tert-Butylimido Complexes of Chromium and Vanadium. X-Ray Crystal Structures of $Cr(NBu^t)Cl_3(MeOCH_2CH_2OMe)$, $Cr[C_6H_4(NH)_2\text{-}o]Cl_2(PMe_2Ph)_2$, $Cr(NBu^t)_2(OSiPh_3)_2$, $Cr(NBu^t)Cl(OC_9H_6N)_2$ and $[(PPh_3)_2][Cr(NBu^t)\{S_2C_2(CN)_2\}_2]$ *

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The compound $Cr(NBu^t)Cl_3$, isolated as its adducts with tetrahydrofuran (thf) and 1,2-dimethoxyethane (dme), has been prepared by chlorination of $Cr(NBu^t)_2Cl_2$. These materials have been used as sources of other chromium compounds such as the neutral adducts $Cr(NBu^t)Cl_3(PR_3)_2$ (R_3 = Me_3, Et_3, Me_2Ph or $EtPh_2$) or $Cr(NBu^t)Cl_2(NC_7H_{13})$ (NC_7H_{13} = quinuclidine) or anionic complexes such as $[PPh_4][Cr(NBu^t)Cl_4]$. The tertiary phosphine complexes in the presence of excess of phosphine are photochemically or thermally reduced to $CrCl_3(PR_3)_3$ and the tertiary phosphinimine. Halide-substitution reactions on $Cr(NBu^t)Cl_3(dme)$ or $[Cr(NBu^t)Cl_4]^-$ with O,N, (O,N) and S ligands give rise to compounds such as *cis*-$Cr(NBu^t)Cl(OC_9H_6N)_2$ (OC_9H_6N = quinolin-8-olate), $[Cr(NBu^t)(mnt)_2]^-$ (mnt = maleonitriledithiolate) and $Cr(NBu^t)Cl(S_2CNEt_2)_2$; cyclic voltammetry of the last two complexes is reported. Evidence for the disproportionation $2Cr^V \longrightarrow Cr^{VI} + Cr^{IV}$ in reactions of alkoxides is given. Reduction of $Cr(NBu^t)Cl_3(dme)$ in the presence of 1,2-bis(dimethylphosphino)ethane (dmpe) gives the chromium(IV) species $[Cr(NBu^t)(dmpe)_2Cl]Cl$. The EPR (X-band) spectra of chromium(V) species at room temperature show hyperfine splitting for ^{53}Cr, ^{14}N and ^{31}P in appropriate compounds with g_{iso} values at 77 K of *ca.* 2.00. The compounds $[V(NBu^t)(NHBu^t)(\mu\text{-}NBu^t)]_2$ and $[V(\mu\text{-}NBu^t)(OSiMe_3)_2]_2$ are also described. The X-ray structures of five compounds have been determined: $Cr(NBu^t)Cl_3(dme)$ is octahedral with a *mer* arrangement of the three chlorines; $Cr[C_6H_4(NH)_2\text{-}o]Cl_2(PMe_2Ph)_2$ is also octahedral, having C_2 symmetry with *trans* phosphines and *cis* chlorines; $Cr(NBu^t)_2(OSiPh_3)_2$ is distorted tetrahedral; $Cr(NBu^t)Cl(OC_9H_6N)_2$ is octahedral with the chelating quinolin-8-olato groups arranged to give *trans* O,O and *cis* N,N geometry; and $[Cr(NBu^t)(mnt)_2]^-$ has a square-pyramidal structure with an axial imido group.

In previous work on *tert*-butylimido compounds of chromium, the chromium(IV) aryls[1] $Cr(NBu^t)_2R_2$ (R = $C_6H_2Me_3$-2,4,6 or $C_6H_3Me_2$-2,6) and their insertion reactions with CO and isocyanides were studied. Recently, similar alkyls, $Cr(NBu^t)_2R_2$ (R = CH_2SiMe_3, CH_2CMe_3 or CH_2CMe_2Ph), were prepared along with $Cr(NBu^t)_2Br_2(py)$ (py = pyridine) and some related compounds.[2] We have also described[3a] the synthesis of the homoleptic compound $Li_2Cr^{VI}(NBu^t)_4$ from $Cr(NBu^t)_2Cl_2$ *via* $Cr(NBu^t)_2(NHBu^t)_2$ and expanded the work[3b] to include a variety of other chromium(VI) species such as $Cr(NBu^t)_2Cl_2(PMe_3)$ and $Cr(NBu^t)_2[\eta^2\text{-}(Bu^tN{=}CMe)]Cl$ as well as chromium(V) dimers $[Cr(NBu^t)X(\mu\text{-}NBu^t)]_2$ (X = Cl or $NHBu^t$). The compound $Cr(NBu^t)_2Cl_2$ has been shown[4] to be reduced on chlorination to give the very useful starting material for synthesis of chromium(V) compounds, $Cr(NBu^t)Cl_3$, and its adducts such as $Cr(NBu^t)Cl_3(thf)_2$ (thf = tetrahydrofuran).

