Stable Homoleptic Metal Alkyls

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Since Frankland's discovery in 1849 of the spontaneously inflammable $ZnEt_2$, metal alkyls have been of considerable interest. The scope of relevant problems is immense, ranging from theoretical or structural studies to organic or biological chemistry. Several compounds, especially the electron-deficient alkyls such as $(LiMe)_4$, $(BeMe_2)_n$, and $(AlMe_3)_2$, have provided significant examples (along with B_2H_6) of covalent molecules in which a simple two-electron two-center bonding model is demonstrably inadequate. Many derivatives have a key role as synthetic reagents, notably the Grignards and alkyls of Li, Zn, Hg, Al, Sn, and Cu. Transition metal alkyls are vital intermediates in metal-catalyzed reactions of olefins or acetylenes, some of which are important in petrochemical, polymer, or heavy organic chemical industry, e.g., alkyls of Ti in Ziegler–Natta polymerizations and of Co in hydroformylation using $Co_2(CO)_8$. Several main group metal alkyls have large tonnage industrial use: $PbEt_4$ as an antiknock gasoline additive; Sn^{IV} compounds as stabilizers for poly(vinyl chloride) and as fungicides or germicides; silicones as rubbers, resins, or paper and textile finishes; and Al derivatives in the manufacture of isoprene or long-chain alcohols. Vitamin B_{12} coenzyme provides a unique example of a naturally occurring metal alkyl, and fission of its Co^{III}–C bond is implicated in the biologically important enzymatic isomerization reactions which it controls.

Inorganic chemists are often fascinated by exploring the potential of a single ligand across the length and breadth of the periodic table. For the case of the ligand R^-, this is the principal theme of our researches in this area and of the present Account. We propose to restrict the scope to homoleptic compounds $(MR_n)_x$. (For compounds $(MX_n)_x$ the term "isoleptic" has been used in the same context [*Inorg. Syn.*, **13**, 73 (1970)]. We prefer to reserve it to describe the relationship between *two or more compounds*: e.g., each of the following *pairs* is isoleptic: (i) $SiMe_4$ and $TiMe_4$ and (ii) Me_3SiCl and Me_3TiCl. Compounds i are homoleptic and ii heteroleptic.) Much of the discussion will focus on species in which the alkyl group R is bulky and has no β hydrogen, especially Me_3SiCH_2 (R^1),[1,2] $(Me_3Si)_2CH$ (R^2), Me_3CCH_2 (R^3), and Me_3SnCH_2 (R^4).[1] The introduction of such ligands in 1970 has significantly broadened the scope of metal alkyl chemistry, especially from the standpoints of increasing the range of available stable compounds, a revision of ideas relating to metal alkyl stability, and the possibility of studying new types of chemical reactions. The word "stable" in the title of this article signifies compounds which do not markedly deteriorate at ambient temperature in a vacuum or in an anhydrous, anaerobic, inert atmosphere.

The classification of inorganic compounds into derivatives of main group elements or of transition metals is often helpful. However, a rigid compartmentalization may be undesirable, and we propose here to knit together the two areas for $(MR_n)_x$ and to include also a third class, that of stable main group metal-centered radicals such as $R^2_3M\cdot$ (M = Si, Ge, or Sn). The last named are discussed because it seems to us illogical to consider paramagnetic transition metal alkyls such as TiR^2_3 and not a species such as $R^2_3Sn\cdot$. Many of the data on compounds such as $(MR^1_n)_x$ are summarized in Table I. From this, it is evident that eight basic propositions, which had until recently been regarded as fundamental,[3] are invalid, at any rate for the above bulky ligands.

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Proposition

Contradictory data

1. Except for group V, main group element alkyls are only stable in the higher oxidation states for elements of variable valency; *e.g.*, $Pb^{IV}Et_4$ but not $Pb^{II}Et_2$, in contrast to, say, chlorides.

Stable alkyls $SnR^2{}_2$ and $PbR^2{}_2$ have been prepared.[4]

2. Homoleptic transition metal alkyls are intrinsically unstable; *e.g.*, $TiMe_4$, unlike, say, $GeMe_4$, decomposes at low temperature.

Stable d^0, d^1, d^2, d^3, and d^{10} homoleptic metal alkyls (Table I),[5] including alkyls of some lanthanides,[6,7] have been prepared.

3. The M–C bond is weak for a transition metal, but stronger for a main group metal.

This is inconsistent with spectroscopic data (see later).

4. The stability of transition metal alkyls is favored by a low metal oxidation state and by the presence of stabilizing ligands such as the potential π acceptors CO, R_3P, or π-$C_5H_5{}^-$. (Rationalizations for propositions 4 and 5 are based on variations in the crystal field splitting parameters, Δ).

Stable high oxidation state homoleptic (*i.e.*, without "stabilizing" ligands) M^{4+} and M^{3+} compounds are exemplified by $MR^1{}_4$[5] and $MR^2{}_3$[6] (M = a transition metal).

5. For an isostructural series of transition metal alkyls, stability increases from left to right along a transition metal series and from top to bottom down the three series; *i.e.*, stability is maximized in a heavy late transition metal such as Pt.

The stable complexes $MR^1{}_4$[5] $MR^2{}_3$[6] are derived from light early transition metals, such as Sc, Ti, V, or Cr.

6. Main group metal-centered radicals are best treated as free radicals rather than organometallic compounds, and are transient species.

The species $R^2{}_2Sn\cdot$[8] and $R^2{}_3Ge\cdot$[9] do not decompose after many weeks at 20°.

7. Alkyl bridging is characteristic of electron-deficient compounds of main group elements only.

In $(CuR^1)_4$[10] the coordination number of C is 5.[11]

8. A bridging alkyl, R, may only be bound to three metal atoms, I, as in $(LiMe)_4$, or two alkyl groups may form a double bridge to two metal atoms, II, as in Al_2Me_6.

