Silylmethyl and Related Complexes. Part 6.[1] Preparation, Properties, and Crystal and Molecular Structure of Tris[bis(trimethylsilyl)methyl]-chromium(III); the Chemistry of Related Compounds of Titanium(III), Vanadium(III), Zirconium(IV), and Hafnium(IV) †

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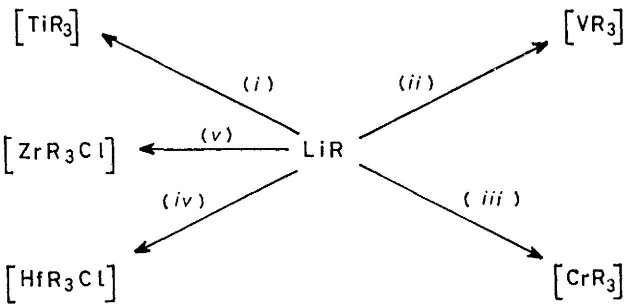
Interaction of Li[$CH(SiMe_3)_2$] in OEt_2 with respectively $CrCl_3$, VCl_3, [$TiCl_3(NMe_3)_2$] or $TiCl_4$, [$VCl_3(NMe_3)_2$], $ZrCl_4$, or $HfCl_4$ gives [MR_3] (M = Cr, V, or Ti) or [$M'R_3Cl$] [M' = Zr or Hf; R = $CH(SiMe_3)_2$] as crystalline products. The monomeric [CrR_3] is highly reactive, giving RH on hydrolysis or with glacial acetic acid, a maroon diamagnetic 1 : 1 adduct with NO {believed to be [$CrR_3(NO)$]}, and $\dot{C}Ph_3$ and a purple solid {believed to be [CrR_3Cl]} with CPh_3Cl. Crystals of [CrR_3] are bright emerald-green, extremely air-sensitive needles, elongated along *c*, in the trigonal space group *P*31*c* (confirmed by structure refinement) with unit-cell dimensions *a* = *b* = 16.120(5), and *c* = 8.793(2) Å, and trap solvent in the cavities of the lattice so formed. The molecule, which is confirmed as monomeric and three-co-ordinate, is non-planar, the Cr atom lying *ca.* 0.3 Å above the plane of the three alkyl carbon atoms [Cr–C 2.07(1) Å, C–Cr–C 117.6(4)°]. Full-matrix least-squares refinement using 548 independent intensities (200 K) has converged to *R* 0.067 (*R'* 0.075). Less detailed analytical and spectroscopic (but not *X*-ray) characterisation is provided for the other new transition-metal alkyls.

NEOPENTYL-type ligands have gained some prominence in recent transition-metal literature.[2] The main emphasis has been on [$CH_2(SiMe_3)$]$^-$, [CH_2Bu^t]$^-$, and variants on these themes, *e.g.* [$CH_2(SiMe_2Ph)$]$^-$ and [CH_2CMe_2Ph]$^-$. Thermally stable transition-metal alkyls derived from a secondary alkyl ligand are still unusual, although in Part 5 reference was made to [$CHPh_2$]$^-$.[1] However, the stabilisation of unusual valence states in main-group organometallic chemistry has been achieved using the bis(trimethylsilyl)methyl ligand [$CH(SiMe_3)_2$]$^-$ (or R$^-$), as in the crystalline MR_2 (M = Ge, Sn, or Pb)[3] and the hydrocarbon-solution-species PR_2,[4] AsR_2,[4] or MR_3 (M = Si, Ge, or Sn).[5]

We now report complementary results on homoleptic early transition-metal alkyls [MR_3] [R = $CH(SiMe_3)_2$; M = Ti, V, or Cr] and the chlorides [MR_3Cl] (M = Zr or Hf). A preliminary communication mentioned some of these findings,[6] and reference to the series of ligands [$CH_{3-n}(SiMe_3)_n$]$^-$ was made in the first of our publications in this area;[7] the compounds [$M(\eta\text{-}C_5H_5)_2R(Cl)$] (M = Zr or Hf) and [$M(\eta\text{-}C_5H_5)_2R$] (M = Ti or V) were described in Part 5.[1]

RESULTS AND DISCUSSION

The reaction of bis(trimethylsilyl)methyl-lithium, LiR, in diethyl ether and a suspension of the appropriate metal chloride, or solution of the metal chloride–amine adduct, afforded the new metal alkyls as shown in Scheme 1. All these compounds are exceedingly moisture- and oxygen-sensitive. Furthermore, they have a very high solubility in hydrocarbons, no doubt due to the hydrophobic sheath of methyl groups. Purification presented a considerable problem, and low-temperature crystallisation from an alkane was adopted; hence the reported yields, which refer to purified products, are often low.



SCHEME 1 Reactions of Li[$CH(SiMe_3)_2$] (LiR) with some anhydrous transition-metal chlorides. (*i*) [$TiCl_3(NMe_3)_2$] or $TiCl_4$; (*ii*) [$VCl_3(NMe_3)_2$]; (*iii*) $CrCl_3$; (*iv*) $HfCl_4$; (*v*) $ZrCl_4$

Similar experiments were carried out with LiR and

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† No reprints available.

[1] Part 5, J. L. Atwood, G. K. Barker, J. Holton, W. E. Hunter, and M. F. Lappert, *J. Amer. Chem. Soc.*, 1977, **99**, 6645.

[2] *Cf.* P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, **7**, 209; *Chem. Rev.*, 1976, **76**, 219.

[3] P. J. Davidson, D. H. Harris, and M. F. Lappert, *J.C.S. Dalton*, 1976, 2268.

