Elimination Stabilized Alkyls. Part I. Chromium, Molybdenum, Tungsten, and Vanadium.[1] †

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The interaction of chlorides of V, Cr, Mo, and W with the lithium or Grignard reagents derived from chloromethyltrimethylsilane produces thermally stable alkyls of formula $V(CH_2SiMe_3)_4$, $VO(CH_2SiMe_3)_3$, $Cr(CH_2SiMe_3)_4$, and $M_2(CH_2SiMe_3)_6$ (M = Mo or W). The compounds have been investigated, where feasible, by i.r., Raman, electronic, e.s.r., and n.m.r. spectroscopy and the various spectral assignments are discussed in terms of proposed structures for the compounds.

EARLY efforts to prepare simple alkyls and aryls of transition metals showed that, generally, these have low thermal stability.[2] It has often been taken implicitly, and sometimes explicitly, that the transition metal to carbon bond is weak and that, following the preparation of the first extensive series of σ-bonded alkyls and aryls[3] in which additional ligands were present, the presence of ligands such as CO, π-C_5H_5, PR_3, *etc.* may increase the strength. Thus, ' By any simple criterion, simple transition-metal alkyls are very unstable,' ' in contrast to the simple alkyls some metal complexes bearing other ligands in addition to alkyl and aryl groups are strikingly stable '[4a] and ' in these compounds [of type π-$(C_5H_5)_2TiR_2$] the electronic energy levels of the metal are filled by π electrons of the sandwich (C_5H_5) group leading to an increase in the stability of the compound as a whole and of the metal to carbon bond in particular.'[4b]

Although metal to carbon bond lengths obtained from *X*-ray data are doubtless in part related to the strength or energy of the bond,[5] attempts to correlate only M–C bond lengths with thermal stabilities of metal alkyl derivatives are doomed to failure. The chemical or thermal stability of compounds tell us nothing about bond strengths and it is necessary to distinguish clearly, as has been done,[6] between thermodynamic and kinetic stability. There are still only few estimates of bond energies and these in compounds with π-bonding ligands, *viz.* (*a*) $Pt{-}C_6H_5$[7] in $(Et_3P)_2PtPh_2$, *ca.* 250 kJ mol^{-1}; (*b*) $Pt{-}CH_3$[8] in π-$C_5H_5PtMe_3$, *ca.* 164 kJ mol^{-1}; and (*c*) $Ti{-}CH_3$ and $Ti{-}C_6H_5$ in $(\pi$-$C_5H_5)_2TiR_2$,[9] *ca.* 250 and

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† No reprints available.

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[9] V. I. Tel'noi, I. B. Rabinovich, V. D. Tikhonov, V. N. Latiaeva, L. I. Vyshinskaia, and G. A. Razuvaev, *Doklady Akad. Nauk, S.S.S.R.*, 1967, **174**, 1374.

350 kJ mol^{-1} respectively. There are also some force-constant data for CH_3TiCl_3 [10] and $CF_3Mn(CO)_5$.[11]

Since (i) there is insufficient bond-energy data to support the view that transition metal to carbon bonds are intrinsically weaker than bonds between carbon and non-transition elements, or between transition elements and oxygen or nitrogen in isolable compounds such as the alkoxides and dialkylamides, *e.g.* $Cr(OEt)_4$ [12a] or $Co[N(SiMe_3)_2]_2$,[12b] (ii) it is clear that the presence of stabilising ligands of the π-acid type is no guarantee of stability [indeed the use of complexes such as $RhH(CO)(PPh_3)_3$ in catalysis depends on the instability of the metal to carbon bond [13]], and (iii) even ethyl groups can be bound to metals in substitution-inert octahedral complexes of Cr^{III}, Co^{III}, and Rh^{III},[14] we were led to suggest [1] that binary alkyls of transition metals should be isolable provided that they are kinetically stable. Although there are several possible paths for the destruction of metal to carbon bonds,[15] one of the commonest is the alkene elimination reaction (1).

$$M\text{–}CH_2CH_2R \rightleftharpoons MH + CH_2\text{=}CHR \qquad (1)$$

This reaction can be inhibited if (*a*) there is a group of type $M\text{–}CH_2\text{–}XHR_n$ where X is any atom that can form a single but not a multiple bond to carbon, or (*b*) the β-carbon atom of the alkyl chain bears atoms or groups of atoms which cannot be as readily transferred to the metal as is hydrogen.

There are large numbers of groups which could serve this purpose, *e.g.* CH_2SnR_3, CH_2HgR, $CH_2Mn(CO)_5$, $CCo_3(CO)_{12}$, $C[B(OMe)_2]_3$, but for accessibility and preparative convenience we have studied [1] the trimethylsilylmethyl group. We now give details of the compounds of Cr, Mo, W, and V. Complexes of CH_2SiMe_3 with π-bonding ligands present have also been described,[16a,b] and the titanium and zirconium compounds have been mentioned [16b] although satisfactory analyses were not obtained. In our own work we have also been unable to obtain the titanium compound pure.

It may be noted that there are a number of known isolable binary alkyls which meet the above criteria. These are the following: (*a*) the benzyls [17] of Ti and Zr, $M(CH_2Ph)_4$.* (*b*) The chelated carborane [18] derivatives such as $Ni[(B_{10}C_2H_{10})_2]_2^{2-}$ which have four metal–carbon bonds. (*c*) Phenyl and perfluorophenyl compounds, *e.g.* $(C_6H_5)_3Cr(C_4H_8O)_3$,[19] $[CuC_6F_5]_8$,[20] AgC_6F_5,[21] $Au(C_6F_5)_3$,[22] and $Ti(C_6H_5)_4$.[23] (*d*) The methyl group cannot of course undergo reaction (1) but other decomposition routes such as homolysis, solvent attack, *etc.* are possible. Nevertheless, simple methyls such as $TiMe_4$ or $MnMe_2$ are considerably more stable than their ethyl analogues [this is true even for $MeMn(CO)_5$ *vs.* $EtMn(CO)_5$] and Me_3MCl_2 ($M = Nb$ or Ta) are reasonably stable at room temperature.[24] Further, there are several anionic methyls of Cu, Co, Fe, Mn, Cr, *etc.*, some of which, notably those of Cr such as Li_3CrMe_6 or $Li_4[Cr_2Me_8]$,[25] are sufficiently stable to isolate and study by *X*-ray crystallography.

It is also to be noted that, where the co-ordination sites necessary for reaction (1) to proceed are blocked, increased stability may result, as in the substitution-inert complexes referred to above. Other examples are the thermally stable adducts of Me_4Ti and $MeTiCl_3$ [26] and also the chelated alkyl [27] tris[*o*-dimethylarsino)-α-tolyl]chromium(III), which is stable to 350°.

One of the best indications of relative stabilities of transition metal alkyls comes from the studies of Tamura and Kochi [28] on the decomposition of dialkyl manganese compounds, prepared *in situ*, which shows that the order is $Me \sim PhCH_2 \sim Me_3CCH_2 \gg Pr^n,Bu^n > Et > Bu^t > Pr^i$. The most stable are clearly those which cannot readily undergo the reaction (1). It is

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* Note that it is possible that an electron pair from the phenyl ring could participate in metal to ligand bonding and give an allylic or tri*hapto* structure as in $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}CH_2Ph)$ (R. B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, 1966, **88**, 532. F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 1969, **91**, 1339). The same argument would hold for other systems with available lone pairs, *e.g.*, CH_2SR (R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1965, **4**, 486). However, for the Ti and Zr benzyls, spectroscopic data (ref. 17) is accommodated by simple σ bonding and this is confirmed by *X*-ray studies on tetrabenzyltitanium (I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccola, *J. Amer. Chem. Soc.*, 1971, **93**, 3787. G. R. Davis, J. A. J. Jarvis, B. T. Kilbourn, and A. J. P. Pioli, *Chem. Comm.*, 1971, 677).

