Subvalent Group 4B Metal Alkyls and Amides. Part 7.[1]
Transition-metal Chemistry of Metal(II) Bis(trimethylsilyl)amides M'(NR₂)₂ (R = SiMe₃; M' = Ge, Sn, or Pb) †

Michael F. Lappert * **and Philip P. Power**
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The transition-metal (M) chemistry of the compounds $M'(NR_2)_2$ (M' = Ge, Sn, or Pb; R = SiMe₃) falls into three categories. These heavy Group 4B atom carbene analogues behave as (a) M'-centred neutral ligands with respect to Lewis acids, (b) co-ordinatively unsaturated fragments, by inserting into transition-metal M–X bonds, or (c) as sources of other bivalent molecules $M'X'_2$. Reactions of class (a) afford complexes in which the Group 4 metal atom is usually [but note: $[W(CO)_5\{SnCl(NR_2)(thf)\}]$ (thf = tetrahydrofuran) in a three-co-ordinate environment, as in $[M(CO)_5\{M'(NR_2)_2\}]$ (M = Cr, Mo, or W; M' = Ge or Sn), trans-$[M(CO)_4\{M'(NR_2)_2\}_2]$ (M = Mo or W, M' = Ge or Sn), $[Sc(\eta\text{-}C_5H_5)_2\text{-}Me\{Sn(NR_2)_2\}]$, or cis-$[Pd(\eta\text{-}C_3H_5)Cl\{M'(NR_2)_2\}]$ (M' = Sn or Pb). Reactions of class (b) afford complexes in which the Group 4 metal atom is in a four-co-ordinated environment, as in $[Mn(CO)_5\text{-}\{SnBr(NR_2)_2\}]$, $[Fe(\eta\text{-}C_5H_5)(CO)_2\{Sn(NR_2)_2X\}]$ (X = F, I, or Me), $[\{Pt(\mu\text{-}Cl)[M'Cl(NR_2)_2](PEt_3)\}_2]$ (M' = Ge, Sn, or Pb), or cis-$[Pd(cod)\{SnCl(NR_2)_2\}_2]$ (cod = cyclo-octa-1,5-diene). A product of a reaction of type (c) is $[Sn\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$. Type (a) reactions are those in which an $M'(NR_2)_2$ ligand either displaces another neutral ligand (CO or olefin) from the inner co-ordination sphere of a transition metal, or effects the nucleophilic cleavage of an $M(\mu\text{-}Cl)_2M$ bridge. Type (b) reactions are insertions of an $M'(NR_2)_2$ moiety into a transition metal–halide or –alkyl bond, while the sole type (c) reaction demonstrates the facility with which the $N(SiMe_3)_2^-$ group is displaced from the Group 4 metal M' by a transition metal-centred nucleophile.

In Part 5 we described the synthesis and physical properties of the coloured, thermochromic diamagnetic, low-melting, monomeric (in C_6H_{12}) metal(II) bis(trimethylsilyl)amides of the Group 4B metals, $M'(NR_2)_2$ (R = SiMe₃): the pale yellow germanium, orange tin, and deep yellow lead compounds.[2] Their He(I) photoelectron spectra showed that they are relatively electron-rich, their first ionisation potentials being lower than those of tertiary phosphines but marginally higher than those of isoelectronic dialkyls $M'[CH(SiMe_3)_2]_2$.[3] Recently we have demonstrated that the compounds $M'(NR_2)_2$ are V-shaped monomers both in the crystal (X-ray, M' = Sn or Pb)[4] and the vapour (M = Ge,[4] Sn,[5] or Pb[4]) with the NM'N angle ranging in the gas phase from 101(1.5) (M' = Ge) to 91(2)° (M' = Pb) [although in the crystal NSnN 104.7(2) and NPbN 103.6(7)°]. It is thus evident that the Group 4B metal atom M' in $M'(NR_2)_2$ is co-ordinatively unsaturated and of a low (+2) oxidation number. The molecules exist under ambient conditions in a singlet electronic ground state, with a stereochemically active lone pair of electrons.

We now present results on the chemical behaviour of the Group 4B metal(II) bis(trimethylsilyl)amides $M'(NR_2)_2$ with some transition-metal(M)-containing reagents which has yielded 23 new compounds containing M–M' bonds, (1)—(23). Preliminary communications have dealt in outline with eight of these: $[Fe(\eta\text{-}C_5H_5)(CO)_2\{Sn(NR_2)_2Me\}]$,[6] $[W(CO)_5\{M'(NR_2)_2\}]$ (M' = Ge[7] or Sn[8]), cis-$[Pd(\eta\text{-}C_3H_5)\text{-}Cl\{M'(NR_2)_2\}]$ (M' = Sn[7] or Pb[8]), $[\{Pt(\mu\text{-}Cl)[M'Cl(NR_2)_2]\text{-}(PEt_3)\}_2]$ (M' = Sn[7] or Pb[8]), and trans-$[W(CO)_4\{Ge\text{-}(NR_2)_2\}_2]$.[8]
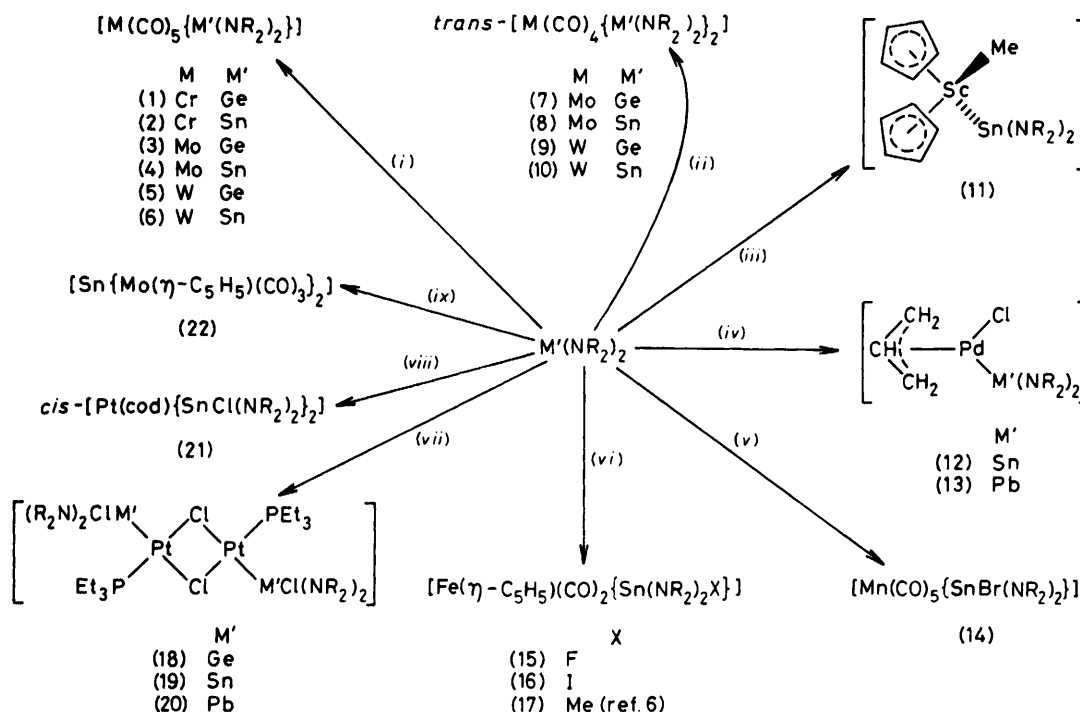
Whereas transition-metal complexes (I), having as ligand $SnCl_3^-$, a derivative, or a germanium or lead analogue, are well known, complexes (II), containing a neutral M̈'XY donor (X,Y being monodentate) are much rarer [L_n represents