In $(CuR^1)_4$ there are single alkyl bridges (III).[11]
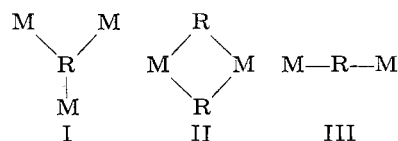
Kinetic stability is proposed as the underlying principle governing the thermal stability of metal alkyls. It is appropriate, therefore, to identify decomposition pathways. One such process is olefin loss by β elimination, hence the significance of ligands which do not possess β-H, such as $Me_3SiCH_2{}^-$. Other possible routes include α, γ, reductive, or binuclear elimination and M–C homolysis. Ligands such as $Me_3SiCH_2{}^-$ must not be regarded intrinsically as "stabilizing." On the contrary, they may enhance a decomposition pathway; thus $(Ph_3P)_3RhR^1$ is less stable than $(Ph_3P)_3RhMe$, presumably because elimination leading to IV is encouraged by

IV
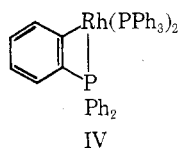
the bulkier ligand.[12] Because transition metal alkyls have available various decomposition routes, it is not

possible to give an invariant order for relative stability of a metal alkyl as a function of M or R. However, often the following stability sequences hold: (i) 1-norbornyl (Nor) > $PhCH_2$ > Me_3SiCH_2 $\approx$ Me_3CCH_2 > Me_3SnCH_2 > Ph > Me $\gg$ Et > *sec*- or *tert*-butyl; (ii) perfluoroalkyl (R_F) > R. Such distinctions are only useful when referring to complexes of the same coordination number; for example, it is not fruitful to discuss the relative stabilities of complexes having $Me_3SiCH_2{}^-$ ($R^1{}^-$) or $(Me_3Si)_2CH^-$ ($R^2{}^-$) ligands by reference to $CrR^1{}_4$ and $CrR^2{}_3$.

Other features which influenced our choice of ligands such as $R^1{}^-$ or $R^2{}^-$ are good hydrocarbon solubility, simple ^1H nmr or esr (for paramagnetic species) spectra, and the analogy with $(Me_3Si)_2N^-$. The latter is isoelectronic with $(Me_3Si)_2CH^-$ and often yields transition metal amides of low coordination number, especially 3.[13] Other ligands which have yielded stable homoleptic transition metal alkyls include $PhCH_2{}^-$ (Ti^{IV}, Zr^{IV}, Hf^{IV}),[14] Me_3PCH_2 (Au^I),[15] a bidentate phosphonium ylide$^-$ (Cr^{III}, Ni^{II}, Cu^I, Ag^I, Au^I),[15,16] *e.g.*, V,[15] Nor$^-$ [as in VI, M = Ti, V, Cr, Mn, Co, Zr, or Hf],[17] and 1-adamantyl$^-$

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(Ti^{IV}).[18] The synthesis of stable metal hexamethyls (*e.g.*, $ZrMe_6^{2-}$,[19] or WMe_6[20]) illustrates the principle that, even with small ligands, the occupancy of a large number of coordination sites (coordination saturation) enhances stability.
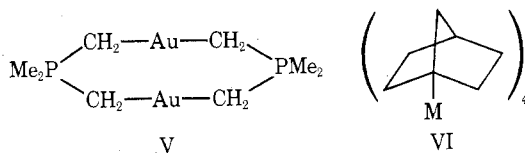
Several reviews are relevant to this Account. They refer to transition metal alkyls[21] or specifically to trimethylsilylmethyls.[5] Elsewhere we shall present a comprehensive account of homoleptic metal σ-hydrocarbyls (this term embraces alkyls, aralkyls, alkenyls, alkynyls, or aryls), with particular reference to stoichiometry, structure, bonding, stability, and thermal decomposition pathways (including data for heteroleptic alkyls).[22] Table I contains data on neopentyl-type ligands.[4,6-11,22-37]
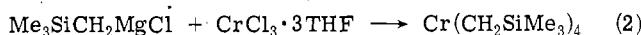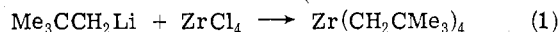
Synthesis

Various procedures have been used, as shown below.

Direct Synthesis. This method is largely limited to Li [in one case, Na; Al (+ H_2 + olefin); or alloys (*e.g.*, NaPb + $RX \rightarrow PbR_4$)], and involves reaction between the metal, preferably as Li "shot" or powder, and alkyl halide, most suitably the chloride for ease of separation of the mole equivalent of Li halide produced. It is surprising that, so far, $Li(CH_2SnMe_3)$ has not proved to be accessible.[27]

Halogen–Alkyl Exchange. Organolithium or Grignard reagents are the most versatile for this procedure, especially where the production of the homoleptic compounds is required. Examples are in eq 1[25] and 2.[28]

$$Me_3CCH_2Li + ZrCl_4 \longrightarrow Zr(CH_2CMe_3)_4 \quad (1)$$

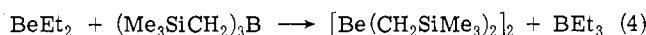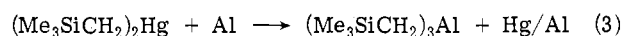$$Me_3SiCH_2MgCl + CrCl_3 \cdot 3THF \longrightarrow Cr(CH_2SiMe_3)_4 \quad (2)$$

Generally preformed metal alkyls are used, but *in situ* reactions have also been employed in the transition metal series, notably in the preparation of $Cr(CH_2CMe_3)_4$[38] and $Ti(1\text{-adamantyl})_4$ (Wurtz method).[18] For the main group metals, forcing conditions are sometimes necessary for replacement of the final halide ligand by a bulky alkyl, *e.g.*, in the preparations of $M(CH_2CMe_3)_4$ (M = Ge).[25] Here the superior reactivity of the organolithium reagent is an advantage, but in other cases use of RLi may lead to undesirable reduction; this is particularly significant for transition metals.[24] The reducing power, which parallels alkylating ability, follows the order: RLi > RMgCl > R_2Mg, and where reduction is significant (*e.g.*, with $TiCl_4$), then the dialkylmagnesium is the reagent of choice.[24] Reagents such as zinc or aluminum alkyls are less reactive, and therefore may be useful for the synthesis of heteroleptic species, *e.g.*, $Cl_3NbR^1_2$ or $Cl_2NbR^1_3$ from $NbCl_5$.[32]

The metal in the halide need not be in the same oxidation state as in the product homoleptic alkyl (*cf.* Table I for Cr^{IV} complexes, which interestingly are accessible from Cr^{III} precursors; see eq 2).

