{Br} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Br} \end{array} \rightleftharpoons \begin{array}{c} \text{Li}-\text{Me} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Br} \end{array} + \begin{array}{c} \text{Li}-\text{Br} \\ \\ \text{Me}-\text{Li} \end{array}$ [(MeLi) ₃ (LiBr)] · [(MeLi)(LiBr)]	28b
3a	MeLi/LiI	Et ₂ O (180 K)	$\begin{array}{c} \text{Li}-\text{Me} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Me} \end{array} + \begin{array}{c} \text{Li}-\text{I} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{I} \end{array} \rightleftharpoons \begin{array}{c} \text{Li}-\text{Me} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{I} \end{array}$ [(MeLi) ₃ (LiI)] [(MeLi) ₂ (LiI) ₂]	28, 310c
3b		THF (183 K)	$\begin{array}{c} \text{Li}-\text{Me} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Me} \end{array} + \begin{array}{c} \text{Li}-\text{I} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{I} \end{array} \rightleftharpoons \begin{array}{c} \text{Li}-\text{Me} \\ \\ \text{Me}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{I} \end{array}$ [(MeLi) ₃ (LiI)] [(MeLi) ₂ (LiI) ₂]	310c
4	PhLi/LiBr	from Et ₂ O	$\begin{array}{c} \text{Et}_2\text{O}-\text{Li}-\text{Ph} \\ \\ \text{Ph}-\text{Li}-\text{Li} \\ \\ \text{Li}-\text{Ph} \\ \\ \text{Et}_2\text{O} \end{array}$ [(PhLi) ₃ (LiBr)] · 3Et ₂ O	60

reverse transcriptase inhibitor efavirenz. Both structural data in solution and in the solid state were obtained. They pointed out

mixtures of solvated 3:1, 2:2, and 1:3 $[(\text{R''C}\equiv\text{CLi})_x \cdot (\text{R}_2\text{NCH}(\text{R}')\text{CH}(\text{Ph})\text{OLi})_y] \cdot n\text{S}$ ($1 \leq n \leq 3$) mixed tetramers at

Table 16. Structures of (N–Li/N’–Li)-HomoMAAs (solid state and solution)

Entry	(N–Li/N’–Li)-homoMAA	Analytical method	Solvent (S)	$[(N\text{-Li})_x \cdot (N'\text{-Li})_y] \cdot nS$	Ref
1	<i>c</i> -Hex ₂ NLi/Me ₂ NLi	NMR	benzene (rt)	 [(<i>c</i> -Hex ₂ NLi)(Me ₂ NLi)]	125
2	HMDSLi/DMEDALi	NMR	pentane/toluene (-110°C)	 [(HMDSLi) ₂ (DMEDALi)] [(HMDSLi) ₃ (DMEDALi)] [(HMDSLi) ₂ (DMEDALi) ₂] [(HMDSLi) ₂ (DMEDALi)] DMEDA	313
3a	Ph(H)C=C=NLi/DALi	X-Ray	TMEDA		314
3b	Ph(H)C=C=NLi/HMDSLi	NMR	toluene/TMEDA		129
3c			THF		315
3d	H ₂ C=C=NLi/CLA	NMR	Et ₂ O		315

equilibrium in THF or DME solution (Scheme 54, top and bottom left).^{59a,309a} By contrast, unsolvated complex mixtures were observed in Et₂O. X-ray crystallographic studies highlighted a cubic tetrameric 1:3 crystalline aggregate isolated from THF.^{309a} More unexpectedly, the unsolvated hexamer [(R”C≡CLi)₂·(R₂NCH(R')CH(Ph)OLi)₄] was observed after crystallization in THF solution of a 2:2 acetylidy/ephedrate mixture (Scheme 54, bottom right).^{309a} The lifetime of this structure was found to be very short in solution, quickly providing a mixture of the 2:2 and 1:3 tetramers.

Switching from the lithium ephedrate derivatives to a (+)-3-carene-derived aminoalkoxide (3-careneOLi, Scheme 55) had the effect of providing a better level of induction in the enantioselective reactions in which the consecutive acetylidy/R*OLi homoMAAs were involved.²⁹⁷ NMR spectroscopic investigations were carried out as an attempt to rationalize such an observation and led to the conclusion that, in THF/pentane medium, a range of solvated 3:1, 2:2, and 1:3 tetrameric

[(RC≡CLi)_x·(3-careneOLi)_y]·nTHF (1 ≤ n ≤ 3) mixed aggregates formed, linked by a series of balanced equilibria (R = c-Pr). Note the observation of two 2:2 complexes, C₂-symmetric and asymmetric, in this medium, whereas only the symmetric isomer was noted in Et₂O and the asymmetric one in Me₂NEt.

Chiral vicinal aminoalkoxide derived from camphor was also combined with lithium cyclopropylacetylidy or phenylacetylidy, and ⁶Li, ¹³C, and ¹⁵N NMR data obtained at low temperature revealed, in THF/pentane solution, asymmetric 3:1 and C₂-symmetric 2:2 mixed tetramers and structures comparable with those already depicted above.^{309b}

3.4. C–Li/Li–X-HomoMAAs

Results are presented for [(MeLi)_x·(LiCl)_y], [(MeLi)_x·(LiBr)_y], [(MeLi)_x·(LiI)_y], and [(PhLi)_x·(LiBr)_y].

The structure of the (C–Li/X–Li)-homoMAA formed after mixing methylolithium and lithium chloride in THF was

Table 17. Structures of (DALi/ROLi)-HomoMAAs (solid state and solution)

Entry	ROLi	Analytical method	Solvent (S)	$[(DALi)_x \cdot (ROLi)_y] \cdot nS$	Ref
1	Me ₂ N-CH ₂ -CH ₂ -OLi DMPOLi	X-ray NMR	hexane	 [(DALi) ₂ (DMPOLi) ₂]	316
2a	ArOLi (X = H, MeO, F Alk = Me, Et, iPr)	NMR	THF (-90°C)	 [(DALi)(ArOLi)]nTHF*	155i
2b			BuOMe HMPA DME TMEDA Et ₃ N (-90°C)	 [(DALi)(ArOLi)]nS* [(DALi) ₂ (ArOLi)]nS*	317
3a	KENOLi-5	X-ray	heptane	 [(DALi) ₂ (KENOLi-5) ₂]	318
3b	KENOLi-1	NMR	THF (-115°C)	 [(DALi)(KENOLi-1)]nS*	319
3c	KENOLi-3	NMR	THF/HMPA (-125°C)	 [(DALi)(KENOLi-3)]nS*	320
3d	KENOLi-6	NMR	THF/HMPA (-125°C)	 [(DALi)(KENOLi-6)]nS*	320
4a	EENOLi-10	NMR	THF HMPA DMPU (-90°C)	 [(DALi)(EENOLi-10)]2S	321
4b			BuOMe (-90°C)	 [(DALi)(EENOLi-10)]2S [(DALi) ₂ (EENOLi-10)]2S	322
4c	EENOLi-11	NMR	HMPA/THF (-80°C)	 [(DALi)(EENOLi-11)]nS* [(DALi) ₂ (EENOLi-11)]diether	323
4d	EENOLi-12	NMR	toluene + chiral diether (-80°C)	 [(DALi)(EENOLi-12)]diether	324

^{*} *n* undetermined.

examined by the NMR technique at $-103\text{ }^{\circ}\text{C}$.¹⁹² From the data obtained, it was found that only one mixed entity was present in the medium, corresponding to the trisolvated dimer $[(\text{MeLi})\cdot(\text{LiCl})]\cdot3\text{THF}$, in equilibrium with the $[\text{MeLi}]_4$ and $[\text{LiCl}]_2$ oligoMAAs (Table 15, entry 1). Structures of the complexes formed between methylolithium and lithium bromide in Et_2O were also evidenced by NMR spectroscopy (Table 15, entry 2a).^{28b,204,205,310} Note as well the preliminary exploration in the solid state.³¹¹ The species observed in the Et_2O solution in the -50 to $-90\text{ }^{\circ}\text{C}$ range were assigned to $[(\text{MeLi})_3\cdot(\text{LiBr})]$, $[(\text{MeLi})_2\cdot(\text{LiBr})_2]$, and $[(\text{MeLi})\cdot(\text{LiBr})_3]$ cubic tetramers in equilibrium with the homogeneous $[\text{MeLi}]_4$ and $[\text{LiBr}]_4$ oligoMAAs.^{28b,204,310c} The proportions of these five possible aggregates were found to follow an almost purely statistical distribution, except for $[(\text{MeLi})\cdot(\text{LiBr})_3]$ species, which always remained less abundant than expected. The latter was actually postulated as being less favored on the basis of aggregation energies obtained from functional theory calculations. Using THF as the sole solvent led to dramatic changes in the NMR spectra (Table 15, entry 2b).^{28b} The oligoMAAs $[\text{MeLi}]_4$ and $[\text{LiBr}]_x$ became the main species (x not determined at this point) with a low contribution of the $[(\text{MeLi})_3\cdot(\text{LiBr})]$ homoMAA and the presence of a significant amount of the $[(\text{MeLi})\cdot(\text{LiBr})]$ dimer. The methylolithium/lithium iodide combination was also studied in Et_2O (Table 15, entry 3a) and THF (Table 15, entry 3b).^{28,310c} In a preliminary NMR investigation run in Et_2O , the single formation of $[(\text{MeLi})_3\cdot(\text{LiI})]$, in equilibrium with the homogeneous precursors $[\text{MeLi}]_4$ and $[\text{LiI}]_x$, was postulated. Using more efficient equipment (58 MHz ${}^6\text{Li}$ instead of 38.8 MHz ${}^7\text{Li}$) and working at lower temperature ($-95\text{ }^{\circ}\text{C}$ instead of $-70\text{ }^{\circ}\text{C}$) allowed a more precise picture of the contents of the solution to be obtained. It would consist of five MAAs that were identified as being the four $[\text{MeLi}]_4$, $[(\text{MeLi})_3\cdot(\text{LiI})]$, $[(\text{MeLi})_2\cdot(\text{LiI})_2]$, and $[(\text{MeLi})\cdot(\text{LiI})_3]$ cubic tetramers and $[\text{LiI}]_x$ oligomer.^{28a} Working in THF once again brought a major change in the composition of the mixture. In this medium, the tetrameric methylolithium oligoMAA remained by far the major species in addition to small amounts of the $[(\text{MeLi})_3\cdot(\text{LiI})]$ and $[(\text{MeLi})_2\cdot(\text{LiI})_2]$ tetrameric complexes as well as the $[(\text{MeLi})\cdot(\text{LiI})]$ mixed dimer.^{310c} Crystallographic data obtained for a $[(\text{PhLi})_x\cdot(\text{LiBr})]$ homoMAA revealed the trisolvated $[(\text{PhLi})_3\cdot(\text{LiBr})]\cdot3\text{Et}_2\text{O}$ complex organized around a cubic tetramer (Table 15, entry 4).⁶⁰ Finally, a DFT study combining a halomethylolithium carbenoid and lithium halides was documented. It was deduced that, in the gas phase as well as in THF solution, mixed dimers, trimers, and tetramers should coexist in the presence of free lithium carbenoids, in proportions depending on the lithium salt.³¹²

3.5. N–Li/N’–Li-HomoMAAs

Results are presented for $[(c\text{-Hex}_2\text{NLi})_x\cdot(\text{Me}_2\text{NLi})_y]$, $[(\text{HMDSLi})_x\cdot(\text{DMEDALi})_y]$, and $[(\text{R}^1\text{R}^2\text{C}=\text{C}\text{NLi})_x\cdot(\text{R}^3\text{R}^4\text{NLi})_y]$ ($\text{R}^3\text{R}^4\text{N} = \text{i-Pr}_2\text{N}, (\text{Me}_3\text{Si})_2\text{N}$, or CLA).

The homoMAAs involving two dissimilar lithium amides are less common. Among those for which structural data are depicted, one can retain the aggregate formed with the couple $c\text{-Hex}_2\text{NLi}/\text{Me}_2\text{NLi}$ (Table 16, entry 1) and highlighted when examining, by NMR at room temperature, the composition of a lithium dicyclohexylamide benzene solution containing an excess (2 equiv) of HMPA.¹²⁵ The dimeric $[(c\text{-Hex}_2\text{NLi})\cdot(\text{Me}_2\text{NLi})]$ complex was characterized, and its formation assigned to a decomposition of HMPA. Another

example of $(\text{N-Li/N'-Li})\text{-homoMAA}$ was obtained by adding HMDSLi to various amounts of N,N -dimethylethylenediamine (DMEDA) in hydrocarbon solution (pentane/toluene mixture), and the resulting mixtures were examined at $-110\text{ }^{\circ}\text{C}$ using the $[{}^6\text{Li}, {}^{15}\text{N}]$ NMR technique (Table 16, entry 2).³¹³ With a 1:0.25 HMDSLi/DMEDA ratio, three unsolvated mixed aggregates were observed and defined as the $[(\text{HMDSLi})_2\cdot(\text{DMEDALi})]$ trimer, $[(\text{HMDSLi})_2\cdot(\text{DMEDALi})_2]$ ladder tetramer, and $[(\text{HMDSLi})\cdot(\text{DMEDALi})]$ dimer. In all structures, the dimethylamino appendage established an intramolecular coordination with a lithium cation. Varying the HMDSLi/DMEDA ratio to 1:0.5 limited the composition of the medium to two aggregates, the trimer becoming nonexistent. Spectra related to 1:0.75 HMDSLi/DMEDA mixture showed three additional aggregates, among which were the monosolvated $[(\text{HMDSLi})_2\cdot(\text{DMEDALi})]\cdot\text{DMEDA}$ trimer and two HMDSLi oligoMAAs. The latter oligomers became the only species in solution in the presence of equimolar amounts of HMDSLi and DMEDA.

Now, most of the studies related to the structure of $(\text{N-Li/N'-Li})\text{-homoMAA}$ were found to implicate for one amide a lithioacetonitrile derivative. Thus, a solid-state structure was obtained from a $\text{Ph(HC=CNLi, DALi, TMEDA}}$ mixture³¹⁴ and pointed to the disolvated mixed dimer $[(\text{Ph(HC=CNLi, DALi)})\cdot2\text{TMEDA}]$ in which each lithium was chelated by a diamine molecule (Table 16, entry 3a). A ${}^6\text{Li}, {}^{15}\text{N}$ NMR-based structural investigation in solution was conducted afterward on a TMEDA-solvated 1:1 lithiophenylacetonitrile/HMDSLi complex.¹²⁹ The data pointed to a disolvated mixed dimer of formula $[(\text{Ph(HC=CNLi, HMDSLi)})\cdot2\text{TMEDA}]$ (Table 16, entry 3b). Note that no aggregation of these two partners was observed in THF. Calculations run on both systems, whether with DALi or HMDSLi, confirmed the observations above.¹²⁹ Finally, the coordination of a chiral lithium amide ($\text{Li-[2-methoxy-(R)-1-phenylethyl][(S)-1-phenylethyl]amide} = \text{R}^R\text{R}^S\text{NLi}$) with lithioacetonitrile has been the subject of structural NMR analyses.³¹⁵ Mixed dimers $[\text{H}_2\text{C}=\text{C}=\text{NLi})\cdot(\text{R}^R\text{R}^S\text{NLi})]$, organized around an N-Li-N-Li quadrilateral, were described either in Et_2O or THF (Table 16, entries 3c,d). However, in Et_2O , this species would be in equilibrium with two isomeric forms showing a central six-membered ring (Table 16, entry 3d). Computational studies run on the latter aggregates allowed an approach on the possible solvation. Only dimers with tetracoordinated lithium atoms were considered.

3.6. N–Li/O–Li-HomoMAAs

Results are presented for $[(\text{DALi})_x\cdot(\text{ROLi})_y]$, $[(\text{HMDSLi})_x\cdot(\text{ROLi})_y]$, $[(\text{TMPLi})_x\cdot(\text{ROLi})_y]$, $[(c\text{-Hex}_2\text{NLi})_x\cdot(\text{ROLi})_y]$, $[(2\text{-adamantyl}_2\text{NLi})_x\cdot(\text{ROLi})_y]$, and $[(\text{CLA})_x\cdot(\text{ROLi})_y]$ homoMAAs (RO = alkoxide, phenoxide or enolate).

Structural studies about $(\text{N-Li/O-Li})\text{-homoMAAs}$ mostly involved the classical lithium amides DALi and HMDSLi. Starting with DALi, structural data were obtained both in the solid state (X-ray diffraction) and solution (NMR spectroscopy) (Table 17). Combining this amide with the lithium alkoxide derived from 1,3-bis(dimethylamino)-2-propanol ($\text{Me}_2\text{NCH}_2\text{CH(Oli)CH}_2\text{NMe}_2 = \text{DMPOLi}$) in hexane at $0\text{ }^{\circ}\text{C}$ led to the obtention of a crystalline structure that was examined through a diffractometer.³¹⁶ A $[(\text{DALi})_2\cdot(\text{DMPOLi})_2]$ complex was highlighted, organized as

Table 18. Structures of (HMDSLi/ROLi)-HomoMAAs (solid state and solution)

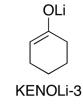
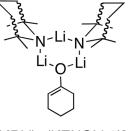
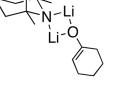
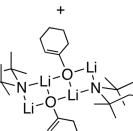
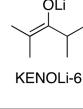
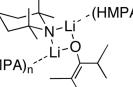
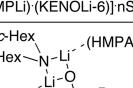
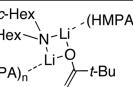
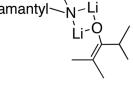
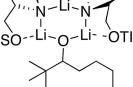
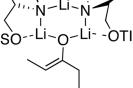
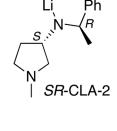
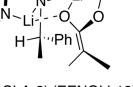
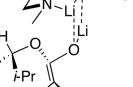
Entry	ROLi	Analytical method	Solvent (S)	$[(\text{HMDSLi})_x \cdot (\text{ROLi})_y] \cdot nS$	Ref
1a		NMR	THF		325
1b		NMR	Me_2NEt (-90°C)		309b
2a		X-ray	DME		326
2b		NMR	Et_3N (0°C)		327
2c		NMR	DME (-90°C)		161c
2d		NMR	DME (-90°C)		161c
2e		NMR	DME (-90°C)		161c
2f		NMR	Me_2NEt (-100°C)		328
3		NMR	THF -90°C		329
4		NMR	THF -75°C		330

^{*} n undetermined.

a ladder-tetramer in which two four-membered $\text{N}-\text{Li}-\text{O}-\text{Li}$ rings were connected through a central $\text{O}-\text{Li}-\text{O}-\text{Li}$ quadrilateral (Table 17, entry 1). In such an arrangement, each lithium cation was found to be coordinated to an N,N -dimethylamino group. Then, examining a 1:1 DALi/DMPOLi mixture in THF solution at room temperature allowed one to observe on the ^6Li NMR spectra the formation of a 1:1 mixed aggregate in equilibrium with a large amount (83%) of both parent partners. However, no more information was given about the exact structure of this aggregate in solution. Next, concerning the association of DALi with a lithium phenoxide ($2\text{-Alk}_2\text{NC(O)}(\text{C}_6\text{H}_3\text{X})\text{OLi} = \text{ArOLi}$, $\text{X} = \text{H}, \text{MeO}, \text{F}$, and $\text{Alk} = \text{Me}, \text{Et}, i\text{-Pr}$) formed while running an anionic Fries rearrangement, quadrilateral mixed dimers $[(\text{DALi}) \cdot (\text{ArO}-$

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Table 19. Structures of (N -Li/ROLi)-HomoMAAs (solid state and solution), for Which NLi = TMPLi, *c*-Hex₂NLi, 2-Adamantyl₂NLi, and CLAs

Entry	N-Li	ROLi	Analytical method	Solvent (S)	$[(N\text{-Li})_x \cdot (\text{ROLi})_y] \cdot n\text{S}^*$	Ref
1a	TMPLi	 KENOLi-3	NMR	THF	 $[(\text{TMPLi})_2(\text{KENOLi-3})] \cdot n\text{S}^*$	331
					 $[(\text{TMPLi}) \cdot (\text{KENOLi-3})] \cdot n\text{S}^*$	320
					 $[(\text{TMPLi})_2(\text{KENOLi-3})_2] \cdot n\text{S}^*$	331
1b		 KENOLi-6	NMR	THF/HMPA	 $(\text{HMPA})_n$	320
					 $[(\text{TMPLi}) \cdot (\text{KENOLi-6})] \cdot n\text{S}^*$	
2	<i>c</i> -Hex ₂ NLi	 KENOLi-1	NMR	C ₆ H ₆ /HMPA	 $(\text{HMPA})_n$	125
3	2-adamantyl ₂ NLi	 KENOLi-6	NMR	THF	 $[(2\text{-adamantyl}_2\text{NLi})(\text{KENOLi-6})] \cdot n\text{S}^*$	126
4a		 ALKOLi	NMR	toluene	 $[(\text{ALKOLi})_2(\text{TIPSO})] \cdot n\text{S}^*$	299c
					$[(\text{ALKOLi})_2(\text{TIPSO})]$	
4b		 KENOLi-10	X-ray NMR	toluene	 $[(\text{CLA-1})_2(\text{TIPSO})]$	332
					$[(\text{CLA-1})_2(\text{KENOLi-10})]$	
4c	 SR-CLA-2	 EENOLi-12	NMR	THF	 $[(\text{SR-CLA-2})_2(\text{i-Pr})] \cdot n\text{S}^*$	333
					$[(\text{SR-CLA-2})_2(\text{EENOLi-12})] \cdot n\text{S}^*$	
					 $[(\text{SS-CLA-2})_2(\text{i-Pr})] \cdot n\text{S}^*$	333

* n undetermined.

$\text{Li}] \cdot n\text{THF}$ (Table 17, entry 2a) were characterized thanks to ^6Li and ^{15}N NMR spectra registered at -90°C in THF, without precise information about the solvation.¹⁵⁵ⁱ Inequivalent ^6Li resonance coming up from a possible chelation with the amide group was not observed, but this does not mean it did not exist, since the Li–Li exchange can run very fast, even at temperatures lower than -120°C . A mixed trimer $[(\text{DALi})_2 \cdot (\text{ArOLi})]$ was additionally observed substituting THF by the other basic solvents BuOMe, HMPA, DME, TMEDA, or Me_2NET (Table 17, entry 2b).³¹⁷ Now, it is with enolates that DALi was found to be mostly associated. Thus, the first structural characterization of a DALi/lithium ketone enolate complex corresponded to an X-ray diffraction analysis and involved lithium 5-(*tert*-butyldimethylsilyloxy)-3,3-dimethylpent-1-en-2-olate [$\text{H}_2\text{C}=\text{C}(\text{OLi})\text{C}(\text{Me})_2\text{CH}_2\text{CH}_2\text{OSi}(\text{Me})_2t\text{-Bu} = \text{KENOLi-5}$].³¹⁸ A ladder-tetramer $[(\text{DALi})_2 \cdot (\text{KENOLi-5})_2]$ arrangement was depicted, assembling, like for the alkoxide above, two N–Li–O–Li quadrilaterals through a central O–Li–O–Li ring (Table 17, entry 3a). In this arrangement, the silyloxy group was found to coordinate the external lithium cations. Studies implicating the lithium ketone enolate derived from pinacolone [$\text{H}_2\text{C}=\text{C}(\text{OLi})t\text{-Bu} = \text{KENOLi-1}$] were also conducted, but attempts to obtain a crystalline sample were unsuccessful. By contrast, in THF solution, the NMR spectra, registered at -115°C , were found to be consistent with the presence of a $[(\text{DALi}) \cdot (\text{KENOLi-1})] \cdot n\text{S}$ mixed dimer (Table 17, entry 3b).³¹⁹ The solvation was not discussed. In the same way, lithium cyclohexenolate (KENOLi-3, Table 17, entry 3c) and lithium 2,4-dimethylpentenolate (KENOLi-6, Table 17, entry 3d) were found to organize with DALi in THF–HMPA solution as 1:1 mixed cyclic dimers $[(\text{DALi}) \cdot (\text{KENOLi-3})] \cdot n\text{S}$ and $[(\text{DALi}) \cdot (\text{KENOLi-6})] \cdot n\text{S}$.³²⁰ Note that if the solvation effect was not precisely evoked for these two examples, the role played by HMPA could be observed as being decisive in the obtention of such mixed aggregates. Indeed, in its absence (only THF), DALi and KENOLi-3 showed no tendency to form a mixed complex. Switching to lithium ester enolates, structural NMR analyses were obtained from a mixture containing equivalent amounts of DALi and lithium *tert*-butoxy(cyclohexylidene)-methanolate (EENOLi-10).³²¹ Spectra registered at -90°C in THF, THF/HMPA, and THF/DMPU underscored the formation of disolvated mixed dimers $[(\text{DALi}) \cdot (\text{EENOLi-10})] \cdot 2\text{S}$, S = THF, HMPA, and DMPU; Table 17, entry 4a). In S = BuOMe, the presence of disolvated mixed dimer was also observed, in addition to disolvated cyclic mixed trimer $[(\text{DALi})_2 \cdot (\text{EENOLi-10})] \cdot 2\text{S}$, Table 17, entry 4b).³²² Lithium enolate derived from a linear β -aminoester [$c\text{-HexCH}(\text{NiPr}_2)\text{CH}=\text{C}(\text{OLi})\text{Ot-Bu} = \text{EENOLi-11}$] was also found to organize, in THF/HMPA solution, as a mixed dimer $[(\text{DALi}) \cdot (\text{EENOLi-11})] \cdot n\text{S}$, Table 17, entry 4c) when added to an excess of DALi.³²³ The solvation was not mentioned and, depending on the procedure used to obtain the complex, one or two stereoisomeric complexes could be identified. In the case of (N–Li/O–Li)-homoMAAs engaging DALi, an NMR study run at -80°C on a toluene solution containing the amide, a chiral diether, and a lithium ester enolate derived from 2,4-dimethylpentan-3-yl isobutyrate [$\text{Me}_2\text{C}=\text{C}(\text{OLi})\text{OCH}(i\text{-Pr})_2 = \text{EENOLi-12}$] highlighted an additional mixed dimer, dicoordinated on one of the lithium cations by the diether $[(\text{DALi}) \cdot (\text{EENOLi-12})] \cdot \text{diether}$, Table 17, entry 4d).³²⁴

Concerning structural data of the (N–Li/O–Li)-homoMAAs consisting of HMDSLi (Table 18), two aggregates

obtained by mixing HMDSLi and a lithium alkoxide were reported. One example was related to the formation of a complex between HMDSLi and the α -aminoalkoxide formed in the 1,2 nucleophilic addition of lithium pyrrolidide onto 2-methylcyclohexanones ($\alpha\text{-AAOLi}$, Table 18, entry 1a).³²⁵ The ^6Li , ^{13}C , and ^{15}N NMR spectra registered in THF showed the presence of a pair of conformers for the disolvated $[(\text{HMDSLi}) \cdot (\alpha\text{-AAOLi})] \cdot 2\text{THF}$ mixed dimer. In the second illustration, HMDSLi was combined in a dimethylethylamine solution with a chiral alkoxide derived from camphor (CAMPHOLi),^{309b} and a disolvated mixed dimer $[(\text{HMDSLi}) \cdot (-\text{CAMPHOLi})] \cdot n\text{Me}_2\text{NET}$ (n not determined), showing an intramolecular coordination between one lithium cation and the camphor moiety, could be observed at low temperature (-90°C) by NMR (Table 18, entry 1b). Then, concerning the use of a lithium ketone enolate as the O–Li partner, a crystalline sample was isolated from a DME solution, for a HMDSLi complex with the ketone enolate derived from pinacolone (KENOLi-1).³²⁶ The disolvated dimer $[(\text{HMDSLi}) \cdot (\text{KENOLi-1})] \cdot 2\text{DME}$ was depicted in which each lithium cation was found to be chelated by one molecule of solvent (Table 18, entry 2a). Studying structures of HMDSLi/lithium enolate derived from 2-methylpentan-3-one (KENOLi-7) aggregates formed in Et_3N solution, using the NMR spectroscopy, afforded the possibility to observe disolvated mixed dimers (Table 18, entry 2b).³²⁷ Two Z and E $[(\text{HMDSLi}) \cdot (\text{KENOLi-7})] \cdot 2\text{NEt}_3$ stereoisomeric complexes were observable if running the enolization at 0°C , while only the E isomer was formed at -78°C . Lithium ketone enolates derived from 1-indanone (KENOLi-8), cyclopentanone (KENOLi-2), and cyclohexanone (KENOLi-3) were also mixed with HMDSLi, and structural data of the corresponding (N–Li/O–Li)-homoMAAs were given in DME solution using the method of continuous variation in conjunction with ^6Li NMR spectroscopy.^{161c} Disolvated mixed dimers $[(\text{HMDSLi}) \cdot (\text{KENOLi-}x)] \cdot 2\text{DME}$ with $x = 8, 2$, and 3 emerged (Table 18, entries 2c–e). Enolization of 2-methylcyclohexanone in the presence of an excess of HMDSLi and dimethylethylamine at -100°C led to the observation by NMR of a disolvated mixed dimer $[(\text{HMDSLi}) \cdot (\text{KENOLi-9})] \cdot 2\text{Me}_2\text{NET}$, Table 18, entry 2f).³²⁸ Switching to lithium ester enolate derived from methyl 3-aminobutanoate (EENOLi-9), a mixed dimer, in which an intramolecular coordination between the amino group and one of the lithium atoms takes place, was depicted in THF at -90°C $[(\text{HMDSLi}) \cdot (\text{EENOLi-9})] \cdot n\text{THF}$, Table 18, entry 3).³²⁹ Note that the solvation by THF was not specified. Similar observations were made from lithium amide enolate derived from 3-amino-N,N-dibutylbutanamide (AENOLi), this time in the presence of a mixed trimer incorporating two HMDSLi units for one enolate $[(\text{HMDSLi}) \cdot (\text{AENOLi})] \cdot n\text{THF}$ and $[(\text{HMDSLi})_2 \cdot (\text{AENOLi})] \cdot n\text{THF}$, Table 18, entry 4).³³⁰

Among other (N–Li/O–Li)-homoMAAs for which structural data were obtained (Table 19), one can mention the NMR results obtained when engaging TMPLi. Putting this lithium amide in the presence of lithium cyclohexenolate (KENOLi-3) in THF led to the observation of a $[(\text{TMPLi})_2 \cdot (\text{KENOLi-3})] \cdot n\text{S}$ cyclic trimer, a $[(\text{TMPLi}) \cdot (\text{KENOLi-3})] \cdot n\text{S}$ cyclic dimer, and a $[(\text{TMPLi})_2 \cdot (\text{KENOLi-3})_2] \cdot n\text{S}$ ladder-tetramer, without precision about the exact solvation (Table 19, entry 1a).³³¹ Running similar spectroscopic analyses in THF/HMPA mixture revealed the mixed dimer as the only observable mixed aggregate, however, without precision about

Table 20. Structures of (N–Li/Li–X)-HomoMAAs (solid state and solution)

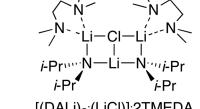
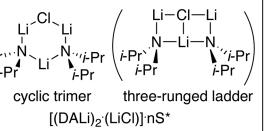
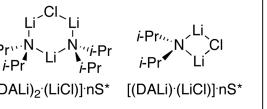
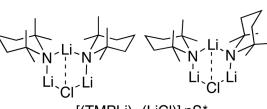
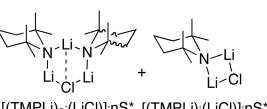
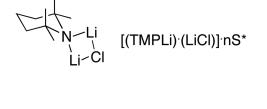
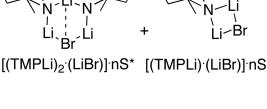
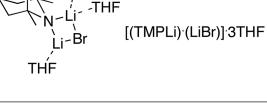
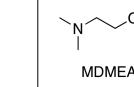
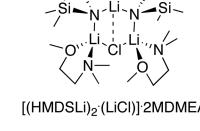
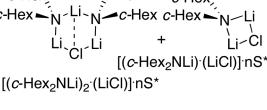
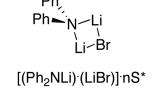
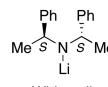
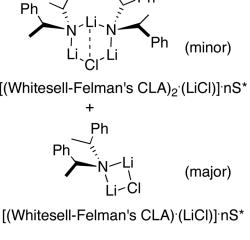
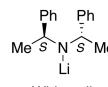
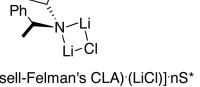
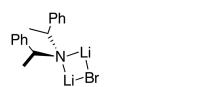
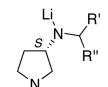
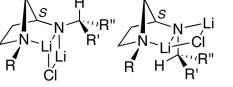
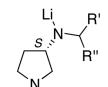
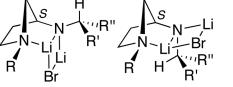
Entry	N-Li	Li-X	Analytical method	Solvent (S)	$[(N\text{-Li})_x \cdot (Li\text{-}X)_y] \cdot nS$	Ref
1a	DALi	LiCl (1 equiv)	X-ray and NMR (-90°C)	toluene + 2 equiv TMEDA		334
1b		LiCl (low cc)	NMR (-115°C)	THF		319 323b
1c		LiCl (high cc)	NMR (-115°C)	THF		319 323b
2a	TMPLi	LiCl (0.3 equiv)	NMR (-100°C)	THF + pentane (3:1)		331
2b		LiCl (0.6 equiv)	NMR (-100°C)	THF + pentane (3:1)		331
2c		LiCl (1.2 equiv)	NMR (-100°C)	THF + pentane (3:1)		331
2d		LiBr (0.5 equiv)	NMR (-100°C)	THF + pentane (3:1)		331
2e		LiBr (1.5 equiv)	NMR (-100°C) + X-ray	THF + pentane (3:1) + X-ray		331 336
3	HMDSLi	LiCl (1 equiv)	X-ray			336
4	c-Hex ₂ NLi	LiCl (1 equiv)	NMR (\geq rt)	THF/toluene (1.5 : 1)		125
5	Ph ₂ NLi	LiBr (0.5 equiv)	NMR (-90°C)	THF/toluene (low cc)		2b,c

Table 20. continued

Entry	N-Li	Li-X	Analytical method	Solvent (S)	$[(N\text{-Li})_x \cdot (Li\text{-}X)_y] \cdot nS$	Ref
6a		LiCl (0.5 equiv)	NMR (-115°C)	THF	 <p>$[(Whitesell\text{-}Felman's\ CLA)_2(LiCl)]nS^+$ $[(Whitesell\text{-}Felman's\ CLA)(LiCl)]nS^+$</p>	337
6b		LiCl (3 equiv)	NMR (-115°C)	THF	 <p>$[(Whitesell\text{-}Felman's\ CLA)(LiCl)]nS^+$</p>	337
6c		LiBr (0.5-3 equiv)	NMR (-115°C)	THF	 <p>$[(Whitesell\text{-}Felman's\ CLA)(LiBr)]nS^+$</p>	337
7a		LiCl (1 equiv)	NMR (-78°C)	THF	 <p>$[(Maddaluno\text{'s}\ CLA)(LiCl)]nS^+$</p>	338
7b		LiBr (1 equiv)	NMR (-78°C)	THF	 <p>$[(Maddaluno\text{'s}\ CLA)(LiBr)]nS^+$</p>	338

* n undetermined.

the exact HMPA solvation effect.³²⁰ Treatment of TMPLi with lithium diisopropylketone enolate (KENOLi-6) also afforded the exclusive formation of $[(TMPLi)\cdot(KENOLi-6)]\cdot nS$ cyclic mixed dimer in the THF/HMPA solvent (Table 19, entry 1b).³²⁰ Here again the precise solvation was not determined. Among other lithium amides associated with lithio-oxygenated derivatives, one can evoke the results obtained by mixing lithium dicyclohexylamide ($c\text{-Hex}_2\text{NLi}$) and ketone enolate derived from pinacolone (KENOLi-1) in benzene/HMPA medium (Table 19, entry 2),¹²⁵ as well as those associating lithium bis(2-adamantyl) amide (2-adamantyl $_2\text{NLi}$) with lithium 2,4-dimethylpentenolate (KENOLi-6) in THF (Table 19, entry 3).¹²⁶ In both cases, the formation of cyclic mixed dimers was highlighted, either $[(c\text{-Hex}_2\text{NLi})\cdot(KENOLi-1)]\cdot nHMPA$ in limited concentration along with the two parent oligoMAAs or $[(2\text{-adamantyl}_2\text{NLi})\cdot(KENOLi-6)]\cdot nS$ quantitatively. Once more, no details were reported about the solvation. Finally, we can tackle structural data about complexes between chiral lithium amides (CLAs) and a lithium alkoxide or enolates (Table 19, entries 4a–c). Running a ^1H and ^{13}C DOSY NMR experiment on mixtures containing Koga–Hilmersson's CLA derived from valine (CLA-1) and lithium 2,2-dimethylheptan-3-olate (ALKOLi) in deuteriated toluene allowed one to characterize an unsolvated trimeric complex incorporating two lithium amide units for one alkoxide ($[(CLA-1)_2\cdot(ALKOLi)]$, Table 19, entry 4a).^{299c} The same chiral amide, in contact with lithium (Z)-pent-2-en-3-olate (KENOLi-10), resulted in crystals from which X-ray analyses also showed an unsolvated 2:1 cyclic mixed trimer (Table 19, entry 4b).^{332a} The $[(CLA-1)_2\cdot(KENOLi-10)]$ crystals were then dissolved in deuteriated toluene, and a similar trimeric

arrangement was highlighted in solution at $-78\ ^\circ\text{C}$.^{332b} By contrast, two 1:1 noncovalent mixed dimers were identified spectroscopically in THF solution between lithium ester enolate EENOLi-12 and two diastereomeric Maddaluno's CLAs (SR-CLA-2 and SS-CLA-2, Table 19, entry 4c).³³³ In these last examples, the solvation was not determined.