We now describe extended studies on the chemistry and structures of chromium(V) imido compounds, their reactions and electron paramagnetic resonance spectra. Analytical and physical data for new compounds are collected in Table 1.

Results and Discussion

Chlorination of $Cr(NBu^t)_2Cl_2$ *to give* $Cr(NBu^t)Cl_3$.—The chlorination of $Cr(NBu^t)_2Cl_2$ in dichloromethane at room temperature results in reduction of Cr^{VI} to Cr^V after 2–3 min as is shown by the change in colour from the orange-red of Cr^{VI} to green-brown of Cr^V. The reduction does not appear sensitive to temperature or stoichiometry of the reactants; on scales > 1 g a slight exothermicity is observed. Excess of chlorine has no further effect on the $Cr(NBu^t)Cl_3$ formed. In hexane intractable products are obtained. Although chlorination of $Cr(NBu^t)_2(OSiMe_3)_2$ has been claimed to give '$Cr(NBu^t)_2Cl_2$' as an orange powder,[5] we have shown that $Cr(NBu^t)_2Cl_2$ is a red crystalline material formed on interaction of the siloxide with BCl_3.[3] Since we find that chlorination of the siloxide under various conditions of solvent and temperature does not give a chromium(V) complex it appears that for successful reduction it is necessary to use $Cr(NBu^t)_2Cl_2$ and CH_2Cl_2 as the preferred reaction medium. This dichloride was also claimed[2] to be formed as a purple oil in 50% yield along with $CrO(NBu^t)(OSiMe_3)$ by interaction of $Cr(NBu^t)_2(OSiMe_3)_2$ with HCl in Et_2O but it was isolated only as $Cr(NBu^t)_2Cl_2(py)$.

Although we have been unable to obtain evidence of intermediates in the chlorination reaction it seems likely that chlorine attacks the electron-rich nucleophilic imido nitrogen with elimination of Bu^tNCl_2, equation (1). The failure of

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* *tert*-Butylimidotrichloro(1,2-dimethoxyethane-κ^2O,O')chromium(V), dichlorobis(dimethylphenylphosphine)(*o*-phenylenediamido-κ^2N,N')chromium(IV), bis(*tert*-butylimido)bis(triphenylsiloxo)chromium(VI), *tert*-butylimidochlorobis(quinolin-8-olato-κ^2N,O)chromium(V) and bis(triphenylphosphoranylidene)ammonium *tert*-butylimidobis(maleonitriledithiolato-κ^2S,S')chromate(V).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.
Non-SI unit employed: G = 10^{-4} T.

