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Group 1 and 2 and Early Transition Metal Complexes Bearing N-Heterocyclic Carbene Ligands: Coordination Chemistry, Reactivity, and Applications

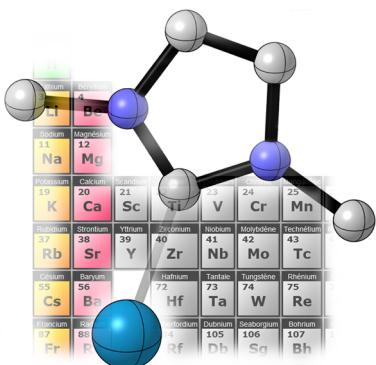
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1. INTRODUCTION

N-Heterocyclic carbenes (NHCs) are omnipresent ligands in coordination and organometallic chemistry, which is reflected

by myriads of applications involving NHC-bearing metal complexes in areas ranging from homogeneous catalysis to material science.^{1–3} Pioneering work in that field was carried out by Wanzlick and Öfele, who first reported the synthesis of such compounds in the late 1960s.^{4,5} The coordination and organometallic chemistry of these at-the-time unusual ligands was then studied by Lappert in the 1970s.⁶ A significant breakthrough was achieved by Bertrand in 1988 with the first isolation of free carbenes and subsequently by Arduengo with the first synthesis and X-ray-determined structural characterization of a N-heterocyclic carbene.^{7,8} Since then, use of these stable NHCs, frequently referred to as “Arduengo-type carbenes”, as ligands for coordination to various metal centers has attracted tremendous attention. These investigations quickly led to, and to some extent came along with, developments on possible applications of the derived NHC metal complexes, most notably in homogeneous catalysis. As of today, the scope of applications of NHC metal complexes is wide and N-heterocyclic carbenes are now at the heart of numerous advances in various chemical fields.

A N-heterocyclic carbene contains a nonbonded singlet lone pair and is an electron-rich neutral donor ligand. Therefore, a strong analogy was early on drawn with phosphine ligands though NHC ligands are different both electronically and sterically. NHCs have been used as phosphine mimics in particular in homogeneous catalysis. The potential of these ligands in catalysis was first demonstrated by Herrmann, and his pioneering work opened the way to intensive research in the area.⁹ Development and applications of metal NHC catalysts, whether regarding transition metal or main group metal derivatives, are well documented, including the use of chiral NHC metal complexes in enantioselective catalysis.^{2d}

In contrast, early transition metal and more generally oxophilic and electropositive metal species supported by N-heterocyclic carbene have been much less investigated, which may be related to the earlier mentioned analogy between phosphine and N-heterocyclic carbene ligands. Phosphine ligands are soft bases and thus preferably bind to mid- or late-transition metals to form adducts that may be significantly

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stabilized by π -back-bonding electron donation from an electron-rich metal center. However, N-heterocyclic carbenes as ligands have no necessary requirement for back-bonding, since they primarily act as exceptionally strong σ -donating L-type ligands. Therefore, the nucleophilic nature of the donating singlet lone pair spans a larger range of metals, including early transition metals or other oxophilic and electron-poor metal centers.

Interestingly, the first examples of NHC complexes were reported with chromium. In 1968, Öfele described species of the type $(\text{NHC})\text{Cr}(\text{CO})_5$. Relatively few studies dealt with NHC early transition metal complexes afterward, but the past decade has witnessed a regained attention for such compounds with various studies on NHC alkali, alkaline earth, lanthanide, or group 13–15 metal complexes. This has led to structurally diverse coordination compounds whose derived reactivity studies are now emerging. For instance, some of these oxophilic metal complexes have found applications in catalysis including amination reactions, olefin polymerization, cyclic esters/carbonates ring-opening polymerization, and ketone hydrosilylation.

On the basis of the above, the field of oxophilic metal compounds ligated by N-heterocyclic ligands and associated reactivity/applications has progressed to the point that a comprehensive review is appropriate. Note that f-block and group 13 metal species bearing NHCs were recently and comprehensively reviewed and thus lie outside the scope of the present work.^{10a,e} Likewise, group 14 and 15 element NHC compounds are also excluded since, for the most part, these derivatives have already been described in previous bibliographical accounts.¹⁰ The present contribution comprehensively reviews group 1 and 2 and early transition metal species (up to group 7 derivatives) supported by N-heterocyclic carbenes. It is structured by group metals with an initial description of group 1 and 2 metals (s-block metal carbenes) and then early transition metals from group 3 to group 7 (from scandium to rhenium). When appropriate and available, the structural features of the metal complexes are discussed. Synthetic aspects along with the derived reactivity and associated applications are continuously addressed.^{11,12}

2. GROUP 1 AND 2 METAL COMPLEXES

2.1. Group 1 Metal Complexes

A number of carbene complexes of M^+ alkali cations have been described and structurally characterized, and on the basis of X-ray data, the metal–carbene interaction in these complexes is essentially ionic with $M-\text{C}_{\text{carbene}}$ contacts in all cases well above the sum of the corresponding covalent radii ($C-M = 2.03-2.08$, $2.30-2.41$, and $2.71-2.76$ Å for $M = \text{Li}$, Na , and K , respectively).¹³ Table 1 compiles the $\text{C}_{\text{carbene}}-M$ bond distances for X-ray-characterized NHC alkali species. In general, going from Li^+ to K^+ leads to formation of weaker

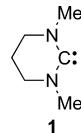
Table 1. Group 1 Carbene–Metal Bond Distances Compiled from the Cambridge Crystallographic Data Centre Database (at the date of manuscript submission)¹⁶

element	$\text{C}_{\text{carbene}}-M$ min (Å)	$\text{C}_{\text{carbene}}-M$ max (Å)	average (Å)	no. of X-ray structures
Li	2.056	2.531	2.134	28
Na	2.439	2.510	2.463	4
K	2.811	3.048	2.915	17

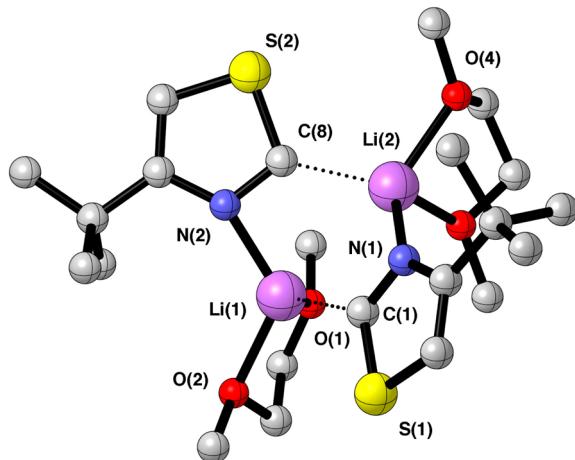
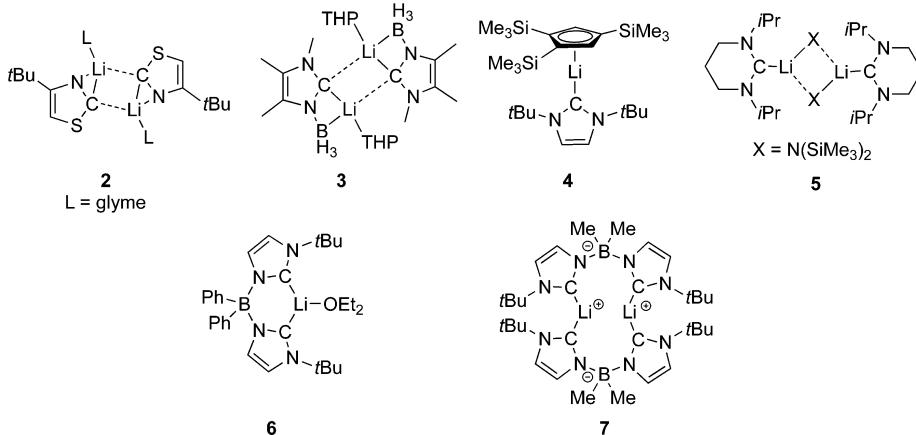
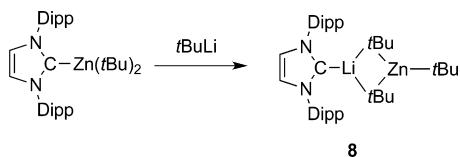
$M-\text{C}_{\text{carbene}}$ adducts, in line with the lower Lewis acidity of the M^+ cation going down column 1. In solution, this is best reflected by the upfield ^{13}C NMR chemical shift of the $\text{C}_{\text{carbene}}$ resonance in carbene complexes of alkali cations (vs free carbene), as illustrated by comparative NMR data for the Li^+ , Na^+ , and K^+ adducts of 1,3-dimethyl-3,4,5,6-tetrahydropyrimid-2-ylidene (Table 2).^{14,15}

Table 2. ^{13}C NMR Chemical Shifts of the $\text{C}_{\text{carbene}}$ Atoms for Alkali Adducts of 1,3-Dimethyl-3,4,5,6-tetrahydropyrimid-2-ylidene¹⁴

	$\text{C}_{\text{carbene}}$ (ppm)
1	242.7
1–Li	219.4
1–Na	224.9
1–K	241.0

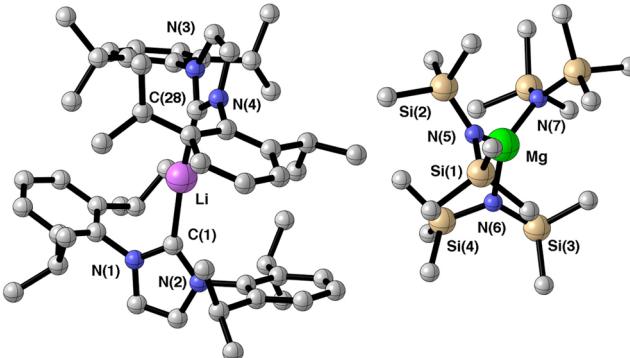
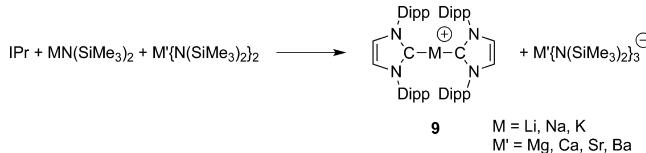


Historically, in 1995, Boche and co-workers first reported on the synthesis of a group 1 carbene species with the synthesis of the lithiated 4-*tert*-butylthiazole 2 (Scheme 1 and Figure 1) via deprotonation of 4-*tert*-butylthiazole with MeLi. The salt compound 2 crystallizes as a dimeric species with rather long bonds between the Li^+ centers and the carbenic carbons [average 2.531(5) Å].¹⁷ A couple of years later, the borane–carbene lithium species 3 was prepared by Siebert and co-workers via deprotonation of the corresponding trimethylimidazole borane adduct (Scheme 1).¹⁸ In the solid state, complex 3 crystallizes as a dimer with two four-coordinate Li centers (Scheme 1) and the Li^+ cations display a short [2.169(5) Å] and a longer [2.339(5) Å] bond distance with the two carbenic carbon atoms. As reported by Arduengo and co-workers, the reaction of free $\text{I}^{\text{t}}\text{Bu}$ carbene with the 1,2,4-tris(trimethylsilyl)-cyclopentadienide lithium salt ($\text{I}^{\text{t}}\text{Bu} = 1,3\text{-di-}tert\text{-butylimidazol-2-ylidene}$) led to the corresponding Li–NHC adduct 4 (Scheme 1), which was structurally characterized by X-ray diffraction.¹⁹ The Li center in 4 bears a η^5 -coordinated Cp ring and a NHC ligand [$\text{Li}-\text{C}_{\text{carbene}} = 2.155(4)$ Å]. In C_6D_6 solution, the carbenic carbon of 2 resonates at δ 190.7 ppm: ca. 20 ppm upfield from the corresponding free carbene. An Li adduct of 1,3-diisopropyl-3,4,5,6-tetrahydropyrimid-2-ylidene (5, Scheme 1) was also isolated via reaction of the latter NHC with $\text{Li}[\text{N}(\text{SiMe}_3)_2]$.²⁰ More recently, Hoffmann and co-workers described access to mono- and dinuclear lithium carbene complexes bearing a bulky bidentate bis-NHC anionic ligand (6 and 7, Scheme 1) via deprotonation of the salt precursor with $^6\text{BuLi}$. Noticeably, the average $\text{Li}-\text{C}_{\text{carbene}}$ bond distances in 6 and 7 [2.089(10) and 2.056(2) Å, respectively] are the shortest $\text{Li}-\text{C}_{\text{carbene}}$ bonds to date.^{21,22} Also, as typically observed in NHC coordination chemistry, the molecular structure of bis-carbene 6 features elongated $\text{C}_{\text{carbene}}-\text{N}$ bonds along with smaller $\text{N}-\text{C}_{\text{carbene}}-\text{N}$ angles relative to those in the azolium precursor. Very recently, an unusual NHC transmetalation reaction from a Zn(II) center to a Li^+ center was reported. Thus, reaction of the sterically bulky NHC–Zn(II) adduct $(\text{I}^{\text{t}}\text{Bu})\text{Zn}(\text{I}^{\text{t}}\text{Bu})_2$ with $^6\text{BuLi}$ led to formation of the NHC–Li heterometallic compound 8 (Scheme 2), as confirmed through X-ray studies.²³

Scheme 1. Molecular Structure of the Carbene Lithium Complexes 2–7 (THP = tetrahydropyran)**Figure 1.** Molecular structure of lithium complex 1. Hydrogen atoms are omitted for clarity. Selected bond lengths (Angstroms) and angles (degrees): C(8)–Li(2), 2.175; C(1)–Li(1), 2.176; N(2)–Li(1), 2.011; N(1)–Li(2), 1.990; C(8)–Li(1), 2.557; C(1)–Li(2), 2.513; C(8)–N(2)–Li(1), 97.98; Li(2)–C(8)–N(2), 125.68.**Scheme 2.** Reaction of the NHC–Zn Adduct (IPr) $\text{Zn}(\text{'Bu})_2$ with 'BuLi 

Interestingly, bis-carbene adducts of Li^+ cations may also be prepared with monodentate NHCs. Thus, addition of IPr [$\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol}-2\text{-ylidene}$] to a 1/1 mixture of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ and $\text{Mg}(\text{N}(\text{SiMe}_3)_2)_2$ produced the lithium magnesiate salt species $[(\text{IPr})_2\text{Li}]^+[\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_3]^-$ (9, Scheme 3).²⁴ This synthetic approach was extended to all heavier alkaline earth metals (Mg, Ca, Sr, Ba), which were isolated as Li^+ , Na^+ , or K^+ salts (Scheme 3).

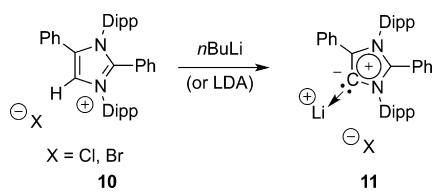
The molecular structure of the lithium magnesiate compound 9 is depicted in Figure 2. The Li cation is two coordinate through two sp^2 -hybridized carbene centers. $\text{C}_{\text{carbene}}\text{–Li}$ bond distances [2.150(4) and 2.154(4) Å] are in the average for this class of compounds (Table 1), and the $\text{C}–$

Scheme 3. Reaction of Free Carbene IPr with Equimolar Quantities of Group 1 and Group 2 Bis(trimethylsilyl)amides (Dipp = 2,6-diisopropylphenyl)**Figure 2.** Molecular structure of the lithium complex 9. Hydrogen atoms are omitted for clarity. Selected bond lengths (Angstroms) and angles (degrees): Li–C(1), 2.150(4); Li–C(28), 2.154(4); Mg–N(5), 2.0257(19); Mg–N(6), 2.0222(19); Mg–N(7), 2.0262(19); C(1)–Li–C(28), 174.5(2); N(1)–C(1)–Li, 123.22(19); N(2)–C(1)–Li, 134.63(18); N(5)–Mg–N(6), 118.76(8); N(6)–Mg–N(7), 120.45(8); N(5)–Mg–N(7), 120.78(8).

$\text{Li}–\text{C}$ bond angle deviates only slightly from linearity [174.5(2)°].

Recent developments in carbene lithium compounds include the isolation and structural characterization of Li^+ adducts bearing abnormal NHCs (α NHCs, i.e., C4 bonded to the metal center). Nearly unknown 5 years, such NHC group 1 adducts may now be considered as key components to access various unusual coordination metal compounds that may display novel reactivity due to the stronger donating ability of α NHCs vs classical NHCs. In 2009, Bertrand and co-workers first reported on the synthesis of an α NHC lithium complex via deprotonation of the corresponding imidazolium protio ligand 10 with lithium diisopropylamide (LDA) (11, Scheme 4).²⁵ In species 11, the ^{13}C NMR resonance for the $\text{C}_{\text{carbene}}$ atom resonates at 190 ppm (vs 201.9 ppm for the corresponding free

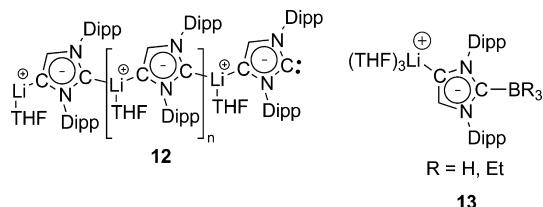
Scheme 4. Formation of the Lithiated Abnormal NHC Complex 11



*a*NHC). In contrast, performing the deprotonation reaction with potassium hexamethyldisilazide (KHMDS) produced the free *a*NHC, thus with no coordination of K⁺ to the carbene center, illustrating the better suitability of potassium salts for generation of free carbenes.