[4] M. J. S. Gynane, A. Hudson, M. F. Lappert, P. P. Power, and H. Goldwhite, *J.C.S. Chem. Comm.*, 1976, 623.

[5] A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Dalton*, 1976, 2369.

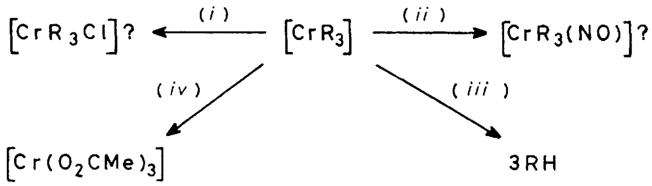
[6] G. K. Barker and M. F. Lappert, *J. Organometallic Chem.*, 1974, **76**, C45.

[7] M. R. Collier, M. F. Lappert, and M. M. Truelock, *J. Organometallic Chem.*, 1970, **25**, C36.

$NbCl_5$, $TaCl_5$, $MoCl_5$, WCl_6, $MnCl_2$, $FeCl_3$, or CuI, but crystalline products were not isolated although reactions did take place. The choice of the lithium reagent LiR may have disadvantages; partly because it is probably a stronger reducing agent than, for example, $Li[CH_2(SiMe_3)]$. Experiments, now in hand,[8] using the Grignard reagent $[Mg\{CH(SiMe_3)_2\}Cl]$ may provide a further range of compounds.

It is interesting that, using $Li[CH_2(SiMe_3)]$(LiR′), each of the metal chlorides mentioned in Scheme 1 or YCl_3 gave $[YR'_3(thf)_2]$(thf = tetrahydrofuran),[9] or $[MR'_4]$ (M = Ti from $TiCl_4$,[10] Zr,[10] Hf,[10], V,[11] or Cr [11]). It thus appears that with the sterically demanding ligands $[CH(SiMe_3)_2]$ (R^-) and $[CH_2(SiMe_3)]^-$ (R'^-) the metal co-ordination number in the derived compound is dependent on the nature of the ligand: three-co-ordination is often preferred with the more bulky R^-, and four-co-ordination usually with the less bulky R'^-. It is, of course, rare in transition-metal chemistry that the geometry of a metal compound is not influenced by the electronic configuration of the metal (Scheme 1 shows d^0, d^1, d^2, and d^3 compounds). However, homoleptic [bis(trimethylsilyl)amido]transition-metal compounds $[M\{N(SiMe_3)_2\}_3]$ have been much studied, notably by Bürger and Bradley and their co-workers, and Hursthouse and his group have *X*-ray data on many of these unusual three-co-ordinate compounds; when M is a d^1—d^5 first-row element, the compounds have a coplanar MN_3 skeleton (*cf.* ref. 12).

The reactions of the Group 4 metal(IV) chlorides are interesting, leading to reduction of $TiCl_4$ to $[TiR_3]$ or substitution for the heavier MCl_4 congeners yielding $[MR_3Cl]$ (M = Zr or Hf) but no tetrakis(alkyl). It seems that a three-co-ordinate alkyl can tolerate (in the steric sense) a fourth co-ligand (see also Scheme 2) provided that it is small. The greater ease of $M^{IV} \longrightarrow M^{III}$ reduction for M = Ti rather than Zr or Hf is well known, and is parallelled in reactions of $[M(\eta\text{-}C_5H_5)_2Cl_2]$ with LiR giving $[M(\eta\text{-}C_5H_5)_2R]$ for M = Ti or V, but $[M(\eta\text{-}C_5H_5)_2R(Cl)]$ for M = Zr or Hf.[1]



SCHEME 2 Aspects of the chemistry of $[Cr\{CH(SiMe_3)_2\}_3]$ ($[CrR_3]$). (*i*) Ph_3CCl, $-CPh_3$ (e.s.r.); (*ii*) NO; (*iii*) aqueous HCl; (*iv*) $MeCO_2H$, $-3RH$

Because of the aerobic sensitivity mentioned above, analysis of the compounds was often conveniently carried out by hydrolysis with dilute aqueous hydrogen chloride, when bis(trimethylsilyl)methane was the sole organic product. This and other reactions of the alkylchromium(III) compound are shown in Scheme 2. The reaction with NO has a parallel; green $[Cr\{N(SiMe_3)_2\}_3]$ similarly yields red, diamagnetic, low-spin d^2 $[Cr\{N(SiMe_3)_2\}_3(NO)]$.[13] Satisfactory crystals of red diamagnetic $[CrR_3(NO)]$ [ν(NO) at 1 672 cm^{-1}] or purple $[CrR_3Cl]$ {ν(CrCl) at 475 cm^{-1}; and $\dot{C}Ph_3$, identified by e.s.r., as the coproduct; *cf.*[11] blue $[CrR'_4]$} have not yet been obtained. However, these experiments support the suggestion made in the preceding paragraph that a small fourth co-ligand can be accommodated, together with three R groups, within the inner co-ordination sphere of a transition metal.

Steric effects are further manifested by the lack of reactivity between $[CrR_3]$ and either CO_2 or $NH(SiMe_3)_2$. Reactive metal alkyls usually undergo carbonation with the former reagent and are expected to yield RH with a protic species.

The colours of the homoleptic metal alkyls $[MR_3]$ are similar to those of the isoelectronic amides $[M\{N(SiMe_3)_2\}_3]$:[12] M = Ti, blue-green (amide, bright blue [14]); M = V, bright blue-green (amide,[12] brown); and M = Cr, bright green (amide,[12] bright green). The chromium alkyl has u.v. bands ($\lambda_{max.}$ in nm, ε in dm^3 mol^{-1} cm^{-1} in parentheses; in C_6H_{12}) at 227 (3×10^4), 266 (1.5×10^4), and 394 (1×10^4) compared with 298 (2.8×10^3), 318 (3.7×10^3), and 395 (3.7×10^3) for $[Cr\{N(SiMe_3)_2\}_3]$ in cyclohexane.[14] These are probably due to charge-transfer and ligand–ligand transitions.