Table 1 Analytical and physical data for new compounds

Compound	Colour	M.p./°C	Analysis (%)			
			C	H	N	Other
1 $\mathrm{Cr(NBu^t)Cl_3(thf)_2}$	Green	110–115	38.4	6.8	3.8	Cl 28.3
			(38.5)	(6.7)	(3.7)	(28.5)
2 $\mathrm{Cr(NBu^t)Cl_3(dme)}$	Green	126–127	29.8	6.0	4.3	Cl 33.1
			(30.0)	(5.9)	(4.4)	(33.3)
3 $\mathrm{Cr(NBu^t)Br_3(dme)}$	Red	148–150	21.8	4.2	2.9	Br 54.4
			(21.3)	(4.2)	(3.1)	(53.0)
4 $\mathrm{Cr(NBu^t)Cl_3(PMe_3)_2}$	Orange-red	162–165	32.5	7.1	3.7	
			(31.5)	(7.1)	(3.7)	
5 $\mathrm{Cr(NBu^t)Cl_3(PEt_3)_2}$	Orange-red	165–167	41.5	8.3	3.1	
			(41.2)	(8.4)	(3.0)	
6 $\mathrm{Cr(NBu^t)Cl_3(PMe_2Ph)_2}$	Orange-red	163–170	47.8	6.2	2.8	
			(47.5)	(6.1)	(2.8)	
7 $\mathrm{Cr(NBu^t)Cl_3(PEtPh_2)_2}$	Orange-red	165–170	58.3	5.9	2.1	
			(58.4)	(5.9)	(2.1)	
8 $\mathrm{Cr(NBu^t)Cl_3(NC_7H_{13})_2}$	Green	220	60.5	9.3	11.2	
			(61.4)	(9.9)	(11.9)	
9 $\mathrm{[PPh_4][Cr(NBu^t)Cl_4]}$	Olive	169–170	54.0	5.2	2.4	Cl 23.4
		(decomp.)	(55.6)	(4.8)	(2.3)	(23.5)
10 $\mathrm{[N(PPh_3)_2][Cr(NBu^t)Cl_4]}$	Olive	162–164	59.6	5.1	3.6	Cl 17.9
		(decomp.)	(59.8)	(4.9)	(3.5)	(17.7)
11 $\mathrm{Cr[C_6H_4(NH)_2\text{-}\mathit{o}]Cl_2(PMe_2Ph)_2}$	Red	250	55.0	5.8	5.8	Cl 15.1
			(55.6)	(5.9)	(5.9)	(15.0)
12 $\mathrm{[Cr(NBu^t)(NHBu^t)_2Cl]_2}$	Dark orange	127–128	46.5	9.3	13.2	
			(47.6)	(9.6)	(13.9)	
13 $\mathrm{[Cr(NBu^t)(NHC_6H_3Cl_2\text{-}2,6)_2Cl]_2}$	Purple	112–114	38.7	3.6	8.6	
			(39.9)	(3.5)	(8.7)	
14 $\mathrm{[Cr(NBu^t)(OSiPh_3)_3]_2}$	Orange	110–112	71.8	6.2	2.0	
			(73.4)	(5.7)	(1.6)	
15 $\mathrm{Cr(NBu^t)_2(OSiPh_3)_2}$	Brown	102–105	70.4	6.3	3.8	
			(70.2)	(6.4)	(3.7)	
16 $\mathrm{Cr(NBu^t)Cl(OC_9H_6N)_2}$	Green	192–197	58.5	4.3	9.2	
			(58.9)	(4.5)	(9.4)	
17 $\mathrm{[N(PPh_3)_2][Cr(NBu^t)(OCMeEtCO_2)]}$	Brown	*ca.* 200	67.3	6.4	3.1	
			(67.1)	(6.2)	(3.1)	
18 $\mathrm{Cr(NBu^t)(salen)Cl}$	Brown	>250	55.2	5.4	9.6	
			(56.5)	(5.8)	(9.8)	
19 $\mathrm{Na[Cr(NBu^t)(CN)_4]}$	Orange	>250	34.0	3.5	25.6	
			(34.3)	(3.2)	(25.1)	
20 $\mathrm{Cr(NBu^t)Cl(S_2CNEt_2)_2}$	Green	162–163	35.8	6.4	9.0	S 26.6
			(37.0)	(6.4)	(9.2)	(28.2)
21 $\mathrm{[N(PPh_3)_2][Cr(NBu^t)(mnt)_2]}$	Blue-green	187–188	61.0	3.9	8.9	S 12.6
			(61.2)	(4.1)	(8.9)	(13.6)
22 $\mathrm{[Cr(NBu^t)(dmpe)_2Cl]Cl}$	Green	>250	38.2	8.4	2.7	
			(38.9)	(8.3)	(2.8)	
23 $\mathrm{[V(NBu^t)(NHBu^t)(\mu\text{-}NBu^t)]_2}$	Red-brown	205–206	54.5	10.5	15.9	
			(54.4)	(10.5)	(15.9)	
24 $\mathrm{[V(\mu\text{-}NBu^t)(OSiMe_3)_2]_2}$	Yellow-brown	146–150	39.9	8.6	4.9	
		(decomp.)	(40.2)	(9.0)	(4.7)	

Table 2 Selected bond lengths (Å) and angles (°) for the complex $\mathrm{Cr(NBu^t)Cl_3(dme)}$