Robinson and co-workers first showed that a classical NHC such as IDipp may be readily deprotonated at the C4 position by *n*BuLi to afford the corresponding anionic NHC dicarbene Li salt (**12**, Scheme 5), as deduced from X-ray diffraction

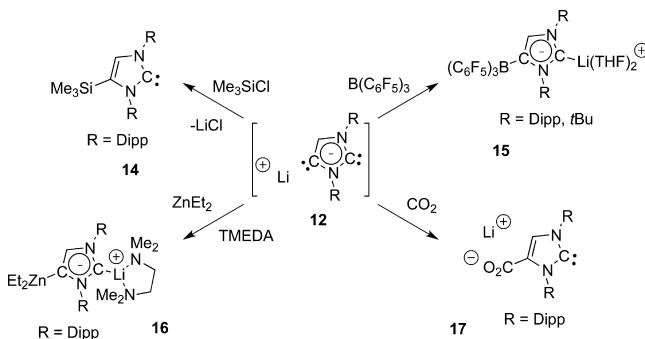
Scheme 5. Molecular Structure of the Lithiated NHCs 12 and 13



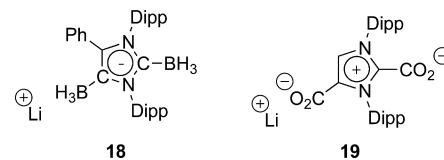
studies.²⁶ In salt **12**, each Li⁺ center coordinates to two NHC moieties, one bonded in a normal fashion [through the C2 NHC carbon; Li—C_{carbene} = 2.175(6) Å] and the other in an abnormal fashion [through the C4 NHC carbon, Li—C_{carbene} = 2.125(6) Å]. In a related manner, the lithium abnormal carbene boron compounds **13** were synthesized via deprotonation of adducts (IDipp)BH₃ and (IDipp)BEt₃ with tBuLi and nBuLi, respectively.²⁷

Subsequent reactivity studies and coordination chemistry of the Li salt **12** and related analogues are now attracting attention. In this regard, various Lewis acids and electrophiles (including Me_3SiCl , $\text{B}(\text{C}_6\text{F}_5)_3$, AlMe_3 , BEt_3 , ZnEt_2 , and CO_2) were found to preferentially react at the more sterically open C4 position (selected examples are depicted in Scheme 6 with formation of compounds **14–17**), though the C2 and C4 sites may both react with reagents such as BH_3 and CO_2 to form the bis-adduct derivatives **18** and **19**, respectively (Scheme 7).^{26,28}

Scheme 6. Selected Examples of Reactivity Studies with the Lithiated Dicarbene 12



Scheme 7. Molecular Structure the Bis-Carbene Adduct 18 and Dicarboxylate Species 19



Li^+ salts of anionic NHCs that are C4-functionalized by a $\text{B}(\text{C}_6\text{F}_5)_3$ moiety, such as species **15**, were demonstrated by Tamm and co-workers to be well-suited ligand precursors for production of *a*NHC Au(I) and Ir(I) compounds, and the derived complexes were successfully used to catalyze enyne rearrangement and alkene hydrogenation reactions, respectively.^{28a,29}

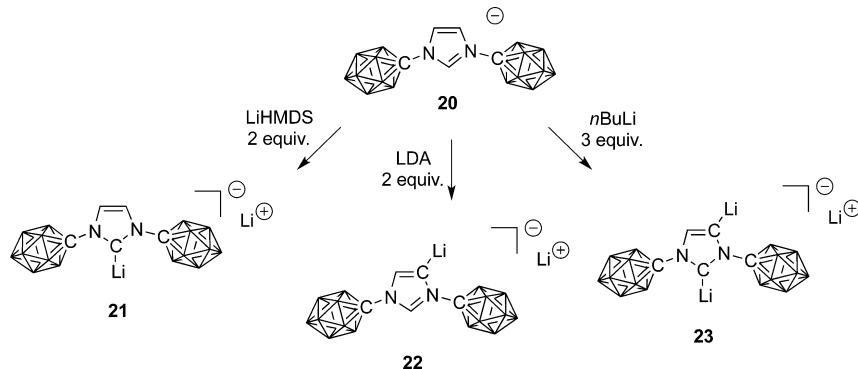
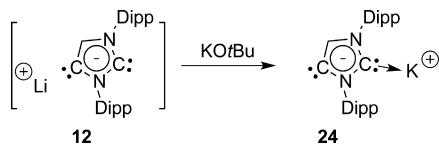
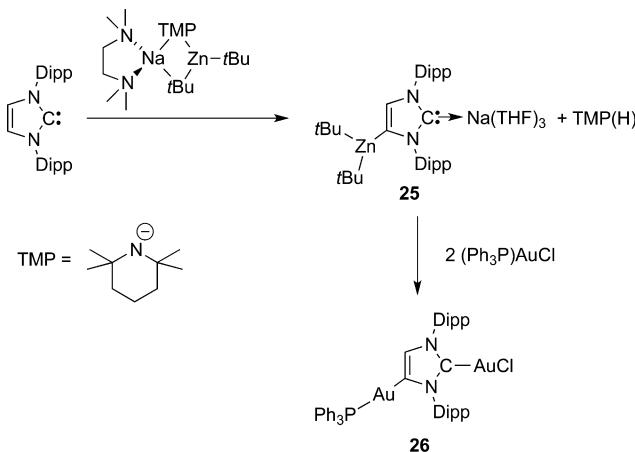
In related studies on anionic NHCs, Lavallo and co-workers isolated and characterized a number of Li salts of carborane-containing NHC anions starting from a formally monoanionic carborane N-functionalized imidazolium salt as the protic ligand.³⁰ Remarkably, the regioselectivity of the deprotonation of salt **20** (i.e., at C2 or C4) is highly dependent upon the nature of the base (Scheme 8), while reaction of **20** with LiHMDS led to formation of the normal NHC–Li dianionic adduct **21** that with LDA resulted in deprotonation at the C4 position to afford the abnormal NHC dianion **22**. It is also noteworthy that imidazolium **20** may be deprotonated twice in the presence of an excess of *n*BuLi to yield the formally trianionic NHC species **23**, found to be dimeric in the solid state through X-ray diffraction studies. Also, in these systems an unusual abnormal-to-normal carbene isomerization process was observed and found to be rapidly promoted by a trace amount of imidazolium salt **20**.

The first structurally characterized $\text{Na}^+ - \text{NHC}$ and $\text{K}^+ - \text{NHC}$ adducts were reported by the groups of Hill and Alder, respectively (compounds 5 and 9, Schemes 1 and 3).^{24,20} The number of X-ray-characterized M–NHC adducts (M = Na^+ , K^+) remains quite limited (Table 1). $\text{C}_{\text{carbene}} - \text{Na}$ bond distances in these structures range from 2.439 to 2.510 Å, while $\text{C}_{\text{carbene}} - \text{K}$ bond lengths may vary from 2.811 to 3.048 Å, in line with primarily electrostatic contacts between the $\text{C}_{\text{carbene}}$ and the Na^+ and K^+ cations.^{31,24}

Access to anionic and/or abnormal NHC sodium and potassium has also been very recently investigated. For instance, Goicoechea and co-workers described the ready synthesis of anionic NHC–K salt **24** via a salt metathesis reaction between the Li compound **12** and KO*t*Bu (Scheme 9).³² In the solid state, compound **24** features close contacts between the K⁺ cation and the C2 carbene of the anionic NHC [K–C_{carbene} = 2.905(2) Å]. As earlier observed for the Li derivative **12**, reaction of Lewis acids with **24** preferentially occurs at the C4 position. Interestingly, access to a Zn(*t*Bu)₂-functionalized NHC–Na species **25** (Scheme 10) was also recently reported via reaction of a TMP-stabilized sodium zincate species (TMP = 2,2,6,6-tetramethylpiperide) with IDipp.²³ This process, which formally results in deprotonation of the NHC ring C4 position by the TMP moiety, may be described as a sodium-mediated zincation. The transmetalation reaction of species **25** to AuCl(PPh₃) led to formation of the dinuclear Au(I) derivative **26** (Scheme 10).

Other examples of lithium and potassium NHC compounds have been reported and typically include (i) polydentate ligands incorporating a carbene ligand with an anionic functional group

Scheme 8. Deprotonation Reactions of the Carborane N-Functionalized Imidazolium Salt 20

Scheme 9. Salt Metathesis between the Li Compound 12 and KO^tBu To Form Anionic NHC–K Salt 24Scheme 10. Synthesis of Zn(*t*Bu)₂-Functionalized NHC–Na Species 25 and Transmetalation Reaction

and (ii) variously functionalized monodentate NHC ligands.³³ Such Li salts are typically prepared as intermediates to subsequently access transition metal, main group metal, or lanthanide NHC species via salt metathesis routes.¹¹ A couple of NHC-supported Li alkynyl species have also been characterized.³⁴

2.2. Group 2 Metal Complexes

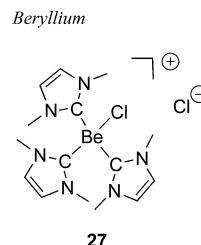
A limited number of group 2 metal NHC adducts have been described and structurally characterized, and the metal–carbene interaction in such coordination compounds is highly ionic with M–C_{carbene} contacts above the sum of the corresponding covalent radii (C–M = 1.71–1.77, 2.14–2.16, 2.46–2.49, 2.60–2.68, and 2.71–2.88 Å for M = Be, Mg, Ca, Sr, and Ba, respectively).¹³ For the C_{carbene}–M bond distances in X-ray-characterized group 2 metal NHC adducts, see Table 3.

2.2.1. Beryllium. The first beryllium carbene compound, the salt [(IMe)₃BeCl]⁺Cl[−] 27 (Scheme 11), was reported by Herrmann and co-workers in the mid-1990s upon treatment of beryllium chloride with three equivalents of 1,3-dimethylimidazolin-2-ylidene (IMe).³⁵ More recently, reaction of Ph₂Be

Table 3. Group 2 Carbene–Metal Bond Distances Compiled from the Cambridge Crystallographic Data Centre Database¹⁶

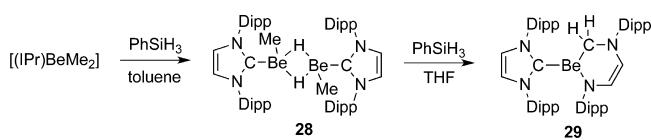
element	C _{carbene} –M min (Å)	C _{carbene} –M max (Å)	average (Å)	no. of X-ray structures
Be	1.765	1.822	1.797	6
Mg	2.201	2.288	2.247	11
Ca	2.593	2.686	2.636	5
Sr	2.731	2.768	2.749	2
Ba	2.914	3.002	2.958	2

Scheme 11. Beryllium NHC Complex 27



with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene afforded the corresponding (NHC)BePh₂ adduct.³⁶ A dimethyl beryllium NHC adduct was also isolated with the IPr ligand. Addition of PhSiH₃ (acting as a reducing agent) to (IPr)BeMe₂ produced the dimeric organoberyllium hydride [(IPr)BeHMe]₂ (28, Scheme 12).³⁷ Further reaction of complex 28 with

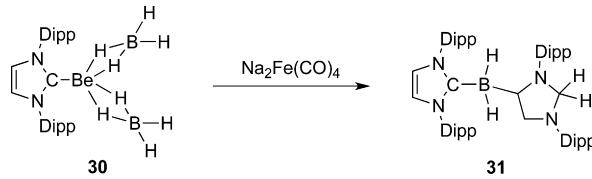
Scheme 12. Preparation of NHC Beryllium Complexes 28 and 29



PhSiH₃ (THF, 80 °C) unexpectedly afforded the ring-expanded product 29 in which the Be center is inserted into one of the C–N bonds of a NHC ligand. Both beryllium complexes were structurally characterized with C_{carbene}–Be bond distances of 1.822(2) and 1.803(5) Å for complexes 28 and 29, respectively. A DFT-based mechanism rationalizing the observed ring expansion was subsequently reported.³⁸

NHC-stabilized beryllium borohydride monomeric species (IDipp)Be(BH₄)₂ (30, Scheme 13) were also recently characterized by Robinson and co-workers and prepared by

Scheme 13. Carbene-Stabilized Beryllium Borohydride Complex 30 and Reaction with $\text{Na}_2\text{Fe}(\text{CO})_4$ ·Dioxane To Give Complex 31



reaction of (IDipp) BeCl_2 with LiBH_4 .³⁹ Remarkably, species 30 reacted with $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot$ dioxane in an unusual manner to afford the novel NHC–boron adduct 31, resulting from hydroboration of the NHC backbone $\text{C}=\text{C}$ double bond and hydrogenation of the C2 carbene atom.

Though unknown so far, low-valent Be species (i.e., $\text{Be}(0)$ or $\text{Be}(I)$) supported by NHC ligands were theoretically predicted to be viable species.⁴⁰

2.2.2. Magnesium. Discrete $\text{Mg}(\text{II})$ –NHC adducts were first synthesized over 20 years ago by Arduengo and co-workers via reaction of MgEt_2 with either IAd or IMes (adamantyl- or mesityl-substituted carbene) to afford the corresponding monoadducts.⁴¹ Analogous adducts were reported and characterized since then.⁴² As typically observed in metal–NHC species, adduct formation was confirmed by the upfield displacement of the ^{13}C NMR $\text{C}_{\text{carbene}}$ chemical shift (ca. 25–30 ppm relative to the free carbene) and by X-ray diffraction studies.

Magnesium complexes incorporating amido-functionalized NHC ligands were initially reported in 2004 by Arnold et al. (Scheme 14, compound 32), and derivatives bearing a tridentate bis-NHC-amide ligand were also synthesized (33, Scheme 14).^{33c,43,44} Meanwhile, Zhang and Kawaguchi also investigated aryloxy-functionalized NHC ligands and reported the corresponding dinuclear Mg complex 34.⁴⁵

Tris-NHC–borate magnesium bromide species 35 (Scheme 14) were also characterized and subsequently used as ligand transfer reagents to produce the corresponding $\text{Fe}(\text{II})$ complexes.^{46,47} Magnesium NHC complexes were also studied as initiators of lactide ring-opening polymerization (ROP). For instance, the $\text{Mg}(\text{II})$ amido derivative 36 readily initiates the ROP of *rac*-lactide at room temperature with a moderate level of control to afford a heterotactic-enriched PLA (PDI = 1.57, 58% heterotacticity, Scheme 15).⁴⁸ It was proposed that ROP initiation proceeds through an initial insertion/ring-opening of lactide into the $\text{C}_{\text{carbene}}\text{–Mg}$ bond (Scheme 15).

Magnesium hydride species may be also stabilized by NHC ligands. Thus, Hill and co-workers isolated magnesium hydride species of general formula $(\text{NHC})_2\text{Mg}_4\text{H}_6[\text{N}(\text{SiMe}_3)_2]_2$ that display a higher hydride/Mg ratio (1:1.5) than any complex

described to date.⁴⁹ NHC-supported Mg alkynyl species have also been characterized.³⁴

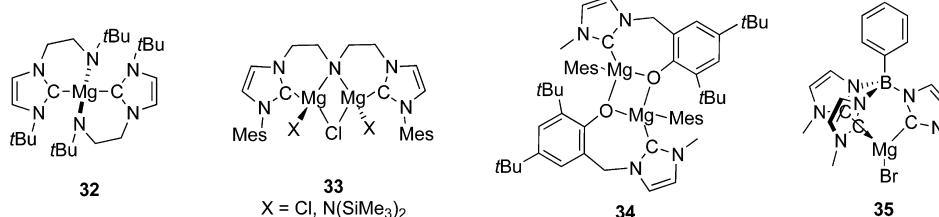
Use of N-heterocyclic carbenes as catalysts for activation of Grignard reagents was recently developed. Addition of a NHC to a Grignard reagent resulted in an enhanced nucleophilicity of the Mg–R moiety, which was exploited in Grignard allylic substitutions.⁵⁰ MgCl_2 was also used as a NHC protecting group and the corresponding $(\text{NHC})\text{MgCl}_2$ adducts utilized as latent precatalysts for solvent-free polymerization of ϵ -caprolactone.⁵¹

2.2.3. Calcium, Strontium, and Barium. The reactivity of NHCs with various alkaline earth metallocenes (Mg , Ca , Sr , Ba) of the type Cp^*_2M was also investigated in the late 1990s by Arduengo and led to adducts of the type $\text{Cp}^*_2\text{M}\text{–}(\text{NHC})$.^{52,53} For the latter species, X-ray structural data along with NMR studies provided insight into the nature of the $\text{C}_{\text{carbene}}\text{–M}$ bond, found to range from somewhat covalent with $\text{Mg}(\text{II})$ to rather ionic with $\text{Ba}(\text{II})$. The heavier alkaline elements (Sr and Ba) are also able to form stable bis-NHC adducts.

