Elimination Stabilized Alkyls. Part II.[1] Neopentyl and Related Alkyls of Chromium(IV)†

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Binary chromium(IV) alkyls, CrR_4, R = CH_2CMe_3, CH_2CMe_2Ph, CH_2CPh_3, and CH_3, have been prepared and characterised by electronic, i.r. and e.s.r. spectroscopy. The electronic and magnetic properties of tetrahedral chromium(IV) compounds are discussed.

IN previous studies on elimination-stabilised alkyls of transition metals, we prepared [1] tetrakis(trimethylsilylmethyl)chromium(IV). Compounds with the metal in the IV oxidation state are uncommon for chromium. The mixed oxides $M^{II}_4CrO_6$, $M^{II}_3CrO_5$ and $M^{II}_2CrO_4$ [2a] (M = Sr or Ba), the oxide CrO_2 [2b] and the ionic fluorides M^ICrF_5, $M^I_2CrF_6$ [3a] and $M^{II}CrF_6$ [3b] (M^I = Li, K, Rb, or Cs; M^{II} = Ba, Sr, Ca, Cd, Hg, or Ag) are well known. The halides, CrX_4 are reported [3a] but only CrF_4 is isolable while $CrCl_4$ and $CrBr_4$ exist in vapours, although $CrCl_4$ appears to be obtained at low temperatures by the action of HCl on $Cr(CH_2SiMe_3)_4$.[1] The best characterised compounds are the trimethylsilylmethyl,[1] the tertiary alkoxides $Cr(OR)_4$,[4] the numerous dialkylamides, *e.g.* $Cr(NEt_2)_4$,[5] some recently reported 1-norbornyl and related alkyls,[6a] and tetrakis(t-butyl)chromium(IV).[6b] The latter compounds have properties similar to the trimethylsilylmethyl [1] and to the related compounds now described.

Synthesis and Chemical Properties of Chromium(IV) *Alkyls.*—Tetra-alkyl chromium compounds, CrR_4, (R = neopentyl, neophyl, tritylmethyl, and methyl) have been prepared by the interaction of the Grignard or lithium reagent derived from the respective chloride with the tetrahydrofuran adduct of chromic chloride, $CrCl_3$,3THF, or in the case of tetramethylchromium, an exchange reaction between methyl-lithium and chromium(IV) t-butoxide. Details are given in the Experimental section. The compounds and some of their properties are listed in Table 1.

The neopentyl, neophyl, and tritylmethyl compounds are purple to red, paramagnetic, crystalline solids; tetramethylchromium is a volatile, thermally unstable, maroon oil. They are all readily soluble in organic solvents and are unaffected by water, alcohols, dilute acids and bases. Tetramethylchromium co-distils *in vacuo* with petrol at −35 °C and tetrakis(neopentyl)chromium sublimes *in vacuo* at 60 °C in good yield, but the other compounds, due to their higher molecular weights, decompose before the sublimation temperature is reached.

The general chemical behaviour of the compounds is similar to that of tetrakis(trimethylsilylmethyl)chromium [1] in that they fail to react with primary aliphatic and aromatic amines, alkyl and aryl tertiary phosphines, ethylene and liquid alkenes and carbon monoxide. Their reactivity towards oxygen and nitric oxide is in the order methyl > neopentyl ~ trimethylsilylmethyl > neophyl ≫ tritylmethyl. The tritylmethyl compound is sufficiently stable towards oxygen to be handled in air during its isolation. The oxygen and nitric oxide reactions of the neopentyl compound have been followed by e.s.r. spectroscopy. Strong mineral acids react with the compounds yielding solutions with Cr^{III} and the respective alkane, and gaseous HCl and chlorine both react to give, initially, the unstable red species believed to be chromium tetrachloride,[1] and ultimately a mixture of Cr^{II} and Cr^{III} chlorides. Tetrakis(benzylchromium-(IV) and bis(1,3-dimethylenetetramethyldisiloxane)-chromium(IV) have been prepared in poor yield and have been only partially characterised by their e.s.r. spectra and, in the case of the chelate, the electronic spectrum. These spectra would not be conclusive on their own, but when compared with the corresponding properties of the well characterised alkyls, the suggested structures seem realistic. The benzyl reaction does not proceed without complications, as the bulk of the chromium remains as chromium(III), with only a very small fraction being oxidised to the chromium(IV) compound. The reaction of the di-Grignard with $CrCl_3$,3THF could

TABLE 1

Properties of chromium(IV) tetra-alkyls

Compound	Colour, form	M.p. (°C)	Electronic spectrum [a]	$\mu_{eff.}$ [b]
$Cr(CH_2CMe_3)_4$	Maroon needles	110	18 500, 21 100 (1090)	2·7
$Cr(CH_2CMe_2Ph)_4$	Purple prisms	*ca.* 120 (dec.)	18 200, 20 500 (1380)	2·8
$Cr(CH_2CPh_3)_4$	Purple prisms	*ca.* 130 (dec.)	17 600, 20 200 [c] (1380)	2·6
$CrMe_4$	Maroon oil	*ca.* −60	20,000, 22 200 (*ca.* 600)	
$Cr(CH_2SiMe_3)_4$ [d]	Purple needles	40	17 100, 19 400 (1060)	2·9

[a] In cm^{-1}, in petroleum solution. Maximum ε_M in parentheses (see text). [b] In B.M., by Evans n.m.r. method. [c] In Benzene. [d] From ref. 1.

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† No reprints available. Preliminary note: W. Mowat and G. Wilkinson, *J. Organometallic Chem.*, 1972, **38**, C35.

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

[2] (*a*) K. A. Wilhelmi and O. Jenssen, *Acta Chem. Scand.*, 1961, **15**, 1415; (*b*) B. L. Chamberland, *Mat. Res. Bull.*, 1967, **2**, 827.

[3] (*a*) H. C. Clark and Y. N. Sadana, *Canad. J. Chem.*, 1964, **42**, 50; (*b*) G. Siebert and W. Hoppe, *Naturwiss.*, 1971, **58**, 95.

[4] E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chisholm, *J. Chem. Soc.* (*A*), 1971, 772.

[5] J. S. Basi, D. C. Bradley, and M. H. Chisholm, *J. Chem. Soc.* (*A*), 1971, 1433.