the sum of all ligands other than one M'XY(Z) attached to M].[9] The first complex of type (II) to have been reported was $[Cr(CO)_5(SnR'_2)]$ [R' = CH(SiMe₃)₂][10] in 1974 (see also ref. 11). Other examples are $[M(CO)_5(M'R'_2)]$ (M = Cr, M' = Ge;[7] M = Mo, M' = Sn or Pb[11]), trans-$[M(CO)_4\text{-}(M'R'_2)_2]$ (M = Cr or W, M' = Ge;[7] M = Cr or Mo, M' = Sn[11]), $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(SnR'_2)]$,[11] $[RhCl(PPh_3)_2\text{-}(SnR'_2)]$,[11] $[PtCl(PEt_3)(SnR'_2)(SnClR'_2)]$,[11] $[Cr(CO)_5\{Ge\text{-}(SR'')_2\}]$ (R'' = Me,[12] $C_6H_2Me_3\text{-}2,4,6$,[12] or $C_6H_2Bu^t_3\text{-}2,4,6$[13]), $[M(CO)_5\{Sn(\eta\text{-}C_5H_4R'')_2\}]$ (M = Cr, Mo, or W, R'' = H; M = Cr or W, R'' = Me),[14] and $[M(CO)_5\{SnCl(PBu^t_2)\}]$ (M = Cr, Mo, or W);[15] three of these have been authenticated by X-ray analysis, $[Cr(CO)_5(M'X_2)]$ [M'X₂ = GeR'_2,[7] SnR'_2,[11] or $Ge(SC_6H_2Me_3\text{-}2,4,6)_2$[12]]. Complexes having $M'(NR_2)_2$ as ligand have been mentioned only in our preliminary communications, see above.[6-8]
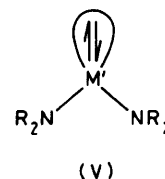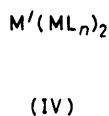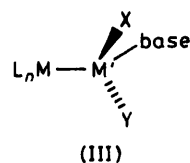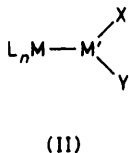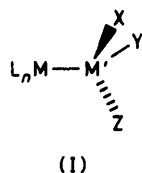
A further type of complex, (III), has a base-stabilised carbene analogue as ligand and the first of these, $[Cr(CO)_5\{M'(L)\text{-}X_2\}]$ (M' = Ge or Sn, X = Me; M' = Sn, X = Bu^t), were described in 1971.[16] Further type (III) complexes are: $[M(CO)_5\{M'Cl_2(thf)\}]$ (M = Cr,[17a] Mo,[17b] or W;[17a] M' = Ge or Sn; thf = tetrahydrofuran), some SnBr₂ or SnI₂ analogues,[17c] or for M = Cr or W some $SnCl_2(PR''_3)$ (R'' = Et, Bu^n, Bu^t, or Ph) analogues;[18] $[M(CO)_5\{Sn(OH)_2(thf)\}]$ (M = Cr or W);[18] $[Cr(CO)_5\{Ge(L)(SC_6H_4Me_3\text{-}2,4,6)_2\}]$ (L = NMe₃, NC₅H₅, or PPh₃);[12] $[M(CO)_5\{SnCl(L)X\}]$ (M = Cr, Mo, or W; L = unspecified base, X = AsBu^t₂ or PBu^t₂);[19] $[Cr(\eta\text{-}arene)(CO)_2\{GeCl_2(L)\}]$ [arene = C_6H_6, $C_6H_3Me_3\text{-}1,3,5$, or $\overline{C_7H_5NS}$ (benzothiazole)];[17a] $[Cr\{SnS(CH_2)_2N(Bu^t)(CH_2)_2S\}\text{-}(CO)_5]$;[20] $[Mn(\eta\text{-}C_5H_4Me)(CO)_2\{GeCl_2(L)\}]$ (L = thf or C_7H_5NS);[17a] $[Fe(CO)_4\{M'Cl_2(L)\}]$ (M' = Sn,[21] L = NC₅H₅ or OSMe₂; M' = Ge,[17a] L = thf or C_7H_5NS); $[Fe(CO)_4\text{-}\{M'R''_2(L)\}]$ (L = thf or NC₅H₅; M' = Sn, R'' = Ph; M' = Pb, R'' = Bu^n or Ph);[22] and $[Ni(CO)_3\{Sn(OSi\text{-}Me_3)_2\}_2]$[23a] (no structural assignment was made). For two of these there are X-ray data [(III), M = Cr, L_n = (CO)₅,

$[M(CO)_5\{M'(NR_2)_2\}]$

	M	M'
(1)	Cr	Ge
(2)	Cr	Sn
(3)	Mo	Ge
(4)	Mo	Sn
(5)	W	Ge
(6)	W	Sn

$trans\text{-}[M(CO)_4\{M'(NR_2)_2\}_2]$

	M	M'
(7)	Mo	Ge
(8)	Mo	Sn
(9)	W	Ge
(10)	W	Sn

(11)

$[Sn\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$
(22)

$cis\text{-}[Pt(cod)\{SnCl(NR_2)_2\}_2]$
(21)

$M'(NR_2)_2$

(12) Sn
(13) Pb

	M'
(18)	Ge
(19)	Sn
(20)	Pb

	X
(15)	F
(16)	I
(17)	Me (ref. 6)

$[Fe(\eta\text{-}C_5H_5)(CO)_2\{Sn(NR_2)_2X\}]$

$[Mn(CO)_5\{SnBr(NR_2)_2\}]$
(14)

Scheme. Aspects of the transition-metal chemistry of the bis[bis(trimethylsilyl)amido]tin(II) compounds and their germanium(II) and lead(II) analogues $M'[N(SiMe_3)_2]_2$ [abbreviated as $M'(NR_2)_2$]. Reactions (*i*)—(*iv*) exemplify their Lewis-base properties, and (*v*)—(*viii*) are valence expansions (2 to 4 for M') or alternatively insertions of $M'(NR_2)_2$ into M–X (X = halide or Me) bonds. (*i*) $[M(CO)_6]$, n-C_6H_{14}, irradiation, 30—40 h, 25 °C; (*ii*) $[M(CO)_4(nbd)]$, n-C_6H_{14}, reflux, 12—24 h; (*iii*) $[Sc(\eta\text{-}C_5H_5)_2(\mu\text{-}Me)_2AlMe_2]$, n-$C_6H_{14}$, 25 °C, 24 h; (*iv*) [{Pd(η-C_3H_5)(μ-Cl)}_2], n-C_6H_{14}–PhMe, 0 °C; (*v*) $[MnBr(CO)_5]$, n-C_6H_{14}, 20 °C, 1 h; (*vi*) $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$, n-$C_6H_{14}$, 25 °C; (*vii*) [{Pt(μ-Cl)Cl(PEt₃)}₂], n-C_6H_{14}, 25 °C; (*viii*) cis-[PtCl₂(cod)], n-C_5H_{12}, 0 °C, 2 h; (*ix*) $[Mo(\eta\text{-}C_5H_5)(CO)_3H]$, n-$C_6H_{14}$, 25 °C

(I)   (II)

(III)   (IV)

(V)