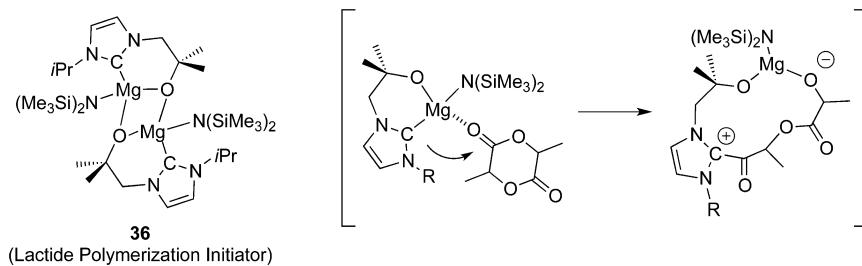
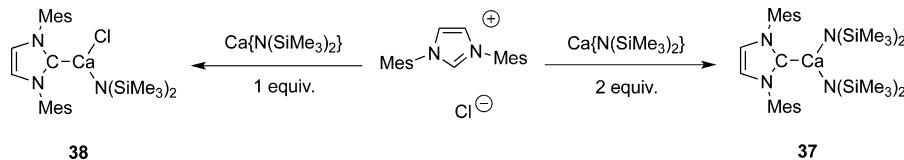
Barrett, Hill, and co-workers investigated NHC coordination chemistry with heavier group 2 bis(trimethylsilyl)amido precursors.⁵⁴ The protonolysis reaction between the azonium IMes·HCl and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]$ (1/2 ratio) led to the corresponding adduct $(\text{IMes})\text{Ca}[\text{N}(\text{SiMe}_3)_2]$ (37, Scheme 16). The methodology was successfully extended to $\text{Sr}(\text{II})$ and $\text{Ba}(\text{II})$ amido analogues. Interestingly, the amine elimination reaction of a 1/1 mixture of IMes·HCl and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]$ afforded the mixed amido–chloride $\text{Ca}(\text{II})$ –NHC species 38. Adduct 38 is presumably an intermediate prior to formation of complex 37. Conversion of 38 to 37 was proposed to proceed (i) via a NHC transfer to unreacted $\text{Ca}[\text{N}(\text{SiMe}_3)_2]$, (ii) via a salt metathesis reaction between 38 and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]$, or (iii) resulting from a Schlenk-like redistribution. The Ca complex 37 was structurally characterized along with its $\text{Sr}(\text{II})$ and $\text{Ba}(\text{II})$ analogues [$\text{C}_{\text{carbene}}\text{–M}$ bond distances = 2.2895(13), 2.4277(14), and 2.579(3) Å, respectively]. Though stable in solution, adduct 37 readily reacted with protic substrates via protonolysis of the $\text{Ca–C}_{\text{carbene}}$ bond. Furthermore, regarding the relative strength of Ca–L Lewis adducts, a series of complexation reactions carried out with various Lewis bases agree with the following decreasing order: $\text{Ph}_3\text{P}=\text{O} > \text{NHC} \approx \text{THF} > \text{PPh}_3$.

Bis(imidazolin-2-ylidene)borate and tris(imidazolin-2-ylidene)borate metal complexes of the heavier alkaline earths were also prepared and structurally characterized.⁵⁵ The bis-NHCs adduct species retain their integrity in the presence of amine donors, a stability ascribed to the strong ionic character of the $\text{M–C}_{\text{carbene}}$ bonds. Thus, these relatively robust systems were further used as precatalysts for the intramolecular hydroamination reaction (Scheme 17). The strontium deriva-

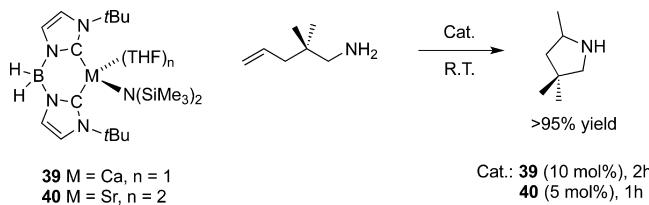
Scheme 14. Amido- and Aryloxy-Functionalized NHC Magnesium Complexes 32–34 and Tris-NHC–Borate Magnesium Bromide 35



Scheme 15. Proposed Lactide Initiation Pathway with Complex 36

Scheme 16. Reaction of $\text{Ca}[\text{N}(\text{SiMe}_3)_2]$ with IMes·HCl

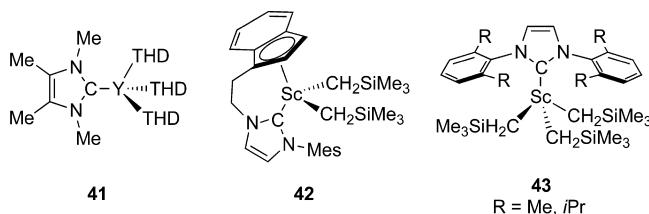
tive **40** was found to be more active than the calcium analogue **39**.

Scheme 17. Intramolecular Hydroamination of Terminal Aminoalkenes Catalyzed by Complexes **39** and **40**

3. EARLY TRANSITION METAL COMPLEXES

3.1. Group 3 Metal Complexes

A group 3 NHC complex, the seven-coordinate Y–NHC adduct **41** (Scheme 18), was first prepared in 1994 by

Scheme 18. First Examples of Yttrium and Scandium NHC Complexes **41** and **42** as Well as scandium NHC Monodentate Complex **43**^a

^aTHD = 2,2,6,6-tetramethylheptane-3,5-dionato.

Arduengo and co-workers via reaction of 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene with tris(2,2,6,6-tetramethylheptane-3,5-dionato)yttrium [$\text{Y}(\text{THD})_3$].⁵⁶ The ^{13}C NMR spectrum of **41** displays a doublet resonance for the carbene atom (δ 199.4 ppm) with a coupling constant of 33 Hz to the ^{89}Y nucleus. The first scandium NHC complexes were only disclosed in 2007 by Cui et al. with the synthesis of the indenyl-functionalized NHC scandium complex **42** via a SiMe_4 elimination reaction between $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ and the indenyl-functionalized NHC.^{57,58} Following a similar approach,

the yttrium analogue was also synthesized and characterized. In the solid state, the Sc(III) center in compound **42** adopts a tetrahedral geometry with a $\text{C}_{\text{carbene}}\text{—Sc}$ bond length of 2.350(3) Å. A Sc(III) derivative supported by a fluorenyl-functionalized NHC ligand was also reported.⁵⁹ Scandium complexes bearing monodentate NHC ligands are also known and structurally characterized, with $\text{C}_{\text{carbene}}\text{—Sc}$ bond lengths of 2.433(9) and 2.412(5) Å for derivatives of **43**, respectively.⁶⁰ Table 4 compiles the $\text{C}_{\text{carbene}}\text{—M}$ bond distances for X-ray

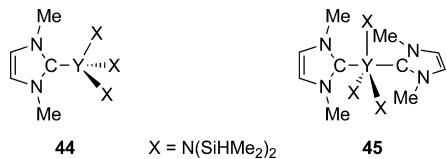
Table 4. Group 3 Carbene–Metal Bond Distances Compiled from the Cambridge Crystallographic Data Centre Database¹⁶

element	C–M min (Å)	C–M max (Å)	average (Å)	no. of X-ray structures
Sc	2.342	2.464	2.426	10
Y	2.501	2.642	2.579	15

characterized NHC group 3 species. The NHC scandium alkyl derivatives **42** and **43** were tested as olefin polymerization catalysts. Though complex **42** and its fluorenyl analogue exhibit low to no activity in isoprene polymerization,^{59,61} they efficiently mediate the copolymerization of ethylene/1-hexene (or 1-octene).⁶² Related half-sandwich Sc(III)–NHC catalysts successfully catalyzed the copolymerization of nonconjugated dienes (i.e., 1,5-hexadiene and 1,6-heptadiene),⁶³ copolymerization of ethylene with norbornene,⁶⁴ and polymerization of methylene butyrolactone derivatives.⁶⁵

NHC–scandium species **43** also exhibit high activities in 1-hexene polymerization or copolymerization with 1-octene (or 1-decene) upon activation with two equivalents of $[\text{Ph}_3\text{C}] [\text{B}(\text{C}_6\text{F}_5)_4]$.⁶⁰

Tris-amido Y(III) derivatives supported by one or two NHC moieties have been described and prepared by reaction of the free carbene with the corresponding tris-amido precursors. Thus, combining $\text{Y}[\text{N}(\text{SiHMe}_2)_2]_3$ with one or two equivalents of IMe led to the corresponding complexes **44** and **45** (Scheme 19).⁶⁶ The ^{13}C NMR spectrum of compound **44** displays a characteristic $\text{C}_{\text{carbene}}$ doublet resonance (δ 190.3 ppm, $^{1}\text{J}_{\text{Y-Carbene}} = 49.6$ Hz) with a $^{1}\text{J}_{\text{Y-Carbene}}$ coupling constant significantly larger than that in the Y–NHC complex **41**. The latter suggested a stronger interaction between the yttrium center and the carbene in **44** versus **41**. As deduced from X-ray

Scheme 19. Yttrium Tris-Amido NHC Complexes

data, the C_{carbene}–Y bond (2.55(1) Å) in **44** is significantly shorter than those in the bis-NHC complex **45** [2.648(8) and 2.671(9) Å].

The coordination of hindered N-heterocyclic carbenes such as iPr or IMes to Y(III) was investigated by Okuda et al.⁶⁷ While the four-coordinate adduct (iPr)₂Y(CH₂SiMe₃)₃ was isolated and characterized upon reaction of iPr with (THF)₂Y(CH₂SiMe₃)₃, C–H activation of an *ortho*-methyl group occurred upon reaction of IMes with (THF)₂Y(CH₂SiMe₃)₃ resulting in formation of the orthometalated compound **46** (Figure 3). The Y–C_{carbene} bond length in **46** [2.6420(16) Å] is

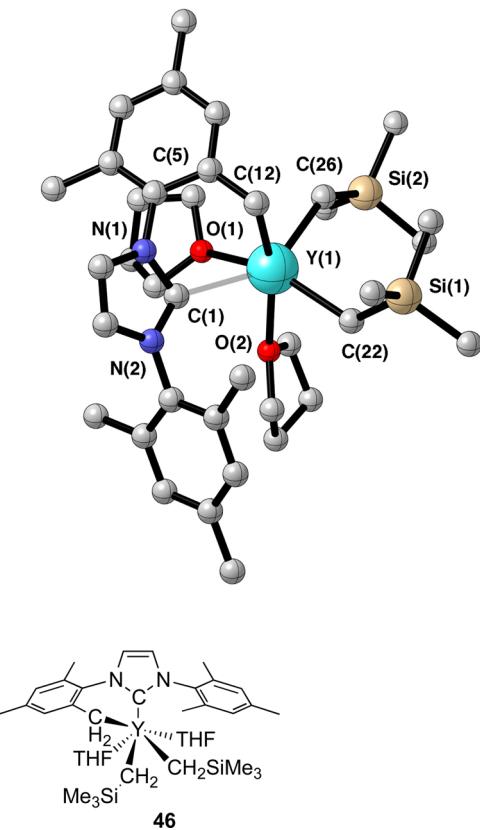
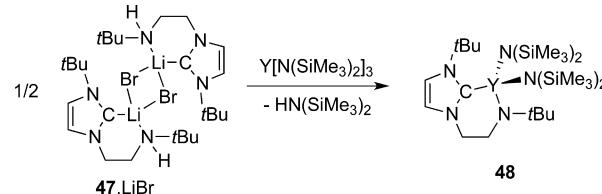


Figure 3. Molecular structure of the scandium complex **46**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Angstroms) and angles (degrees): Y(1)–C(1), 2.6420(16); Y(1)–C(12), 2.4995(16); Y(1)–C(22), 2.4285(16); Y(1)–C(26), 2.4263(17); Y(1)–O(1), 2.4761(11); C(1)–Y(1)–C(12), 70.25(5); O(1)–Y(1)–C(26), 83.54(5).

longer than those in other Y–NHC compounds despite the value of the Y–C_{carbene} coupling constant [¹J_{YC} = 37.3 Hz, δ(C_{carbene}) = 194.1 ppm].

In view of the rather labile NHC coordination to oxophilic and electropositive metal centers such as group 3 M(III) salts, introduction of an anionic (or dianionic) amido/alkoxide tether onto the NHC ligand was developed to promote robust attachment of the carbene moiety to the oxophilic metal center.

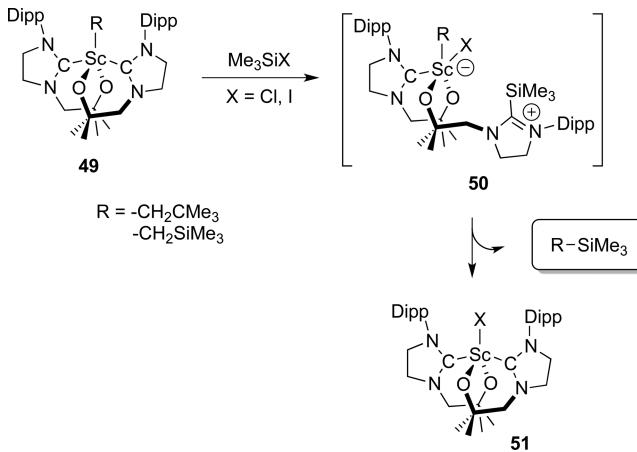
The first report on such metal NHC complexes by Arnold et al. in 2003 involved the synthesis and characterization of the amine–carbene Y–NHC chelate complex **48** prepared via an amine elimination reaction between precursor **47**·LiBr and Y[N(SiMe₃)₂]₃ (Scheme 20).^{33d,31b,68} The ¹J_{YC} coupling

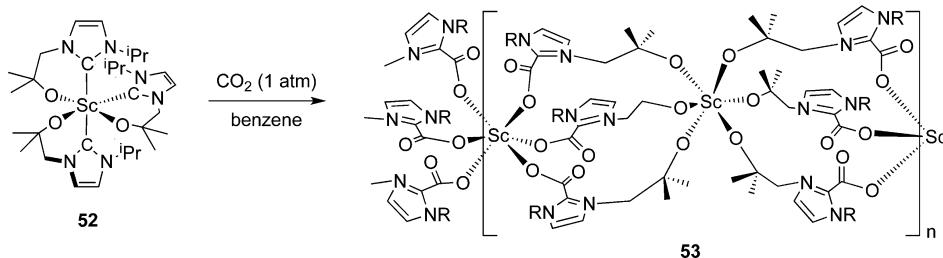
Scheme 20. Synthesis of Amido NHC Complex 48

constant of the Y–C_{carbene} (δ 186.3 ppm, ¹J_{YC} = 54.7 Hz) in species **48** remains the largest to date. X-ray analysis showed a pseudotetrahedral geometry at the Y(III) center with a C_{carbene}–Y bond length of 2.501(5) Å. Complex **48** readily dissociates upon addition of Lewis bases such as tetramethylethylenediamine (tmEDA) or Ph₃P=O but retains its integrity in the presence of THF, Et₂O, PPh₃, or Me₃NO. Acting as a bifunctional catalyst akin to its magnesium analogue **36** (Scheme 15), complex **48** initiates the ring-opening polymerization of lactide for production of well-defined poly(lactide).⁶⁹

Arnold et al. recently reported on reactivity studies of Sc(III) and Y(III) carbyl complexes supported by tethered bidentate alkoxide-saturated NHC ligands with Me₃SiX (X = Cl, I), resulting in carbon–silicon and carbon–carbon bond formation by elimination reactions. For example, treatment of the Sc alkyl complex **49** with Me₃SiX (X = Cl, I) led to intermediate **50**, arising from cleavage of the Sc(III)–C_{carbene} bond and attachment of the SiMe₃ group to the C_{carbene} atom (Scheme 21). The latter is unstable and slowly converts into the corresponding complex **51** with elimination of R–SiMe₃ (R = CH₂SiMe₃, CH₂CMe₃) and thus with formation of a C–Si bond.⁷⁰

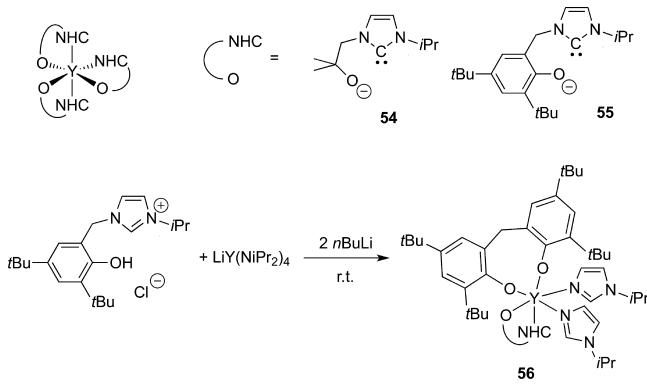
Reaction of (THF)₃ScCl₃ with three equivalents of a tethered bidentate alkoxide-saturated NHC ligand afforded the corresponding homoleptic species **52** in good yield (Scheme 22). X-ray diffraction studies confirmed the molecular structure of the chiral complex (the asymmetric unit contains both enantiomers; mean C_{carbene}–Sc bond distance 2.436 Å).

Scheme 21. Formation of C–Si Bonds upon Addition of Halosilane to Sc–NHC Complexes

Scheme 22. Reaction of the Sc(III)–NHC Complex 52 with CO₂

Variable-temperature ¹H NMR studies of complex 52 suggested a labile coordination of the NHC to the Sc(III) center. Such a feature was exploited for frustrated-Lewis-pair-type reactivity with CO₂ or CS₂. Thus, species 52 readily reacted with CO₂ via insertion into all three Sc–C_{carbene} bonds to form the coordination polymer 53 (Scheme 22). In contrast, only up to two equivalents of CS₂ reacted with the homoleptic complex 52 to yield formation of a dithiocarboxylated imidazolium Sc(III) derivative.⁷¹

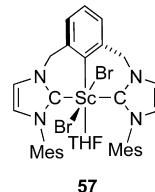
Coordination of bidentate NHC-containing ligands with an alkoxide (or phenoxide) tether to Y(III) was also studied. Several homoleptic NHC-incorporating complexes were reported, and two representative examples are depicted in Scheme 23.⁷² For instance, reaction of (THF)₃YCl₃ with three

Scheme 23. Yttrium Homoleptic Complexes 54 and 55 and Room-Temperature Reaction of a Phenol–Imidazolium Salt with Li[Y(NiPr₂)₄] Leading to Formation of Complex 56

equivalents of the corresponding alkoxide–NHC potassium salt produced the homoleptic complex 54.⁷³ The NHC–phenoxide yttrium species 55 was prepared from the corresponding imidazolium salt, two equivalents of *n*BuLi, and Li[Y(NiPr₂)₄] at –78 °C.⁷⁴ When conducted at room temperature, the latter reaction led, unexpectedly, to isolation of the mono-NHC bis-phenolate chelate 56, which results from partial decomposition of the chelating ligand (Scheme 23).

