

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 $(\text{LiMe})_4$, $(\text{BeMe}_2)_n$, and $(\text{AlMe}_3)_2$, 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 $\text{Co}_2(\text{CO})_8$. 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 $\text{Co}^{\text{III}}\text{-C}$ 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 $(\text{MR}_n)_x$. (For compounds $(\text{MX}_n)_x$ 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} $(\text{Me}_3\text{Si})_2\text{CH}$ (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 $(\text{MR}_n)_x$ and to include also a third class, that of stable main group metal-centered radicals such as $\text{R}^2_3\text{M}\cdot$ ($\text{M} = \text{Si, Ge, or Sn}$). 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 $\text{R}^2_3\text{Sn}\cdot$. Many of the data on compounds such as $(\text{MR}^1_n)_x$ 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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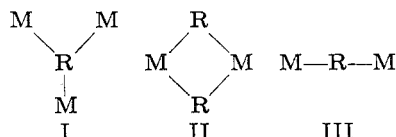
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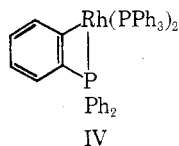
Peter J. Davidson is a research chemist with Johnson Matthey Ltd., London. He obtained his B.Sc. from the University of Bristol in 1968. From 1968 to 1970 he was a research chemist with Midland Silicones Ltd., Barry, and then spent the next 3 years working for his D.Phil. with M. F. Lappert.

Proposition

1. Except for group V, main group element alkyls are only stable in the higher oxidation states for elements of variable valency; e.g., $\text{Pb}^{\text{IV}}\text{Et}_4$ but not $\text{Pb}^{\text{II}}\text{Et}_2$, in contrast to, say, chlorides.
2. Homoleptic transition metal alkyls are intrinsically unstable; e.g., TiMe_4 , unlike, say, GeMe_4 , decomposes at low temperature.
3. The M-C bond is weak for a transition metal, but stronger for a main group metal.
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 $\pi\text{-C}_5\text{H}_5^-$. (Rationalizations for propositions 4 and 5 are based on variations in the crystal field splitting parameters, Δ).
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.
6. Main group metal-centered radicals are best treated as free radicals rather than organometallic compounds, and are transient species.
7. Alkyl bridging is characteristic of electron-deficient compounds of main group elements only.
8. A bridging alkyl, R, may only be bound to three metal atoms, I, as in $(\text{LiMe})_4$, or two alkyl groups may form a double bridge to two metal atoms, II, as in Al_2Me_6 .



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 $\text{Me}_3\text{SiCH}_2^-$. Other possible routes include α , γ , reductive, or binuclear elimination and M-C homolysis. Ligands such as $\text{Me}_3\text{SiCH}_2^-$ must not be regarded intrinsically as "stabilizing." On the contrary, they may enhance a decomposition pathway; thus $(\text{Ph}_3\text{P})_3\text{RhR}^1$ is less stable than $(\text{Ph}_3\text{P})_3\text{RhMe}$, presumably because elimination leading to IV is encouraged by



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

(4) P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 317 (1973).

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Contradictory data

Stable alkyls SnR_2 and PbR_2 have been prepared.⁴

Stable d^0 , d^1 , d^2 , d^8 , and d^{10} homoleptic metal alkyls (Table I),⁵ including alkyls of some lanthanides,^{6,7} have been prepared.

This is inconsistent with spectroscopic data (see later).

Stable high oxidation state homoleptic (i.e., without "stabilizing" ligands) M^{4+} and M^{3+} compounds are exemplified by $\text{MR}^{1,5}$ and MR_2^6 (M = a transition metal).

The stable complexes $\text{MR}^{1,5}$ MR_2^6 are derived from light early transition metals, such as Sc, Ti, V, or Cr.

The species R_2Sn^8 and R_2Ge^9 do not decompose after many weeks at 20°.