A toluene solution of $[Cr\{CH(SiMe_3)_2\}_3]$ under strictly anaerobic conditions gave no detectable e.s.r. signal at 20 °C. However, if dry air was admitted into the system a very intense multiplet was observed at *g ca.* 2.0, attributed to a dioxygen compound. On cooling to −100 °C, a further pure specimen of $[CrR_3]$ in toluene under anaerobic conditions showed two broad lines at *g ca.* 2.0 and *ca.* 3.9. By analogy with e.s.r. results for $[Cr\{N(SiMe_3)_2\}_3]$, these signals are assigned to $g_\perp$ and $g_\parallel$ (found at *ca.* 2.0 and *ca.* 4.0 in the amide and interpreted in terms of a trigonal crystal field for a d^3 configuration).[15] The specimen believed to be $[CrR_3(NO)]$ gave no e.s.r. absorption in toluene at −100 °C. A solution of $[TiR_3]$ in toluene at 20 °C gave a strong signal at *g* 1.968; this was an asymmetric quartet, attributed to hyperfine coupling [*a*(H) 6 G] * with three equivalent α protons. The *g* value is in the range expected for Ti^{III}; *e.g.* $[Ti\{N(SiMe_3)_2\}_3]$ has $g_{av.}$ at 1.911.[15] The vanadium(III) alkyl showed no e.s.r. absorption, whether as solid or as a frozen solution in toluene.

The magnetic susceptibility of the chromium(III) alkyl

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* Throughout this paper: 1 G = 10^{-4} T; 1 B.M. ≈ 9.27×10^{-24} A m^2.

[8] J. Jeffery and M. F. Lappert, unpublished work.

[9] M. F. Lappert and R. Pearce, *J.C.S. Chem. Comm.*, 1973, 126.

[10] Part 1, M. R. Collier, M. F. Lappert, and R. Pearce, *J.C.S. Dalton*, 1973, 445.

[11] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

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[13] D. C. Bradley, M. B. Hursthouse, C. W. Newing, and A. J. Welch, *J.C.S. Chem. Comm.*, 1972, 567.

[14] E. C. Alyea, D. C. Bradley, R. G. Copperthwaite, and K. D. Sales, *J.C.S. Dalton*, 1973, 185.

[15] D. C. Bradley, R. G. Copperthwaite, S. A. Cotton, K. D. Sales, and J. F. Gibson, *J.C.S. Dalton*, 1973, 191.

corresponded to *ca.* 3.8 B.M. at 20 °C by (average from three determinations) the Gouy balance method for the crystalline material and *ca.* 3.3 B.M. in solution [3.25 at 35 °C (average from three measurements)] by ^{1}H n.m.r. The latter value showed insignificant variation over the range −63 to 35 °C. This may be compared with a temperature-invariant (−150 to 25 °C) value [14] of 3.7(2) (crystal) or 3.74 B.M. ($C_6H_{11}Me$ solution) for $[Cr\{N(SiMe_3)_2\}_3]$. These results are appropriate for a spin-only value corresponding to three unpaired spins.

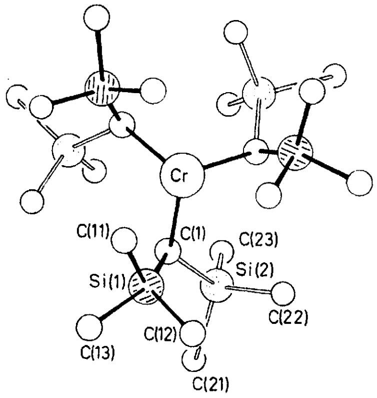

FIGURE 1 Molecular structure of $[Cr\{CH(SiMe_3)_2\}_3]$ with hydrogen atoms omitted, showing the atomic numbering sequence. The unlabelled atoms are symmetry related to the labelled atoms