M' = Sn; XY(base) = $Bu^t_2(NC_5H_5)$[24] or $S(CH_2)_2N(Bu^t)$-$(CH_2)_2S$[20]], as well as for the related compound $[Ni(CO)_3$-$\{Ge(OBu^t)(\mu\text{-}OBu^t)_2Ge(OBu^t)\}Ni(CO)_3]$.[23b]

Five compounds have been reported of a fourth type of complex, $[M'(ML_n)_2]$ (IV), in which the Main group metal M' has the even lower [cf. (I)—(III)] co-ordination number of two. The first to have been described was claimed to have the formula $[Sn\{W(\eta\text{-}C_5H_5)(CO)_3\}_2]$,[25] obtained from $2[W(\eta\text{-}C_5H_5)(CO)_3H]$ and $Sn(\eta\text{-}C_5H_4Me)_2$ and subsequent recrystallisation from CH_2Cl_2; re-examination[26] showed that the product of a related reaction, using $Sn(\eta\text{-}C_5H_5)_2$, was $[SnH\{W(\eta\text{-}C_5H_5)(CO)_3\}_3]$ which upon recrystallisation from CH_2Cl_2 afforded $[SnCl\{W(\eta\text{-}C_5H_5)(CO)_3\}_3]$. Authentic examples are $[Ge\{Mn(\eta\text{-}C_5H_4Me)(CO)_2\}_2]$[27] (for which the X-ray data show a linear MnGeMn skeleton consistent with double bonding between Ge and Mn), $[Ge\{Mn(\eta\text{-}C_5Me_5)$-$(CO)_2\}_2]$[28] (X-ray data show[29] linear MnGeMn), and

recently[30] the complexes $[GeX\{Co(CO)_4\}]$ [X = F or Co-$(CO)_4$]. These cobalt complexes were characterised as the 1-germacyclopenta-3-enes by trapping with 2,3-dimethyl-buta-1,3-diene to give products of formula (II) (and curiously were claimed as the 'first germylenes with germanium–transition metal bonds').
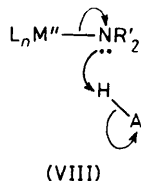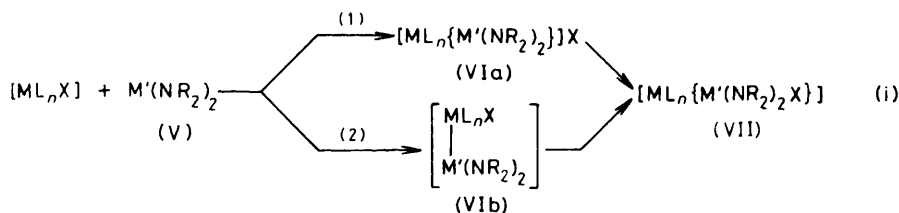
Results and Discussion

The electron-rich nature and co-ordination unsaturation of the bis[bis(trimethylsilyl)amido]metal(II) complexes (V) is demonstrated by their ability to function as (*a*) *metal-centred nucleophiles* to give products of formula (II), or (*b*) *substrates for insertion* into transition–metal–anionic ligand bonds to yield complexes (I). These reaction types are illustrated by those designated as (*i*)—(*iv*) in the Scheme for class (*a*) and (*v*)—(*viii*) for class (*b*) reactions. As a result of either type of process the co-ordination number of the Group 4B metal M' is increased from two in the free amide (V) to three for class (*a*), or four for class (*b*), the respective products being (II) and (I).

It is likely that the reaction pathway for class (*b*) reactions leading to the ultimate product (VII) often involves initial class (*a*) behaviour to form an intermediate (VI). The latter is either (1) a salt (VIa) or (2) a covalent molecule (VIb); if the latter, then the final step is a 1,2-shift of the anionic

$$[ML_nX] + M'(NR_2)_2 \xrightarrow{(1)} [ML_n\{M'(NR_2)_2\}]X \text{ (VIa)}$$
$$\text{(V)} \xrightarrow{(2)} \left[\begin{array}{c} ML_nX \\ | \\ M'(NR_2)_2 \end{array}\right] \text{ (VIb)} \longrightarrow [ML_n\{M'(NR_2)_2X\}] \quad \text{(i)} \quad \text{(VII)}$$

$$L_nM''{-}NR'_2 \cdots H {-} A$$

(VIII)

ligand X^- from the transition metal M to the Main Group 4B metal M', equation (i). In this paper the group X = F, Cl, I, or Me, but in principle is such that X^- is a good leaving group when attached to M.

The transformation (V) —► (VII) may be regarded as a carbene-like insertion reaction into an M–X bond and is already particularly well known, for example for $[ML_nCl] + SnCl_2 \longrightarrow [M(SnCl_3)L_n]$ systems where $[ML_nCl] = cis\text{-}[Pt(Cl)-H(PEt_3)_2]$.[9] Reactions of this nature are often erroneously termed oxidative additions at M'; this nomenclature is incorrect, since a ligand such as $SnCl_3^-$ unquestionably has tin in the same formal oxidation state (+2) as the starting material, e.g. $SnCl_2$. In the present context the carbene-like insertion reaction into an M–X bond results in valence expansion for M', from 2 in (V) to 4 in compound (VII). (We are not concerned with questions of electron distribution but of nomenclature; as to the former, see ref. 31.)

Metal amides may often be useful reagents by virtue of the fact that the metal–nitrogen bond is readily cleaved.[32] This is particularly the case if the metal (M'') is significantly electropositive, whence there is a weak and polar $\overset{\delta+}{M''}{-}\overset{\delta-}{N}\overset{\diagup}{\diagdown}$ bond with the amide reacting as a nitrogen-centred nucleophile, e.g. with respect to a proton-active substrate HA, as shown in (VII). In the context of the chemical behaviour of the Group 4B metal(II) amides, $M'(NR_2)_2$ (V), such reactions have been demonstrated for the following $Sn(NR_2)_2$–HA systems, equation (ii): HA = HO_2CMe,[6] HOEt, HCl, HC_5H_5, $HSPh$,[8]

$$M'(NR_2)_2 + 2HA \longrightarrow M'A_2 + 2NHR_2 \quad \text{(ii)}$$

HSR''' {$R''' = C_6H_2Bu^t_3\text{-}2,4,6$ or $C_6H_3Pr^i_2\text{-}2,6$ [also for the lead(II) analogue]},[13] or HOR'''' [$R'''' = C_6H_2Bu^t_2\text{-}2,6\text{-Me-4}$; also for the germanium(II) and lead(II) analogues],[33] to yield SnA_2 (or GeA_2[33] or PbA_2,[13,33] for A = SR''' or OR''''). We now show that $Sn(NR_2)_2$ may function as (c) a nitrogen-centred nucleophile with respect to a transition-metal hydride [(ix) in the Scheme] to yield $[Sn\{Mo(\eta\text{-}C_5H_5)-(CO)_3\}_2]$, (22). This example [equation (ii), A = $Mo(\eta\text{-}C_5H_5)(CO)_3$] thus represents a third class of transition-metal behaviour of bis[bis(trimethylsilyl)amido]metal(II) complexes (V), for which mechanism (VIII) seems to be appropriate.