Access to ($\kappa^3\text{-}C,C',C''$)Sc(III) pincer chelates 57 (Scheme 24) was achieved via a salt metathesis reaction between ScCl₃ and the *in situ* generated corresponding bis-NHC phenide Li salt.⁷⁵ Anionic 3-borane-1-alkylimidazol-2-ylidene were used as ligands with scandium.⁷⁶ The anionic tetracarbene Sc complex (NHC)₄Sc[–]Li⁺ was synthesized by reaction of the Li species 3 (Scheme 1) with ScCl₃.¹⁸

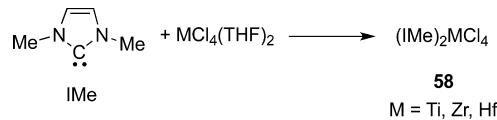
A theoretical study of the coordination of 2,6-bis(imidazole-2-ylidene)pyridine tridentate ligand to Sc(III) and Y(III) conducted by Maron and Bourissou concluded on essentially ionic metal–ligand bonds with a small covalent contribution.⁷⁷

Scheme 24. ($\kappa^3\text{-}C,C',C''$)Sc(III) Pincer Chelates 57

3.2. Group 4 Metal Complexes

NHC adducts of group 4 metals were first reported by Herrmann and co-workers in 1994 (58, Scheme 25) and

Scheme 25. Group 4 NHC Complexes Adducts via THF Substitution

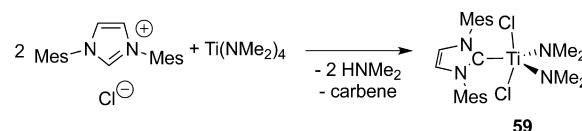


prepared via ligand substitution of the corresponding metal halide THF adducts.⁷⁸ This strategy was inspired by substitution of a CO ligand in hexacarbonyl group 6 compounds with IMe carbene ligand to afford the corresponding complexes (IMe)M(CO)₅ (M = Cr, Mo, W).⁷⁹

Alternatively, direct addition of a NHC to an early transition metal precursor may lead to the corresponding NHC–M adducts. For instance, (NHC)TiCl₄ (NHC = 1,3-dialkyl-4,5-dimethylimidazol-2-ylidene) was produced upon combining the free carbene with TiCl₄. Likewise, various monodentate adducts such as (NHC)₂TiF₄,^{80,81} (NHC)TiCl₂(NMe₂)₂,^{82,83} and benzannulated NHC Ti complex (NHC)TiCl₄⁸⁴ and also bidentate adducts with imino-N-heterocyclic carbene ligands have been described.⁸⁵ Note that careful hydrolysis of (NHC)TiCl₄ led to a well-defined μ -oxo Ti(IV)–NHC complex, as determined by XRD studies.⁸⁶

The amine elimination approach was found to be an effective and a direct method to access group 4 NHC species from azolium precursors as first shown by Cowley and co-workers.⁸⁷ Thus, the amine elimination reaction of two equivalents of the azolium (IMes)·HCl with Ti(NMe₂)₄ led to the NHC complex (IMes)TiCl₂(NMe₂)₂ 59, isolated in 45% yield (Scheme 26). In

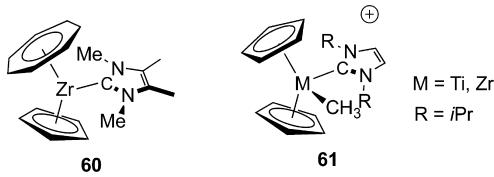
Scheme 26. Synthesis of the Ti–NHC Complex 59 via Amine Elimination



the solid state, adduct **59** features a central Ti metal center in a distorted trigonal bipyramidal geometry with the amido ligands and IMes occupying the equatorial positions. The Cl–Ti–Cl angle [163.93(6) $^{\circ}$] significantly deviates from ideal linear coordination. The C_{carbene}…Cl distances [3.103(5) and 3.120(5) Å] lie considerably below the sum of van der Waals radii for carbon and chlorine (3.65 Å), which was ascribed to a bonding overlap between the chlorine lone pairs and the formally vacant NHC p orbital. Such an interaction, which may be seen as a back-bonding from the chlorine lone pairs to the Ti-coordinated NHC, agrees with a fairly electrophilic C_{carbene} atom and supports the view that the coordinated NHC moiety in early transition metal species may exhibit Fischer-type carbene behavior.

Monodentate NHC adducts of Zr and Hf such as (NHC)₂MCl₄ have also been reported and structurally characterized.⁸⁸ The molecular structure of the bis-NHC species (IMes)ZrCl₂(NMe₂)₂ is also consistent with short C_{carbene}…Cl intramolecular contacts akin to those of the titanium congener.⁸⁹ Reaction of the Zr(II) metallocene [$(\eta^7\text{-C}_7\text{H}_7)\text{Zr}(\eta^5\text{-C}_5\text{H}_5)$] with tetramethylimidazolin-2-ylidene yielded the corresponding adduct **60** as confirmed from X-ray studies (Scheme 27). In contrast, PMe₃ only weakly

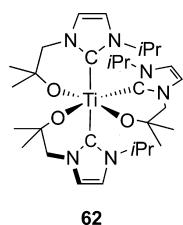
Scheme 27. Zr Metallocene NHC Complexes **60** and **61**



coordinates to the latter Zr(II) species, which precluded isolation of the corresponding Me₃P–Zr adduct.^{90–92} Treatment of [Cp₂TiCH₃(THF)]⁺ with 1,3-diisopropylimidazol-2-ylidene gave the corresponding NHC adduct [Cp₂TiCH₃(NHC)]⁺ **61** by THF displacement. The conformational orientation of the ligand indicates that the ligand acts as a pure σ donor.^{93–95}

As discussed above with group 2 and 3 metal NHC species, introduction of an anionic or a dianionic tether onto the NHC ligand may favor robust attachment of the carbene moiety to transition metals. For example, bidentate-tethered alkoxide NHC ligands were successfully used for synthesis of the octahedral titanium(III) tris(carbene) homoleptic complex **62** (Scheme 28).⁹⁶ The latter was compared with its yttrium analogue **54** for possible experimental evidence of a π -bonding component in the C_{carbene}–M bond. The yttrium complex **54** displays a rather lengthened metal M–C_{carbene} bond (~2.59 Å), whereas that of the titanium complex **62** is substantially shorter

Scheme 28. Titanium(III) Tris(carbene) Homoleptic Complex **62**



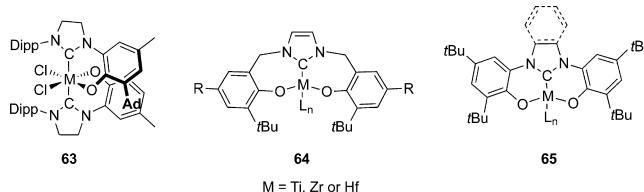
(2.28 Å). After correcting these values by the ionic radii (1.46 vs 1.55 Å for Ti and Y, respectively), it was suggested that the shorter Ti–C_{carbene} vs Y–C_{carbene} distances may result from a M → C_{carbene} π -back-bonding contribution in the Ti(III) complex **62** (Table 5). However, DFT investigations suggested that the shorter M–C_{carbene} bond in **62** vs **54** may be due to the smaller size and thus more polarizing nature of the Ti center.⁷³

Table 5. Group 4 Carbene–Metal Bond Distances Compiled from the Cambridge Crystallographic Data Centre Database¹⁶

element	oxidation state	C–M min (Å)	C–M max (Å)	average (Å)	no. of X-ray structures
Ti	III	2.178	2.349	2.263	7
	IV	2.165	2.324	2.240	25
Zr	IV	2.296	2.471	2.402	25
Hf	IV	2.343	2.405	2.374	3

The coordination chemistry of tethered bidentate phenoxide NHC ligands was first studied with nickel and palladium metals to afford robust complexes.⁹⁷ Later, this class of bidentate ligands was also shown to form stable chelates with Ti(IV) and Zr(IV). For instance, the octahedral group 4 complexes **63** were synthesized via double deprotonation of the azonium precursor and subsequent salt metathesis reaction with TiCl₄(THF)₂ or ZrCl₄ (Scheme 29).^{98,99} These NHC metal

Scheme 29. NHC-Incorporating Pincer-Type Chelating Ligands with Group 4 Transition Metals



derivatives displayed moderate activities ethylene polymerization catalysis upon activation with MAO (up to 76 kg·mol_{cat}⁻¹·h⁻¹). C₂-symmetric bis-phenoxide–NHC chelating ligands were demonstrated to be well-suited ligands to access robust group 4 NHC chelate complexes. Kawaguchi and co-workers first reported on such coordination compounds in 2003 (**64**, M = Ti, L = 2 Cl, THF, R = tBu). Upon MAO activation, the titanium complex catalyzes ethylene polymerization with an activity of 290 kg·mol_{cat}⁻¹·h⁻¹·bar⁻¹.¹⁰⁰ Various complexes of type **64** have been reported since then with derivatives of the following general formula: LTiBr₂(THF), LTi(CH₂Ph)₂, LTiMe₂, LZrCl₂(THF), LZr(CH₂Ph)₂, LZr(CH₂Ph)₂, or homoleptic complexes L₂M (L = bis-phenolate NHC ligand; M = Ti, Zr).^{101–104} Notably, the latter compounds include a very recent report on chiral saturated carbene group 4 complexes of type **64** (Ti, Zr, and Hf). Some of these complexes promote controlled ROP of rac-lactide for production of heterotactic-enriched PLA.¹⁰⁵

Seeking more robust NHC-incorporating pincer-type chelating ligands, we developed group 4 NHC compounds bearing a bis-phenoxide–NHC tridentate ligand in which two phenoxide moieties are directly connected to the nitrogen atoms of a central NHC (**65**, Scheme 29).¹⁰⁶ It was envisioned that such a structure may be suitable for coordination to a variety of metal centers across the periodic table, including early transition

metals.¹⁰⁷ Group 4 complexes bearing such tridentate are indeed readily accessible in high yields via an alcohol elimination route. For instance, reaction of azolium **66**·HCl with $M(OiPr)_4$ afforded the corresponding carbene complexes **67** (Scheme 30, Figure 4).^{108–110} Figure 3 depicts the

Scheme 30. Group 4 Complexes **67** Obtained via Alcohol Elimination Route

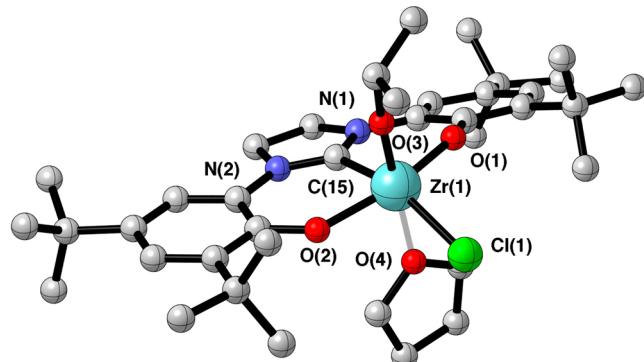
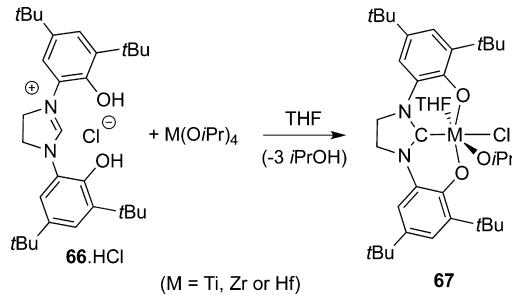
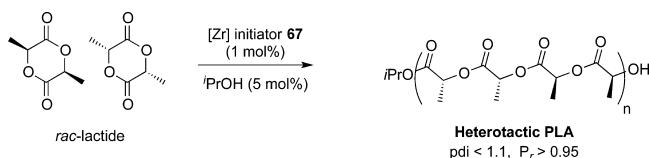


Figure 4. Molecular structure of **67** ($M = Zr$). Hydrogen atoms are omitted for clarity. Selected bond lengths (Angstroms) and angles (degrees): $Zr(1)-O(1)$, 2.001(2); $Zr(1)-O(2)$, 1.991(2); $Zr(1)-O(3)$ = 1.912(3); $Zr(1)-O(4)$, 2.350(2); $Zr(1)-Cl(1)$, 2.493(1); $Zr(1)-C(15)$ = 2.360(3); $C(15)-Zr(1)-Cl(1)$, 156.32(8); $O(2)-Zr(1)-C(15)$, 76.26(9); $O(2)-Zr(1)-Cl(1)$, 98.88(7); $O(3)-Zr(1)-O(4)$, 179.45(11).

molecular structure of the $Zr(IV)$ -NHC derivative $LZr(OiPr)_2(Cl)(THF)$, evidencing the effective *mer*-coordination of the OCO^{2-} tridentate ligand [$C_{\text{carbene}}-Zr$ bond distance = 2.360(3) Å] with a Zr center in a distorted octahedral environment.

The titanium alkoxide **67** efficiently mediates controlled ROP of *rac*-lactide to produce chain-length controlled and atactic PLA. Going from Ti to Zr dramatically improved both the ROP activity and the stereoselectivity, with the Zr analog allowing a highly controlled and heteroselective ROP of *rac*-lactide at room temperature (Scheme 31). Remarkably, these excellent levels of polymerization control and stereoselectivity are unaltered under immortal ROP conditions, i.e., in the presence of an excess of *i*PrOH (vs metal initiator) acting as a

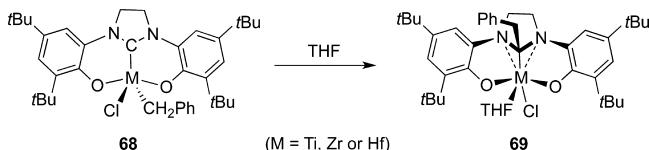
Scheme 31. Highly Stereoselective ROP of Lactide in the Presence of Zr Complex **67**



chain transfer agent. The zirconium ROP initiator also allowed access to well-defined and highly heterotactic poly(lactic acid)-poly(trimethyl carbonate) block copolymers via a sequential ROP of trimethylene carbonate (TMC) and *rac*-lactide.¹⁰⁸

Zr benzyl derivatives of the type **68** were also prepared via a toluene elimination reaction between azolium **66**·HCl and $Zr(CH_2Ph)_4$ to yield the chloro benzyl Zr species **68** in high yield (Scheme 32). Unexpectedly, the latter is quite reactive in

Scheme 32. THF-Promoted Rearrangement of the Zr Complex **68**

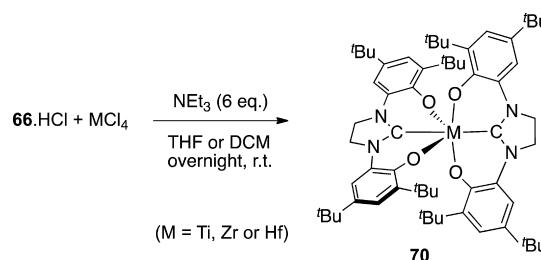


the presence of a Lewis base such as THF to readily rearrange into an unusual heptacoordinate Zr -THF adduct (**69**, Scheme 32), as deduced from X-ray crystallographic studies.^{111,112} This unprecedented reactivity, reflecting a clear-cut Fisher-type carbene behavior for species **68** (i.e., an electrophilic carbene carbon), was rationalized by DFT calculations.

Access to the zirconium and hafnium dibenzyl derivatives (of species **68**) may be readily performed upon reaction of one equivalent of $PhCH_2MgBr$ with species **68**. These were then converted into the corresponding anilinium benzyl cationic species upon a protonolysis reaction with $[HNMe_2Ph][B(C_6F_5)_4]$. The anilinium $Zr-CH_2Ph^+$ cation ($OCO)^+Zr-(CH_2Ph)(NMe_2Ph)^+$ catalyzes at room temperature the highly regioselective oligomerization of 1-hexene with a marked preference for trimer formation.¹¹⁰ Addition of a phosphine ligand to a related NHC complex switches it from a 1-hexene oligomerization to a polymerization catalyst.¹¹³ The titanium complexes **67** were also successfully used as initiators of the cyclohexene oxide/ CO_2 copolymerization.¹¹⁴ In the presence of bis(triphenylphosphine)iminium chloride or nitrite salts as cocatalysts, a high degree of carbonate linkage (>99%) was observed.

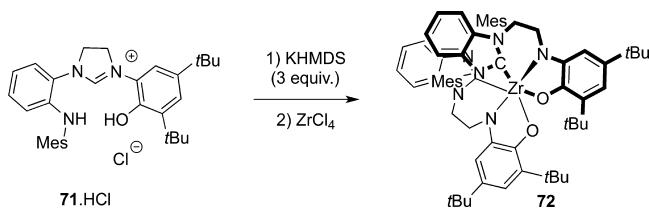
Reaction of two equivalents of proligand **66**·HCl and group 4 precursor McI_4 ($M = Ti$, Zr , or Hf) in the presence of triethylamine gave the corresponding homoleptic complex **70** in excellent yield (Scheme 33).¹¹⁵ The robust and air-stable complexes **70** could be studied by cyclic voltammetry, and the one-electron oxidized complexes agreed with formation of a ligand-centered radical species. Interestingly, the Zr and Hf complexes are luminescent and constitute the first examples of emissive nonmetallocene group 4 metal complexes.

Scheme 33. Synthesis of Homoleptic NHC Group 4 Complexes **70**



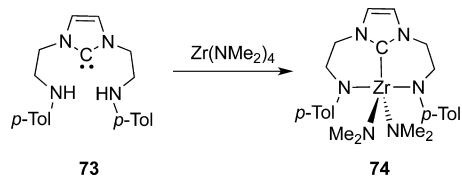
The coordination chemistry of an unsymmetrical tridentate dianionic N-heterocyclic carbene was recently investigated with Zr(IV). Triple deprotonation of the azonium salt **71**·HCl followed by addition of $ZrCl_4$ led to formation of the bis(benzimidazolylidene)zirconium homoleptic complex **72**, resulting from rearrangement of the imidazolyl unit into a benzimidazolyl moiety (Scheme 34).¹¹⁶ The latter ligand-based rearrangement seems to occur upon deprotonation of the azonium salt.