[6] (*a*) B. K. Bower and H. G. Tennent, *J. Amer. Chem. Soc.*, 1972, **94**, 2512; (*b*) W. Kruse, *J. Organometallic Chem.*, 1972, **42**, C39.

lead to two products after an aqueous extraction; the above chelate, or the tetra-alkyl $Cr(CH_2SiMe_2OSiMe_3)_4$. The rhombic splitting observed in the e.s.r. favours the chelate structure. It was not possible to isolate the pure compound as it readily disproportionates to give a reddish-purple, involatile chromium(III) species.

The magnetic and electronic properties are discussed later.

Tetrakis(neopentyl)chromium(IV) *and the Tetrakis(neopentyl)chromate*(III) *Ion*.—The interaction, in tetrahydrofuran (THF), of neopentyl-lithium with $CrCl_3$,3THF produces a blue-black solution stable only in THF, and we formulate this species as $Cr(CH_2CMe_3)_4^-$ by its spectroscopic properties and by analogy to the trimethylsilylmethyl analogue.[1] Attempts to isolate a crystalline solid by addition of large cations failed. The solution is oxidised immediately by trace amounts of oxygen or benzoyl peroxide to the maroon tetrakis(neopentyl)chromium(IV) and the latter may be reduced electrolytically or chemically to the blue anion. Coulometric measurements on an ethanolic solution with tetra-n-butylammonium iodide as supporting electrolyte show a reduction wave at a half-wave potential of *ca.* −1·65 V *vs.* the saturated calomel electrode.

The interaction of neopentylmagnesium chloride with $CrCl_3$,3THF does not produce the tetra-alkyl in a one-step process as is the case with the trimethylsilylmethyl compound. Addition of up to 2 equivalents produces an orange species which can be isolated as a petroleum soluble crystalline compound, readily disproportionating to give the tetra-alkyl on standing or more rapidly by the action of water or air. The X-band (9·2 GHz) e.s.r. spectrum of the frozen orange solution shows bands at 202, 520, and 850 mT which may be attributed to a species having $S = 1$ and $D \simeq 0{\cdot}5$ cm^{-1}. The bands observed at 202 and 850 mT are due to molecules with their principal axis nearly parallel to the magnetic field and the other due to molecules with this axis perpendicular to the field. The presence of a strong distortion suggests that this is a mixed species $Cr[CH_2CMe_3]_nCl_{4-n}$ and the absence of splitting in the perpendicular band at 520 mT indicates near-axial symmetry implying $n = 1$ or 3. This compound was too sensitive to obtain a reliable analysis. On addition of further Grignard reagent, the colour becomes initially blue, but reverts to the orange colour until an ' end-point ' is reached at *ca.* 3 equivalents, after which the colour remains an intense, deep blue. This blue solution is stable only in ether, and addition of air, water, or petroleum causes immediate disproportionation or oxidation to the maroon tetra-alkyl. Attempts to crystallise the blue compound failed. The e.s.r. spectrum of this solution, which showed a broad line at g *ca.* 2 with a sharp line at its centre, is ambiguous but probably indicates octahedral chromium(III).

The reaction of $Cr(CH_2CMe_3)_4$ with nitric oxide yields a solution in which three species are observed in the room temperature e.s.r. spectrum. There is a free radical with hyperfine structure attributable to one nitrogen atom and four equivalent protons, which is probably the dineopentyl nitroxide radical, $(Me_3CCH_2)_2NO\cdot$. The spin Hamiltonian parameters are: $g = 2{\cdot}0062(3)$, $a_N = 1{\cdot}30(2)$ mT and $a_4 = 0{\cdot}75(2)$ mT. The other two compounds contain chromium bonded to nitrogen and the stronger of these has $g = 1{\cdot}9730(5)$ and $a_N = 0{\cdot}59(2)$ mT with a chromium hyperfine structure that was not sufficiently well resolved for the magnitude of the coupling to be established. The other spectrum is about one third as intense and overlaps with the other chromium-nitrogen compound preventing accurate measurements. The g-factor is 1·968 and the nitrogen hyperfine splitting 0·6 mT.

The reaction with oxygen is rapid, giving brown solutions containing a mixture of products. The e.s.r. spectra of solutions exposed to a trace of oxygen reveal two transient $S = \frac{1}{2}$ species analogous to the species A and D observed with $Cr(CH_2SiMe_3)_4$ [1] but with substantially smaller proton hyperfine couplings. (Table 2).

TABLE 2

Spin Hamiltonian parameters for oxidation products of $Cr(CH_2XMe_3)_4$

	X	g	a_1/mT	a_2/mT	a_6/mT
A	C	1·986(1)	1·07(1)		0·43(1)
D	C	1·9790(5)		0·45(3)	
A	Si [a]	1·9836(3)	1·32(1)		0·50(1)
D	Si [a]	1·9725(5)		0·66(1)	

[a] Data from ref. 1.

Tetrakis(neophyl)chromium(IV).—The interaction of neophylmagnesium chloride with $CrCl_3$,3THF produces tetrakis(neophyl)chromium(IV) as maroon crystals after oxidation or disproportionation of a deep blue solution in an analogous way to the neopentyl reaction. The lithium reagent was not prepared but the existence of the $Cr(CH_2CMe_2Ph)_4^-$ ion was established by coulometric measurements on the tetra-alkyl. A solution in acetone with tetra-n-butylammonium iodide as supporting electrolyte shows a one electron reduction wave at a half-wave potential of *ca.* −1·97 V *vs.* the saturated calomel electrode.

Tetrakis(tritylmethyl)chromium(IV).—The interaction of tritylmethyl-lithium with $CrCl_3$,3THF at −78° produces the anion $Cr(CH_2CPh_3)_4^-$ which is readily oxidised by air to the air-stable, purple tetrakis(tritylmethyl)chromium(IV). The reaction must be carried out at −78° because above this temperature there is appreciable rearrangement of the lithium reagent to give $PhCH_2{\cdot}CPh_2Li$.[7] The latter does react to form a purple species, but on warming to room temperature, decomposition occurs rapidly, presumably due to interaction of the β hydrogen atoms. Coulometric measurements of a solution of the chromium(IV) alkyl in acetone show a one electron reduction wave at half-wave potential of *ca.* −1·99 V *vs.* the saturated calomel electrode.