In $(\text{CuR}^1)_4$,¹⁰ the coordination number of C is 5,¹¹

In $(\text{CuR}^1)_4$ there are single alkyl bridges (III).¹¹

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 > $\text{Me}_3\text{SiCH}_2 \approx \text{Me}_3\text{CCH}_2$ > Me_3SnCH_2 > Ph > $\text{Me} \gg \text{Et} > \text{sec-}$ 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 $\text{Me}_3\text{SiCH}_2^-$ (R^{1-}) or $(\text{Me}_3\text{Si})_2\text{CH}^-$ (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 $(\text{Me}_3\text{Si})_2\text{N}^-$. The latter is isoelectronic with $(\text{Me}_3\text{Si})_2\text{CH}^-$ 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-

(13) Cf. D. C. Bradley, *Advan. Inorg. Chem. Radiochem.*, 15, 259 (1972).

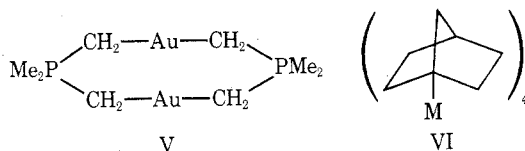
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(Ti^{IV}).¹⁸ The synthesis of stable metal hexamethyls (*e.g.*, ZrMe₆²⁻,¹⁹ or WMe₆²⁰) illustrates the principle that, even with small ligands, the occupancy of a large number of coordination sites (coordination saturation) enhances stability.



Several reviews are relevant to this account. They refer to transition metal alkyls²¹ 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}

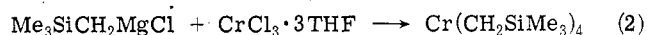
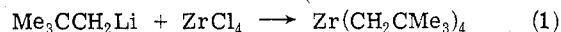
Synthesis

Various procedures have been used, as shown below.

Direct Synthesis. This method is largely limited to Li [in one case, Na; Al (+ H₂ + olefin); or alloys (*e.g.*, NaPb + RX \rightarrow PbR₄)], 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(CH₂SnMe₃) has not proved to be accessible.²⁷

Halogen-Alkyl Exchange. Organolithium or Grignard reagents are the most versatile for this proce-

cedure, especially where the production of the homoleptic compounds is required. Examples are in eq 1²⁵ and 2.²⁸

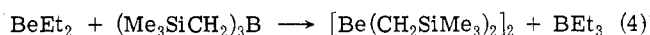
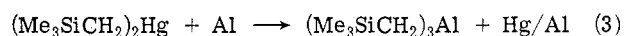


Generally preformed metal alkyls are used, but *in situ* reactions have also been employed in the transition metal series, notably in the preparation of Cr(CH₂CMe₃)₄³⁸ and Ti(1-adamantyl)₄ (Wurtz method).¹⁸ For the main group metals, forcing conditions are sometimes necessary for replacement of the final halide ligand by a bulky alkyl, *e.g.*, in the preparations of M(CH₂CMe₃)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 > R₂Mg, and where reduction is significant (*e.g.*, with TiCl₄), 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.*, Cl₃NbR¹⁻² or Cl₂NbR¹⁻³ from NbCl₅.³²

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).

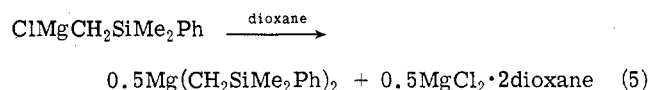
Where the appropriate metal halide is unsuitable, perhaps due to low solubility, a complex may be used: *e.g.*, TiCl₃·2Me₃N for TiR₂.⁶ Alternatively, for CrBu-*t*₄, the nonexistence of CrCl₄ prompted the use of Cr(OBu-*t*)₄ with LiBu-*t*.³⁸

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 3³⁹ and 4.³⁷



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



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)₂ of Neopentyl Type [R = $\text{Me}_3\text{SiCH}_2(\text{R}^1)$, $(\text{Me}_2\text{Si})_2\text{CH}(\text{R}^2)$, $\text{Me}_2\text{CCH}_2(\text{R}^3)$, $\text{Me}_2\text{SnCH}_2(\text{R}^4)$, $\text{Me}_2\text{OC}_6\text{H}_4\text{SiMe}_2\text{CH}_2(\text{R}^5)$, $\text{Me}_2\text{PhSiCH}_2(\text{R}^6)$, $\text{MePh}_2\text{SiCH}_2(\text{R}^7)$, $\text{Me}_2\text{PhCCH}_2(\text{R}^8)$, or $\text{Ph}_3\text{CCH}_2(\text{R}^9)$]^a