Scheme 34. Rearrangement of the Aniline–Phenol Azonium Precursor **71**·HCl Yielding the Zr Complex **72**



The coordination chemistry of tridentate amino-bis(N-heterocyclic carbene) ligands with Ti(IV) and Zr(IV) precursors was also investigated.^{33d} Zirconium complexes supported by bis-amido NHC tridentate ligands are known as well. For instance, amine or alkyl elimination reaction of tridentate carbene **73** with Zr(IV) alkyl/amido precursors provided access to various Zr(IV)–NHC adducts.^{117–119} Note that carbene **73** is a stable entity and may be readily generated via deprotonation of the appropriate azonium precursor. For instance, aminolysis of $Zr(NMe_2)_4$ with carbene **73** afforded the corresponding κ^3 -(bis-amido–NHC) chelate complex **74** in good yield (Scheme 35). Various amido, chloro, and alkyl

Scheme 35. Zirconium Complex **74** of a Tridentate-NHC Ligand



group 4 derivatives were also prepared and characterized. Figure 5 displays the molecular structure of the bis-[(trimethylsilyl)methyl] zirconium derivative $LZr(CH_2SiMe_3)_2$ (**75**), which may be produced either by carbylation of the dichloro precursor or by a protonolysis reaction between **73** and $Zr(CH_2SiMe_3)_4$. In the solid state, the geometry around the Zr(IV) metal center is distorted trigonal bipyramidal, with the tridentate NHC-containing ligand coordinating in *mer*-fashion. The C_{carbene}–Zr bond length is 2.415(3) Å, which is in accordance with related structures.¹¹⁹

κ^3 -(Bis-amido–NHC) Hf and Zr dimethyl derivatives of type **75** were tested in the polymerization of ethylene (activation with $[Ph_3C][B(C_6F_5)_4]$).¹²⁰ Moderate activity was observed with the derived Zr methyl cation ($125\text{ kg}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}\cdot\text{atm}^{-1}$), possibly reflecting the fast decomposition of the catalytically active cationic species under polymerization conditions. The hafnium dialkyl complexes insert carbon monoxide as well as isocyanides to yield η^2 -acyl and η^2 -iminoacyl derivatives, respectively.

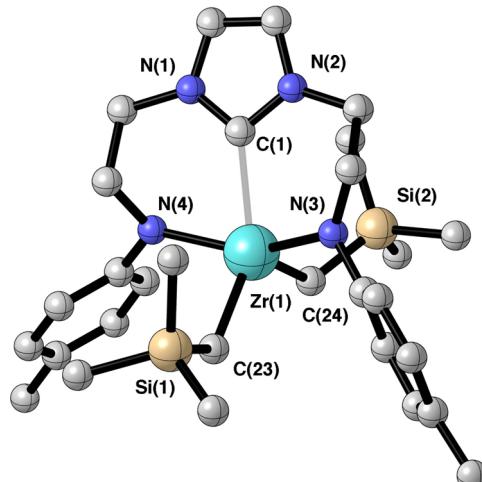
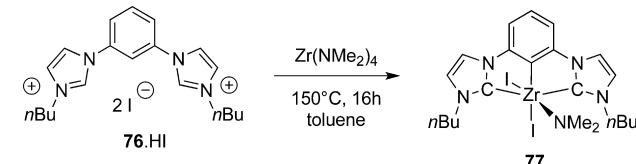


Figure 5. Molecular structure of the Zr NHC complex **75**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Angstroms) and angles (degrees): Zr(1)–C(1), 2.415(3); Zr(1)–N(3), 2.173(2); Zr(1)–N(4), 2.135(2); Zr(1)–C(23), 2.238(3); Zr(1)–C(24), 2.254(3); N(3)–Zr(1)–C(1), 78.23(9); N(4)–Zr(1)–C(1), 76.27(9); C(24)–Zr(1)–C(1), 115.29(10); N(4)–Zr(1)–N(3), 148.73(9).

Anionic bis-NHC tridentate pincer ligands may also be suited for coordination to early transition metal centers.^{2g} Complexes incorporating a tridentate pincer ligand bound to the metal center via a central metal–C σ bond and two lateral M–NHC dative bonds have been reported by Hollis and co-workers.^{121,122} Such ligand design was envisioned for more robust metal NHC compounds, a feature of interest in homogeneous catalysis.¹²² Reaction of the bis(imidazolium) precursor **76**·HI with $Zr(NMe_2)_4$ in toluene and subsequent heating quantitatively led to the desired complex $LZrI_2(NMe_2)$ (**77**, Scheme 36). Complex **77** could be structurally characterized by X-ray

Scheme 36. Synthesis of Bis(carbene) Complex **77**



diffraction studies and exhibit a shorter C_{carbene}–Zr bond length [2.367(3) and 2.362(3) Å] than those in nonchelated NHC–Zr species (2.43–2.46 Å). The pincer complex **77** exhibited good catalytic activity in the intramolecular hydroamination reaction. Selected examples are gathered in Table 6.¹²³ In particular, these reactions proceeded in high yield with *gem*-dialkyl amino–alkene substrates allowing formation of pyrrolidine derivatives in high yield (entries 1 and 2). Monosubstituted alkenyl amines afforded low conversions, and unsubstituted substrates did not react at all. Though formation of piperidine is possible (entry 3), larger ring size cyclic amine products could not be generated (entry 4). The hafnium congener $LHfI_2(NMe_2)$ and the titanium complexes $LTiI(NMe_2)_2$ and $LTiCl(NMe_2)_2$ were also tested for hydroamination but were less active than their Zr counterparts.^{124,125}

Hollis and co-workers recently found that the nature of the halogen ligand in $LMX(NMe_2)_2$ (M = group 4 metal, X = halide) significantly influences the rate of the hydroamination

Table 6. Hydroamination in the Presence of 5 mol % of Zr Complex 77

	Amine	Product	Time	Conv.
1			50 min	>98%
2			38 h	88%
3			2 h	90%
4			49 h	-

reaction. Table 7 displays Zr and Hf compounds that were evaluated in hydroamination of 2,2-diphenylpent-4-ene-1-

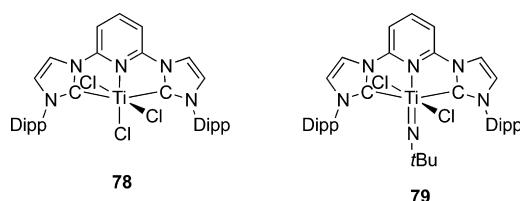
Table 7. Impact of Metal and Halogen Ligands on the Rate of Hydroamination

M	X	time	conversion (%)	Precatalyst:
Zr	I	50 min	>98	
	Br	10 h	>98	
	Cl	18 h	>98	
Hf	I	4.5 h	98	
	Br	23 h	64	
	Cl	23 h	8	

amine. Complexes with iodide ligands performed best with the following order of reactivity: I > Br > Cl and Zr > Hf.¹²⁶

Bis-NHC CNC-type pincer ligands of the type L₃ were first used with Pd and, later on, coordinated onto early transition metal complexes (Scheme 37). The Ti(III) complex 78 was prepared from (THF)₃TiCl₃ and the free bis(carbene)pyridine, whereas the imido Ti(IV) complex 79 was synthesized from

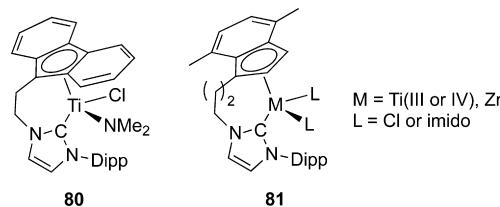
Scheme 37. Titanium Bis(carbene)pyridine Complexes 78 and 79



Ti(NtBu)Cl₂(pyridine)₃.^{127,128} The pincer complex 78 was tested in ethylene polymerization, and an activity of 791 kg·mol⁻¹·bar⁻¹·h⁻¹ was observed when activated with 500 equiv of MAO cocatalyst.

Group 4 complexes comprising an annulated ligand with a pendant NHC group have also been studied.^{129,58,31c} The titanium(III) complex 80 formed upon a reduction reaction of the Ti(IV) bis-amido precursor TiCl₂(NMe₂)₂ with the corresponding potassium fluorenyl NHC salt. Indenyl-functionalized N-heterocyclic carbene complexes of Ti(IV), Ti(III), and Zr(IV) were also prepared by salt metathesis reactions, and the bidentate coordination mode was confirmed by X-ray diffraction studies (Scheme 38, complexes 81).

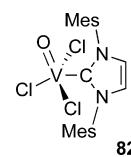
Scheme 38. Group 4 Complexes Comprising an Annulated Ligand with a Pendant NHC



3.3. Group 5 Metal Complexes

Reaction of free carbene IMes with trichloro–oxo–vanadium V(=O)Cl₃ led to the first NHC V(V) adduct complex 82, which, remarkably, is air stable both in the solid state and in dichloromethane solution (Scheme 39).¹³² As deduced from

Scheme 39. Vanadium Oxo Carbene Adduct 82



solid-state structural data, short distances between the C_{carbene} atom and the cis-disposed chlorides are observed [2.849(2) and 2.887(2) Å, i.e., well below the sum of the van der Waals radii for C and Cl (3.49 Å)] (Table 8). The angles between the carbene atom, the vanadium center, and the cis chloride are also rather acute (81.04° and 82.20°). These structural parameters are consistent with the existence of C_{carbene}–Cl interactions and in line with DFT calculations that concluded on a bonding overlap between the chlorine lone pairs and the formally vacant p orbital of the carbene. These calculations also indicated a

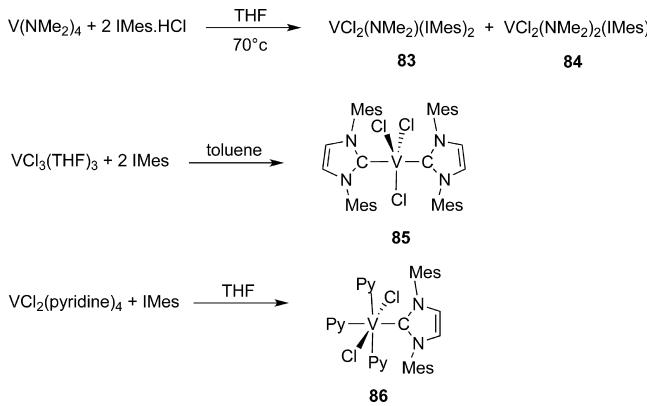
Table 8. Group 5 Carbene–Metal Bond Distances Compiled from the Cambridge Crystallographic Data Centre Database¹⁶

element	oxidation state	C–M min (Å)	C–M max (Å)	average (Å)	no. of X-ray structures
V	II	2.161	2.257	2.216	3
	III	2.127	2.266	2.187	6
	IV	2.104	2.187	2.157	3
	V	2.136	2.203	2.170	3
Nb	III	2.203	2.206	2.205	1
	V	2.396	2.396	2.396	1
Ta	V	2.225	2.408	2.306	5

significant contribution of the vanadium d orbital to the bonding overlap.

Reaction of V(IV) precursor $\text{V}(\text{NMe}_2)_4$ with two equivalents of IMes·HCl afforded the corresponding V(III) bis-NHC adduct $\text{VCl}_2(\text{NMe}_2)(\text{IMes})_2$ **83** in ca. 65% yield and the V(IV) complex $\text{VCl}_2(\text{NMe}_2)_2(\text{IMes})$ **84** in ca. 20% yield (Scheme 40).

Scheme 40. Syntheses of Vanadium(II), -(III), and -(IV) Comprising NHC Carbene Ligands

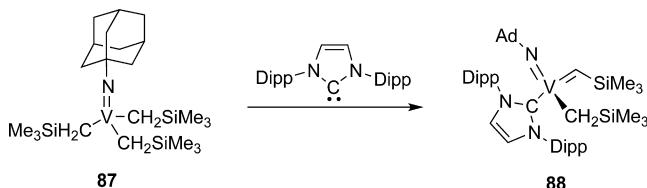


Both compounds are paramagnetic.⁸⁹ $\text{VCl}_2(\text{NMe}_2)(\text{IMes})_2$ **83** was characterized by X-ray diffraction studies. The geometry around the metal is that of a distorted square pyramid with the two carbene ligands trans to one another [$\text{C}_{\text{carbene}}-\text{V}$ bond distances of 2.238(3) and 2.237(2) Å]. Reaction of $\text{VCl}_3(\text{THF})_3$ with two equivalents of IMes afforded the compound $\text{VCl}_3(\text{IMes})_2$ **85** in 70% yield as a d^2 -paramagnetic NMR- and EPR-silent complex. The $\text{C}_{\text{carbene}}-\text{V}$ bond distances in **85** are slightly longer than in the analogue **83** [2.262(3) and 2.266(2) Å]. Both complexes **83** and **85** display short distances between the carbene carbon and the chlorine atoms, again supporting the presence of intramolecular interactions as discussed for complex **82** (vide supra). A V(II) NHC complex was also reported upon pyridine displacement with the carbene ligand.^{89,78} Thus, reaction of $\text{VCl}_2(\text{pyridine})_4$ with one equivalent of IMes afforded $\text{VCl}_2(\text{IMes})(\text{pyridine})_3$ **86** as a d^3 -paramagnetic, NMR- and EPR-silent complex.

The first (NHC) NbCl_5 adduct compounds were very recently reported upon reaction of IPr or IMes with NbCl_5 and structurally characterized.¹³³ Niobium and tantalum precursors of formula $\text{MCl}_4(\text{pyridine})_2$ have been used to generate the corresponding Nb(IV) and Ta(IV) NHC complexes $\text{MCl}_4(\text{NHC})_2$ (NHC = IMe) via pyridine replacement.⁷⁸

Reaction of IPr ligand with the vanadium imido compound $\text{V}(=\text{N}-\text{Ad})(\text{CH}_2\text{SiMe}_3)_3$ **87** (Ad = adamantyl) led to formation of the V–NHC adduct $\text{V}(\text{CHSiMe}_3)(\text{NAd})(\text{CH}_2\text{SiMe}_3)(\text{IPr})$ **88**, incorporating an alkyl, an alkylidene, and a NHC ligand (Scheme 41).¹³⁴ Formation of **88** thus

Scheme 41. V(V) Imido Carbene Complex 88



involves a NHC-promoted α -hydrogen elimination at a $\text{V}-\text{CH}_2\text{SiMe}_3$ group to form a vanadium alkylidene complex of the type $\text{V}=\text{CHSiMe}_3$. The $\text{V}-\text{C}$ bond distances for the alkyl, alkylidene, and NHC are 2.069(3), 1.829(3), and 2.172(2) Å, respectively. Figure 6 displays the molecular structure of complex **88**. Compound **88** exhibited low activity in the ring-opening metathesis polymerization of norbornene.

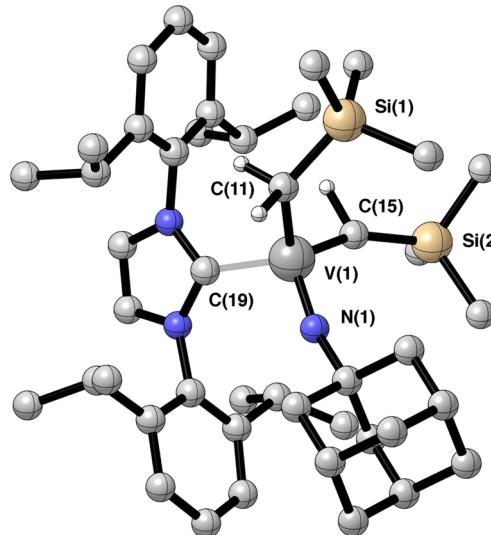
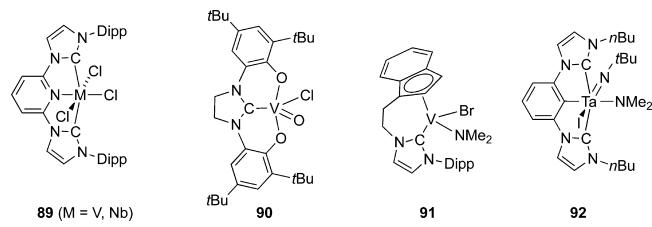


Figure 6. Molecular structure of the vanadium complex **88**. Hydrogen atoms are omitted for clarity (with exception of alkyl and alkylidene). Selected bond lengths (Angstroms) and angles (degrees): $\text{V}(1)-\text{C}(19)$, 2.172(2); $\text{V}(1)-\text{C}(11)$, 2.069(3); $\text{V}(1)-\text{C}(15)$, 1.829(3); $\text{V}(1)-\text{N}(1)$, 1.637(2); $\text{C}(15)-\text{V}(1)-\text{C}(19)$, 101.96(11); $\text{C}(11)-\text{V}(1)-\text{C}(19)$, 115.26(11); $\text{C}(11)-\text{V}-\text{C}(15)$ 111.10(12).

Several bidentate or tridentate NHC ligands were reported to stabilize group 5 metals, and these are depicted in Scheme 42.

