

UNUSUAL METAL ALKYLs

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Abstract - Initial objectives were to obtain novel thermally stable homoleptic metal complexes $[MR'_n]$: (i) d- or f-block metal alkyls, (ii) subvalent diamagnetic main-group element alkyls (carbene analogues), and (iii) paramagnetic alkyls of main-group elements (alkyl-radical analogues). Subsequently, further targets became (iv) compounds with bridging alkyl ligands for d- or f-block metals, and (v) heteroleptic complexes in which a bulky alkyl group $[(Me_3Si)_2CH=R]$ allowed the incorporation within the metal inner co-ordination sphere of unexpected co-ligands. Compounds discussed included those listed in Table 4. Among the physical methods used were dynamic n. m. r., e. s. r., X-ray diffraction, and calorimetry.

INTRODUCTION AND INITIAL OBJECTIVES

Until 1970 thermally stable homoleptic metal alkyls $[MR'_n]$ did not include (i) transition metal compounds or (ii) subvalent main-group metal alkyls. We took the view that such derivatives could be made kinetically stable by appropriate choice of ligand R'^- , so that decomposition pathways would be energetically unfavourable. Studies concentrated on neopentyl-type ligands, especially $Me_3SiCH_2^-$ (R''^-) and $(Me_3Si)_2CH^-$ (R^-) (Ref. 1); complementary results in area (i) came from G. Wilkinson's group (Ref. 2). Stable compounds are listed in Tables 1 and 2.

TABLE 1 Stable sub-valent main-group metal homoleptic alkyls, MR'_n [$R = (Me_3Si)_2CH$]

Type	Compound	Comments
$\overset{\cdot\cdot}{M}R_2$ \underline{s}^2	GeR ₂ , SnR ₂ , PbR ₂	Monomers in C ₆ H ₁₂ ; (SnR ₂) ₂ in solid
$\overset{\cdot\cdot}{M}R_2$ \underline{s}^1	PR ₂ , AsR ₂	Monomers in PhMe or vapour; π -radicals
$\overset{\cdot}{M}R_3$ \underline{s}^1	SiR ₃ , GeR ₃ , SnR ₃ , GeAr ₃ (Ar = Mes* or C ₆ H ₅ Me ₂ -2, 6)	Monomers in PhMe; σ -radicals

* Cf. Ref. 19

The presence of bridging alkyl ligands between 2 or more metal centres was formerly regarded as characteristic only of the electron-deficient alkyls of Li, Be, Mg, or Al, but crystallographically-authenticated examples now include alkyls of d- and f-block elements (Table 3, see also Ref. 1).

NEW RESULTS

It is now becoming apparent that bulky alkyl groups, such as $R = (Me_3Si)_2CH$ or $R'' = Me_3SiCH_2$, may stabilise unusual complexes. Examples, discussed in the lecture and largely unpublished, are in Table 4.

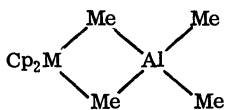
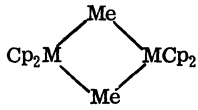
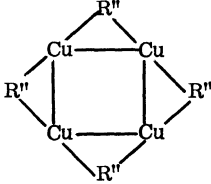
The oxidative addition of PhBr to SnR₂ is catalysed by a trace of EtBr (Ref. 16). The use of T. H. F. rather than C₆H₆ as solvent favours the formation of SnR₂Br₂ at the expense of SnR₂(Br)Ph. These, and earlier e. s. r. and optical activity data, favour the mechanism of Scheme 1. The compounds SnR₂X(R') [$R = (Me_3Si)_2CH$] show diastereotopic Me₃Si signals (Ref. 29); SnR₃Cl is a discrete distorted tetrahedral monomer in the solid state (Ref. 29).