Electronic type	Compound	Preparation			Appearance	Comments	Ref
		Method ^b	Yield, %	Starting material			
s ¹	SnR_2^3	2		SnR_2^3	Characterized by esr in C_6H_6 or C_6H_{10} , quartet centered at $g = 2.0094$ ($g_{\perp} = 2.016$, $g_{\parallel} = 1.994$), $a(^{117}\text{Sn}) = 1698$ G and $a(^{119}\text{Sn}) = 1776$ G; $a(^1\text{H}) = 2.1$ G. No signal decay after 750 hr at 20°	8	
s ¹	GeR_2^3	1 and then 2		$\text{GeCl}_2 \cdot \text{diox}$ or GeI_2	Characterized by esr in C_6H_6 or C_6H_{10} , quartet centered at $g = 2.0078$; $a(^{73}\text{Ge}) = 91.8$ G; $a(^1\text{H}) = 3.8$ G.	9	
s ¹	SiR_2^3	1 and then 2		Si_2Cl_6	Characterized by esr in C_6H_6 , quartet centered at $g = 2.0027$, $a(^{29}\text{Si}) = 192.6$ G; $a(^1\text{H}) = 4.8$ G; half-life at 30° in C_6H_6 ~9 min	23	
s ²	SnR_2^2	1	71	SnCl_2	Monomer in C_6H_6 ; low first ionization potential (7.42 eV); Mössbauer shows IS = 0.06 mm sec ⁻¹ (rel. to $\alpha\text{-Sn}$) and QS = 2.31 mm sec ⁻¹ ; behaves as a good donor in transition metal chemistry; e.g., + $\text{Mo}(\text{CO})_6 \rightarrow \text{R}_2\text{SnMo}(\text{CO})_5$ First IP = 7.23 eV; good donor: cf. $\text{R}_2\text{PbMo}(\text{CO})_5$	4	
s ²	PbR_2^2	1	3	PbCl_2	Monomer in C_6H_6 ; ^1H nmr shows each R^1 to be equivalent	4	
(d ⁰)	$\text{ScR}_3 \cdot 2\text{THF}$	1	69	ScCl_3	Colorless cryst, mp 43–45°	7	
(d ⁰)	$\text{ScR}_3 \cdot 2\text{THF}$	1	73	ScCl_3	Colorless cryst, mp 62–63°	7	
d ⁰	ScR_3^3	1	95	ScCl_3	Colorless cryst, mp 66–68°	7	
(d ⁰)	$\text{YR}_3 \cdot 2\text{THF}$	1	54	YCl_3	Colorless cryst, mp 115–120°	7	
d ⁰	YR_3^3	1	70	YCl_3	Colorless cryst, mp 48–50°	6	
(d ⁰)	$\text{YR}_3 \cdot 2\text{THF}$	1	54	YCl_3	Colorless cryst, mp 78–79°	7	
d ⁰	TiR_4^4	1	73	TiCl_4	Pale-yellow, mp 0–1°, bp ~25° (10 ⁻³ mm)	24	
d ⁰	TiR_4^4	1	26	TiCl_4	Monomer in C_6H_6	25, 26	
d ⁰	TiR_4^4	1	80	TiCl_4	Half-life ~12 hr at 20°	27	
d ⁰	TiR_4^6	1	50–75	TiCl_4	Monomer in C_6H_6	24	
d ⁰	TiR_4^4	1	60	TiCl_4	Monomer in C_6H_6	24	
d ⁰	ZrR_4^4	1	60–90	ZrCl_4	Monomer in C_6H_6	24	
d ⁰	ZrR_3^3	1	68	ZrCl_4	Monomer in C_6H_6	25, 26	