In its ligand-displacement reactions [class (a), (i)—(iv) in the Scheme] the Main Group 4B metal(II) amide clearly behaves very similarly to a tertiary phosphine. Thus, it is possible to displace CO or norbornadiene (nbd) from the co-ordination sphere of a metal(0) carbonyl, $[M(CO)_6]$ or $cis\text{-}[M(CO)_4-(nbd)]$ (M = Cr, Mo, or W), to give $[M(CO)_5\{M'(NR_2)_2\}]$, (1)—(6), or $trans\text{-}[M(CO)_4\{M'(NR_2)_2\}_2]$, (7)—(10), respect-

ively; or alternatively to cleave a $(\mu\text{-Me})_2$ or $(\mu\text{-Cl})_2$ bridge between two transition-metal centres, to afford the complexes $[Sc(\eta\text{-}C_5H_5)_2Me\{Sn(NR_2)_2\}]$, (11), and $[Pd(\eta\text{-}C_3H_5)Cl\{M'-(NR_2)_2\}]$ (M' = Sn or Pb), (12) and (13), respectively.

The insertion reactions [class (b), (v)—(viii) in the Scheme] show a closer analogy between $M'(NR_2)_2$ and carbon monoxide rather than PR_3; but then CO is isolobal with CH_2 or $M'-(NR_2)_2$. The reaction sequence for conversion of a transition-metal alkyl $[ML_nX]$ (X = alkyl) into the corresponding acyl $[ML_n\{C(=O)X\}]$ is associative and implicates an intermediate carbonylmetal complex [analogue of (VI), in which $M'-(NR_2)_2 = CO$, equation (i)[34]]. It is generally assumed that the subsequent mechanism involves an intramolecular alkyl migration in the latter, rather than CO insertion into the metal–alkyl bond, although this has only been rigorously demonstrated for $[Mn(CO)_5Me] \longrightarrow [Mn(CO)_5\{C(=O)Me\}]$ and related systems. By analogy, it is likely, therefore, that the conversion of (V) into (VII) [equation (i)] involves migration of X from (VI), and hence the 'insertion' nomenclature may be mechanistically misleading.

While with respect to their class (a) and (b) reactions the amides $M'(NR_2)_2$, (V), behave as co-ordinatively unsaturated species, this is not so for class (c), where the analogy is more evidently with that of a carboxylic acid amide, cf. (VIII). This leads us to predict a novel method of preparing acyl-transition-metal complexes, equation (iii).

$$[ML_nH] + MeC(=O)NMe_2 \longrightarrow$$
$$[M\{C(=O)Me\}L_n] + NHMe_2 \quad \text{(iii)}$$
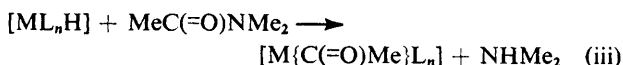
An outline of the reaction conditions used for preparing the new compounds containing M–M' bonds is provided in the Scheme. In Table 1 we summarise data on yields, appearance, and microanalyses. In Table 2 are listed selected (see assignments) carbonyl-stretching frequencies for the new Group 6 transition-metal carbonyl complexes $[M(CO)_5-\{M'(NR_2)_2\}]$, (1)—(6), and $trans\text{-}[M(CO)_4\{M'(NR_2)_2\}_2]$, (7)—(10), together with similar data on related complexes in which the ligand L in $[M(CO)_5L]$ or $trans\text{-}[M(CO)_4L_2]$ is $M'[CH-(SiMe_3)_2]_2$ (M' = Ge or Sn), PPh_3, or the electron-rich carbene $\overline{:CN(Et)(CH_2)_2NEt}$. Hydrogen-1 n.m.r. and i.r. data for the complexes of Sc^{III}, Mn^I, Fe^{II}, Pd^{II}, and Pt^{II}, (11)—(21), are shown in Table 3.

All of the carbonylmetal(0)–germanium or –tin complexes (1)—(10) are extremely air-sensitive, but they are thermally stable. In the case of the disubstituted species, (7)—(10) the product was exclusively the trans complex (as deduced from i.r. data) and no evidence was found for the presence of the cis isomer. Attempts to prepare tris-substituted species $[M-(CO)_3\{M'(NR_2)_2\}_3]$, by reaction of $Sn(NR_2)_2$ with tricarbonyl-mesitylenetungsten(0), were unsuccessful. Steric effects probably play a major role in preventing the formation of either the cis disubstituted metal(0) or tris[bis(amido)tin(II)]-metal(0) complexes.

I.r. spectra of the carbonylmetal complexes (1)—(10) were recorded in n-hexane solution and are interpreted (Table 2) on the basis of C_{4v} skeletal symmetry in the case of $[M(CO)_5L]$

Table 1. Yields, m.p.s, colours, and analytical data for transition-metal complexes derived from bis[bis(trimethylsilyl)amido]tin(II) compounds or their analogues from $Ge(NR_2)_2$, $Pb(NR_2)_2$, or $SnCl(NR_2)$ (R = $SiMe_3$)

Compound	Yield (%) [a]	M.p. (θ_c/°C)	^{1}H N.m.r. (CH$_3$) in C$_6$D$_6$ (τ)	Colour	Found (Required) (%)		
					C	H	N
(1) [Cr(CO)$_5${Ge(NR$_2$)$_2$}]	40	90 (decomp.)	9.58	Yellow	34.5 (34.8)	6.1 (6.2)	4.7 (4.8)
(2) [Cr(CO)$_5${Sn(NR$_2$)$_2$}]	50	58—60	9.62	Orange-yellow	32.9 (32.2)	5.4 (5.7)	4.4 (4.4)
(3) [Mo(CO)$_5${Ge(NR$_2$)$_2$}]	25	Pasty	9.66	Yellow	32.6 (32.4)	5.8 (5.8)	4.2 (4.45)
(4) [Mo(CO)$_5${Sn(NR$_2$)$_2$}]	25	Pasty	9.63	Yellow	30.1 (30.2)	5.1 (5.4)	3.9 (4.1)
(5) [W(CO)$_5${Ge(NR$_2$)$_2$}]	30	96—98	9.64	Yellow	29.1 (29.4)	5.1 (5.15)	3.8 (4.0)
(6) [W(CO)$_5${Sn(NR$_2$)$_2$}] [b]	35	87—89	9.62	Yellow	26.9 (27.6)	4.7 (4.8)	3.6 (3.7)
(7) trans-[Mo(CO)$_4${Ge(NR$_2$)$_2$}$_2$]	60	145—148	9.48	Yellow	33.6 (33.8)	7.1 (7.2)	5.4 (5.6)
(8) trans-[Mo(CO)$_4${Sn(NR$_2$)$_2$}$_2$]	65	78—80 (decomp.)	9.66	Orange	30.8 (30.9)	6.6 (6.7)	5.2 (5.15)
(9) trans-[W(CO)$_4${Ge(NR$_2$)$_2$}$_2$]	55	90—92 (decomp.)	9.47	Yellow	30.7 (31.1)	6.8 (6.7)	5.6 (5.2)
(10) trans-[W(CO)$_4${Sn(NR$_2$)$_2$}$_2$]	60	162—164 (decomp.)	9.53	Orange	28.1 (28.6)	6.0 (6.2)	4.6 (4.8)
(11) [Sc(η-C$_5$H$_5$)$_2$Me{Sn(NR$_2$)$_2$}]	c	Oil	d	Pale yellow	c	c	c
(12) [Pd(η-C$_3$H$_5$)Cl{Sn(NR$_2$)$_2$}] [b]		(Decomp. at ca. 20 °C)	d	Yellow	27.4 (28.9)	6.6 (6.2)	4.5 (4.2)
(13) [Pd(η-C$_3$H$_5$)Cl{Pb(NR$_2$)$_2$}]	65	80—82 (decomp.)	d	Dark yellow	25.1 (25.3)	6.0 (5.8)	3.0 (3.9)
(14) [Mn(CO)$_5${SnBr(NR$_2$)}]		Oil	d	Orange	26.6 (28.5)	4.9 (5.1)	3.5 (3.9)
(15) [Fe(η-C$_5$H$_5$)(CO)$_2${Sn(NR$_2$)$_2$F}]	85	>100 (decomp.)	d	Pale yellow	35.1 (35.9)	6.6 (6.5)	4.1 (4.4)
(16) [Fe(η-C$_5$H$_5$)(CO)$_2${Sn(NR$_2$)$_2$I}]	80	Oil	d	Yellow	30.2 (30.7)	5.3 (5.6)	3.5 (3.8)
(17) [Fe(η-C$_5$H$_5$)(CO)$_2${Sn(NR$_2$)$_2$Me}] [e]	c	Oil	d	Orange-red	c	c	c
(18) trans-[{Pt(μ-Cl)[GeCl(NR$_2$)$_2$](PEt$_3$)}$_2$]	c	Oil	d	Pale yellow	c	c	c
(19) trans-[{Pt(μ-Cl)[SnCl(NR$_2$)$_2$](PEt$_3$)}$_2$] [b]	79	164—166	d	Pale yellow	26.1 (26.2)	6.3 (6.2)	3.3 (3.4)
(20) trans-[{Pt(μ-Cl)[PbCl(NR$_2$)$_2$](PEt$_3$)}$_2$]	70	(Decomp. at ca. 0 °C)	d	Pale yellow	c	c	c
(21) cis-[Pt(cod){SnCl(NR$_2$)$_2$}$_2$]	c	(Decomp. at ca. 25 °C)	d	Pale yellow	c	c	c
(22) [Sn{Mo(η-C$_5$H$_5$)(CO)$_3$}$_2$]	70	Crystals [c]	c	Dark red	31.1 (31.5)	1.7 (1.7)	c
(23) [W(CO)$_5${SnCl(NR$_2$)(thf)}]	33	>90 (decomp.)	c	Pale yellow	25.0 (25.3)	3.6 (3.7)	2.0 (2.0)