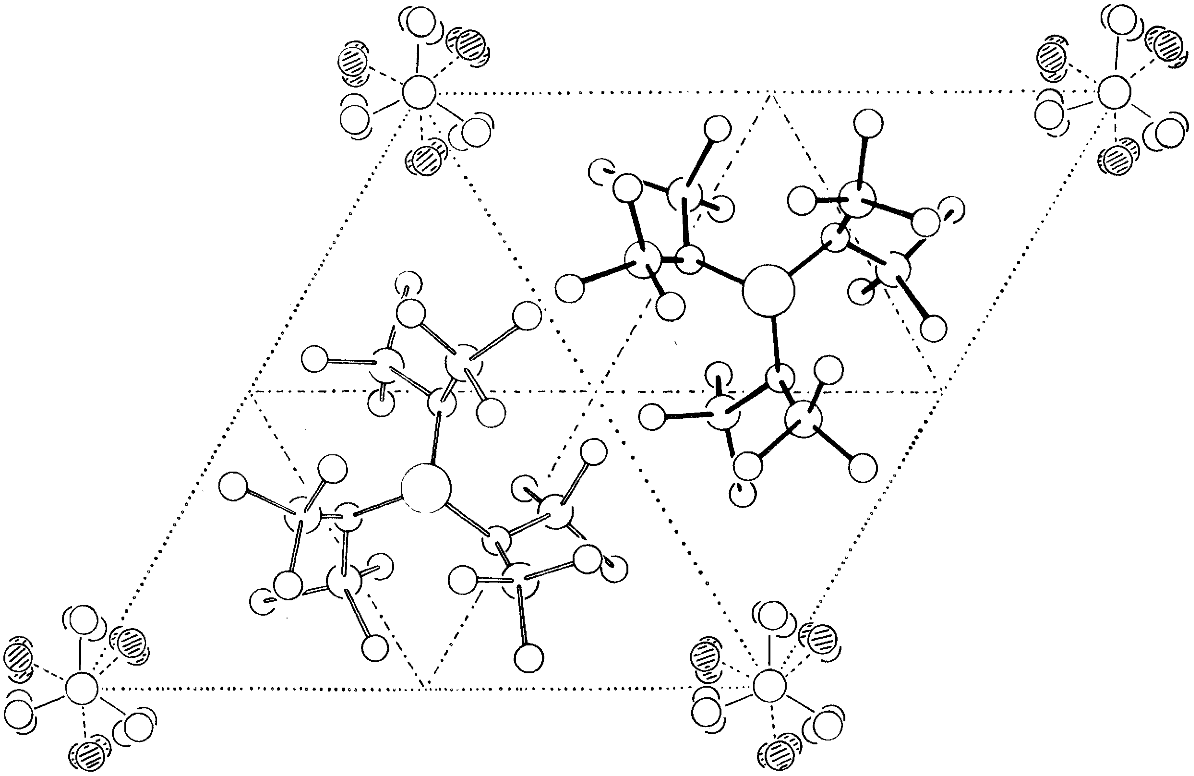

FIGURE 2 Unit-cell contents viewed down the unique axis *c* towards the origin. Open circles indicate solvent atoms lying at *z*, hatched circles those at *z* + ½ respectively. Atoms lying on the C_3 axis through the origin are shown as one ' atom ' only

The chromium(III) alkyl gave a solution molecular weight (cryoscopy in C_6H_6) corresponding to the monomer (Found: *M* 498. $C_{21}H_{57}CrSi_6$ requires *M* 530). Mass spectra of each of the compounds were uninformative, thermal decomposition occurring on attempted sublimation into the mass-spectrometer inlet.

The solution i.r. spectra showed features attributable to vibrations associated with the $CH(SiMe_3)_2$ ligand. Apart from the compound supposed to be $[CrR_3(NO)]$ [ν(NO) at 1 672 cm^{-1}], diagnostic features were found only below *ca.* 500 cm^{-1}. The chlorides $[MR_3Cl]$ had ν(MCl) bands (in n-C_6H_{14}) at 475 (M = Cr), 368 (Zr), or 350 cm^{-1} (Hf). Metal–carbon stretching modes were found at 403 and 432 ($[TiR_3]$), 400 and 460 ($[VR_3]$), 403 and 449 ($[CrR_3]$), 415 and 443 ($[ZrR_3Cl]$), and 414 and 424 cm^{-1} ($[HfR_3Cl]$); the presence of two vibrations suggests a non-planar MC_3 skeleton.

The diamagnetic compounds showed the expected singlets for each of $Si(CH_3)_3$ (τ 9.5—9.6) and C*H* (*e.g.* τ 8.8 for $[ZrR_3Cl]$) in the ^{1}H n.m.r. spectra (in C_6D_6).

Molecular Structure of $[Cr\{CH(SiMe_3)_2\}_3]$.—The overall molecular structure, omitting H atoms, with the atomic-numbering sequence is shown in Figure 1, the unit-cell contents in Figure 2, and internuclear distances and angles in Table 1. The three-co-ordinate nature of the compound has been confirmed and, unlike the triamido-compounds,[16,17] it is non-planar. The deviation from

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

[17] D. C. Bradley, M. B. Hursthouse, and D. F. Rodesiler, *Chem. Comm.*, 1969, 14.

TABLE 1

Bond lengths (Å) and angles (°) for $[Cr\{CH(SiMe_3)_2\}_3]$ with estimated standard deviations in parentheses

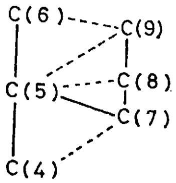
(*a*) Non-hydrogen atoms

Cr–C(1)	2.07(1)	C(1)–Cr–C(1′) [a]	117.6(4)
C(1)–Si(1)	1.87(1)	Si(1)–C(1)–Si(2)	118.2(6)
C(1)–Si(2)	1.87(1)	Cr–C(1)–Si(1)	113.5(6)
		Cr–C(1)–Si(2)	116.8(9)
Si(1)–C(11)	1.88(1)	C(11)–Si(1)–C(12)	107.8(7)
Si(1)–C(12)	1.89(2)	C(12)–Si(1)–C(13)	106.4(9)
Si(1)–C(13)	1.89(2)	C(13)–Si(1)–C(11)	107.0(8)
Si(2)–C(21)	1.88(2)	C(21)–Si(2)–C(22)	107.2(6)
Si(2)–C(22)	1.86(2)	C(22)–Si(2)–C(23)	109.8(9)
Si(2)–C(23)	1.86(2)	C(23)–Si(2)–C(21)	104.1(9)

(*b*) Hydrogen atoms [b]