3.7. N–Li/Li–X–HomoMAAs

Results are presented for $[(DALi)_x \cdot (LiCl)_y]$, $[(TMPLi)_x \cdot (LiCl)_y]$, $[(TMPLi)_x \cdot (LiBr)_y]$, $[(HMDSLi)_x \cdot (LiCl)_y]$, $[(c\text{-Hex}_2\text{NLi})_x \cdot (LiCl)_y]$, $[(Ph_2\text{NLi})_x \cdot (LiBr)_y]$, and $[(CLA)_x \cdot (LiX)_y]$ ($X = Cl, Br$).

The heteroMAA made of lithium diisopropylamide and lithium chloride (Table 20, entry 1) probably figures among the most structurally described examples of N–Li/Li–X species. Data both in the solid state³³⁴ and solution^{319,320,323b,331,335} have been reported for this system, in support of ab initio calculations.³³⁵ In the solid-state structure,³³⁴ isolated from a toluene solution containing 2 equiv of TMEDA, a disolvated mixed trimer accounting for two molecules of monosolvated lithium amide for one of lithium chloride was highlighted (Table 20, entry 1a). The $[(DALi)_2 \cdot (LiCl)] \cdot 2\text{TMEDA}$ complex thus obtained was described as a three-runged ladder. The same crystals were then dissolved in toluene to be analyzed in solution, thanks to the NMR technique $[-90 < T (\text{°C}) < 0]$.³³⁵ More or less the same trimeric skeleton could be identified, although an intramolecular fluxional process implicating open trimers and intramolecularly bridging TMEDA was pointed to under these conditions. Examining the DALi/LiCl homoMAA structure at $-115\ ^\circ\text{C}$ in THF solution^{319,323b} also led, at low LiCl concentration, to the observation of a 2:1 lithium amide/

Table 21. Structures of (O–Li/Li–X)-HomoMAAs (solid state and solution)

Entry	O-Li	Li-X	Analytical method	Solvent (S)	$[(O\text{-Li})_x \cdot (Li\text{-X})_y] \cdot nS$	Ref
1		LiCl	NMR (-78°C)	THF	 [(PhCH(Me)OLi) ₃ (LiCl)] _n THF*	339
2a		LiCl	NMR (-90°C)	S = 1,3-dioxolane or THF	 S = 1,3-dioxolane or THF [(ArOLi)(LiCl)] _n S*	340
2b		LiI	NMR (-80°C)	Et ₂ O	 [(ArOLi) ₃ (LiI)] _n Et ₂ O* [(ArOLi) ₂ (LiI) ₂] _n Et ₂ O* (minor) (major)	153e
3a		LiCl	NMR (-50°C)	S = 1,3-dioxolane	 [(KENOLi-11) ₃ (LiCl)] _n S*	163
3b		LiBr	X-ray	TMEDA	 [(KENOLi-6)(LiBr)] ₂ TMEDA	336
3c		LiI	X-ray	TMEDA	 [(KENOLi-6)(LiI)] ₂ TMEDA	336

* *n* undetermined.

lithium chloride arrangement, albeit no precision was given about the solvation. A cyclic $[(DALi)_2 \cdot (LiCl)] \cdot nS$ trimer was advanced (Table 20, entry 1b), without excluding the possibility of forming a three-runged ladder. Working at higher LiCl concentration favored the appearance of the cyclic $[(DALi) \cdot (LiCl)] \cdot nS$ mixed dimer (Table 20, entry 1c).³¹⁹ Those aggregates turned out to be nonexistent in solution when HMPA was added to the THF solution.³²⁰

The structure in solution of TMPLi/LiX (X = Cl, Br) homoMAAs was documented in 1991.³³¹ NMR Spectra run at -100 °C in THF/pentane (3:1) solution and varying the amount of lithium chloride led to the successive conclusions (Table 20, entries 2a–c): (i) at 0.3 equiv LiCl, $[(TMPLi)_2 \cdot (LiCl)] \cdot nS$ trimers (two conformational isomers, symmetrical and unsymmetrical) formed next to monomeric and dimeric TMPLi oligoMAAs; (ii) at 0.6 equiv LiCl, all TMPLi oligoMAAs disappeared to mix either as $[(TMPLi)_2 \cdot (LiCl)] \cdot nS$ trimers or $[(TMPLi) \cdot (LiCl)] \cdot nS$ dimer; (iii) at 1.2 equiv LiCl, the mixed dimer became by far

the major entity. The solvation was not discussed for all the above sequence. Working with LiBr revealed slightly different than LiCl (Table 20, entries 2d,e). The introduction of 0.5 equiv of LiBr led to a mixture of a single symmetrical $[(TMPLi)_2 \cdot (LiBr)] \cdot nS$ trimer, a significant amount of cyclic $[(TMPLi) \cdot (LiBr)]$ dimer, and the two monomeric and dimeric TMPLi oligoMAAs. After increasing the amount of LiBr to 1.5 equiv, only the mixed dimer was observed, in addition to free LiBr. This dimer was isolated in the solid state and depicted as being solvated by three molecules of THF.^{336a}

Among other lithium amide/lithium halide homoMAAs for which structural data were obtained, one can include the cases of (i) HMDSLi and lithium chloride that gave, in the presence of 2-methoxy-N,N-dimethylethanamine ($\text{Me}_2\text{NCH}_2\text{CH}_2\text{OMe}$, MDMEA), a solid-state structure depicted by X-ray diffraction as a disolvated three-runged ladder structure incorporating two solvated molecules of HMDSLi surrounding one molecule of LiCl (Table 20, entry 3);^{336a} (ii) dicylohexylolithium amide and lithium chloride, which were found to form, at -90 °C in

THF/toluene (1.5:1) solvent, a 2:1 $[(c\text{-Hex}_2\text{NLi})_2\cdot(\text{LiCl})]\cdot nS$ mixed trimer and a 1:1 $[(c\text{-Hex}_2\text{NLi})\cdot(\text{LiCl})]\cdot nS$ mixed dimer (n undetermined, Table 20, entry 4);¹²⁵ and (iii) lithium diphenylamide and lithium bromide that quantitatively arranged, in THF/toluene (1.2:1) at -90°C , as a cyclic 1:1 $[(\text{Ph}_2\text{NLi})\cdot(\text{LiBr})]\cdot n\text{THF}$ mixed dimer, probably trisolvated ($n = 3$, Table 20, entry 5).^{2b,c} Increasing THF concentration led to the dissociation of the latter mixed aggregate.

The structures of N–Li/Li–X-homoMAAs involving a chiral lithium amide have also been studied. Thus, the aggregations of LiCl, LiBr, and LiI with Whitesell–Felman’s CLA were examined by NMR in THF at -115°C (Table 20, entries 6a–c).³³⁷ Introducing increasing amounts of LiCl onto a Whitesell–Felman’s CLA solution in THF led to the successive formation of four species, as detailed in the following (Table 20, entries 6a,b): (i) in the absence of lithium halide, the amide was found to be mostly present as a dimeric oligoMAA, in addition to small amount of monomer; (ii) the addition of 0.5 equiv of LiCl led to a mixture containing a large amount of dimeric Whitesell–Felman’s CLA-oligoMAA, traces of a mixed three-runged ladder trimer $[(\text{Whitesell–Felman’s CLA})_2\cdot(\text{LiCl})]\cdot nS$, and significant amount of mixed cyclic dimer $[(\text{Whitesell–Felman’s CLA})\cdot(\text{LiCl})]\cdot nS$; and (iii) working with 3 equiv of lithium chloride was in favor of the exclusive presence of the mixed dimer. With LiBr, the mixed trimer was not observed at any lithium halide concentration. The single formation of mixed dimer $[(\text{Whitesell–Felman’s CLA})\cdot(\text{-LiBr})]\cdot nS$ was accompanied by a not negligible amount of dimeric Whitesell–Felman’s CLA-oligoMAA, even in the presence of 3 equiv of lithium bromide (Table 20, entry 6c). By contrast, LiI did not alter the aggregation state of the amide. As another example of CLA/LiX homoMAA, one can cite the complexes fully described in THF from NMR data between Maddaluno’s CLA and LiCl or LiBr (Table 20, entries 7a,b).³³⁸ Maddaluno’s CLA derived from a 3-aminopyrrolidine skeleton was seen as adopting an azanorbornyl-like conformation due to an intramolecular coordination between the lithium cation and the pyrrolidinic nitrogen. Both LiCl and LiBr salts showed a high affinity for this lithium amide in THF at -78°C , preserving the norbornyl-like folding and leading quantitatively to the mixed dimers $[(\text{Maddaluno’s CLA})\cdot(\text{LiCl})]\cdot nS$ and $[(\text{Maddaluno’s CLA})\cdot(\text{LiBr})]\cdot nS$. The thermodynamic preference for mixed aggregation between this amide and LiX was confirmed by static DFT calculations. Note that, for all structures referring to CLA partners, the solvation was not determined.

3.8. O–Li/Li–X-HomoMAAs

Results are presented for $[(\text{PhCH}(\text{Me})\text{OLi})_x\cdot(\text{LiCl})_y]$, $[(\text{Ar-OLi})_x\cdot(\text{LiCl})_y]$, $[(\text{ArOLi})_x\cdot(\text{LiI})_y]$, $[(\text{Me}_2\text{C}=\text{C}(\text{Ph})\text{OLi})_x\cdot(\text{LiCl})_y]$, $[(\text{Me}_2\text{C}=\text{C}(\text{i-Pr})\text{OLi})_x\cdot(\text{LiBr})_y]$, and $[(\text{Me}_2\text{C}=\text{C}(\text{i-Pr})\text{OLi})_x\cdot(\text{LiI})_y]$.

The literature proved to be very poor about structural data related to O–Li/Li–X homoMAAs incorporating a lithium alkoxide. Note only the very recent results obtained when analyzing by NMR at -78°C the affinity of PhCH(Me)OLi with LiCl in THF.³³⁹ In this single example, the formation of a mixed tetramer accounting for three molecules of alkoxide for one molecule of lithium chloride was highlighted $[(\text{PhCH}(\text{Me})\text{OLi})_3\cdot(\text{LiCl})]\cdot n\text{THF}$, Table 21, entry 1). Note that the solvation was not determined.

Contrariwise, variously substituted lithium phenoxides have been mixed with lithium salts in 1,3-dioxolane or THF, and the

NMR spectra run at -80 or -90°C extricate structural data.³⁴⁰ Thus, lithium 2,6-dimethyl-, 4-bromo-2,6-dimethyl-, and 2,4,6-tribromophenoxides led to mixed cyclic dimers when put in the presence of 1 equiv of LiCl in these two solvents $[(\text{ArOLi})\cdot(\text{LiCl})]\cdot nS$, S = dioxolane or THF, Table 21, entry 2a). In Et₂O, lithium 3,5-dimethylphenoxide was found to form mixed tetramers with LiI.^{153e} The 3:1 $[(\text{ArOLi})_3\cdot(\text{LiI})]\cdot n\text{Et}_2\text{O}$ mixed tetramer was identified as the major complex, in addition to a minor amount of the 2:2 $[(\text{ArOLi})_2\cdot(\text{LiI})_2]\cdot n\text{Et}_2\text{O}$ tetramer (Table 21, entry 2b).^{153e} Note that the solvation was not clearly established for all of these examples (n undetermined).

Among O–Li/Li–X homoMAAs involving lithium enolates, one can mention the results obtained with lithioisobutyronone $[\text{Me}_2\text{C}=\text{C}(\text{Ph})\text{OLi}$, KENOLi-11] in the presence of an equimolar amount of lithium chloride in dioxolane. NMR analyses run at low temperature (about -50°C) evidenced a cubic tetrameric arrangement made of three molecules of enolate and one molecule of lithium chloride, the solvation not being discussed $[(\text{KENOLi-11})_3\cdot(\text{LiCl})]\cdot nS$, S = dioxolane; Table 21, entry 3a).¹⁶³ Complementarily, X-ray measurements were performed on crystals obtained after mixing LiBr or LiI with lithium 2,4-dimethylpent-2-en-3-olate $[\text{Me}_2\text{C}=\text{C}(\text{i-Pr})\text{OLi}$, KENOLi-6] in the presence of TMEDA.³³⁶ Both structures were found to correspond to the disolvated mixed cyclic dimers $[(\text{KENOLi-6})\cdot(\text{LiBr})]\cdot 2\text{TMEDA}$ (Table 21, entry 3b) and $[(\text{KENOLi-6})\cdot(\text{LiI})]\cdot 2\text{TMEDA}$ (Table 21, entry 3c), respectively.

The Li,Li-homoMAAs’ structures that are presented above are mainly corresponding to mixed dimers or cubic tetramers. A few examples correspond to ladder arrangements, and very rarely, trimers show up. Most of the mixed aggregates depicted above have the particularity of changing the initial reactivity, either in terms of yield or selectivity, of the parent partners. In some cases, the association has the effect of accelerating the kinetics, and thus the yields, of the transformations involved. This is, for example, the case for a mixture of *t*-BuLi and *i*-PrLi used to carry on the metalation of indene: pure tetrameric *t*-BuLi was revealed to be less reactive than the *t*-BuLi/*i*-PrLi mixed aggregate.^{294b} As another application, one can evoke the chemical results obtained when running enantioselective nucleophilic 1,2-additions of alkyllithiums onto aldehydes: the alkyllithium/chiral lithium amide mixed aggregates reacted with the electrophile faster than the free alkyllithium introduced in excess in the reaction medium, since quantitative yields and high enantioselectivities could be reached.¹³² By contrast, the formation of a mixed complex may reduce the reactivity, as observed sometimes when adding lithium halides.^{177b} The same lithium halide can also have a beneficial effect on the stereoselectivities.³³⁹ Such variable behaviors on deprotonation and nucleophilic addition reactions are actually presented and discussed on the basis of the structure/reactivity relationship in the companion review entitled “Mixed Aggregate (MAA): A Single Concept for All Dipolar Organometallic Aggregates. 2. Syntheses and Reactivities of Homo/HeteroMAAs”.

4. HeteroMAAs

In this section, the organo(bi)metallic species made of two organometallic partners with nonidentical metals are called “heteroMAAs”. The anionic moieties can be similar or totally distinct. This definition gathers the Schlosser–Lochmann superbases and the ate complexes. The most used and known structures, from an organic chemist’s point of view, will be presented: Li,Na-, Li,K-, and Na,K-heteroMAAs (Schlosser–

Table 22. Solid-State Structures of Homoleptic Li_nNa_m, Li_nK_m, and Na_nK_m-HeteroMAAs

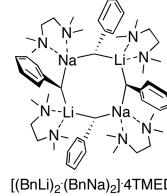
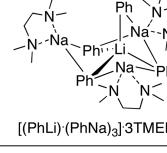
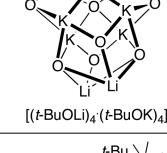
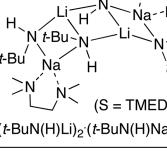
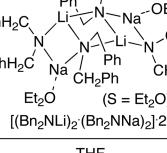
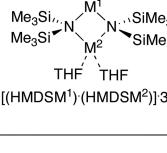
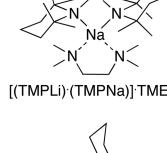
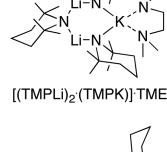
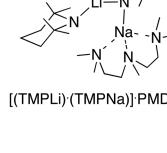
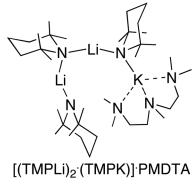
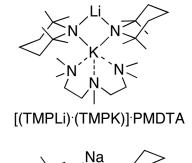
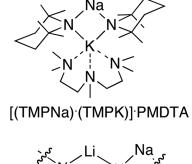
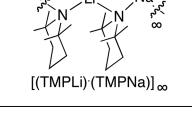
Entry	R-Li	R-M (M = Na or K)	Analytical method	Solvent (S)	$[(R\text{-Li})_x \cdot (R\text{-M})_y] \cdot nS$	Ref
1	MeLi	MeNa	X-ray	Et ₂ O	-	209a
2	BnLi	BnNa	X-ray	toluene + TMEDA	 [(BnLi) ₂ (BnNa) ₂]·4TMEDA	343
3	PhLi	PhNa	X-ray	hexane + TMEDA	 [(PhLi)(PhNa) ₃]·3TMEDA	344
4	<i>t</i> -BuOLi	<i>t</i> -BuOK	X-ray	TMEDA	 [(t-BuOLi) ₄ (t-BuOK) ₄]*	345
5	<i>t</i> -BuN(H)Li	<i>t</i> -BuN(H)Na	X-ray	hexane + TMEDA	 [(t-BuN(H)Li) ₂ (t-BuN(H)Na) ₂]·2S (S = TMEDA)	346
6	Bn ₂ NLi	Bn ₂ NNa	X-ray	Et ₂ O	 [(Bn ₂ NLi) ₂ (Bn ₂ NNa) ₂]·2S (S = Et ₂ O)	347
7a 7b 7c	HMDSLi HMDSLi -	HMDSNa HMDSK HMDSNa/HMDSK	X-ray	pentane + THF	 [(HMDSM ¹)·(HMDSM ²)·3THF]	348
8a	TMPLi	TMPNa		TMEDA	 [(TMPLi)·(TMPNa)]·TMEDA	
8b	TMPLi	TMPK		TMEDA	 [(TMPLi) ₂ (TMPK)]·TMEDA	349
8c	TMPLi	TMPNa		PMDTA	 [(TMPLi)·(TMPNa)]·PMDTA	
			X-ray			

Table 22. continued

Entry	R-Li	R-M (M = Na or K)	Analytical method	Solvent (S)	$[(R\text{-Li})_x \cdot (R\text{-M})_y] \cdot nS$	Ref
8d	TMPLi	TMPK		PMDTA	 [(TMPLi) ₂ (TMPK)]PMDTA	
8e	TMPLi	TMPK		PMDTA	 [(TMPLi)(TMPK)]PMDTA	349
8f	-	TMPNa/TMPK		PMDTA	 [(TMPNa)(TMPK)]PMDTA	
8g	TMPLi	TMPNa		none	 [(TMPLi)(TMPNa)] _∞	

*The *t*-Bu appendages have been omitted for clarity.

Lochmann superbases), as well as magnesate, aluminate, and zincate derivatives.

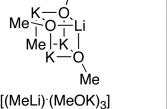
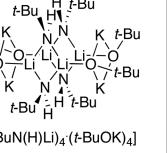
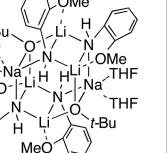
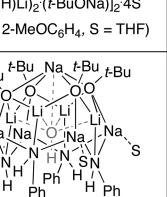
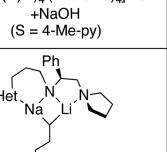
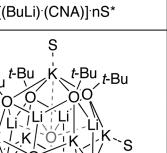
4.1. Li,Na-, Li,K-, and Na,K-HeteroMAAs

4.1.1. Homoleptic Li,Na-, Li,K-, and Na,K-HeteroMAAs. Results are presented for $[(\text{MeLi})_x \cdot (\text{MeNa})_y]$, $[(\text{BnLi})_x \cdot (\text{BnNa})_y]$, $[(\text{PhLi})_x \cdot (\text{PhNa})_y]$, $[(t\text{-BuOLi})_x \cdot (t\text{-BuOK})_y]$, $[(t\text{-BuN(H)Li})_x \cdot (t\text{-BuN(H)Na})_y]$, $[(\text{Bn}_2\text{NLi})_x \cdot (\text{Bn}_2\text{NNa})_y]$, $[(\text{HMDSLi})_x \cdot (\text{HMDSNa})_y]$, $[(\text{HMDSLi})_x \cdot (\text{HMDSK})_y]$, $[(\text{HMDSNa})_x \cdot (\text{HMDSK})_y]$, $[(\text{TMPLi})_x \cdot (\text{TMPNa})_y]$, $[(\text{TMPLi})_x \cdot (\text{TMPK})_y]$, and $[(\text{TMPNa})_x \cdot (\text{TMPK})_y]$.

The ability for mixed organoalkali bases consisting of lithium and sodium or potassium derivatives to act as powerful deprotonating reagents over those containing only lithium has been widely demonstrated.^{4b,5,341} Concerning structural information about these reactants, much less has been reported until now.³⁴² Among relevant information on this matter, one can distinguish data obtained for homoleptic Li,Na-, Li,K-, and Na,K-heteroMAAs, made of similar anionic moieties, from those comprising unsimilar anionic partners (heteroleptic). The complexes $[(\text{MeLi})_x \cdot (\text{MeNa})_y]$,^{209a} $[(\text{BnLi})_x \cdot (\text{BnNa})_y]$,³⁴³ $[(\text{PhLi})_x \cdot (\text{PhNa})_y]$,³⁴⁴ $[(t\text{-BuOLi})_x \cdot (t\text{-BuOK})_y]$,³⁴⁵ $[(t\text{-BuN(H)Li})_x \cdot (t\text{-BuN(H)Na})_y]$,³⁴⁶ $[(\text{Bn}_2\text{NLi})_x \cdot (\text{Bn}_2\text{NNa})_y]$,³⁴⁷ $[(\text{HMDSLi})_x \cdot (\text{HMDSNa})_y]$,³⁴⁸ $[(\text{HMDSLi})_x \cdot (\text{HMDSK})_y]$,³⁴⁸ $[(\text{HMDSNa})_x \cdot (\text{HMDSK})_y]$,³⁴⁸ $[(\text{TMPLi})_x \cdot (\text{TMPNa})_y]$,³⁴⁹ $[(\text{TMPLi})_x \cdot (\text{TMPK})_y]$,³⁴⁹ and $[(\text{TMPNa})_x \cdot (\text{TMPK})_y]$ ³⁴⁹ belong to the first category (Table 22). Regarding the MeLi/MeNa mixture, the question of forming a mixed complex was raised when synthesizing methylsodium by the reaction of methylolithium with sodium *tert*-butoxide in diethyl ether. Depending upon the reaction conditions, variable amounts of MeLi were found in the newly formed MeNa preparation, with Na/Li going from 36:1 to 3:1. Crystallographic data highlighted a polymeric arrangement of 24 cubic tetrameric $[\text{MeNa}]_4$ units, in which eight cavities were present, able to incorporate

$[\text{MeLi}]_4$ items with a maximum $[\text{MeNa}]_4/[\text{MeLi}]_4$ ratio of 3:1 (Table 22, entry 1). The BnLi/BnNa complex was observed running the metalation of toluene in the presence of equimolar amounts of BuLi and BuNa, plus 2 equiv of TMEDA.³⁴³ It organized as the TMEDA-tetrasolvated planar 2:2 mixed tetramer $[(\text{BnLi})_2 \cdot (\text{BnNa})_2] \cdot 4\text{TMEDA}$ (Table 22, entry 2), in which the metal cations were found to interchange in the bulk crystal. A TMEDA–phenyllithium/phenylsodium adduct was also isolated in the solid state, and included three molecules of solvated phenylsodium for one molecule of unsolvated phenyllithium.³⁴⁴ In this $[(\text{PhLi}) \cdot (\text{PhNa})_3] \cdot 3\text{TMEDA}$ aggregate, the lithium occupied a central tetrahedral position, being linked to the four phenyl appendages. The three sodium atoms were all coordinated to a molecule of TMEDA. Two of them were also linking to two phenyl moieties, while three were linked to the third one (Table 22, entry 3). Examining oxygenated anionic species, one can evoke the $[(t\text{-BuOLi})_x \cdot (t\text{-BuOK})_y]$ heteroMAA synthesized from its homonuclear parents in the presence of TMEDA. It crystallized in a TMEDA-free form incorporating eight alkoxide units and four atoms of each metal. A 16-vertex and 12-square-faced $[(t\text{-BuOLi})_4 \cdot (t\text{-BuOK})_4]$ polyhedron was described (Table 22, entry 4).³⁴⁵ As an example of lithium/sodium bisamide, one can cite the ladder-tetramer structure derived from *t*-BuNH₂ and solvated by two molecules of TMEDA through the sodium atoms.³⁴⁶ Thus, a $[(t\text{-BuN(H)Li})_2 \cdot (t\text{-BuN(H)Na})_2] \cdot 2\text{TMEDA}$ laddering arrangement was depicted, assembling two N–Li–N–Na quadrilaterals through a central N–Li–N–Li ring (Table 22, entry 5). A comparable organization was observed from crystals isolated from a Bn₂NLi/Bn₂NNa mixture in Et₂O.³⁴⁷ The $[(\text{Bn}_2\text{NLi})_2 \cdot (\text{Bn}_2\text{NNa})_2] \cdot 2\text{Et}_2\text{O}$ ladder-tetramer heteroMAA was deduced from crystallographic analyses (Table 22, entry 6). Mixed-alkali-metal bis(trimethylsilyl)amide bases have also been the subject of structural analyses by crystallography.³⁴⁸ Thus, $[(\text{HMDSLi})_x \cdot (\text{HMDSNa})_y]$,

Table 23. Structures of Heteroleptic Li,Na- and Li,K-HeteroMAAs

Entry	R-Li	R'-M (M = Na or K)	Analytical method	Solvent (S)	$[(R\text{-Li})_x \cdot (R'\text{-M})_y] \cdot nS$	Ref
1	MeLi	MeOK	theoretical data	-		351
2	<i>t</i> -BuN(H)Li	<i>t</i> -BuOK	X-ray	C ₆ H ₆		352
3	2-MeOC ₆ H ₄ N(H)Li or <i>t</i> -BuLi	<i>t</i> -BuONa or MeOC ₆ H ₄ N(H)Na	X-ray	THF		353
4	PhN(H)Li or <i>t</i> -BuLi	<i>t</i> -BuONa or PhN(H)Na	X-ray	4-Me-pyridine		354
5	BuLi	Het- <i>CH</i> ₂ - <i>CH</i> (<i>Ph</i>)- <i>N</i> (<i>Na</i>) (Het = Me ₂ N or MeO) Koga-O'Brien CNA	NMR	THF (-80°C)		355
6	KENOLi-2 or <i>t</i> -BuOLi	<i>t</i> -BuOK or KENOK	X-ray	THF		356

^{*}*n* undetermined.

$[(\text{HMDSLi})_x \cdot (\text{HMDSK})_y]$, and $[(\text{HMDSNa})_x \cdot (\text{HMDSK})_y]$ aggregates were isolated in the solid state after mixing equimolar amounts of each component in pentane/THF mixture and cooling down to -40°C . X-ray diffraction underscored the THF-trisolvated cyclic mixed dimers $[(\text{HMDSLi}) \cdot (\text{HMDSNa})] \cdot 3\text{THF}$, $[(\text{HMDSLi}) \cdot (\text{HMDSK})] \cdot 3\text{THF}$, and $[(\text{HMDSNa}) \cdot (\text{HMDSK})] \cdot 3\text{THF}$ (Table 22, entry 7). A series of Li,Na-, Li,K-, and Na,K-TMP compounds was studied as well in the presence of TMEDA and PMDTA.³⁴⁹ Crystallographic structures (Table 22, entry 8) were established for (i) $[(\text{TMPLi}) \cdot (\text{TMPNa})] \cdot \text{TMEDA}$, which was found to correspond to a TMEDA-monosolvated cyclic mixed dimer organized around a N–Li–N–Na quadrilateral; (ii) $[(\text{TMPLi})_2 \cdot (\text{TMPK})] \cdot \text{TMEDA}$, depicted as a TMEDA-monosolvated 2:1 mixed trimer forming a central cyclic N–Li–N–Li–N–K core; (iii) $[(\text{TMPLi}) \cdot (\text{TMPNa})] \cdot \text{PMDTA}$, corre-

sponding to a PMDTA-monosolvated open mixed dimer, while the $[(\text{TMPLi}) \cdot (\text{TMPK})] \cdot \text{PMDTA}$ and $[(\text{TMPNa}) \cdot (\text{TMPK})] \cdot \text{PMDTA}$ congeners presented a cyclic N–M–N–K ($\text{M} = \text{Li}$ or Na) central core; and (iv) $[(\text{TMPLi})_2 \cdot (\text{TMPK})] \cdot \text{PMDTA}$, arranged as a PMDTA-monosolvated open 2:1 mixed trimer. In all these monosolvated aggregates, the amino ligands were found to coordinate preferentially the biggest metal. In the absence of additive, a polymeric arrangement was reported for the TMPLi/TMPNa mixture ($[(\text{TMPLi}) \cdot (\text{TMPNa})]_\infty$). Finally, one can mention the crystallized species derived from a β -ethyl ester keto-enolate and isolated from a $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ /cryptand mixture. An unsolvated dimeric complex, all arranged around a single lithium atom and next to free potassium cation, was highlighted.³⁵⁰

4.1.2. Heteroleptic Li,Na- and Li,K-HeteroMAAs.

Results are presented for $[(\text{MeLi})_x \cdot (\text{MeOK})_y]$, $[(\text{t-BuN(H)})_x \cdot (\text{t-BuOK})_y]$, $[(\text{BuLi}) \cdot (\text{CNA})] \cdot nS^*$, $[(\text{KENOLi-2})_4 \cdot (\text{t-BuOK})_4] \cdot 5S + \text{KOH}$ ($S = \text{THF}$), and $[(\text{TMPLi})_2 \cdot (\text{TMPK})] \cdot \text{PMDTA}$.

Table 24. Structures of Homoleptic Li,Mg-HeteroMAAs

Entry	R-Li	R ₂ Mg	Analytical method	Solvent (S)	[$(RLi)_x(R_2Mg)_y \cdot nS$]	Ref
1a			NMR	Et ₂ O THF ^a	 [(MeLi) ₂ (Me ₂ Mg)] _n S ^b [(MeLi) ₃ (Me ₂ Mg)] _n S ^b	361a,b
1b	MeLi	Me ₂ Mg	X-ray	TMEDA	 [(MeLi) ₂ (Me ₂ Mg)] ₂ TMEDA [(MeLi) ₂ (Me ₂ Mg) ₂] ₂ TMEDA	361c
2	PhC≡CLi	(PhC≡C) ₂ Mg	X-ray	TMEDA	 [(PhCCLi)((PhCC) ₂ Mg)] ₂ 2TMEDA	362
3a	PhLi	Ph ₂ Mg	NMR	Et ₂ O	 [(PhLi) ₂ (Ph ₂ Mg)] _n S ^{b,c} + [(PhLi)(Ph ₂ Mg)] _n S ^{b,d} (S = S _{n1} +S _{n2})	363
3b			X-ray	TMEDA	 [(PhLi) ₂ (Ph ₂ Mg) ₂] ₂ TMEDA	364
3c	2,4,6- <i>i</i> -Pr ₃ C ₆ H ₂ Li	(2,4,6- <i>i</i> -Pr ₃ C ₆ H ₂) ₂ Mg	X-ray	THF	 [(2,4,6- <i>i</i> -Pr ₃ C ₆ H ₂ Li)((2,4,6- <i>i</i> -Pr ₃ C ₆ H ₂) ₂ Mg)] THF	235d
4	BnLi	Bn ₂ Mg	X-ray	TMEDA	 {[Bn ₄ MgLi]}TMEDA ⁻ {[Li] ₂ TMEDA} ⁺	362
5a				hexane/toluene	 [HMDSLi](HMDS ₂ Mg)]	365
5b	HMDSLi	HMDS ₂ Mg	X-ray	THF	 {[HMDSLi](HMDS ₂ Mg)} THF	97

Table 24. continued

Entry	R-Li	R ₂ Mg	Analytical method	Solvent (S)	[(RLi) _x ·(R ₂ Mg) _y]·nS	Ref
5c				pyridine	<p>[(HMDSLi)·(HMDS₂Mg)]·nS</p>	97
6	c-Hex ₂ NLi	(c-Hex ₂ N) ₂ Mg	X-ray	THF	<p>[(c-Hex₂NLi)·((c-Hex₂N)₂Mg)]·nS</p>	97
7a	Bn ₂ NLi	(Bn ₂ N) ₂ Mg	X-ray	donor-free	<p>[(Bn₂NLi)₂·((Bn₂N)₂Mg)]</p>	240a
7b				pyridine	<p>[(Bn₂NLi)·((Bn₂N)₂Mg)]·nS</p>	240a

^aThe trimer was the only species observed in THF. ^bn undetermined. ^cIf PhLi/Ph₂Mg > 2. ^dIf PhLi/Ph₂Mg < 2.