[a] These refer to purified compounds. [b] Data from ref. 8. [c] Not recorded. [d] See Table 3. [e] Data from D. H. Harris, D. Phil. (Sussex), 1975.

Table 2. I.r. data (carbonyl region $\nu_{max.}$, cm^{-1}) for complexes [M(CO)$_5$L] and trans-[M(CO)$_4$L$_2$] [a]

	L = Ge[N(SiMe$_3$)$_2$]$_2$		Sn[N(SiMe$_3$)$_2$]$_2$		Ge[CH(SiMe$_3$)$_2$]$_2$ [b]		Sn[CH(SiMe$_3$)$_2$]$_2$ [c]		PPh$_3$ [d]		:CN(Et)(CH$_2$)$_2$NEt [e]	
(a) [M(CO)$_5$L] [f]												
	a_1 (1)	a_1 (2)	a_1 (1)	a_2 (2)	a_1 (1)	a_1 (2)	a_1 (1)	a_1 (2)	a_1 (1)	a_1 (2)	a_1 (1)	a_1 (2)
M = Cr	2 064	1 925	2 063	1 929	2 053	1 934	2 053	1 942	2 066	1 942	2 056	1 924
Mo	2 077	1 936	2 076	1 928	2 058	1 938	2 068	1 950	2 073	1 952	2 060	1 928
W	2 069	1 932	2 073	1 931	2 076	1 932	—	—	2 075	1 938	2 060	1 927
(b) trans-[M(CO)$_4$L$_2$] (all e_u bands)												
M = Cr	—		—		1 903		1 901		1 897		—	
Mo	1 938		1 938		1 914		1 919		1 887		1 840	
W	1 933		1 931		1 907		—		—		1 845	

[a] In n-hexane solution. [b] From S. J. Miles, D. Phil. (Sussex), 1977. [c] From ref. 11a. [d] From D. M. Adams, 'Metal–Ligand and Related Vibrations,' Edward Arnold, London, 1967, p. 98. [e] From M. F. Lappert, P. L. Pye, and G. M. McLaughlin, J. Chem. Soc., Dalton Trans., 1977, 1272; M. F. Lappert and P. L. Pye, ibid., p. 1283; P. B. Hitchcock, M. F. Lappert, and P. L. Pye, ibid., p. 460. [f] Four bands were observed: the a_1 (1) is that at highest wavenumber and a_1 (2) the strong band at lowest wavenumber.

(the strong e_u being omitted) or D_{4h} symmetry for the complexes [M(CO)$_4$L$_2$] (only the strong e_u is listed). With the former complexes (1)—(6), the assignments for the a_1(2), the strongest band, suggest that the ligands M'(NR$_2$)$_2$ are comparable in π-acceptor function to electron-rich carbenes. For each of the bis-substituted complexes (7)—(10), however, the position of the strong e_u mode indicates that the M'(NR$_2$)$_2$ ligands are more effective at removing charge from the metal than the carbenes. It is probable that the π-acceptor/σ-

donor ratio is relatively high for the Group 4B metal complexes. A further interesting feature is that the e_u frequencies are in most cases ca. 10 cm^{-1} higher for the amides than for the alkyl analogues. This may be due to the greater electronegativity of nitrogen, reducing the σ-donor ability of the M' atom.

In addition to the Group 6A transition metal-M'(NR$_2$)$_2$ complexes (1)—(10), reactions of M'(NR$_2$)$_2$ with various other metal carbonyls, [Fe(CO)$_5$], [Fe$_2$(CO)$_9$], [Mn$_2$(CO)$_{10}$],

Table 3. Some i.r. and n.m.r. data for transition metal–Main Group 4 metal(II) amide complexes (11)—(21)

	^{1}H N.m.r. chemical shifts (τ) in C_6D_6		I.r. (cm^{-1})	
Compound	Si(CH_3)$_3$	Other	ν(MN$_2$)	Other
(11)	9.68	4.73 (s, η-C$_5$H$_5$), 9.89 (s, Sc–CH$_3$)	405w, 365m	510w, 480w [ν(ScC)]
(12)	9.72	4.96 (m, CH), 6.88 (d of d, CH$_2$) ^{a}	395w	370m {ν[Pd(η-C$_3$H$_5$)]}, 270m [ν(PdCl)]
(13)	9.43	4.95 (m, CH), 7.08 (d of d, CH$_2$) ^{b}	400w	360m (br) {ν[Pd(η-C$_3$H$_5$)]}, 260m [ν(PdCl)]
(14)	9.34		410s, 373s	
(15)	Insoluble		408s, 372s	
(16)	9.46	5.66 (s, η-C$_5$H$_5$)	411s, 371s	
(17) ^{d}	9.46	9.03 (Sn–CH$_3$),^{c} 5.71 (η-C$_5$H$_5$) ^{e}		2 013s, 1 962s [ν(CO)]
(18)	9.41	8.8 (m, CH_3CH$_2$), 7.76 (m, CH$_3$CH_2)	380m	
(19)	9.3	8.8 (m, CH_3CH$_2$), 7.76 (m, CH$_3$CH_2)	405s, 370s	
(20)	9.38	8.78 (m, CH_3CH$_2$), 7.75 (m, CH$_3$CH_2)	370m	
(21)	9.28	7.03 (m)	405s, 370s	

^{a} J = 13 Hz. ^{b} J = 12 Hz. ^{c} ^2J(^{119}Sn–^{1}H) 40.0 Hz. ^{d} From D. H. Harris, D. Phil. (Sussex), 1975. ^{e} ^2J(^{119}Sn–^{1}H) 6 Hz.

or [Co$_2$(CO)$_8$], were also examined, but invariably led to a mixture of products. Attempts to separate these using a Florosil column resulted in decomposition. For example, reaction of either Ge(NR$_2$)$_2$ or Sn(NR$_2$)$_2$ with tetracarbonyl-nickel(0) in n-pentane afforded a yellow solution with i.r. bands in the CO region at 2 047, 2 030, 2 016, and 1 997 cm^{-1}, indicating the presence of mono- and bis-substituted species [Ni(CO)$_{4-n}$ {M'(NR$_2$)$_2$}$_n$] (n = 1 or 2). Attempts to isolate complexes by removal of solvent and [Ni(CO)$_4$] *in vacuo* yielded a metallic nickel deposit and a mixture of unidentified products.