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[11] F. A. Cotton and R. M. Wing, *J. Organometallic Chem.*, 1967, **9**, 511.

[12] (*a*) E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chisholm, *J. Chem. Soc.* (*A*), 1971, 772; (*b*) D. C. Bradley and K. J. Fischer, *J. Amer. Chem. Soc.*, 1971, **93**, 2058.

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[14] See *e.g.*, M. D. Johnson and N. Winterton, *J. Chem. Soc.* (*A*), 1970, 507; K. Thomas, J. A. Osborn, A. R. Powell, and G. Wilkinson, *ibid.*, 1968, 1801.

[15] See *e.g.*, R. P. A. Sneeden and H. H. Zeiss, *J. Organometallic Chem.*, 1970, **22**, 713; 1970, **26**, 101; 1971, **27**, 89. G. M. Whitesides, I. R. Stedronsky, C. P. Casey, and J. S. Filippo, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 1426; J. Dvorak, R. J. O'Brien, and W. Santo, *Chem. Comm.*, 1970, 411.

[16] (*a*) B. Wozniak, D. Ruddick, and G. Wilkinson, *J. Chem. Soc.*, 1971, 3116; (*b*) M. R. Collier, M. F. Lappert, and M. M. Truelock, *J. Organometallic Chem.*, 1970, **25**, C36.

[17] U. Zucchini, E. Abizzati, and U. Giannini, *J. Organometallic Chem.*, 1971, **26**, 357.

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[19] W. Herwig and H. H. Zeiss, *J. Amer. Chem. Soc.*, 1959, **81**, 4798; see also G. M. Whitesides and W. J. Ehmann, *ibid.*, 1970, **92**, 5625.

[20] A. Cairncross, J. R. Roland, R. M. Henderson, and W. A. Sheppard, *J. Amer. Chem. Soc.*, 1970, **92**, 3187.

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[22] L. G. Vaughan and W. A. Sheppard, *J. Organometallic Chem.*, 1970, **22**, 739.

[23] G. A. Razuvaev, *Doklady Akad. Nauk.*, *S.S.S.R.*, 1970, **191**, 620 (*Chem. Abs.*, **73**, 149,956k).

[24] G. L. Juvinall, *J. Amer. Chem. Soc.*, 1964, **86**, 4202.

[25] J. Krausse, G. Marx, and G. Schödel, *J. Organometallic Chem.*, 1970, **21**, 159; J. Krausse and G. Schödel, *ibid.*, 1971, **27**, 59.

[26] R. Tabacchi and A. Jacot-Guillarmod, *Chimia*, 1970, **24**, 271; R. J. H. Clark and A. J. McAless, *J. Chem. Soc.* (*A*), 1970, 2026; G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *ibid.*, 1971, 1920.

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[28] M. Tamura and J. Kochi, *J. Organometallic Chem.*, 1971, **29**, 111.

of note that we have now prepared isolable neopentyls[29] of V, Cr, Mo, *etc.*, which are similar to those of the 'silicon analogues' now discussed and which we shall describe in detail later.

In short, therefore, despite the present lack of M–C bond-energy data, it is probable that the transition metal to carbon bond is no weaker than bonds between carbon and other metallic elements and that the main purpose of additional ligands, π-acid or otherwise, in stabilizing compounds with metal–carbon σ-bonds is merely the blocking of the co-ordination sites required for decomposition reactions to proceed.

Trimethylsilylmethyl Compounds

The compounds are obtained by conventional procedures by interaction of the metal chloride with the lithium or Grignard reagent derived from Me_3SiCH_2Cl. Details are given in the Experimental section. The compounds and some of their properties are listed in Table 1. They have been studied where feasible by various spectroscopic techniques.

TABLE 1

Trimethylsilylmethyl (R) compounds of transition metals

Compd.	Colour, form	M.p. (°C)	Electronic spectrum (cm^{-1}, ε)
VR_4	Dark green needles	43	15,625, 23,600 (310) and weak broad band in far i.r.
VOR_3	Lemon yellow needles	75	Rising absorption in u.v. weak shoulder at 26,600
$[CrR_4]^-$	Blue-green anion		7800 (50); 16,250 (760)
CrR_4	Purple-red needles	40	19,000 (1060)
Mo_2R_6	Yellow plates	99	Rising absorption in u.v.
W_2R_6	Orange-brown plates	110	Rising absorption in u.v. with weak band at 21,300

The Tetrakis(trimethylsilylmethyl)chromate(III) *Ion*.—The interaction, in tetrahydrofuran (THF), of $LiCH_2SiMe_3$ and the tetrahydrofuran adduct, $CrCl_3,3THF$, produces a blue-green solution. The blue-green species is stable in THF, but attempts to isolate crystalline salts by addition of tetra-alkylammonium and other large cations failed. The solutions are immediately oxidised by air to the purple-red chromium(IV) species discussed below. The green species can be formulated as the tetrahedral ion $Cr(CH_2SiMe_3)_4^-$ on the following grounds: (*a*) the ion is oxidised to $Cr(CH_2SiMe_3)_4$ and the latter in THF is reduced chemically, *e.g.*, by sodium amalgam, or electrolytically, to the green anion. Coulometric measurements confirm a one-electron reduction step; the polarogram of 10^{-4}M-ethanolic solution of $Cr(CH_2SiMe_3)_4$ with tetra-n-butylammonium iodide as supporting electrolyte shows a reduction wave at a half-wave potential *ca.* −1·28V *vs.* the saturated calomel electrode. Hence we have a reversible reaction,

$$Cr(CH_2SiMe_3)_4^- = Cr(CH_2SiMe_3)_4 + e.$$

(*b*) The electronic properties of the green species suggest that it is one of the few known examples of tetrahedral Cr^{III}.[30–32]

The electronic absorption spectrum (Table 1) is inconsistent with octahedral or three-co-ordinate chromium(III),[32] and agrees well with the spectrum for tetrahedral chromium(III) in salts of Cr^{III} 12-heteropolytungstates (8300 and 16,000 cm^{-1}). The observed bands are assigned to the $^4T_1(F) \longrightarrow {}^4T_2(F)$ and $^4T_1(F) \longrightarrow {}^4A_2(F)$ and $^4T_1(P)$ transitions respectively. This assignment yields values of Δ *ca.* 8800 cm^{-1} and *B ca.* 700 cm^{-1}. The broad band at 16,250 cm^{-1} in $Cr(CH_2SiMe_3)_4^-$ has a shoulder at 19,000 cm^{-1} which could be due to partial resolution of the $^4T_1(F) \longrightarrow {}^4A_2(F)$ and $^4T_1(P)$ transitions, but may be due to a trace of the Cr^{IV} species. The magnetic properties are discussed later.

Tetrakis(trimethylsilylmethyl)chromium(IV).—The compound $Cr(CH_2SiMe_3)_4$ is remarkably unreactive other than towards oxygen. It is unaffected by most solvents, by primary aliphatic and aromatic amines, ethylenediamine, alkyl and aryl tertiary phosphines, carbon disulphide, ethylene and liquid alkenes, phenylacetylene, succinimide, triphenylmethyl tetrafluoroborate, and by carbon monoxide at 100° and 200 p.s.i.