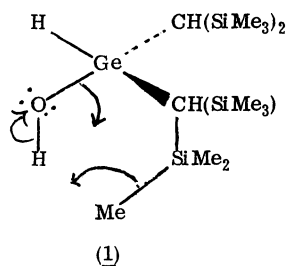
TABLE 2 Stable transition-metal homoleptic alkyls $[\{\text{MR}'_n\}_x]$

Type	$\text{R}' = \text{Me}_3\text{SiCH}_2 (\text{R}'')$	$\text{R}' = (\text{Me}_3\text{Si})_2\text{CH} (\text{R})$
$[\{\text{MR}'_x\}]$	$[\{\text{CuR}'_4\}]$	\underline{d}^{10}
$[\{\text{MR}'_2\}_x]$	$[\{\text{MnR}'_2\}_\infty]^a$	\underline{d}^5
$[\{\text{MR}'_3\}_x]$	$[\{\text{MoR}'_3\}_2]^a$	\underline{d}^3
	$[\{\text{WR}'_3\}_2]^a$	\underline{d}^3
		$[\text{TiR}_3] \quad \underline{d}^1$ $[\text{VR}_3] \quad \underline{d}^2$ $[\text{CrR}_3] \quad \underline{d}^3$
$[\{\text{MR}'_4\}_x]$	$[\text{TiR}'_4], [\text{ZrR}'_4], [\text{HfR}'_4]$	\underline{d}^0
	$[\text{VR}'_4]^a$	\underline{d}^1
	$[\text{CrR}'_4]^a$	\underline{d}^2
	$[\{\text{ReR}'_4\}_3]^a$	\underline{d}^3

^aG. Wilkinson, *et al.* (Ref. 2)

TABLE 3 Stable transition- or lanthanide-metal bridging alkyls

Compound type	Specific examples	Ref.
	$\text{M} = \text{Sc}, \text{Y}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$	3
	$\text{M} = \text{Y}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{or Yb}$	4
	$\text{R}' = \text{Me}_3\text{SiCH}_2 (\text{R}'')$	5
$[\{\text{MnR}'_2\}_n]$	$n = \infty, \text{R}' = \text{Me}_3\text{SiCH}_2; n = 2, \text{R}' = \text{PhMe}_2\text{CCH}_2$	6



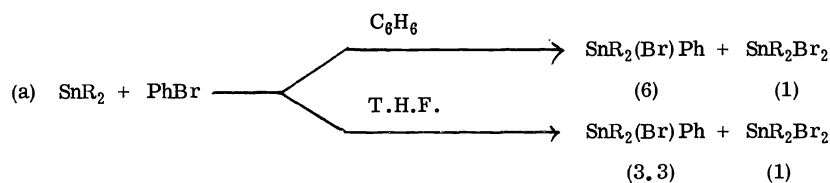
The yellow germanium(II) alkyl, GeR_2 , hydrolyses instantly upon exposure to the atmosphere to give the white, volatile $\text{HGe}^+[\text{CH}(\text{SiMe}_3)_2][\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{O}^-)]$ (Ref. 10), for which there is spectroscopic and crystallographic evidence. The unexpectedly facile C-Si cleavage is attributed to initial oxidative-addition and then a reaction involving a cyclic transition state (1).

Although SnR_3 is indefinitely stable in presence of SnR_2 in $n\text{-C}_6\text{H}_{14}$ (Ref. 1), the diamagnetic dimer can be made and gives rise to a number of unusual organotin compounds (Ref. 11) (Scheme 2).

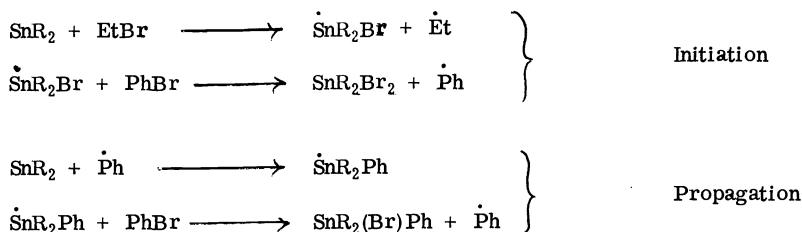
TABLE 4 The use of the $(\text{Me}_3\text{Si})_2\text{CH}^-$ ligand to stabilise unusual complexes