Scheme 42. Vanadium, Niobium, and Tantalum Complexes Bearing Bidentate or Tridentate NHC Ligands

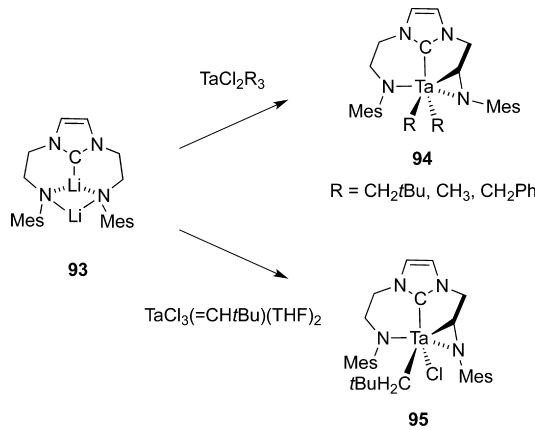


The V(III) complex **89** could be cleanly oxidized (by 4-methylmorpholine N-oxide) to the corresponding paramagnetic V(IV) oxo complex $\text{LV}(=\text{O})\text{Cl}_2$.^{127,128} Coordination of a bis-NHC pyridyl ligand has also been recently investigated with niobium(III). Like the vanadium(V) complex **82**, the bisphenolate V(V)–NHC species **90** is air stable whether in the solid state or in benzene solution.¹⁰⁶ The V(III) complex **91** resulted from reaction of $\text{V}(\text{NMe}_2)_4$ with the corresponding indenyl imidazolium salt and thus proceeded with a reduction to V(III).^{31c,130} The V(III) complex $\text{CpVCl}_2(\text{IMes})$ was also accessed via a direct protonolysis reaction of Cp_2VCl with IMes·HCl and proceeded with elimination of CpH .¹³⁵ Anionic 3-borane-1-alkylimidazol-2-ylidene has also been used to stabilize V(III) species.^{76,18} More recently, Hollis and co-

workers investigated the coordination chemistry of (CCC) bis-NHC pincer ligand with tantalum(V) such as compound **92**.¹³⁶

Fryzuk et al. investigated the coordination chemistry of the tridentate diamido-N-heterocyclic carbene ligand **73** with tantalum(V).¹³⁷ Aminolysis or alkane elimination reactions with **73** afforded bidentate chelates with a remaining pendant amine donor. Metathesis reactions of the dilithiated NHC precursor and Ta(V) precursors were more successful. Interestingly, reaction of dilithiated precursor **93** with $TaCl_2R_3$ produced the metallaaziridine complex **94**, arising from cyclometalation of one of the 6-membered chelate rings (Scheme 43). DFT calculations concluded on a lowest energy

Scheme 43. Reactivity of Dilithiated NHC **93 with Ta(V)**



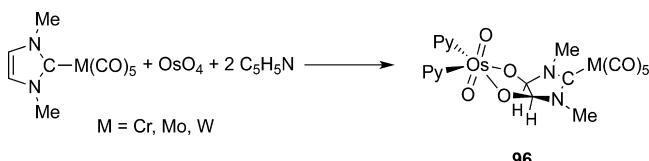
pathway involving a Ta alkylidene transient species that may subsequently undergo a C–H activation. This proposal was validated by (i) reaction of **93** with an alkylidene precursor, found to cleanly afford the metallaaziridine compound **95**, and (ii) deuterium labeling studies.

3.4. Group 6 Metal Complexes

Coordination of NHCs to tetracarbonyl- and pentacarbonyl-chromium complexes was pioneered by Öfele over 40 years ago.^{5,138–141} Since then, numerous Cr(0) complexes of general formula $(NHC)Cr(CO)_5$ or $(NHC)_2Cr(CO)_4$ have been synthesized and characterized.^{142,143} Interestingly, the pentacarbonyl-chromium NHC complex undergoes osmylation to yield the unusual and stable bimetallic complex **96**, which was structurally characterized (Scheme 44).¹⁴⁴ Such reactivity was brought forward as evidence for the nonaromaticity of imidazol-2-ylidene ligands, a point being much debated in the literature.^{2a}

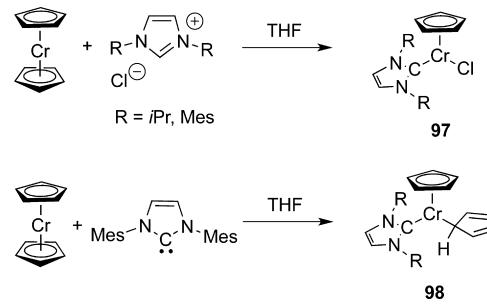
A number of monodentate chromium–NHC adducts (Cr in various oxidation states) are known. For instance, the reactivity of NHCs with Cr(II) metallocene complexes has been studied.¹⁴⁵ The protonolysis reaction of chromocene with the imidazolium chloride salt IMes·HCl or iPr·HCl afforded the

Scheme 44. Oxy Functionalization of Metal-Coordinated Imidazol-2-ylidene Carbenes



corresponding 14-electron Cr(II) complexes of the type $CpCr(NHC)Cl$ via a CpH elimination reaction (**97**, Scheme 45), both adducts isolated as highly air-sensitive species.¹⁴⁶

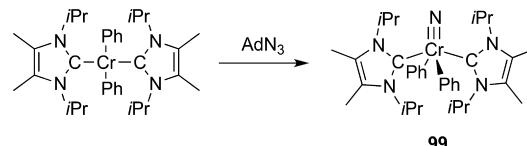
Scheme 45. Synthesis of NHC Chromium(II) Metallocene Complexes



Subsequent oxidation of $CpCr(iPr)_2Cl$ with $PbCl_2$ or $CpCr(IMes)_2Cl$ with $CHCl_3$ produced the corresponding Cr(III) NHC dichloro complex of general formula $CpCr(NHC)Cl_2$.¹⁴⁷ Alternatively, reaction of chromocene with free IMes led to compound $(\eta^1-C_5H_5)(\eta^5-C_5H_5)Cr(IMes)_2$ **98**, the first thermally stable $(C_5H_5)_2CrL$ -type complex.¹⁴⁸

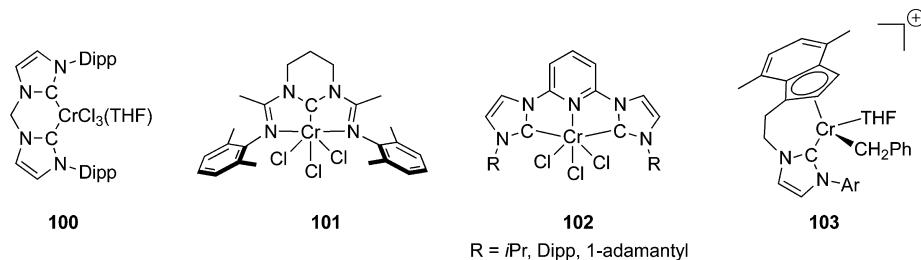
There are examples of chromium(II) bis-NHC adducts of the type $(NHC)_2CrCl_2$ or $(NHC)_2CrR_2$.^{149–151} The reactivity of such organochromium(II) species with 1-azidoadamantane was studied and the corresponding nitridochromium Cr(V) compound isolated in good yield (**99**, Scheme 46).¹⁵²

Scheme 46. Reaction of a Cr(II) Complex with 1-Azidoadamantane Yielding Organonitridochromium(V) **99**



Several chromium complexes supported by a chelating bis-NHC ligand were characterized and subsequently evaluated in ethylene polymerization catalysis (Scheme 47).^{153,154} For example, the chromium(III) complex **100** (upon MAO activation) exhibited a low polymerization activity, and ill-defined poly(ethylene) was produced. Also, such complexes may be readily reduced into their Cr(II) analogues due to the soft character of the carbene ligand and of Cr(II) vs Cr(III). The tridentate bis(imino)carbene complex **101** is an active ethylene polymerization catalyst with an average activity of $27 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{bar}^{-1}\cdot\text{h}^{-1}$.¹⁵⁵ Gibson et al. described the synthesis of Cr(III) complexes based on tridentate pincer ligands that are exceptionally active in ethylene polymerization.¹⁵⁶ Thus, chromium complexes **102** in combination with MAO are highly effective in ethylene oligomerization. For instance, derivative **102** (with R = Dipp, Scheme 47) displayed an oligomerization activity of up to $40\,440 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{bar}^{-1}\cdot\text{h}^{-1}$, and the produced α -olefins followed a Schulz–Flory distribution. The polymerization mechanism was studied, and the chelating ligand coordination mode was found to be crucial to promote oligomerization.¹⁵⁷ Indenyl-functionalized NHC complexes of chromium(III) **103** (Scheme 47) also mediated the ethylene oligomerization/polymerization, though with moderate activity.¹⁵⁸ Likewise, amidine- and amidinate-functionalized

Scheme 47. Examples of Chromium NHC Complexes Used as Ethylene Polymerization Catalysts

 $R = i\text{Pr}$, Dipp, 1-adamantyl

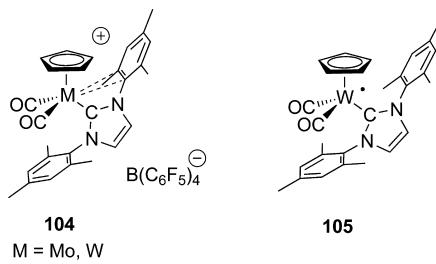
NHC complexes of Cr catalyze ethylene polymerization with a low activity.¹⁵⁹ NHC coordination may be detrimental to catalytic performance as highlighted by Chen and co-workers, who reported that chromium-catalyzed conversion of glucose to 5-hydroxymethylfurfural was less effective upon addition of NHC ligands.¹⁶⁰ Since ionic liquids (typically imidazolium salts) are commonly used in biomass conversion, such an observation is of significant interest for process development.

Monodentate NHC adducts of molybdenum(0) and tungsten(0) carbonyl complexes have been the subject of numerous studies.^{79,142,143,161–164} Such NHC adducts typically derive from substitution of a carbonyl ligand in hexacarbonyl group 6 compounds with a NHC ligand.

Molybdenum(II) and tungsten(II) complexes containing a cyclopentadienyl ligand or a π -allyl ligand may also be stabilized by N-heterocyclic carbene ligands.^{165,166} Notably, cationic formally 16-electron complexes $\text{CpM}(\text{CO})_2(\text{IMes})^+\text{B}(\text{C}_6\text{F}_5)_4^-$ ($\text{M} = \text{Mo, W}$; **104**, Scheme 48) have been isolated and

Table 9. Group 6 Carbene–Metal Bond Distances Compiled from the Cambridge Crystallographic Data Centre Database¹⁶

element	oxidation state	C–M min (Å)	C–M max (Å)	average (Å)	no. of X-ray structures
Cr	V	2.110	2.111	2.110	1
	III	2.037	2.245	2.116	21
	II	2.032	2.180	2.127	16
	I	2.049	2.053	2.051	1
	0	2.125	2.157	2.138	5
Mo	VI	2.173	2.173	2.173	1
	II	2.161	2.303	2.233	17
	0	2.257	2.332	2.304	15
W	VI	2.222	2.222	2.222	1
	II	2.131	2.284	2.220	10
	I	2.165	2.223	2.194	2
	0	2.197	2.301	2.268	14

Scheme 48. $[\text{CpM}(\text{CO})_2(\text{IMes})]^+$ **104** and $[\text{CpW}(\text{CO})_2(\text{IMes})]$ **105** Tungsten Complexes

characterized by synchrotron X-ray diffraction studies. The NHC ligand in cations **104** coordinated dissymmetrically, with close contacts between one mesityl group and the metal center through η^2 -arene interactions.¹⁶⁷ The bond distances in these η^2 -arene interactions were found to be 2.901(13) and 3.072(13) Å for W and 2.78 and 3.02 Å for Mo (Table 9). These complexes showed modest catalytic activity for hydrogenation of $\text{Et}_2\text{C}=\text{O}$.^{165c}

The equimolar reaction of $[\text{CpW}(\text{CO})_2(\text{IMes})](\text{MeCN})^+\text{PF}_6^-$ and $[\text{CpW}(\text{CO})_2(\text{IMes})]\text{K}(18\text{-crown-6})^+$ resulted in quantitative formation of the radical species $[\text{CpW}(\text{CO})_2(\text{IMes})]^\bullet$ (**105**) through a comproportionation reaction (Scheme 48).^{168,169} The 17-electron radical species **105** could be isolated and characterized by NMR, IR, and EPR spectroscopies and X-ray diffraction studies. Derivative **105** is a rare example of a stable third-row metal monomeric radical. DFT calculations concluded on the presence of bulky mesityl groups being crucial for monomer stability. The 17-electron chromium analogue $[\text{CpCr}(\text{CO})_2(\text{IMe})]^\bullet$ was also isolated and characterized.¹⁷⁰ The reactivity of these W–NHC adducts with

H_2 was thoroughly studied.¹⁷¹ In particular, the bond energy values of the W–H bonds in $\text{CpW}(\text{CO})_2(\text{IMes})\text{H}$, $[\text{CpW}(\text{CO})_2(\text{IMes})\text{H}]^{+*}$, and the dihydride $[\text{CpW}(\text{CO})_2(\text{IMes})(\text{H})_2]^+$ were estimated via thermochemical measurements. The strong electron-donating properties of the IMes ligand was confirmed by the measured acidity difference between $\text{CpW}(\text{CO})_2(\text{IMes})\text{H}$ and $\text{CpW}(\text{CO})_2(\text{PMe}_3)\text{H}$ ($\text{pK}_a = 31.9$ and 26.6 in CH_3CN , respectively).

Cationic $\text{CpM}(\text{CO})_2(\text{IMes})^+\text{B}(\text{C}_6\text{F}_5)_4^-$ ($\text{M} = \text{Mo, W}$) complexes **104** were successfully used as catalysts for hydrosilylation of ketones and esters, the W(II) complex being much more active than its Mo(II) analogue.¹⁷² For example, hydrosilylation of pentan-3-one by triethylsilane catalyzed by species **104** yielded the desired product in 89% yield after 1 h (ketone/silane/catalyst in a 100/120/0.2 ratio, no solvent). Remarkably, these salt catalysts precipitate at the end of the reaction due to the nonpolar nature of the medium at the end of the reaction (a polar liquid substrate at the start of the reaction versus a nonpolar liquid product at the end). The solid could be recovered and reused up to 5 times. The cationic hydrido species A and B were identified as the resting states of this hydrosilylation catalysis (Figure 7). Species C was also observed during the catalytic reaction. The dihydride species B resulting from reaction of the ketone adduct cation C with traces of H_2 (produced by reaction of silane with residual water) was found to inhibit the hydrosilylation reaction. On the basis of previous studies, the authors proposed an ionic hydrogenation mechanism as displayed in Figure 7.¹⁷³

The indenyl-functionalized triethylborane adduct of NHC **106** may be used as a convenient NHC source to access the Mo(II) NHC adduct **107** in high yield (Scheme 49).¹⁷⁴ The latter indicates that the protection of a NHC moiety by BEt_3

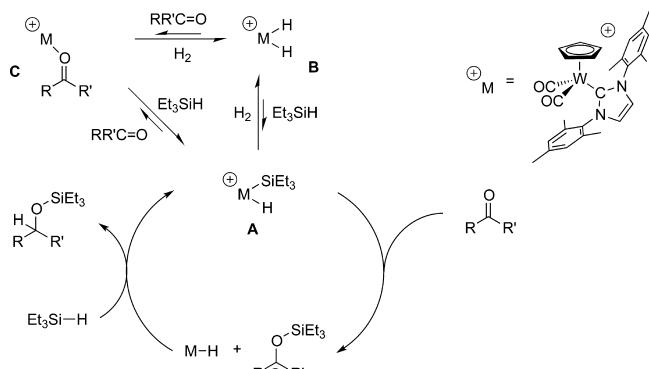
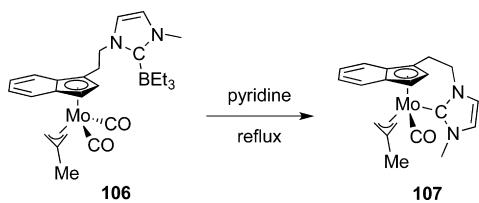


Figure 7. Proposed mechanism for the hydrosilylation catalyzed by the tungsten complex **103**.

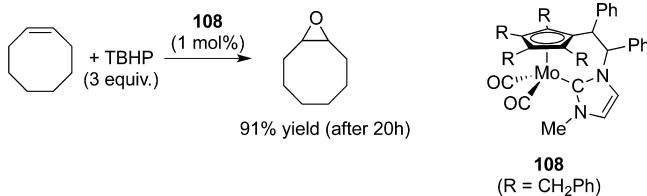
can effectively control NHC coordination ability to a metal center.

Scheme 49. Mononuclear Chelate-Type Mo Complex 107



Royo et al. investigated the reactivity of Mo(II) complexes containing cyclopentadienyl-functionalized NHCs toward olefin epoxidation.¹⁷⁵ The reaction was carried out with *tert*-butylhydroperoxide (TBHP) as the oxidant in the presence of 1 mol % of Mo–NHC species (Scheme 50). The best results

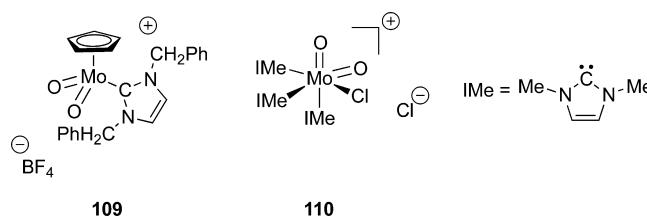
Scheme 50. Epoxidation of Cyclooctene Catalyzed by Mo Complex 108



were achieved using the bulky Mo catalyst **108** with selective oxidation of cyclooctene to the corresponding epoxide with no side product formation. The robustness of these NHC complexes under oxidative conditions allowed for longer reaction time (91% yield after 20 h), compensating for the observed low TOFs. The Mo(II) salt species $[\text{CpMo}(\text{CO})_2(\text{IMes})]^+\text{BF}_4^-$ also effectively catalyzes the epoxidation of olefins, with TOF values comparable to those of $\text{CpMo}(\text{CO})_3\text{Cl}$.^{165a,176,177} The stability of the M–NHC ligand bonds in these Mo(II)–NHC compounds was investigated under oxidative conditions and permitted characterization of high-valent molybdenum Cp–NHC dioxo Mo(VI) complexes such as **109** (Scheme 51).^{165a} The Mo–C_{carbene} bond length in **109** [2.173(4) Å] is, as expected, shorter than that in $\text{CpMo}(\text{CO})_2(\text{IBz})\text{Cl}$ [2.221(3) Å] or $[\text{CpMo}(\text{CO})_2(\text{IBz})]^+\text{BF}_4^-$ [2.2287(18) Å] due to the high oxidation state of Mo(VI).