However, it will react with tetracyanoethylene in refluxing toluene and with hexafluorobut-2-yne at 100° in a sealed tube. Although unaffected by water and dilute mineral acids, concentrated HCl and H_2SO_4 give green solutions containing Cr^{III} and tetramethylsilane is lost.

On treatment of $Cr(CH_2SiMe_3)_4$ in pentane at low temperatures with either hydrogen chloride or chlorine, a red soluble species is formed. This decomposes above −40° to give a solid which contains only chromium and chlorine, and a clear solution. The solid is a mixture of variable colour and contains Cr^{II} and Cr^{III} chloride; the pentane solution contains several compounds by g.l.c., but the major component is Me_4Si.

The red species is probably $CrCl_4$ which has previously been reported only in the vapor phase when $CrCl_3$ is heated in chlorine.[33]

Both $Cr(CH_2SiMe_3)_4^-$ and $Cr(CH_2SiMe_3)_4$ react with nitric oxide to give two or more brown petroleum-soluble products which are still under investigation; the Cr^{IV} t-butoxide gives only one product.[34]

The electronic spectrum of $Cr(CH_2SiMe_3)_4$ consists of a single strong band at 19,000 cm^{-1}, for which there are two possible assignments. If the symmetry is tetrahedral this transition would be $^3A_2 \longrightarrow {}^3T_1(F)$ and

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[29] F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Comm.*, 1971, 1079.

[30] D. H. Brown, *J. Chem. Soc.*, 1962, 3322.

[31] D. J. Machin, D. F. C. Morris, and E. L. Short, *J. Chem. Soc.*, 1964, 4658.

[32] E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chisholm, *Chem. Comm.*, 1968, 495.

[33] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 2nd edn., Wiley, New York, 1966.

[34] D. C. Bradley and C. W. Newing, *Chem. Comm.*, 1970, 219.

assuming B *ca.* 700 cm^{-1} we may calculate Δ *ca.* 12,500 cm^{-1}, which seems reasonable when compared with $Cr(CH_2SiMe_3)_4^-$ ($\Delta = 8800$ cm^{-1}) and $Cr(OEt)_4$ ($\Delta = 9430$ cm^{-1}).[12a] This interpretation requires a band $^3A_2 \longrightarrow {}^3T_2$ at 12,500 cm^{-1} which is not observed, but is expected to be weak as it is symmetry-forbidden. A second strong band $^3A_2 \longrightarrow {}^3T_1(P)$ is predicted at about 30,000 cm^{-1} but would be masked by the even stronger charge-transfer bands.

An alternative assignment has been proposed for $Cr(NEt_2)_4$[35] which, like $Cr(CH_2SiMe_3)_4$ has a single strong band. It was considered that there was a very strong distortion of the tetrahedron to D_{2d} symmetry, and that the observed transition at 13,700 cm^{-1} was $^3B_1[(a_1)^1(b_1)^1] \longrightarrow {}^3A_2[(b_2)^1(b_1)^1]$. Either of these assignments appears to be tenable for $Cr(CH_2SiMe_3)_4$.

The magnetic properties are discussed later.

Hexakis(*trimethylsilylmethyl*)-*dimolybdenum and -ditungsten*.—From the interaction of the Grignard reagent with $MoCl_5$ or WCl_6 in ether the compounds $M_2(CH_2SiMe_3)_6$ are obtained, (Table 1 *). These compounds are isomorphous and isostructural by X-ray diffraction. The n.m.r. spectra (Table 2) are also virtually identical and the physical properties of the compounds are also similar. They sublime *in vacuo* at *ca.* 120° and are stable in air over short periods of time although on prolonged exposure they darken and the end product of oxidation appears to be the blue molybdenum or tungsten oxide.

TABLE 2

Nuclear magnetic resonance spectra of trimethylsilylmethyl (R), compounds (τ values in deuteriobenzene)

Compound	CH_3	CH_2	Remarks
VOR_3	9·90	Centre 7·5b	$CH_3 : CH_2 = 9 : 2$
Mo_2R_6	9·65	7·85	$CH_3 : CH_2 = 9 : 2$
W_2R_6	9·75	8·10	$CH_3 : CH_2 = 9 : 2$ $J(^{183}W–CH_2) = 10$ Hz
SnR_4	9·96	10·18	$J(^{117,119}Sn–CH_2) = 70$ Hz
PbR_4	9·96	9·48	$J(^{207}Pb–CH_2) = 80$ Hz
$PbClR_3$	9·83	8·85	$J(^{207}Pb–CH_2) = 90$ Hz

Both compounds are soluble in petroleum, benzene, and ether, the molybdenum compound giving yellow and tungsten compound intense orange-brown solutions; in absence of air these solutions are stable for at least a week, but are rapidly oxidised in air.

The i.r. spectra are almost identical and as noted later are consistent with the observed structure.

The compounds are more reactive than the tetra-alkylchromium. Water, dilute acids and bases, and ethanol do not react with the molybdenum compound but the tungsten compound reacts rapidly. Concentrated mineral acids produce tetramethylsilane. On heating the molybdenum compound in aqueous 12N-HCl, in the absence of air, it dissolves to give a pale yellow-green solution from which the yellow-green solid $Rb_3Mo_2Cl_8$ is obtained on addition of rubidium chloride.[36] On refluxing the alkyl in glacial acetic acid molybdenum(II) acetate is formed quantitatively. It is most probable that the Mo–Mo bond remains intact in both reactions.

The reaction with nitric oxide is rapid at room temperature, but no simple product could be isolated. Carbon monoxide reacts with both compounds at room temperature and pressure but several products are formed sequentially and the systems have not yet been studied in detail.

Tetrakis(*trimethylsilylmethyl*)*vanadium*(IV) *and Oxotris*(*trimethylsilylmethyl*)*vanadium*(V).—From the interaction of the lithium or Grignard reagents with VCl_4, the compound $V(CH_2SiMe_3)_4$ is obtained. This is similar to $Cr(CH_2SiMe_3)_4$ being very volatile, sublimable *in vacuo* at room temperature, and very soluble in petroleum and benzene, *etc.* It is very air-sensitive, inflaming in air, although under nitrogen at −30° it is stable indefinitely. Also, unlike the chromium compound, it is decomposed by aqueous solutions, alcohols and chlorinated solvents. However, it does not react under mild conditions with CO, CS_2, SO_2, alkenes, acetylenes, or tertiary phosphines, but does react with NO, tetracyanoethylene, hexafluorobut-2-yne, dry ammonia, and alkylamines.

The intense visible spectrum of $V(CH_2SiMe_3)_4$ is consistent with a non-centrosymmetric structure and the spectrum compares with those found for similar compounds,[37] *i.e.*, $V(OBu)_4$, 10,900, 13,900 cm^{-1} and $V(NR_2)_4$, 13,300, 17,600 cm^{-1}, but with a very strong field, as is the case for the alkylchromium.

On passing a petroleum solution of $V(CH_2SiMe_3)_4$ through a cellulose column, the colour changes to pale yellow and from this solution needles of oxotris(trimethylsilylmethyl)vanadium(V) are obtained. The compound can be made directly from $VOCl_3$ and a deficiency of the Grignard reagent; if excess of Grignard is used, reduction to $V(CH_2SiMe_3)_4$ occurs. The oxo-compound is relatively air stable, sublimable *in vacuo* at 70°, but is somewhat light sensitive. It is unaffected by water and alcohols and is readily soluble in petroleum, benzene, and ether. The compound does not react under mild conditions with CO, tertiary phosphines, or primary amines.