For all the homoleptic metal carbonyls mentioned above, attempts to make the lead analogues by thermal or photochemical displacement reactions led to decomposition, as evident from the observed metal deposits, due no doubt to facile decomposition of Pb(NR$_2$)$_2$ by intense light or refluxing in n-hexane or benzene. A reaction between [Mo(CO)$_5$-(thf)] and Pb(NR$_2$)$_2$ also afforded an immediate precipitate of lead metal.

Curiously, for the palladium(II) complexes *cis*-[Pd(η-C$_3$H$_5$)Cl{M'(NR$_2$)$_2$}], (12) and (13), the tin(II) derivative (12) was much less thermally stable than the lead analogue (13) decomposing in *ca.* 30 min at 25 °C but being stable at −30 °C. The lead(II) derivative (13) probably did not decompose significantly before melting at *ca.* 80—82 °C. A plausible explanation is that if the products of decomposition involve an M'^{IV} species the latter would be less favoured for lead than for tin. A possible decomposition pathway of this type would yield a palladium(0) complex [*e.g.* with (V) as ligands] and M'(C$_3$H$_5$)Cl(NR$_2$)$_2$. Thus the amide (V) is envisaged as capable of functioning as a reducing agent. Such a reaction has been demonstrated in the conversion of PR'''Cl$_2$ into R'''P=PR''' using a cyclic tin(II) amide as a powerful dechlorinating reagent (R''' = C$_6$H$_2$Bu$^t_3$-2,4,6).[35]

The insertion reactions of M'(NR$_2$)$_2$ with transition-metal halides [(v)—(viii) in the Scheme] were carried out in n-hexane and proceeded in high yield. Difficulties were encountered in the complete purification of complexes (14)—(21), due to their tendency to form either an oil or an intractable (ionic) solid, (15), material. The platinum compounds (18)—(20) are interesting because the corresponding reactions of [{Pt(μ-Cl)Cl(PEt$_3$)}$_2$] with Sn[CH(SiMe$_3$)$_2$]$_2$, *i.e.* SnR'$_2$, gave [PtCl(PEt$_3$)(SnR'$_2$)(SnClR'$_2$)].[11] This may illustrate the weaker nucleophilicity of Sn(NR$_2$)$_2$ compared with SnR'$_2$. I.r. and n.m.r. data indicate that both the PtCl bonds of [PtCl$_2$(cod)] (cod = cyclo-octa-1,5-diene) suffer insertion by Sn(NR$_2$)$_2$; however, due to the instability of complex (21) (it readily decomposes at >0 °C) analytical data are not available.

Experimental

All the manipulative operations were carried out under rigorously anaerobic conditions, as described in Part 2.[11a] Spectroscopic instrumentation was as previously.[1,2] The Group 6A transition metal(0) hexacarbonyls were commercial samples. Other starting materials were prepared by published procedures: [M(CO)$_4$(nbd)],[36] [Sc(η-C$_5$H$_5$)$_2$(μ-Me)$_2$AlMe$_2$],[37] [{Pd(η-C$_3$H$_5$)(μ-Cl)}$_2$],[38] [MnBr(CO)$_5$],[39] [Fe(η-C$_5$H$_5$)(CO)$_2$-X] (X = F, I, or Me),[40] [{Pt(μ-Cl)Cl(PEt$_3$)}$_2$],[41] [PtCl$_2$(cod)],[42] and [Mo(η-C$_5$H$_5$)(CO)$_3$H].[43]

Reactions of Bis[bis(trimethylsilyl)amido]-derivatives of Germanium(II), *Tin*(II), *or Lead* (II).—*With Group 6A metal hexacarbonyls.* Hexacarbonylchromium(0) (0.44 g, 2 mmol) was added slowly to a solution of bis[bis(trimethylsilyl)-amido]tin (0.44 g, 1 mmol) in n-hexane (30 cm^3). The solution was irradiated with u.v. light for 30 h affording a yellow solution. This was reduced in volume to *ca.* 10 cm^3 *in vacuo*, cooled to −78 °C, and filtered. The volume of the filtrate was further reduced to *ca.* 3 cm^3, cooled to −78 °C, and filtered. Cooling the filtrate to −78 °C afforded the yellow crystalline *compound* (2) (0.16 g, 29%). From the mother-liquors a further crop of crystals was isolated by cooling.

The other monogermanio- and stannio-derivatives of Cr, Mo, and W, (1) and (3)—(6), were prepared similarly (see Table 1 for details). With the lead amide severe photodecomposition took place affording a deposit of lead metal, and no complexes were isolated

With tetracarbonyl(norbornadiene)-molybdenum(0) *or -tungsten*(0). Tetracarbonyl(norbornadiene)molybdenum(0) (0.5 g, 1.6 mmol) was added to a solution of bis[bis(trimethylsilyl)-amido]germanium (1.4 g, 3.5 mmol) in n-hexane (25 cm^3) and the mixture was refluxed for 24 h. The resultant orange solution was cooled, the volume reduced *in vacuo* to *ca.* 5 cm^3, and filtered. The filtrate was cooled to −78 °C, affording the yellow crystalline *compound* (7) (0.79 g, 48%), and a further crop of crystals was isolated from the mother-liquors.

The other bis-germanio- and -stannio-derivatives of Mo and W, (8)—(10), were prepared similarly (Table 1 for details), but reaction of a tetracarbonyl(norbornadiene)metal(0) complex and the lead(II) amide afforded a deposit of lead metal; no new complexes were isolated.

Reaction of Sn[N(SiMe$_3$)$_2$]$_2$ with [Sc(η-C$_5$H$_5$)$_2$(μ-Me)$_2$Al-Me$_2$].—The tin(II) amide (0.37 g, 0.6 mmol) in n-hexane (20 cm^3) was added slowly to a suspension of the scandium(III) tetramethylaluminate (0.6 mmol) in n-hexane (20 cm^3). The mixture gradually became pale yellow and was filtered, after

stirring for 24 h. The volatiles were removed *in vacuo*, affording a pale yellow oil. An i.r. spectrum was recorded and it showed bands attributable to Al_2Me_6, η-C_5H_5 groups, $N(SiMe_3)_2$ groups, and Sn–N stretching. The ^{1}H n.m.r. spectrum was recorded after the residue had been under high vacuum for several hours; this showed peaks at τ 4.73, 9.68, and 9.89 in the ratio *ca.* 3 : 6 : 1, which supports the formulation of the product as that of complex (11).