d ⁰	ZrR ₄	1	ZrCl ₄	90	Pale-yellow oil	Half-life ~15 hr at 20°	27
d ⁰	ZrR ₆	1	ZrCl ₄	66	Off-white cryst, mp 12-14°	Monomer in C ₆ H ₆	24
d ⁰	HfR ₄	1	HfCl ₄	96	Colorless, mp 8-10°, bp ~50° (10 ⁻³ mm)		24
d ⁰	HfR ₄	1	HfCl ₄	59	Colorless cryst, mp 115-116°		25
d ⁰	HfR ₄	1	HfCl ₄	90	Pale-yellow oil	Half-life ~15 hr at 20°	27
d ¹	VR ₄	1	VCl ₄ or VOCl ₃	30	Deep-green cryst, mp 43°	μ _{eff} = 1.55 BM at 308 K; esr	28
d ¹	TiR ₂	1	TiCl ₃ ·2Me ₃ N	5	Blue cryst	Esr: g = 1.97 (quartet)	6
d ²	VR ₃	1	VCl ₃ ·2Me ₃ N	5	Blue-gray cryst		6
d ²	CrR ₄	1	CrCl ₃ ·3THF	30	Purple cryst, mp 40°, subl. 30° (10 ⁻⁴ mm)	μ _{eff} = 2.89 BM at 296 K	28
d ²	CrR ₄	1	CrCl ₃ ·3THF	30	Maroon cryst, mp 110°	Esr; μ _{eff} = 2.7 BM	29
d ²	CrR ₄	1	CrCl ₃ ·3THF	30	Purple cryst, mp 120° dec	Esr; X-ray ³⁰ shows distorted tetrahedron	29, 30
d ²	CrR ₄	1	CrCl ₃ ·3THF	20	Purple cryst, mp 130° dec	Esr	29
d ²	CrR ₂	1	CrCl ₃	70	Green cryst		6
d ³	(MoR ₃) ₂	1	MoCl ₅	15	Yellow cryst, mp 99°	μ _{eff} = 3.6 BM at 296 K; esr: g = 2.0, 3.9; monomer in C ₆ H ₆ ; diamagnetic red CrR ₃ ·NO (p _{NO} 1605 cm ⁻¹) X-Ray ³¹ shows short Mo-Mo; diamagnetic	28, 31
d ³	(MoR ₃) ₂	1	MoCl ₅	15	Yellow cryst, mp 135-138°	Diamagnetic	26
d ³	(WR ₃) ₂	1	WCl ₆	20	Orange-brown cryst, mp 110°	Isosstructural with (MoR ₃) ₂	28
d ¹⁰	(CuR ¹) ₄	1	CuI	70	Colorless cryst, mp 78-79° dec	With LiR ¹ → pale-violet LiCuR ₂ ; X-ray ¹¹ shows square-planar Cu ₄ cluster with single R ¹ bridges	10, 11
d ¹⁰	ZnR ₂	1	ZnCl ₂	90	Colorless, bp 44° (1.5 mm)	ZnC ₂ linear from ir	32
d ¹⁰	HgR ₂	1	HgCl ₂	49	Colorless, bp 49-50°		33a
d ¹⁰	HgR ₂	1	HgCl ₂	77	Colorless, mp 35°, bp 108° (4 mm)		33b
d ¹⁰	HgR ₂	1	HgCl ₂	29	Colorless cryst, mp 31-33°		34
d ¹⁰	HgR ₂	1 and then R ⁸ HgCl + Na ₂ SnO ₂	HgCl 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: LiR¹, LiR², LiR³, LiR⁴, NaR³, BeR^{1/2}, BeR², BeR³, MgR², MgR³, BR¹, BR², BR³, BR⁴, AlR³, AlR⁴, GeR², SnR³, SnR⁴, SnR⁵, PbR¹, PbR², PbR³, PbR⁴, PR¹, PR², PR³, AsR³, SbR¹, and BiR¹. ^b The numbers in this column refer to: 1, halogen-alkyl exchange (usually with RMgX or RLi); or 2, photochemical disproportionation.