The n.m.r. spectrum (Table 2) has a sharp methyl resonance but the methylene peak is *ca.* 150 Hz wide evidently due to coupling with ^{51}V(spin $\frac{7}{2}$) which should produce eight lines, although these are not resolved, possibly due to interaction with the nuclear quadrupole or to exchange broadening resulting from intramolecular fluxional behaviour.

Vibrational Spectra of Trimethylsilylmethyl Compounds.—I.r. and, where possible, Raman spectra have been measured (see Tables 3 and 4) for the compounds and,

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* The Mo compound was originally believed to be $Mo(CH_2SiMe_3)_4$, ref. 1.

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[36] M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, 1969, **9**, 1060.

[37] E. C. Alyea and D. C. Bradley, *J. Chem. Soc.* (*A*), 1969, 2330.

TABLE 3

Infrared and Raman spectra of $ClCH_2SiMe_3$, $Sn(CH_2SiMe_3)_4$, and $Pb(CH_2SiMe_3)_4$

$ClCH_2SiMe_3$		$Sn(CH_2SiMe_3)_4$		$Pb(CH_2SiMe_3)_4$	
I.r. (cm^{-1}) [a]	Raman [b]	I.r. (cm^{-1}) [a]	Raman [b]	I.r. (cm^{-1}) [a]	Raman [b]
		2950	2958 (2)	2949vs	2955 (4)
		2930sh,vs			
		2890m	2894 (20)	2893s	2887 (8)
		2800sh,w		2800w	
		1925vw		1925vw	
		1850vw		1848vw	
		1460vw		1461vw	
		1440w	1451	1441w	
		1400m	1413 (2)	1401m	1415 (1)
		1358w	1364 (2)	1358w	1363 (3)
		1297w		1292w	
1278m					
1261sh	1265w	1260s	1261 (1)	1260vs	1262 (2)
1251vs	1256w	1248vvs	1249 (1)	1249vvs	1249 (2)
1175m	1181w				
1102m	1108w				
		1007vs	1003 (20)	990vs	993br (*ca.* 40)
		956m	971	945m	948 (2)
930w					
865sh		850vvs	856	850vvs	855 (2)
850vvs	*ca.* 854br,w	830vvs	835 (2)	830vvs	834 (2)
789m					
759s		758vs	758 (1)	760vs	758 (2)
742m [c]	744 (40) 0·48	720vs	727 (3)	714 vs	725 (7) p
700s [d]	704 (11) 0·80	686s	690 (12) dp	688s	691 (10) dp
		670sh	672 (<1)	670sh	
641s [e]	645 (6) 0·45				
		612w	613 (35) p	610sh	609 (20) p
581m	587 (100) 0·42	595s		595m	
		575m		579	
		510s	511 (15)		
			482 (100) p	475s	480 (20)
					456 (100) p
288s	291 (13) 0·58	282m	283 (4)	275m	270 (10)
			269 (4)		
234m	239 (45) 0·81	241m	247sh	241m	242sh
		230sh	234 (40)	230sh	230 (20) dp
	205 (60) 0·72		184 (20)		
			167 (20) p		164 (55) p
	128 (*ca.* 1)		118 (40)		106 (20)

[a] Liquid state. [b] Liquid, the numbers in parentheses are approximate estimates of the intensity of the lines. [c] νC–Cl. [d] νC–Si (E). [e] νSi–C (A_1).

TABLE 4

Infrared spectra of transition-metal trimethylsilylmethyl compounds [a]

$Cr(CH_2SiMe_3)_4$	$Mo_2(CH_2SiMe_3)_6$	$W_2(CH_2SiMe_3)_6$	$V(CH_2SiMe_3)_4$	$VO(CH_2SiMe_3)_3$
1257vs	1259s	1256s	1256s	1255s
1245vs	1244vs	1243vs	1245vs	1242s
	1165vw	*ca.* 1100vw	1118vw	*ca.* 1080vbr, w
	1092vw		1040vw	*ca.* 1012vbr, w
1015w	1015vw	1010vw	1020vw	
	945s	955s		988 [b]
900vs	932s	940s		920s
884vs	882s	887vs	880vvbr, vs	
				862vvs
835vvbr, vvs	835vvbr, vvs	840vvbr, vvs	840vvbr, vvs	829vvs
744vs	740vs	743vs	741vs	746m
730s	720sh	730sh	720s	720s
693vs	691s	695vs		
681vs	680vs	681vs	686vs	681s
669sh	669sh	669sh	669sh	
612m	616m	619m	612m	610w
		560sh		
536m	534w	550m		522s
515m	484s	490s	504s	468m
	ca. 440vw	455sh	430m	
279m	281m	275m	275m	
234m	253m	249m	242m	
	242sh	235m	232m	

[a] In mulls, CS_2 and benzene solutions. [b] V=O stretch.

for comparison purposes, the spectra of Me_3SiCH_2Cl and $(Me_3SiCH_2)_4M$ (M = Sn, Pb) are included. Several groups of bands appear in all of the spectra at nearly identical positions and may be assigned without ambiguity to $SiMe_3$ group vibrations.[38] Thus the $SiMe_3$ group remains largely unaffected in all these molecules and can be considered as an independent vibrating system. The characteristic bands appear at: (i) *ca.* 3000—2900 cm^{-1}, weak bands in both the i.r. and Raman for CH stretches of $-CH_3$ and, overlapping, $-CH_2-$; (ii) *ca.* 1400—1460 cm^{-1}, several medium to weak bands overlapping to some extent assignable as CH_3 deformations. The in-plane deformations of the $-CH_2-$ groups also occur here; (iii) *ca.* 1260—1240 cm^{-1}. All spectra show a strong sharp doublet in the i.r. This appears to be the characteristic[39] symmetric deformation of CH_3–Si which in Me_3Si groups has two components of unequal intensity. In the Raman, the corresponding line is rather weak and broad; (iv) *ca.* 950—800 cm^{-1}. The strong i.r. bands arise from methyl rocking vibrations probably coupled with Si–C stretches; they are useful in providing structural information. For Me_3Si the absorption is *ca.* 840 and 770 cm^{-1}; the bands are weak and broad in the Raman; (v) *ca.* 400—200 cm^{-1}. Here there are low-frequency modes involving the C_3–Si– angular motions.

There are some bands in the region *ca.* 1200—950 cm^{-1} which appear to be sensitive to the nature of X in XCH_2SiMe_3. Thus the bands of medium intensity at 1175 and 1102 cm^{-1} in $ClCH_2SiMe_3$ are shifted in the metal compounds to the 1000—880 cm^{-1} region and the frequencies are unique for each compound: the bands appear in $VO(CH_2SiMe_3)_3$ at 920 cm^{-1}; at 880 cm^{-1} as a very strong broad band in $V(CH_2SiMe_3)_4$; at 945, 932, and 882 cm^{-1} in $Mo_2(CH_2SiMe_3)_6$; at 900 and 884 cm^{-1} in $Cr(CH_2SiMe_3)_4$; at 990 and 954 cm^{-1} in $Pb(CH_2SiMe_3)_4$; at 1007 and 956 cm^{-1} in $Sn(CH_2SiMe_3)_4$. These *X*-sensitive bands are fundamentals involving largely the various $-CH_2-$ angular movements, predominately wagging and twisting. Assignments in the 750—400 cm^{-1} region are now discussed.