Where the appropriate metal halide is unsuitable, perhaps due to low solubility, a complex may be used: *e.g.*, $TiCl_3 \cdot 2Me_3N$ for TiR^2_3,[6] Alternatively, for $CrBu\text{-}t_4$, the nonexistence of $CrCl_4$ prompted the use of $Cr(OBu\text{-}t)_4$ with $LiBu\text{-}t$.[38]

Transalkylation. This method is useful where either especially pure halogen-free materials are required or where the above methods are unsuitable. Examples are shown in eq 3[39] and 4.[37]

$$(Me_3SiCH_2)_2Hg + Al \longrightarrow (Me_3SiCH_2)_3Al + Hg/Al \quad (3)$$

$$BeEt_2 + (Me_3SiCH_2)_3B \longrightarrow [Be(CH_2SiMe_3)_2]_2 + BEt_3 \quad (4)$$

This procedure has yet to be used in the transition series, but developments are expected in view of the current interest in reactions of condensed metal vapors which may provide the necessary activated metal source.[40]

Disproportionation. This may be effected chemically, thermally, or photolytically. Dialkylmagnesium compounds may be obtained, albeit somewhat impure, by precipitation of magnesium chloride as a Lewis base adduct (dioxanate) from solutions of the Grignard reagent, as in eq 5.[24]

$$ClMgCH_2SiMe_2Ph \xrightarrow{\text{dioxane}}$$

$$0.5Mg(CH_2SiMe_2Ph)_2 + 0.5MgCl_2 \cdot 2\text{dioxane} \quad (5)$$
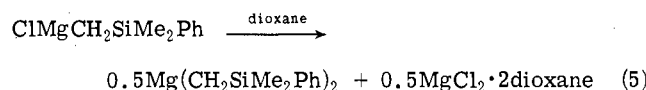
A novel photochemical disproportionation has recently been discovered which leads to the production of stable metal(III) alkyls of the group IVb metals.

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Table I

Stable Homoleptic Metal Alkyls $(MR_n)_x$ of Neopentyl Type $[R = Me_3SiCH_2(R^1), (Me_3Si)_2CH(R^2), Me_3CCH_2(R^3), Me_3SnCH_2(R^4), o\text{-}MeOC_6H_4SiMe_2CH_2(R^5), Me_2PhSiCH_2(R^6), MePh_2SiCH_2(R^7), Me_2PhCCH_2(R^8),$ or $Ph_3CCH_2(R^9)]^a$

Electronic type	Compound	Preparation Method[b]	Yield, %	Starting material	Appearance	Comments	Ref
s^1	SnR^2_3	2		SnR^2_2		Characterized by esr in C_6H_6 or C_6H_{14}, quartet centered at $g = 2.0094$ $(g_\perp = 2.016, g\| = 1.994)$, $a(^{117}Sn) = 1698$ G and $a(^{119}Sn) = 1776$ G; $a(^1H) = 2.1$ G. No signal decay after 750 hr at 20°	8
s^1	GeR^2_3	1 and then 2		$GeCl_2 \cdot diox$ or GeI_2		Characterized by esr in C_6H_6 or C_6H_{14}, quartet centered at $g = 2.0078$; $a(^{73}Ge) = 91.8$ G; $a(^1H) = 3.8$ G.	9
s^1	SiR^2_3	1 and then 2		Si_2Cl_6		Characterized by esr in C_6H_6, quartet centered at $g = 2.0027$, $a(^{29}Si) = 192.6$ G; $a(^1H) = 4.8$ G; half-life at 30° in C_6H_6 ~9 min	23
s^2	SnR^2_2	1	71	$SnCl_2$	Red cryst, mp 135–137°	Monomer in C_6H_6; low first ionization potential (7.42 eV); Mössbauer shows IS = 0.06 mm sec⁻¹ (rel. to α-Sn) and QS = 2.31 mm sec⁻¹; behaves as a good donor in transition metal chemistry: *e.g.*, $+ Mo(CO)_6 \rightarrow R^2_2SnMo(CO)_5$	4
s^2	PbR^2_2	1	3	$PbCl_2$	Purple cryst, mp 43–45°	First IP = 7.23 eV; good donor: *cf.* $R^2_2PbMo(CO)_5$	4
d^0	$ScR^1_3 \cdot 2THF$	1	69	$ScCl_3$	Colorless cryst, mp 62–63°	Monomer in C_6H_6; ¹H nmr shows each R^1 to be equivalent	7
d^0	$ScR^3_3 \cdot 2THF$	1	73	$ScCl_3$	Colorless cryst, mp 66–68°	Monomer in C_6H_6; ¹H nmr shows each R^3 to be equivalent	7
d^0	ScR^5_3	1	95	$ScCl_3$	Colorless cryst, mp 115–120°		7
d^0	$YR^1_3 \cdot 2THF$	1	54	YCl_3	Colorless cryst, mp 48–50°	Monomer in C_6H_6; ¹H nmr shows each R^1 to be equivalent, $J(^{89}YC^1H) = 2.5$ Hz	7
d^0	YR^3_3	1	70	YCl_3	Colorless cryst	$J(^{89}YC^1H) = 2.4$ Hz	6
d^0	$YR^3_3 \cdot 2THF$	1	54	YCl_3	Colorless cryst, mp 78–79°	Monomer in C_6H_6; ¹H nmr shows each R^3 to be equivalent, $J(^{89}YC^1H) = 2.5$ Hz	7
d^0	TiR^1_4	1	73	$TiCl_4$	Pale-yellow, mp 0–1°, bp ~25° (10⁻³ mm)	Monomer in C_6H_6	24
d^0	TiR^3_4	1	26	$TiCl_4$	Yellow cryst, mp 105–107° dec	Monomer in C_6H_6	25, 26
d^0	TiR^4_4	1	80	$TiCl_4$	Pale-yellow oil	Half-life ~12 hr at 20°	27
d^0	TiR^6_4	1	50–75	$TiCl_4$	Pale green-yellow, mp ~0°	Monomer in C_6H_6	24
d^0	TiR^7_4	1	60	$TiCl_4$	Pale yellow	Monomer in C_6H_6	24
d^0	ZrR^1_4	1	60–90	$ZrCl_4$	Colorless, mp 10–11°, bp ~25(10⁻³ mm)	Monomer in C_6H_6	24
d^0	ZrR^3_4	1	68	$ZrCl_4$	Colorless, mp 108–111° dec	Monomer in C_6H_6	25, 26