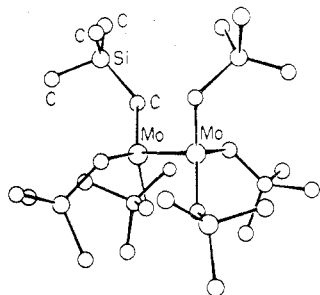


Figure 1. The molecular structure of $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$:³¹ Mo-Mo, 2.167 Å; Mo-CH₂, 2.131 Å; ∠Mo-Mo-CH₂, 100.6°; ∠Mo-CH₂-Si, 121.1°.

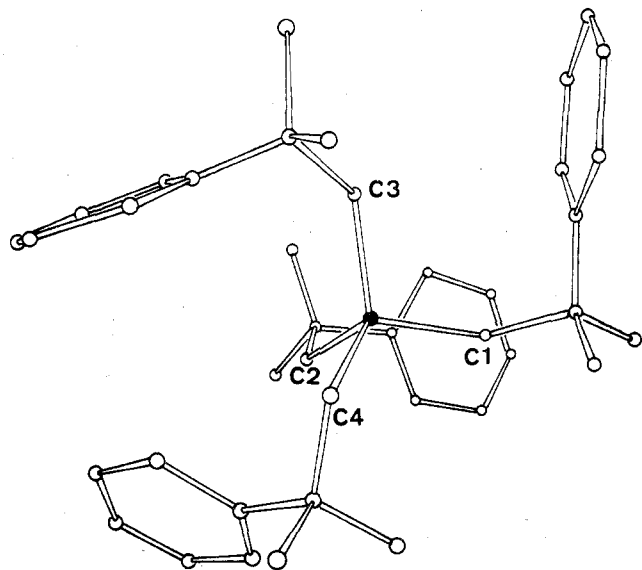
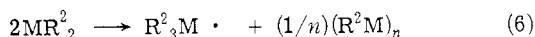


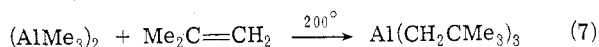
Figure 2. The molecular structure of $\text{Cr}(\text{CH}_2\text{CPhMe}_2)_4$:³⁰ Cr-C, 2.05 Å; ∠Cr-C-C (mean), 123.5°.

Thus, irradiation (visible light) of a benzene or hexane solution of $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ gives the stable radical $\text{R}^2_3\text{Sn}\cdot$, as in eq 6 ($M = \text{Sn}$).⁸ The radical



$\text{R}^2_3\text{Sn}\cdot$ 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 $\text{R}^2_3\text{Si}\cdot$ ²³ and $\text{R}^2_3\text{Ge}\cdot$ ⁹ were prepared by photolysis of the products from $\text{Si}_2\text{Cl}_6\text{-LiR}^2$ and $\text{GeCl}_2\cdot\text{dioxane-LiR}^2$, 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



Miscellaneous. Oxidative addition $[\text{Ni}^0 + (\text{Ph}_3\text{C})_2]$ to give bis(trityl)nickel⁴² 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.

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

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

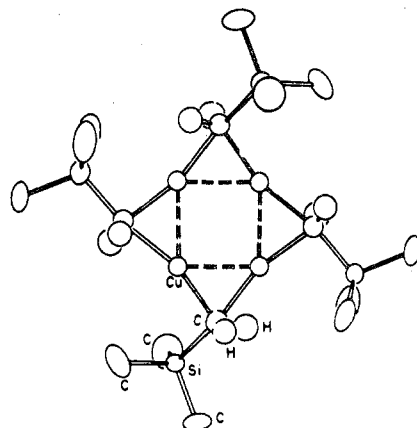


Figure 3. The molecular structure of $(\text{CuCH}_2\text{SiMe}_3)_4$:¹¹ Cu-Cu, 2.417 Å; Cu-C (mean), 2.02 Å; ∠C-Cu-C, 164°; $\text{Cu}_4\text{C}_4\text{Si}_2$ coplanar; centrosymmetric.