(a) *The lead and tin compounds.* When the CH_2SiMe_3 group is bound to a heavy metal, interaction with the perpendicular movement of the $SiMe_3$ ν_{asym} stretching mode occurs, and the degenerate *E* mode of the local C_{3v} symmetry is split into a doublet. The ν_{asym} Si–C doublets have the following values: $Pb(CH_2SiMe_3)_4$, 714, 688; $Sn(CH_2SiMe_3)_4$, 720, 686; $Cr(CH_2SiMe_3)_4$, 693, 681; $[Mo(CH_2SiMe_3)_3]_2$, 691, 680; $V(CH_2SiMe_3)_4$, 686; $[W(CH_2SiMe_3)_3]_2$, 681, 695; $VO(CH_2SiMe_3)_3$, 681 cm^{-1}. The two strong Raman counterparts appear in the spectra of the liquid Pb and Sn tetra-alkyl compounds. For $Pb(CH_2SiMe_3)_4$ the depolarization factors could be measured for the 725 and 691 cm^{-1} bands, the former being polarized and the latter depolarized thus showing a splitting of the *E* mode into two components, one of them strongly polarized.

The low-frequency spectra of the lead and tin tetra-alkyl compounds are very similar. Although their structure is unknown it is reasonable to assume that they are tetrahedral with site-group T_d for which we expect only one intense band (*F* mode) in the i.r. and in the Raman its depolarized counterpart, plus one very strong A_1 polarized line. Thus we assign the strong i.r. bands at 475 cm^{-1} (Raman, 480 cm^{-1}, dp) in $Pb(CH_2SiMe_3)_4$ and at 510 cm^{-1} (Raman 511 cm^{-1} dp) in $Sn(CH_2SiMe_3)_4$ to the Pb–C and Sn–C triply degenerate *F* mode, respectively, and the very strong and polarized lines at 456 cm^{-1} in the lead and 482 cm^{-1} in the tin compounds to the totally symmetric Pb–C and Sn–C stretching modes respectively.

The weak i.r. bands at 610 and 612 cm^{-1} in the lead and tin tetra-alkyls have strong and polarized Raman counterparts so that these frequencies can be assigned with certainty to the ν_{sym} Me_3SiCH_2. No other polarized band occurs.

The i.r. bands at 579 and 595 cm^{-1} in $Pb(CH_2SiMe_3)_4$ and 575 and 595 cm^{-1} in the tin analogue can be explained as combinations of fundamentals and such an assignment is quite satisfactory. The lowest Raman lines observed for the lead and tin compounds are strong and slightly asymmetric bands at *ca.* 106 and 118 cm^{-1} respectively. They doubtlessly represent a superposition of lines associated with the MC_4 angular skeletal movements and we thus tentatively assign the two bands at *ca.* 575 and 595 cm^{-1} in both molecules as combinations of the low-frequency fundamentals with the strong *F* metal–carbon mode.

(b) *The transition-metal compounds.* Very great difficulty in obtaining Raman spectra was experienced due to decomposition, absorption, and heating effects in the beam. However, comparison of the i.r. spectra with those of the tin and lead compounds allows tentative interpretation and support for structural proposals.

In the region above 600 cm^{-1} the i.r. spectra are essentially identical with those of the tin and lead species. Since the number of active metal–carbon vibrations is essential for assigning site symmetry we have assumed here that all bands in the 550—430 cm^{-1} region arise from metal–carbon modes and that no Si–C symmetric vibrations fall within this range. The description of the bands in this region as M–C vibrations is only approximate since they are likely to be coupled with CH_2SiC_3 vibrations. The low-frequency skeletal modes fall in the region 400—100 cm^{-1} and involve the various angular motions which are more difficult to identify with certainty. The bands around 300—200 cm^{-1} can be mainly associated with CH_2SiMe_3 angular motions by comparison with the i.r. spectrum of $ClCH_2SiMe_3$ and those below 200 cm^{-1} mainly with C–M–C and M–C–$SiMe_3$ angular movements.

$VO(CH_2SiMe_3)_3$. The two bands 468m, 522s cm^{-1} suggest C_{3v} symmetry and the former is assigned to the A_1 mode and the latter to the *E* mode of the V–C stretch.

$V(CH_2SiMe_3)_4$. Two i.r. bands are observed at 504 and 430 cm^{-1}. The low-frequency value of the latter

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[38] H. Bürger, *Organometallic Chem. Rev.*, 1968, **3**, 425.

[39] A. L. Smith, *Spectrochim. Acta*, 1960, **16**, 87.

suggests a totally symmetric A_1 vibration and this can be interpreted in terms of a C_{4v} square-pyramidal structure (active A_1 and E modes in the i.r.) with the unpaired electron occupying the apical position. A T_d structure distorted towards C_{4v} is also likely.

$Cr(CH_2SiMe_3)_4$. The i.r. has two medium bands at 515 and 536 cm^{-1}, respectively both in a mull and in solution. It seems reasonable to ascribe these bands to non-totally symmetric vibrations since the A_1 mode would probably occur at a lower frequency, as observed for the other compounds discussed above. A tetrahedral symmetry distorted along the C_2 axis, *i.e.*, D_{2d} site symmetry, is acceptable since two i.r.-active bands, B_2 and E, are to be expected.

$[Mo(CH_2SiMe_3)_3]_2$ and $[W(CH_2SiMe_3)_3]_2$. The solid-state spectra of these compounds are almost identical.

The X-ray structural data [29] indicate that the molecules have D_3 symmetry, which requires the following species for the M–C vibrations: A_1 (Raman), A_2 (i.r.), $2E$ (i.r. and Raman). The i.r. has three bands in the range as expected; for molybdenum, 440, 484, and 534 cm^{-1}. The two latter are probably the E modes and the first the A_2 mode. The only band that could be observed in the Raman due to the uncertain experimental conditions, *ca.* 440 cm^{-1}, is probably the strong A_1 mode which appears to be nearly coincident in frequency values with the A_2 mode.

We may make a simple MO treatment for these molecules. Defining the metal–metal vector as the z axis we may divide the metal d orbitals into three symmetry types. d_{z^2} has σ, d_{zx}, d_{yz} have π and $d_{x^2-y^2}$, d_{xy} have δ symmetry about the z axis. The Mo–Mo–C angle is *ca.* 90° and it is believed the metal–ligand bond has very little π character so we may deduce that the strength of bonding to the ligands and therefore the energies of the d orbitals lie in the order $\sigma \simeq \pi \ll \delta$. The d orbitals are also involved in metal–metal bonding so that we expect that the lowest energy d orbitals are σ- and π-metal–metal bonding orbitals which will accommodate the six d electrons of the two Mo^{3+} ions, yielding a molybdenum–molybdenum triple bond.

The staggered conformation arises from interligand repulsion, there being no electronic factor favouring the eclipsed form as there is in $Re_2Cl_8^{2-}$.[40a] In the latter compound the eclipsed form is stabilized by the existence of a fourth (δ) bond between the metal atoms. Such a bond would not in fact have the same effect in $[Mo(CH_2SiMe_3)_3]_2$ since in this compound with a three-fold symmetry axis the δ orbitals do not have their degeneracy lifted by ligand interactions.

This treatment must be regarded with some caution as it takes no account of interelectronic repulsions which may dominate the electronic structure of metal–metal bonds.[40b] There is indeed little π bonding to the ligands and the rather large $Si-CH_2-Mo$ and $Mo-Mo-CH_2$ angles (121·1 and 100·6°) probably result from steric factors due to the bulky Me_3Si groups.