Reactions of Bis[bis(trimethylsilyl)amido]-derivatives of Tin(II) or Lead(II) with Di(η-allyl)-di-μ-chloro-dipalladium-(II).—Bis[bis(trimethylsilyl)amido]lead(II) (0.5 g, 0.95 mmol) in n-hexane (10 cm³) was added dropwise to a cooled (0 °C) suspension of [{Pd(η-C_3H_5)Cl}$_2$] (0.165 g, 0.45 mmol) in toluene (20 cm³). The solid gradually dissolved and the resultant yellow suspension was stirred for 2 h and filtered rapidly. The filtrate was concentrated to *ca.* 5 cm³; addition of a small volume of n-hexane afforded, on cooling, the yellow crystalline *complex* (13) (0.43 g, 65%). The *tin analogue* (12) was prepared similarly, but was unstable.

Reactions of Bis[bis(trimethylsilyl)amido]tin(II).—With bromopentacarbonylmanganese(I). The title bromo-complex (0.22 g, 0.8 mmol) was added slowly to a solution of Sn-[N(SiMe₃)₂]₂ (0.35 g, 0.8 mmol) in n-hexane (30 cm³). The orange solution instantly became paler and after stirring for 1 h the solvent was removed *in vacuo* to afford an orange-yellow oil which could not be crystallised or distilled without decomposition, but is formulated as complex (14) (0.5 g, 88%).

With dicarbonyl(cyclopentadienyl)iron(II) complexes. The compound Sn[N(SiMe₃)₂]₂ (0.33 g, 0.75 mmol) in n-hexane (25 cm³) was added dropwise to a suspension of [Fe(η-C₅H₅)(CO)₂F] (0.145 g, 0.7 mmol), or the iodo-analogue (0.21 g, 0.71 mmol), in n-hexane (15 cm³). In each case there was an instantaneous reaction affording a yellow solution (I⁻) or a pale yellow precipitate (F⁻). Removal of volatiles *in vacuo* afforded the appropriate *complex* (15) or (16). Attempts at recrystallisation were unsuccessful, due to the sparing insolubility of (15) and the excessive solubility of (16).

Dropwise addition of a yellow solution of [Fe(η-C₅H₅)-(CO)₂Me] (0.232 g, 1.21 mmol) in benzene (10 cm³) to an orange-yellow solution of Sn[N(SiMe₃)₂]₂ (0.532 g, 1.21 mmol) in the same solvent (10 cm³) produced no visible sign of reaction. The mixture was stirred for 2 d at *ca.* 25 °C and was then refluxed for 12 h. Filtration, removal of volatiles from the filtrate at *ca.* 20 °C (10^{-3} Torr), and extraction of the residue into n-hexane afforded (as shown by i.r., n.m.r., and analysis) impure complex (17) contaminated with starting materials and a trace of [{Fe(η-C₅H₅)(CO)₂}₂]. Repeated extractions with n-C₅H₁₂ and crystallisations failed to afford pure complex (17), and attempted microdistillation (b.p. 60 °C, 10^{-3} Torr) gave the dimeric iron(I) carbonyl.

With [RhCl(PPh₃)₃] or [NiCl₂(PPh₃)₂]. A solution of Sn[N(SiMe₃)₂]₂ (*ca.* 1 mmol) in benzene (10 cm³) was added dropwise to a stirred solution of the rhodium or nickel compound (*ca.* 1 mmol) in benzene (10 cm³). In each case a brown solution resulted and although i.r. spectra showed that tin–chloride bond formation had taken place, no pure products were isolated.

With [Co₂(CO)₈], [Fe(CO)₅], [Fe₂(CO)₉], [Fe₃(CO)₁₂], or [Mn₂(CO)₁₀]. In each case a solution of Sn[N(SiMe₃)₂]₂ (*ca.* 1 mmol) in n-hexane (20 cm³) was treated with the appropriate metal carbonyl in a 1 : 1 ratio. Reaction was induced in each case by photolysis or by refluxing. All of the metal carbonyl reacted (i.r. evidence). Attempts at isolating pure products by chromatography were unsuccessful, due to decomposition of the complexes on the Florisil columns.

With tetracarbonylnickel(0). A solution of Sn[N(SiMe₃)₂]₂

(0.44 g, 1 mmol) and [Ni(CO)₄] (0.6 g, 3.5 mmol) in n-pentane (20 cm³) was refluxed for 4 h and allowed to cool. An i.r. spectrum of the yellow solution showed that most of the tetracarbonyl had reacted to yield a monosubstituted nickel tricarbonyl. Removal of the volatiles *in vacuo* yielded a metallic deposit, and no pure product was isolated.

Reactions of Bis[bis(trimethylsilyl)amido]-derivatives of Germanium(II), Tin(II), or Lead(II) with trans-Di-μ-chloro-dichlorobis(triethylphosphine)diplatinum(II).—The tin(II) amide (0.25 g, 0.5 mmol) in n-hexane (10 cm³) was slowly added to a stirred suspension of the platinum dimer (0.192 g, 0.25 mmol) in n-hexane (25 cm³). The suspension gradually dissolved, affording a yellow solution which, having been filtered and cooled, afforded pale yellow crystals of *complex* (19) (0.35 g, 79%). A similar experiment, but using an excess of Sn[N-(SiMe₃)₂]₂ (0.5 mmol) and [{Pt(μ-Cl)Cl(PEt₃)}₂], gave a significantly reduced yield, and unreacted Sn[N(SiMe₃)₂]₂ was recovered.

Reaction of [{Pt(μ-Cl)Cl(PEt₃)}₂] with bis[bis(trimethylsilyl)-amido]lead(II) in a 1 : 2 ratio, under identical conditions, afforded pale yellow crystals of the lead *complex* (20) which decomposed rapidly (*ca.* 30 min) at 25 °C and slowly even at 0 °C.

Reaction of [{Pt(μ-Cl)Cl(PEt₃)}₂] with Ge[N(SiMe₃)₂]₂ in a 2 : 1 molar ratio afforded a pale yellow oil which could not be recrystallised or distilled; however, analytical, i.r., and n.m.r. data indicated that a germanium analogue (18) of complexes (19) and (20) had been formed.

Reaction of [PtCl₂(cod)] with Sn[N(SiMe₃)₂]₂.—The tin(II) amide (0.351 g, 0.8 mmol) in n-pentane (10 cm³) was added dropwise to a suspension of dichloro(cyclo-octa-1,5-diene)-platinum(II) (0.15 g, 0.4 mmol) in n-pentane (25 cm³) at 0 °C. The solid gradually dissolved, affording a pale yellow solution which, after stirring for 2 h, was quickly filtered. The volume of the solution was reduced to *ca.* 10 cm³ *in vacuo*, and cooling to −78 °C afforded the pale yellow crystalline *compound* (21). The complex decomposed at 25 °C in *ca.* 5 min.

Reaction of Sn[N(SiMe₃)₂]₂ with [Mo(η-C₅H₅)(CO)₃H].—The tin(II) amide (0.4 g, 0.92 mmol) in n-hexane (20 cm³) was treated slowly with the hydrido-complex (0.44 g, 1.8 mmol). The solution gradually became dark red and, after stirring for 2 h, the volatiles were removed. The residue was recrystallised from a CH₂Cl₂–n-hexane mixture affording dark red crystals of *compound* (22).

Reaction between [Bis(trimethylsilyl)amido]chlorotin(II) and Pentacarbonyl(tetrahydrofuran)tungsten(0).—To a solution of [W(CO)₅(thf)], synthesised by u.v. irradiation of [W(CO)₆] (0.5 g, 1.43 mmol) in tetrahydrofuran (25 cm³) for 6 h, was added SnCl[N(SiMe₃)₂] (0.40 g, 1.3 mmol). The solution was stirred for 2 h and the volatiles removed *in vacuo*. n-Hexane (10 cm³) was added to the residue, and the solution was cooled to −78 °C for *ca.* 15 min and then filtered. The filtrate was reduced to a volume of *ca.* 4 cm³ *in vacuo*, and cooling to −78 °C afforded pale yellow crystals which were purified by two further recrystallisations from toluene to yield *compound* (23) (0.3 g, 33%).