C(1)–H(1)	1.44	Si(1)–C(1)–H(1)	82
		Si(2)–C(1)–H(1)	108
		Cr–C(1)–H(1)	112
C(11)–H(111)	0.94	H(111)–C(11)–H(112)	111
C(11)–H(112)	0.96	H(112)–C(11)–H(113)	105
C(11)–H(113)	0.99	H(113)–C(11)–H(111)	106
C(12)–H(121)	0.94	H(121)–C(12)–H(122)	119
C(12)–H(122)	0.86	H(122)–C(12)–H(123)	105
C(12)–H(123)	0.92	H(123)–C(12)–H(121)	116
C(13)–H(131)	0.83	H(131)–C(13)–H(132)	85
C(13)–H(132)	1.18	H(132)–C(13)–H(133)	129
C(13)–H(133)	0.94	H(133)–C(13)–H(131)	95
C(21)–H(211)	1.20	H(211)–C(21)–H(212)	100
C(21)–H(212)	1.03	H(211)–C(21)–H(213)	108
C(21)–H(213)	0.93	H(212)–C(21)–H(213)	108
C(22)–H(221)	0.90	H(221)–C(22)–H(222)	113
C(23)–H(222)	0.94	H(221)–C(22)–H(223)	112
C(22)–H(223)	1.03	H(222)–C(22)–H(223)	106
C(23)–H(231)	1.09	H(231)–C(23)–H(232)	117
C(23)–H(232)	1.01	H(231)–C(23)–H(233)	83
C(23)–H(233)	0.85	H(232)–C(23)–H(233)	96

(*c*) Solvent atoms [c]



C(4)–C(5)	1.30	C(7)–C(5)–C(7′)	112
C(5)–C(6)	1.12	C(4)–C(5)–C(8)	94
C(5)–C(7)	1.54	C(4)–C(5)–C(7)	74
C(5)–C(8)	1.68	C(7)–C(5)–C(8)	27
C(4)–C(7)	1.72	C(7)–C(5)–C(8′)	138
C(7)–C(9)	1.22	C(7)–C(5)–C(8″)	101
C(7)–C(8)	0.77	C(5)–C(8)–C(6)	34
C(8)–C(9)	0.64	C(5)–C(8)–C(9)	94
C(6)–C(9)	1.72	C(8)–C(6)–C(8′)	96
C(6)–C(8)	1.95	C(8)–C(6)–C(9)	18
		C(8)–C(6)–C(9′)	111
		C(8)–C(6)–C(9″)	103

[a] C(*n*′) indicates a symmetry-related atom. [b] Positional parameters were not refined, therefore no estimated standard deviations are given. [c] The relation of the atoms and the C_3 axis through 0,0,0 [C(4)] is as follows: C(*n*′) and C(*n*″) indicate the atoms situated at the other two equivalent positions related by the three-fold axis through the origin.

planarity (0.32 Å), although small, is nonetheless significant and the orientation of the trimethylsilyl groups is such that any intermolecular contacts are minimised. The closest approach of hydrogen atoms, which occurs between two symmetry-related ligands on the same Cr atom, and based on the unrefined atomic co-ordinates of the hydrogen atoms, is 2.1 Å [H(223) and H(132)].

The previously studied triamido-compounds are planar, except for those of Eu and Sc [12] where a heavy-metal disorder is proposed for the solid,[18] giving rise to an essentially pyramidal molecule. There exists, however, the possibility of π interaction between $M-\ddot{N}$ or $\ddot{N}-Si$ in these complexes,[12] whereas if we assume not to have lost the α-hydrogen atoms then no such possibility exists for the title compound.

The Cr–C separation [2.07(1) Å] compares well with that found in $[Cr\{CH_2(SiMe_3)\}_4]$ [2.05(2) Å],[19] and is not vastly different from the values reported for Cr–C(sp^2) in $[Cr\{CH_2(SiMe_3)\}(bipy)_2]$ of 2.107(9) Å,[20] where the ligand $CH_2(SiMe_3)$ lies *trans* to bipyridyl and the compound is octahedral. The C–Cr–C angle (117°) is consistent with a slightly distorted planar configuration. The mean Si-C(Cr) separation [1.87(1) Å] is in accord with the few known values, *e.g.*[21] 1.90 Å (mean) in $[Cr(CO)_5\{Ge[CH(SiMe_3)_2]_2\}]$ and likewise the C-Si-C angles (107° mean) compared with [21] 108° in $[Cr(CO)_5\{Ge[CH(SiMe_3)_2]_2\}]$. Similarly, the Si–$CH_3$ bond lengths [mean 1.88(2) Å] are in good agreement with 1.8 Å (mean) in $[\{Cu[CH_2(SiMe_3)]\}_4]$.[22] The Si-C(1)-Si angle is much larger than tetrahedral (118°, *cf.*[23] 115° in $[Cr(CO)_5\{Ge[CH(SiMe_3)_2]_2\}]$), presumably to minimise methyl–hydrogen interaction within each ligand itself, and the tilt of the CSi_2 plane to the CrC_3 plane (57°) reduces contacts between symmetry-related ligands on the same metal atom. The α-hydrogen atoms have been included in the calculations at a position located from the electron-density map, but are unrefined and hence the angles around C(1) appear rather distorted tetrahedral.

As stated below, the ' solvent ' atoms cannot be organised into any obvious geometry, hence their parameters are presented without comment.

EXPERIMENTAL

Manipulative procedures, solvent purification, and synthetic methods including the synthesis of $CHCl(SiMe_3)_2$ have been described previously.[3,10] The compounds $[TiCl_3(NMe_3)_2]$ and $[VCl_3(NMe_3)_2]$ were prepared by published methods.[23] Electronic spectra were obtained using a Cary 14 spectrometer, e.s.r. spectra with a Varian E3 instrument, magnetic moments in solution by Evans' ^1H n.m.r. method,[24] and i.r. (Perkin-Elmer 457), ^1H n.m.r. (Varian HA100), and ^{13}C n.m.r. (Jeol PFT100) spectra with standard instrumentation.