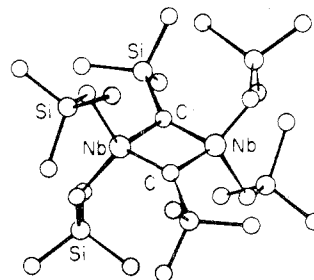


Figure 4. The molecular structure of $\text{Nb}_2(\text{CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$:⁴⁶ Nb-C (mean), 1.974 Å; Nb-CH₂ (mean), 2.160 Å; ∠C-Nb-C, 85.6°; ∠Nb-C-Nb, 94.4°; Nb...Nb, 2.897 Å; ∠Nb-C-Si, 119.8°; ∠Nb-C-Si, 142.4°.

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 $(\text{LiMe})_4$;⁴³ for Be, Mg, or Al derivatives, two alkyl groups are often doubly bridging (II), as in Al_2Me_6 .⁴⁴ In $(\text{CuR}^1)_4$, 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 $(\text{MoR}^1_3)_2$,³¹ CrR^8_4 ,³⁰ and $(\text{CuR}^1)_4$,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 $\text{Cr}(\text{CH}_2\text{CMe}_2\text{Ph})_4$, 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 $(\text{MoR}^1_3)_2$ has been attributed to a triple bond, and the large Si-CH₂-Mo angle is

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

(44) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, 21, 986 (1953).

(45) R. Mason and D. M. P. Mingos, *J. Organometal. Chem.*, 50, 53 (1973).

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

(47) Cf., D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 72, 545 (1972).

probably caused by steric repulsion.³¹ It is surprising that in $(\text{CuR}^1)_4$ 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 $\text{R}^1\text{-R}^9$ (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 ($\text{M} = \text{Sn, Pb, Ti, Zr, Hf, V, or Cr; R}^1 = \text{Me}_3\text{SiCH}_2$), but with the bulky ligand $(\text{Me}_3\text{Si})_2\text{CH}$ (R^2) complexes are obtained in lower coordination number: MR^2_3 ($\text{M} = \text{Si, Ge, Sn, Y, Ti, V, or Cr}$) and MR^2_2 ($\text{M} = \text{Sn or Pb}$) (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., $\text{Cr}^{\text{IV}}\text{R}^1_4$ and $(\text{Mo}^{\text{III}}\text{R}^1_3)_2$.

The very high values for metal (^{117}Sn , ^{119}Sn , ^{73}Ge , or ^{29}Si) hyperfine coupling constants (esr) in R^2_3M ($\text{M} = \text{Sn, Ge, or Si}$) suggest that these metal-centered radicals are not planar,^{8,9,23} in contrast to alkyl radicals such as $\text{CH}_3\cdot$.

The He(I) photoelectron spectra of several compounds of formula MR_4 [$\text{M} = \text{Si, Ge, Sn, Ti, Zr, Hf, or Cr; R} = \text{Me}_3\text{SiCH}_2$ (R^1) or Me_3CCH_2 (R^3)] have been examined;⁴⁸ the $\sigma(\text{M-C})$ 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., $\bar{E}(\text{B-C}) = 81.7 \pm 2.7 \text{ kcal mol}^{-1}$ in BET_3 and $\bar{E}(\text{Sn-C}) = 46.2 \pm 2.1 \text{ kcal mol}^{-1}$ 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 $\text{Ph} > \text{Me} > \text{Et}$. 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(PMe₂Ph)₂ X-ray and spectroscopic results show that the *trans* influence of R has little sensitivity to substitution or hybridization effects ($\text{R} = \text{Me}_3\text{SiCH}_2$, $\text{CH}_2=\text{CH}$, or $\text{PhC}\equiv\text{C}$, compared with $\text{R} = \text{Me}$).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 $\text{Me}_3\text{M}\cdot$;⁵² there is no particular gain in delocalization energy relative to Me_4M , in contrast to $\text{Me}_3\text{C}\cdot$ relative to Me_4C . $\text{Ph}_3\text{Si}\cdot$ is destabilized with respect to $\text{Me}_3\text{Si}\cdot$ by ca. $14.1 \text{ kcal mol}^{-1}$ (contrast $\text{Ph}_3\text{C}\cdot$ *vis-à-vis* $\text{Me}_3\text{C}\cdot$).⁵³ Infrared and Raman spectra for MR_4 ($\text{M} = \text{Sn, Ti, Zr, Hf, V, or Cr; R} = \text{Me}_3\text{SiCH}_2$)^{5,25} show that the MC_4 asymmetric stretching mode falls in the range $470\text{--}530 \text{ cm}^{-1}$, 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 molecular-ity 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 $[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{M}\cdot$ 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 $\text{M} = \text{Ge or Sn}$ providing no inducement to hydrogen abstraction.^{8,9} The corresponding silyl radical $\text{R}^2_3\text{Si}\cdot$ 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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(55) F. M. Rossi, P. A. McCusker, and G. F. Hennion, *J. Org. Chem.*, **32**, 1233 (1967).