Li)_x·(t-BuOK)_y], [(2-MeOC₆H₄N(H)Li)_x·(t-BuONa)_y], [(PhN(H)Li)_x·(t-BuONa)_y], [(BuLi)_x·(Koga–O’Brien CNA)_y] (CNA = chiral sodium amide), and [(pinacolone lithium enolate)_x·(t-BuOK)_y].

Concerning structural knowledge about heteroleptic Li,Na-and Li,K-heteroMAAs (i.e., the presence of two distinct anionic skeletons; Table 23), one would expect that LiC-KOR (BuLi/t-BuOK) and LiDA-KOR (DALi/t-BuOK), the most known and used superbases, have aroused the most curiosity and evidence. Unfortunately, it has not been possible until now to settle on an efficient analytical technique for these entities. In a theoretical study, a simple computational model was set up and consisted of approaching a probable structure of LiC-KOR with the MeLi/MeOK components.³⁵¹ Dimeric, trimeric, and tetrameric mixed arrangements were computed. The cubic tetramer [(MeLi)·(MeOK)₃] proved to be the most favorable composition of an energy point of view (Table 23, entry 1). In such a combination, the more striking feature was the complete splitting of the methide and lithium anions that occupy opposite vertices in the cubic tetramer. For structures approaching LiDA-KOR, one can mention the crystallographic data obtained by mixing t-BuN(H)Li and t-BuOK. The X-ray data afforded an unsolvated unusual centrosymmetric molecular structure [(t-BuN(H)Li)₄·(t-BuOK)₄] (Table 23, entry 2).³⁵² Other analogues, this time involving sodium metal instead of potassium, such as the 2-MeOC₆H₄N(H)Li/t-BuONa (or t-BuOLi/2-MeOC₆H₄N(H)Na) complex³⁵³ and the PhN(H)Li/t-BuONa (or t-BuOLi/PhN(H)Na) aggregate,³⁵⁴ were characterized by X-ray crystallography. With the first mixture, a THF-solvated complex of formula [(2-MeOC₆H₄N(H)Li)₂·(t-BuONa)]₂·4THF was depicted as being constructed from fusing four Li–N–Na–O rings with two Li–N–Li–N quadrilaterals (Table 23, entry 3). In the second application, the crystals obtained in the presence of 4-methylpyridine (4-Me-py) highlighted a tetrasolvated 16-vertex dome-shaped core

of formula [(PhN(H)Li)₄·(t-BuONa)₄]·4(4-Me-py)-NaOH, the sodium hydroxide molecule being encapsulated inside the dome (Table 23, entry 4). The structure derived from the Koga–O’Brien sodium amide (Koga–O’Brien CNA) and butyllithium mixtures proved to be more simple.³⁵⁵ Indeed, a cyclic mixed heterodimer [(BuLi)·(Koga–O’Brien CNA)]·nS, in which sodium was found to be part of a six-membered ring while lithium would occupy the center of a five-membered chelate, was evidenced thanks to an NMR spectroscopic study run in THF (Table 23, entry 5). The solvation was not discussed for this example. Finally, we will consider the crystal structure of a heteroMAA containing ketone enolate and *tert*-butoxide moieties with lithium and potassium metals.³⁵⁶ Both synthetic strategies reacting preformed lithium or potassium enolate derived from pinacolone (KENOLi-1 or KENOK) and potassium or lithium *tert*-butoxide (t-BuOK or t-BuOLi), respectively, led to the same aggregate composed of four enolate units, four alkoxy groups, four lithium, and four potassium cations arranged in a 17-vertex dome-shaped core similar to that depicted (Table 23, entry 4). The entire structure was solvated by five molecules of THF and incorporated a potassium hydroxide molecule, leading in this way to the general formula [(KENOLi-2)₄·(t-BuOK)₄]·5THF-KOH or [(t-BuOLi)₄·(KENOK)₄]·5THF-KOH (Table 23, entry 6). Note that an alternative to study the structural properties of RM/R’OLi mixtures consisted of working with compounds containing both functionalities. Thus, lithium 4,6-dimethyl-2-sodiomethylphenoxide was isolated in the solid state after reacting sodium 2,4,6-trimethylphenoxide with butyllithium in hexane containing TMEDA.³⁵⁷ The single-crystal X-ray analysis revealed a cubic tetrameric aggregate.

4.2. M,Mg-HeteroMAAs (M = Li, Na, K)

Li,Mg-, Na,Mg-, and K,Mg-heteroMAAs, more commonly named lithium, sodium, and potassium magnesates, proved their efficiency as peculiar nucleophilic³⁵⁸ as well as basic³⁵⁹

reactants. Aspects about their structure in both the solid state and solution have been evoked in several reviews.^{1e,g,6b,342,360}

4.2.1. Homoleptic M,Mg-HeteroMAAs. Homoleptic M,Mg-heteroMAAs are made of three (or four) identical anionic moieties and two distinct metals that are a magnesium atom and, for the most encountered cases that are depicted in the present review, an alkaline metal. At this stage of the review, a question arises about the conventions to adopt for the writing of the homoleptic heteroMAAs' formula. Two representations were retained. One clearly distinguishes the nature and proportions of the two parent partners (for instance $[(RM)_x \cdot (R_2Mg)_y]$ if homoleptic M,Mg-heteroMAA). The other possibility gathers the anionic ligands (except for halides) in front of the metallic elements (for instance $R_{x+2y}Mg_yM_x$). The first representation was chosen for a matter of clarity in the present review, focused on structural aspects of the aggregates, whereas the second notation was found more convenient to depict synthetic results, which is the case in the companion review.

4.2.1.1. Homoleptic Li,Mg-HeteroMAAs. Results are presented for $[(MeLi)_x \cdot (Me_2Mg)_y]$, $[(PhC\equiv CLi)_x \cdot ((PhC\equiv C)_2Mg)_y]$, $[(PhLi)_x \cdot (Ph_2Mg)_y]$, $[(2,4,6-i-Pr_3C_6H_2Li)_x \cdot ((2,4,6-i-Pr_3C_6H_2)_2Mg)_y]$, $[(BnLi)_x \cdot (Bn_2Mg)_y]$, $[(HMDSLi)_x \cdot (HMDS_2Mg)_y]$, $[(c-Hex_2NLi)_x \cdot ((c-Hex_2N)_2Mg)_y]$, and $[(Bn_2NLi)_x \cdot ((Bn_2N)_2Mg)_y]$.

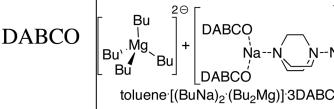
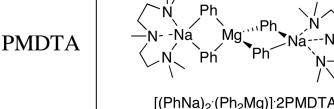
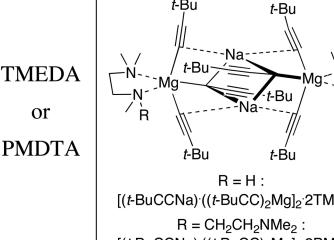
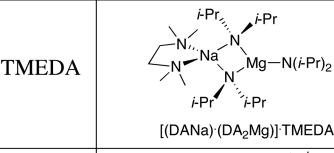
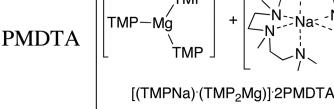
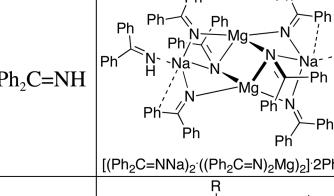
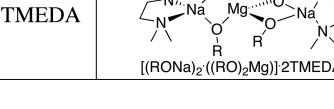
Structures of alkali metal magnesates started to be explored in the mid-1960s when running a 7Li and 1H NMR study on homoleptic species $[(RM)_x \cdot (R_2Mg)_y] \cdot nS$ ($M = Li, Na, K; nS =$ solvation) in ethereal solutions.²⁹² First, concerning homoleptic Li,Mg-MAAs (Table 24), diethyl ether solutions of methyl-lithium with dimethylmagnesium were examined by varying the temperature, and the NMR spectra suggested the formation of mixed trimeric and tetrameric complexes of $[(MeLi)_2 \cdot (Me_2Mg)] \cdot nEt_2O$ and $[(MeLi)_3 \cdot (Me_2Mg)] \cdot nEt_2O$ formula, respectively (Table 24, entry 1a).^{361a} In the proposed structures, the tetramer was postulated as adopting a cubic arrangement with three Li vertices and one Mg vertex, of which only one methyl group was involved in the cubic aggregate, the geometry of the magnesium atom being tetrahedral in this case. The trimer was depicted as two quadrilaterals sharing a vertex that would be occupied by a magnesium atom (tetragonal or tetrahedral: not determined). The same mixture was then studied in THF, still by NMR, and in this more polar solvent, the 3:1 tetrameric complex was not observed anymore.^{361b} In these two studies, the solvation was not discussed (n undetermined). Using TMEDA afforded two crystalline structures, a disolvated mixed trimer and a disolvated mixed tetramer, in which two or three cyclic dimeric cores were connected to each other through vertices occupied by tetrahedral magnesium atoms $\{[(MeLi)_2 \cdot (Me_2Mg)] \cdot 2TMEDA$ and $[(MeLi)_2 \cdot (Me_2Mg)] \cdot 2TMEDA$, Table 24, entry 1b].^{361c} Switching to homoleptic Li,Mg-MAAs made of phenylacetylidyne anionic moieties,³⁶² X-ray data were obtained on crystals grown in the presence of TMEDA and highlighted the formation of a mixed complex in which the magnesium atoms established in a trigonal bipyramidal manner coordinations with three $PhC\equiv C$ and one TMEDA ligand next to a C-Li-C-Li core $\{[(PhC\equiv CLi) \cdot ((PhC\equiv C)_2Mg)]_2 \cdot 2TMEDA$, Table 24, entry 2]. Examining by the NMR technique the phenyllithium/diphenylmagnesium combination in Et_2O was in favor of the single observation of a 2:1 trimer when the $PhLi/Ph_2Mg$ ratio was >2 $\{[(PhLi)_2 \cdot (Ph_2Mg)] \cdot nEt_2O$, Table 24, entry 3a].³⁶³ The exact structural arrangement of the trimer was not precise. If this

ratio was less than two, a 1:1 dimeric complex was identified as well $\{[(PhLi) \cdot (Ph_2Mg)] \cdot nEt_2O$, Table 24, entry 3a]. Note that the solvation was not discussed for the two latter samples (n undetermined). Complementarily, mixing PhLi and Ph_2Mg with TMEDA had the effect of affording a crystalline structure, and the related X-ray analysis pointed out a disolvated 1:1 tetrameric aggregate made of three cyclic dimeric cores connected to each other through vertices occupied by tetrahedral magnesium atoms $\{[(PhLi)_2 \cdot (Ph_2Mg)]_2 \cdot 2TMEDA$, Table 24, entry 3b].³⁶⁴ With the bulkier aromatic unit 2,4,6-i- $Pr_3C_6H_2$, crystals grown in THF solution corresponded to a 1:1 monosolvated cyclic dimer $\{[(2,4,6-i-Pr_3C_6H_2Li) \cdot ((2,4,6-i-Pr_3C_6H_2)_2Mg)] \cdot THF$, Table 24, entry 3c].^{235d} The $BnLi/Bn_2Mg/TMEDA$ mixture³⁶² led to a solid-state structure of formula $[(BnLi)_2 \cdot (Bn_2Mg)] \cdot 2TMEDA$. A separated ion pair arrangement was identified opposing the $\{[Li] \cdot 2TMEDA\}^+$ cation to the $\{[Bn_2MgLi] \cdot TMEDA\}^-$ anion (Table 24, entry 4). Homoleptic M,Mg-MAAs involving amido ligands were also analyzed. Thus, HMDSLi and $HMDS_2Mg$ were mixed in hydrocarbon medium or in the presence of THF and then pyridine, and their aggregation was characterized by NMR spectroscopy and X-ray crystallography.^{97,365} First, crystals obtained in hexane/toluene solution from a 2:1 HMDSLi/ $HMDS_2Mg$ ratio revealed an unsolvated dinuclear arrangement based on a near-planar N-Mg-N-Li quadrilateral $\{[(HMDSLi) \cdot (HMDS_2Mg)]$, Table 24, entry 5a].²⁶⁵ In such a structure, the magnesium atom was found to be trigonal planar, being connected to three HMDS ligands, whereas the lithium atom was tetrahedral because of intramolecular coordinations observed between this cation and two HMDS units. The solid-state samples isolated from THF or pyridine solutions also highlighted mixed cyclic dimers, this time solvated by one molecule of THF or pyridine on lithium, thus presenting both the Mg and Li cations in a trigonal planar geometry $\{[(HMDSLi) \cdot (HMDS_2Mg)] \cdot THF$ and $\{[(HMDSLi) \cdot (HMDS_2Mg)] \cdot pyr$, Table 24, entries 5b,c].⁹⁷ In the same way, the combination of c -Hex₂NLi and $(c$ -Hex₂N)₂Mg in THF resulted in a monosolvated mixed cyclic dimeric crystalline structure $\{[(c-Hex_2NLi) \cdot ((c-Hex_2N)_2Mg)] \cdot THF$, Table 24, entry 6].⁹⁷ For its part, the $Bn_2NLi/(Bn_2N)_2Mg$ equimolar mixture in donor-free medium provided crystals for which structural data were different from those depicted above. A 2:1 mixed trimer showed up, viewed as two heterometallic Mg-N-Li-N rings fused through a tetrahedral Mg center $\{[(Bn_2NLi)_2 \cdot ((Bn_2N)_2Mg)]$, Table 24, entry 7a].^{240a} Addition of pyridine to the above equimolar mixture resulted in the formation of a monosolvated mixed dimer $\{[(Bn_2NLi) \cdot ((Bn_2N)_2Mg)] \cdot pyr$, Table 24, entry 7b].^{240a} Lithium amides ($Me_2NCH_2CH_2(Bn)NLi$ and $((Me_2NCH_2CH_2)(Bn)N)_2Mg$ were reacted in toluene solution and crystals formed, accounting for a 2:1 trimeric aggregate made of two cyclic dimeric cores connected to each other through a tetrahedral Mg vertex and with two intramolecular coordinations of the NMe_2 groups per lithium ($\{[(Me_2NCH_2CH_2)(Bn)NLi]_2 \cdot [(Me_2NCH_2CH_2)(Bn)N]_2Mg\}$).³⁶⁶

4.2.1.2. Homoleptic Na,Mg-HeteroMAAs. Results are presented for $[(BuNa)_x \cdot (Bu_2Mg)_y]$, $[(PhNa)_x \cdot (Ph_2Mg)_y]$, $[(t-BuC\equiv CNa)_x \cdot ((t-BuC\equiv C)_2Mg)_y]$, $[(DANa)_x \cdot (DA_2Mg)_y]$, $[(TMPNa)_x \cdot (TMP_2Mg)_y]$, $[(Ph_2C\equiv NNa)_x \cdot (Ph_2C\equiv N)_2Mg)_y]$, and $[(RONa)_x \cdot ((RO)_2Mg)_y]$.

Among homoleptic Na,Mg-MAAs that have been structurally investigated (Table 25), one can evoke the complex formed

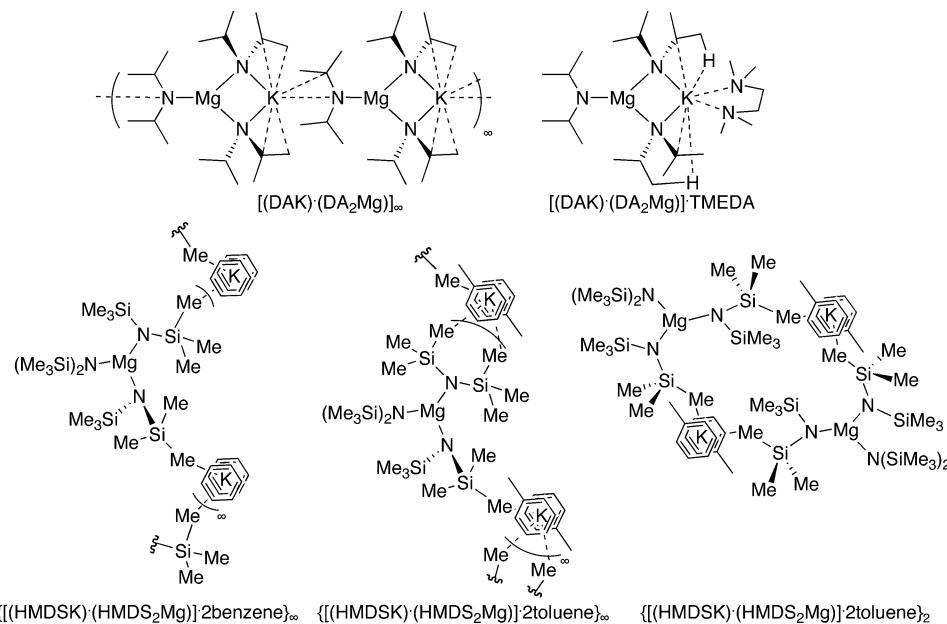
Table 25. Structures of Homoleptic Na,Mg-HeteroMAAs

Entry	R-Na	R ₂ Mg	Analytical method	Solvent (S)	[(RNa) _x ·(R ₂ Mg) _y]·nS	Ref
1	BuNa	Bu ₂ Mg	X-ray	DABCO		367
2	PhNa	Ph ₂ Mg	X-ray	PMDTA		234
3	t-BuCCNa	(t-BuCC) ₂ Mg	X-ray	TMEDA or PMDTA		234
4	i-Pr ₂ NNa (DANa)	(i-Pr ₂ N) ₂ Mg (DA ₂ Mg)	X-ray	TMEDA		368
5	TMPNa	TMP ₂ Mg	X-ray	PMDTA		369
6	Ph ₂ C=NNa	(Ph ₂ C=N) ₂ Mg	X-ray	Ph ₂ C=NH		370
7	RONa ^a	(RO) ₂ Mg ^a	X-ray	TMEDA		220b

^aR = 2,4,6-Me₃C₆H₂C(=CH₂)

when mixing in toluene BuNa and Bu₂Mg in the presence of DABCO.³⁶⁷ The crystal structure obtained incorporated two molecules of BuNa for one molecule of Bu₂Mg, the whole complex including one molecule of toluene and three molecules of DABCO (toluene·[(BuNa)₂·(Bu₂Mg)]·3DABCO, Table 25, entry 1) and was made of separated cationic {toluene·[-Na]₂·3DABCO}²⁺ and anionic [Bu₄Mg]²⁻ moieties. Reaction of phenylsodium with diphenylmagnesium in the presence of PMDTA led to a complex for which a solid-state structure could be examined.²³⁴ An associated ion pair dissolved 2:1 trimeric aggregate was reported, organized as two Ph-Na-Ph-Mg quadrilaterals connected to each other through a tetrahedral Mg vertex, each Na cation being surrounded by one molecule of PMDTA [(PhNa)₂·(Ph₂Mg)]·2PMDTA, Table 25, entry 2). Treating phenylsodium, diphenylmagnesium, and *tert*-butylethyne in the presence of TMEDA or PMDTA yielded the [(t-BuC≡CNa)·((t-BuC≡C)₂Mg)]₂·2TMEDA and [(t-BuC≡CNa)·((t-BuC≡C)₂Mg)]₂·2PMDTA.

[(DANa)-(DA₂Mg)]·TMEDA aggregates.²³⁴ In these arrangements, the two magnesium atoms were trigonal bipyramidal, being linked to three acetylide units and two nitrogens of a molecule of TMEDA or PMDTA, both facing a Na-C-Na-C central dimeric core (Table 25, entry 3). Among structures depicted for homoleptic sodium tris-amide magnesiates, one can retain the results obtained for the tris-diisopropylamide congener crystallized in the presence of TMEDA.³⁶⁸ It evidenced an associated ion pair arrangement, organized around a Na-N-Mg-N core in which the magnesium atom adopted a planar trigonal geometry, being linked to the three amido moieties. A tetrahedral geometry was observed for the sodium cation, coordinated to the two amido groups part of the quadrilateral and the two nitrogens of one TMEDA unit [(DANa)-(DA₂Mg)]·TMEDA, Table 25, entry 4). Attempts to isolate the analogue sodium tris-TMP magnesate TMEDA-solvate were unsuccessful in contrast to the PMDTA solvate.³⁶⁹ The latter was found to correspond to a separated ion-pair system for

Scheme 56. Structures of Homoleptic K,Mg-HeteroMAAs^{368,371}

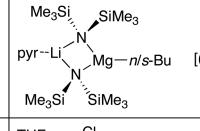
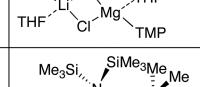
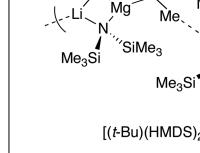
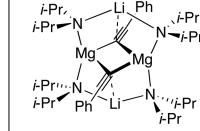
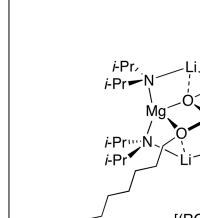
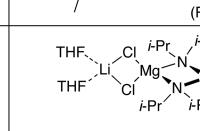
which the magnesium was surrounded by the three TMP ligands in a planar trigonal geometry, the hexacoordinated sodium atom being linked to two molecules of triamine ($\{[(\text{TMPNa}) \cdot (\text{TMP}_2\text{Mg})] \cdot 2\text{PMDTA}$ or $\{[\text{TMP}_3\text{Mg}]^-, [\text{Na} \cdot 2\text{PMDTA}]^+\}$; Table 25, entry 5). An example involving ketimido ligands derived from diphenylmethane imine was also depicted. A dissolved disodium dimagnesium complex was highlighted in the solid state. It organized around an N–Mg–N–Mg quadrilateral adjacent, through the Mg–N–Mg sides, to two six-membered Mg–N–Mg–N–Na–N rings ($[(\text{Ph}_2\text{C}=\text{NNa})_2 \cdot (\text{Ph}_2\text{C}=\text{N})_2\text{Mg}] \cdot 2\text{Ph}_2\text{C}=\text{NH}$, Table 25, entry 6).³⁷⁰ Note also the reaction between 2,4,6-trimethylacetophenone and $[(\text{BuNa}) \cdot (\text{Bu}_2\text{Mg})]$ in the presence of TMEDA that afforded, among other products, the dissolved trimeric complex $[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{C}(=\text{CH}_2)\text{ONa})_2 \cdot ((2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{C}(=\text{CH}_2)\text{O})_2\text{Mg}] \cdot 2\text{TMEDA}$. This alkoxide complex organized according to two O–Na–O–Mg dimeric cores connected through a tetrahedral Mg vertex, each Na ion being surrounded by one molecule of TMEDA (Table 25, entry 7).^{220b} This motif is also called the Weiss motif.

4.2.1.3. Homoleptic K,Mg-HeteroMAAs. Results are presented for $[(\text{DAK})_x \cdot (\text{DA}_2\text{Mg})_y]$ and $[(\text{HMDSK})_x \cdot (\text{HMDS}_2\text{Mg})_y]$.

Mainly homoleptic tris-amido K,Mg-MAAs have been the object of structural investigations, in the solid state. Thus, working with the diisopropylamido ligand, two potassium–magnesium complexes were characterized: a polymeric chain and a TMEDA solvate.³⁶⁸ In the first aggregate, the unit was made of a N–Mg–N–K dimeric core connected to two others thanks to N–K interactions possible between the potassium atom and the DA appendage of the magnesium metal not involved in the N–Mg–N–K quadrilateral ($[(\text{DAK}) \cdot (\text{DA}_2\text{Mg})]_\infty$, Scheme 56, top left). The arrangement was reduced to the dimeric core when solvated by TMEDA, the latter establishing a double coordination with the potassium metal ($[(\text{DAK}) \cdot (\text{DA}_2\text{Mg})] \cdot \text{TMEDA}$, Scheme 56, top right). Note that in these two structures, agostic interactions were also postulated between the alkaline and diisopropyl fragments. Switching to K,Mg-MAAs incorporating three hexamethyldisilazane ligands,³⁷¹ crystals isolated from benzene or toluene solutions corresponded to polymeric structures in which the magnesium was linked in a trigonal planar manner to the three HMDS groups. Two of the latter were found to coordinate, through their methyl groups (one per HMDS appendage with benzene as the solvent and two per HMDS if toluene used), with a potassium cation. The alkaline metal was also observed in the environment of two molecules of the aromatic solvent t h a n k s t o π -cation interactions ($\{[(\text{HMDSK}) \cdot (\text{HMDS}_2\text{Mg})] \cdot 2\text{benzene}\}_\infty$ and $\{[(\text{HMDSK}) \cdot (\text{HMDS}_2\text{Mg})] \cdot 2\text{toluene}\}_\infty$, Scheme 56, bottom left and middle). In the case of toluene, an additional supramolecular structure was isolated. It consisted in a tetrakisolvated 16-membered ring connecting two $[(\text{HMDSK}) \cdot (\text{HMDS}_2\text{Mg})]$ units. The global organization of the ligands and metals was revealed to be similar with the polymeric isomer depicted earlier, as well as for the solvation ($\{[(\text{HMDSK}) \cdot (\text{HMDS}_2\text{Mg})] \cdot 2\text{toluene}\}_2$, Scheme 56, bottom right).

4.2.2. Heteroleptic M,Mg-HeteroMAAs. Heteroleptic M,Mg-heteroMAAs, which involve the three ligands R¹, R², and R³, can be separated into two categories depending on whether R³ = R² ≠ R¹ or R³ ≠ R² ≠ R¹. The second type, for which the name “bis-heteroleptic M,Mg-heteroMAAs” is here attributed, will not be represented in the actual review. In term of synthesis, heteroleptic M,Mg-heteroMAAs can result from the reaction between a pure alkaline reagent and a homo- or a heteroleptic magnesium entity. They can also be reached from the deprotonation of a protonated entity by a homoleptic M,Mg-heteroMAA. In all cases, the resulting MAA was found to structurally organize in a way that now prevents the $[(\text{R}^1\text{M})_x \cdot (\text{R}^2\text{R}^3\text{Mg})_y]$ general notation (although it would always be possible to redistribute arbitrarily the anionic and cationic units to fit with a $[(\text{R}^1\text{M})_x \cdot (\text{R}^2\text{R}^3\text{Mg})_y]$ formula, but the latter would remain too far from the real structural organizations observed). The representation $[(\text{R}^1)(\text{R}^2)_2\text{MgM}]_z$ was chosen to account for the species discussed in the present section, with z = 1 corresponding to monomers and z = 2 to dimers.

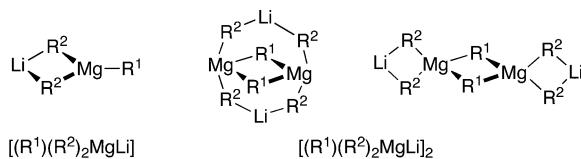
Table 26. Structures of Heteroleptic Li,Mg-HeteroMAAs

Entry	$(R^1)(R^2)_2MgLi$	Analytical method	Solvent (S)	$[(R^1)(R^2)_2MgLi]_z \cdot nS$	Ref
1	$(Bu)(HMDS)_2MgLi$	X-ray	pyridine		97
2	$(TMP)(Cl)_2MgLi$	X-ray	THF		251
3	$(t\text{-}Bu)(HMDS)_2MgLi$	X-ray	none		372
4	$(PhC\equiv C)(DA)_2MgLi$	X-ray	none		373
5	$(RO)(DA)_2MgLi$ (R = octyl)	X-ray	none		374
6	$(DA)(Cl)_2MgLi$	X-ray	THF		375

4.2.2.1. Heteroleptic Li,Mg-HeteroMAAs. Results are presented for $(n/s\text{-}Bu)(HMDS)_2MgLi$, $(TMP)(Cl)_2MgLi$, $(t\text{-}Bu)(HMDS)_2MgLi$, $(PhC\equiv C)(DA)_2MgLi$, $(RO)(DA)_2MgLi$, and $(DA)(Cl)_2MgLi$.

X-ray analyses information about the structure of heteroleptic Li,Mg-heteroMAAs $[(R^1)(R^2)_2MgLi]_z$ has been reported only recently, since 2001 (Table 26). Mainly three structural frames were identified whether $z = 1$ or $z = 2$ (Scheme 57). The

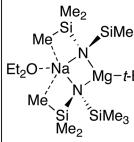
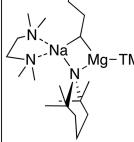
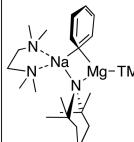
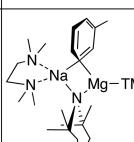
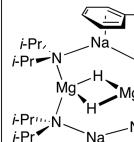
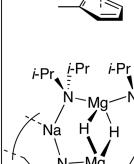
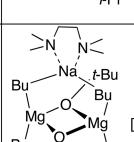
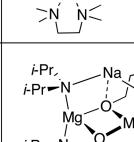
Scheme 57. Structural Frames Encountered for $[(R^1)(R^2)_2MgLi]$ and $[(R^1)(R^2)_2MgLi]_2$



$[(R^1)(R^2)_2MgLi]$ monomers formed an $\text{Li}-\text{R}^2-\text{Mg}-\text{R}^2$ quadrilateral arrangement, keeping the ligand R^1 fixed on the magnesium atom on the outside position of the square core. The $[(R^1)(R^2)_2MgLi]_2$ dimers were found to organize on the basis of a central $\text{Mg}-\text{R}^1-\text{Mg}-\text{R}^1$ quadrilateral either surrounded on each side by $\text{Mg}-\text{R}^2-\text{Li}-\text{R}^2-\text{Mg}$ bridges or linked to two lateral $\text{Mg}-\text{R}^2-\text{Li}-\text{R}^2$ quadrilaterals through tetrahedral magnesium cationic vertices.

Thus, treating, in the presence of pyridine, 2 equiv of HMDS with 1 equiv of the homoleptic $[(BuLi)\cdot(Bu_2Mg)]$ heteroMAA afforded a new species isolated in the solid state and amounting to the $[(Bu)(HMDS)_2MgLi]\cdot\text{pyr}$ monosolvated aggregate that organized around a $\text{Li}-\text{N}-\text{Mg}-\text{N}$ quadrilateral (Table 26, entry 1).⁹⁷ The $s\text{-}BuLi$ analogue was isolated and characterized following the same study and led to comparable results. The deprotonation of TMPh by the heteroleptic magnesium reactant $i\text{-PrMgCl}$ in the presence of LiCl in THF afforded a crystalline species corresponding to the trisolvated $[(TMP)(Cl)_2MgLi]\cdot 3\text{THF}$ complex that included a $\text{Li}-\text{Cl}-\text{Mg}-\text{Cl}$ core (Table 26, entry 2).²⁵¹ Combining equimolar quantities of $t\text{-}BuLi$ and HMDS_2Mg in hydrocarbon solvents led to a solid-state polymeric arrangement made of $[(t\text{-}Bu)(HMDS)_2MgLi]$ units, the polymeric sequence being ensured thanks to Me–Li agostic interactions ($[(t\text{-}Bu)(HMDS)_2MgLi]_\infty$, Table 26, entry 3).³⁷² Crystals of the heteroleptic Li,Mg-heteroMAA made of phenylacetylide and diisopropylamide moieties were retrieved from a hexane solution, after reacting $[(DALi)\cdot(DA_2Mg)]$ with $\text{PhC}\equiv\text{CH}$ in an equimolar amount.³⁷³ The unsolvated $[(PhC\equiv C)(DA)_2MgLi]_2$ dimeric complex was depicted with a central $\text{Mg}-\text{C}-\text{Mg}-\text{C}$ quadrilateral surrounded on each side by $\text{Mg}-\text{N}-\text{Li}-\text{N}-\text{Mg}$ bridges fastened by C–Li interactions (Table 26, entry 4). The same homoleptic amido Li,Mg-heteroMAA was put in the presence of a stoichiometric amount of ROH alcohol (octanol, R = $\text{CH}_3(\text{CH}_2)_7$) in hexane, and a

Table 27. Structures of Heteroleptic Na,Mg-HeteroMAAs

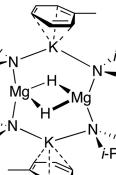
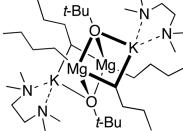
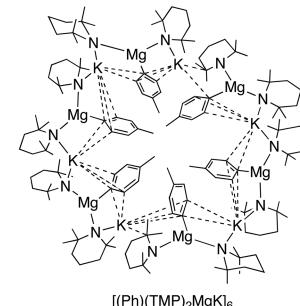
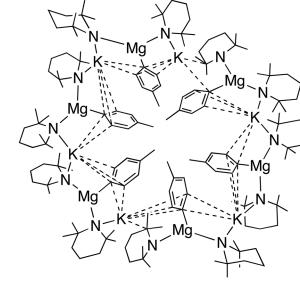
Entry	$(R^1)(R^2)_2MgNa$	Analytical method	Solvent (S)	$[(R^1)(R^2)_2MgNa]_2 \cdot nS$	Ref
1	$(t\text{-Bu})(\text{HMDS})_2MgNa$	X-ray	Et_2O		372
2	$(\text{Bu})(\text{TMP})_2MgNa$	X-ray	TMEDA		376
3	$(\text{Ph})(\text{TMP})_2MgNa$	X-ray	TMEDA		376
4	$(\text{Tol})(\text{TMP})_2MgNa$	X-ray	TMEDA		377
5a	$(\text{H})(\text{DA})_2MgNa$	X-ray	toluene		378a
5b					378c
6	$(t\text{-BuO})(\text{Bu})_2MgNa$	X-ray	TMEDA		379
7	$(\text{RO})(\text{DA})_2MgNa$ (R = butyl or octyl)	X-ray	none		374

comparable arrangement was depicted from the crystals of the resulting product $[(\text{RO})(\text{DA})_2\text{MgLi}]_2$, Table 26, entry 5).³⁷⁴ Mixing equimolar amounts of DALi and MgCl_2 in THF led to crystals, the structure of which corresponded to the tetrasolvated $[(\text{DA})(\text{Cl})_2\text{MgLi}]_2 \cdot 4\text{THF}$ aggregate showing three twisted quadrilaterals, among which there is a central $\text{Mg}-\text{DA}-\text{Mg}-\text{DA}$ core (Table 26, entry 6).³⁷⁵ From these few examples, it would be premature to establish an obvious link between the nature of the solvant used and the size (monomer or dimer) of the aggregate.