	Compound	Halide	Method[b]	Yield, %	Physical properties	Comments	Ref
d^0	$ZrR^4{}_4$	$ZrCl_4$	1	90	Pale-yellow oil	Half-life ~15 hr at 20°	27
d^0	$ZrR^6{}_4$	$ZrCl_4$	1	66	Off-white cryst, mp 12–14°	Monomer in C_6H_6	24
d^0	$HfR^1{}_4$	$HfCl_4$	1	96	Colorless, mp 8–10°, bp ~50° (10^{-2} mm)		24
d^0	$HfR^3{}_4$	$HfCl_4$	1	59	Colorless cryst, mp 115–116°		25
d^0	$HfR^4{}_4$	$HfCl_4$	1	90	Pale-yellow oil	Half-life ~15 hr at 20°	27
d^1	$VR^1{}_4$	VCl_4 or $VOCl_3$	1	30	Deep-green cryst, mp 43°	μ_{eff} = 1.55 BM at 308 K; esr	28
d^1	$TiR^2{}_3$	$TiCl_3\cdot2Me_3N$	1	5	Blue cryst	Esr: g = 1.97 (quartet)	6
d^2	$VR^2{}_3$	$VCl_3\cdot2Me_3N$	1	5	Blue-gray cryst		6
d^2	$CrR^1{}_4$	$CrCl_3\cdot3THF$	1	30	Purple cryst, mp 40°, subl. 30° (10^{-4} mm)	μ_{eff} = 2.89 BM at 296 K	28
d^2	$CrR^3{}_4$	$CrCl_3\cdot3THF$	1	30	Maroon cryst, mp 110°	Esr; μ_{eff} = 2.7 BM	29
d^2	$CrR^8{}_4$	$CrCl_3\cdot3THF$	1	30	Purple cryst, mp 120° dec	Esr; X-ray[30] shows distorted tetrahedron	29, 30
d^2	$CrR^9{}_4$	$CrCl_3\cdot3THF$	1	20	Purple cryst, mp 130° dec	Esr	29
d^3	$CrR^2{}_3$	$CrCl_3$	1	70	Green cryst	μ_{eff} = 3.6 BM at 296 K; esr: g = 2.0, 3.9; monomer in C_6H_6; diamagnetic red $CrR^2{}_3\cdot$NO (ν_{NO} 1605 cm^{-1})	6
d^3	$(MoR^1{}_3)_2$	$MoCl_5$	1	15	Yellow cryst, mp 99°	X-Ray[31] shows short Mo–Mo; diamagnetic	28, 31
d^3	$(MoR^3{}_3)_2$	$MoCl_5$	1	15	Yellow cryst, mp 135–138°	Diamagnetic	26
d^3	$(WR^1{}_3)_2$	WCl_6	1	20	Orange-brown cryst, mp 110°	Isostructural with $(MoR^1{}_3)_2$	28
d^{10}	$(CuR^1)_4$	CuI	1	70	Colorless cryst, mp 78–79° dec	With $LiR^1 \rightarrow$ pale-violet $LiCuR^1{}_2$; X-ray[11] shows square-planar Cu_4 cluster with single R^1 bridges	10, 11
d^{10}	$ZnR^1{}_2$	$ZnCl_2$	1	90	Colorless, bp 44° (1.5 mm)	ZnC_2 linear from ir	32
d^{10}	$HgR^1{}_2$	$HgCl_2$	1	49	Colorless, bp 49–50° (0.35 mm)		33a
d^{10}	$HgR^2{}_2$	$HgCl_2$	1	77	Colorless, mp 35°, bp 108° (4 mm)		33b
d^{10}	$HgR^3{}_2$	$HgCl_2$	1	29	Colorless cryst, mp 31–33°		34
d^{10}	$HgR^8{}_2$	$HgCl_2$	1 and then $R^8HgCl + Na_2SnO_2$	85	Colorless cryst, mp 26–26.5°		35
d^{10}	$Hg[C(SiMe_3)_3]_2$	$HgCl_2$					36