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(49) Cf. J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970; H. A. Skinner, *Advan. Organometal. Chem.*, **2**, 49 (1964).

(50) Cf. M. F. Lappert, "The Chemistry of Boron and its Compounds," E. L. Muetterties, Ed., New York, N. Y., 1967, p 433.

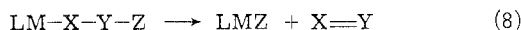
(51) M. R. Collier, C. Eaborn, B. Jovanović, M. F. Lappert, Lj. Manojlović-Muir, K. W. Muir, and M. M. Truelock, *J. Chem. Soc., Chem. Commun.*, 613 (1972); C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organometal. Chem.*, **60**, C70 (1973).

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

Compound	Decomposition conditions	Products and comments	Ref
(BeMe ₂) _n	200°	CH ₄ + (CH ₂ Be) _n $\xrightarrow{\Delta}$ (Be ₂ C) _n	54
B(CH ₂ CMe ₃) ₃		Stable at 227°	55
Al(CH ₂ CMe ₃) ₃	~200°	Me ₃ Al + Me ₂ C=CH ₂	41
SiMe ₄	~700°	Diverse products with linkage SiCSi predominating	56
Hg(CH ₂ SiMe ₃) ₂	200°	Hg + Me ₄ Si + Me ₃ SiCH ₂ HgCH ₂ SiMe ₃ CH ₂ CH ₂ SiMe 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 ₂ CMe ₃) ₄	C ₆ H ₆ ; M = Ti, 60°, t _{1/2} ~14.5 hr	Me ₄ C + black solid, hydrogen in Me ₄ Si not derived from solvent	25
	M = Zr, 80°, t _{1/2} ~80 hr		
	M = Hf, 90°, t _{1/2} ~900 hr		
M(CH ₂ SiMe ₃) ₄	C ₆ H ₆ ; M = Ti, 80°, t _{1/2} ~125 hr	Me ₃ Si + black solid, hydrogen in Me ₄ Si not derived from solvent	24, 25
	M = Zr, 80°, t _{1/2} ~150 hr		
	M = Hf, 90°, t _{1/2} ~350 hr		
M(CH ₂ SnMe ₃) ₄	C ₆ H ₆ ; M = Ti, 80°, t _{1/2} ~30 min	(Me ₃ SnCH ₂) ₂ + black solid	27
	M = Zr, 80°, t _{1/2} ~30 min	+ Me ₄ Sn	
	M = Hf, 80°, t _{1/2} ~30 min		
Zr(CH ₂ Ph) ₄	Ca. 130°	C ₆ H ₆ + PhMe + (PhCH ₂) ₂ + Ph ₂ CH ₂ + C ₂ H ₆ + black solid	14a, 59
Cr(CH ₂ CMe ₃) ₄		Stable at 80° in heptane	38
CrBu-t ₄	Heptane, 70°, t _{1/2} ~4.5 min	Principally Me ₃ CH + Me ₂ C=CH ₂ + Cr (with 5% C)	38
WMe ₅	Neat, 25°	CH ₄ + C ₂ H ₆ (trace) + black solid (contains C, H, W)	20
(CuCH ₂ SiMe ₃) ₄	PhMe, 80°	Cu + Me ₄ Si + (Me ₃ Si) ₂ CH ₂ + (Me ₃ SiCH ₂) ₂ + PhCH ₂ CH ₂ SiMe 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



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.