Magnetic Properties of Paramagnetic Trimethylsilylmethyl Compounds.—The species $[Cr(CH_2SiMe_3)_4]^-$, $Cr(CH_2SiMe_3)_4$, and $V(CH_2SiMe_3)_4$ are paramagnetic and have been studied by bulk susceptibility and e.s.r. measurements.

$[Cr(CH_2SiMe_3)_4]^-$. This ion in THF solution has a magnetic moment of 3·7 B.M. measured by Evans' n.m.r. line-shift method at 308 K. The e.s.r. spectrum of the frozen solution was recorded at *ca.* 100 K. This showed a species having $S = \frac{1}{2}$, $g_{\parallel} = 2{\cdot}0 \pm 0{\cdot}05$, and $g_{\perp} = 3{\cdot}9 \pm 0{\cdot}1$. This is expected for a quartet state ($S = \frac{3}{2}$) having a very large zero-field splitting;[41] similar behaviour has been reported for the trigonal planar Cr^{III} compounds, $Cr(NPr^i_2)_3$.[42]

The tetrahedral ion $[Cr(CH_2SiMe_3)_4]^-$ has a ground term $^4T_1$ and is therefore closely analogous to the octahedral d^7 ion which has been analysed in detail.[43] The only modification required for application of this theory to tetrahedral d^3 is to change the sign of the spin–orbit coupling parameter. The detection of an e.s.r. spectrum at a temperature as high as 100 K indicates that the orbital triplet of the ground term must have been split by a distortion of the tetrahedron leaving an orbital-singlet ground state.

These observations may be translated into the formalism of ref. 43 by writing $\frac{3}{2} > \gamma > 1$ and $\delta \ll -\zeta$. We find that the ground state is $|M_s, 0\rangle$ and has $S = \frac{3}{2}$, $g = 2$, and D *ca.* $-\gamma^2\zeta^2/9\delta$. $\zeta(=3\lambda)$ is 273 cm^{-1} for the free chromium(III) ion[44] while $|\delta|$ will probably lie in the range 300—1000 cm^{-1} as it must be greater than ζ but will, presumably, be an order of magnitude smaller than the ligand-field splitting Δ which is known from the optical spectrum to be *ca.* 9000 cm^{-1}. We therefore calculate that D is *ca.* $+10$ cm^{-1} which is large enough to give the observed spectrum with its fictitious spin of $\frac{1}{2}$. There is also a low-lying ^2E term which is mixed with the ground state by spin–orbit coupling to give an additional contribution to D of $2\zeta^2/3\delta'$ where δ' is the energy of the θ component of ^2E, which is presumably split in the low symmetry.

If a trace of oxygen is present an additional intense line appears having $g = 1{\cdot}98 \pm 0{\cdot}02$. Bradley *et al.*,[42] report a similar line obtained when $Cr(NPr^i_2)_3$ is exposed to oxygen and attributed this to an unstable oxygen complex, which explanation also seems applicable to $[Cr(CH_2SiMe_3)_4]^-$. If more oxygen is admitted, the $g = 1{\cdot}98$ signal becomes even stronger and a new spectrum appears due to the oxidized compound, $Cr(CH_2SiMe_3)_4$.

$Cr(CH_2SiMe_3)_4$. In the solid state this compound has a magnetic moment of 2·89 B.M. at 296 K measured on a Gouy–Rankine balance. At room temperature

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[40a] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1967, **5**, 924.

[40b] C. K. Jørgenson, 'Absorption Spectra and Bonding in Complexes,' Pergamon, 1962, p. 207.

[41] J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, Cambridge, 1961, p. 349.

[42] D. C. Bradley, M. B. Hursthouse, and C. W. Newing, *Chem. Comm.*, 1971, 411.

[43] Ref. 41, pp. 360—363.

[44] A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions,' Oxford University Press, Oxford, 1970, p. 399.

the e.s.r. spectrum of a solution in petroleum or toluene consists of a single broad line with $g = 1{\cdot}993 \pm 0{\cdot}005$. When the solution is cooled, this line broadens and then splits into two lines which sharpen and move apart while a new line appears at *ca.* 1600 *g* until a well resolved spectrum is obtained (Figure 1, lower) which is typical of a triplet ($S = 1$) state with axial symmetry in a rigid matrix. Up to this point the line-shape variation closely resembles that predicted for a triplet species which is rotating slowly.[45] On further cooling, the apparent zero-field splitting continues to increase but the line width passes through a minimum of *ca.* 12·5 mT about 150 K and begins to rise while at the same time a new, narrow line appears having *g ca.* 2 (Figure 1 upper). If we consider the spectrum when the line width is a minimum, we find a spin Hamiltonian $\mathscr{H}_s = g\beta H . S + D(S_z^2 - S^2/3)$ where $g = 1{\cdot}989 \pm 0{\cdot}005$ and $D = 0{\cdot}053 \pm 0{\cdot}010$ cm^{-1}, which is similar to that found for FeO_4^{2-} ($g = 2{\cdot}0$; $D = 0{\cdot}09$ cm^{-1}) in the only reported single-crystal e.s.r. study of a distorted-tetrahedral d^2 system.[46]

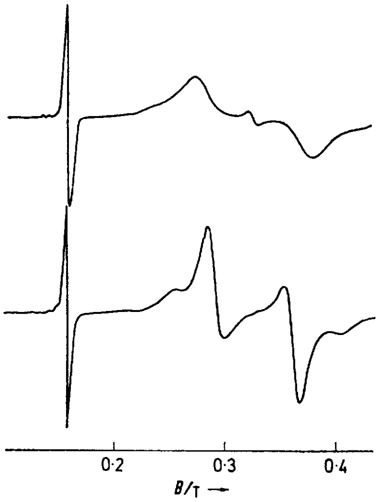

FIGURE 1 Electron spin resonance spectrum of $Cr(CH_2SiMe_3)_4$ in toluene; lower, 165 K; upper 100 K

Recently attempts have been reported to observe e.s.r. spectra of $Cr(OBu^t)_4$ and several compounds of the form $Cr(NR_2)_4$.[12a,33] No spectra were detected at 100 K or above, but at 10 K a spectrum was found for $Cr(OBu^t)_4$ which is quite unlike those of $Cr(CH_2SiMe_3)_4$ or other tetrahedral d^2 systems.[35,47] These results suggest either rapid spin–lattice relaxation and/or a large zero-field splitting, both of which are unexpected for a tetrahedral d^2 system which normally has an orbitally non-degenerate $^3A_2$ ground state.

$Cr(CH_2SiMe_3)_4$, like $[Cr(CH_2SiMe_3)_4]^-$ and $Cr(NPr^i_2)_3$,[48] yields a number of new species if exposed to a trace of oxygen. These all have $S = \frac{1}{2}$, *g ca.* 2, and an extensive hyperfine structure involving two, four, or seven ligand nuclei. Spin Hamiltonian parameters for mobile solution spectra are listed in Table 5. The anisotropic spectra in frozen solutions were generally masked by the much stronger $Cr(CH_2SiMe_3)_4$ spectrum, but a frozen solution spectrum of the species C has been obtained. This had $g_\parallel = 2{\cdot}008 \pm 0{\cdot}005$ and $g_\perp = 1{\cdot}977 \pm 0{\cdot}005$, while the ligand-hyperfine structure was almost isotropic. The isotropy of the splittings suggests that they are due to protons. The pairs (or sextets) of equivalent nuclei presumably being methylene protons of the trimethylsilylmethyl group.