ᵃ Also prepared have been a number of alkyls of other main group elements: LiR^1, LiR^2, LiR^3, LiR^5, LiR^6, NaR^3, $BeR^1{}_2$ (a dimer in C_6H_6),[37] $BeR^3{}_2$, $MgR^3{}_2$, $MgR^6{}_2$, $BR^1{}_3$, $BR^3{}_3$, $BR^4{}_3$, $AlR^1{}_3$, $AlR^3{}_3$, $GeR^3{}_4$, $SnR^1{}_4$, $SnR^3{}_4$, $SnR^8{}_4$, $PbR^1{}_4$, $PbR^3{}_4$, $PR^1{}_3$, $AsR^1{}_3$, $SbR^1{}_3$, and $BiR^1{}_3$. ᵇ The numbers in this column refer to: 1, halogen-alkyl exchange (usually with RMgX or RLi); or 2, photochemical disproportionation.
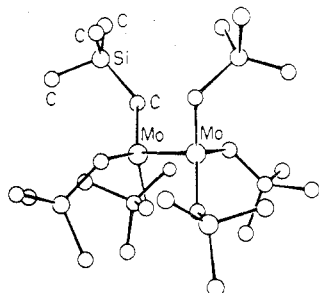
Figure 1. The molecular structure of $Mo_2(CH_2SiMe_3)_6$:[31] Mo–Mo, 2.167 Å; Mo–CH₂, 2.131 Å; ∠Mo–Mo–CH₂, 100.6°; ∠Mo–CH₂–Si, 121.1°.
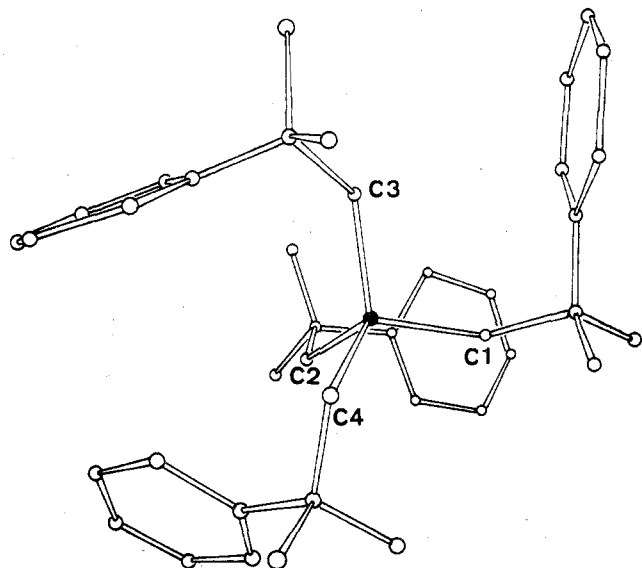
Figure 2. The molecular structure of $Cr(CH_2CPhMe_2)_4$:[30] Cr–C, 2.05 Å; ∠Cr–C–C (mean), 123.5°.

Figure 3. The molecular structure of $(CuCH_2SiMe_3)_4$:[11] Cu–Cu, 2.417 Å; Cu–C (mean), 2.02 Å; ∠C–Cu–C, 164°; $Cu_4C_4Si_2$ coplanar; centrosymmetric.
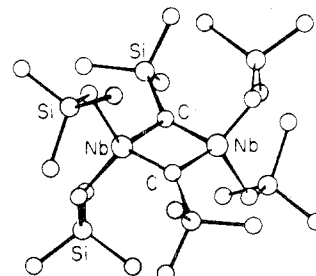
Figure 4. The molecular structure of $Nb_2(CSiMe_3)_2(CH_2SiMe_3)_4$:[46] Nb–C (mean), 1.974 Å; Nb–CH₂ (mean), 2.160 Å; ∠C–Nb–C, 85.6°; ∠Nb–C–Nb, 94.4°; Nb···Nb, 2.897 Å; ∠Nb–C–Si, 119.8°; ∠Nb–C–Si, 142.4°.

Thus, irradiation (visible light) of a benzene or hexane solution of $Sn[CH(SiMe_3)_2]_2$ gives the stable radical $R^2_3Sn\cdot$, as in eq 6 (M = Sn).[8] The radical

$$2MR^2_2 \longrightarrow R^2_3M\cdot + (1/n)(R^2M)_n \qquad (6)$$

$R^2_3Sn\cdot$ was unequivocally characterized by esr as the only paramagnetic species in solution. There was no metal deposit (in contrast to the lead mirror formed by photolysis of the Pb analog), and it was inferred that the transient Sn^I coproduct oligomerized to di- or tetravalent species. The radicals $R^2_3Si\cdot$[23] and $R^2_3Ge\cdot$[9] were prepared by photolysis of the products from Si_2Cl_6–LiR^2 and $GeCl_2\cdot$dioxane–LiR^2, respectively.

Insertion. For complexes with the neopentyl structure this route is of limited application, requiring olefin insertion into the M–C bond of a stable precursor, as in eq 7.[41]

$$(AlMe_3)_2 + Me_2C=CH_2 \xrightarrow{200°} Al(CH_2CMe_3)_3 \qquad (7)$$

Miscellaneous. Oxidative addition [Ni⁰ + $(Ph_3C)_2$ to give bis(trityl)nickel][42] and metalation (e.g., from Me_3PCH_2 to give complexes such as V)[15,16] are other procedures which have been used for homoleptic metal alkyls.

Structures, Bonding, and Some Ground-State Properties

The alkyl group is usually a terminal ligand bonding to the metal *via* a two-electron two-center orbital. However, it may be bridging as in the electron-deficient main group element compounds. For the lithium derivatives, an alkyl group bridges three metal atoms (I), as in $(LiMe)_4$;[43] for Be, Mg, or Al derivatives, two alkyl groups are often doubly bridging (II), as in Al_2Me_6.[44] In $(CuR^1)_4$, each Me_3SiCH_2 group provides a single bridge between two Cu atoms (III).[11] A multicenter molecular orbital scheme may be used to describe the bonding in all these compounds.[45]

For the neutral complexes listed in Table I, single-crystal X-ray diffraction data are available for $(MoR^1_3)_2$,[31] CrR^8_4,[30] and $(CuR^1)_4$,[11] as shown in Figures 1–3. A closely related Nb compound (Figure 4)[46] is not strictly within our terms of reference, having a bridging carbene ligand.[47] In $Cr(CH_2CMe_2Ph)_4$, the CrCC angles are all significantly greater than the tetrahedral angle, with consequential dense packing of alkyl and aryl groups.[30] The very short Mo–Mo distance in $(MoR^1_3)_2$ has been attributed to a triple bond, and the large Si–CH₂–Mo angle is

(41) W. Pfohl, *Justus Liebigs Ann. Chem.*, **629**, 207 (1960).