4.2.2.2. Heteroleptic Na,Mg-HeteroMAAs. Results are presented for $(t\text{-Bu})(\text{HMDS})_2MgNa$, $(\text{Bu})(\text{TMP})_2MgNa$, $(\text{Ph})(\text{TMP})_2MgNa$, $(\text{Tol})(\text{TMP})_2MgNa$, $(\text{H})(\text{DA})_2MgNa$, $(t\text{-BuO})(\text{Bu})_2MgNa$, and $(\text{RO})(\text{DA})_2MgNa$.

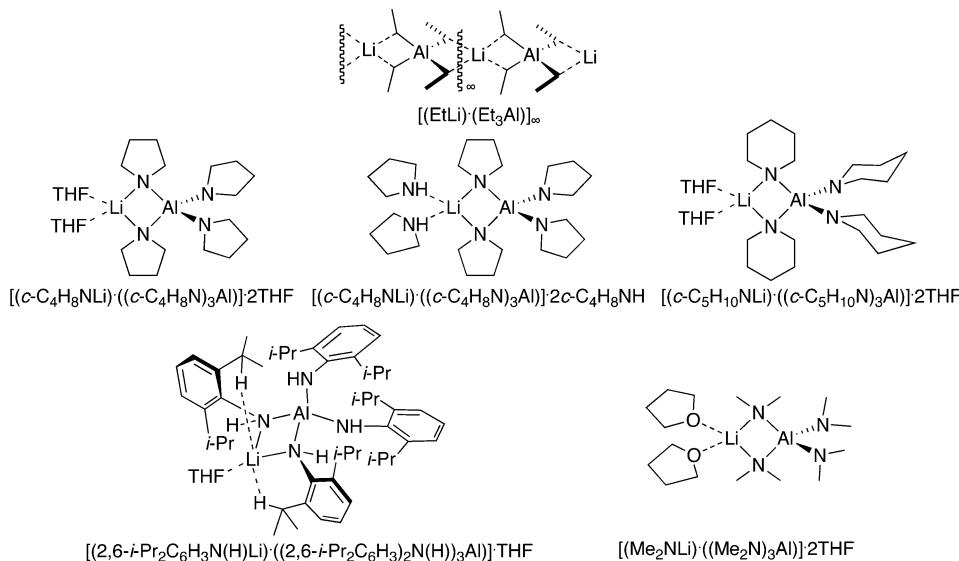
Monomers $[(R^1)(R^2)_2MgNa]$ and dimers $[(R^1)(R^2)_2MgNa]_2$ were also found for heteroleptic Na,Mg-heteroMAAs (Table 27). Thus, mixing 2 mol equiv of HMDSNa with 1 mol equiv of $t\text{-BuMgCl}$ in hydrocarbon/ether solution led to the crystalline disolvated $[(t\text{-Bu})(\text{HMDS})_2MgNa] \cdot \text{Et}_2\text{O}$ aggregate, which organized around a $\text{Na}-\text{N}-\text{Mg}-\text{N}$ quadrilateral.³⁷² The sodium cation was

Table 28. Structures of Heteroleptic K,Mg-HeteroMAAs

Entry	$(R^1)(R^2)_2MgK$	Analytical method	Solvent (S)	$[(R^1)(R^2)_2MgK]_n \cdot nS$	Ref
1	$(H)(DA)_2MgK$	X-ray	toluene		378b
2	$(t\text{-}BuO)(Bu)_2MgK$	X-ray	TMEDA		379
3	$(Ph)(TMP)_2MgK$	X-ray	none		380
4	$(Tol)(TMP)_2MgK$	X-ray	none		380

strongly coordinated with one molecule of diethyl ether, while weakly establishing symmetric connections with two methyl groups of the silyl appendages (Table 27, entry 1). The introduction of TMP units in the composition of the magnesate led to a slight reorganization of the resulting $[(R)(TMP)_2MgNa]$ monomer. Probably for steric reason, only one amido group was involved in the quadrilateral that became of Na–C–Mg–N general formula. Thus, mixing the homoleptic Na,Mg-heteroMAA $[(BuNa)\cdot(Bu_2Mg)]$ with TMHP in the presence of TMEDA led to crystals of $[(Bu)(TMP)_2MgNa]\cdot TMEDA$,³⁷⁶ for which a Na–C–Mg–N quadrilateral structure was depicted, the sodium atom being tetrahedral since already dicoordinated and additionally chelated by one molecule of TMEDA (Table 27, entry 2). Replacing the butyl ligand by a phenyl or a tolyl led to the $[(Ph)(TMP)_2MgNa]\cdot TMEDA$ ³⁷⁶ and $[(Tol)(TMP)_2MgNa]\cdot TMEDA$ ³⁷⁷ aggregates designed identically (Table 27, entries 3 and 4, respectively). Refluxing the homoleptic $[(BuNa)\cdot(Bu_2Mg)]$ heteroMAA with 3 equiv of diisopropylamine in toluene led first to the homoleptic $[(DANa)\cdot(DA_2Mg)]$ heteroMAA, which rapidly rearranged thermally thanks to a hydride transfer coming from a $CH(Me)_2$ appendage. It resulted in the dissolved $[(H)(DA)_2MgNa]_2$

dimer made of a central Mg–H–Mg–H quadrilateral, surrounded on each side by Mg–N–Na–N–Mg bridges. Each sodium cation was found to be coordinated to one molecule of toluene thanks to π –cation interactions ($[(H)(DA)_2MgNa]_2 \cdot 2$ toluene, Table 27, entry 5a).^{378a} The same synthesis was repeated in hexane, and a polymeric arrangement then showed up, connecting the dimeric cores depicted in toluene through Na···i-Pr agostic interactions ($[(H)(DA)_2MgNa]_\infty$, Table 27, entry 5b).^{378c} A comparable structural frame was observed in the solid state for the $[(t\text{-}BuO)(Bu)_2MgNa]_2 \cdot 2$ TMEDA³⁷⁹ species (with a central Mg–O–Mg–O quadrilateral this time), a complex obtained by reacting molar equivalents of $t\text{-}BuONa$ and Bu_2Mg in the presence of TMEDA (Table 27, entry 6). The two molecules of diamine were found to chelate each sodium atom. Mixing in hexane an excess of $[(BuNa)\cdot(Bu_2Mg)]$ with isopropylamine and then introducing slowly butanol or octanol led to unsolvated $[(RO)(DA)_2MgNa]_2$ aggregates, isostructural to the two previous complexes.³⁷⁴ Note, however, the additional coordinations between the “external” sodium atoms and the “central” oxygens (Table 27, entry 7).

Scheme 58. Crystalline Structures of Homoleptic Li,Al-HeteroMAAs^{266c,384–386}

4.2.2.3. Heteroleptic K,Mg-HeteroMAAs. Results are presented for $(\text{H})(\text{DA})_2\text{MgK}$, $(t\text{-BuO})(\text{Bu})_2\text{MgK}$, $(\text{Ph})(\text{TMP})_2\text{MgK}$, and $(\text{Tol})(\text{TMP})_2\text{MgK}$.

Higher-size aggregates, from dimers to hexamers, were depicted for heteroleptic K,Mg-heteroMAAs (Table 28). A first dimeric example corresponded to crystals of an amido-hydride species obtained by boiling benzylpotassium, dibutylmagnesium, and lithium diisopropylamine in toluene. The arrangement was made of a central Mg–H–Mg–H quadrilateral surrounded by two Mg–N–K–N–Mg external bridges. The potassium cations were each solvated by a molecule of toluene $[(\text{H})(\text{DA})_2\text{MgK}]_2\cdot 2\text{toluene}$, Table 28, entry 1).^{378b} The second dimer that has been the subject of structural descriptions, still in the solid state, was obtained after mixing molar equivalents of $t\text{-BuOK}$ and Bu_2Mg in the presence of TMEDA. Unlike its sodium counterpart mentioned earlier, a disolvated structural frame arranging three quadrilaterals connected through Mg–O sides was highlighted with the sequences Mg–O–Mg–O for the central core and Mg–C–K–O for the two external ones $[(t\text{-BuO})(\text{Bu})_2\text{MgK}]_2\cdot 2\text{TMEDA}$, Table 28, entry 2).³⁷⁹ Hexapotassium–hexamagnesium 24-membered macrocycles were reported for $[(\text{Ph})(\text{TMP})_2\text{MgK}]_6$ ³⁸⁰ and $[(\text{Tol})(\text{TMP})_2\text{MgK}]_6$ ³⁸⁰ obtained as crystalline samples after reacting the homoleptic $[(\text{TMPK})\cdot(\text{TMP}_2\text{Mg})]$ synthesized in situ with benzene or toluene, respectively (Table 28, entry 3).

The three following series of studies run on M,Mg-heteroMAAs structural elucidations are also of high interest; however, not detailed in the present review: (i) investigations presenting composition of “simple” M,Mg-heteroMAAs ($M = \text{Li}, \text{Na}, \text{K}$) without exact description of the concerned structures,^{295,381} (ii) syntheses and characterizations of “crown ethers” MAA’s isolated after exposure to oxygen,³⁸² and (iii) a description of heteroleptic M,Mg-heteroMAA intermediates resulting from the single or double deprotonation of aromatic species by MAA reactants.^{369,383}

4.3. M,Al-HeteroMAAs ($M = \text{Li}, \text{Na}, \text{K}$)

Structural aspects of Li,Al-, Na,Al-, and K,Al-heteroMAAs $R^1R^2R^3R^4\text{AlM}$, more commonly named lithium, sodium, and potassium aluminates, respectively, have been mentioned in few reviews.^{1c,360b} Knowledge about the arrangement of

“simple” homoleptic M,Al-heteroMAAs and those for heteroleptic M,Al-heteroMAAs is evoked below.

4.3.1. Homoleptic M,Al-HeteroMAAs. By comparison with the magnesium congeners mentioned above, the homoleptic M,Al-heteroMAAs are represented here with the $[(RM)_x\cdot(R_3\text{Al})_y]\cdot nS$ general formula, while being aware that the $R_{x+3y}\text{Al}_yM_x$ notation can also be used.

4.3.1.1. Homoleptic Li,Al-HeteroMAAs. Results are presented for $[(\text{EtLi})_x\cdot(\text{Et}_3\text{Al})_y]$, $[(c\text{-C}_4\text{H}_8\text{NLi})_x\cdot((c\text{-C}_4\text{H}_8\text{N})_3\text{Al})_y]$, $[(c\text{-C}_5\text{H}_{10}\text{NLi})_x\cdot((c\text{-C}_5\text{H}_{10}\text{N})_3\text{Al})_y]$, $[(2,6-i\text{-Pr}_2\text{C}_6\text{H}_3\text{N}(\text{H})\text{Li})_x\cdot((2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)_2\text{N}(\text{H}))_3\text{Al}]_y$, and $[(\text{Me}_2\text{NLi})_x\cdot((\text{Me}_2\text{N})_3\text{Al})_y]$.

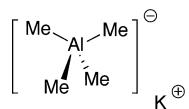
Crystals of lithium tetraethylaluminates were obtained after mixing in benzene equimolar amounts of triethylaluminum and ethyllithium. The structure was determined by X-ray diffraction methods and was found to consist of an unsolvated polymeric linear chain alternating lithium and aluminum cations, both presenting a tetrahedral geometry $[(\text{EtLi})\cdot(\text{Et}_3\text{Al})]_\infty$, Scheme 58, top).³⁸⁴ Apart from this example, mostly amido homoleptic Li,Al-heteroMAAs were characterized. Thus, pyrrolidino and piperidino species were synthesized in THF by reacting pyrrolidine and piperidine, respectively, with lithium aluminum hydride in an about 4:1 ratio. The pyrrolidino sample was first examined by NMR and two differently solvated 1:1 dimeric aggregates, one by two molecules of THF and the other by two molecules of protonated pyrrolidine, were depicted $\{[(c\text{-C}_4\text{H}_8\text{NLi})\cdot((c\text{-C}_4\text{H}_8\text{N})_3\text{Al})]\cdot 2\text{THF}$ and $[(c\text{-C}_4\text{H}_8\text{NLi})\cdot((c\text{-C}_4\text{H}_8\text{N})_3\text{Al})]\cdot 2\cdot c\text{-C}_4\text{H}_8\text{NH}$, Scheme 58, left and middle).^{266c} The recovery of the two crystalline solids, isolated from the NMR solution or slightly modifying the synthetic procedure, supported the formation of two complexes made of a nonplanar Li–N–Al–N quadrilateral. The structure of the piperidino derivative was similar to that of the pyrrolidino sample in THF, being based on a Li–N–Al–N ring with bridging piperidine groups and disolvated on the lithium cation by two molecules of solvent $\{[(c\text{-C}_5\text{H}_{10}\text{NLi})\cdot((c\text{-C}_5\text{H}_{10}\text{N})_3\text{Al})]\cdot 2\text{THF}$, Scheme 58, right).^{266c} Li/Al complexes engaging 2,6-*i*-Pr₂C₆H₃N(H) amido moieties were prepared in THF by reaction of AlCl₃ with 2,6-*i*-Pr₂C₆H₃N(H)Li in a 1:4 ratio, and the X-ray analyses highlighted a monosolvated dimeric core in which lithium was intramolecularly coordinated to hydrogen atoms of isopropyl

appendages $\{[(2,6-i\text{-Pr}_2\text{C}_6\text{H}_3\text{N}(\text{H})\text{Li})\cdot((2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)_2\text{N}(\text{H}))_3\text{Al}]\}\cdot\text{THF}$, Scheme 58 bottom left].³⁸⁵ Finally, one can evoke the amido homoleptic Li,Al-heteroMAA made of four dimethylamido ligands that could be isolated in the solid state as a THF solvate.³⁸⁶ The structure was found to correspond to an Li–N–Al–N quadrilateral in which both Li and Al cations presented a tetrahedral geometry, aluminum being linked to the four amido moieties, while lithium would coordinate two amido groups and two molecules of THF $\{[(\text{Me}_2\text{NLi})\cdot((\text{Me}_2\text{N})_3\text{Al})]\cdot2\text{THF}$, Scheme 58 bottom right}.

4.3.1.2. Homoleptic K,Al-HeteroMAAs. Results are presented for $[(\text{MeK})_x\cdot(\text{Me}_3\text{Al})]$.

The crystal structure of the potassium tetramethylaluminum MAA was determined from X-ray powder diagrams. This species was found to organize as a separated ionic pair in which the Al atom was coordinated by the four methyl groups in a distorted tetrahedral array, and no covalent interaction was present between this anionic part and the alkali cation $[(\text{MeK})\cdot(\text{Me}_3\text{Al})]$, Scheme 59).³⁸⁷ In the presence of PMDTA, the potassium cation was found to establish six coordinations with the nitrogens of two molecules of the triamine.

Scheme 59. Crystalline Structure of $[(\text{MeK})\cdot(\text{Me}_3\text{Al})]$ ³⁸⁷



4.3.2. Heteroleptic M,Al-HeteroMAAs. As for the heteroleptic M,Mg-heteroMAAs, the heteroleptic M,Al-heteroMAAs are given the $[(\text{R}^1)(\text{R}^2)(\text{R}^3)(\text{R}^4)\text{AlM}]_z$ general formula and are considered as monomeric species if $z = 1$ and dimeric if $z = 2$.

4.3.2.1. Heteroleptic Li,Al-HeteroMAAs. Results are presented for $(\text{H})(t\text{-Bu})_3\text{AlLi}$, $(\text{HMDS})(\text{H})_3\text{AlLi}$, $((\text{Me}_3\text{Si})_3\text{C})(\text{H})_3\text{AlLi}$, $((\text{Me}_2\text{PhSi})_3\text{C})(\text{H})_3\text{AlLi}$, $((\text{Me}_3\text{Si})_3\text{C})(\text{EtO})_3\text{AlLi}$, $((\text{Me}_3\text{Si})_3\text{C})(t\text{-BuO})_3\text{AlLi}$, $((\text{Me}_3\text{Si})_3\text{C})(\text{MeS})_3\text{AlLi}$, $(\text{TMP})(i\text{-Bu})_3\text{AlLi}$, $(\text{TMP})(\text{Ph})_3\text{AlLi}$, and $(\text{HMDS})_2(\text{H})_2\text{AlLi}$.

Mostly crystallographic data were obtained for heteroleptic Li,Al-heteroMAAs (Table 29). The reaction of *tert*-butyllithium with aluminum trihalides in pentane led to a mixture of four compounds among which the unsolvated dimeric complex $[(\text{H})(t\text{-Bu})_3\text{AlLi}]_2$ organized as an aggregate of three adjacent quadrilaterals: a central Li–H–Li–H core surrounded by two Li–H–Al–C_{t-Bu} four-membered rings (Table 29, entry 1).^{263a} A dimeric aggregate was also depicted for the $(\text{HMDS})(\text{H})_3\text{AlLi}$ heteroMAA isolated in the solid state after reacting an equivalent of hexamethyldisilylamine with LiAlH₄ in diethyl ether. This time, a Li–H–Al–H–Li–H–Al–H eight-membered ring, solvated by four molecules of Et₂O (two per lithium), was characterized $\{[(\text{HMDS})(\text{H})_3\text{AlLi}]_2\cdot4\text{Et}_2\text{O}$, Table 29, entry 2).³⁸⁸ The $((\text{Me}_3\text{Si})_3\text{C})(\text{H})_3\text{AlLi}$ and $((\text{Me}_2\text{PhSi})_3\text{C})(\text{H})_3\text{AlLi}$ species, synthesized in THF by mixing $(\text{Me}_3\text{Si})_3\text{CLI}$ or $(\text{Me}_2\text{PhSi})_3\text{CLI}$ with LiAlH₄, were found, in the solid state, to be isostructural to the $(\text{HMDS})(\text{H})_3\text{AlLi}$ compound $\{[(\text{Me}_3\text{Si})_3\text{C})(\text{H})_3\text{AlLi}]_2\cdot4\text{THF}$ and $\{[(\text{Me}_2\text{PhSi})_3\text{C})(\text{H})_3\text{AlLi}]_2\cdot4\text{THF}$, Table 29, entry 3).³⁸⁹ Keeping the $(\text{Me}_3\text{Si})_3\text{C}$ ligand, but switching from hydrides to alkoxy groups, had the effect of reducing the size of the MAA, since monomeric arrangements made of a Li–O–Al–O quadrilateral were highlighted in those cases. Thus, the THF-

solvated $\{[(\text{Me}_3\text{Si})_3\text{C})(\text{EtO})_3\text{AlLi}\}\cdot2\text{THF}$ ^{390b} (Table 29, entry 4a) and $\{[(\text{Me}_3\text{Si})_3\text{C})(t\text{-BuO})_3\text{AlLi}\}\cdot\text{THF}$ ^{390a} (Table 29, entry 4b) solid-state monomers were fully described. Crystals of the thiolato analogous derivative $((\text{Me}_3\text{Si})_3\text{C})(\text{MeS})_3\text{AlLi}$ were also prepared from a THF solution, and X-ray analyses showed a disolvated monomer containing an Li–S–Al–S four-membered ring $\{[(\text{Me}_3\text{Si})_3\text{C})(\text{MeS})_3\text{AlLi}\}\cdot2\text{THF}$, Table 29, entry 5).^{390c} The $(\text{TMP})(i\text{-Bu})_3\text{AlLi}$ MAA reactant could be crystallized by means of adding *N,N*-diisopropylbenzamide as a solvating agent. A monomer made of an Li–N–Al–C quadrilateral solvated by one molecule of benzamide was thus identified $\{[(\text{TMP})(i\text{-Bu})_3\text{AlLi}]\cdot\text{PhC(O)Ni-Pr}_2$, Table 29, entry 6).^{16,391} Reacting TMPLi with Ph₃Al in THF in the presence of TMEDA led to the $[\text{TMEDA-Li-2THF}]^-,[\text{(TMP)-(Ph)}_3\text{Al}]^-$ separated ion pair arrangement (Table 29, entry 7).³⁹² The heteroleptic Li,Al-heteroMAA $(\text{HMDS})_2(\text{H})_2\text{AlLi}$ differs from the previous one by the proportions of each of the ligands ($\text{R}_2\text{R}'_2\text{AlLi}$ instead of $\text{RR}'_3\text{AlLi}$). This reactant was found to crystallize from Et₂O solution as a monomeric species organized around a disolvated Li–H–Al–H quadrilateral $\{[(\text{HMDS})_2(\text{H})_2\text{AlLi}]\cdot2\text{Et}_2\text{O}$, Table 29, entry 8).³⁸⁸

Among other examples,^{390b,393} crystal structures of metalated intermediates resulting from aromatic deprotonations³⁹⁴ or reactions with TMEDA/PMDTA³⁹⁵ have been reported in the literature but are not detailed here.

4.3.2.2. Heteroleptic Na,Al-HeteroMAAs. Results are presented for $(\text{TMP})(i\text{-Bu})_3\text{AlNa}$.

The only example of heteroleptic Na,Al-heteroMAA for which a crystallographic structural description could be obtained was synthesized by mixing TMPNa, *i*-Bu₃Al, and TMEDA. The molecular structure featured a TMEDA-solvated monomeric Na–N–Al–C ring ($[(\text{TMP})(i\text{-Bu})_3\text{AlNa}]\cdot\text{TMEDA}$, Scheme 60).³⁹⁶

4.3.2.3. Heteroleptic K,Al-HeteroMAAs. Results are presented for $(\text{H})(\text{Me})_3\text{AlK}$ and $(t\text{-BuO})(\text{Me})_3\text{AlK}$.

The heteroleptic K,Al-HeteroMAA $\text{H}(\text{Me})_3\text{AlK}$ was formed by decomposition of $(\text{H}_3\text{Si})(\text{Me})_3\text{AlK}$ in Et₂O. This compound crystallized as a separated ion pair comprising an anionic moiety made of an aluminum atom tetracoordinated by the hydrogen and the three methyl groups next to an isolated potassium cation $[\text{K}^+][(\text{H})(\text{Me})_3\text{Al}]^-$, Scheme 61).³⁹⁷ A polymeric arrangement made of dimeric units interconnected by K···MeAl interactions was highlighted for the $(t\text{-BuO})(\text{Me})_3\text{AlK}$ compound isolated in the solid state after reacting $(\text{Bn}_2\text{NH})\text{Me}_3\text{Al}$ with *t*-BuOK in toluene. The crystal structure of the dimeric core consisted of five four-membered rings taking on a diamond shape and potassium cations supporting seven coordinations $\{[(t\text{-BuO})(\text{Me})_3\text{AlK}]_2\cdot\text{PMDTA}\}_\infty$.^{387b}

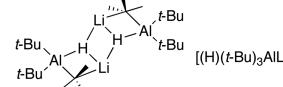
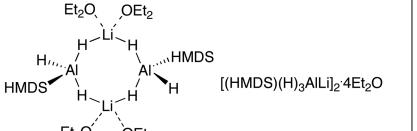
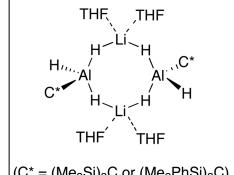
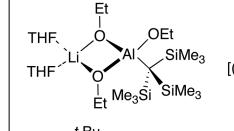
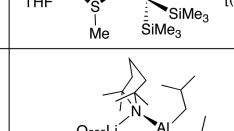
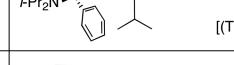
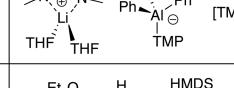
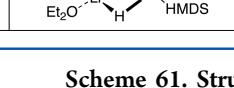
4.4. M,Zn-HeteroMAAs (M = Li, Na, K, Mg)

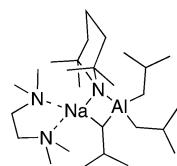
Li,Zn-, Na,Zn-, and K,Zn-MAAAs, more commonly named lithium, sodium, and potassium zincates, are probably the most known ate complexes, as evidenced by the many reviews dedicated to this class of compounds.^{1c–e,g,h,6b}

4.4.1. Homoleptic M,Zn-HeteroMAAs. As above, homoleptic M,Zn-heteroMAAs are given the $[(\text{RM})_x\cdot(\text{R}_2\text{Zn})_y]$ general formula instead of $\text{R}_{x+2y}\text{Zn}_y\text{M}_x$.

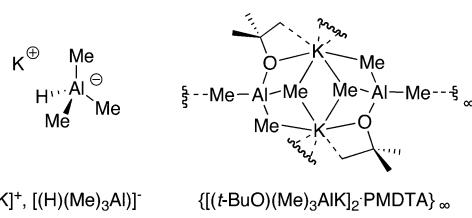
4.4.1.1. Homoleptic Li,Zn-HeteroMAAs. Results are presented for $[(\text{MeLi})_x\cdot(\text{Me}_2\text{Zn})_y]$, $[(t\text{-BuLi})_x\cdot(t\text{-Bu}_2\text{Zn})_y]$, $\{[(\text{Me}_3\text{Si})_2\text{CHLi}]_x\cdot[(\text{Me}_3\text{Si})_2\text{CH}_2\text{Zn}]_y\}$, $[(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Li})_x\cdot((2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{Zn}]_y$, and $[(\text{Me}_2\text{NLi})_x\cdot((\text{Me}_2\text{N})_2\text{Zn}]_y$.

Table 29. Structures of Heteroleptic Li_xAl-HeteroMAAs

Entry	(R ¹) _x (R ²) _m AlLi	Solvent (S)	[R ¹] _x (R ²) _m AlLi] _n S	Ref
1	(H)(t-Bu) ₃ AlLi	none		263a
2	(HMDS)(H) ₃ AlLi	Et ₂ O		388
3	((Me ₃ Si) ₃ C)(H) ₃ AlLi ((Me ₂ PhSi) ₃ C)(H) ₃ AlLi	THF		389
4a	((Me ₃ Si) ₃ C)(EtO) ₃ AlLi	THF		390b
4b	((Me ₃ Si) ₃ C)(t-BuO) ₃ AlLi			390a
5	((Me ₃ Si) ₃ C)(MeS) ₃ AlLi	THF		390c
6	(TMP)(i-Bu) ₃ AlLi	N,N-di-iso-propyl benzamide		391
7	(TMP)(Ph) ₃ AlLi	TMEDA/THF		392
8	(HMDS) ₂ (H) ₂ AlLi	Et ₂ O		388

Scheme 60. X-ray Analyses of [(TMP)(i-Bu)₃AlNa]·TMEDA³⁹⁶

It is only recently, in 2009, that the structure of the basic lithium trimethylzincate has been elucidated. Crystals of such species were obtained after reacting dimethylzinc with an equimolar amount of methylolithium in the presence of PMDTA or diglyme in a toluene/Et₂O mixture at 0 °C and then freezing at -45 °C. X-ray analyses of the species grown with the triamine showed a Li–Me–Zn–Me four-membered ring as the central motif, the zinc atom being planar trigonal and the lithium establishing three coordinations with the PMDTA

Scheme 61. Structures of [K]⁺, [(H)(Me)₃Al]⁻³⁹⁷ and {[(t-BuO)(Me)₃AlK]₂·PMDTA}_∞^{387b}

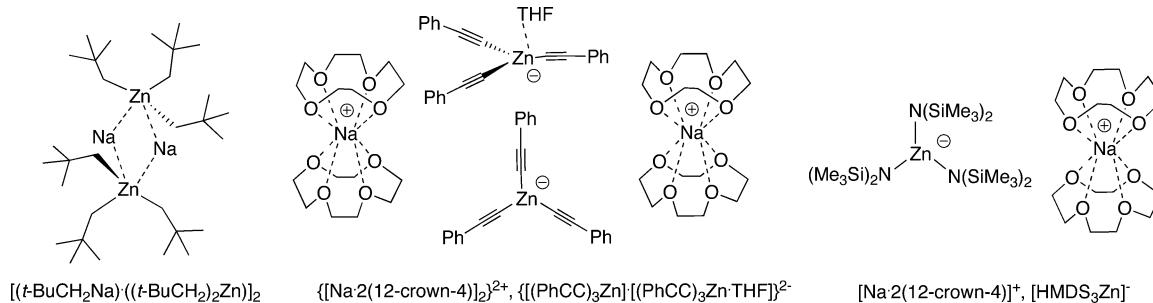
solvating agent and two with methyl groups ($[(\text{MeLi}) \cdot (\text{Me}_2\text{Zn})] \cdot \text{PMDTA}$, Table 30, entry 1a).^{398d} A separated ion-pair system rather formed when diglyme was used as the additive.^{398d} In this arrangement, the three methyl ligands were attached to the zinc atom while the lithium cation was hexacoordinated separately by two molecules of the triether ($\{[\text{Li} \cdot 2\text{diglyme}]^+, [\text{Me}_3\text{Zn}]^-\}$, Table 30, entry 1b). The highly coordinated dilithium tetramethyl zinate parent was also

Table 30. Structures of Homoleptic Li_xZn-HterOMAs

Entry	R-Li	R ₂ Zn	Solvent (S)	[R-Li] _x ·[R ₂ Zn] _y ·nS	Ref
1a			PMDTA	 [(MeLi) ₁ ·(Me ₂ Zn)]·PMDTA	398d
1b			diglyme	 {[Li·2diglyme] ⁺ ·[Me ₃ Zn] ⁻ }	398d
1c	MeLi	Me ₂ Zn	none	 {2[Li] ⁺ ·[Me ₄ Zn] ²⁻ }	398a
1d			TMEDA	 [(MeLi) ₂ ·(Me ₂ Zn)]·2TMEDA	398e
2	(Me ₃ Si) ₂ CHLi	((Me ₃ Si) ₂ CH) ₂ Zn	TMEDA/Et ₂ O	 {TMEDA[Li]·2Et ₂ O} ⁺ , {((Me ₃ Si) ₂ CH) ₂ Zn}	400
3a	2-Me ₂ NCH ₂ -C ₆ H ₄ Li	(2-Me ₂ NCH ₂ -C ₆ H ₄) ₂ Zn	THF	 [(RLi) ₁ ·(R ₂ Zn)]·THF (R = 2-Me ₂ NCH ₂ C ₆ H ₄)	401
3b			none	 [(RLi) ₂ ·(R ₂ Zn)]	401
4	Me ₂ NLi	(Me ₂ N) ₂ Zn	TMEDA	 [(Me ₂ NLi) ₁ ·((Me ₂ N) ₂ Zn)] ₂ ·2TMEDA	398e

isolated in the solid state from a hexane solution, actually much earlier, in the late 1960s, and an unsolvated separated ionic pair was depicted ($\{2[\text{Li}]^+, [\text{Me}_4\text{Zn}]^{2-}\}$, Table 30, entry 1c).^{398a} Growing the crystals of this species in the presence of TMEDA changed the arrangement into a contacted ion pair made of two Li–Me–Zn–Me quadrilaterals joined by a tetrahedral zinc atom.^{398e} The lithium cations were found to be each chelated by a molecule of diamine ($[(\text{MeLi})_2 \cdot (\text{Me}_2\text{Zn})] \cdot 2\text{TMEDA}$, Table 30, entry 1d). Both tri- and tetramethyl zinc derivatives were examined in solution thanks to the NMR technique.^{398b,c} In THF at low temperature (-20°C), the dianionic structure of the highly coordinated species was supported.^{398b} On the other hand, at -80°C , an equilibrium was attested between the tri- and the tetramethyl derivatives, however, strongly in favor of the trimethyl entity.^{398c} The bulkier analogue dilithium tetra-*t*-butylzincate showed its efficiency in halogen–metal exchange reactions, and spectral studies reinforced by computational investigations in the gas and liquid phase (THF)

indicated a huge stabilization of a dianion-type zincate, mainly due to the strong steric hindrance of the ligands.³⁹⁹ However, no structure was drawn for this example. Separated ions were also observed in the solid state for the lithium tris[bis(trimethylsilyl)methyl]zinc compound crystallized in the presence of both TMEDA and Et₂O.⁴⁰⁰ The lithium cation was found to be tetrahedrally coordinated to the two nitrogens of the TMEDA molecule and the oxygen atoms of two Et₂O units. The zinc metal was observed as being trigonal planar, establishing links with three (Me₃Si)₂CH ligands ($\{\text{TMEDA} \cdot [\text{-Li}] \cdot 2\text{Et}_2\text{O}\}^+, \{[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{Zn}\}^-$, Table 30, entry 2). Two homoleptic Li_xZn-heteroMAAs, incorporating three or four 2-Me₂NCH₂C₆H₄ ligands, were synthesized and crystallized.⁴⁰¹ Both corresponded to associated ion pair arrangements, probably due to the presence of intramolecular coordinations between the metallic parts and the dimethylamino appendages. The tricoordinated entity organized around a seven-membered ring, in which both Zn and Li metallic partners were

Scheme 62. X-ray Structures of Homoleptic Na,Zn-HeteroMAAs^{402,403}

additionally linked by one and two NMe₂ groups, respectively. Note that a molecule of THF also solvated lithium. In the tetracoordinated species, two Li–C–Zn–C quadrilaterals joined by a tetrahedral Zn vertex formed, each external lithium cation being twice attached to two NMe₂ appendages {[2-(2-Me₂NCH₂C₆H₄Li)·((2-Me₂NCH₂C₆H₄)₂Zn]}·THF and {[2-(2-Me₂NCH₂C₆H₄Li)₂·((2-Me₂NCH₂C₆H₄)₂Zn]}, Table 30, entries 3a and 3b, respectively}. Lithium zincate made of dimethylamino ligands was also examined.^{398e} In the presence of TMEDA, a dimeric trisubstituted zinc lithio derivative was highlighted thanks to X-ray analyses. The related structure showed three quadrilaterals attached through tetrahedral zinc atoms and thus a central Zn–N–Zn–N core next to two lateral Zn–N–Li–N four-membered rings, each lithium being also coordinated to the two nitrogen atoms of a molecule of TMEDA {[Me₂NLi]·((Me₂N)₂Zn)}₂·2TMEDA, Table 30, entry 4).