Tetramethylchromium(IV).—The exchange reaction between $Cr(OBu^t)_4$ and a large excess of freshly prepared

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[7] E. Grovenstein, jun., and L. P. Williams, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 412.

methyl-lithium in petroleum yields an unstable maroon solution of tetramethylchromium(IV). This product is not obtained if a co-ordinating solvent, *e.g.*, diethyl ether or THF, is used, and probably for this reason the reaction of $Cr(OBu^t)_4$ with methylmagnesium chloride[8] does not yield tetramethylchromium. This exchange reaction has been also recently reported independently[6b] and used to prepare $Cr(t\text{-butyl})_4$ while Me_4Cr and other alkyls were characterised in solution. Addition of ligands such as tertiary amines and phosphines, or carbon monoxide to the $CrMe_4$–MeLi solution produces orange solutions which appear to contain chromium(III), probably either $CrMe_3L_3$ (*cf.* $CrMe_3$,3THF[9a]) or a lithium methylchromate.[9b]

If the tetramethylchromium and the petroleum are co-distilled out of the reaction mixture *in vacuo* and collected at −78°, the resulting solution is considerably less stable than when the excess of lithium reagent is present. It decomposes slowly at −60° and rapidly at room temperature. In this purer state, the compound seems more reactive towards amines and phosphines than the other chromium(IV) compounds but no adducts could be isolated.

A petroleum-free sample (see Experimental section) was prepared and a mass spectrum obtained, but this showed no chromium-containing species, hardly surprising due to the very low thermal stability of the compound.

Infrared Spectra.—The i.r. spectra of the isolable compounds is dominated by the ligand vibrations, very few of which change significantly in the alkyls. Most of these vibrations are well-known aliphatic and aromatic bands and have not been included in Table 3. This lists only bands from 700 to 250 cm⁻¹. For a near-tetrahedral structure two i.r. active bands are expected for Cr–C between 500 and 400 cm⁻¹ as observed.

TABLE 3

I.r. spectra of chromium(IV) tetra-alkyls [a]

$Cr(CH_2CMe_3)_4$	$Cr(CH_2CMe_2Ph)_4$	$Cr(CH_2CPh_3)_4$	
	700s	700s	
		693s	
		672	sharp, w
		640	
		633	
		625	
		620	
	601m	610	
590m	584w	573w	
	563w	550w	
555s	550sh	528w	
	534m	513w	
		500m	
508m			
	481m	485m	
450w			
	424m	410w(br)	
400vw	400vw		
378m		322vw	
293m	280		

[a] In cm⁻¹ from 700—250 cm⁻¹ in Nujol or Vaseline mulls.

Electron Spin Resonance Spectra.—The e.s.r. spectrum of $Cr[CH_2SiMe_3]_4$ has been described in an earlier paper[1] and was found to have an unexpected temperature dependence. Further measurements have been carried out on this compound with more precise control of temperature and concentration in order to understand these phenomena. Similar studies were carried out with the alkyls $Cr[CH_2CMe_3]_4$, $Cr[CH_2CMe_2Ph]_4$, and $Cr[CH_2CPh_3]_4$. A preliminary note on e.s.r. studies of some chromium(IV) alkyls including $Cr[CH_2CMe_3]_4$ and $Cr[CH_2CMe_2Ph]_4$ has recently appeared.[6b,10]

The e.s.r. spectrum of CrR_4 (where $R = CH_2SiMe_3$ or CH_2CMe_3) solutions in petroleum or toluene at temperatures greater than 140 K is exactly as predicted for a triplet species with a random rotational motion.[11] At 140 K the line-width passes through a minimum and both it and the fine structure splitting increase on further cooling. Also, at low temperatures there is an additional line having $g \simeq 2$ which cannot be assigned to any transition of the $^3A_2$ ground state of the alkyl.

It is now clear that the $g \simeq 2$ resonance is due to some magnetically concentrated phase that separates from the solution at low temperatures, presumably because of reduced solubility. A solution in petroleum, in which CrR_4 is extremely soluble at room temperature, that is not more than 10^{-3} M, does not show the sharp line. On the other hand a solution in benzene, in which CrR_4 is much less soluble at room temperature, shows only a broad line with $g \simeq 2$ unless the concentration is *ca.* 10^{-4}M or less in which case a normal triplet state spectrum is observed in addition to the $g = 2$ line.

It is possible to obtain supersaturated frozen solutions by plunging tubes containing the solution into liquid nitrogen. These samples have weaker $g = 2$ signals than others of the same concentration that were frozen slowly. If such a supersaturated solution in petroleum is warmed to 135 K or more the $g = 2$ signal grows in intensity until it is the same as that of the slowly frozen solution. This process takes *ca.* 1 h at 135 K and is faster at higher temperatures. Solutions in benzene behave similarly but temperatures of 200 K or more are required before this equilibration occurs at a perceptible rate.

The $g = 2$ signal is not identical with the spectrum of pure solid CrR_4, which is also a single line with $g \simeq 2$ but with a different line width, so one must presume that the separated phase in the frozen solution samples incorporates some of the solvent. These phenomena are displayed in a more extreme manner by $Cr[CH_2CPh_3]_4$. In all solvents tried except benzene a single broad line (150 mT) centred on $g = 2$ was always observed. In benzene there is a similar broad line, but, provided the solution was frozen rapidly, a number of additional sharp

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[8] T. Tsuda and J. K. Kochi, *Bull. Chem. Soc. Japan*, 1972, **44**, 648.

[9] (*a*) H. H. Zeiss and R. P. A. Sneedon, *Angew. Chem. Internat. Edn.*, 1967, **6**, 435; (*b*) J. Krausse, G. Marx, and G. Schödl, *J. Organometallic Chem.*, 1970, **21**, 159.

[10] G. A. Ward, W. Kruse, B. K. Bower, and J. C. W. Chien, *J. Organometallic Chem.*, 1972, **42**, C43.

[11] (*a*) J. R. Norris and S. I. Weissman, *J. Phys. Chem.*, 1969, **73**, 3119; (*b*) J. H. Freed, G. V. Bruno, and C. Polnaszch, *J. Chem. Phys.*, 1971, **55**, 5270.

lines are detected. These lines are not accurately reproducible or isotropic so they cannot be a true frozen solution spectrum. Nevertheless some features are almost reproducible; such as the splitting of the outermost pair of lines allowing a rough estimate of *D* and it is also possible to make a very tentative estimate of a rhombic component *E* of the zero-field splitting. The lines are very narrow (*ca.* 2·5 mT) compared to the other alkyls of which Cr[CH$_2$CMe$_3$]$_4$ has the narrowest lines with 6·0 mT width at 145 K. The behaviour of Cr[CH$_2$CPh$_3$]$_4$ is probably due to its low solubility relative to the other alkyls in all solvents except benzene in which its solubility is about the same as the others.