Complex	Complex
1. $[\text{InR}_3]$	7. $[\text{MR}_3\text{Cl}]^-$ (M = Er, Yb)
2. $\text{HGe}(\text{R})^+ \{ \text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{O})^- \}$	8. $[\text{ZrCp}_2(\text{R})\text{Y}]$ (Y = H, Me, Et, Pr^{n} , Bu^{n} , CH_2SiMe_3 , or Ph)
3. $[\text{Cr}(\text{CO})_5\{\text{MR}_2\}]$ (M = Ge or Sn) <i>J. C. S. Chem. Comm.</i> , 1977, 458; <i>J. C. S. Dalton</i> , 1976, 2275	9. $[\text{ZrCp}_2(\text{R})(\begin{smallmatrix} \text{N} \\ \\ \text{N} \end{smallmatrix})]$
4. $\text{SnR}_3\text{-OH}$	10. $[\text{ZrCp}_2(\text{R})\text{-N}_2\text{-ZrCp}_2\text{R}]$
5. $\text{SnR}_3\text{-NO?}$	11. Other unusual heteroleptic compounds include $[\text{MR}'_4]^-$ (M = Y, Er, Yb; R' = Me_3SiCH_2), $[\text{MR}'_3\text{Cl}]^-$ (M = Er, Yb; R' = Me_3SiCH_2), and $[\text{ZrCp}_2(\overset{\text{O}}{\parallel}\text{CR}'\text{R}')] (R' = \text{Me}_3\text{SiCH}_2)$
6. $[\text{MgRCl}(\text{OEt}_2)_2]$	

SCHEME 1 Oxidative-addition: catalytic and solvent effects (relative ratios in parentheses)



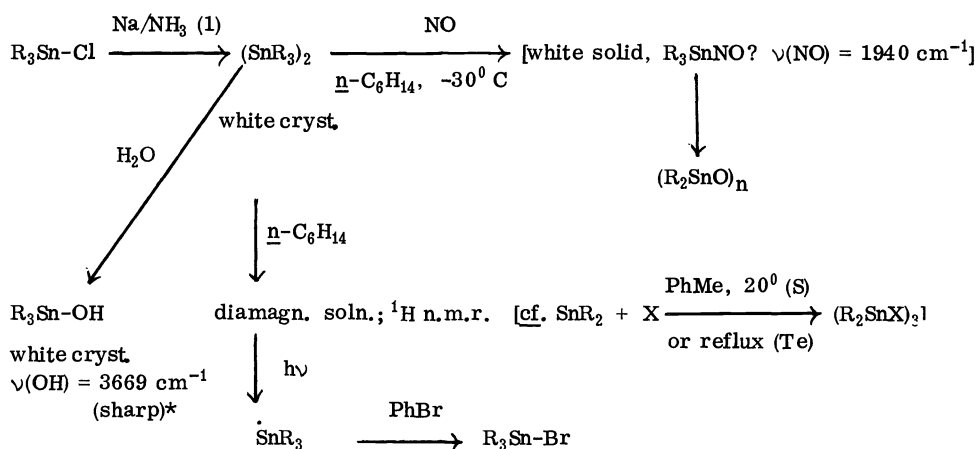
(b) Mechanism



A new persistent germanium-centred radical is $\text{Ge}(\text{C}_6\text{H}_5\text{Me}_{2-2,6})_3$, obtained under photolysis from $\text{GeAr}_3\text{-Cl}$ and the electron-rich olefin $\text{=CN}(\text{Et})\text{CH}_2\text{CH}_2\text{NEt}_2$ (Ref. 18). The e.s.r. spectrum in toluene at 20° C shows $g = 2.0080$, $a(^1\text{H}) = 0.065$ mT, and $a(^{73}\text{Ge}) = 0.669$ mT; there is coincidental equivalence of all proton couplings (due to twisting of the aromatic rings into a propeller arrangement about the Ge), the eighteen lines correspond to the central 18 of the binomial expansion of 28. Recently $\text{Ge}(\text{C}_6\text{H}_2\text{Me}_{3-2,4,6})_3$ has been obtained by classical methods (Ref. 19).