TABLE 5

Spin Hamiltonian parameters for oxidation products of $Cr(CH_2SiMe_3)_4$

	g	a_1	a_2	a_2'	a_6	a_{Cr}
A	1·9836(3)	1·32(1)			0·50(1)	
B	1·9873(3)		0·96(1)	0·51(1)		
C	1·9869(3)		0·91(1)	0·57(1)		1·32(2)
D	1·9725(5)		0·66(1)			1·69(2)

a_{Cr} Is the hyperfine splitting due to ^{53}Cr and the a_i are due to ligand nuclei, the subscript *i* indicating the number of equivalent nuclei concerned. Hyperfine couplings are expressed in mT and the numbers in brackets are the errors in the last significant figure.

All these species are stable at 77 K but decay rapidly at room temperature, C having a half-life *ca.* 60 min and D *ca.* 10 min. C may also be destroyed by degassing a solution in which it has been detected. Relatively little is known about A and B as they have only been observed on one occasion each and no method for obtaining them at will has yet been discovered.

The species D is clearly differentiated from the others by its *g* factor, line-width, and instability. Furthermore D has never been observed unless either B or C is also present (Figure 2).

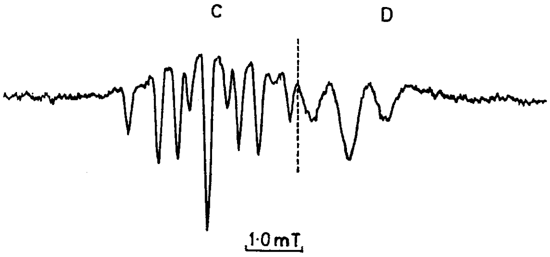

FIGURE 2 Second derivative e.s.r. spectrum of oxidation products C and D of $Cr(CH_2SiMe_3)_4$

There are no examples reported of chromium(III) having $S = \frac{1}{2}$, although this is, in principle, possible, so it seems probable that these species are chromium(V). Several compounds of the form $[CrOX_5]^{2-}$ have been studied by e.s.r.[49,50] and their spin Hamiltonians resemble those of the oxidation products of $Cr(CH_2SiMe_3)_4$.

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[45] J. R. Norris and S. I. Weissman, *J. Phys. Chem.*, 1969, **73**, 3119.

[46] A. Carrington, D. J. E. Ingram, K. A. K. Lott, D. S. Schonland, and M. C. R. Symons, *Proc. Roy. Soc.*, 1960, *A* **254**, 101.

[47] W. C. Holton, J. Schneider, and T. L. Estle, *Phys. Rev.*, 1964, **133***A*, 1638; A. Carrington, D. J. E. Ingram, D. S. Schonland, and M. C. R. Symons, *J. Chem. Soc.*, 1956, 4710.

[48] C. W. Chien, W. Kruse, D. C. Bradley, and C. W. Newing, *Chem. Comm.*, 1970, 1177.

[49] H. Kon and N. E. Sharpless, *J. Chem. Phys.*, 1965, **42**, 906.

[50] N. S. Garifyanov, S. E. Kamenev, and J. V. Ovchinnikov, *Zhur. fiz. Khim.*, 1969, **43**, 609, 611.

For example $[CrOCl_5]^{2-}$ has $g_{\parallel} = 2{\cdot}008$ and $g_{\perp} = 1{\cdot}974$ but this close agreement is probably fortuitous.

$V(CH_2SiMe_3)_4$. Solutions of this compound less than 10^{-3}M in petroleum show a typical vanadium(IV) spectrum of eight lines, with a g factor of $1{\cdot}968 \pm 0{\cdot}001$ and hyperfine coupling of $50 \pm 1 \times 10^{-4}$ cm^{-1}. On cooling, the lines broaden as the tumbling of the molecules becomes slow,[51] until at 100—120 K a rigid-matrix spectrum appears [Figure 3 lower]. We may measure $g_{\parallel} = 1{\cdot}974 \pm 0{\cdot}001$ and $A_{\parallel} = 111 \pm 1 \times 10^{-4}$ cm^{-1}, but it is impossible to obtain the remaining parameters $g_{\perp}$ and $A_{\perp}$. Further cooling leads to a new spectrum, which is rather poorly resolved [Figure 3 upper].

If the concentration is greater than 10^{-3}M, the mobile solution spectrum is broadened and on cooling the rigid-matrix stage is not observed. The very low temperature spectrum is only slightly concentration dependent.

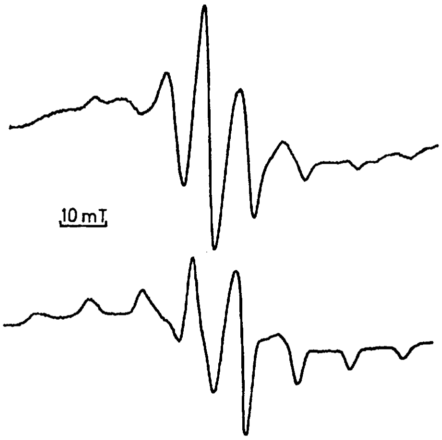

FIGURE 3 Electron spin resonance spectrum of $V(CH_2SiMe_3)_4$ 5×10^{-4}M in petroleum; lower, 105 K; upper, 95 K

It is apparent that the temperature dependence of the line-shape is very similar for $V(CH_2SiMe_3)_4$ and $Cr(CH_2SiMe_3)_4$. The low-temperature increase of line width may possibly be due to random small distortions in the environment of the metal ion,[52] presumably caused by interaction between the molecule and the solvent. Such distortions would be averaged out at higher temperatures and one might expect that at low enough temperatures they would be frozen and no further increase of line width would occur.

Solid $V(CH_2SiMe_3)_4$ at room temperature has a single very broad line [100 mT], which at 100 K becomes narrower [4 mT] and asymmetric. $g_{\perp} = 1{\cdot}99 \pm 0{\cdot}01$ and $g_{\parallel} < g_{\perp}$.

The mobile-solution spin Hamiltonian is comparable to that for $V(OBu^t)_4$,[53] but g is closer to the free-spin value and the hyperfine splitting is less. This may be attributed to the greater $e \longrightarrow t_2$ excitation energy of the alkyl, as shown by the visible spectrum, which implies stronger bonding and more extensive delocalization of the unpaired electron. The g factors calculated for the frozen solution and solid states are much too high to be compatible with the mobile-solution spectra, but this conflict is not very serious as we have already postulated that the spin Hamiltonian is rather sensitive to the surroundings of the molecule.

The magnetic moment has been measured by n.m.r. line shifts in benzene solution at 308 K and was 1·55 B.M., while in the solid a value of 1·30 B.M. was found using a Gouy–Rankine balance. Such low values are not unusual for vanadium(IV) compounds[54] and presumably indicate some form of intermolecular spin coupling.

EXPERIMENTAL

Microanalyses by Beller, Göttingen, Bernhard, Mülheim, and Imperial College Microanalytical Laboratories. Metal analyses were obtained using a Perkin-Elmer Atomic Absorption instrument model 303.

Spectroscopic Instruments.—Perkin-Elmer R-14 and Varian HA-100 n.m.r. spectrometers, Varian E-12 X-band e.s.r. spectrometer. I.r. spectra were recorded on a Perkin-Elmer model 325 spectrophotometer calibrated with polystyrene over the region 5000—200 cm^{-1}. Liquid samples were run as films between KBr plates and in standard liquid cells for the region 4000—450 cm^{-1} and between polyethylene plates in the region 450—200 cm^{-1}. Raman spectra were obtained in capillary tubes using a Cary model 81 spectrophotometer with a CRL 52M6 argon–krypton laser. Qualitative information on polarization was obtained by the method of polarized incident light.