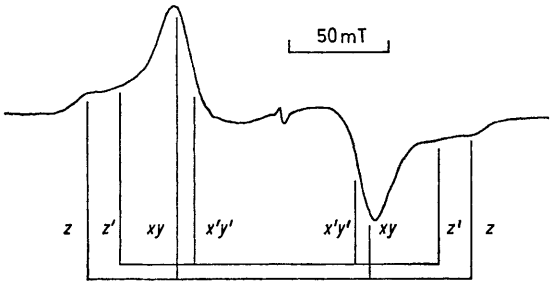

FIGURE 1 E.s.r. spectrum of a petroleum solution of Cr(CH$_2$SiMe$_3$)$_4$ at 115 K, showing the presence of two $S = 1$ species

The anomalous line broadening of Cr[CH$_2$SiMe$_3$]$_4$ at low temperatures is similarly interpreted as being due to a mixture of two species, both of which remain in solution. At temperatures below 125 K the *z*-component of the spectrum splits into two (Figure 1). The resolution is clearest at 115 K since below 110 K one of the *z*-lines is hidden beneath the strong *x,y* line and the overall spectrum appears to be broadened rather than split. The fine structure splitting of both spectra tend to limits at sufficiently low temperatures (Figure 2). The change of the splitting at higher temperatures may be attributed to three effects. There may be a genuine temperature dependence of the spin–spin coupling tensor (*D*), molecular tumbling reduces the measured splitting, and it is possible that the two spectra are due to two conformers of Cr[CH$_2$SiMe$_3$]$_4$ which may interchange rapidly at temperatures above 125 K. A similar resolution into two conformers at low temperatures has already been postulated for Mo[NMe$_2$]$_4$ which has a low temperature splitting in the electronic spectrum.[12] Two conformers of Cr[CH$_2$SiMe$_3$]$_4$ may be visualised related to each other by rotation of the chromium–carbon bond in exactly the same way as those considered for Mo[NMe$_2$]$_4$.

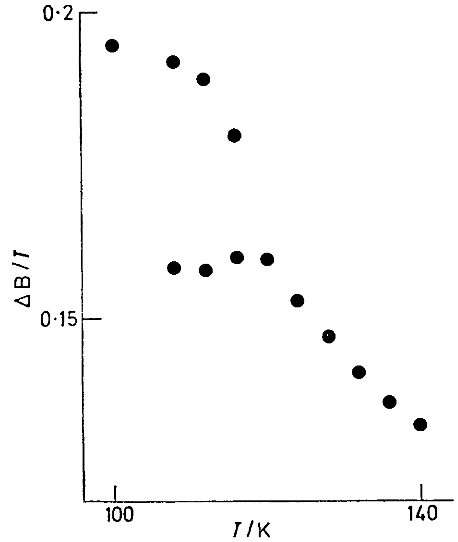

FIGURE 2 Temperature dependence of the fine structure splitting (Δ*H*) of the *z*-component of the e.s.r. spectrum of Cr(CH$_2$SiMe$_3$)$_4$

The *x,y* lines of Cr[CH$_2$CMe$_3$]$_4$, behave in the same fashion as those of Cr[CH$_2$SiMe$_3$]$_4$, so we may presume that there is a similar resolution into two species, but in the neopentyl the spin–spin interaction is much weaker and consequently it is never possible to resolve the *z*-lines of the spectrum. (Figure 3).

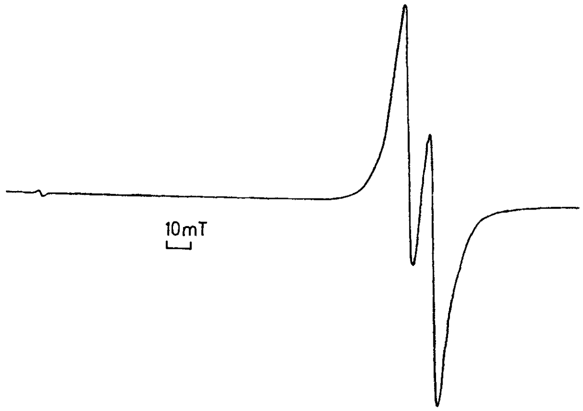

FIGURE 3 E.s.r. spectrum of a petroleum solution of Cr(CH$_2$CMe$_3$)$_4$ (*ca.* 3 × 10^{-4}M) at 125 K

A spectrum of two species is also detected in frozen solutions of Cr[CH$_2$CMe$_2$Ph]$_4$. In this case the difference between the two forms is so great that the *x,y* line and the *x',y'* line are resolved, but the *z'* line is always concealed under the *x,y* one. An alternative hypothesis of a single species of rhombic symmetry was also considered, but could not fit the spectrum. There is no minimum line-width with this compound at *ca.* 145 K since the splitting giving rise to the apparent line-width increase on further cooling of Cr[CH$_2$CMe$_3$]$_4$ or Cr[CH$_2$SiMe$_3$]$_4$ is already resolved and, as is to be expected, the line-width is a minimum at the lowest temperature accessible (*ca.* 100 K).

E.s.r. spectra were also observed with solutions of CrMe$_4$, Cr[CH$_2$Ph]$_4$ and Cr[(CH$_2$SiMe$_2$)$_2$O]$_2$ but were not well enough characterised to permit such detailed study. CrMe$_4$ has such a small zero-field splitting that its spectrum merely consists of a single broad line at *g ca.* 2 which considered alone is ambiguous. We shall note

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[12] D. C. Bradley and M. H. Chisholm, *J. Chem. Soc.* (*A*), **1971**, 2741.

later a correlation between the e.s.r. and electronic spectra which predicts $D \simeq 0$ for $CrMe_4$, so that we conclude that this is indeed a tetrahedral d^2 species.

Spin Hamiltonian parameters of all the alkyls are collected in Table 4.

The *X*-band e.s.r. spectra obtained by Ward *et al.*[10] show, in each case, a single sharp line at *ca.* 0·33 T and a much weaker line at *ca.* 0·16 T. This is in marked conflict with the findings reported above and suggests that they are observing the $g \simeq 2$ magnetically concentrated phase spectrum. The concentrations reported [3×10^{-3}M for $Cr(CH_2CMe_3)_4$] are rather high.