Some interesting steric effects on (a) reactivity, (b) ^{31}P chemical shifts, and (c) $>\ddot{\text{P}}-\text{C}<$ and $>\ddot{\text{P}}-\ddot{\text{N}}<$ rotational barriers, are summarised in Table 5 (Ref. 21).

A new transition-metal homoleptic alkyl is $[\text{MnR}_2]_n$ (Ref. 23), prepared from the crystalline $[\text{MgR}(\text{Cl})(\text{OEt}_2)_2]$. The latter is a $\mu\text{-Cl}_2$ -bridged centrosymmetric dimer (Ref. 15). The Grignard reagent is also the starting material of choice for obtaining GeR_2 or PbR_2 [R = $(\text{Me}_3\text{Si})_2\text{CH}$]. The compounds $[\text{CrR}_3]$ (Ref. 24) and $[\text{InR}_3]$ (Ref. 7) are isomorphous, the metal lying 0.2 to 0.3 Å out of the plane of the surrounding three carbon atoms.

SCHEME 2 Some reactions of $(\text{SnR}_3)_2$, $\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$ * Cf. Ref. 17 for $(\text{Me}_3\text{Sn-OH})_\infty$ TABLE 5 Some unusual steric effects in organophosphorus compounds [$\text{R} = \text{Me}_3\text{Si})_2\text{CH}$]

Compound	Reactivity	$\delta(^{31}\text{P})$ (p.p.m. rel. to 85% H_3PO_4)	
$\text{R}_2\text{P-H}^{\text{a}}$	None with LiMe or $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$		
$\text{R}_2\text{P-Cl}^{\text{a}}$	(a) None with $\text{Bu}^{\text{t}}\text{-NH}_2$ or $\text{LiNPr}^{\text{i}}_2$ (b) $\rightarrow \text{R}_2\text{PY}$ with LiY ($\text{Y} = \text{Me}$ or NMe_2)	-154 (cf. usual range -120 to -80^0)	$\text{P} \begin{array}{l} \nearrow \text{C, } T_{\text{C}} = 168 \text{ K, } \Delta G^\ddagger = 8.5 \\ \searrow \text{ [cf. 6.3 for } \text{Bu}^{\text{t}}_2\text{PCl (Ref. 20)]} \end{array}$
$\text{R}_2\text{P-PR}_2^{\text{a}}$	$\rightleftharpoons 2 : \text{PR}_2^{\text{b}}$ in C_6H_{14}	+120 (cf. usual range +60 to -40^0)	
$\text{R}'\text{P} \begin{array}{l} \nearrow \\ \text{Cl} \end{array} \text{NMe}_2$			$\text{P} \begin{array}{l} \nearrow \text{N barriers } (\Delta G^\ddagger = 9 \text{ to } 12) \\ \searrow \end{array}$ (a) $\text{R}' = \text{Me} > \text{Et} > \text{Pr}^{\text{i}} > \text{Bu}^{\text{t}}$ (b) $\text{Me} \approx \text{R}$

^aDiastereotopic Me_3Si groups. ^bFor PR_2 or AsR_2 , see ref. 22

We previously noted for complexes $[\text{ML}_4]$ ($\text{M} = \text{Ti}, \text{Zr},$ or Hf ; $\text{L} = \text{CH}_2\text{CMe}_3, \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{Ph}, \text{NMe}_2, \text{OPr}^{\text{i}},$ or Cl) the following trends in thermochemical bond energy terms $\bar{E}(\text{M-L})$: (a) $\text{Ti} \ll \text{Zr} < \text{Hf}$, (b) $\text{alkyl} < \text{NMe}_2 \approx \text{Cl} < \text{OPr}^{\text{i}}$, and (c) $\text{CH}_2\text{CMe}_3 < \text{CH}_2\text{SiMe}_3 \approx \text{CH}_2\text{Ph}$ (Ref. 25). Trend (c) is also followed in the linear $[\text{ZnR}'_2]$ (Ref. 26); but for amides, bond strengths decrease in the order $\text{Zn} > \text{Cd} > \text{Hg}$. From preliminary X-ray data on $[\text{ZrCp}_2\text{R}'_2]$, bond lengths $\text{Zr-CH}_2\text{CMe}_3 > \text{Zr-CH}_2\text{SiMe}_3$ reflect trend (c) (Ref. 15 and 23).