Molybdenum and tungsten η^3 -allyl dicarbonyl complexes

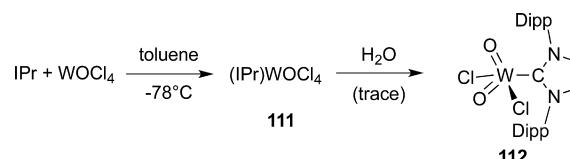
Scheme 51. Molecular Structure of Mo Complex **109** and Proposed Structure for Complex **110**



bearing NHC ligands were also evaluated as cyclooctene epoxidation catalysts using H_2O_2 as oxidant. Decomposition of the NHC-based catalysts to the corresponding imidazolium cation clearly indicated the vulnerability of the coordinated NHCs under the studied reaction conditions.¹⁷⁸

Herrmann et al. first disclosed the synthesis and characterization of a NHC–Mo(VI) adduct in 1996.¹⁷⁹ In particular, these early studies led to preparation of the tris-NHC cationic complex $[\text{MoO}_2\text{Cl}(\text{IMe})_3]^+\text{Cl}^-$ (**110**, Scheme 51) via reaction of three equivalents of IMe with $\text{MoO}_2\text{Cl}_2(\text{THF})_2$. Following a similar approach, bis-NHC adducts of the type $\text{MO}_2\text{Cl}_2(\text{NHC})_2$ ($\text{M} = \text{Mo}$ or W) were also synthesized.^{179,180} Likewise, reaction of WOCl_4 with IPr gave formation of the expected monoadduct $(\text{IPr})\text{WOCl}_4$ (**111**, Scheme 52), which

Scheme 52. Synthesis of NHC W(VI) Oxo Complexes



readily hydrolyzed in the presence of residual water to yield the dioxo derivative $(\text{IPr})\text{WO}_2\text{Cl}_2$ (**112**).¹⁸¹ As deduced from the X-ray-determined molecular structure of **112** (Figure 8), both oxo ligands lie in the equatorial plane with a chloride and the carbene ligand in the axial positions. The coordinated NHC in **112** is tilted toward one chloride ligand resulting in an acute Cl–W–C_{carbene} angle [79.27(11)°] and a short Cl–C_{carbene} distance (2.930 Å), a situation reminiscent to that earlier discussed for $\text{VOCl}_3(\text{IMes})$ **82**.

Alternatively, production of Mo NHC complexes may also be achieved via functionalization of the corresponding $\text{Mo}(\eta^1\text{-N-imidazole})$ species, as elegantly demonstrated by Díaz, López, Riera et al.¹⁸² Thus, deprotonation of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{bipy})(\text{CO})_2(\eta^1\text{-N-IMes})]^+(\text{OTf})^-$ complexes **113** ($\text{R} = \text{Me}$, Mes) yielded the neutral complexes **114** via deprotonation of the C2–H atom and a subsequent rearrangement (Scheme 53). It may be noted that metal complexes supported by such carbanionic ligands are rare.^{183,184} Reaction of complexes **114** with electrophilic reagents such as trifluoromethanesulfonic acid or methyl trifluoromethanesulfonate led to NHC complexes (**115** and **116**, Scheme 53) via protonation (or alkylation) of the unsubstituted N atom of the imidazole ring. The Mo–C_{carbene} distance in complexes **115** ($\text{R} = \text{Mes}$, 2.240(3) Å) and **116** ($\text{R} = \text{Mes}$, 2.252(4) Å) are similar to that in related Mo(II) NHC complexes.¹⁸⁵ Interestingly, reaction of **114** with $(\text{Ph}_3\text{P})\text{AuCl}$ afforded the corresponding dinuclear Au–NHC Mo cations of type **117**. The more carbophilic Au(I) center thus resulted in a NHC translocation from Mo(II) to the Au(I) center.

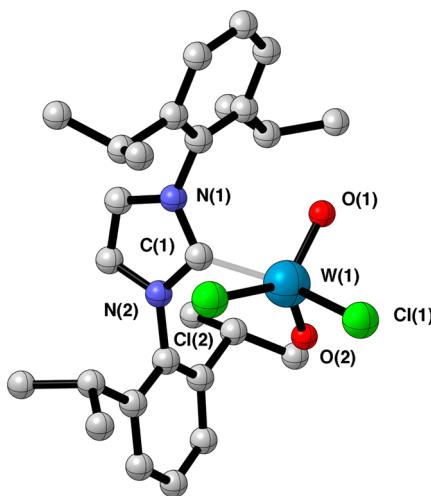
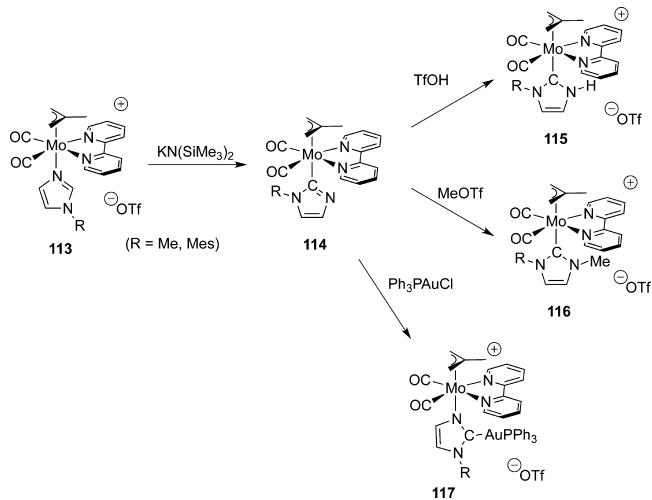


Figure 8. Molecular structure of the tungsten complex **112**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Angstroms) and angles (degrees): C(1)–W(1), 2.223(4); O(1)–W(1), 1.704(3); O(2)–W(1), 1.699(3); Cl(1)–W(1), 2.3461(12); Cl(2)–W(1), 2.3669(13); O(1)–W(1)–C(1), 91.82(15); O(2)–W(1)–Cl(2), 125.38(11); O(1)–W(1)–Cl(2), 125.52(12); C(1)–W(1)–Cl(2), 79.27(11); Cl(1)–W(1)–Cl(2), 83.78(5); Cl(2)–W(1)–C(1)–N(1), 90.77.

Scheme 53. Reactivity of Mo(II) Complex **113**

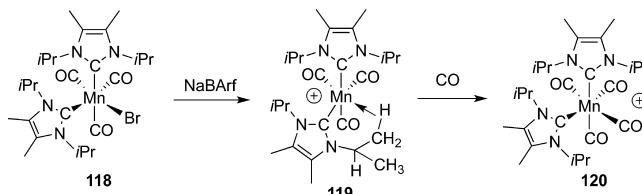


3.5. Group 7 Metal Complexes

Lappert and Pye reported the first example of a manganese species bearing an N-heterocyclic carbene in 1977.^{186,187} Heating dimeric $(\text{SiMe}_2)_2$ in the presence of $\text{CpMn}(\text{CO})_3$ afforded the corresponding NHC complexes $\text{CpMn}(\text{CO})_2(\text{SiMe}_2)$ and $\text{MnBr}(\text{CO})_3(\text{SiMe}_2)_2$ in very low yields (<1% and 5%, respectively). Since then, several groups have reported the synthesis of manganese NHC complexes mainly through multicomponent reactions.^{188,189}

The bis-iPr Mn(I) adduct **118** was ionized with NaBARf (BARf = tetrakis[(3,5-trifluoromethyl)phenyl] borate) to produce cation **119** via halide abstraction (Scheme 54). An agostic interaction between a N-iPr substituent and the Mn(I) center was evidenced in solution at 208 K by ^1H NMR (Scheme 54).¹⁹⁰ Addition of CO resulted in the bis-NHC adduct **120**, which was X-ray characterized. The photochemistry of Mn(I) NHC complexes of general formula

Scheme 54. Neutral and Cationic NHC Mn(I) Complexes



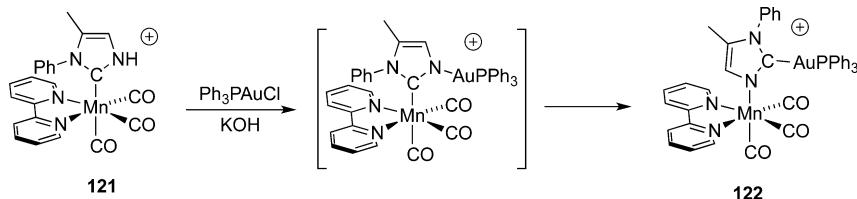
$\text{CpMn}(\text{NHC})(\text{CO})_2$ was also studied, upon exposure to UV light, generation of the 16-electron species of the type $\text{CpMn}(\text{NHC})(\text{CO})$, also featuring a C–H agostic interaction of the NHC ligand.^{191,192}

Replacement of one pyridine ring with a NHC moiety in Mn(I) complexes of general formula $\text{fac-}[\text{MnBr}(\text{bipy})(\text{CO})_3]$, a class of compounds of interest as electrocatalysts for the two-electron reduction of CO_2 to CO ,¹⁹³ was studied. Compounds of the type $\text{fac-}[\text{MnBr}(\text{C–N})(\text{CO})_3]$ supported by a NHC–pyridine bidentate ligand were thus evaluated for electrocatalytic reduction of CO_2 to CO and exhibited a catalytic activity comparable to that of $\text{fac-}[\text{MnBr}(\text{bipy})(\text{CO})_3]$ species. However, functionalization of such Mn–NHC compounds (via the NHC moiety) should be easier, which is an attractive feature for catalyst optimization.¹⁹⁴

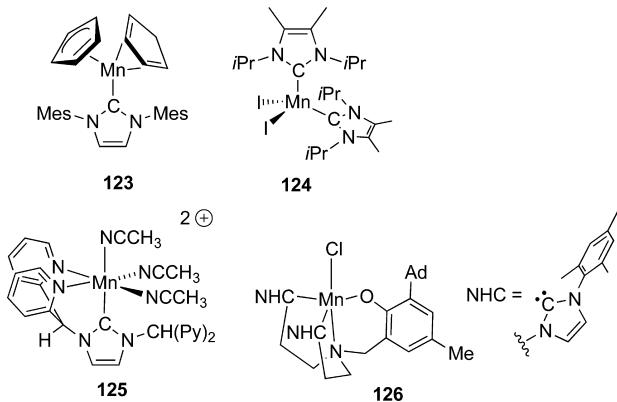
Ruiz et al. studied several $\text{fac-}[\text{Mn}(\text{NHC})(\text{CO})_3(\text{dppe})]^+$ and $\text{fac-}[\text{Mn}(\text{NHC})(\text{CO})_3(\text{bipy})]^+$ complexes as carbene transfer agents to a cationic Au(I) fragment $[\text{Au}(\text{L})]^+$ ($\text{L} = \text{PPh}_3$, $\text{CN}-\text{Ar}$). Scheme 55 displays a representative example of such reactivity with the reaction of the Mn(I)–NHC adduct **121** with PPh_3AuCl in the presence of KOH to produce the heterobimetallic derivative **122**. As discussed earlier for related Mo NHC species (vide supra), this rearrangement is most likely promoted by the softer character of Au(I) vs Mn(I).

Lugan, Sortais, and co-workers recently demonstrated that manganese(I) NHC complexes $\text{CpMn}(\text{CO})_2(\text{NHC})$ are active catalysts for hydrosilylation of various ketones and aldehydes under UV radiation.¹⁹⁷ The reactivity of Cp_2Mn with NHC carbenes was also studied. For example, IMes readily reacted with Cp_2Mn to generate the corresponding Mn–NHC adduct $(\eta^2-\text{C}_5\text{H}_5)(\eta^4-\text{C}_5\text{H}_5)\text{Mn}(\text{IMes})$ **123**, a formally 15-electron complex (Scheme 56).¹⁹⁸ Bis-carbene adducts $(\eta^1-\text{C}_5\text{H}_5)(\eta^2-\text{C}_5\text{H}_5)\text{Mn}(\text{NHC})_2$ are also known and may be prepared with a less sterically demanding carbene such as tetramethylimidazol-2-ylidene. Few Mn(II) NHC adducts of general formula $(\text{NHC})_n\text{MnX}_2$ ($n = 1$ or 2, X = halogen, alkyl, aryl) have thus far been synthesized.^{199,33g,200} These include the bis-carbene Mn(II) compound **124** (Scheme 56), prepared by reaction of iPr with 0.5 equiv of MnI_2 , with a solid state molecular structure featuring a Mn(II) center in a distorted tetrahedral geometry and $\text{C}_{\text{carbene}}-\text{M}$ bond lengths of 2.210(4) and 2.204(4) Å (Table 10).²⁰¹ Smith and Long studied the coordination chemistry of a five-coordinate ligand incorporating an axial NHC and four equatorial pyridine donors.²⁰² The latter chelating ligand showed a strong tendency to stabilize 6-coordinate complexes with low-spin configurations (M = Fe, Co, Ni, Cu) but was unable to either enforce a low-spin state or fully accommodate the Mn(II) ion. The Mn(II) complex **125** bearing a tridentate bis-pyridine-NHC-type ligand was nevertheless prepared and structurally characterized [$\text{Mn}-\text{C}_{\text{carbene}} = 2.213(2)$ Å]. Meyer and collaborators investigated two novel N-anchored tripodal ligands, combining a NHC and phenolate

Scheme 55. NHC–Manganese(I) Complex 121 as Transfer Agent to a Gold Fragment



Scheme 56. NHC Manganese(II) Complexes 123–126

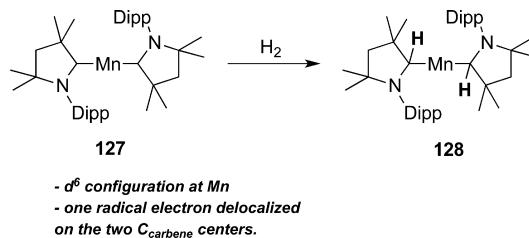
Table 10. Group 7 Carbene–Metal Bond Distances Compiled from the Cambridge Crystallographic Data Centre Database¹⁶

element	oxidation state	C–M min (Å)	C–M max (Å)	average (Å)	no. of X-ray structures
Mn	V	2.054	2.054	2.054	1
	IV	1.932	2.103	2.008	1
	III	1.983	2.014	2.001	2
	II	2.175	2.276	2.217	13
	I	1.998	2.120	2.046	6
	0	2.093	2.093	2.093	1
	Tc	2.070	2.232	2.179	4
Re	V	2.154	2.233	2.197	15
	I	2.114	2.248	2.203	23
	0	2.126	2.172	2.149	1

donors [mono(carbene) bis(phenolate) or bis(carbene) mono(phenolate)], for coordination to Mn(II).²⁰³ The corresponding high-spin Mn(II) chelate 126 was prepared by reaction of anhydrous MnCl₂ and the in-situ-generated bis(carbene) mono(phenolate) ligand. Access to the reactive metal center for activation of organic substrates remains possible with such chelates due to the flexibility of the ligand backbone, unlike what is observed with Mn(II) complexes supported by the more rigid tris-NHC TIMEN ligand (vide infra).²⁰⁴ Mn(II) compounds supported by bis(carbene) mono(phenolate) ligand were used as catalysts in bleaching laundry.²⁰⁵

Roesky, Frenking, and co-workers recently reported on unusual two-coordinate Mn species of the type (CAAC)Mn, 127 and 128, respectively (Scheme 57, CAAC = cyclic alkyl(amino)carbene).²⁰⁶ Preparation of the Mn(I) species 127 was performed via reaction of the corresponding free CAAC with MnCl₂ to produce the Mn(II) bis-adduct (CAAC)MnCl₂ that was subsequently reduced with KC₈ to form 127 (Scheme 57). Magnetic measurements on compound 127 agree with a d⁶ configuration at the Mn center and one radical electron delocalized on the two C_{carbene} atoms.

Scheme 57. Two-Coordinate Mn Compounds Stabilized by Two CAAC Ligands

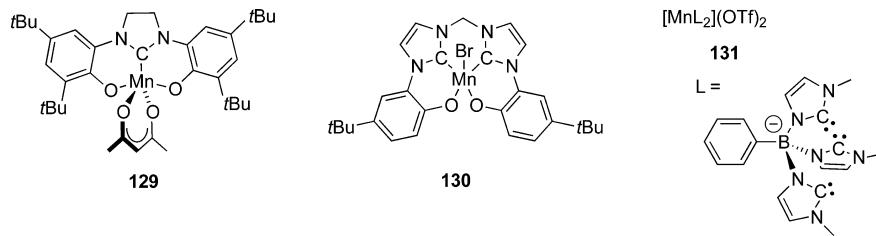
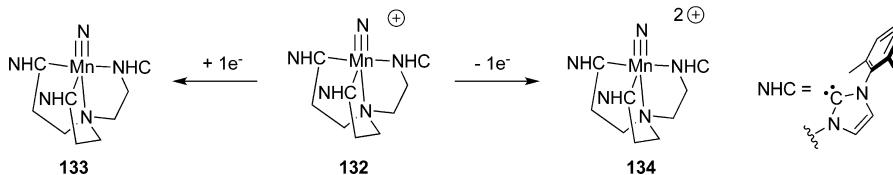
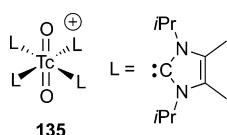
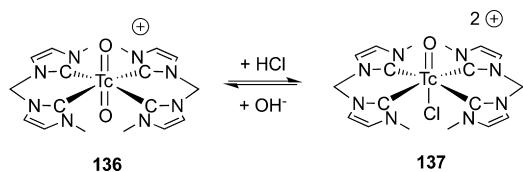


Remarkably, compound 127 undergoes a facile splitting of H₂ to form the Mn(II) species 128.