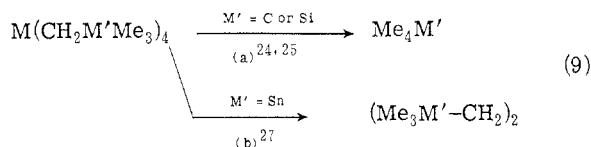
Migration of hydrogen is preferred, and this is a factor which accounts for the enhanced stability of complexes with a neopentyl-like structure. When Y is silicon, elimination would be of a relatively unstable silaolefin.

Examples are to be found in the decomposition of CrBu-t₄ to give *inter alia* Me₂C=CH₂,³⁸ and of Al(CH₂CMe₃)₃ to give AlMe₃ and Me₂C=CH₂.⁴¹ 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-t₄) 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



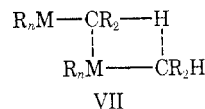
0–40° for M = Ti, Zr, or Hf (Ti the least stable), is probably a case of reductive elimination;²⁷ direct participation of free radicals is unlikely because toluene does not alter the nature of the products.

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 4⁴⁶ may be regarded



as an intermediate in the decomposition of hypothetical Nb(CH₂SiMe₃)₅ (from NbCl₅-LiR⁺) by loss of 4 mol of SiMe₄.

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



(61) M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, 948 (1973); N. G. Hargreaves, R. J. Puddephatt, L. H. Sutcliffe, and P. J. Thompson, *ibid.*, 861 (1973).

(62) M. P. Brown, A. K. Holliday, and G. M. Way, *J. Chem. Soc., Chem. Commun.*, 532 (1973).

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α carbon. This is a principal factor governing the greater stability of $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$ and $\text{Ti}(\text{CH}_2\text{SiMe}_3)_4$ 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. $(\text{CuCH}_2\text{SiMe}_3)_4$ 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 decomposition 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 $(\text{MR}_n)_x$, and thus we can expect a major increase in the range of homoleptic complexes using ligands such as $(\text{Me}_3\text{Si})_2\text{CH}^-$, 2,2,3-trimethylnorbornyl⁻, or $\text{Me}_2\text{P}(\text{CH}_2)(\text{CH}_2)^-$. For example, whereas the group IV radicals $\text{R}^2_3\text{M}\cdot$ ($\text{M} = \text{Si}, \text{Ge}, \text{or Sn}$) are at present the only metal-centered main group element radicals to be stable at room temperature, extensions to the isoelectronic ion radicals $\text{R}^2_3\text{In}\cdot^-$ and $\text{R}^2_3\text{Sb}\cdot^+$ 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 $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{M}\cdot$ ($\text{M} = \text{Ge or Sn}$) have been made).⁶⁵ Among main group element neutral compounds, new stable s^2

and s^1 complexes, such as $(\text{MR}^2)_n$ ($\text{M} = \text{Ga}, \text{In}, \text{or Tl}$) or $\text{R}^2\text{Hg}-\text{HgR}^2$, 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 $(\text{Me}_3\text{Si})_3\text{C}^-$ (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 4²⁶ 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_2O_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 $\text{Zr}(\text{CH}_2\text{SiMe}_3)_4$]. Finally, with regard to (iii) we point to the new area of heavy group IV main group metal donors: *e.g.*,⁴ R^2_2M with $\text{M}'(\text{CO})_6$ yields $\text{R}^2_2\text{MM}'(\text{CO})_5$ or *trans*- $(\text{R}^2_2\text{Sn})_2\text{M}'(\text{CO})_4$ ($\text{M} = \text{Sn or Pb}$, $\text{M}' = \text{Cr or Mo}$).

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(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).