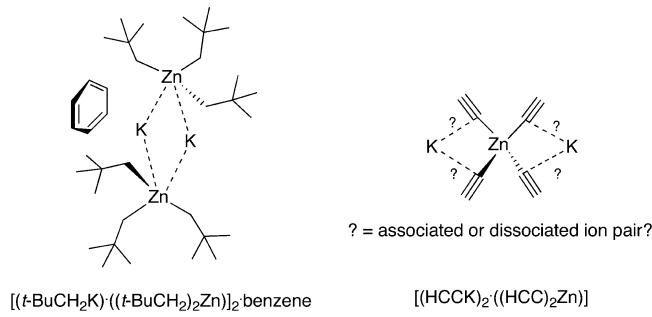
4.4.1.2. Homoleptic Na,Zn-HeteroMAAs. Results are presented for [(t-BuCH₂Na)_x·((t-BuCH₂)₂Zn)_y], [(PhC≡CNa)_x·((PhC≡C)₂Zn)_y], and [(HMDSNa)_x·(HMDS₂Zn)_y].

Among the few homoleptic Na,Zn-heteroMAAs for which structural aggregates have been elucidated, one can mention the derivative involving the t-BuCH₂ ligand.⁴⁰² Crystallographic data showed a (t-BuCH₂)₂Zn moiety, the zinc atom being trigonal planar. A weak interaction of this zinc part with the sodium atom was evoked and such Na,Zn complex was described as being dimeric {[t-BuCH₂Na]·((t-BuCH₂)₂Zn)}₂, Scheme 62, left). As regards the phenylacetylide ligand PhC≡C, a separated ion pair arrangement was reported from X-ray analyses of a sample isolated from a THF solution containing 12-crown-4 polyether.⁴⁰³ The complex was actually found to be also a dimer with two (PhC≡C)₃Zn units perpendicular to each other, one being solvated by a molecule of THF. In each anionic entity, zinc was trigonal planar. The two sodium counterions were separately inserted in two polyether crown skeletons {[Na·2(12-crown-4)]₂}²⁺, {[PhC≡C]₃Zn]·[(PhC≡C)₃Zn·THF]}²⁻, Scheme 62, middle). If one switches to amido ligands such as HMDS in the presence of 12-crown-4,⁴⁰³ a separated ion pair system was also observed in the solid state, this time as a monomeric aggregate {[Na·2(12-crown-4)]⁺, [HMDS₃Zn]⁻, Scheme 62, right).

4.4.1.3. Homoleptic K,Zn-HeteroMAAs. Results are presented for [(t-BuCH₂K)_x·((t-BuCH₂)₂Zn)_y] and [(HC≡CK)_x·((HC≡C)₂Zn)_y].

The homoleptic K,Zn-heteroMAA made of t-BuCH₂ ligands was found, in the solid state, to be quasi-isostructural to its sodium analogue depicted earlier, i.e., a dimeric triorganozincate facing two trisubstituted planar trigonal zinc moieties separated by two potassium cations.⁴⁰² The only difference lies in the fact that the K complex incorporates a molecule of

benzene, solvent from which the crystals were isolated. Note that the bigger size of the K⁺ ion, vs that of the Na⁺ ion, resulted in K–Zn and Zn–Zn distances longer than those measured with the Na parent {[t-BuCH₂K]·((t-BuCH₂)₂Zn)}₂·benzene, Scheme 63, left). Otherwise, the

Scheme 63. X-ray Structures of Homoleptic K,Zn-HeteroMAAs^{402,404}

crystal structure of the acetylenic K,Zn derivative was established from X-ray powder data, and a tetracoordinated zinc moiety was depicted next to two potassium cations. The issue of being in the presence of either an associated or dissociated ion pair was actually not clearly specified {[HC≡CK]₂·((HC≡C)₂Zn)}, Scheme 63, right).⁴⁰⁴

4.4.1.4. Homoleptic Mg,Zn-HeteroMAAs. Results are presented for [(Bn₂Mg)_x·(Bn₂Zn)_y].

To end the homoleptic M,Zn-heteroMAA section, one can add the results obtained for the magnesium zincate incorporating benzylic ligands.⁴⁰⁵ The addition of Bn₂Mg to 2 equivalents of Bn₂Zn in THF yielded a single complex that crystallized and thus could be characterized by X-ray crystallography in addition to NMR analyses. A separated ion-pair arrangement was highlighted, composed of two tricoordinated Bn₃Zn units next to a THF-hexasolvated magnesium cation {[Mg·6THF]²⁺, 2[Bn₃Zn]⁻}, Scheme 64).

4.4.2. Heteroleptic M,Zn-HeteroMAAs. The heteroleptic M,Zn-heteroMAAs presented in this section correspond to compounds with the $[(R)_x(R')_yZnM_{(x+y)-z}]_z$ general formula, where M is an alkali metal, with z = 1 designating a monomer

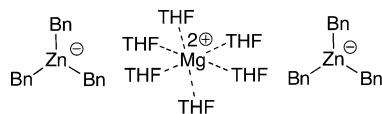
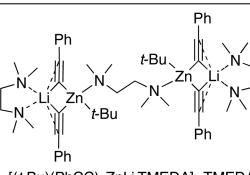
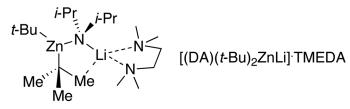
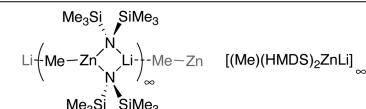
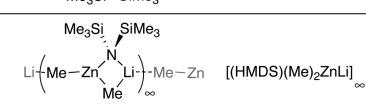
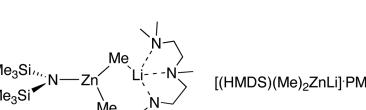
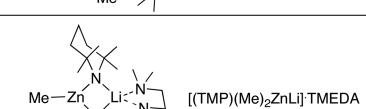
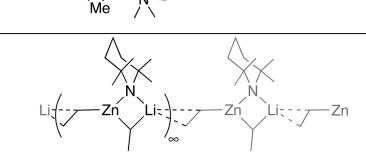
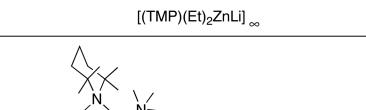
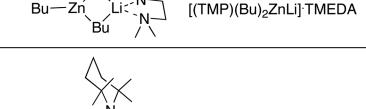
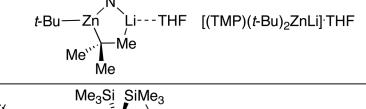
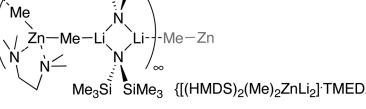
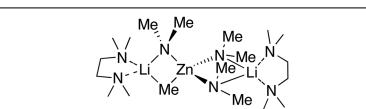
Scheme 64. X-ray Structure of a Homoleptic Mg,Zn-HeteroMAA⁴⁰⁵

Table 31. Crystallographic Structures of Heteroleptic Li_xZn-HeteroMAAs

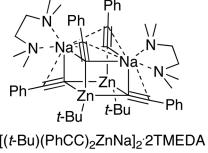
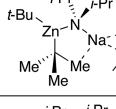
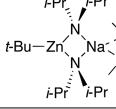
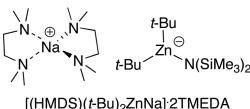
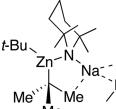
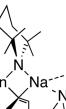
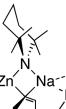
Entry	(R ¹) _x (R ²) _y ZnLi _{(x+y)-2}	Solvent (S)	[(R ¹) _x (R ²) _y ZnLi _{(x+y)-2}] _z ·nS	Ref
1	(t-Bu)(PhC≡C) ₂ ZnLi	TMEDA	 [(t-Bu)(PhC≡C)2ZnLi] ₂ ·TMEDA	274b
2	(DA)(t-Bu) ₂ ZnLi	TMEDA	 [(DA)(t-Bu) ₂ ZnLi] ₂ ·TMEDA	274b
3	(Me)(HMDS) ₂ ZnLi	none	 [(Me)(HMDS) ₂ ZnLi] _n	406a
4a		none	 [(HMDS)(Me) ₂ ZnLi] _n	406b
4b	(HMDS)(Me) ₂ ZnLi	PMDTA	 [(HMDS)(Me) ₂ ZnLi]·PMDTA	406b
5	(TMP)(Me) ₂ ZnLi	TMEDA	 [(TMP)(Me) ₂ ZnLi]·TMEDA	407
6	(TMP)(Et) ₂ ZnLi	none	 [(TMP)(Et) ₂ ZnLi] _n	408
7	(TMP)(Bu) ₂ ZnLi	TMEDA	 [(TMP)(Bu) ₂ ZnLi]·TMEDA	409
8	(TMP)(t-Bu) ₂ ZnLi	THF	 [(TMP)(t-Bu) ₂ ZnLi]·THF	410
9	(HMDS) ₂ (Me) ₂ ZnLi ₂	TMEDA	 [(HMDS) ₂ (Me) ₂ ZnLi ₂]·TMEDA	407
10	(Me)(Me ₂ N) ₃ ZnLi ₂	TMEDA	 [(Me)(Me ₂ N) ₃ ZnLi ₂]·2TMEDA	398e
11	(CLA)(Et) ₂ ZnLi ₂	THF	 [(CLA)(Et) ₂ ZnLi ₂]·THF	411

and $z = 2$ a dimer. Structural data were mainly related to crystallographic analyses.

4.4.2.1. *Heteroleptic Li_xZn-HeteroMAAs*. Results are presented for (t-Bu)(PhC≡C)₂ZnLi, (DA)(t-Bu)₂ZnLi, (Me)-

(HMDS)₂ZnLi, (HMDS)(Me)₂ZnLi, (TMP)(Me)₂ZnLi, (TMP)(Et)₂ZnLi, (TMP)(Bu)₂ZnLi, (TMP)(t-Bu)₂ZnLi, (HMDS)₂(Me)₂ZnLi₂, (Me)(Me₂N)₃ZnLi₂, and (CLA)-(Et)₂ZnLi₂.

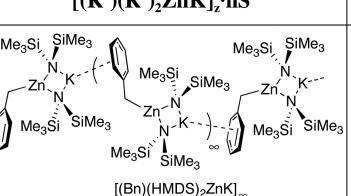
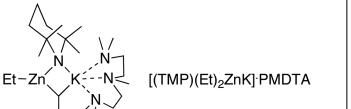
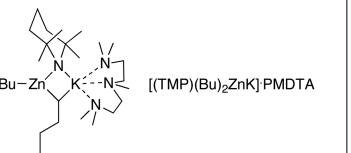
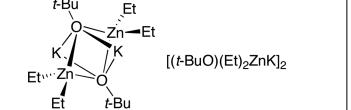
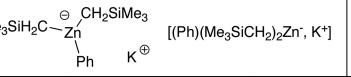
Table 32. Crystallographic Structures of Heteroleptic Na_xZn-HeteroMAAs

Entry	(R ¹)(R ²) ₂ ZnNa or (R ¹)(R ²)(R ³)ZnNa	Solvent (S)	[(R ¹)(R ²) ₂ ZnNa] _x ·nS or [(R ¹)(R ²)(R ³)ZnNa] _x ·nS	Ref
1	(t-Bu)(PhC≡C) ₂ ZnNa	TMEDA	 [(t-Bu)(PhC≡C)2ZnNa] ₂ ·2TMEDA	274b
2	(DA)(t-Bu) ₂ ZnNa	TMEDA	 [(DA)(t-Bu) ₂ ZnNa]·TMEDA	274b
3	(t-Bu)(DA) ₂ ZnNa	TMEDA	 [(t-Bu)(DA) ₂ ZnNa]·TMEDA	412b
4	(HMDS)(t-Bu) ₂ ZnNa	TMEDA	 [(HMDS)(t-Bu) ₂ ZnNa]·2TMEDA	412b
5	(TMP)(t-Bu) ₂ ZnNa	TMEDA	 [(TMP)(t-Bu) ₂ ZnNa]·TMEDA	412a
6	(TMP)(Ph)(t-Bu)ZnNa	TMEDA	 [(TMP)(Ph)(t-Bu)ZnNa]·TMEDA	412a
7	(TMP)(x-MeC ₆ H ₅)(t-Bu)ZnNa (x = 3 or 4)	TMEDA	 [(TMP)(x-MeC ₆ H ₅)(t-Bu)ZnNa]·TMEDA	413

Although most heteroleptic Li_xZn-heteroMAAs for which structural data (Table 31) were obtained include in their composition an amido ligand, one can retain the particular case of the bimetallic *tert*-butyl diacetylide species (t-Bu)(PhC≡C)₂ZnLi, isolated in the solid state while reacting dialkylamide zincate (DA)(t-Bu)₂ZnLi with phenylacetylene in the presence of TMEDA.^{274b} The molecular structure of this amido-free zincate was found as corresponding to a trisolvated dimer with two TMEDA-(Li-C^{sp}-Zn-C^{sp}) four-membered rings linked to each other through a TMEDA bridge setting up between two zinc atoms [(t-Bu)(PhC≡C)₂ZnLi·TMEDA]₂·TMEDA,^{274b} Table 31, entry 1). In the same structural authentication, the crystallographic structure of the reactant (DA)(t-Bu)₂ZnLi was also determined. A TMEDA-solvated monomeric associated ion pair was reported, which included a five-membered Li-N-Zn-C-C ring, the lithium cation being linked to a methyl group of the *tert*-butyl appendage instead of the hindered quaternary carbon. The second t-Bu group was simply linked to the zinc atom on the outside of the pentacycle, preserving the almost trigonal geometry of the metal. The lithium cation was additionally chelated by a molecule of TMEDA [(DA)(t-Bu)₂ZnLi]·TMEDA, Table 31, entry 2).^{274b} Reacting dimethylzinc, butyllithium, and hexamethyldisilazane in the 1:2:2 ratio led to colorless needle crystals. Their structure corresponded to a polymeric arrangement made of (Me)-

(HMDS)₂ZnLi units organized around a Li-N-Zn-N quadrilateral, with the methyl group occupying the third (external) coordination site on the Zn atom and ensuring the link between the various units via Li-Me interactions ([(Me)-(HMDS)₂ZnLi]_∞, Table 31, entry 3).^{406a} The analogue (HMDS)(Me)₂ZnLi is part of a series of dialkylamido zincates (HMDS)(Alk)₂ZnM (M = Li, Na, K) that received particular attention due to their high degree of selectivity in aromatic deprotonation reactions. These species were isolated in the solid state as an unsolvated aggregate^{406b} but were also solvated by PMDTA.^{406b} The solvent-free form was obtained by recrystallization from hexane-toluene mixture, and a contacted ion-pair polymeric chain structure made of four-membered Li-N-Zn-C_{Me} rings, linked thanks to Me-Li interactions, was highlighted ([(HMDS)(Me)₂ZnLi]_∞, Table 31, entry 4a).^{406b} The crystallographic structure of the PMDTA adduct was also depicted as an ion-contacted entity; this time it was not polymeric but organized around an uncyclic core based on a planar trigonal zinc atom linked to the solvated tricoordinated lithium cation through a Me bridge ([(HMDS)-(Me)₂ZnLi]·PMDTA, Table 31, entry 4b).^{406b} Replacing the triamine by diamine TMEDA caused a significant change, since a polymeric arrangement with units considering two lithium atoms for one zinc and including two HMDS anionic parts in addition to the two methyl ones now formed

Table 33. Crystallographic Structures of Heteroleptic K_nZn-HeteroMAAs

Entry	(R ¹)(R ²) ₂ ZnK	Solvent (S)	[(R ¹)(R ²) ₂ ZnK] _n S	Ref
1	(Bn)(HMDS) ₂ ZnK	none		414
2	(TMP)(Et) ₂ ZnK	PMDTA		415
3	(TMP)(Bu) ₂ ZnK	PMDTA		415b
4	(t-BuO)(Et) ₂ ZnK	none		416
5	(Ph)(Me ₃ SiCH ₂) ₂ ZnK	none		402

((HMDS)₂(Me)₂ZnLi₂).⁴⁰⁷ Against all odds, this stoichiometry did not refer to a tetrasubstituted zinc atom but showed up as Li—N—Li—N quadrilaterals linked to each other thanks to Me—Zn—Me bridges, the zinc metal, now tetrahedral, being found to support two additional coordinations with the nitrogens of a molecule of TMEDA ($\{[(\text{HMDS})_2(\text{Me})_2\text{ZnLi}_2]\cdot\text{TMEDA}\}_\infty$, Table 31, entry 9).⁴⁰⁷ Switching to the TMP-amido derivatives, structural data were obtained for the (TMP)(Me)₂ZnLi,⁴⁰⁷ (TMP)(Et)₂ZnLi,⁴⁰⁸ (TMP)(Bu)₂ZnLi,⁴⁰⁹ and $[(\text{TMP})(\text{t}-\text{Bu})_2\text{ZnLi}]_\infty$ ⁴¹⁰ combinations in the presence of TMEDA or not. All were found to correspond to associated ion pairs. The structure of (TMP)(Me)₂ZnLi was described as a four-membered Li—N—Zn—C_{Me} ring solvated on the lithium atom by the two nitrogens of a molecule of TMEDA ($[(\text{TMP})(\text{Me})_2\text{ZnLi}]\cdot\text{TMEDA}$, Table 31, entry 5).⁴⁰⁷ Compound (TMP)(Et)₂ZnLi was isolated in the solid state from a hydrocarbon medium, and the crystallographic data showed a polymeric sequence made of Li—N—Zn—C_{Et} quadrilaterals linked to each other thanks to Li—Et interactions ($[(\text{TMP})(\text{Et})_2\text{ZnLi}]_\infty$, Table 31, entry 6).⁴⁰⁸ The (TMP)(Bu)₂ZnLi species revealed structural similarity with its Me analogue in the presence of TMEDA ($[(\text{TMP})(\text{Bu})_2\text{ZnLi}]\cdot\text{TMEDA}$, Table 31, entry 7).⁴⁰⁹ In THF, a five-membered Li—N—Zn—C—C_{Me} ring was found for the (TMP)(t-Bu)₂ZnLi arrangement, lithium being solvated by one molecule of the ethereal solvent ($[(\text{TMP})(\text{t}-\text{Bu})_2\text{ZnLi}]\cdot\text{THF}$, Table 31, entry 8).⁴¹⁰ The structure of higher-order heteroleptic Li_nZn-heteroMAAs was also reported (Table 31, entries 9 and 10). Thus, the EXAFS (extended X-ray absorption fine structure) spectroscopy technique, in addition to NMR and Raman analyses, supported the idea that (NC)(Me)₃ZnLi₂ and (NCS)(Me)₃ZnLi₂ were zinc-tetracoordinated structures, however, without affording indisputable structural diagrams.^{398b} In contrast, the (Me)(Me₂N)₃ZnLi₂ reactant could be isolated in the solid state from

a solution containing TMEDA, and fully analyzed by X-ray crystallography. A spiro arrangement made of two nonidentical quadrilaterals linked by a tetrahedral zinc atom was underlined. Both Li—N—Zn—N and Li—N—Zn—Me four-membered rings were chelated on the lithium cations by a molecule of TMEDA ($[(\text{Me})(\text{Me}_2\text{N})_3\text{ZnLi}_2]\cdot 2\text{TMEDA}$, Table 31, entry 10).^{398e} Finally, one can mention the case of the alkylamido lithium—zinc organobimetallic entity employing a chiral bis-amide derived from a piperazine. The latter was found to adopt, in THF, a boat conformation in order to pinch the zinc metal that in this case became tetrahedrally tetracoordinated ($[(\text{CLA})(\text{Et})_2\text{ZnLi}_2]$, Table 31, entry 11).⁴¹¹ The solvation was not evoked for this example.

4.4.2.2. Heteroleptic Na_nZn-HeteroMAAs. Results are presented for (t-Bu)(PhC≡C)₂ZnNa, (DA)(t-Bu)₂ZnNa, (t-Bu)(DA)₂ZnNa, (HMDS)(t-Bu)₂ZnNa, (TMP)(t-Bu)₂ZnNa, (TMP)(Ph)(t-Bu)ZnNa, and (TMP)(4-MeC₆H₅)(t-Bu)ZnNa.

Studies examining the synergic effects of mixed alkali metal zinc bases attested that the identity of the alkali metal could affect decisively the course of the reaction. Thus, sodium zincates (then potassium and magnesium depicted later) were synthesized and few of them led to structural depictions (Table 32). First, for the (t-Bu)(PhC≡C)₂ZnNa reactant obtained in the solid state by mixing (DA)(t-Bu)₂ZnNa with 2 equiv of phenylacetylene in the presence of TMEDA, a dimeric arrangement organized around a disolvated cubic tetramer was highlighted ($[(\text{t}-\text{Bu})(\text{PhC}\equiv\text{C})_2\text{ZnNa}]_2\cdot 2\text{TMEDA}$, Table 32, entry 1).^{274b} The zincate precursor (DA)(t-Bu)₂ZnNa was also crystallized in the same medium and a structure comparable to its lithium congener was underlined; i.e., a Na—N—Zn—C—Me pentacycle solvated by one molecule of TMEDA fixed on the sodium atom was emphasized ($[(\text{DA})(\text{t}-\text{Bu})_2\text{ZnNa}]\cdot\text{TMEDA}$, Table 32, entry 2).^{274b} The same compound was found to undergo a slow disproportionation

after 48 h at room temperature, affording the alkylbis(amido) zincate (*t*-Bu)(DA)₂ZnNa. Crystals of this new entity corresponded to a four-membered Na—N—Zn—N ring system solvated on the sodium atom by a molecule of TMEDA ([(*t*-Bu)(DA)₂ZnNa]·TMEDA, Table 32, entry 3).^{412b} The amido zincate (HMDS)(*t*-Bu)₂ZnNa was isolated as colorless crystals in the same study (presence of TMEDA) and a solvent-separated ion-pair arrangement was mentioned in this case. In such a crystalline structure, the zinc atom was found to be trigonal planar, being coordinated to the HMDS and the two *tert*-butyl ligands, while the sodium cation was surrounded by two molecules of TMEDA in a pseudotetrahedral geometry ([(*t*-Bu)(DA)₂ZnNa]·2TMEDA, Table 32, entry 4).^{412b} The (TMP)(*t*-Bu)₂ZnNa congener was prepared and also isolated in the crystalline form as its TMEDA adduct. An associated ion-pair molecular structure, based on a monosolvated Na—N—Zn—C—Me pentacycle, was depicted from the X-ray analyses ([(*t*-Bu)(TMP)₂ZnNa]·TMEDA, Table 32, entry 5).^{412a} Finally, one can cite two examples of bis-heteroleptic Na,Zn heteroMAA, (TMP)(Ph)(*t*-Bu)ZnNa and (TMP)(4-MeC₆H₅)(*t*-Bu)ZnNa. Both were isolated in the solid state in the presence of TMEDA and were found isostructural, arranging around TMEDA-solvated Na—N—Zn—C_{aryl} quadrilaterals {[*(t*-Bu)(Ph)(*t*-Bu)ZnNa]·TMEDA}^{412a} and {[*(t*-Bu)(4-MeC₆H₅)(*t*-Bu)ZnNa]·TMEDA},⁴¹³ Table 32, entries 6 and 7, respectively.

4.4.2.3. Heteroleptic K,Zn-HeteroMAAs. Results are presented for (Bn)(HMDS)₂ZnK, (TMP)(Et)₂ZnK, (TMP)-(*t*-Bu)₂ZnK, (*t*-BuO)(Et)₂ZnK, and (Ph)(Me₃SiCH₂)₂ZnK.

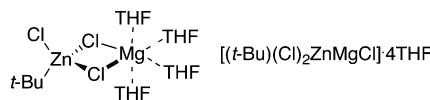
Concerning at this point molecular structures of heteroleptic K,Zn-heteroMAAs (Table 33), one can mention the benzyl bisamido product (Bn)(HMDS)₂ZnK obtained by reacting [(HMDSK)·(HMDS₂Zn)] with toluene. This species was found to exist in the crystals as an infinite spiral chain made of K—N—Zn—N quadrilaterals linked to each others thanks to π-cation (Ph—K) interactions ([(*Bn*)(HMDS)₂ZnK]_∞, Table 33, entry 1).⁴¹⁴ Two dialkylamido potassium zincates, i.e., (TMP)(Et)₂ZnK⁴¹⁵ and (TMP)(*t*-Bu)₂ZnK,^{415b} were synthesized in the presence of PMDTA and isolated in the solid state. Both species showed a molecular structure organized around a four-membered K—N—Zn—C ring solvated on the potassium by the three nitrogens of a molecule of triamine ([(*t*-Bu)(Et)₂ZnK]·PMDTA and [(*t*-Bu)(Et)₂ZnK]·PMDTA, Table 33, entries 2 and 3, respectively). Crystals were also obtained for the dialkyl alkoxy zincate (*t*-BuO)(Et)₂ZnK, and an octahedral-like geometry was observed for this compound, forming a dimer. Two oxygen atoms occupied opposite tops of the octahedral and were linked to two zinc and two potassium atoms, the two zinc entities being arranged to describe a central quadrilateral ([(*t*-BuO)(Et)₂ZnK]₂, Table 33, entry 4).⁴¹⁶ Finally, the molecular structure of (Ph)(Me₃SiCH₂)₂ZnK was reached when reacting [(Me₃SiCH₂K)·((Me₃SiCH₂)₂Zn)] with benzene. The crystalline complex was found to consist of a separated ion pair ([(*Ph*)(Me₃SiCH₂)₂Zn[−], K⁺], Table 33, entry 5).⁴⁰²

4.4.2.4. Heteroleptic Mg,Zn-HeteroMAAs. Results are presented for (*t*-Bu)(Cl)₂ZnMgCl.

The reaction between ZnCl₂ and *t*-BuMgCl in THF afforded the crystalline mixed alkyl chloride magnesium zincate (*t*-Bu)(Cl)₂ZnMgCl, for which the structure corresponded to an associated ion pair arrangement made of a Mg—Cl—Zn—Cl quadrilateral tetrasolvated on the magnesium atom by four

molecules of THF and in which the zinc metal was tetrahedral ([(*t*-Bu)(Cl)₂ZnMgCl]·4THF, Scheme 65).⁴¹⁷

Scheme 65. Crystallographic Structure of (*t*-Bu)(Cl)₂ZnMgCl Grown in THF⁴¹⁷



As for the magnesium and the aluminum heteroMAAs, the molecular structures of zincates made of complex ligands or corresponding to intermediates of aromatic deprotonation reactions⁴¹⁸ are not detailed in the present review.

As regards general conclusions on heteroMAAs structures, one can observe that, unlike Li,Li-homoMAAs, a wide range of structures exist, going from mixed dimers, often organized around a quadrilateral, to macromolecules able to contain up to eight mixed organometallic units. Polymeric arrangements are also encountered. In the case of quadrilateral mixed dimers, which remain the most characterized, or least presumed (by calculation), structures, one can notice that for organometallic parent partners presenting a minimum of two R anionic moieties (R₂Mg, R₂Zn, R₃Al), one of those anion will distinguish from the other(s) being part of the quadrilateral core. For this ligand, surrounded by two metals, a higher reactivity, as base or nucleophile, is observed.^{418n,o,419} As for the homoMAAs, the reader is invited to consult the following review in this issue (part 2) regarding structure/reactivity correlations of heteroMAAs on deprotonation and nucleophilic addition purposes.

5. CONCLUSION

In this review, our aim has been to gather the knowledge acquired about the structures for dipolar organometallic aggregates made of elements from the top of the Mendeleev classification. Those species have been classified into three categories named oligoMAA when a single organometallic species is involved, homoMAA for mixed entities implying a single sort of metal, and heteroMAA if two different metallic partners are associated. Of course, the subject is not exhaustively covered because of the huge work done in this field. However, the structures of most common organo(bi)metallic reactants used in organic chemistry should be discussed here. Structural depictions of heteroMAA intermediates, mostly resulting from deprotonation reactions, recently covered the field. It has been decided to not detail those results here, as they should be the object of a review on their own.

AUTHOR INFORMATION

Corresponding Author

*A.H.M: phone, 33 235 522 438; fax, 33 235 522 971; e-mail, anne.harrison@univ-rouen.fr. F.M.: phone, 33 223 236 931; fax, 33 223 236 955.

Notes

The authors declare no competing financial interest.

Biographies



Anne Harrison-Marchand obtained her Ph.D. in Chemistry in 1995 from the University of Nantes. Her doctoral research was carried out in the laboratory of Dr. J. Villiéras, under the supervision of Drs. A. Guingant and J.-P. Pradère. She then spent a year and a half occupying a postdoctoral position (with a Marie-Curie Training Grant) in the group of Prof. A. Pelter at the University of Wales, Swansea, U.K. From January 1997 to August 1999, she worked on industrial projects: first, with Rhône-Poulenc Rorer in the group of Prof. A. Barrett at the Imperial College of London (U.K.) and, second, with UCBPharma in the group of Prof. G. Guillaumet at Orléans (France). She was offered an Assistant Professor position (HDR in 2008) at the University of Rouen in September 1999. She has expertise in two distinct areas related to asymmetric heterocycloadditions and enantioselective nucleophilic additions of organo(bi)metallic reactants. The latter problem is currently her main focus and consists of both exploring new synthetic methodologies and understanding their stereochemical outcomes thanks to analyses of the species directly in solution.



Florence Mongin obtained her Ph.D. in Chemistry in 1994 from the University of Rouen under the supervision of Prof. Guy Quéguiner. After a two-year stay at the Institute of Organic Chemistry of Lausanne as a postdoctoral fellow with Prof. Manfred Schlosser, she returned to the University of Rouen as an Assistant Professor in 1997 (HDR in 2003). Besides research activities concerning the functionalization of heteroaromatic compounds using lithium and magnesium reagents and the synthesis of biologically active compounds, she got involved in catalysis studies, notably for the activation of C–F bonds and the transition metal C–C bond formation using Grignard reagents in the presence of reactive functional groups. She has thus a strong expertise in the functionalization of aromatic and heterocyclic compounds, in the synthesis and use of metal bases, and in metal-catalyzed coupling reactions. She took up her present position in 2005 as Professor at the University of Rennes and was appointed Junior Member of the Institut

Universitaire de France in 2009. Her present scientific interests include the functionalization of aromatic compounds with recourse to bimetallic bases. The synergies brought out by combining lithium and magnesium, lithium and zinc, lithium and cadmium, lithium and copper, lithium and cobalt, and lithium and iron reagents have been evidenced in the course of the last seven years. Extensions to asymmetric synthesis are currently under investigation.

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REFERENCES

- (1) For early observations, see: (a) Wittig, G.; Meyer, F. J.; Lange, G. *Justus Liebigs Ann. Chem.* **1951**, 571, 167. (b) Tochtermann, W. *Angew. Chem., Int. Ed.* **1966**, 5, 351. For recent reviews, see: (c) Linton, D. J.; Schooler, P.; Wheatley, A. E. H. *Coord. Chem. Rev.* **2001**, 223, 53. (d) Wheatley, A. E. *New. J. Chem.* **2004**, 28, 435. (e) Mulvey, R. E. *Organometallics* **2006**, 25, 1060. (f) Naka, H.; Uchiyama, M.; Matsumoto, Y.; Wheatley, A. E. H.; McPartlin, M.; Morey, J. V.; Kondo, Y. *J. Am. Chem. Soc.* **2007**, 129, 1921. (g) Mulvey, R. E.; Mongin, F.; Uchiyama, M.; Kondo, Y. *Angew. Chem., Int. Ed.* **2007**, 46, 3802. (h) Mulvey, R. E. *Acc. Chem. Res.* **2009**, 42, 743.
- (2) Among preliminary references using this term, see: (a) Jackman, L. M.; Dunne, T. S. *J. Am. Chem. Soc.* **1985**, 107, 2805. (b) DePue, J. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, 110, 5518. (c) DePue, J. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, 110, 5524.
- (3) See, for example: (a) Hilmersson, G.; Davidsson, Ö. *Organometallics* **1995**, 14, 912. (b) Granander, J.; Sott, R.; Hilmersson, G. *Chem.—Eur. J.* **2006**, 12, 4191.
- (4) (a) Caubère, P. *Chem. Rev.* **1993**, 93, 2317. (b) Gros, P.; Fort, Y. *Eur. J. Org. Chem.* **2002**, 3375. (c) Gros, P.; Fort, Y. *Eur. J. Org. Chem.* **2009**, 4199.
- (5) (a) Lochmann, L.; Pospisil, J.; Vodnansky, J.; Trekoval, J.; Lim, D. *Collect. Czech. Chem. Commun.* **1965**, 30, 2187. (b) Schlosser, M. J. *Organomet. Chem.* **1967**, 8, 9. (c) Schlosser, M.; Strunk, S. *Tetrahedron Lett.* **1984**, 25, 741. (d) Margot, C.; Matsuda, H.; Schlosser, M. *Tetrahedron* **1990**, 46, 2425.
- (6) (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, 56, 151. (b) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1501. (c) Williard, P. G. Carbanions of Alkali and Alkaline Earth Cations: Synthesis and Structural Characterization. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: London, 1991; Vol. 1, p 1. (d) Beswick, M. A.; Wright, D. S. Alkali Metals. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, 1995; Vol. 1, p 1. (e) Ruhlandt-Senge, K.; Henderson, K. W.; Andrews, P. C. Alkali Metal Organometallics: Structure and Bonding. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Meyer, K., Eds.; Elsevier: Oxford, 2007; Vol. 2, p 1. (f) Gessner, V. H.; Däschlein, C.; Strohmann, C. *Chem.—Eur. J.* **2009**, 15, 3320. (g) Hanusa, T. P. Alkaline Earth Organometallics. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Meyer, K., Eds.; Elsevier: Oxford, 2007; Vol. 2, p 67. (h) Mitra, A.; Atwood, D. A. Aluminum Organometallics. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Housecroft, C. E., Eds.; Elsevier: Oxford, 2007; Vol. 3, p 265. (i) Stahl, L.; Smoliakova, I. P. Zinc Organometallics. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Meyer, K., Eds.; Elsevier: Oxford, 2007; Vol. 2, p 309. (j) Stey, T.; Stalke, D. *Patai Series: The Chemistry of Organolithium Compounds*; Rappoport, Z., Marek, I., Eds.; John Wiley & Sons, Ltd: New York, 2004; Vol. 1, Chapter 2, p 47.