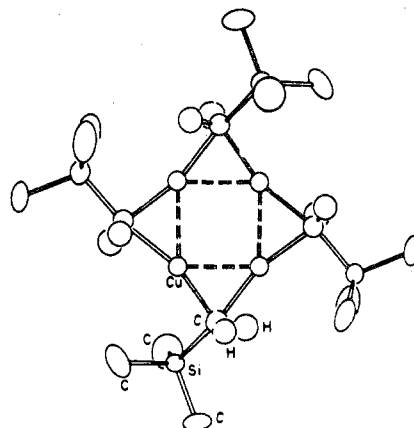(42) G. Wilke and H. Schott, *Angew. Chem., Int. Ed. Engl.*, **5**, 583 (1966).

(43) E. Weiss and E. A . C. Lucken, *J. Organometal. Chem.*, **2**, 197 (1964).

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(46) F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1477 (1971).

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probably caused by steric repulsion.[31] It is surprising that in $(CuR^1)_4$ the formally d^{10} Cu atoms are in a planar environment with the methylene carbons in the same plane as the Cu_4 square;[11] bonding may be described in terms of linear (CCuC) coordination at Cu with Cu-Cu bonding relatively unimportant.

Because of the bulk of neopentyl and related alkyl ligands, such as R^1-R^9 (Table I), it is not surprising that the metal coordination number is affected primarily by the nature of the ligand rather than the oxidation state and electronic configuration of the metal. Thus, on the one hand there is the extensive series MR^1_4 (M = Sn, Pb, Ti, Zr, Hf, V, or Cr; R^1 = Me_3SiCH_2), but with the bulky ligand $(Me_3Si)_2CH$ (R^2) complexes are obtained in lower coordination number: MR^2_3 (M = Si, Ge, Sn, Y, Ti, V, or Cr) and MR^2_2 (M = Sn or Pb) (see Table I). Similarly, whereas homoleptic methyls of Be, or Mg, and Al are polymers and dimer, respectively, corresponding neopentyl-like complexes are found as smaller aggregates. Increasing the size of the metal may lead to a decrease in oxidation state, e.g., $Cr^{IV}R^1_4$ and $(Mo^{III}R^1_3)_2$.

The very high values for metal (^{117}Sn, ^{119}Sn, ^{73}Ge, or ^{29}Si) hyperfine coupling constants (esr) in $R^2_3M\cdot$ (M = Sn, Ge, or Si) suggest that these metal-centered radicals are not planar,[8,9,23] in contrast to alkyl radicals such as $CH_3\cdot$.

The He(I) photoelectron spectra of several compounds of formula MR_4 [M = Si, Ge, Sn, Ti, Zr, Hf, or Cr; R = Me_3SiCH_2 (R^1) or Me_3CCH_2 (R^3)] have been examined;[48] the σ(M-C) orbital for each is in the range 8-9 eV, and there is thus no evidence that, for these related compounds, occupied electronic energy levels differ significantly for main group and transition-metal complexes. From much data on standard heats of formation of homoleptic alkyls of the main group elements,[49] it is clear that M-C bond strengths are not especially low: e.g., $\bar{E}$(B-C) = 81.7 ± 2.7 kcal mol^{-1} in BEt_3 and $\bar{E}$(Sn-C) = 46.2 ± 2.1 kcal mol^{-1} in $SnEt_4$. General trends are that M-C mean thermochemical bond energy terms, $\bar{E}$, within a group fall with increasing mass of M, and for a given M in the order Ph > Me > Et. Hence conjugative and hyperconjugative effects may have a small role, as has been most extensively discussed for B.[50] This is not likely to be important for transition metals, because in the series *trans*-Pt(R)-Cl(PMe_2Ph)_2 X-ray and spectroscopic results show that the trans influence of R has little sensitivity to substitution or hybridization effects (R = Me_3Si-CH_2, CH_2=CH, or PhC≡C, compared with R = Me).[51] Now that numerous homoleptic transition metal alkyls are available (Table I), it should be relatively straightforward to obtain thermochemical

data by calorimetry. Such information is available for the radicals $Me_3M\cdot$;[52] there is no particular gain in delocalization energy relative to Me_4M, in contrast to $Me_3C\cdot$ relative to Me_4C. $Ph_3Si\cdot$ is destabilized with respect to $Me_3Si\cdot$ by ca. 14.1 kcal mol^{-1} (contrast $Ph_3C\cdot$ vis-à-vis $Me_3C\cdot$).[53] Infrared and Raman spectra for MR_4 (M = Sn, Ti, Zr, Hf, V, or Cr; R = Me_3SiCH_2)[5,25] show that the MC_4 asymmetric stretching mode falls in the range 470-530 cm^{-1}, which suggests that the MC_4 asymmetric stretching force constant and hence MC bond strength is largely independent of the electronic structure of the metal.

Decomposition Pathways for Metal σ-Hydrocarbyls

Thermal decomposition of a metal alkyl often affords a complex mixture. Although it is not always possible to ascertain all the product-forming reactions it is important, for an analysis of the comparative stability of these complexes, to establish rate-determining decomposition pathways and to assess their relative importance within the various combinations of metal and ligand. Our first objective is to identify these pathways, and results are summarized in Table II.[10,14a,20,24,25,27,38,41,54-59] Because there are limited data on homoleptic compounds, reference should be made to the much more extensive results on heteroleptic complexes, but this will be deferred to another paper.[22]

Metal-carbon bond breaking may formally be uni- or bimolecular. A unimolecular process involves either (a) migration of a substituent from the alkyl group to the metal (α, β, γ, etc., elimination) or (b) M-C homolysis. The pathways of higher molecularity result in disproportionation or formation of clusters (referred to below as binuclear eliminations). The principles for decomposition pathways for metal-centered radicals are qualitatively those applicable to organic radicals, but disproportionation routes to metallo olefins are unfavorable, and atom-abstraction reactions (e.g., of H or Hal) are influenced by bond strengths (e.g., of M-H or M-Hal). The stability of the group IV radicals $[(Me_3Si)_2CH]_3M\cdot$ in benzene or hexane is thus attributed to the bulk of the ligand (R^2) making dimerization unlikely and to the low M-H bond strength for M = Ge or Sn providing no inducement to hydrogen abstraction.[8,9] The corresponding silyl radical $R^2_3Si\cdot$ is less stable and decays by a pseudo-first-order reversible process which may be that of Si-H bond making and breaking.