TABLE 4

Spin Hamiltonian parameters of frozen solutions of CrR_4

R	T/K	$g_{\parallel}$	$g_{\perp}$	D/cm^{-1}	E/cm^{-1}
Me	110	*ca.* 1·99 [a]		*ca.* 0·005	
CH_2CMe_3	145		1·990(3)	0·011(1)	
CH_2CMe_2Ph	110		1·988(5)	0·021(5)	
	110		1·992(5)	0·049(5)	
CH_2CPh_3 [b]	110	*ca.* 2·0 [a]		0·07	0·01
CH_2SiMe_3 [c]	145	1·986(3)	1·990(3)	0·063(5)	
	110	1·986(3)	1·989(3)	0·073(5)	
	110	1·981(3)	1·989(3)	0·089(5)	
$\frac{1}{2}\{(CH_2SiMe_2)_2O\}$	145	1·994(5) [a]		0·123(10)	0·017(3)
CH_2Ph	110	*ca.* 2·0 [a]		*ca.* 0·2	

[a] Average *g*-factor. [b] Provisional values from improperly frozen solutions. [c] These parameters are considered to be more accurate than those of ref. 1.

Spectroscopic Properties of Chromium(IV) *Compounds. Electronic Spectra.*—The ground state for a tetrahedral d^2 molecule is $^3A_2(e^2)$ and, considering only *d*-electron transitions, there are three excited triplets, $^3T_2(et_2)$, $^3T_1(et_2)$ and $^3T_1(t_2{}^2)$. The electric dipole operator transforms as T_2 so that the $^3A_2 \longrightarrow {}^3T_1$ transitions are allowed but $^3A_2 \longrightarrow {}^3T_2$ is forbidden. In the strong field limit $^3A_2 \longrightarrow {}^3T_1(t_2)$ is also forbidden as it is a two electron transition, but it is usually found that the interelectronic electrostatic interaction mixes the two $^3T_1$ states and therefore two $^3A_2 \longrightarrow {}^3T_1$ absorption bands are expected.

If the tetrahedron suffers a tetragonal distortion, reducing the symmetry to D_{2d}, the degeneracy of the triplets is partially lifted. The T_2 states are split into an orbital singlet and a doublet, $B_2 + E$, and T_1 is similarly split into $A_2 + E$. The ground state becomes $^3B_1$ and electric dipole transitions are allowed to $^3A_2$ and ^3E. In particular this means that the transition to the ^3E state derived from $^3T_2$ becomes allowed, but its intensity will remain relatively low.

A qualitative description of the behaviour of the energy levels may be obtained by assuming that they depend on only three parameters Δ, δ and B. Δ is the energy difference between the t_2 and the *e*-antibonding orbitals of primarily *d* character, δ is the splitting of the t_2-orbitals and B is an effective Racah parameter for the interelectronic repulsion. This treatment is necessarily an approximation since it neglects any splitting of the *e* (π-bonding) orbitals and it assumes that the electrostatic repulsion can be treated simply by taking reduced values of B and, tacitly, of A. The former is probably justified for the alkyls, which can only π-bond by a form of hyperconjugation [13] but is clearly inappropriate for the dialkylamides.

The inadequacy of a single electrostatic repulsion parameter B has been discussed for the isoelectronic tetrahedral vanadium(III) ion [14a] and more elaborate treatments have been described [14b] but, in the present case the data is too fragmentary for these to be useful.

Alkyls.—All the chromium(IV) alkyls have an absorption band at *ca.* 500 nm and then rapidly rising absorption towards shorter wavelength. The oscillator strength of the 500 nm band is *ca.* 0·02 which is remarkably large for formally *d–d* transitions, but is not unreasonably so for a highly covalent non-centrosymmetric system.[15] The band is asymmetric and may be reconstructed as two components with intensities in the ratio 2 : 1 with the stronger at the shorter wavelength. There is also another much weaker shoulder at *ca.* 667 nm.

This spectrum is assigned to a system of slightly elongated tetrahedral symmetry (D_{2d}), with the two strong bands at *ca.* 500 nm being assigned to the transitions $^3B_1 \longrightarrow {}^3E(T_1)$ and $^3B_1 \longrightarrow {}^3A_2(T_1)$. The splitting of the $^3T_1$ state is almost independent of the alkyl group, varying only in the range 2200—2700 cm^{-1} with no obvious relation to the distortion as implied by the e.s.r. parameter D. The centre of gravity of the $^3A_2 \longrightarrow {}^3T_1$ band does show a marked correlation with D varying from 21 500 cm^{-1} for $CrMe_4$ to 18 600 cm^{-1} for $Cr(CH_2SiMe_3)_4$.

The third band is an order of magnitude weaker and cannot be located very accurately. It is at *ca.* 15 000 cm^{-1} and is not significantly dependent on the alkyl group. A number of assignments may be considered, but none is very satisfactory:

(i) $^3B_1 \longrightarrow {}^3E(T_2)$: This permits us to calculate parameters Δ *ca.* 14 500 cm^{-1}, B *ca.* 450 cm^{-1} and δ *ca.* 2 500 cm^{-1}, which are quite acceptable values, but is is difficult to understand why the energy of $^3T_2$ should be independent of the alkyl group while that of $^3T_1$ changes substantially.

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[14] (*a*) E. König and G. Thomas, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1173; (*b*) C. K. Jørgensen, ' Modern Aspects of Ligand Field Theory,' North-Holland, Amsterdam, London, 1971, p. 302.

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(ii) $^3B_1 \longrightarrow {}^1A_1(A_1)$: The indifference of the transition energy to the ligand field suggests a spin-forbidden transition within the e^2 configuration. Assuming that $C = 4\,B$ we find that B *ca.* 450 cm^{-1}, while a similar assignment, $^3B_1$ to states derived from the ^1E state of a tetrahedron, yields B *ca.* 900 cm^{-1}. The former seems preferable, since the latter value of B implies rather slight covalent interaction in conflict with the e.s.r. data to be considered later.

Alkoxides.—The electronic spectrum of, for example, $\text{Cr(OBu}^t)_4$ is exactly as expected for a nearly regular tetrahedron, with $\Delta = 9\,430\ \text{cm}^{-1}$ and $B = 795\ \text{cm}^{-1}$.[4] This assignment is, however, incompatible with the electronic spectrum of $\text{Cr(OBu}^t)_4^-$, which has been interpreted as being due to a tetrahedral d^3-ion having $\Delta = 11\,200\ \text{cm}^{-1}$ and $B = 560\ \text{cm}^{-1}$,[16] since it is improbable that an ion MX_4^- should have a greater ligand field splitting than the corresponding MX_4. One explanation for this paradox is that $\text{Cr(OBu}^t)_4^-$ is not tetrahedral, but a polymer;[16] or alternatively the assignment of the $\text{Cr(OBu}^t)_4$ spectrum is incorrect.