The first lanthanide-metal alkyls are listed in Table 6 (Ref. 12); an X-ray analysis of a single crystal of $[\text{Li}(\text{T.H.F.})_4][\text{YbR}_3\text{Cl}]$ shows a distorted tetrahedral arrangement of valences around ytterbium (Ref. 15).

In $[\text{YCp}_2\text{Me}_2\text{AlMe}_2]$ there is fluxional behaviour as between bridging and terminal Me groups: when $\text{Cp} = \text{Me}_3\text{SiC}_5\text{H}_4$, ΔG^\ddagger is $18.7 \text{ kcal mol}^{-1}$, compared with $15.8 \text{ kcal mol}^{-1}$ for $\text{Cp} = \text{C}_5\text{H}_5$ (Ref. 27).

TABLE 6 Some stable lanthanide-metal alkyls

Compound type	$[\text{MR}'_3(\text{T.H.F.})_2]^{\text{a}}$	$[\text{MR}'_3\text{Cl}]^-$	$[\text{MR}'_4]^-$
Examples	M = Tb, Er, Yb R' = Me ₃ SiCH ₂ (R'')	M = Er, Yb R' = (Me ₃ Si) ₂ CH (R)	M = Er, Yb (Y) R' = Me ₃ SiCH ₂

^aCf. Sc, Y: Ref. 1

Some new hexane-soluble zirconium(IV) heteroleptic alkyls include compounds (2)-(6) (Cp = C₅H₅-η). Some of these, (3)-(6), show that at low temperature (< 238-303 K) there is a preferred conformer (7), which implies a high barrier (ca. 15 kcal mol⁻¹) to Zr-C rotation (Ref. 13).

$[\text{ZrCp}_2\text{R}'_2]$

(2) R' = Ph₂CH (Ref. 28)

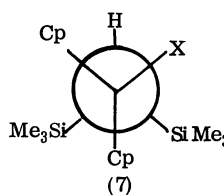
$[\text{ZrCp}_2(\text{X})\text{R}]$

(3) X = Buⁿ (Ref. 28)

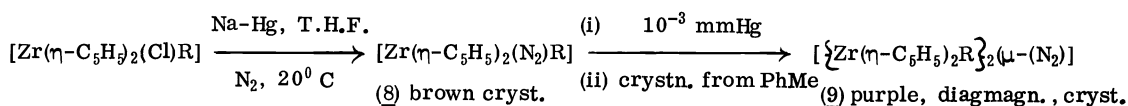
(4) X = Cl (Ref. 28)

(5) X = H (Ref. 13)

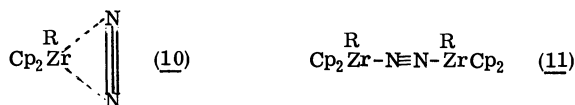
(6) X = Me, Et, Prⁿ, CH₂SiMe₃,
or Ph (Ref. 13)



Finally, reduction of a Zr^{IV} chloro-alkyl under N₂ surprisingly leads to incorporation of dinitrogen into the products (8) and (9) (Ref. 14):



Neither compound (8) nor compound (9) show $\nu(\text{N}_2)$. The former complex, unlike the latter, is paramagnetic. In the e.s.r. spectrum (T.H.F., 20^o C), complex (8) shows a 1:2:3:2:1 quintet due to coupling [$a(^{14}\text{N}) = 0.375 \text{ mT}$] with two equivalent ¹⁴N atoms [or a 1:2:1 triplet for the ¹⁵N₂-isotopomer, $a(^{15}\text{N}) = 0.45 \text{ mT}$]. The preferred structures based on these data are (10) and (11) respectively.



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* Items 10-16, 18, 21, 23, 24, and 26; 27 refer to unpublished work, (at the University of Sussex, unless otherwise stated).

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