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(51) M. R. Collier, C. Eaborn, B. Jovanović, M. F. Lappert, Lj. Manojlović-Muir, K. W. Muir, and M. M. Truelock, *J. Chem. Soc., Chem. Commun.*, 613 (1972); C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organometal. Chem.*, 60, C70 (1973).

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(53) J. M. Gaidis, P. R. Briggs, and T. W. Shannon, *J. Phys. Chem.*, 75, 974 (1971).

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Table II
Selected Data on the Thermal Decomposition of Homoleptic Metal Alkyls

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Compound	Decomposition conditions	Products and comments	Ref
$(BeMe_2)_n$	200°	$CH_4 + (CH_2Be)_n \xrightarrow{\Delta} (Be_2C)_n$	54
$B(CH_2CMe_3)_3$		Stable at 227°	55
$Al(CH_2CMe_3)_3$	~200°	$Me_3Al + Me_2C=CH_2$	41
$SiMe_4$	~700°	Diverse products with linkage SiCSi predominating	56
$Hg(CH_2SiMe_3)_2$	200°	$Hg + Me_4Si + Me_3SiCH_2HgCH_2SiMe_2CH_2CH_2SiMe_3$	57
$TiMe_4$	Heptane, 10°	CH_4 + black solid (contains C, H, Ti), hydrogen in CH_4 not derived from solvent	58
$M(CH_2CMe_3)_4$	C_6H_6: M = Ti, 60°, $t_{1/2}$ ~14.5 hr	Me_4C + black solid, hydrogen in Me_4Si not derived from solvent	25
	M = Zr, 80°, $t_{1/2}$ ~80 hr		
	M = Hf, 90°, $t_{1/2}$ ~900 hr		
$M(CH_2SiMe_3)_4$	C_6H_6: M = Ti, 80°, $t_{1/2}$ ~125 hr	Me_4Si + black solid, hydrogen in Me_4Si not derived from solvent	24, 25
	M = Zr, 80°, $t_{1/2}$ ~150 hr		
	M = Hf, 90°, $t_{1/2}$ ~350 hr		
$M(CH_2SnMe_3)_4$	C_6H_6: M = Ti, 80°, $t_{1/2}$ ~30 min	$(Me_3SnCH_2)_2$ + black solid +Me_4Sn	27
	M = Zr, 80°, $t_{1/2}$ ~30 min		
	M = Hf, 80°, $t_{1/2}$ ~30 min		
$Zr(CH_2Ph)_4$	*Ca.* 130°	$C_6H_6 + PhMe + (PhCH_2)_2 + Ph_2CH_2 + C_2H_6$ + black solid	14a, 59
$Cr(CH_2CMe_3)_4$		Stable at 80° in heptane	38
$CrBu-t_4$	Heptane, 70°, $t_{1/2}$ ~4.5 min	Principally $Me_3CH + Me_2C=CH_2$ + Cr (with 5% C)	38
WMe_6	Neat, 25°	$CH_4 + C_2H_6$ (trace) + black solid (contains C H, W)	20
$(CuCH_2SiMe_3)_4$	PhMe, 80°	$Cu + Me_4Si + (Me_3Si)_2CH_2 + (Me_3SiCH_2)_2 + PhCH_2CH_2SiMe_3 + (PhCH_2)_2$	10

Some of the mechanistic discussion that follows is conjectural, often being based on qualitative rather than quantitative information. More extensive kinetic studies are clearly required.

β Elimination. This is represented by the general eq 8. For a simple alkyl (X = Y = a saturated C

$$LM-X-Y-Z \longrightarrow LMZ + X=Y \quad (8)$$
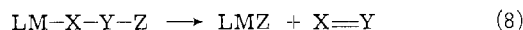
atom, and Z = H or another alkyl group) this demands migration of a β-H or alkyl from carbon to metal in a concerted manner, with formation of an alkene.
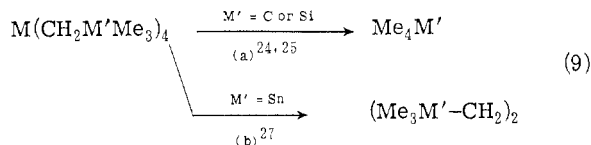
Migration of hydrogen is preferred, and this is a factor which accounts for the enhanced stability of complexes with a neopentyl-like structure. When Y is silicon, elimination would be of a relatively unstable silaolefin.

Examples are to be found in the decompositon of $CrBu-t_4$ to give *inter alia* $Me_2C=CH_2$,[38] and of $Al(CH_2CMe_3)_3$ to give $AlMe_3$ and $Me_2C=CH_2$.[41] There are no examples of alkyl migrations in the transition series. It should be noted that a suitable transition-state geometry is required with a vacant coordination position (*cf.* the severely crowded $CrBu-t_4$) while the dihedral angle of the M–C–C–Z moiety should approach zero.

α Elimination. This involves fragmentation of a species of the type LMC–QQ′Q″ to give LM–Q (Q = H, OR, or halogen) and a carbene moiety CQ′Q″. It is of synthetic utility: compounds with M = Hg, Sn, Li, Zn, *e.g.*, can act as carbene transfer reagents. In most of these reactions free carbenes are not involved.[60] This pathway is not established for transition-metal homoleptic alkyls.