Preparation.—Tris[bis(trimethylsilyl)methyl]chromium(III). Bis(trimethylsilyl)methyl-lithium (4.5 mmol) in diethyl ether (12 cm^3) was added dropwise to a suspension of chromium(III) chloride (0.235 g, 1.5 mmol) in diethyl

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[19] V. Gramlich and K. Pfefferkorn, *J. Organometallic Chem.*, 1973, **61**, 247.

[20] J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, *J.C.S. Dalton*, 1973, 1497.

[21] M. F. Lappert, S. J. Miles, P. P. Power, A. J. Carty, and N. J. Taylor, *J.C.S. Chem. Comm.*, 1977, 458.

[22] Part 4, J. A. J. Jarvis, R. Pearce, and M. F. Lappert, *J.C.S. Dalton*, 1977, 999.

[23] M. W. Duckworth, G. W. A. Fowles, and P. T. Greene, *J. Chem. Soc.* (*A*), 1967, 1592.

[24] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

ether (40 cm^3) at -78 °C. The solution changed from brown to green as the mixture was allowed to warm slowly to room temperature. After stirring for 2 h, volatiles were removed *in vacuo*, and the residue was extracted with n-hexane (60 cm^3) and filtered to give a deep green solution. This was concentrated (to *ca.* 20 cm^3) and cooled to -20 °C giving bright green *crystals* (0.56 g, 71%) (Found: C, 47.3; H, 11.0; Cr, 10.0; Si, 31.4. $C_{21}H_{57}CrSi_6$ requires C, 47.6; H, 10.8; Cr, 9.8; Si, 31.8%).

Tris[bis(trimethylsilyl)methyl]titanium(III). Bis(trimethylsilyl)methyl-lithium (10.0 mmol) in diethyl ether (26 cm^3) was added dropwise to a solution of $[TiCl_3(NMe_3)_2]$ (0.503 g, 3.26 mmol) in diethyl ether (20 cm^3) at -60 °C. On warming slowly to room temperature a blue-black solution was formed from which, after stirring for 2 h, all the volatiles were removed. The resulting blue-green oil was extracted with n-hexane (30 cm^3) to give a dark green solution. This was concentrated (to *ca.* 10 cm^3) and cooled to -20 °C, whereupon blue-green crystals of the product (0.1 g, 6%) were deposited. The compound was found to be extremely sensitive to handling and it was impossible to prepare a sample for elemental analysis. Hydrolysis, with dilute acid, of a portion (0.033 5 g) in an n.m.r. tube gave bis(trimethylsilyl)methane (0.213 mmol by ^{1}H n.m.r. using a PhMe solution in benzene as calibrant. $C_{21}H_{57}Si_6Ti$ requires 0.20 mmol).

Tris[bis(trimethylsilyl)methyl]vanadium(III). Bis(trimethylsilyl)methyl-lithium (7.3 mmol) in diethyl ether (11 cm^3) was added dropwise to a solution of $[VCl_3(NMe_3)_2]$ (0.665 g, 2.4 mmol) at -60 °C. The solution changed from purple to green and was allowed to warm to room temperature. After stirring (2 h) all the volatiles were removed to give a green oil which was extracted with n-hexane (30 cm^3) and filtered. Concentration of the resulting green solution and cooling to -20 °C gave bright blue-green *crystals* (0.18 g, 14%) (Found: C, 46.4; H, 10.5. $C_{21}H_{57}Si_6V$ requires C, 47.7; H, 10.8%). The crystals were extremely sensitive to handling and readily became contaminated with a black tar.

Tris[bis(trimethylsilyl)methyl]chlorozirconium(IV). Bis(trimethylsilyl)methyl-lithium (16.4 mmol) in diethyl ether (35 cm^3) was added dropwise to a slurry of zirconium(IV) chloride (1.27 g, 5.5 mmol) in diethyl ether (30 cm^3) at room temperature. The resulting white slurry was stirred for 24 h, whereafter volatiles were removed *in vacuo* yielding an off-white powder. Extraction with *n*-hexane (40 cm^3) gave a pale yellow solution which was filtered, concentrated, and cooled to -20 °C, yielding white *crystals* (1.5 g, 45%) (Found: C, 41.5; H, 9.5; Cl, 6.0; Zr, 15.5. $C_{21}H_{57}ClSi_6Zr$ requires C, 41.7; H, 9.5; Cl, 5.9; Zr, 15.1%).

Tris[bis(trimethylsilyl)methyl]chlorohafnium(IV). Bis(trimethylsilyl)methyl-lithium (17.6 mmol) in diethyl ether (28 cm^3) was added dropwise to a slurry of hafnium(IV) chloride (1.92 g, 6.0 mmol) in diethyl ether (30 cm^3) at room temperature. The resulting cloudy yellow solution was stirred for 24 h. Volatiles were removed *in vacuo* yielding a pale yellow oily solid. Extraction with n-hexane (30 cm^3) and filtration yielded a pale yellow solution which was concentrated and cooled to -20 °C, yielding white *crystals* (2.2 g, 53%) (Found: C, 36.2; H, 8.5; Cl, 5.4; Hf, 26.1. $C_{21}H_{57}ClHfSi_6$ requires C, 36.4; H, 8.3; Cl, 5.1; Hf, 25.8%).

Attempted Preparations.—Tris[bis(trimethylsilyl)methyl]-scandium(III) *or -lanthanum*(III). Typically, $Li[CH(SiMe_3)_2]$ (3 mol) in diethyl ether was added to a stirred slurry of the metal(III) chloride (1 mol) in toluene at room temperature. Stirring was continued for up to 1 week. Volatiles were removed *in vacuo* and the resulting solid was extracted with toluene. Filtration followed by concentrating and cooling of the resulting solution to -20 °C yielded, in both cases, white crystals identified by their n.m.r. spectra as being those of $Li[CH(SiMe_3)_2]$.