Preparations.—All preparations and other operations were carried out in oxygen-free nitrogen or *in vacuo*. Chloromethyltrimethylsilane (Peninsular Chemrearch Inc.) was used as received. Solvents were dried and degassed before use. Petroleum used had b.p. 60—80° unless otherwise stated.

TABLE 6

Analytical data for trimethylsilylmethyl compounds

	Required			Found		
Compound	C	H	Metal	C	H	Metal
$C_{16}H_{44}Si_4V$	48·1	11·0	12·8	47·3	10·6	12·6
$C_{12}H_{33}OSi_3V$	43·9	10·1	15·5	44·3	9·8	15·3
$C_{16}H_{44}CrSi_4$	48·0	11·0	13·0	47·2	10·4	13·2
$C_{24}H_{66}Mo_2Si_6$	40·3	9·2	26·9	41·0	9·3	26·8
$C_{24}H_{66}Si_6W_2$	32·3	7·4	41·4	32·1	7·0	41·2

Analytical data is collected in Table 6. Chromatography was carried out using acid-washed alumina (Spencer Chemicals for Industry, Type H) and cellulose powder (Whatman CF-11). G.l.c. analyses were obtained using a Perkin-Elmer F-11 instrument with Kent Chromalog integrator, flame-ionization detector, and squalene columns.

Trimethylsilylmagnesium chloride was prepared in

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[51] M. S. Itzkowitz, *J. Chem. Phys.*, 1967, **46**, 3048.

[52] I. M. Brown, S. I. Weissman, and L. C. Snyder, *J. Chem. Phys.*, 1965, **42**, 1105.

[53] For spectra of this and also $V(OMe)_4$, $V(OEt)_4$, $V(NMe_2)_4$, and $V(NEt_2)_4$ see C. E. Holloway, F. E. Mabbs, and W. R. Smail, *J. Chem. Soc.* (*A*), 1968, 2980; E. C. Alyea and D. C. Bradley, *ibid.*, 1969, 2330; D. C. Bradley, R. H Moss, and K. D. Sales, *Chem. Comm.*, 1969, 1255.

[54] J. Selbin, *Chem. Rev.*, 1965, **65**, 153.

diethyl ether as *ca.* 1M solution;[55] the yields were over 90%. The lithium reagent was prepared in cyclohexane.[56] When specially pure reagent was required the solvent was stripped and the lithium alkyl sublimed (10^{-4} mmHg, 105°), re-dissolved in an appropriate solvent and standardized; g.l.c. tests of these solutions showed only traces of $(Me_3SiCH_2)_2$ and Me_4Si.

Tetrakis(*trimethylsilylmethyl*)*vanadium*(IV).—(a) *From* $VOCl_3$. To a solution of trimethylsilylmethylmagnesium chloride (300 mmol) in diethyl ether (250 ml) was added $VOCl_3$ (5 ml, 50 mmol) in diethyl ether (150 ml) dropwise at room temperature over *ca.* 1 h. The deep green solution was filtered through a frit, and the solvent was removed from the filtrate; the residue was extracted with petroleum giving a deep green solution. After concentration *in vacuo* to 200 ml, cooling to −78°, and collection at that temperature, the product was recrystallized from petroleum (150 ml) at −30° giving dark green *needles*, which were filtered cold, washed with chilled petroleum, and dried *in vacuo* (4 g, 20%).

(b) *From* VCl_4. To a solution of trimethylsilylmethyllithium (13 mmol) in petroleum (50 ml) was added VCl_4 (0·3 ml, 3 mmol) in petroleum (5 ml) at −78°. The mixture was stirred and slowly warmed to room temperature to give a green solution which was filtered, concentrated *in vacuo* to 20 ml, and cooled to −78°. The crystals were treated as above (yield, *ca.* 30%).

Oxotris(*trimethylsilylmethyl*)*vanadium*(V).—A green petroleum solution of $V(CH_2SiMe_3)_4$ (as obtained above before crystallization) was absorbed on a cellulose column and eluted slowly with petroleum under nitrogen. The green band initially formed turned yellow as it moved down the column. The eluate was collected, concentrated, and cooled to 0° to give yellow *needles* (*ca.* 50% based on VCl_4).

The Tetrakis(*trimethylsilylmethyl*)*chromate*(III) *Ion*.—To a suspension of $CrCl_3$,3THF (3·8 g, 10 mmol) in THF (100 ml) at −78°, was added dropwise, during 30 min, a freshly prepared solution of pure trimethylsilylmethyl-lithium (45 mmol) in THF (50 ml). An immediate reaction gave a blue-green solution which was allowed to warm to room temperature and filtered. The reaction appears to be essentially quantitative. Attempts to isolate crystalline salts by the addition of a variety of large cations were unsuccessful. The solution may be oxidized to $Cr(CH_2SiMe_3)_4$ in high yield by traces of air but this compound is best made as follows.

Tetrakis(*trimethylsilylmethyl*)*chromium*(IV).—To a suspension of $CrCl_3$,3THF (7·5 g, 20 mmol) in diethyl ether (150 ml), was added dropwise, during 15 min, trimethylsilylmethylmagnesium chloride (90 mmol) in diethyl ether (100 ml). The deep purple mixture was stirred for a further 30 min and then hydrolysed with saturated ammonium chloride solution (100 ml). After separation, the ether layer was dried ($MgSO_4$), decanted, and concentrated to *ca.* 20 ml. The solution was transferred to an alumina column and eluted with petroleum. The purple fraction was collected and concentrated to small volume when purple crystals of the *compound* were obtained by cooling at −78°. After chromatography the yield was *ca.* 2·5 g (30%). This petroleum solution is sufficiently pure for use in studies of reactions. The crude product can also be purified by sublimation at 30°, 10^{-4} mmHg.

Hexakis(*trimethylsilylmethyl*)*dimolybdenum*(III).—To a solution of trimethylsilylmethylmagnesium chloride (110 mmol) in diethyl ether (100 ml), was added $MoCl_5$ (5·4 g, 20 mmol) in diethyl ether (50 ml) at room temperature during 1 h; the mixture was then stirred for 5 h. After filtration and removal of the solvent, the brown oily residue was extracted with light petroleum (b.p. 30—40°) to give a dark brown solution. This was concentrated *in vacuo* to *ca.* 20 ml, transferred to an alumina column, and eluted with petroleum. The yellow fraction on slow concentration *in vacuo* gave crystals of the *compound* (1g, 15%).

Hexakis(*trimethylsilylmethyl*)*ditungsten*(III).—To a solution of trimethylsilylmethylmagnesium chloride (110 mmol) in diethyl ether (150 ml) was added a slurry of WCl_6 (10 g, 25 mmol) in diethyl ether (300 ml) at room temperature during 1 h with vigorous stirring. The green colour formed initially gradually turned red-brown. After being stirred for 2 h the solution was decanted and the solvent was removed. The brown oily residue was extracted with petroleum (b.p. 30—40°), concentrated *in vacuo* to *ca.* 30 ml, transferred to a cellulose column, and eluted with petroleum. Concentration of the red-brown fraction to *ca.* 30 ml and cooling to −40° gave light brown *crystals*. These were filtered off at −40°, washed with chilled petroleum, and dried *in vacuo* (2 g, 20%).

Lead and Tin Compounds.—These were prepared by published methods and had properties as described: $Sn(CH_2SiMe_3)_4$,[57] and $Pb(CH_2SiMe_3)_4$.[58] The purity was checked by analysis, m.p., and n.m.r. spectra.

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