Lack of Reaction.—Between [{Mo(η-C₅H₅)(CO)₃}₂] and Sn[N(SiMe₃)₂]₂. The title metal(I) carbonyl (0.8 g, 1.63 mmol) was added to a solution of the tin(II) amide (0.72 g, 1.64 mmol) in n-hexane (30 cm³), and the mixture was refluxed for 10 h, then cooled and filtered affording an orange filtrate and unreacted crystals of the molybdenum compound (analysis, i.r.). Removal of volatiles *in vacuo* from the filtrate

afforded an orange oil which was identified as crude Sn-[N(SiMe₃)₂]₂, from i.r. and n.m.r. spectra.

Between bis[bis(trimethylsilyl)amido]tin(II) and [IrCl(N₂)-(PPh₃)₂]. The iridium(I) complex (0.3 g, 0.38 mmol) was added slowly to a stirred solution of Sn[N(SiMe₃)₂]₂ (0.17 g, 0.4 mmol) in n-hexane (20 cm³). Most of the iridium(I) complex (i.r.) was recovered upon filtration, and the filtrate on removal of volatiles *in vacuo* afforded crude Sn[N(SiMe₃)₂]₂ (i.r., n.m.r.).

Acknowledgements

References

1 Part 6, M. J. S. Gynane, M. F. Lappert, S. J. Miles, A. J. Carty, and N. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1977, 2009.
2 Part 5, M. S. J. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, and M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.*, 1977, 2004.
3 D. H. Harris, M. F. Lappert, J. B. Pedley, and G. J. Sharp, *J. Chem. Soc., Dalton Trans.*, 1976, 945.
4 T. Fjeldberg, H. Hope, M. F. Lappert, P. P. Power, and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1983, 639.
5 M. F. Lappert, P. P. Power, M. J. Slade, L. Hedberg, K. Hedberg, and V. Schomaker, *J. Chem. Soc., Chem. Commun.*, 1979, 369.
6 D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895.
7 M. F. Lappert, S. J. Miles, P. P. Power, A. J. Carty, and N. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1977, 458.
8 M. F. Lappert and P. P. Power, *Adv. Chem. Ser.*, 1976, 157, 70.
9 *cf.*, K. M. Mackay and B. K. Nicholson, in ' Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 6, pp. 1043—1114.
10 J. D. Cotton, P. J. Davidson, D. E. Goldberg, M. F. Lappert, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1974, 893.
11 (a) Part 2, J. D. Cotton, P. J. Davidson, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2275; (b) Part 3, J. D. Cotton, P. J. Davidson, J. D. Donaldson, M. F. Lappert, and J. Silver, *ibid.*, p. 2286.
12 P. Jutzi, W. Steiner, E. König, G. Huttner, A. Frank, and U. Schubert, *Chem. Ber.*, 1978, 111, 606.
13 P. B. Hitchcock, M. F. Lappert, B. J. Samways, and E. L. Weinberg, *J. Chem. Soc., Chem. Commun.*, 1983, 1492.
14 A. B. Cornwell, P. G. Harrison, and J. A. Richards, *J. Organomet. Chem.*, 1976, 108, 47.
15 W-W. du Mont and B. Neudert, *Chem. Ber.*, 1978, 111, 2267.
16 T. J. Marks, *J. Am. Chem. Soc.*, 1971, 93, 7090.
17 (a) P. Jutzi and W. Steiner, *Chem. Ber.*, 1976, 109, 3473; (b) H. Behrens, M. Moll, and E. Sixtus, *Z. Naturforsch., Teil B*, 1977,

32, 1105; (c) D. Uhlig, H. Behrens, and E. Lindner, *Z. Anorg. Allg. Chem.*, 1973, 401, 233.
18 W-W. du Mont and H-J. Kroth, *Z. Naturforsch., Teil B*, 1980, 35, 700.
19 W-W. du Mont, J. L. Lefferts, and J. J. Zuckerman, *J. Organomet. Chem.*, 1979, 166, 347.
20 A. Tzschach, K. Jurkschat, M. Scheer, J. Meunier-Piret, and M. van Meerssche, *J. Organomet. Chem.*, 1983, 259, 165.
21 A. B. Cornwell and P. G. Harrison, *J. Chem. Soc., Dalton Trans.*, 1975, 2017.
22 T. J. Marks and A. R. Newman, *J. Am. Chem. Soc.*, 1973, 95, 769; G. W. Grynkewich, B. Y. K. Ho, T. J. Marks, D. L. Tomaja, and J. J. Zuckerman, *Inorg. Chem.*, 1973, 12, 2522.
23 (a) W-W. du Mont and M. Grenz, *Z. Naturforsch., Teil B*, 1983, 38, 113; (b) M. Grenz, E. Hahn, W-W. du Mont, and J. Pickhardt, *Angew. Chem., Int. Ed. Engl.*, 1984, 23, 61.
24 M. A. Brice and F. A. Cotton, *J. Am. Chem. Soc.*, 1973, 95, 4529.
25 P. G. Harrison and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 1973, 940.
26 T. S. Dory, J. J. Zuckerman, C. D. Hoff, and J. W. Connolly, *J. Chem. Soc., Chem. Commun.*, 1981, 521.
27 W. Gäde and E. Weiss, *J. Organomet. Chem.*, 1981, 213, 451.
28 W. A. Herrmann, J. Weichmann, U. Küsthardt, A. Schäfer, R. Hörlein, C. Hecht, E. Voss, and R. Serrano, *Angew. Chem., Int. Ed. Engl.*, 1983, 22, 979.
29 I. Bernal and J. D. Korp, cited in ref. 28.
30 A. Castel, P. Rivière, J. Satgé, J. J. Moreau, and R. J. P. Corriu, *Organometallics*, 1983, 2, 1498.
31 D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, 1969, 8, 1771; G. W. Parshall, *ibid.*, 1972, 11, 433.
32 *cf.*, M. F. Lappert, P. P. Power, A. R. Sanger, and R. C. Srivastava, 'Metal and Metalloid Amides,' Horwood-Wiley, Chichester, 1980
33 B. Çetinkaya, I. Gümrükçü, M. F. Lappert, J. L. Atwood, R. D. Rogers, and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1980, 102, 2088.
34 *cf.*, J. K. Kochi, 'Organometallic Mechanisms and Catalysis,' Academic Press, New York, 1978, pp. 557—561.
35 M. Veith, V. Huch, J-P. Majoral, G. Bertrand, and G. Manuel, *Tetrahedron Lett.*, 1983, 4219.
36 *cf.*, R. B. King, 'Organometallic Synthesis,' eds. J. J. Eisch and R. B. King, Academic Press, New York, 1965, vol. 1, p. 124.
37 J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1979, 45.
38 R. Hüttel, J. Kratzer, and M. Bechten, *Chem. Ber.*, 1961, 94, 766.
39 Ref. 36, p. 174.
40 Ref. 36, pp. 175 and 176.
41 R. J. Goodfellow and L. M. Venanzi, *J. Chem. Soc.*, 1965, 7533.
42 K. A. Jensen, *Acta Chem. Scand.*, 1953, 7, 866.
43 S. A. Keppie and M. F. Lappert, *J. Organomet. Chem.*, 1969, 19, P5.