Other homoleptic transition-metal alkyls using $Li[CH(SiMe_3)_2]$. Typically, $Li[CH(SiMe_3)_2]$ was added dropwise to a slurry of the metal halide in diethyl ether at -78 °C. The resulting mixture was then allowed to warm to room temperature and stirring was continued until no further colour change was observed. Following the standard work-up procedure described previously, no crystalline product was obtained from reactions with $NbCl_5$, $TaCl_5$, $MoCl_5$, WCl_6, $MnCl_2$, $FeCl_3$, or CuI.

Reactions of $[Cr\{CH(SiMe_3)_2\}_3]$.—(*a*) *With nitrogen monoxide*. Typically, $[Cr\{CH(SiMe_3)_2\}_3]$ (0.126 g, 0.24 mmol) was dissolved in n-hexane (10 cm^3) and NO (0.24 mmol) was condensed in at -196 °C. The mixture was then allowed to warm to room temperature with stirring. The original green solution rapidly darkened, changing from brown through to brick-red and after 30 min all the volatiles were removed to give a diamagnetic maroon solid. Attempts to recrystallise this from n-hexane failed, and the compound was unstable over long periods in solution, depositing a brown solid. A solution i.r. spectrum gave ν(NO) at 1 672 cm^{-1}. We believe that the species formed in this reaction is $[CrR_3(NO)]$.

(*b*) *With trityl chloride*. The compound $[CrR_3]$ (0.390 g, 0.74 mmol) was dissolved in n-hexane (10 cm^3) and solid trityl chloride (0.205 g, 0.75 mmol) was added with stirring at room temperature. Over a period of 6 h the solution changed from deep green through brown to purple. On removal of the volatiles *in vacuo* a purple solid was formed which could not be crystallised. An i.r. spectrum of the solid (in n-hexane) showed ν(CrC) at 390 and 450 cm^{-1} and a band at 475 cm^{-1} attributed to ν(CrCl). A similar experiment performed in an e.s.r. tube showed the formation of $\dot{C}Ph_3$ as the reaction proceeded.

(*c*) *With various reagents*. Mixing the chromium(III) alkyl (in n-hexane) and hexamethyldisilazane or carbon dioxide gave no indication that reaction had occurred, and after work-up the chromium(III) alkyl was recovered in good yield.

Reactions of a Metal(III) *Alkyl with Protic Reagents*.—(*a*) *Aqueous hydrogen chloride*. Quantitative hydrolyses were carried out by allowing a known weight of the compound to react in dilute aqueous hydrogen chloride at *ca.* 20 °C. The bis(trimethylsilyl)methane which instantly formed was extracted as an upper layer in a separating funnel into a known concentration of toluene in benzene (typically, 0.449 mmol PhMe in 1 cm^3 of C_6H_6). The amount of $CH_2(SiMe_3)_2$ formed was determined by ^{1}H n.m.r. spectroscopy, by integration of the $Si(CH_3)$ and $PhCH_3$ resonances.

(*b*) *Glacial acetic acid*. A sample of the chromium(III) alkyl and an equimolar quantity of the acid at 20 °C instantly and quantitatively afforded $CH_2(SiMe_3)_2$ and chromium(III) acetate. The compounds were separated on the vacuum line and were identified by ^{1}H n.m.r. and i.r. spectroscopy, respectively.

X-*Ray Structure Analysis*.—The data crystal, size 0.45 × 0.20 × 0.15 mm, obtained at low temperature from n-pentane–n-hexane, was mounted under nitrogen and sealed in a Lindemann glass capillary using a cyanoacrylate adhesive. The normal epoxy-resins attacked the crystals after mounting; presumably the small amount of admixed air escapes on hardening and is sufficient to decompose the small sample. Intensity data were collected at reduced temperature (200 K) using a Syntex four-circle diffractometer in the range $2.9 \leqslant 2\theta \leqslant 50°$ with Mo-K_α radiation (graphite monochromator) according to methods described earlier.[25] Using the criterion $I \geqslant 1.5\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation derived from counting statistics, 548 of the 879 intensities recorded were deemed independent and observable and only these were used in the solution and refinement of the structure. The data were corrected for Lorentz and polarisation effects, but not for X-ray absorption since careful measurement and indexing of the crystal faces were hindered by the mode of mounting and the linear absorption coefficient is in fact not large. The lack of an absorption correction does not give rise to any systematic errors in the results presented below.

Crystal Data.—$C_{21}H_{57}CrSi_6$, $M = 530.2$,* Trigonal, space group $P31c$, $a = b = 16.120(5)$, $c = 8.793(2)$ Å, $Z = 2$,* $U = 1\,978.8$ Å^3 (200 K), $F(000) = 582$,* $D_c = 0.89$ g cm^{-3},* Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 4.8 cm^{-1}.

Structure Solution and Refinement.—The molecular structure (Figure 1) was solved by difference density syntheses following successful location of the Cr atom from a three-dimensional Patterson synthesis. The ambiguity in the space group existing at this stage was resolved by careful investigation of both acentric and centric Fourier maps. The disorder of the alkyl C atom [C(1)], indicated in the electron-density distribution for $P\bar{3}1c$ about the C_2 axis required in this centric space group, perpendicular to the three-fold axis through the chromium atom, was not supported by subsequent refinements of such a disordered planar molecule. Also, an assumption must be made *a priori* that the α-hydrogen atom on C(1) exhibits a 50% disorder about this C_2 axis, or does not exist at all. Although approximate two-fold symmetry does exist in the refined structure, there is no crystallographic constraint to produce an exactly planar molecule in the chosen acentric space group $P31c$, in which the refinement converges with the three α-C atoms forming a plane below the chromium atom. Other tests confirmed the correct assignment of the space group as $P31c$ and also that of the enantiomorph presented herein.