- (7) (a) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47. (b) Mulvey, R. E. *J. Am. Chem. Soc. Rev.* **1991**, *20*, 167.
- (8) (a) Streitwieser, A.; Bachrach, S. M.; Dorigo, A.; Schleyer, P. v. R. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; p 1. (b) Sapse, A.-M.; Jain, D. C.; Raghavachari, K. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; p 45.
- (9) Pratt, L. M.; Khan, I. M. *J. Comput. Chem.* **1995**, *16*, 1067.
- (10) Verstraete, P.; Deffieux, A.; Fritsch, A.; Rayez, J. C.; Rayez, M. T. *J. Mol. Struct.: THEOCHEM* **2003**, *631*, 53.
- (11) Jemmis, E. D.; Gopakumar, G. In *The Chemistry of Organolithium Compounds*; Rappoport, Z., Marek, I., Eds.; Wiley: New York, 2004; p 1.
- (12) (a) Brown, T. L.; Rogers, M. T. *J. Am. Chem. Soc.* **1957**, *79*, 1859. (b) Brown, T. L.; Rogers, M. T. *Acta Crystallogr.* **1957**, *10*, 465. (c) Brown, T. L. *Adv. Organomet. Chem.* **1965**, *3*, 365.
- (13) (a) Dietrich, H. *Z. Naturforsch.* **1959**, *14b*, 739. (b) Dietrich, H. *Acta Crystallogr.* **1963**, *16*, 681. (c) Dietrich, H. *J. Organomet. Chem.* **1981**, *205*, 291.
- (14) (a) Weiss, E.; Lucken, E. A. *C. J. Organomet. Chem.* **1964**, *2*, 197. (b) Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265. (c) Köster, H.; Thoenes, D.; Weiss, E. *J. Organomet. Chem.* **1978**, *160*, 1. (d) Ogle, C. A.; Huckabee, B. K.; Johnson, H. C., IV; Sims, P. F.; Winslow, S. D.; Pinkerton, A. A. *Organometallics* **1993**, *12*, 1960. (e) Walfort, B.; Lameyer, L.; Weiss, W.; Herbst-Irmer, R.; Bertermann, R.; Rocha, J.; Stalke, D. *Chem.—Eur. J.* **2001**, *7*, 1417.
- (15) (a) Strohmann, C.; Strohfeldt, K.; Schildbach, D.; McGrath, M. J.; O'Brien, P. *Organometallics* **2004**, *23*, 5389. (b) Strohmann, C.; Dilks, S.; Strohfeldt, K. *Organometallics* **2006**, *25*, 41. (c) Strohmann, C.; Gessner, V. H. *J. Am. Chem. Soc.* **2007**, *129*, 8952.
- (16) Zerger, R.; Rhine, W.; Stucky, G. *J. Am. Chem. Soc.* **1974**, *96*, 6048.
- (17) (a) Siemeling, U.; Redecker, T.; Neumann, B.; Stammler, H.-G. *J. Am. Chem. Soc.* **1994**, *116*, 5507. (b) Strohmann, C.; Gessner, V.; Damme, A. *Chem. Commun.* **2008**, 3381.
- (18) (a) Strohmann, C.; Strohfeldt, K.; Schildbach, D. *J. Am. Chem. Soc.* **2003**, *125*, 13672. (b) Strohmann, C.; Gessner, V. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 4566. (c) Strohmann, C.; Gessner, V. H. *J. Am. Chem. Soc.* **2008**, *130*, 11719.
- (19) (a) Nichols, M. A.; Williard, P. G. *J. Am. Chem. Soc.* **1993**, *115*, 1568. (b) Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *J. Am. Chem. Soc.* **1993**, *115*, 1573.
- (20) Kottke, T.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 580.
- (21) (a) Strohmann, C.; Seibel, T.; Strohfeldt, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 4531. (b) Strohmann, C.; Gessner, V. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 8281. (c) Gessner, V. H.; Strohmann, C. *J. Am. Chem. Soc.* **2008**, *130*, 14412. (d) Gessner, V. H.; Strohmann, C. *Organometallics* **2010**, *29*, 1858.
- (22) (a) Lappert, M. F.; Engelhardt, L. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1323. (b) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827. (c) Teclie, B.; Maqsudur Rahman, A. F. M.; Oliver, J. P. *J. Organomet. Chem.* **1986**, *317*, 267.
- (23) Fraenkel, G.; Adams, D. G.; Williams, J. *Tetrahedron Lett.* **1963**, *4*, 767.
- (24) (a) Brown, T. L.; Dickerhoof, D. W.; Bafus, D. A. *J. Am. Chem. Soc.* **1962**, *84*, 1371. (b) Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 2174.
- (25) (a) McKeever, L. D.; Waack, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* **1968**, *90*, 3244. (b) McKeever, L. D.; Waack, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* **1969**, *91*, 1057.
- (26) (a) Fraenkel, G.; Fraenkel, A. M.; Geckle, M. J.; Schloss, F. J. *Am. Chem. Soc.* **1979**, *101*, 4745. (b) Fraenkel, G.; Henrichs, M.; Hewitt, J. M.; Su, B. M.; Geckle, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 3345.
- (27) (a) Thomas, R. D.; Jensen, R. M.; Young, T. C. *Organometallics* **1987**, *6*, 565. (b) Thomas, R. D.; Clarke, M. T.; Young, T. C. *J. Organomet. Chem.* **1987**, *328*, 239. (c) Gallagher, D. J.; Kerrick, S. T.; Beak, P. *J. Am. Chem. Soc.* **1992**, *114*, 5872. (d) Carbone, G.; O'Brien, P.; Hilmersson, G. *J. Am. Chem. Soc.* **2010**, *132*, 15445.
- (28) (a) Eppers, O.; Günther, H. *Helv. Chim. Acta* **1990**, *73*, 2071. (b) Günther, H. *J. Braz. Chem. Soc.* **1999**, *10*, 241.
- (29) Bauer, W. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse A. M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; p 125.
- (30) Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664.
- (31) (a) Margerison, D.; Newport, J. P. *Trans. Faraday Soc.* **1963**, *2058*. (b) West, P.; Waack, R. *J. Am. Chem. Soc.* **1967**, *89*, 4395.
- (32) Weiner, M.; Vogel, G.; West, R. *Inorg. Chem.* **1962**, *1*, 654.
- (33) (a) Andrews, L. *J. Chem. Phys.* **1967**, *47*, 4834. (b) West, R.; Glaze, W. *J. Am. Chem. Soc.* **1961**, *83*, 3580.
- (34) (a) Waack, R.; Doran, M. A. *J. Am. Chem. Soc.* **1963**, *85*, 1651. (b) Waack, R.; Doran, M. A. *J. Phys. Chem.* **1963**, *67*, 148. (c) Waack, R.; Doran, M. A. *J. Phys. Chem.* **1964**, *68*, 1148.
- (35) (a) Berkowitz, J.; Bafus, D. A.; Brown, T. L. *J. Phys. Chem.* **1961**, *65*, 1380. (b) Chinn, J. W.; Lagow, R. *J. Organometallics* **1984**, *3*, 75.
- (36) (a) Zgonnik, V. N.; Kalnin'sh, K. K.; Nikolaev, N. I.; Shadrina, E. Y. *Russ. Chem. Bull.* **1972**, *21*, 1881. (b) Brown, T. L.; Gerteis, R. L.; Bafus, D. A.; Ladd, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 2135.
- (37) Bergander, K.; He, R.; Chandrakumar, N.; Eppers, O.; Günther, H. *Tetrahedron* **1994**, *50*, 5861.
- (38) (a) Qu, B.; Collum, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 9355. (b) Bartlett, P. D.; Goebel, C. V.; Weber, W. P. *J. Am. Chem. Soc.* **1969**, *91*, 7425.
- (39) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308.
- (40) (a) McGarrity, J. F.; Ogle, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 1805. (b) McGarrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H.-R. *J. Am. Chem. Soc.* **1985**, *107*, 1810.
- (41) Keresztes, I.; Williard, P. G. *J. Am. Chem. Soc.* **2000**, *122*, 10228.
- (42) (a) Saá, J. M.; Martorell, G.; Frontera, A. *J. Org. Chem.* **1996**, *61*, 5194. (b) Waldmüller, D.; Kotsatos, B. J.; Nichols, M. A.; Williard, P. G. *J. Am. Chem. Soc.* **1997**, *119*, 5479. (c) Hoffmann, D.; Collum, D. B. *J. Am. Chem. Soc.* **1998**, *120*, 5810. (d) Rutherford, J. L.; Hoffmann, D.; Collum, D. B. *J. Am. Chem. Soc.* **2002**, *124*, 264.
- (43) Fraenkel, G.; Beckenbaugh, W. E.; Yang, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 6878.
- (44) Fraenkel, G.; Henrichs, M.; Hewitt, M.; Su, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 255.
- (45) (a) Hartwell, G. E.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4625. (b) McKeever, L. D.; Waack, R. *J. Am. Chem. Soc., Chem. Commun.* **1969**, *750*.
- (46) Thomas, R. D.; Clarke, M. T.; Jensen, R. M.; Young, T. C. *Organometallics* **1986**, *5*, 1851.
- (47) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371.
- (48) Bates, T. F.; Clarke, M. T.; Thomas, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5109.
- (49) (a) Bauer, W.; Hampel, F. *J. Am. Chem. Soc., Chem. Commun.* **1992**, *903*. (b) Bauer, W.; Griesinger, C. *J. Am. Chem. Soc.* **1993**, *115*, 10871.
- (50) (a) Sorger, K.; Bauer, W.; Schleyer, P. v. R.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1594. (b) Braun, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 430.
- (51) (a) Knorr, R.; Freudenreich, J.; Polborn, K.; Nöth, H.; Linti, G. *Tetrahedron* **1994**, *50*, 5845. (b) Polt, R. L.; Stork, G.; Carpenter, G. B.; Williard, P. G. *J. Am. Chem. Soc.* **1984**, *106*, 4276.
- (52) Gassman, P. G.; Valcho, J. J.; Proehl, G. S.; Cooper, C. F. *J. Am. Chem. Soc.* **1980**, *102*, 6519.
- (53) Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *J. Am. Chem. Soc.* **1997**, *119*, 1072.
- (54) (a) Schubert, B.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 496. (b) Schubert, B.; Weiss, E. *Chem. Ber.* **1983**, *116*, 3212.
- (55) Geissler, M.; Kopf, J.; Schubert, B.; Weiss, E.; Neugebauer, W.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 587.
- (56) Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1972.
- (57) Hässig, R.; Seebach, D. *Helv. Chim. Acta* **1983**, *66*, 2269.

- (58) Fraenkel, G.; Pramanik, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1527.
- (59) (a) Thompson, A.; Corley, E. G.; Huntington, M. F.; Grabowski, E. J. J.; Remenar, J. F.; Collum, D. B. *J. Am. Chem. Soc.* **1998**, 120, 2028. (b) Briggs, T. F.; Winemiller, M. D.; Collum, D. B.; Parsons, R. L.; Davulcu, A. H., Jr.; Harris, G. D.; Fortunak, J. M.; Confalone, P. N. *J. Am. Chem. Soc.* **2004**, 126, 5427. (c) Qu, B.; Collum, D. B. *J. Org. Chem.* **2006**, 71, 7117.
- (60) Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1983**, 105, 5320.
- (61) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, 111, 3157.
- (62) Schümann, U.; Kopf, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 215.
- (63) Dinnebier, R. E.; Behrens, U.; Olbrich, F. *J. Am. Chem. Soc.* **1998**, 120, 1430.
- (64) (a) Ladd, J. A. *Spectrochim. Acta* **1966**, 22, 1157. (b) Ladd, J. A.; Parker, J. *J. Organomet. Chem.* **1971**, 28, 1. (c) Fraenkel, G.; Adams, D. G.; Dean, R. R. *J. Phys. Chem.* **1968**, 72, 944. (d) Jones, A. J.; Grant, D. M.; Russell, J. G.; Fraenkel, G. *J. Phys. Chem.* **1969**, 73, 1624.
- (65) Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1984**, 106, 4627.
- (66) Eppers, O.; Günther, H. *Helv. Chim. Acta* **1992**, 75, 2553.
- (67) Reich, H. J.; Green, D. P.; Medina, M. A.; Goldenberg, W. S.; Guðmundsson, B. Ö.; Dykstra, R. R.; Phillips, N. H. *J. Am. Chem. Soc.* **1998**, 120, 7201.
- (68) Wehman, E.; Jastrzebski, J. T. B. H.; Ernsting, J.-M.; Grove, D. M.; van Koten, G. *J. Organomet. Chem.* **1988**, 353, 133.
- (69) Sott, R.; Häkansson, M.; Hilmersson, G. *Organometallics* **2006**, 25, 6047.
- (70) (a) Fraenkel, G.; Dayagi, S.; Kobayashi, S. *J. Phys. Chem.* **1968**, 72, 953. (b) Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, 4, 2117. (c) Fraenkel, G.; Subramanian, S.; Chow, A. *J. Am. Chem. Soc.* **1995**, 117, 6300. (d) Ruhlandt-Senge, K.; Ellison, J. J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, 115, 11353.
- (71) (a) Schiemenz, B.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 2150. (b) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, 119, 2847. (c) Hardman, N. J.; Twamley, B.; Stender, M.; Baldwin, R.; Hino, S.; Schiemenz, B.; Kauzlarich, S. M.; Power, P. P. *J. Organomet. Chem.* **2002**, 643–644, 461.
- (72) (a) Dietrich, H.; Mahdi, W.; Stork, W. *J. Organomet. Chem.* **1988**, 349, 1. (b) Wehman, E.; Jastrzebski, J. T. B. H.; Ernsting, J.-M.; Grove, D. M.; van Koten, G. *J. Organomet. Chem.* **1988**, 353, 145. (c) Wheatley, A. E. H. *Eur. J. Inorg. Chem.* **2003**, 3291. (d) Reich, H. J.; Goldenberg, W. S.; Sanders, A. W.; Jantzi, K. L.; Tzschucke, C. C. *J. Am. Chem. Soc.* **2003**, 125, 3509. (e) Gossage, R. A.; Jastrzebski, J. T. B. H.; van Koten, G. *Angew. Chem., Int. Ed.* **2005**, 44, 1448. (f) Kronenburg, C. M. P.; Rijnberg, E.; Jastrzebski, J. T. B. H.; Kooijman, H.; Lutz, M.; Spek, A. L.; Gossage, R. A.; van Koten, G. *Chem.—Eur. J.* **2005**, 11, 253.
- (73) (a) Waack, R.; Doran, M. A.; Baker, E. B.; Olah, G. A. *J. Am. Chem. Soc.* **1966**, 88, 1272. (b) McKeever, L. D.; Waack, R. *J. Organomet. Chem.* **1971**, 28, 145. (c) Takahashi, K.; Kondo, Y.; Asami, R.; Inoue, Y. *Org. Magn. Res.* **1974**, 6, 580. (d) Bywater, S.; Lachance, P.; Worsfold, D. *J. Phys. Chem.* **1975**, 79, 2148.
- (74) Patterson, S. P.; Karle, I. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, 92, 1150.
- (75) Hage, M.; Ogle, C. A.; Rathman, T. L.; Hubbard, J. L. *Main Group Met. Chem.* **1998**, 21, 777.
- (76) Zarges, W.; Marsch, M.; Harms, K.; Boche, G. *Chem. Ber.* **1989**, 122, 2303.
- (77) (a) Arnold, J.; Knapp, V.; Schmidt, J. A. R.; Shafir, A. *J. Chem. Soc., Dalton Trans.* **2002**, 3273. (b) Davidson, M. G.; Garcia-Vivo, D.; Kennedy, A. R.; Mulvey, R. E.; Robertson, S. D. *Chem.—Eur. J.* **2011**, 17, 3364.
- (78) (a) Zarges, W.; Marsch, M.; Harms, K.; Koch, W.; Frenking, G.; Boche, G. *Chem. Ber.* **1991**, 124, 543. (b) Fraenkel, G.; Duncan, J. H.; Martin, K.; Wang, J. *J. Am. Chem. Soc.* **1999**, 121, 10538.
- (79) Brooks, J. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, 94, 7333.
- (80) Bartlett, R. A.; Dias, H. V. R.; Power, P. P. *J. Organomet. Chem.* **1988**, 341, 1.
- (81) Sandel, V. R.; Freedman, H. H. *J. Am. Chem. Soc.* **1963**, 85, 2328.
- (82) Fraenkel, G.; Martin, K. V. *J. Am. Chem. Soc.* **1995**, 117, 10336.
- (83) (a) Hoffmann, R. W.; Rühl, T.; Chemla, F.; Zahneisen, T. *Liebigs Ann. Chem.* **1992**, 719. (b) Hoffmann, R. W.; Rühl, T.; Harbach, J. *Liebigs Ann. Chem.* **1992**, 725. (c) Ruhland, T.; Hoffmann, R. W.; Schade, S.; Boche, G. *Chem. Ber.* **1995**, 128, 551. (d) Strohmann, C.; Lehmen, K.; Wild, K.; Schildbach, D. *Organometallics* **2002**, 21, 3079.
- (84) (a) Schade, S.; Boche, G. *J. Organomet. Chem.* **1998**, 550, 359. (b) Schade, S.; Boche, G. *J. Organomet. Chem.* **1998**, 550, 381. (c) Kühnen, M.; Günther, H.; Amoureaux, J.-P.; Fernández, C. *Magn. Reson. Chem.* **2002**, 40, 24.
- (85) Köster, H.; Weiss, E. *Chem. Ber.* **1982**, 115, 3422.
- (86) Schümann, U.; Weiss, E.; Dietrich, H.; Mahdi, W. *J. Organomet. Chem.* **1987**, 322, 299.
- (87) (a) Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1961**, 26, 4797. (b) West, P.; Purmort, J. I.; McKinley, S. V. *J. Am. Chem. Soc.* **1968**, 90, 797. (c) Brownstein, S.; Bywater, S.; Worsfold, D. *J. J. Organomet. Chem.* **1980**, 199, 1.
- (88) (a) Johnson, C. S., Jr.; Weiner, M. A.; Waugh, J. S.; Seyferth, D. *J. Am. Chem. Soc.* **1961**, 83, 1306. (b) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, 101, 5459. (c) Neugebauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1980**, 198, C1. (d) Stähle, M.; Schlosser, M. *J. Organomet. Chem.* **1981**, 220, 277. (e) Benn, R.; Rufinska, A. *J. Organomet. Chem.* **1982**, 239, C19. (f) Ahlbrecht, H.; Zimmermann, K.; Boche, G.; Decher, G. *J. Organomet. Chem.* **1984**, 262, 1.
- (89) Winchester, W. R.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 177.
- (90) (a) Seyferth, D.; Jula, T. F. *J. Organomet. Chem.* **1967**, 8, P13. (b) Burley, J. W.; Young, R. N. *J. Chem. Soc. B: Phys. Org.* **1971**, 1018. (c) Bates, R. B.; Beavers, W. A. *J. Am. Chem. Soc.* **1974**, 96, 5001. (d) Fraenkel, G.; Halasa, A. F.; Mochel, V.; Stumpe, R.; Tate, D. *J. Org. Chem.* **1985**, 50, 4563. (e) Fraenkel, G.; Winchester, W. R. *J. Am. Chem. Soc.* **1989**, 111, 3794. (f) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, 112, 2582. (g) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, 112, 1382. (h) Boche, G.; Fraenkel, G.; Cabral, J.; Harms, K.; van Eikema Hommes, N. J. R.; Lohrenz, J.; Marsch, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, 114, 1562. (i) Balzer, H.; Berger, S. *Chem. Ber.* **1992**, 125, 733. (j) Cabral, J.; Fraenkel, G. *J. Am. Chem. Soc.* **1992**, 114, 9067. (k) Fraenkel, G.; Winchester, W. R. *Organometallics* **1990**, 9, 1314. (l) Fraenkel, G.; Cabral, J. A. *J. Am. Chem. Soc.* **1993**, 115, 1551. (m) Fraenkel, G.; Qiu, F. *J. Am. Chem. Soc.* **1996**, 118, 5828. (n) Fraenkel, G.; Qiu, F. *J. Am. Chem. Soc.* **1997**, 119, 3571. (o) Fraenkel, G.; Cabral, J.; Lanter, C.; Wang, J. *J. Org. Chem.* **1999**, 64, 1302. (p) Fraenkel, G.; Duncan, J. H.; Wang, J. *J. Am. Chem. Soc.* **1999**, 121, 432. (q) Fraenkel, G.; Qiu, F. *J. Am. Chem. Soc.* **2000**, 122, 12806. (r) Fraenkel, G.; Chow, A.; Fleischer, R.; Liu, H. *J. Am. Chem. Soc.* **2004**, 126, 3983. (s) Fraenkel, G.; Liu, H. *J. Am. Chem. Soc.* **2004**, 126, 5202. (t) Fraenkel, G.; Gallucci, J.; Liu, H. *J. Am. Chem. Soc.* **2006**, 128, 8211. (u) Fraenkel, G.; Chen, X.; Gallucci, J.; Ren, Y. *J. Am. Chem. Soc.* **2008**, 130, 4140.
- (91) (a) Collum, D. B. *Acc. Chem. Res.* **1992**, 25, 448. (b) Jones, A. C.; Sanders, A. W.; Bevan, M. J.; Reich, H. J. *J. Am. Chem. Soc.* **2007**, 129, 3492. (c) Collum, D. B.; McNeil, A. J.; Ramirez, A. *Angew. Chem., Int. Ed.* **2007**, 46, 3002.
- (92) Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *J. Am. Chem. Soc.* **1991**, 113, 8187.
- (93) Bernstein, M. P.; Romesberg, F. E.; Fuller, D. J.; Harrison, A. T.; Collum, D. B.; Liu, Q.-Y.; Williard, P. G. *J. Am. Chem. Soc.* **1992**, 114, 5100.
- (94) Williard, P. G.; Salvino, J. M. *J. Org. Chem.* **1993**, 58, 1.
- (95) (a) Rogers, R. D.; Atwood, J. L.; Grüning, R. J. *Organomet. Chem.* **1978**, 157, 229. (b) Mootz, D.; Zinnius, A.; Böttcher, B. *Angew. Chem., Int. Ed.* **1969**, 8, 378.
- (96) (a) Engelhardt, L. M.; May, A. S.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1671. (b) Lappert, M. F.; Slade, M. J.;

- Singh, A.; Atwood, J. L.; Rogers, R. D.; Shakir, R. *J. Am. Chem. Soc.* **1983**, *105*, 302. (c) Engelhardt, L. M.; Jolly, B. S.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1986**, *39*, 1337.
- (97) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Rodger, P. J. A.; Rowlings, R. B. *J. Chem. Soc., Dalton Trans.* **2001**, 1477.
- (98) Power, P. P.; Xiaojie, X. *J. Chem. Soc., Chem. Commun.* **1984**, 358.
- (99) Williard, P. G.; Liu, Q.-Y. *J. Am. Chem. Soc.* **1993**, *115*, 3380.
- (100) Barr, D.; Clegg, W.; Hodgson, S. M.; Lamming, G. R.; Mulvey, R. E.; Scott, A. J.; Snaith, R.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1241.
- (101) (a) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 285. (b) Armstrong, D. R.; Mulvey, R. E.; Walker, G. T.; Barr, D.; Snaith, R.; Clegg, W.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1988**, 617.
- (102) Clegg, W.; Liddle, S. T.; Mulvey, R. E.; Robertson, A. *Chem. Commun.* **1999**, 511.
- (103) Barnett, N. D. R.; Clegg, W.; Horsburgh, L.; Lindsay, D. M.; Liu, Q.-Y.; Mackenzie, F. M.; Mulvey, R. E.; Williard, P. G. *Chem. Commun.* **1996**, 2321.
- (104) (a) Armstrong, D. R.; Barr, D.; Clegg, W.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 869. (b) Armstrong, D. R.; Barr, D.; Clegg, W.; Hodgson, S. M.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wright, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 4719.
- (105) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1987**, 716.
- (106) Kennedy, A. R.; Klett, J.; O'Hara, C. T.; Mulvey, R. E.; Robertson, G. M. *Eur. J. Inorg. Chem.* **2009**, 5029.
- (107) Boche, G.; Marsch, M.; Harms, K. *Angew. Chem.* **1986**, *98*, 373.
- (108) (a) van Vliet, G. L. J.; de Kanter, F. J. J.; Schakel, M.; Klumpp, G. W.; Spek, A. L.; Lutz, M. *Chem.—Eur. J.* **1999**, *5*, 1091. (b) van Vliet, G. L. J.; Luitjes, H.; Schakel, M.; Klumpp, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 1643.
- (109) Kim, Y.-J.; Bernstein, M. P.; Galiano-Roth, A. S.; Romesberg, F. E.; Williard, P. G.; Fuller, D. J.; Harrison, A. T.; Collum, D. B. *J. Org. Chem.* **1991**, *56*, 4435.
- (110) (a) Galiano-Roth, A. S.; Collum, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 6772. (b) Li, D.; Keresztes, I.; Hopson, R.; Williard, P. G. *Acc. Chem. Res.* **2009**, *42*, 270. (c) Li, D.; Hopson, R.; Li, W.; Liu, J.; Williard, P. G. *Org. Lett.* **2008**, *10*, 909.
- (111) Remenar, J. F.; Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1997**, *119*, 5567.
- (112) Rutherford, J. L.; Collum, D. B. *J. Am. Chem. Soc.* **2001**, *123*, 199.
- (113) (a) Romesberg, F. E.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5751. (b) Ma, Y.; Ramirez, A.; Singh, K. J.; Keresztes, I.; Collum, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 15399.
- (114) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1995**, *117*, 9863.
- (115) Romesberg, F. E.; Bernstein, M. P.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 3475.
- (116) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 6009.
- (117) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1996**, *118*, 2217.
- (118) (a) Collum, D. B. *Acc. Chem. Res.* **1993**, *26*, 227. (b) Lucht, B. L.; Bernstein, M. P.; Remenar, J. F.; Collum, D. B. *J. Am. Chem. Soc.* **1996**, *118*, 10707.
- (119) Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 794.
- (120) Renaud, P.; Fox, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 5702.
- (121) Armstrong, D. R.; Garcia-Alvarez, P.; Kennedy, A. R.; Mulvey, R. E.; Robertson, S. D. *Chem.—Eur. J.* **2011**, *17*, 6725.
- (122) (a) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 7949. (b) Remenar, J. F.; Lucht, B. L.; Kruglyak, D.; Romesberg, F. E.; Gilchrist, J. H.; Collum, D. B. *J. Org. Chem.* **1997**, *62*, 5748.
- (123) Romesberg, F. E.; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 2112.
- (124) Galiano-Roth, A. S.; Michaelides, E. M.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2658.
- (125) Aubrecht, K. B.; Collum, D. B. *J. Org. Chem.* **1996**, *61*, 8674.
- (126) Sakuma, K.; Gilchrist, J. H.; Romesberg, F. E.; Cajthami, C. E.; Collum, D. B. *Tetrahedron Lett.* **1993**, *34*, 5213.
- (127) Rutherford, J. L.; Collum, D. B. *J. Am. Chem. Soc.* **1999**, *121*, 10198.
- (128) Aubrecht, K. B.; Lucht, B. L.; Collum, D. B. *Organometallics* **1999**, *18*, 2981.
- (129) Carlier, P. R.; Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 11602.
- (130) Grotjahn, D. B.; Sheridan, P. M.; Al Jihad, I.; Ziurys, L. M. *J. Am. Chem. Soc.* **2001**, *123*, 5489.
- (131) See, for instance: (a) Whitesell, J. K.; Felman, S. W. *J. Org. Chem.* **1980**, *45*, 755. (b) Cox, P. J.; Simpkins, N. S. *Tetrahedron: Asymmetry* **1991**, *2*, 1. (c) Bunn, B. J.; Simpkins, N. S. *J. Org. Chem.* **1993**, *58*, 533. (d) Koga, K. *Pure Appl. Chem.* **1994**, *66*, 1487. (e) Simpkins, N. S. *Pure Appl. Chem.* **1996**, *68*, 691. (f) Hodgson, D. M.; Gibbs, A. R.; Lee, G. P. *Tetrahedron* **1996**, *52*, 14361. (g) O'Brien, P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1439.
- (132) See, for instance: (a) Eleveld, M. B.; Hogeweine, H. *Tetrahedron Lett.* **1984**, *25*, 5187. (b) Arvidsson, P. I.; Davidsson, Ö.; Hilmersson, G. *Tetrahedron: Asymmetry* **1999**, *10*, 527. (c) Granander, J.; Sott, R.; Hilmersson, G. *Tetrahedron: Asymmetry* **2003**, *14*, 439. (d) Harrison-Marchand, A.; Valnot, J.-Y.; Corruble, A.; Duguet, N.; Oulyadi, H.; Desjardins, S.; Fressigné, C.; Maddaluno, J. *Pure Appl. Chem.* **2006**, *78*, 321. (e) Duguet, N.; Petit, S. M.; Marchand, P.; Harrison-Marchand, A.; Maddaluno, J. *J. Org. Chem.* **2008**, *73*, 5397.
- (133) (a) Juaristi, E.; Beck, A. K.; Hansen, J.; Matt, T.; Mukhopadhyay, T.; Simson, M.; Seebach, D. *Synthesis* **1993**, 1271. (b) Duguet, N.; Harrison-Marchand, A.; Maddaluno, J.; Tomioka, K. *Org. Lett.* **2006**, *8*, 5745.
- (134) Edwards, A. J.; Hockey, S.; Mair, F. S.; Raithby, P. R.; Snaith, R.; Simpkins, N. S. *J. Org. Chem.* **1993**, *58*, 6942.
- (135) Armstrong, D. R.; Henderson, K. W.; Kennedy, A. R.; Kerr, W. J.; Mair, F. S.; Moir, J. H.; Moran, P. H.; Snaith, R. *J. Chem. Soc., Dalton Trans.* **1999**, 4063.
- (136) Andrews, P. C.; Duggan, P. J.; Maguire, M.; Nichols, P. J. *Chem. Commun.* **2001**, 53.
- (137) Sato, D.; Kawasaki, H.; Shimada, I.; Arata, Y.; Okamura, K.; Date, T.; Koga, K. *J. Am. Chem. Soc.* **1992**, *114*, 761.
- (138) (a) Hilmersson, G.; Davidsson, Ö. *J. Org. Chem.* **1995**, *60*, 7660. (b) Hilmersson, G.; Davidsson, Ö. *J. Organomet. Chem.* **1995**, *489*, 175. (c) Hilmersson, G.; Arvidsson, P. I.; Davidsson, Ö.; Häkansson, M. *Organometallics* **1997**, *16*, 3352. (d) Hilmersson, G.; Arvidsson, P. I.; Davidsson, Ö.; Häkansson, M. *J. Am. Chem. Soc.* **1998**, *120*, 8143. (e) Hilmersson, G. *Chem.—Eur. J.* **2000**, *6*, 3069. (f) Arvidsson, P. I.; Davidsson, Ö. *Angew. Chem., Int. Ed.* **2000**, *39*, 1467. (g) Pettersen, D.; Amedjkouh, M.; Nilsson Lill, S. O.; Ahlberg, P. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1397. (h) Sott, R.; Granander, J.; Dinér, P.; Hilmersson, G. *Tetrahedron: Asymm.* **2004**, *15*, 267. (i) Dinér, P. *Tetrahedron: Asymmetry* **2010**, *21*, 2733. (j) Kagan, G.; Li, W.; Li, D.; Hopson, R.; Williard, P. G. *J. Am. Chem. Soc.* **2011**, *133*, 6596. (k) Rönnholm, P.; Hilmersson, G. *ARKIVOC* (Gainesville, FL, U. S.) **2011**, 200.
- (139) Johansson, A.; Pettersson, A.; Davidsson, Ö. *J. Organomet. Chem.* **2000**, *608*, 153.
- (140) (a) Khan, A. Z.-Q.; de Groot, R. W.; Arvidsson, P. I.; Davidsson, Ö. *Tetrahedron: Asymmetry* **1998**, *9*, 1223. (b) Arvidsson, P. I.; Hilmersson, G.; Ahlberg, P. *J. Am. Chem. Soc.* **1999**, *121*, 1883. (c) Olsson, R. I.; Ahlberg, P. *Tetrahedron: Asymmetry* **1999**, *10*, 3991.
- (141) (a) Corruble, A.; Valnot, J.-Y.; Maddaluno, J.; Prigent, Y.; Davoust, D.; Duhamel, P. *J. Am. Chem. Soc.* **1997**, *119*, 10042. (b) Yuan, Y.; Desjardins, S.; Harrison-Marchand, A.; Oulyadi, H.; Fressigné, C.; Giessner-Prettre, C.; Maddaluno, J. *Tetrahedron* **2005**, *61*, 3325.
- (142) (a) Bains, M. S. *Can. J. Chem.* **1964**, *42*, 945. (b) Talalaeva, T. V.; Tsareva, G. V.; Simonov, A. P.; Kocheshkov, K. A. *Russ. Chem. Bull.* **1964**, *13*, 595. (c) Kamiensky, C. W.; Lewis, D. H. *J. Org. Chem.* **1965**, *30*, 3498.