The low value of Δ is a necessary result of assigning a very weak transition *ca.* 9 000 cm^{-1} to $^3A_2 \longrightarrow {}^3T_2$. An alternative possibility is $^3A_2 \longrightarrow {}^1E$ which implies B *ca.* 550 cm^{-1}. There is a strong band at *ca.* 15 000 cm^{-1}, which is very similar in shape and intensity to the 20 000 cm^{-1} band of the alkyls and probably due to the same $^3A_2 \longrightarrow {}^3T_1$ transition. Taking $B = 550\ \text{cm}^{-1}$ we may calculate Δ *ca.* 11 500 cm^{-1} and δ *ca.* 2 000 $\text{cm}^{-}{}_{1}$. This assignment, which requires an additional $^3A_2 \longrightarrow {}^3T_1$ band at *ca.* 27 000 cm^{-1} is much more in line with the spectra of CrR_4 and Cr(OR)_4^-.

Dialkylamides.—The only *d–d* band observed for the dialkylamides is at 13 700 cm^{-1}. Bradley *et al.* assign this to the $^3B_1 \longrightarrow {}^3A_2$ transition of an elongated tetrahedron,[5] but there seems to be no reason why it should not be the $^3B_1 \longrightarrow {}^3E(T_1)$ transition of a flattened tetrahedron. If we assume that the other transition to $^3T_1$ is at $>25\,000\ \text{cm}^{-1}$ we find that the centre of gravity of $^3T_1$ is at $>21\,200\ \text{cm}^{-1}$ or $>17\,500\ \text{cm}^{-1}$ according to whether the molecule is elongated or flattened. We know that visible–u.v. transitions in $\text{V(NR}_2)_4$ are at lower frequency than those for VR_4 [17,1] so that we favour the latter.

It would also seem that one cannot entirely discount the possibility of a fairly regular tetrahedron ($\Delta < 11\,500\ \text{cm}^{-1}$, $B > 550\ \text{cm}^{-1}$) since the missing $^3A_2 \longrightarrow {}^3T_1$ transition may be rather weak (*cf.* $\text{Cr(OBu}^t)_4$).

Paramagnetic Resonance.—*The g-factor*. The *g*-factors for a d^2 ion in a site of axially distorted tetrahedral symmetry are given by equations (1).

$$\left.\begin{aligned} g_{\parallel} &= 2{\cdot}0023 - \frac{8\lambda_{\parallel}}{W[^3B_2(T_2)]} \\ g_{\perp} &= 2{\cdot}0023 - \frac{8\lambda_{\perp}}{W[^3E(T_2)]} \end{aligned}\right\} \qquad (1)$$

The best characterised e.s.r. spectra are those of $\text{Cr[CH}_2\text{SiMe}_3]_4$ which have $g_{\parallel} = 1{\cdot}984(3)$ and $g_{\perp} = 1{\cdot}989$ (1).

Both assignments (i) and (ii) of the 15 000 cm^{-1} absorption band lead to the same values at room temperature for $W[^3B_2(T_2)]$ and $W[^3E(T_2)]$ which are *ca.* 12 500 and 15 000 cm^{-1} respectively yielding $\lambda_{\parallel} = 31 \pm 5\ \text{cm}^{-1}$ and $\lambda_{\perp} = 28 \pm 3\ \text{cm}^{-1}$. The free ion spin–orbit coupling parameter for chromium(IV) is $\lambda_0 = \zeta_0/2 = 164\ \text{cm}^{-1}$,[18] so that the reduction factor $\lambda/\lambda_0 = 0{\cdot}18 \pm 0{\cdot}04$ is remarkably small, but not unprecedently so, similar values having been reported with, for example, $\text{Mn}^{\text{IV}}\text{O}_6$ [19] and Mo(CN)_8^{3-}.[20]

There are several different mechanisms which combine to reduce the effective spin–orbit coupling. The most important of these are:

(1) Delocalisation of electrons in the nominally metal $3d$-orbitals.[21]

(2) Reduction of the effective charge of the metal ion, and consequent reduction of λ_0 by charge transfer in the filled t_2 bonding orbitals which are nominally localised on the ligands.[22]

(3) Spin–orbit coupling between the $^3A_2$ ground state which belongs to the configuration $(\text{core})(t_2)^6(de)^2(dt_2)^0$ and a charge transfer state of symmetry T_2 and energy W' belonging to the configuration $(\text{core})(t_2)^5(de)^3(dt_2)^0$.[22,23]

Taking all of these into account we may write for the effective spin–orbit coupling parameter

$$\lambda = \lambda_0'[P - (1 - P)W/W'] \qquad (2)$$

where P is the fraction of d-orbital character in the lowest excited t_2 orbital and λ_0 is the free ion spin–orbit coupling parameter for chromium in the oxidation state:

$$Q = 4 - 6(1 - P) = 6P - 2 \qquad (3)$$

Equations (2) and (3) neglect the possibility of π-bonding which is probably justified as alkyl ligands may only π-bond by hyperconjugation. Also neglected is the possibility of admixing chromium $4p$ character into the t_2-orbitals. It has been proposed that this effect is important for tetrahedral cupric complexes,[24-26] but this is not established with any certainty.[27-29]

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We could use equations (2) and (3) to estimate P if we had a value of W', which is not available since ${}^3A_2 \longrightarrow {}^3T_2$ transitions are forbidden. If we neglect the charge transfer term altogether (by setting $W' = \infty$), we find $P = 0{\cdot}25 \pm 0{\cdot}04$ and $Q = -0{\cdot}5$ which seems an unreasonable situation. There is intense absorption in the u.v. from *ca.* 25 000 cm^{-1} so we may tentatively suggest that $W' \simeq 2W \simeq 28\,000$ cm^{-1} in which case $P = 0{\cdot}50 \pm 0{\cdot}03$ and $Q = +1{\cdot}0$. The value of P is not very sensitive to W', since as W' varies from 21 000 cm^{-1} to 35 000 cm^{-1} P only varies from 0·55 to 0·46. These values indicate *extreme* delocalisation of the ' chromium $3d$ '-orbitals, which may partly be due to approximate nature of equation (2). A more elaborate analysis of the g-factor is possible and would be analogous to that of distorted tetrahedral CrO_4^{3-} [30] in which the formally chromium(v) ion has $Q \simeq +1{\cdot}9$. The more detailed treatment would require too many additional parameters to be very significant and it would not alter the overall conclusion of very strong delocalisation between metal and carbon σ-orbitals.

An effective charge Q of *ca.* 1·0 is unusually small [30] and, if it is not an artefact of the simple theoretical model, it would offer an explanation for the rather paradoxical sensitivity of these compounds to decomposition by oxidation.