Reductive Elimination. This pathway, the reverse of oxidative addition, provides a route to cleavage of metal–carbon bonds. It is especially important at the end of the transition series for heteroleptic compounds and is inevitably confined to metals having

stable oxidation states differing by two units; some of these reactions may, however, proceed by homolysis.[61] It is remarkable that related group IV alkyls can have distinctly different decomposition pathways, as shown in eq 9. Reaction 9b, which proceeds at
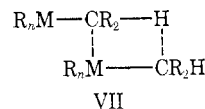
$$M(CH_2M'Me_3)_4 \begin{array}{c} \xrightarrow[(a)^{24,25}]{M' = C \text{ or } Si} Me_4M' \\ \searrow_{(b)^{27}}^{M' = Sn} (Me_3M'-CH_2)_2 \end{array} \quad (9)$$

0–40° for M = Ti, Zr, or Hf (Ti the least stable), is probably a case of reductive elimination;[27] direct participation of free radicals is unlikely because toluene does not alter the nature of the products.

Binuclear Elimination. This is characterized primarily by the nature of the decomposition products: alkane and a solid containing linkages of the types $(LM)_2C=$, $(LM)_3C-$, or $(LM)_4C$ (such a compound may be the Nb product of Figure 4).[46] The reactions are best documented for the methyls of metals, both of the main group or the transition series, *e.g.*, eq 10.[62] The Nb compound of Figure 4[46] may be regard-

$$BMe_3 \longrightarrow (MeB)_6(CH)_4 \quad (10)$$

ed as an intermediate in the decomposition of hypothetical $Nb(CH_2SiMe_3)_5$ (from $NbCl_5–LiR^1$) by loss of 4 mol of $SiMe_4$.

The transition state is probably of the type VII, and reaction will be inhibited by substitution at the

<div align="center">

$R_nM—CR_2—H$
$R_nM——CR_2H$

VII

</div>

(60) *Cf.* D. Seyferth, *Accounts Chem. Res.*, **5**, 65 (1972); D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, **2**, 99 (1973).

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α carbon. This is a principal factor governing the greater stability of Ti(CH$_2$CMe$_3$)$_4$ and Ti-(CH$_2$SiMe$_3$)$_4$ compared with TiMe$_4$.

Homolysis. Among the best examples of homoleptic complexes which undergo decomposition by this route are the homoleptic alkyls of Hg^{II} and also others from Zn^{II}, Cd^{II}, Si^{IV}, Ge^{IV}, Sn^{IV}, and Pb^{IV}.[63] In the transition series, homolysis is relatively uncommon, *i.e.*, it is usually a path of relatively higher activation energy and is used only when other processes are hindered or blocked. (CuCH$_2$SiMe$_3$)$_4$ appears to decompose by this pathway,[10] and it has been postulated to play a minor role in decomposition of TiMe$_4$.[58] For the Cu^{I} case, the evidence is based on the isolation of benzyl derivatives when decompositon was carried out in toluene.[10] The use of species such as *t*-BuNO as a radical trap may help to establish such mechanisms.[61,64]

Conclusions and Prognostications

It has already been stressed that the choice of the alkyl ligand often determines the coordination number and oxidation state of the metal in (MR$_n$)$_x$, and thus we can expect a major increase in the range of homoleptic complexes using ligands such as (Me$_3$Si)$_2$CH$^-$, 2,2,3-trimethylnorbornyl$^-$, or Me$_2$P-(CH$_2$)(CH$_2$)$^-$. For example, whereas the group IV radicals R$_3$M· (M = Si, Ge, or Sn) are at present the only metal-centered main group element radicals to be stable at room temperature, extensions to the isoelectronic ion radicals R$^2{}_3$In·$^-$ and R$^2{}_3$Sb·$^+$ and to other group III–V species are to be anticipated, as well as to related complexes using ligands other than alkyls (stable amidometal radicals [(Me$_3$Si)$_2$N]$_3$M· (M = Ge or Sn) have been made).[65] Among main group element neutral compounds, new stable s^2

and s^1 complexes, such as (MR^2)$_n$ (M = Ga, In, or Tl) or R^{2}Hg–HgR^2, may prove to be accessible. For transition-metal complexes, further developments, especially for the 4d^n, 5d^n, 4f^n, and 5f^n metals, are awaited; two-coordinate metal complexes may be favored by still more bulky ligands such as (Me$_3$Si)$_3$C$^-$ (which has already been used for Hg^{II}).[36]

New bonding situations may emerge, and we look forward to single-bridging (bulky) σ-hydrocarbyl ligands in the transition-metal series beyond Cu^I. Structural studies will have an important role and we await with interest elucidation of the geometry of, for example, the monomeric dialkyls of Sn and Pb.

The isolation and characterization of intermediates in thermal decompositions may provide further points of interest. For example, compounds related to the niobium compound of Figure 4[26] may be discovered.

We have not here been concerned with the potentially very extensive chemistry of metal alkyls, but in conclusion we draw attention to three areas of significance: (i) their use as reagents in organic chemistry (*e.g.*,[66] for copper alkyls), (ii) their role as monometallic catalysts possibly on Al$_2$O$_3$ or SiO$_2$ supports, or intermediates, and (iii) their potential as ligands. As for (ii), we refer to α-olefin polymerization [*e.g.*,[67] catalyzed by group IV or V transition metal alkyls, such as Zr(CH$_2$SiMe$_3$)$_4$]. Finally, with regard to (iii) we point to the new area of heavy group IV main group metal donors: *e.g.*,[4] R$^2{}_2$M with M'(CO)$_6$ yields R$^2{}_2$MM'(CO)$_5$ or *trans*-(R$^2{}_2$Sn)$_2$M'(CO)$_4$ (M = Sn or Pb, M' = Cr or Mo).

(63) *Cf.* S. J. W. Price in "Comprehensive Chemical Kinetics," C. H. Bamford and C. F. H. Tipper, Ed., Vol. 4, Elsevier, Amsterdam, 1972, p 197.

(64) D. J. Cardin, M. F. Lappert, and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, 350 (1973).

(65) D. H. Harris, M. F. Lappert, and P. W. Lednor, unpublished work, 1974.

(66) *Cf.* J. F. Normant, *Synthesis*, 63 (1972).

(67) See, *e.g.*, D. G. H. Ballard, *Advan. Catal.*, 23, 263 (1973).