- (143) (a) Wheatley, P. J. *Nature* **1960**, *185*, 681. (b) Wheatley, P. J. *J. Am. Chem. Soc.* **1960**, *82*, 4270. (c) Weiss, E.; Büchner, W. *Angew. Chem., Int. Ed.* **1964**, *3*, 152.
- (144) Starikova, Z. A.; Turevskaya, E. P.; Turova, N. Y.; Yanovsky, A. I. *J. Chem. Soc., Dalton Trans.* **2000**, *3237*.
- (145) (a) Chisholm, M. H.; Drake, S. R.; Naiini, A. A.; Streib, W. E. *Polyhedron* **1991**, *10*, 805. (b) Nekola, H.; Olbrich, F.; Behrens, U. Z. *Anorg. Allg. Chem.* **2002**, *628*, 2067.
- (146) Allan, J. F.; Nassar, R.; Specht, E.; Beatty, A.; Calin, N.; Henderson, K. W. *J. Am. Chem. Soc.* **2004**, *126*, 484.
- (147) Simonov, A. P.; Bessonov, V. A.; Shapiro, I. O.; Shigorin, D. N. *Theor. Exp. Chem.* **1966**, *2*, 602.
- (148) Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *J. Am. Chem. Soc.* **1996**, *118*, 12183.
- (149) (a) Hvoslef, J.; Hope, H.; Murray, B. D.; Power, P. P. *J. Am. Chem. Soc., Chem. Commun.* **1983**, *1438*. (b) Beck, G.; Hitchcock, P. B.; Lappert, M. F.; MacKinnon, I. A. *J. Am. Chem. Soc., Chem. Commun.* **1989**, *1312*.
- (150) (a) Williard, P. G.; Salvino, J. M. *Tetrahedron Lett.* **1985**, *26*, 3931. (b) Arnett, E. M.; Nichols, M. A.; McPhail, A. T. *J. Am. Chem. Soc.* **1990**, *112*, 7059. (c) Nichols, M. A.; McPhail, A. T.; Arnett, E. M. *J. Am. Chem. Soc.* **1991**, *113*, 6222.
- (151) Strohmann, C.; Seibel, T.; Schildbach, D. *J. Am. Chem. Soc.* **2004**, *126*, 9876.
- (152) Armstrong, D. R.; Davies, J. E.; Davies, R. P.; Raithby, P. R.; Snaith, R.; Wheatley, A. E. H. *New. J. Chem.* **1999**, *35*.
- (153) (a) Jackman, L. M.; Lange, B. C. *Tetrahedron* **1977**, *33*, 2737. (b) Jackman, L. M.; DeBrosse, C. W. *J. Am. Chem. Soc.* **1983**, *105*, 4177. (c) Jackman, L. M.; Smith, B. D. *J. Am. Chem. Soc.* **1988**, *110*, 3829. (d) Jackman, L. M.; Petrei, M. M.; Smith, B. D. *J. Am. Chem. Soc.* **1991**, *113*, 3451. (e) Jackman, L. M.; Rakiewicz, E. F.; Benesi, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 4101. (f) Jackman, L. M.; Cizmeciyani, D.; Williard, P. G.; Nichols, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 6262.
- (154) (a) Shobatake, K.; Nakamoto, K. *Inorg. Chim. Acta* **1970**, *4*, 485. (b) Cole, M. L.; Junk, P. C.; Proctor, K. M.; Scott, J. L.; Strauss, C. R. *Dalton Trans.* **2006**, *3338*.
- (155) (a) Cetinkaya, B.; Gümrükçü, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086. (b) Kociok-Köhn, G.; Pickardt, J.; Schumann, H. *Acta Crystallogr.* **1991**, *C47*, 2649. (c) Vilardo, J. S.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1998**, *17*, 769. (d) van der Schaaf, P. A.; Hogerheide, M. P.; Grove, D. M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc., Chem. Commun.* **1992**, *1703*. (e) van der Schaaf, P. A.; Jastrzebski, J. T. B. H.; Hogerheide, M. P.; Smeets, W. J. J.; Spek, A. L.; Boersma, J.; van Koten, G. *Inorg. Chem.* **1993**, *32*, 4111. (f) Khanjin, N. A.; Menger, F. M. *J. Org. Chem.* **1997**, *62*, 8923. (g) Boyle, T. J.; Pedrotty, D. M.; Alam, T. M.; Vick, S. C.; Rodriguez, M. A. *Inorg. Chem.* **2000**, *39*, 5133. (h) Rosen, T. C.; Kirschbaum, K.; Giolando, D. M. *Inorg. Chem. Acta* **2005**, *358*, 3680. (i) Singh, K. J.; Collum, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 13753.
- (156) De Vries, T. S.; Goswami, A.; Liou, L. R.; Gruver, J. M.; Jayne, E.; Collum, D. B. *J. Am. Chem. Soc.* **2009**, *131*, 13142.
- (157) Gruver, J. M.; Liou, L. R.; McNeil, A. J.; Ramirez, A.; Collum, D. B. *J. Org. Chem.* **2008**, *73*, 7743.
- (158) (a) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624. (b) Valnot, J.-Y.; Maddaluno, J. *Patai Series: The Chemistry of Organolithium Compounds; Rappoport, Z., Marek, I., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 2006; Vol. 2, Chapter 8, p 525.*
- (159) Wen, J. Q.; Grutzner, J. B. *J. Org. Chem.* **1986**, *51*, 4220.
- (160) (a) Amstutz, R.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2617. (b) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 3345. (c) Laube, T.; Dunitz, J. D.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1373. (d) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 462. (e) Pospisil, P. J.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1992**, *114*, 7585.
- (161) (a) Suzuki, M.; Koyama, H.; Noyori, R. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 259. (b) Suzuki, M.; Koyama, H.; Noyori, R. *Tetrahedron* **2004**, *60*, 1571. (c) Liou, L. R.; McNeil, A. J.; Ramirez, A.; Toombes, G. E. S.; Gruver, J. M.; Collum, D. B. *J. Am. Chem. Soc.* **2008**, *130*, 4859. (d) Biddle, M. M.; Reich, H. J. *J. Org. Chem.* **2006**, *71*, 4031.
- (e) Kolonko, K. J.; Biddle, M. M.; Guzei, I. A.; Reich, H. J. *J. Am. Chem. Soc.* **2009**, *131*, 11525. (f) Suzuki, M.; Koyama, H.; Noyori, R. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 259.
- (162) Nichols, M. A.; Leposa, C. M.; Hunter, A. D.; Zeller, M. J. *Chem. Crystallogr.* **2007**, *37*, 825.
- (163) (a) Jackman, L. M.; Haddon, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 3687. (b) Jackman, L. M.; Szeverenyi, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 4954. (c) Jackman, L. M.; Lange, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 4494. (d) Jackman, L. M.; Scarmoutzos, L. M.; DeBrosse, C. W. *J. Am. Chem. Soc.* **1987**, *109*, 5355.
- (164) (a) Abbotto, A.; Streitwieser, A. *J. Am. Chem. Soc.* **1995**, *117*, 6358. (b) Abu-Hasanayn, F.; Stratakis, M.; Streitwieser, A. *J. Org. Chem.* **1995**, *60*, 4688. (c) Abbotto, A.; Leung, S. S.-W.; Streitwieser, A.; Kilway, K. V. *J. Am. Chem. Soc.* **1998**, *120*, 10807. (d) Streitwieser, A.; Leung, S. S.-W.; Kim, Y.-J. *Org. Lett.* **1999**, *1*, 145. (e) Leung, S. S.-W.; Streitwieser, A. *J. Org. Chem.* **1999**, *64*, 3390. (f) Streitwieser, A.; Wang, D. Z.-R. *J. Am. Chem. Soc.* **1999**, *121*, 6213. (g) Streitwieser, A.; Juaristi, E.; Kim, Y.-J.; Pugh, J. K. *Org. Lett.* **2000**, *2*, 3739.
- (165) (a) Goto, M.; Akimoto, K.-I.; Aoki, M.; Shindo, M.; Koga, K. *Tetrahedron Lett.* **1999**, *40*, 8129. (b) Wang, D. Z.; Kim, Y.-J.; Streitwieser, A. *J. Am. Chem. Soc.* **2000**, *122*, 10754.
- (166) Waldmüller, D.; Mayer, B.; Braun, M.; Hanuschik, A.; Krüger, C.; Guenot, P. *Chem. Ber.* **1992**, *125*, 2779.
- (167) Jastrzebski, J. T. B. H.; van Koten, G.; Christophersen, M. J. N.; Stam, C. H. *J. Organomet. Chem.* **1985**, *292*, 319.
- (168) Kagan, G.; Li, W.; Sun, C.; Hopson, R.; Williard, P. G. *J. Org. Chem.* **2011**, *76*, 65.
- (169) Seebach, D.; Amstutz, R.; Laube, T.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5403.
- (170) Jastrzebski, J. T. B. H.; van Koten, G. *Inorg. Chim. Acta* **1988**, *142*, 169.
- (171) Williard, P. G.; Tata, J. R.; Schlessinger, R. H.; Adams, A. D.; Iwanowicz, E. *J. Am. Chem. Soc.* **1988**, *110*, 7901.
- (172) Boche, G.; Langlotz, I.; Marsch, M.; Harms, K. *Chem. Ber.* **1994**, *127*, 2059.
- (173) (a) Wang, J. S.; Jérôme, R.; Warin, R.; Teyssié, P. *Macromolecules* **1993**, *26*, 1402. (b) Wang, J. S.; Jérôme, R.; Warin, R.; Zhang, H.; Teyssié, P. *Macromolecules* **1994**, *27*, 3376.
- (174) (a) McNeil, A. J.; Toombes, G. E. S.; Chandramouli, S. V.; Vanasse, B. J.; Ayers, T. A.; O'Brien, M. K.; Lobkovsky, E.; Gruner, S. M.; Marohn, J. A.; Collum, D. B. *J. Am. Chem. Soc.* **2004**, *126*, 5938. (b) Liou, L. R.; McNeil, A. J.; Toombes, G. E. S.; Collum, D. B. *J. Am. Chem. Soc.* **2008**, *130*, 17334.
- (175) Bauer, W.; Daub, J.; Rapp, K. M. *Chem. Ber.* **1983**, *116*, 1777.
- (176) Bauer, W.; Laube, T.; Seebach, D. *Chem. Ber.* **1985**, *118*, 764.
- (177) (a) Snaith, R.; Wright, D. S. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; p 227. (b) Hevia, E.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 6448.
- (178) Wong, M. K.; Popov, A. I. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3615.
- (179) Ohtaki, H.; Wada, H. *J. Sol. Chem.* **1985**, *14*, 209.
- (180) Raston, C. L.; Whitaker, C. R.; White, A. H. *J. Am. Chem. Soc., Dalton Trans.* **1988**, *991*.
- (181) Raston, C. L.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 341.
- (182) Gingl, F.; Hiller, W.; Strähle, J.; Borgholte, H.; Dehncke, K. Z. *Anorg. Allg. Chem.* **1991**, *606*, 91.
- (183) (a) Schmuck, A.; Leopold, D.; Wallenhauer, S.; Seppelt, K. *Chem. Ber.* **1990**, *123*, 761. (b) Hahn, F. E.; Rupprecht, S. Z. *Naturforsch.* **1991**, *46b*, 143.
- (184) Mitzel, N. W.; Lustig, C. Z. *Naturforsch.* **2001**, *56b*, 443.
- (185) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Am. Chem. Soc., Chem. Commun.* **1984**, *79*.
- (186) Raston, C. L.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 1925.
- (187) Hoffmann, D.; Dorigo, A.; Schleyer, P. v. R.; Reif, H.; Stalke, D.; Sheldrick, G. M.; Weiss, E.; Geissler, M. *Inorg. Chem.* **1995**, *34*, 262.

- (188) Raston, C. L.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 987.
- (189) Durant, F.; Verbist, J.; van Meerssche, M. *Bull. Soc. Chim. Belges* **1966**, 75, 806.
- (190) Durant, F.; Gobillon, Y.; Piret, P.; van Meerssche, M. *Bull. Soc. Chim. Belges* **1966**, 75, 52.
- (191) Fernández, I.; Martínez-Viviente, E.; Breher, F.; Pregosin, P. S. *Chem.—Eur. J.* **2005**, 11, 1495.
- (192) Lecachey, B.; Oulyadi, H.; Lameiras, P.; Harrison-Marchand, A.; Gérard, H.; Maddaluno, J. *J. Org. Chem.* **2010**, 75, 5976.
- (193) Reich, H. J.; Borst, J. P.; Dykstra, R. R.; Green, D. P. *J. Am. Chem. Soc.* **1993**, 115, 8728.
- (194) Raston, C. L.; Robinson, W. T.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1990**, 43, 1163.
- (195) Patalinghug, W. C.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1990**, 43, 635.
- (196) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Crystallogr. Spectrosc. Res.* **1984**, 14, 29.
- (197) Amstutz, R.; Dunitz, J. D.; Laube, T.; Schweizer, W. B.; Seebach, D. *Chem. Ber.* **1986**, 119, 434.
- (198) Raston, C. L.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1989**, 42, 201.
- (199) (a) Hall, S. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1983**, 22, 4070. (b) Davidson, M. G.; Snaith, R.; Stalke, D.; Wright, D. S. *J. Org. Chem.* **1993**, 58, 2810.
- (200) Barr, D.; Doyle, M. J.; Mulvey, R. E.; Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1989**, 318.
- (201) Neumann, F.; Hampel, F.; Schleyer, P. v. R. *Inorg. Chem.* **1995**, 34, 6553.
- (202) Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Russel, C. A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1993**, 3265.
- (203) Raston, C. L.; Whitaker, C. R.; White, A. H. *Inorg. Chem.* **1989**, 28, 163.
- (204) Desjardins, S.; Flinois, K.; Oulyadi, H.; Davoust, D.; Giessner-Prettre, C.; Parisel, O.; Maddaluno, J. *Organometallics* **2003**, 22, 4090.
- (205) Novak, D. P.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, 94, 3793.
- (206) Nöth, H.; Waldhör, R. Z. *Naturforsch.* **1998**, 53b, 1525.
- (207) Brym, M.; Jones, C.; Junk, P. C.; Kloth, M. Z. *Anorg. Allg. Chem.* **2006**, 632, 1402.
- (208) Doria, C.; Köppen, R.; Baum, E.; Stösser, G.; Köhnlein, H.; Schnöckel, H. *Inorg. Chem.* **2000**, 39, 1534.
- (209) (a) Weiss, E.; Sauermann, G.; Thirase, G. *Chem. Ber.* **1983**, 116, 74. (b) Weiss, E.; Corbelin, S.; Cockcroft, J. K.; Fitch, A. N. *Chem. Ber.* **1990**, 123, 1629.
- (210) Weiss, E.; Sauermann, G. *J. Organomet. Chem.* **1970**, 21, 1.
- (211) (a) Schade, C.; Bauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, 295, C25. (b) Pi, R.; Bauer, W.; Brix, B.; Schade, C.; Schleyer, P. v. R. *J. Organomet. Chem.* **1986**, 306, C1.
- (212) (a) Schümann, U.; Behrens, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1989**, 28, 476. (b) den Besten, R.; Brandsma, L.; Spek, A. L.; Kanters, J. A.; Veldman, N. *J. Organomet. Chem.* **1995**, 498, C6.
- (213) Schade, C.; Schleyer, P. v. R.; Dietrich, H.; Mahdi, W. *J. Am. Chem. Soc.* **1986**, 108, 2484.
- (214) Zalkin, A.; Templeton, D. H. *J. Phys. Chem.* **1956**, 60, 821.
- (215) Lorenzen, N. P.; Kopf, J.; Olbrich, F.; Schümann, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 1441.
- (216) Andrews, P. C.; Armstrong, D. R.; Clegg, W.; MacGregor, M.; Mulvey, R. E. *J. Chem. Soc., Chem. Commun.* **1991**, 497.
- (217) (a) Weiss, E. *Z. Anorg. Allg. Chem.* **1964**, 332, 197. (b) Chandran, K.; Nithya, R.; Sankaran, K.; Gopalan, A.; Ganesan, V. *Bull. Mater. Sci.* **2006**, 29, 173.
- (218) Schmidt, P.; Lochmann, L.; Schneider, B. *J. Mol. Struct.* **1971**, 9, 403.
- (219) (a) Kunert, M.; Dinjus, E.; Nauck, M.; Sieler, J. *Chem. Ber.* **1997**, 130, 1461. (b) Fraser, M. E.; Fortier, S.; Markiewicz, M. K.; Rodrigue, A.; Bovenkamp, J. W. *Can. J. Chem.* **1987**, 65, 2558.
- (220) (a) Cambillau, C.; Bram, G.; Corset, J.; Riche, C. *Can. J. Chem.* **1982**, 60, 2554. (b) Hevia, E.; Henderson, K. W.; Kennedy, A. R.; Mulvey, R. E. *Organometallics* **2006**, 25, 1778.
- (221) Mulvey, R. E.; Clegg, W.; Barr, D.; Snaith, R. *Polyhedron* **1986**, 5, 2109.
- (222) (a) Weiss, E.; Sauermann, G. *Angew. Chem., Int. Ed.* **1968**, 7, 133. (b) Weiss, E.; Sauermann, G. *Chem. Ber.* **1970**, 103, 265. (c) Weiss, E.; Lambertsen, T.; Schubert, B.; Cockcroft, J. K. *J. Organomet. Chem.* **1988**, 358, 1.
- (223) Weiss, E. *Helv. Chim. Acta* **1963**, 46, 2051.
- (224) Greiser, T.; Weiss, E. *Chem. Ber.* **1979**, 112, 844.
- (225) Chisholm, M. H.; Drake, S. R.; Naiini, A. A.; Streib, W. E. *Polyhedron* **1991**, 10, 337.
- (226) Dinnebier, R. E.; Pink, M.; Sieler, J.; Norby, P.; Stephens, P. W. *Inorg. Chem.* **1998**, 37, 4996.
- (227) He, X.; Noll, B. C.; Beatty, A.; Mulvey, R. E.; Henderson, K. W. *J. Am. Chem. Soc.* **2004**, 126, 7444.
- (228) (a) Riche, C.; Pascard-Billy, C.; Cambillau, C.; Bram, G. *J. Chem. Soc. Chem. Commun.* **1977**, 183. (b) Cambillau, C.; Bram, G.; Corset, J.; Riche, C.; Pascard-Billy, C. *Tetrahedron* **1978**, 34, 2675. (c) Sarthou, P.; Bram, G.; Guibe, F.; Corset, J. *Tetrahedron* **1980**, 36, 1043.
- (229) For crystallographic and structural data of homoleptic and heteroleptic magnesium compounds, see: (a) Kuhn, N.; Schulten, M.; Boese, R.; Bläser, D. *J. Organomet. Chem.* **1991**, 421, 1. (b) Henderson, K. W.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *J. Organomet. Chem.* **1992**, 439, 237. (c) Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1994**, 465, 1. (d) Henderson, K. W.; Mulvey, R. E.; Dorigo, A. E. *J. Organomet. Chem.* **1996**, 518, 139. (e) Teng, W.; Englisch, U.; Ruhlandt-Senge, K. *Inorg. Chem.* **2000**, 39, 3875. (f) Vargas, W.; Englisch, U.; Ruhlandt-Senge, K. *Inorg. Chem.* **2002**, 41, 5602. (g) Westerhausen, M.; Bollwein, T.; Makropoulos, N.; Piotrowski, H. *Inorg. Chem.* **2005**, 44, 6439. (h) Tang, Y.; Zakharov, L. N.; Rheingold, A. L.; Kemp, R. A. *Organometallics* **2005**, 24, 836. (i) Squiller, E. P.; Pajerski, A. D.; Whittle, R. R.; Richey, H. G., Jr. *Organometallics* **2006**, 25, 2465. (j) Jastrzebski, J. T. B. H.; Boersma, J.; Van Koten, G. *Pataï Series: The Chemistry of Organomagnesium Compounds; Rappoport, Z., Marek, I., Eds.; John Wiley & Sons, Ltd: New York, 2008; Vol. 1, p 1.* (k) Jiménez-Halla, J. O. C.; Bickelhaupt, F. M.; Solà, M. *J. Organomet. Chem.* **2011**, 696, 4104.
- (230) (a) Weiss, E. *J. Organomet. Chem.* **1964**, 2, 314. (b) Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1970**, 22, 241. (c) Kress, J.; Bougeard, D.; Novak, A. *Spectrochim. Acta* **1977**, 33A, 161. (d) Greiser, T.; Kopf, J.; Thoenes, D.; Weiss, E. *J. Organomet. Chem.* **1980**, 191, 1. (e) Viebrock, H.; Weiss, E. *J. Organomet. Chem.* **1994**, 464, 121. (f) Yousef, R. I.; Walforth, B.; Rüffer, T.; Wagner, C.; Schmidt, H.; Herzog, R.; Steinborn, D. *J. Organomet. Chem.* **2005**, 690, 1178.
- (231) (a) Weiss, E. *J. Organomet. Chem.* **1965**, 4, 101. (b) Kress, J.; Novak, A. *J. Organomet. Chem.* **1976**, 121, 7. (c) Pajerski, A. D.; BergStresser, G. L.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, 110, 4844.
- (232) Barnett, N. D. R.; Clegg, W.; Mulvey, R. E.; O'Neil, P. A.; Reed, D. *J. Organomet. Chem.* **1996**, 510, 297.
- (233) Starowieyski, K. B.; Lewinski, J.; Wozniak, R.; Lipkowski, J.; Chrost, A. *Organometallics* **2003**, 22, 2458.
- (234) Geissler, M.; Kopf, J.; Weiss, E. *Chem. Ber.* **1989**, 122, 1395.
- (235) (a) Stucky, G.; Rundle, R. E. *J. Am. Chem. Soc.* **1964**, 86, 4825. (b) Thoenes, D.; Weiss, E. *Chem. Ber.* **1978**, 111, 3381. (c) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Organomet. Chem.* **1990**, 393, 315. (d) Waggoner, K. M.; Power, P. P. *Organometallics* **1992**, 11, 3209. (e) Eriksson, H.; Örtendahl, M.; Håkansson, M. *Organometallics* **1996**, 15, 4823.
- (236) (a) Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Henderson, L. C.; Herber, C.; Liddle, S. T.; Loroño-González, D.; Parkin, A.; Parsons, S. *Chem.—Eur. J.* **2003**, 9, 4820. (b) Schrock, R. R. *J. Organomet. Chem.* **1976**, 122, 209.
- (237) (a) Bradley, D. C.; Hursthause, M. B.; Ibrahim, A. A.; Malik, K. M. A.; Mottevali, M.; Möseler, R.; Powell, H.; Runnacles, J. D.; Sullivan, A. C. *Polyhedron* **1990**, 9, 2959. (b) Westerhausen, M. *Inorg. Chem.* **1991**, 30, 96. (c) Westerhausen, M.; Schwarz, W. Z. *Organ. Allg. Chem.* **1992**, 609, 39.

- (238) Olmstead, M. M.; Grigsby, W. J.; Chacon, D. R.; Hascall, T.; Power, P. P. *Inorg. Chim. Acta* **1996**, *251*, 273.
- (239) Yang, K.-C.; Chang, C.-C.; Huang, J.-Y.; Lin, C.-C.; Lee, G.-H.; Wang, Y.; Chiang, M. Y. *J. Organomet. Chem.* **2002**, *648*, 176.
- (240) (a) Clegg, W.; Henderson, K. W.; Mulvey, R. E.; O'Neil, P. A. *J. Chem. Soc., Chem. Commun.* **1994**, *769*. (b) Clegg, W.; Craig, F. J.; Henderson, K. W.; Kennedy, A. R.; Mulvey, R. E.; O'Neil, P. A.; Reed, D. *Inorg. Chem.* **1997**, *36*, 6238.
- (241) (a) Schibilla, H.; Le Bihan, M.-T. *Acta Crystallogr.* **1967**, *23*, 332. (b) Pércaud, M.-C.; Le Bihan, M.-T. *Acta Crystallogr.* **1968**, *B24*, 1502. (c) Halut-Desportes, S. *Acta Crystallogr.* **1977**, *B33*, 599. (d) Allan, J. F.; Clegg, W.; Henderson, K. W.; Horsburgh, L.; Kennedy, A. R. *J. Organomet. Chem.* **1998**, *559*, 173.
- (242) Halut-Desportes, S.; Bois, C. *Acta Crystallogr.* **1979**, *B35*, 2205.
- (243) Coates, G. E.; Ridley, D. *J. Chem. Soc. (A)* **1967**, 56.
- (244) Conway, B.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; Weatherstone, S. *Dalton Trans.* **2005**, 1532.
- (245) Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; Weatherstone, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1709.
- (246) Armstrong, D. R.; Clegg, W.; Mulvey, R. E.; Rowlings, R. B. *J. Chem. Soc., Dalton Trans.* **2001**, 409.
- (247) Magnuson, V. R.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 1427.
- (248) Henderson, K. W.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *Polyhedron* **1993**, *12*, 2535.
- (249) Henderson, K. W.; Allan, J. F.; Kennedy, A. R. *Chem. Commun.* **1997**, 1149.
- (250) Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 4800.
- (251) García-Alvarez, P.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Klett, J.; Mulvey, R. E.; O'Hara, C. T.; Weatherstone, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 8079.
- (252) (a) Coates, G. E.; Heslop, J. A.; Redwood, M. E.; Ridley, D. J. *Chem. Soc. (A)* **1968**, 1118. (b) Moreno, C. A.; Hughes, D. L.; Bochmann, M. *Polyhedron* **2007**, *26*, 2523.
- (253) Ashby, E. C.; Nackashi, J.; Parris, G. E. *J. Am. Chem. Soc.* **1975**, *97*, 3162.
- (254) (a) Ashby, E. C.; Becker, W. E. *J. Am. Chem. Soc.* **1963**, *85*, 118. (b) Walker, F. W.; Ashby, E. C. *J. Am. Chem. Soc.* **1969**, *91*, 3845. (c) Mori, T.; Kato, S. *J. Phys. Chem. A* **2009**, *113*, 6158.
- (255) (a) Stucky, G. D.; Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 1002. (b) Guggenberger, L. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1964**, *86*, 5344. (c) Toney, J.; Stucky, G. D. *Chem. Commun.* **1967**, *1168*. (d) Guggenberger, L. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 5375. (e) Vallino, M. *J. Organomet. Chem.* **1969**, *20*, 1. (f) Spek, A. L.; Voorbergen, P.; Schat, G.; Blomberg, C.; Bickelhaupt, F. *J. Organomet. Chem.* **1974**, *77*, 147. (g) Holloway, C. E.; Melnik, M. *Coord. Chem. Rev.* **1994**, *135/136*, 287. (h) Hörner, W.; Bertagnoli, H. *J. Organomet. Chem.* **2002**, *649*, 128.
- (256) (a) Sakamoto, S.; Imamoto, T.; Yamaguchi, K. *Org. Lett.* **2001**, *3*, 1793. (b) Yamaguchi, K.; Sakamoto, S. *JEOL News* **2002**, *28A*, 2.
- (257) (a) Pitzer, K.; Gutowsky, H. S. *J. Am. Chem. Soc.* **1946**, *68*, 2204. (b) Lewis, P. H.; Rundle, R. E. *J. Chem. Phys.* **1953**, *21*, 986. (c) Muller, N.; Pritchard, D. E. *J. Am. Chem. Soc.* **1960**, *82*, 248. (d) Ramey, K. C.; O'Brien, J. F.; Hasegawa, I.; Borchert, A. E. *J. Phys. Chem.* **1965**, *69*, 3418. (e) Williams, K. C.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 5460. (f) Vranka, R. G.; Amma, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 3121. (g) McGrady, G. S.; Turner, J. F. C.; Ibberson, R. M.; Prager, M. *Organometallics* **2000**, *19*, 4398.
- (258) Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5362.
- (259) Mitzel, N. W.; Lustig, C. Z. *Naturforsch.* **2004**, *59b*, 1532.
- (260) Leman, J. T.; Landry, C. C.; Barron, A. R. *Main Group Met. Chem.* **1993**, *16*, 193.
- (261) (a) Atwood, J. L.; Hrnčir, D. C.; Shakir, R.; Dalton, M. S.; Priester, R. D.; Rogers, R. D. *Organometallics* **1982**, *1*, 1021. (b) Atwood, J. L.; Priester, R. D.; Rogers, R. D.; Canada, L. G. *J. Incl. Phenom.* **1983**, *1*, 61. (c) Robinson, G. H.; Bott, S. G.; Elgamal, H.; Hunter, W. E.; Atwood, J. L. *J. Incl. Phenom.* **1985**, *3*, 65. (d) Robinson, G. H.; Zhang, H.; Atwood, J. L. *J. Organomet. Chem.* **1987**, *331*, 153. (e) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 1494. (f) Sangokoya, S. A.; Lee, B.; Pennington, W. T.; Robinson, G. H. *J. Coord. Chem.* **1989**, *19*, 331.
- (262) (a) Yamamoto, O.; Yamada, Y. *Tokyo Kogyo Shikensho Hokoku* **1964**, *59*, 489. (b) Yamamoto, O. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1125. (c) Kolomeer, M. G.; Stovbun, E. V.; Gachkovski, V. F.; Vainshtein, E. F. *Dokl. Akad. Nauk SSSR* **1973**, *212*, 403.
- (263) (a) Lehmkühl, H. *Angew. Chem.* **1964**, *76*, 817. (b) Uhl, W. Z. *Anorg. Allg. Chem.* **1989**, *570*, 37. (c) McMahon, C. N.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 3129. (d) Uhl, W.; Abel, T.; Kösters, J.; Rogel, F. *Z. Naturforsch.* **2008**, *63b*, 117.
- (264) (a) Malone, J. F.; McDonald, W. S. *Chem. Commun.* **1967**, 444. (b) Malone, J. F.; McDonald, W. S. *J. Chem. Soc. Dalton* **1972**, 2646. (c) Zhou, S.; Chuang, D.-W.; Chang, S.-J.; Gau, H.-M. *Tetrahedron: Asymmetry* **2009**, *20*, 1407.
- (265) (a) Maqsudur Rahman, A. F. M.; Siddiqui, K. F.; Oliver, J. P. *Organometallics* **1982**, *1*, 881. (b) Maqsudur Rahman, A. F. M.; Siddiqui, K. F.; Oliver, J. P. *J. Organomet. Chem.* **1987**, *319*, 161.
- (266) (a) Kovar, R. A.; Ashby, E. C. *Inorg. Chem.* **1971**, *10*, 893. (b) Waggoner, K. M.; Olmstead, M. M.; Power, P. P. *Polyhedron* **1990**, *9*, 257. (c) Andrianarison, M. M.; Ellerby, M. C.; Gorrell, I. B.; Hitchcock, P. B.; Smith, J. D.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1996**, 211.
- (267) Beard, B. C. *J. Raman Spectrosc.* **2004**, *35*, 1006.
- (268) (a) Benn, R.; Janssen, E.; Lehmkühl, H.; Rufinska, A. J. *Organomet. Chem.* **1987**, *333*, 169. (b) Rhine, W. E.; Eyman, D. P.; Schauer, S. *J. Polyhedron* **1999**, *18*, 905. (c) Francis, J. A.; McMahon, C. N.; Bott, S. G.; Barron, A. R. *Organometallics* **1999**, *18*, 4399.
- (269) (a) Davidson, M. G.; Elilio, D.; Less, S. L.; Martin, A.; Raithby, P. R.; Snaith, R.; Wright, D. S. *Organometallics* **1993**, *12*, 1. (b) Petrie, M. A.; Ruhland-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1135.
- (270) (a) Lewinski, J.; Wheatley, A. E. H. *Top. Organomet. Chem.* **2013**, *41*, 1. (b) Kroll, W. R.; Naegle, W. *J. Organomet. Chem.* **1969**, *19*, 439. (c) Saito, S.; Yamamoto, H. *Chem. Commun.* **1997**, 1585. (d) Ménard, G.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2011**, *50*, 8396. (e) Ménard, G.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2012**, *51*, 4409. (f) Ménard, G.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2012**, *51*, 8272. (g) Lewinski, J.; Zachara, J.; Gos, P.; Grabska, E.; Kopec, T.; Madura, I.; Marcinia, W.; Prowotorow, I. *Chem.—Eur. J.* **2000**, *6*, 3215. (h) Kumar, S. S.; Singh, S.; Raesky, H. W.; Magull, J. *Inorg. Chem.* **2005**, *44*, 1199. (i) Beachley, O. T. *Inorg. Chem.* **1981**, *20*, 2825. (j) Chakraborty, D.; Chen, E. Y.-X. *Organometallics* **2002**, *21*, 1438. (k) Li, X.; Cheng, X.; Song, H.; Cui, C. *Organometallics* **2007**, *26*, 1039. (l) Kingsley, N. B.; Kirschbaum, K.; Mason, M. R. *Organometallics* **2010**, *29*, 5927. (m) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4531. (n) Hardman, N. J.; Cui, C.; Roesky, H. W.; Fink, W. H.; Power, P. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2172. (o) Nelson, S. G.; Peelen, T. J.; Wan, Z. *J. Am. Chem. Soc.* **1999**, *121*, 9742. (p) Nelson, S. G.; Kim, B.-K.; Peelen, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 9318.
- (271) (a) Suryanarayana Rao, K.; Stoicheff, B. P.; Turner, R. *Can. J. Phys.* **1960**, *38*, 1516. (b) Thiele, K.-H. Z. *Anorg. Allg. Chem.* **1962**, *319*, 183. (c) Thiele, K.-H. Z. *Anorg. Allg. Chem.* **1963**, *322*, 71. (d) Thiele, K.-H. Z. *Anorg. Allg. Chem.* **1963**, *325*, 156. (e) Wissing, E.; Kaupp, M.; Boersma, J.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 2349. (f) Hursthouse, M. B.; Motavalli, M.; O'Brien, P.; Walsh, J. R. *Organometallics* **1991**, *10*, 3196. (g) Coward, K. M.; Jones, A. C.; Steiner, A.; Bickley, J. F.; Smith, L. M.; Pemble, M. E. *J. Chem. Soc., Dalton Trans.* **2000**, 3480. (h) Thomas, F.; Schulz, S.; Nieger, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5668. (i) Bacsa, J.; Hanke, F.; Hindley, S.; Odedra, R.; Darling, G. R.; Jones, A. C.; Steiner, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 11685. (j) Lewinski, J.; Sliwinski, W.; Dranka, M.; Justyniak, I.; Lipkowski, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 4826. (k) Lewinski, J.; Suwala, K.; Kubisiak, M.; Ochal, Z.; Justyniak, I.; Lipkowski, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 7888. (l) Cozzi, P. G.; Mignogna, A.; Vicennati, P. *Adv. Synth. Catal.* **2008**, *350*, 975. (m) Maury, J.; Feray, L.; Bazin, S.; Clément, J.-L.; Marque, S. R. A.; Siri, D.; Bertrand, M. P. *Chem.—Eur. J.* **2011**, *17*, 1586.
- (272) (a) Huang, X.; Sun, H.; Wang, X.; Liu, Y. J.; You, X.; Sun, X. *Main Group Met. Chem.* **1996**, *19*, 161. (b) Andrews, P. C.; Raston, C.