Zero-field splitting. In the approximation of equations (1) we may write the zero-field splitting D as:

$$D = 4\left\{\frac{\lambda^2{}_\perp}{W[{}^3E(T_2)]} - \frac{\lambda^2{}_\parallel}{W[{}^3P_2(T_2)]}\right\} - 4\left\{\frac{\lambda^2{}_\perp}{W[{}^1E(T_2)]} - \frac{\lambda^2{}_\parallel}{W[{}^1P_2(T_2)]}\right\} \quad (4)$$

$$\simeq 4\lambda^2\delta\left[\frac{1}{\Delta^2} - \frac{1}{(\Delta + 8B + 2C)^2}\right] - 8\lambda(\lambda_\parallel - \lambda_\perp)\left[\frac{1}{\Delta} - \frac{1}{\Delta + 8B + 2C}\right] \quad (5)$$

There are also contributions to D from spin–orbit coupling to charge transfer states. These lead to additional terms in equations (4) and (5), which, in contrast to corresponding terms in the g-factor, have the same sign as those due to spin–orbit coupling within the nominally d-orbitals. We therefore expect that a zero-field splitting calculation based on equations (4) and (5) would require a greater effective spin–orbit coupling than did the g-factor calculations. It is not possible to make any quantitative estimate of the appropriate value of λ since, given P and Q the value is very sensitive to Δ'. A further difficulty is the possibility of anisotropic spin–orbit coupling.

We shall rather arbitrarily adopt a value of $\lambda = 52 \simeq \lambda_0'/2$ for the following calculations which should only be considered as indicating an order of magnitude. If we take $\Delta \simeq 14\,500$ cm^{-1}, $\delta = 2\,500$ cm^{-1} and $B = C/4 = 450$ cm^{-1} we find that the first term of equation (5) is *ca.* 0·08 cm^{-1} and the second term is $-0{\cdot}04$ $(\lambda_\parallel - \lambda_\perp)$ so that the observed values of D in the range 0·10 to 0·005 cm^{-1} for the alkyls seem acceptable.

The value of D decreases with increasing energy of the 500 nm transition (Tables 1 and 4) which is as expected from the Δ^{-1} and Δ^{-2} dependence in equation (5) but the dependence is remarkably abrupt and more seriously, there is no relation between D and δ. This suggests that the simple treatment implied by equation (4) is inadequate for this system.[31]

Paramagnetic Resonance of Alkoxides and Dialkylamides.—An e.s.r. spectrum has been described for $Cr[OBu^t]_4$. This consists of a broad ($\sim$0·2 T) line centred at 0·15 T ($g \simeq 4$), two sharp lines having $g \simeq 2$ and a broad line at 0·85 T.[4,32] The sharp lines are probably spurious, $S = \frac{1}{2}$ impurities or a magnetically concentrated phase, while the 0·85 T line could be due to gaseous oxygen. The experiment was performed at 10 K but the geometry of the e.s.r. cavity was such that gaseous oxygen could be present.[33]

The $g = 4$ line is probably the forbidden $\Delta M = \pm 2$ transition and there are at least two possible explanations for the absence of the normal $\Delta M = \pm 1$ lines.

(i) There is a very large value of D, but E is small enough to permit observation of the $\Delta \mathrm{M} = \pm 2$ transition. We have seen that the theoretical calculation of D is extremely difficult, but we may extrapolate the correlation between D and the energy of the ${}^3T_1$ manifold and predict that D will indeed be rather large.

(ii) The molecules are randomly distorted, so that the $\Delta M = \pm 1$ lines which occur at fields which depend on D as $D/g\beta$ will be very broad, while the $\Delta M = \pm 2$ line is independent of D in first order and suffers a comparatively small broadening and remains observable.

The disappearance of the $g = 4$ line at 77 K is presumably due to rapid spin lattice relaxation. For spin-multiplets the relaxation becomes faster when the zero-field splitting is large [compare for example haemoglobin [34] with other $d^5({}^6A_2)$ systems].

No e.s.r. spectrum of $Cr(NR_2)_4$ has been detected,[5] and no measurements below 77 K have been reported, and this system is presumably analogous to the alkoxides.

The Nature of the Distortion.—A possible explanation of the independence of the distortion parameters D and δ may lie in the existence of two distinct respects in which the molecules may deviate from regular tetrahedral symmetry. The CrC_4 core may not be a regular tetrahedron, but, even if it is, the distribution of non-nearest-neighbour atoms of the ligands is unlikely to conform to the point group T_d.

In the latter case, the central ion will experience a field of lower than tetrahedral symmetry if the electron

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distribution on the ligating atom is not axially symmetric about the Cr–C bond. We therefore expect that the spectroscopic properties of $Cr(CH_2R)_4$ will indicate a distortion that depends on the difference between H and R as electron donors. Reference to Table 4 shows that this is indeed the case for the zero-field splitting D and the same reasoning predicts a very large value for $Cr(OR)_4$ and $Cr(NR_2)_4$.

We therefore suggest that the splitting δ of the $^3T_1$ state is due to gross distortion of the CrC_4 core, which is approximately the same for all alkyls, and that the next-nearest-neighbours make a negligible contribution, while for D the opposite is true. It is, however, difficult to understand why this should be so. If it is indeed the case, we anticipate that a tertiary alkyl would give rise to a rather small zero-field splitting. It is therefore unfortunate that Ward *et al.* have not obtained ' frozen solution ' spectra.[10] Nevertheless one anticipates that the line width of the magnetically concentrated species will be positively correlated with D, so that it is encouraging that the tertiary alkyls (norbornyl and CMe_3) have narrow e.s.r. lines of width 1·4 mT and 1·7 mT while the primary alkyls give broader lines : neopentyl 4·8 mT and neophyl 7·0 mT.

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 R14 and R12A 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}. Samples were run between KBr plates for the region 4000—450 cm^{-1} and between polyethylene plates in the region 500—200 cm^{-1}. Electronic spectra were recorded on a Cary 14 spectrophotometer as solutions in light petroleum or tetrahydrofuran. Mass spectra were recorded on a A.E.I. MS9.

Preparations.—All preparations and other operations were carried out in oxygen-free nitrogen, argon (for preparation of lithium reagents), or *in vacuo*, unless otherwise stated.