Despite location of the complete molecule, the residual (R) remained unexpectedly high at 0.19, and there was considerable electron density in the channels formed by the packing of the two molecules in the unit cell (Figure 2), and situated around the C_3 axis through the cell origin. Addition of these rather diffuse peaks as carbon atoms produced an almost featureless difference density synthesis and more importantly removed the previously unexplained variations in the molecular parameters within the complex itself. All the attempts made to organise these ‘ atoms ’ into any recognisable molecule of solvent met with little success and the results presented below are a best fit of disordered solvent atoms within the cavities of the solid-state structure. This nearest ordered fit is achieved by assuming partial occupation of each site with concomitant rotational disorder about the three-fold axis. The original electron-density maxima were used as an indication of the frequency of population of the individual sites. These values were fixed, after refinements including the population parameters as variables indicated that these were not unreasonable in magnitude. Since the repeat distance $\frac{c}{2}$ in the cavity is shorter that the ‘ length ’ of n-pentane, a 1 : 1 occupation of these sites cannot occur, but it is not obvious, however, from the geometry of the refined partial atoms how to define the solvent molecule. There are no residuals >0.5 e Å^3 or < -0.2 e Å^3 in the final density synthesis and these do in fact remain predominantly in the cavity regions spilling out from the existing solvent atoms. Refinement

TABLE 2

Final positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses

Atom	x	y	z
Cr	0.333 3	0.666 7	0.250 0
Si(1)	0.543 9(3)	0.715 8(3)	0.384 7(7)
Si(2)	0.539 6(3)	0.828 6(3)	0.086 9(7)
C(1)	0.478 1(9)	0 721 3(8)	0.213 1(14)
H(1)	0 500 0	0.650 0	0.160 0
C(11)	0.458 9(10)	0.632 8(10)	0.532 7(16)
H(111)	0.416 7	0.652 6	0.568 5
H(112)	0.424 8	0.568 0	0.497 0
H(113)	0.496 0	0.632 0	0.622 9
C(12)	0.622 1(13)	0.835 4(13)	0.477 5(21)
H(121)	0.660 0	0.860 0	0.390 0
H(122)	0.592 0	0.863 0	0.513 0
H(123)	0.660 0	0.825 0	0.545 0
C(13)	0.625 5(13)	0.667 6(13)	0.330 5(18)
H(131)	0.670 0	0.700 0	0.270 0
H(132)	0.580 0	0.630 0	0.220 0
H(133)	0.610 0	0.610 0	0.380 0
C(21)	0.664 1(14)	0.855 5(13)	0.036 6(21)
H(211)	0.690 0	0.820 0	−0.060 0
H(212)	0.700 0	0.850 0	0.130 0
H(213)	0.690 0	0.920 0	0.013 0
C(22)	0.550 5(12)	0.938 6(12)	0.174 6(20)
H(221)	0.600 0	0.970 0	0.240 0
H(222)	0.560 0	0.970 0	0.080 0
H(223)	0.490 0	0.930 0	0.230 0
C(23)	0.477 7(12)	0.806 0(12)	−0.099 2(20)
H(231)	0.460 0	0.740 0	−0.160 0
H(232)	0.442 0	0.840 0	−0.130 0
H(233)	0.520 0	0.845 0	−0.165 0
‘ Solvent ’			
C(4)	0.0	0.0	0.0
C(5)	0.0	0.0	0.147(3)
C(6)	0.0	0.0	0.274(4)
C(7)	0.10	0.02	0.16
C(8)	0.12	0.05	0.23
C(9)	0.12	0.06	0.16

TABLE 3

Equations of some least-squares planes in the form $Ax + By + Cz = D$, where x, y, and z are fractional co-ordinates. Distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): C(1), C(1′), C(1″)

$$-0.006x + 0.001y + 8.793z = 1.871$$

[Cr 0.325, Si(1) 1.508, Si(2) −1.110]

Plane (2): C(1), Si(1), Si(2)

$$-11.363x + 12.097y + 0.540z = 4.306$$

[Cr 1.159]

The angle between planes (1) and (2) is 57.3°

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* Omitting the contribution from included solvent. It was not possible to measure the density experimentally, due to the extreme air sensitivity of the crystals, but the space-group symmetry and reasonable value for D_c in comparison with other similar compounds [26] supports the conclusion that $Z = 2$.

[25] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[26] A. J. Welch, Ph.D. Thesis, University of London, 1974.

was therefore concluded when the shift-to-error for all the atoms showed a maximum of 0.4, and a mean of 0.1, in the final cycles of full-matrix least-squares refinement. Only the Cr and Si atoms were given anisotropic thermal parameters, and although almost every hydrogen atom was located from the later electron-density maps neither their positions nor thermal parameters were refined. Those not located were given calculated positional parameters and inclusion of all the hydrogen-atom contributions to the structure-factor calculations as non-variable parameters in the refinement gave a final R value of 0.067 (R' 0.075).

Internuclear distances and angles are given in Table 1, the final atomic positional co-ordinates in Table 2, and the equations of some least-squares planes in Table 3. The computational work was carried out at the University of London Computing Centre, using the '*X*-Ray' system of programs. Scattering factors used were those of ref. 27 for Cr and Si, of ref. 28 for C, and ref. 29 for H. Corrections were made for the effects of anomalous dispersion for Cr and Si (Cr, $\Delta f'$ 0.284, $\Delta f''$ 0.624; Si, $\Delta f'$ 0.072, $\Delta f''$ 0.071). Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. 22215 (8 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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