- L.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 779.
 (c) Krahmer, J.; Beckhaus, R.; Saak, W.; Haase, D. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1696.
- (273) (a) Lewinski, J.; Dranka, M.; Bury, W.; Sliwinski, W.; Justyniak, I.; Lipkowski, J. *J. Am. Chem. Soc.* **2007**, *129*, 3096. (b) Lennartson, A.; Hedström, A.; Hakansson, M. *Organometallics* **2010**, *29*, 177.
- (274) (a) Wooten, A.; Carroll, P. J.; Maestri, A. G.; Walsh, P. *J. Am. Chem. Soc.* **2006**, *128*, 4624. (b) Clegg, W.; García-Alvarez, J.; García-Alvarez, P.; Graham, D. V.; Harrington, R. W.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; Russo, L. *Organometallics* **2008**, *27*, 2654.
- (275) (a) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1990**, *9*, 2243. (b) Dickson, R. S.; Fallon, G. D.; Zhang, Q.-Q. *J. Chem. Soc., Dalton Trans.* **2000**, *1973*.
- (276) (a) Brooker, S.; Bertel, N.; Stalke, D.; Noltemeyer, M.; Roesky, H. W.; Sheldrick, G. M.; Edelmann, F. T. *Organometallics* **1992**, *11*, 192. (b) Cole, S. C.; Coles, M. P.; Hitchcock, P. B. *Dalton Trans.* **2003**, *3663*. (c) Chisholm, M. H.; Gallucci, J. C.; Yin, H.; Zhen, H. *Inorg. Chem.* **2005**, *44*, 4777.
- (277) (a) Weidenbruch, M.; Herrndorf, M.; Schäfer, A.; Pohl, S.; Saak, W. *J. Organomet. Chem.* **1989**, *361*, 139. (b) Sun, Y.; Piers, W. E.; Parvez, M. *Can. J. Chem.* **1998**, *76*, 513.
- (278) Westerhausen, M.; Wieneke, M.; Rademacher, B. B.; Schwarz, W. *Chem. Ber.* **1997**, *130*, 1499.
- (279) Rees, W. S., Jr.; Just, O.; Schumann, H.; Weimann, R. *Polyhedron* **1998**, *17*, 1001.
- (280) Rees, W. S., Jr.; Green, D. M.; Hesse, W. *Polyhedron* **1992**, *11*, 1697.
- (281) Armstrong, D. R.; Forbes, G. C.; Mulvey, R. E.; Clegg, W.; Tookey, D. M. *J. Chem. Soc., Dalton Trans.* **2002**, 1656.
- (282) Luo, B.; Kucera, B. E.; Gladfelter, W. L. *Polyhedron* **2006**, *25*, 279.
- (283) Westerhausen, M.; Bollwein, T.; Pfitzner, A.; Nilges, T.; Deiseroth, H.-J. *Inorg. Chim. Acta* **2001**, *312*, 239.
- (284) Westerhausen, M.; Bollwein, T.; Makropoulos, N.; Schneiderbauer, S.; Suter, M.; Nöth, H.; Mayer, P.; Piotrowski, H.; Polborn, K.; Pfitzner, A. *Eur. J. Inorg. Chem.* **2002**, 389.
- (285) Westerhausen, M.; Wieneke, M.; Schwarz, W. *J. Organomet. Chem.* **1999**, *572*, 249.
- (286) (a) Shearer, H. M. M.; Spencer, C. B. *Chem. Commun.* **1966**, *194*. (b) Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr.* **1980**, *B36*, 2046.
- (287) Matsui, Y.; Kamiya, K.; Nishikawa, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1828.
- (288) Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12160.
- (289) Lewinski, J.; Dutkiewicz, M.; Lesiuk, M.; Sliwinski, W.; Zelga, K.; Justyniak, I.; Lipkowski, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 8266.
- (290) Olmstead, M. M.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 3379.
- (291) Westerhausen, M.; Wieneke, M.; Schwarz, W. *J. Organomet. Chem.* **1996**, *522*, 137.
- (292) Brown, T. L. *Acc. Chem. Res.* **1968**, *1*, 23.
- (293) Paté, F.; Oulyadi, H.; Harrison-Marchand, A.; Maddaluno, J. *Organometallics* **2008**, *27*, 3564.
- (294) (a) Weiner, M. A.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 485. (b) Peascoe, W.; Applequist, D. E. *J. Org. Chem.* **1973**, *38*, 1510.
- (295) Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1967**, *89*, 1607.
- (296) (a) Pratt, L. M.; Newman, A.; St Cyr, J.; Johnson, H.; Miles, B.; Lattier, A.; Austin, E.; Henderson, S.; Hershey, B.; Lin, M.; Balamraju, Y.; Sammonds, L.; Cheramie, J.; Karnes, J.; Hymel, E.; Woodford, B.; Carter, C. *J. Org. Chem.* **2003**, *68*, 6387. (b) Balamraju, Y.; Sharp, C. D.; Gammill, W.; Manuel, N.; Pratt, L. M. *Tetrahedron* **1998**, *54*, 7357.
- (297) Parsons, R. L., Jr.; Fortunak, J. M.; Dorow, R. L.; Harris, G. D.; Kauffman, G. S.; Nugent, W. A.; Winemiller, M. D.; Briggs, T. F.; Xiang, B.; Collum, D. B. *J. Am. Chem. Soc.* **2001**, *123*, 9135.
- (298) (a) Arvidsson, P. I.; Ahlberg, P.; Hilmersson, G. *Chem.—Eur. J.* **1999**, *5*, 1348. (b) Arvidsson, P. I.; Hilmersson, G.; Davidsson, Ö. *Chem.—Eur. J.* **1999**, *5*, 2348. (c) Hilmersson, G.; Malmros, B. *Chem.—Eur. J.* **2001**, *7*, 337.
- (299) (a) Williard, P. G.; Sun, C. *J. Am. Chem. Soc.* **1997**, *119*, 11693. (b) Li, D.; Sun, C.; Liu, J.; Hopson, R.; Li, W.; Williard, P. G. *J. Org. Chem.* **2008**, *73*, 2373. (c) Liu, J.; Li, D.; Sun, C.; Williard, P. G. *J. Org. Chem.* **2008**, *73*, 4045.
- (300) (a) Fressigné, C.; Corruble, A.; Valnot, J.-Y.; Maddaluno, J.; Giessner-Prettre, C. *J. Organomet. Chem.* **1997**, *549*, 81. (b) Prigent, Y.; Corruble, A.; Valnot, J.-Y.; Maddaluno, J.; Duhamel, P.; Davoust, D. *J. Chim. Phys.* **1998**, *95*, 401. (c) Corruble, A.; Davoust, D.; Desjardins, S.; Fressigné, C.; Giessner-Prettre, C.; Harrison-Marchand, A.; Houte, H.; Lasne, M.-C.; Maddaluno, J.; Oulyadi, H.; Valnot, J.-Y. *J. Am. Chem. Soc.* **2002**, *124*, 15267.
- (301) Pratt, L. M.; Kwon, O.; Ho, T. C.; Nguyen, N. V. *Tetrahedron* **2008**, *64*, 5314.
- (302) Brown, T. L.; Ladd, J. A.; Newman, G. N. *J. Organomet. Chem.* **1965**, *3*, 1.
- (303) (a) DeLong, G. T.; Pannell, D. K.; Clarke, M. T.; Thomas, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 7013. (b) DeLong, G. T.; Hoffmann, D.; Nguyen, H. D.; Thomas, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 11998.
- (304) Thomas, R. D.; Huang, H. *J. Am. Chem. Soc.* **1999**, *121*, 11239.
- (305) (a) Halaska, V.; Lochmann, L. *Collect. Czech. Chem. Commun.* **1973**, *38*, 1780. (b) Marsch, M.; Harms, K.; Lochmann, L.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 308.
- (306) (a) Khatabil, H. K.; Gros, P. C.; Fort, Y.; Ruiz-López, M. F. *J. Org. Chem.* **2008**, *73*, 9393. (b) Khatabil, H. K.; Gros, P. C.; Fort, Y.; Ruiz-López, M. F. *J. Am. Chem. Soc.* **2010**, *132*, 2410.
- (307) (a) Goldfuss, B.; Khan, S. I.; Houk, K. N. *Organometallics* **1999**, *18*, 2927. (b) Goldfuss, B.; Steigelmann, M.; Rominger, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4133. (c) Goldfuss, B.; Steigelmann, M.; Rominger, F.; Urtel, H. *Chem.—Eur. J.* **2001**, *7*, 4456.
- (308) Sun, X.; Winemiller, M. D.; Xiang, B.; Collum, D. B. *J. Am. Chem. Soc.* **2001**, *123*, 8039.
- (309) (a) Xu, F.; Reamer, R. A.; Tillyer, R.; Cummins, J. M.; Grabowski, E. J. J.; Reider, P. J.; Collum, D. B.; Huffman, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 11212. (b) Briggs, T. F.; Winemiller, M. D.; Xiang, B.; Collum, D. B. *J. Org. Chem.* **2001**, *66*, 6291.
- (310) (a) Waack, R.; Doran, M. A.; Baker, E. B. *Chem. Commun.* **1967**, *1291*. (b) Kieft, R. L.; Novak, D. P.; Brown, T. L. *J. Organomet. Chem.* **1974**, *77*, 299. (c) Fox, T.; Hausmann, H.; Günther, H. *Magn. Reson. Chem.* **2004**, *42*, 788.
- (311) Glaze, W.; West, R. *J. Am. Chem. Soc.* **1960**, *82*, 4437.
- (312) Pratt, L. M.; Merry, S.; Nguyen, S. C.; Quan, P.; Thanh, B. T. *Tetrahedron* **2006**, *62*, 10821.
- (313) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1996**, *118*, 3529.
- (314) (a) Zarges, W.; Marsch, M.; Harms, K.; Boche, G. *Angew. Chem.* **1989**, *101*, 1424. (b) Zarges, W.; Marsch, M.; Harms, K.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1392.
- (315) Sott, R.; Granander, J.; Hilmersson, G. *Chem.—Eur. J.* **2002**, *8*, 2081.
- (316) Henderson, K. W.; Walther, D. S.; Williard, P. G. *J. Am. Chem. Soc.* **1995**, *117*, 8680.
- (317) Riggs, J. C.; Singh, K. J.; Yun, M.; Collum, D. B. *J. Am. Chem. Soc.* **2008**, *130*, 13709.
- (318) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 5539.
- (319) Galiano-Roth, A. S.; Kim, Y.-J.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5053.
- (320) Romesberg, F. E.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 9198.
- (321) Sun, X.; Collum, D. B. *J. Am. Chem. Soc.* **2000**, *122*, 2459.
- (322) Ramirez, A.; Sun, X.; Collum, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 10326.
- (323) (a) Ma, Y.; Collum, D. B. *J. Am. Chem. Soc.* **2007**, *129*, 14818. (b) Ma, Y.; Hoepker, A. C.; Gupta, L.; Faggion, M. F.; Collum, D. B. *J. Am. Chem. Soc.* **2010**, *132*, 15610.
- (324) Yamamoto, Y.; Yasuda, Y.; Oulyadi, H.; Maddaluno, J.; Tomioka, K. *Tetrahedron* **2010**, *66*, 2470.
- (325) Zhao, P.; Condo, A.; Keresztes, I.; Collum, D. B. *J. Am. Chem. Soc.* **2004**, *126*, 3113.

- (326) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 8602.
 (327) Godenschwager, P. F.; Collum, D. B. *J. Am. Chem. Soc.* **2008**, *130*, 8726.
 (328) Zhao, P.; Collum, D. B. *J. Am. Chem. Soc.* **2003**, *125*, 14411.
 (329) McNeil, A. J.; Toombes, G. E. S.; Gruner, S. M.; Lobkovsky, E.; Collum, D. B.; Chandramouli, S. V.; Vanasse, B. J.; Ayers, T. A. *J. Am. Chem. Soc.* **2004**, *126*, 16559.
 (330) McNeil, A. J.; Collum, D. B. *J. Am. Chem. Soc.* **2005**, *127*, 5655.
 (331) Hall, P. L.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 9575.
 (332) (a) Sun, C.; Williard, P. G. *J. Am. Chem. Soc.* **2000**, *122*, 7829.
 (b) Li, D.; Sun, C.; Williard, P. G. *J. Am. Chem. Soc.* **2008**, *130*, 11726.
 (333) Lecache, B.; Duguet, N.; Oulyadi, H.; Fressigné, C.; Harrison-Marchand, A.; Yamamoto, Y.; Tomioka, K.; Maddaluno, J. *Org. Lett.* **2009**, *11*, 1907.
 (334) Mair, F. S.; Clegg, W.; O'Neil, P. A. *J. Am. Chem. Soc.* **1993**, *115*, 3388.
 (335) Clegg, W.; Greer, J. C.; Hayes, J. M.; Mair, F. S.; Nolan, P. M.; O'Neil, P. A. *Inorg. Chim. Acta* **1997**, *258*, 1.
 (336) (a) Henderson, K. W.; Dorigo, A. E.; Liu, Q.-Y.; Williard, P. G.; Schleyer, P. v. R.; Bernstein, P. R. *J. Am. Chem. Soc.* **1996**, *118*, 1339. (b) Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Robertson, G. M.; Robertson, S. D. *Angew. Chem., Int. Ed.* **2011**, *50*, 8375.
 (337) Sugawara, K.; Shindo, M.; Noguchi, H.; Koga, K. *Tetrahedron Lett.* **1996**, *37*, 7377.
 (338) Paté, F.; Duguet, N.; Oulyadi, H.; Harrison-Marchand, A.; Fressigné, C.; Valnot, J.-Y.; Lasne, M.-C.; Maddaluno, J. *J. Org. Chem.* **2007**, *72*, 6982.
 (339) Lecache, B.; Fressigné, C.; Oulyadi, H.; Harrison-Marchand, A.; Maddaluno, J. *Chem. Commun.* **2011**, *47*, 9915.
 (340) Jackman, L. M.; Rakiewicz, E. F. *J. Am. Chem. Soc.* **1991**, *113*, 1202.
 (341) (a) Wittig, G.; Ludwig, R.; Polster, R. *Chem. Ber.* **1955**, *88*, 294.
 (b) Wittig, G.; Bickelhaupt, F. *Chem. Ber.* **1958**, *91*, 865. (c) Wittig, G.; Benz, E. *Chem. Ber.* **1958**, *91*, 873. (d) Lochmann, L.; Trekoval, J. *J. Organomet. Chem.* **1979**, *179*, 123. (e) Schlosser, M. *Pure Appl. Chem.* **1988**, *60*, 1627. (f) Mordini, A. *Adv. Carbanion Chem.* **1992**, *1*, 1. (g) Schlosser, M. *Mod. Synth. Methods* **1992**, *6*, 227. (h) Schlosser, M.; Desponds, O.; Lehmann, R.; Moret, E.; Rauchschwalbe, G. *Tetrahedron* **1993**, *49*, 10175. (i) Schlosser, M.; Faigl, F.; Franzini, L.; Geneste, H.; Katsoulos, G.; Zhong, G. F. *Pure Appl. Chem.* **1994**, *66*, 1439. (j) Mongin, F.; Maggi, R.; Schlosser, M. *Chimia* **1996**, *50*, 650. (k) Lochmann, L. *Eur. J. Inorg. Chem.* **2000**, *1115*. (l) Schlosser, M. *Organometallics in Synthesis*, 2nd ed.; Schlosser, M., Ed.; Wiley: New York, 2002; Chapter I. (m) Deagostino, A.; Prandi, C.; Venturello, P. *Curr. Org. Chem.* **2003**, *7*, 821. (n) Schlosser, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 376.
 (342) Mulvey, R. E. *Chem. Soc. Rev.* **1998**, *27*, 339.
 (343) Baker, D. R.; Clegg, W.; Horsburgh, L.; Mulvey, R. E. *Organometallics* **1994**, *13*, 4170.
 (344) Schümann, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 584.
 (345) Clegg, W.; Drummond, A. M.; Liddle, S. T.; Mulvey, R. E.; Robertson, A. *Chem. Commun.* **1999**, 1569.
 (346) Clegg, W.; Henderson, K. W.; Horsburgh, L.; Mackenzie, F. M.; Mulvey, R. E. *Chem.—Eur. J.* **1998**, *4*, 53.
 (347) Baker, D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *J. Am. Chem. Soc.* **1993**, *115*, 6472.
 (348) (a) Williard, P. G.; Nichols, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 9671. (b) Nichols, M. A.; Waldmüller, D.; Williard, P. G. *J. Am. Chem. Soc.* **1994**, *116*, 1153.
 (349) Armstrong, D. R.; Kennedy, A. R.; Mulvey, R. E.; Robertson, S. D. *Chem.—Eur. J.* **2011**, *17*, 8820.
 (350) Cambillau, C.; Bram, G.; Corset, J.; Riche, C. *Nouv. J. Chim.* **1979**, *3*, 9.
 (351) Ghigo, G.; Tonachini, G.; Venturello, P. *Tetrahedron* **1996**, *52*, 7053.
 (352) Kennedy, A. R.; MacLellan, J. G.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 3245.
 (353) Holland, R.; Jeffery, J. C.; Russel, C. A. *J. Chem. Soc., Dalton Trans.* **1999**, 3331.
 (354) Kennedy, A. R.; MacLellan, J. G.; Mulvey, R.; Robertson, A. *J. Chem. Soc., Dalton Trans.* **2000**, 4112.
 (355) Johansson, A.; Hilmersson, G.; Davidsson, Ö. *Organometallics* **2002**, *21*, 2283.
 (356) Williard, P. G.; MacEwan, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 7671.
 (357) Harder, S.; Streitwieser, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1066.
 (358) (a) Mukaiyama, T.; Soai, K.; Sato, T.; Shimizu, H.; Suzuki, K. *J. Am. Chem. Soc.* **1979**, *101*, 1455. (b) Noyori, R.; Suga, S.; Kawai, K.; Okada, S.; Kitamura, M. *Pure Appl. Chem.* **1988**, *60*, 1597. (c) Fleming, F. F.; Gudipati, V.; Steward, O. W. *Org. Lett.* **2002**, *4*, 659. (d) Hatano, M.; Matsumura, T.; Ishihara, K. *Org. Lett.* **2005**, *7*, 573. (e) Hatano, M.; Suzuki, S.; Ishihara, K. *Synlett* **2010**, 321.
 (359) (a) Kondo, J.; Inoue, A.; Shinokubo, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2085. (b) Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. *Chem.—Eur. J.* **2002**, *8*, 1730. (c) Fukuhara, K.; Takayama, Y.; Sato, F. *J. Am. Chem. Soc.* **2003**, *125*, 6884. (d) Dumouchel, S.; Mongin, F.; Trécourt, F.; Quéguiner, G. *Tetrahedron* **2003**, *59*, 8629. (e) Cottet, F.; Schlosser, M. *Eur. J. Org. Chem.* **2004**, 3793. (f) Awad, H.; Mongin, F.; Trécourt, F.; Quéguiner, G.; Marsais, F.; Blanco, F.; Abarca, B.; Ballesteros, R. *Tetrahedron Lett.* **2004**, *45*, 6697. (g) Awad, H.; Mongin, F.; Trécourt, F.; Quéguiner, G.; Marsais, F. *Tetrahedron Lett.* **2004**, *45*, 7873. (h) Bayh, O.; Awad, H.; Mongin, F.; Hoarau, C.; Trécourt, F.; Quéguiner, G.; Marsais, F.; Blanco, F.; Abarca, B.; Ballesteros, R. *Tetrahedron* **2005**, *61*, 4779. (i) Bentabed-Ababsa, G.; Blanco, F.; Derdour, A.; Mongin, F.; Trécourt, F.; Quéguiner, G.; Ballesteros, R.; Abarca, B. *J. Org. Chem.* **2009**, *74*, 163. (j) Bellamy, E.; Bayh, O.; Hoarau, C.; Trécourt, F.; Quéguiner, G.; Marsais, F. *Chem. Commun.* **2010**, *46*, 7043.
 (360) (a) Mulvey, R. E. *Chem. Commun.* **2001**, 1049. (b) Westerhausen, M. *Dalton Trans.* **2006**, 4755.
 (361) (a) Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4140. (b) Seitz, L. M.; Little, B. F. *J. Organomet. Chem.* **1969**, *18*, 227. (c) Greiser, T.; Kopf, J.; Thoenes, D.; Weiss, E. *Chem. Ber.* **1981**, *114*, 209.
 (362) Schubert, B.; Weiss, E. *Chem. Ber.* **1984**, *117*, 366.
 (363) Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1967**, *89*, 1602.
 (364) Thoenes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726.
 (365) Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B. *J. Am. Chem. Soc.* **1998**, *120*, 7816.
 (366) Clegg, W.; Henderson, K. W.; Mulvey, R. E.; O'Neil, P. A. *J. Am. Chem. Soc., Chem. Commun.* **1993**, 969.
 (367) Andrikopoulos, P. C.; Armstrong, D. R.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T. *Chem. Commun.* **2005**, 1131.
 (368) Hevia, E.; Kenley, F. R.; Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B. *Eur. J. Inorg. Chem.* **2003**, 3347.
 (369) Graham, D. V.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Talmard, C. *Chem. Commun.* **2006**, 417.
 (370) Clegg, W.; Dale, S. H.; Graham, D. V.; Harrington, R. W.; Hevia, E.; Hogg, L. M.; Kennedy, A. R.; Mulvey, R. E. *Chem. Commun.* **2007**, 1641.
 (371) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Roberts, B. A.; Rowlings, R. B. *Organometallics* **2002**, *21*, 5115.
 (372) Andrikopoulos, P. C.; Armstrong, D. R.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Rowlings, R. B.; Weatherstone, S. *Inorg. Chim. Acta* **2007**, *360*, 1370.
 (373) García-Alvarez, J.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E. *Dalton Trans.* **2008**, 1481.
 (374) Drewette, K. J.; Henderson, K. W.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Rowlings, R. B. *Chem. Commun.* **2002**, 1176.
 (375) Armstrong, D. R.; García-Alvarez, P.; Kennedy, A. R.; Mulvey, R. E.; Parkinson, J. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 3185.
 (376) Hevia, E.; Gallagher, D. J.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Talmard, C. *Chem. Commun.* **2004**, 2422.

- (377) Andrikopoulos, P. C.; Armstrong, D. R.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Talmard, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 3459.
- (378) (a) Gallagher, D. J.; Henderson, K. W.; Kennedy, A. R.; O'Hara, C. T.; Mulvey, R. E.; Rowlings, R. B. *Chem. Commun.* **2002**, *376*. (b) Andrikopoulos, P. C.; Armstrong, D. R.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Rowlings, R. B. *Eur. J. Inorg. Chem.* **2003**, *3354*. (c) Graham, D. V.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T. *Acta Crystallogr.* **2006**, *C62*, m366.
- (379) Barnett, N. D. R.; Clegg, W.; Kennedy, A. R.; Mulvey, R. E.; Weatherstone, S. *Chem. Commun.* **2005**, *375*.
- (380) Andrews, P. C.; Kennedy, A. R.; Mulvey, R. E.; Raston, C. L.; Roberts, B. A.; Rowlings, R. B. *Angew. Chem., Int. Ed.* **2000**, *39*, 1960.
- (381) (a) Ashby, E. C.; Arnott, R.; Srivastava, S. *Inorg. Chem.* **1975**, *14*, 2422. (b) Screttas, C. G.; Micha-Screttas, M. *Organometallics* **1984**, *3*, 904. (c) Screttas, C. G.; Micha-Screttas, M. *J. Organomet. Chem.* **1985**, *290*, 1. (d) Screttas, C. G.; Micha-Screttas, M. *J. Organomet. Chem.* **1986**, *316*, 1. (e) Hanawalt, E. M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4983. (f) Hanawalt, E. M.; Farkas, J., Jr.; Richey, H. G., Jr. *Organometallics* **2004**, *23*, 416.
- (382) See, for instance: (a) Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 3180. (b) Kennedy, A. R.; Mulvey, R. E.; Raston, C. L.; Roberts, B. A.; Rowlings, R. B. *Chem. Commun.* **1999**, *353*. (c) Drummond, A. M.; Gibson, L. T.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Rowlings, R. B.; Weightman, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 2382.
- (383) See, for instance: (a) Armstrong, D. R.; Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 131. (b) Andrikopoulos, P. C.; Armstrong, D. R.; Clegg, W.; Gilfillan, C. J.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Parkinson, J. A.; Tooke, D. M. *J. Am. Chem. Soc.* **2004**, *126*, 11612. (c) Armstrong, D. R.; Clegg, W.; Dale, S. H.; Graham, D. V.; Hevia, E.; Hogg, L. M.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E. *Chem. Commun.* **2007**, *598*. (d) Conway, B.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E. *Chem. Commun.* **2007**, *2864*.
- (384) Gerteis, R. L.; Dickerson, R. E.; Brown, T. L. *Inorg. Chem.* **1964**, *3*, 872.
- (385) Beswick, M. A.; Choi, N.; Harmer, C. N.; McPartlin, M.; Mosquera, M. E. G.; Raithby, P. R.; Tombul, M.; Wright, D. S. *Chem. Commun.* **1998**, *1383*.
- (386) Böck, S.; Nöth, H.; Rahm, P. Z. *Naturforsch.* **1988**, *43b*, 53.
- (387) (a) Wolfrum, R.; Sauermann, G.; Weiss, E. *J. Organomet. Chem.* **1969**, *18*, 27. (b) Craig, F. J.; Kennedy, A. R.; Mulvey, R. E.; Spicer, M. D. *Chem. Commun.* **1996**, *1951*.
- (388) Heine, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 854.
- (389) Eaborn, C.; Gorrell, I. B.; Hitchcock, P. B.; Smith, J. D.; Tavakkoli, K. *Organometallics* **1994**, *13*, 4143.
- (390) (a) Avent, A. G.; Chen, W.-Y.; Eaborn, C.; Gorrell, I. B.; Hitchcock, P. B.; Smith, J. D. *Organometallics* **1996**, *15*, 4343. (b) Chen, W.-Y.; Eaborn, C.; Gorrell, I. B.; Hitchcock, P. B.; Hopman, M.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1997**, *4689*. (c) Chen, W.-Y.; Eaborn, C.; Gorrell, I. B.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **2000**, *2313*.
- (391) García-Alvarez, J.; Hevia, E.; Kennedy, A. R.; Klett, J.; Mulvey, R. E. *Chem. Commun.* **2007**, *2402*.
- (392) Langer, J.; Krieck, S.; Görts, H.; Kreisel, G.; Seidel, W.; Westerhausen, M. *New J. Chem.* **2010**, *34*, 1667.
- (393) (a) Rutherford, D.; Atwood, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 11535. (b) Atwood, D. A.; Rutherford, D. *Organometallics* **1996**, *15*, 436. (c) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sözerli, S. E. *Organometallics* **1998**, *17*, 4322. (d) Eaborn, C.; El-Hamruni, S. M.; Hill, M. S.; Hitchcock, P. B.; Hopman, M.; Le Gouic, A.; Smith, J. D. *J. Organomet. Chem.* **2000**, *597*, 3. (e) Conway, B.; Kennedy, A. R.; Mulvey, R. E.; Robertson, S. D.; García-Alvarez, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 3182. (f) Muñoz, M. T.; Urbaneja, C.; Temprado, M.; Mosquera, M. E. G.; Cuenca, T. *Chem. Commun.* **2011**, *47*, 11757.
- (394) See for instance: (a) Naka, H.; Morey, J. V.; Haywood, J.; Eisler, D. J.; McPartlin, M.; García, F.; Kudo, H.; Kondo, Y.; Uchiyama, M.; Wheatley, A. E. H. *J. Am. Chem. Soc.* **2008**, *130*, 16193.
- (b) Crosbie, E.; García-Alvarez, P.; Kennedy, A. R.; Klett, J.; Mulvey, R. E.; Robertson, S. D. *Angew. Chem., Int. Ed.* **2010**, *49*, 9388.
- (c) Mulvey, R. E.; Armstrong, D. R.; Conway, B.; Crosbie, E.; Kennedy, A. R.; Robertson, S. D. *Inorg. Chem.* **2011**, *50*, 12241.
- (395) Conway, B.; García-Alvarez, J.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; Robertson, S. D. *Organometallics* **2009**, *28*, 6462.
- (396) García-Alvarez, J.; Graham, D. V.; Kennedy, A. R.; Mulvey, R. E.; Weatherstone, S. *Chem. Commun.* **2006**, *3208*.
- (397) Hencken, G.; Weiss, E. *J. Organomet. Chem.* **1974**, *73*, 35.
- (398) (a) Weiss, E.; Wolfrum, R. *Chem. Ber.* **1968**, *101*, 35. (b) Uchiyama, M.; Kondo, Y.; Miura, T.; Sakamoto, T. *J. Am. Chem. Soc.* **1997**, *119*, 12372. (c) Mobley, T. A.; Berger, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3070. (d) Merkel, S.; Stern, D.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 6350. (e) Armstrong, D. R.; Dougan, C.; Graham, D. V.; Hevia, E.; Kennedy, A. R. *Organometallics* **2008**, *27*, 6063.
- (399) Furuyama, T.; Yonehara, M.; Arimoto, S.; Kobayashi, M.; Matsumoto, Y.; Uchiyama, M. *Chem.—Eur. J.* **2008**, *14*, 10348.
- (400) Westerhausen, M.; Rademacher, B.; Schwarz, W. Z. *Anorg. Allg. Chem.* **1993**, *619*, 675.
- (401) Rijnberg, E.; Jastrzebski, J. T. B. H.; Boersma, J.; Kooijman, H.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 2239.
- (402) Purdy, A. P.; George, C. F. *Organometallics* **1992**, *11*, 1955.
- (403) Putzer, M. A.; Neumüller, B.; Dehnische, K. *Z. Anorg. Allg. Chem.* **1997**, *623*, 539.
- (404) Weiss, E.; Plass, H. *J. Organomet. Chem.* **1968**, *14*, 21.
- (405) Rijnberg, E.; Jastrzebski, J. T. B. H.; Boersma, J.; Kooijman, H.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1997**, *541*, 181.
- (406) (a) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B.; Clegg, W.; Liddle, S. T.; Wilson, C. C. *Chem. Commun.* **2000**, *1759*. (b) Armstrong, D. R.; Herd, E.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Clegg, W.; Russo, L. *Dalton Trans.* **2008**, *1323*.
- (407) Graham, D. V.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E. *Organometallics* **2006**, *25*, 3297.
- (408) Kondo, Y.; Morey, J. V.; Morgan, J. C.; Naka, H.; Nobuto, D.; Raithby, P. R.; Uchiyama, M.; Wheatley, A. E. H. *J. Am. Chem. Soc.* **2007**, *129*, 12734.
- (409) Barley, H. R. L.; Clegg, W.; Dale, S. H.; Hevia, E.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2005**, *44*, 6018.
- (410) Clegg, W.; Dale, S. H.; Hevia, E.; Honeyman, G. W.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 2370.
- (411) Eriksson, J.; Arvidsson, P. I.; Davidsson, Ö. *Chem.—Eur. J.* **1999**, *5*, 2356.
- (412) (a) Andrikopoulos, P. C.; Armstrong, D. R.; Barley, H. R. L.; Clegg, W.; Dale, S. H.; Hevia, E.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E. *J. Am. Chem. Soc.* **2005**, *127*, 6184. (b) Armstrong, D. R.; Clegg, W.; Dale, S. H.; García-Alvarez, J.; Harrington, R. W.; Hevia, E.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T. *Chem. Commun.* **2008**, *187*.
- (413) Armstrong, D. R.; García-Alvarez, J.; Graham, D. V.; Honeyman, G. W.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E. *Chem.—Eur. J.* **2009**, *15*, 3800.
- (414) Clegg, W.; Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Liddle, S. T. *Chem. Commun.* **2003**, *406*.
- (415) (a) Conway, B.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Klett, J.; Mulvey, R. E. *Chem. Commun.* **2008**, *2638*. (b) Clegg, W.; Conway, B.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; Russo, L.; Wright, D. S. *Chem.—Eur. J.* **2009**, *15*, 7074.
- (416) Fabicon, R. M.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1412.
- (417) Hevia, E.; Chua, J. Z.; García-Alvarez, P.; Kennedy, A. R.; McCall, M. D. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 5294.
- (418) (a) Westerhausen, M.; Wieneke, M.; Ponikwar, W.; Nöth, H.; Schwarz, W. *Organometallics* **1998**, *17*, 1438. (b) Walfort, B.; Leedham, A. P.; Russel, C. A.; Stalke, D. *Inorg. Chem.* **2001**, *40*, S668. (c) Prust, J.; Hohmeister, H.; Stasch, A.; Roesky, H. W.; Magull, J.; Alexopoulos, E.; Usón, I.; Schmidt, H.-G.; Noltemeyer, M. *Eur. J.*

Inorg. Chem. **2002**, 2156. (d) Boss, S. R.; Haigh, R.; Linton, D. J.; Schooler, P.; Shields, G. P.; Wheatley, A. E. H. *Dalton Trans.* **2003**, 1001. (e) Hevia, E.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E. *J. Am. Chem. Soc.* **2005**, 127, 13106. (f) Clegg, W.; Dale, S. H.; Drummond, A. M.; Hevia, E.; Honeyman, G. W.; Mulvey, R. E. *J. Am. Chem. Soc.* **2006**, 128, 7434. (g) Clegg, W.; Dale, S. H.; Harrington, R. W.; Hevia, E.; Honeyman, G. W.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2006**, 45, 2374. (h) Armstrong, D. R.; Clegg, W.; Dale, S. H.; Hevia, E.; Hogg, L. M.; Honeyman, G. W.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2006**, 45, 3775. (i) Clegg, W.; Dale, S. H.; Hevia, E.; Hogg, L. M.; Honeyman, G. W.; Mulvey, R. E.; O'Hara, C. T. *Angew. Chem., Int. Ed.* **2006**, 45, 6548. (j) Hitchcock, P. B.; Lappert, M. F.; Wei, X.-H. *Dalton Trans.* **2006**, 1181. (k) Seggio, A.; Lannou, M.-I.; Chevallier, F.; Nobuto, D.; Uchiyama, M.; Golhen, S.; Roisnel, T.; Mongin, F. *Chem.—Eur. J.* **2007**, 13, 9982. (l) Armstrong, D. R.; Drummond, A. M.; Balloch, L.; Graham, D. V.; Hevia, E.; Kennedy, A. R. *Organometallics* **2008**, 27, 5860. (m) García, F.; McPartlin, M.; Morey, J. V.; Nobuto, D.; Kondo, Y.; Naka, H.; Uchiyama, M.; Wheatley, A. E. H. *Eur. J. Org. Chem.* **2008**, 644. (n) Clegg, W.; Conway, B.; Hevia, E.; McCall, M. D.; Russo, L.; Mulvey, R. E. *J. Am. Chem. Soc.* **2009**, 131, 2375. (o) Armstrong, D. R.; Blair, V. L.; Clegg, W.; Dale, S. H.; García-Alvarez, J.; Honeyman, G. W.; Hevia, E.; Mulvey, R. E.; Russo, L. *J. Am. Chem. Soc.* **2010**, 132, 9480. (p) Balloch, L.; Kennedy, A. R.; Mulvey, R. E.; Rantanen, T.; Robertson, S. D.; Snieckus, V. *Organometallics* **2011**, 30, 145. (419) Nobuto, D.; Uchiyama, M. *J. Org. Chem.* **2008**, 73, 1117.