Chloromethyltrimethylsilane, 1,3-bis(chloromethyl)tetramethyldisiloxane (Peninsular Chemresearch), neopentyl chloride (K and K Laboratories), benzyl chloride (B.D.H.), and methyl bromide (B.O.C.) were used as received. Neophyl chloride was prepared by the alkylation of benzene with 3-chloro-2-methylpropane using sulphuric acid as a catalyst[35] and tritylmethyl chloride was prepared by the reaction of trityl-sodium with dichloromethane[36] and recrystallised before use. Tetrakis(t-butoxy)chromium(IV) was prepared by the method of Krauss and Munster[37] and purified by sublimation. Solvents were dried and degassed prior to use. Petroleum had b.p. 30—40° except for chromatography when it had b.p. 60—80°. Chromatography was carried out using acid washed alumina (Spencer Chemicals for Industry, Type H).

Tetrakis(trimethylsilylmethyl)chromium(IV).—This was prepared as in ref. 1.

The Tetrakis(neopentyl)chromate(III) *Ion*.—Neopentyllithium was prepared in cyclohexane in the same way as the silicon analogue.[38]

To the stirred suspension of $CrCl_3$,3THF (1·4 g, 4 mmol) in THF (50 ml) at −40°, was added dropwise over 15 min a solution of neopentyl-lithium (16 mmol) in THF. An immediate reaction gave a dark blue-black solution which was allowed to warm to room temperature and filtered. The reaction appears to be quantitative. The solution may be oxidised to $Cr(CH_2CMe_3)_4$ by bubbling through it small quantities of air until the colour changes to a deep maroon, but the tetra-alkyl is more conveniently prepared as follows.

Tetrakis(neopentyl)chromium(IV).—To a stirred suspension of $CrCl_3$,3THF (1 g, 3 mmol) in diethyl ether (50 ml) was added dropwise at room temperature over 10 min a solution of neopentylmagnesium chloride[39] (13 mmol) in diethyl ether (25 ml). The deep blue mixture was allowed to stir for 1 h until it became maroon. The solution was then hydrolysed with saturated ammonium chloride solution (100 ml) and after separation, the ether layer dried ($MgSO_4$), decanted and concentrated to *ca.* 5 ml. The solution was transferred to an alumina column and the complex eluted with petroleum. The maroon fraction was collected and concentrated to small volume and cooled to −30°. Crystals of the *compound* separated and were collected at this temperature (0·3 g, 30%) (Found: C, 72·2; H, 13·0; Cr, 14·5. $C_{20}H_{44}Cr$ requires C, 71·4; H, 13·9; 14·7%).

Tetrakis(neophyl)chromium(IV).—To a stirred suspension of $CrCl_3$,3THF (6 g, 15 mmol) in diethyl ether (100 ml) was added dropwise over 10 min at room temperature a solution of neophylmagnesium chloride[40] (60 mmol) in diethyl ether (40 ml). The dark blue mixture was allowed to stir for 1 h, then sufficient air was bubbled through the solution until it turned to a deep burgundy colour. This solution was then hydrolysed with saturated ammonium chloride solution and extracted into petroleum, dried, (Na_2SO_4) concentrated to 15 ml and transferred to an alumina column. The wine colour absorbed on the column and after sufficient petrol had been passed down to wash out organic impurities the column was washed with toluene, and the coloured fraction collected, concentrated, and petroleum added. On chilling to −60 °C, crystals of the *compound* separated and were collected at this temperature (1·1 g, 30%) (Found: C, 81·3; H, 9·0; Cr, 9·0. $C_{40}H_{52}Cr$ requires C, 82·2; H, 8·9; Cr, 8·9%).

Tetrakis(tritylmethyl)chromium(IV).—To a stirred suspension of $CrCl_3$,3THF (1·8 g, 5 mmol) in THF (100 ml) at −78°, was added as rapidly as possible, a solution of tritylmethyl-lithium (25 mmol) in THF (50 ml) at −78°. A reaction took place at once and the colour of the lithium reagent disappeared, but by the end of the addition, the bright red colour of the lithium reagent predominated. The solution was allowed to warm to room temperature and air bubbled through until the colour changed to purple (2—3 min). The reaction mixture was hydrolysed and

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extracted into toluene and chromatographed on alumina, eluting with toluene. Fine purple crystals of the *compound* were obtained by concentration of the toluene solution and addition of petroleum (1·1 g, 20%) (Found: C, 88·6; H, 6·4; Cr, 5·0. $C_{80}H_{68}Cr$ requires C, 88·9; H, 6·3; Cr, 4·8%).

Tetramethylchromium(IV).—To a suspension of freshly prepared methyl-lithium (*ca.* 2·0 g, 100 mmol) in petroleum (30 ml) was added a solution of $Cr(OBu^t)_4$ (1·0 g, 3 mmol) in petroleum (20 ml). The mixture was allowed to stir at room temperature for 15 min and the maroon solution filtered. On distillation *in vacuo* the volatiles were collected at −78 °C yielding a petroleum solution of the *compound* free from methyl-lithium. Yield before distillation is probably quantitative, after distillation *ca.* 10—20%.

Petroleum-free $CrMe_4$ may be prepared by treating solid chromium(IV) *t*-butoxide with solid methyl-lithium at 30° *in vacuo,* collecting the volatile products, and separating the tetramethylchromium by trap-to-trap distillation *in vacuo.*

Tetrakis(*benzyl*)*chromium*(IV).—To a stirred solution of $CrCl_3$,3THF (1·0 g, 2·5 mmol) in THF (100 ml) at −20 °C was added a solution of benzyl-lithium[41] (10 mmol) in benzene (25 ml). The reaction mixture was allowed to warm to room temperature and stirred for 20 min. The dark solution was filtered, the solvent removed *in vacuo* and the black, sticky residue extracted with petroleum. A very dilute, pale reddish-brown solution was obtained which was extremely air and moisture sensitive, and was characterised as the *compound* by its e.s.r. spectrum. The yield was very poor.

Bis(1,3-*dimethylenetetramethyldisiloxane*)*chromium*(IV).—The di-Grignard reagent derived from 1,3-bis(chloromethyl)-tetramethyldisiloxane was prepared in a similar way to the trimethylsilylmethyl Grignard reagent[42] and a sample was hydrolysed and shown by n.m.r. to be essentially hexamethyldisiloxane.

To a stirred solution of $CrCl_3$,3THF (1·2 g, 3 mmol) in THF (100 ml) at room temperature were added dropwise over 15 min 6 mmol of the di-Grignard reagent in diethyl ether (25 ml). The reaction mixture was stirred for 15 min and hydrolysed with saturated ammonium chloride solution, extracted into petroleum and chromatographed on alumina. On removal of solvent *in vacuo* at room temperature a purple oil was obtained and characterised as the *compound* by its e.s.r. and electronic spectra.

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