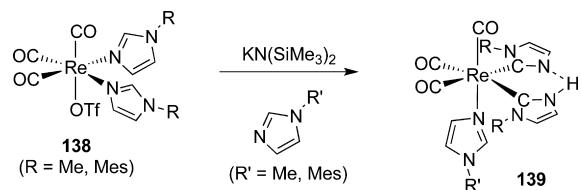
Manganese(III) NHC complexes are rare.²⁰⁷ Scheme 58 displays two examples of Mn(III) complexes stabilized by carbene–phenolate ligands (129 and 130).^{106,208} Examples of Mn(IV) complexes are also scarce and include the homoleptic Mn(IV) zwitterion 131, which bears two tris(carbene)borate PhB(MeIm)₃⁻ units (Scheme 58).^{209,210} The latter is thermally stable unlike any other homoleptic Mn(IV) complexes.²¹¹ The tris(carbene) ligand TIMEN is able to stabilize Mn(III) to Mn(V) nitrides complexes (Scheme 59).²¹² The Mn(IV) nitrido complex 132 was derived from photolysis of the Mn(II) azido derivative [(TIMEN)Mn(–N=N=N)]⁺ and may be either reduced to the Mn(III) nitride 133 (in the presence of potassium graphite) or oxidized to the Mn(V) nitride 134 via reaction with one equivalent of NOBF₄. Both complexes 133 and 134 are nonmagnetic (*s* = 0 ground state) and were thoroughly characterized via spectroscopic and computational studies.

There are only a few technetium NHC complexes thus far reported with the first example being published in 2003 by Abram et al. (Scheme 60).^{213,214} The technetium(V) dioxo tetracarbene adduct complex 135 was prepared from TcOCl₃(PPh₃)₂, (TcOCl₄)(NBu₄), or Tc₂O₃Cl₄(pyridine)₄ in the presence of excess iPr. The Tc center in complex 135 adopts a distorted octahedral geometry with the oxo moieties being trans to one another while the NHC ligands occupy the equatorial positions. Tc–NHC nitrido complexes have been also isolated.^{215,216} Braband et al. recently described the synthesis of water-stable TcO₂–NHC complexes. Homoleptic complex 136 stabilized by the bidentate ligand 1,1'-methylene-3,3'-dimethyl-4,4'-diimidazoline-2,2'-diylidene displays a unique pH-dependent reactivity (Scheme 61). Under acidic conditions, one oxo ligand of complex 136 is reversibly replaced by a chloride ligand to yield the corresponding mono-oxo Tc–NHC species 137. Both complexes 136 and 137 were X-ray characterized through diffraction studies. Such water-stable Tc(V) compounds are of great interest for development of ^{99m}Tc–NHC complexes suitable for radiopharmaceutical applications.²¹⁷

Among group 7 transition metals, coordination of NHCs to rhenium has by far been the most studied. Re–NHC complexes

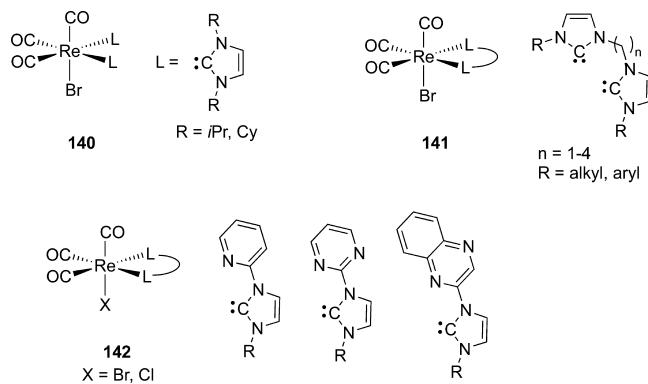
Scheme 58. NHC Manganese(III) Complexes **129** and **130** and NHC Manganese(IV) Complexes **131****Scheme 59.** Manganese(III), -(IV), and -(V) Nitride Complexes Stabilized by the Tripodal Ligand TIMEN**Scheme 60.** Technetium(V) Dioxo Tetracarbene Adduct Complex **135****Scheme 61.** Water-Stable Tc(V) Dioxo NHCs Complexes **136** and **137**

are known with Re(I), -(V), -(VI), or -(VII). The chemistry of Re(I) and NHC recently attracted attention due to the luminescence properties of the resulting coordination complexes.²¹⁸ The first Re(I) NHC complex was reported in 1992 by Herrmann et al.²¹⁹ Since then, a number of Re complexes have been prepared primarily through multicomponent reactions.^{190,220,221} Rhenium(I) carbonyl *N*-alkylimidazole complexes $[\text{Re}(\text{Im})_3(\text{CO})_3]^+$ may readily be deprotonated by a strong base to form the corresponding NHC–Re complexes after a rearrangement reaction similar to that observed for the Mo complexes 113 (vide supra).²²² Similarly, the rhenium complex $\text{Re}(\text{OTf})(\text{CO})_3(\text{N-RIm})_2$ (138) reacted with KHMDS and one equivalent of alkyl-imidazole to afford the bis(carbene) Re(I) 139, in which the Re(I) center is formally coordinated by a imidazol-2-yl anionic ligand, a neutral NH-incorporating imidazole-2-yl carbene, and a N-bonded imidazole (Scheme 62).²²³ In the latter, the N–H of the

Scheme 62. Synthesis of the Bis-Carbene Re(I) Species **139**

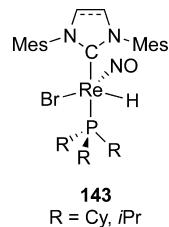
neutral NHC acts as a hydrogen-bond donor stabilizing the unsubstituted nitrogen atom of the imidazole-2-yl anionic ligand and contributes to the coplanarity of the two heterocyclic ligands, as observed from X-ray diffraction studies.

Tricarbonyl rhenium(I) bis(carbene) complexes $(\text{NHC})_2\text{ReBr}(\text{CO})_3$ are easily accessible from the precursor $[\text{NEt}_4]_2[\text{ReBr}_3(\text{CO})_3]$ combined with either a monodentate NHC or a bidentate NHC ligand (140 and 141, Scheme 63).²²⁴ Such neutral species could easily be converted to the

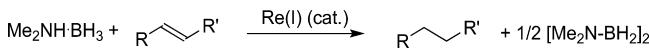
Scheme 63. Tricarbonyl Rhenium(I) NHC Complexes **140–142**

corresponding acetonitrile cationic species by treatment with a silver salt.²²⁵ Coordination to Re(I) of bidentate ligands combining a N-heterocyclic carbene with a nitrogen-based ligand (such as compound 142, Scheme 63) allowed access to luminescent complexes, some being of interest for production of OLED devices.²²⁶

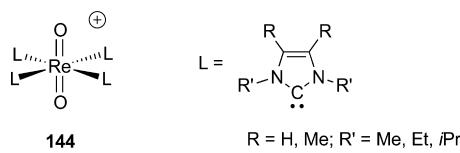
Rhenium(I) hydride complexes of the type $[(\text{NHC})\text{ReBrH}-(\text{NO})(\text{PR}_3)]$ (143, NHC = IMes or SIMes; R = Cy, iPr; Scheme 64) may be prepared by a phosphine substitution reaction between $[\text{ReBrH}(\text{NO})(\text{PR}_3)_2]$ and the corresponding NHC.²²⁷ The Re(I)–SIMes adducts were structurally characterized, and all complexes were tested as catalysts of the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ for production of $[\text{Me}_2\text{N-BH}_2]_2$ and H_2 . Compound $[(\text{IMes})\text{ReBrH}(\text{NO})(\text{P}(i\text{Pr})_3)]$ performed best with a complete dehydrocoupling reaction within 1 h at 75 °C (1 mol % cat.). These rhenium(I) hydride complexes were further evaluated in olefin hydrogenation using

Scheme 64. Rhenium(I) Hydride Complex 143

$\text{Me}_2\text{NH}\cdot\text{BH}_3$ as a H_2 source (Scheme 65) with species $[(\text{IMes})\text{ReBrH}(\text{NO})(\text{P}(i\text{Pr})_3)]$ and its diphosphine analogue $[\text{ReBrH}(\text{NO})(\text{P}i\text{Pr}_3)_2]$ being the most effective catalyst.²²⁸

Scheme 65. Transfer Hydrogenation of Olefins Using $\text{Me}_2\text{NH}\cdot\text{BH}_3$ as Hydrogen Donor

Various rhenium(V) NHC complexes have been prepared.²¹³ For instance, reaction of an excess of free NHC with $\text{ReOCl}_3(\text{PPh}_3)_2$ and subsequent addition of a trace amount of water yielded tetra-NHC dioxorhenium(V) complexes of general structure 144 (Scheme 66).^{229–231} The geometry

Scheme 66. Tetra-NHC Dioxorhenium(V) Complex 144

around the metal is octahedral with the oxo ligands occupying the axial positions. Figure 9 displays the molecular structure of one such $[\text{ReO}_2(\text{NHC})_4]^+$ compound with 1,3-diisopropyl-

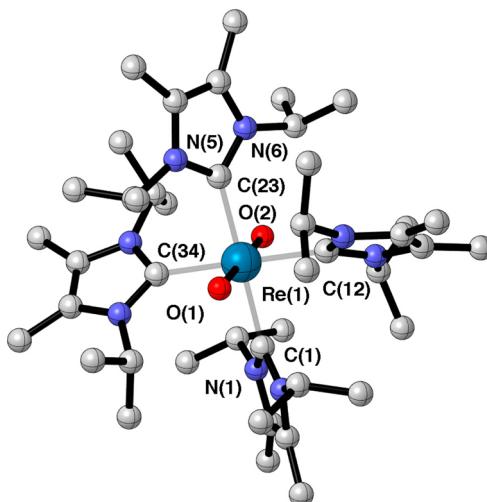
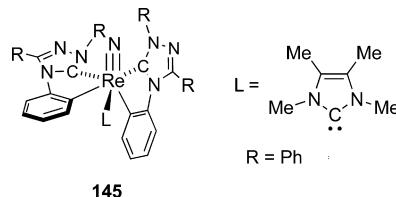


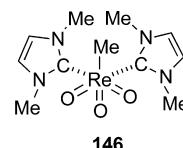
Figure 9. Molecular structure of 144 $[\text{ReO}_2(\text{L})_4]^+$ (Scheme 66, R = Me, R' = iPr). Hydrogen atoms are omitted for clarity. For all 'Pr groups, only the $\text{CH}(\text{Me})_2$ carbons are shown for clarity. Selected bond lengths (Angstroms) and angles (degrees): Re(1)–C(1), 2.20(1), Re(1)–C(21), 2.21(1), Re(1)–C(41), 2.19(1), Re(1)–C(61), 2.20(1), Re(1)–O(1), 1.773(7), Re(1)–O(2), 1.768(7), O(1)–Re(1)–O(2), 179.4(3), O(1)–Re(1)–C(1), 90.2(4).

substituted 4,5-dimethylimidazol-2-ylidene as the NHC ligand. In these derivatives, the Re–C_{carbene} bond lengths range from 2.19(1) to 2.20(1) Å, consistent with the NHC ligands being essentially σ donors, while the Re–O distances are 1.773(7) and 1.768(7) Å. All these complexes are remarkably stable, and interestingly and unlike what is observed for $[\text{ReO}_2(\text{pyridine})_4]^+$, the four equatorial NHC ligands do not readily exchange, reflecting the nonlabile nature of the M–NHC bonds. Mono-oxo and nitrido Re complexes have also been described.^{232–234} Scheme 67 displays a Re(V) nitrido

Scheme 67. Rhenium(V) Nitrido Complex 145

complex 145 supported by 1,2,4-triazolylidene and imidazolylidene ligands and in which the two 1,2,4-triazolylidene ligands underwent an *ortho*-phenyl C–H activation.²¹⁶

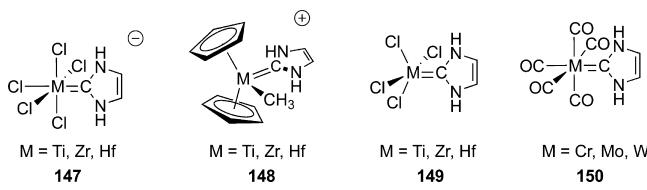
Surprisingly, only one Re(VII)–NHC adduct has been described to date. Reaction of IMe with ReO_3Me formed the corresponding six-coordinate bis-carbene adduct 146 in good yield (Scheme 68).⁷⁸

Scheme 68. Rhenium(VII) NHC Complex 146**4. COMPUTATIONAL STUDIES ON THE NATURE OF THE M–NHC BOND**

A few computational investigations on the nature and dissociation energies of the M–NHC bond in group 1–7 metal NHC complexes have been reported, and these results are thoroughly discussed in a recent review by Cavallo and co-workers.²³⁵ As estimated through DFT calculations by Frenking and co-workers, the M–NHC bond dissociation energies (BDE) in the metal NHC adducts (NHC)–MCl₄ (M = Ti, Zr, Hf) and (NHC)–M(CO)₅ (M = Cr, Mo, W) roughly lie at 30 and 50 kcal·mol^{−1}, respectively, in line with stronger bonding with an increase d-electron count on the metal center.^{236a} Accordingly, higher BDE values were found for group 8 and 11 analogues (NHC)M(CO)₄ (M = Fe, Ru, Os) and (NHC)MCl (M = Cu, Ag, Au) with values around 55 and 70 kcal·mol^{−1}, respectively.

The nature of the M–NHC bond in oxophilic and Lewis acidic metal complexes (such as group 1 and 2 and early transition metal species) is best described as covalent with a variable, yet always substantial, electrostatic/ionic contribution. Using a series of group 4 and 6 NHC adducts (Scheme 69), Jacobsen and co-workers estimated through computational work that the electrostatic component (vs the orbital interaction component) to the total bonding energy (of the M–NHC bond) ranges from 25% for the anionic group 4 species 147 to 65% for the Zr–NHC methyl cation 148. Similar electrostatic

Scheme 69. Model Group 4 and 6 NHC Adducts Studied Computationally



contributions, roughly 45–50% (of the total bonding energy), were found for the neutral group 4 and 6 adducts **149** and **150**, respectively.²³⁷ Other computational studies on group 4, 6, 8, and 10 NHC complexes concluded in all cases on the largest contribution of the electrostatic term in the M–NHC attractive interactions.²³⁶

Regardless of the exact extent to which orbital interactions contribute the overall M–NHC bond energy, the covalent character of the M–NHC bond is well established and gaining insight into the type of orbital interactions, i.e., involvement σ -type and/or π -type interactions, between the NHC ligand and the metal center constitute valuable information for synthetic chemists to better understand the structural and reactivity patterns of M–NHC species. Early calculations by Erker and co-workers on the nature of M–NHC in group 4 (IV) metallocene NHC adducts concluded on the NHC ligand solely acting as a pure σ character, as typically expected upon NHC coordination to a d⁰ metal center.⁹⁴ However, subsequent theoretical studies (involving energy decomposition analysis) by Cavallo and co-workers on (formally) d⁰ group 4 complexes **147** and **148** showed that the π component of the M–NHC bond may account for at least 10% of the overall orbital interaction (vs 90% for the σ component).²³⁷ Logically, the π component is found to be more significant as the formal d-electron count increases on the metal center.^{237,238} Thus, for group 6 species **150** the π component is estimated to be 14% (in average), while the M–NHC bond features a 20% π character in group 10 complexes (NHC)MCl (M = Cu, Ag, Au). The π component of the M–NHC bond in the studied d⁰ metal complexes includes π^* back-donation (from the metal to NHC) as the major contribution but also contains a substantial component due to π donation from the NHC to the electron-poor metal center (average for complexes **147** and **148**: 65% π^* back-donation vs 35% NHC π donation). As the metal center becomes more electron rich, the π^* back-donation is increasingly prominent relative to the NHC π donation. For instance, the NHC π donation lies at 23% and 10% (average) of the overall M–NHC π bonding in group 6 species **150** and group 10 complexes of the type (NHC)MCl (M = Cu, Ag, Au), respectively.

5. CONCLUSION

Over the past 10–15 years, studies on early transition metal complexes supported by N-heterocyclic carbene ligands have certainly established this class of compounds as viable and valuable species of potential usefulness for various applications. The trends of the coordination chemistry and associated structural patterns of such derivatives seem now well established. Despite the more polar nature of the M–C_{carbene} bond (vs late transition metal analogues), ingenious ligand design (through, for instance, use of anionic NHC-containing multidentate ligands) may ensure formation of remarkably stable and robust metal chelates well suited for various chemical

applications. In this regard and in particular, the potential applications of early transition metal NHC complexes in catalysis remain a field to be explored and developed taking advantage of the robustness/stability imparted to the resulting metal-based catalytically active components. Recent and promising reports on the use of early transition metal NHC complexes in homogeneous catalysis include, most notably, their ability to effectively mediate ketone hydrosilylation, olefin/cyclic esters polymerization, and olefin hydroamination reactions. Furthermore, it seems reasonable to expect in the coming years various other applications of this class of coordination compounds by analogy with the numerous possibilities already offered by the widely studied late transition metal NHC species. Finally, from a more fundamental point of view, combination of a intrinsically reactive metal center (since essentially oxophilic and Lewis acidic) with the exceptional electronic and steric stabilization provided by NHCs is likely to allow stabilization of unusual structural motifs yet to be uncovered, this being the source of novel reactivity and thus new potentialities for this family of NHC metal compounds.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The authors declare no competing financial interest.

Biographies



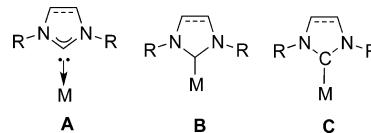
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