Cl(2)–Cr	2.326(4)	Cl(1)–Cr	2.251(4)
O(1)–Cr	2.079(8)	O(2)–Cr	2.200(8)
Cl(3)–Cr	2.289(5)	N–Cr	1.594(9)
Cl(1)–Cr–Cl(2)	90.9(2)	O(1)–Cr–Cl(2)	87.0(3)
O(1)–Cr–Cl(1)	166.5(2)	O(2)–Cr–Cl(2)	88.4(3)
O(2)–Cr–Cl(1)	89.8(3)	O(2)–Cr–O(1)	76.8(3)
Cl(3)–Cr–Cl(2)	171.8(1)	Cl(3)–Cr–Cl(1)	92.1(2)
Cl(3)–Cr–O(1)	88.2(3)	Cl(3)–Cr–O(2)	84.0(3)
N–Cr–Cl(2)	93.7(3)	N–Cr–Cl(1)	96.2(4)
N–Cr–O(1)	97.2(4)	N–Cr–O(2)	173.6(3)
N–Cr–Cl(3)	93.6(4)	C(2)–O(1)–Cr	113.3(6)
C(12)–O(1)–Cr	121.6(7)	C(1)–O(2)–Cr	110.9(6)
C(11)–O(2)–Cr	125.2(6)	C(10)–N–Cr	172.6(6)

$$\mathrm{2Cr(NBu^t)_2Cl_2 + 3Cl_2 \longrightarrow 2Cr(NBu^t)Cl_3 + 2Bu^tNCl_2} \quad (1)$$

$\mathrm{Cr(NBu^t)Cl_3}$ to react with more $\mathrm{Cl_2}$ is presumably due to the bonding $\mathrm{Bu^tN}\overset{\rightarrow}{=}\mathrm{Cr}$ with involvement of the lone pair on nitrogen in N–Cr bonding. As far as we are aware this procedure is the only entry to monoimidochromium(V) species. Attempts to form such imido compounds by reactions of $\mathrm{CrOCl_3}$[6] or salts of the anion $\mathrm{[CrOCl_4]^-}$ with isocyanates, silylamines or amines failed to give the imido species. Also present studies on the reduction of $\mathrm{Cr(NBu^t)_2Cl_2}$ with standard reducing agents in the presence of Lewis bases did not give chromium(V) imido complexes.

The $\mathrm{Cr(NBu^t)Cl_3}$, which forms an oil, cannot be crystallised; the solution in $\mathrm{CH_2Cl_2}$ is stable at room temperature. Addition of thf, 1,2-dimethoxyethane (dme) and other ligands readily gives high yields of adducts, generally $\mathrm{Cr(NBu^t)Cl_3L_2}$ some of which are crystalline but some, as with pyridine, substituted pyridines or acetonitrile, are oils. Addition of $\mathrm{Cl^-}$ gives the anion $\mathrm{[Cr(NBu^t)Cl_4]^-}$. Chromium(V) oxo analogues of these imido species, $\mathrm{CrOCl_3L}$ (L = 2,2′-bipyridine or 4,4′-dimethyl-2,2′-bipyridine) are known,[7] as well as $\mathrm{CrOCl_3}$ and the anion $\mathrm{[CrOX_4]^-}$ (X = F, Cl or Br).[8]

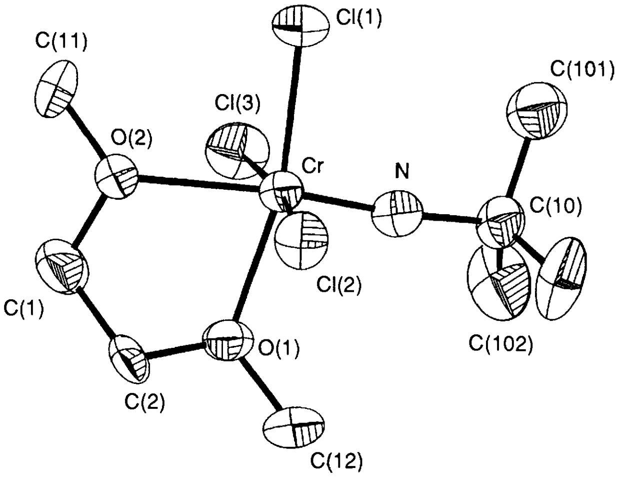


Fig. 1 The structure of $\text{Cr(NBu}^t\text{)Cl}_3\text{(dme)}$

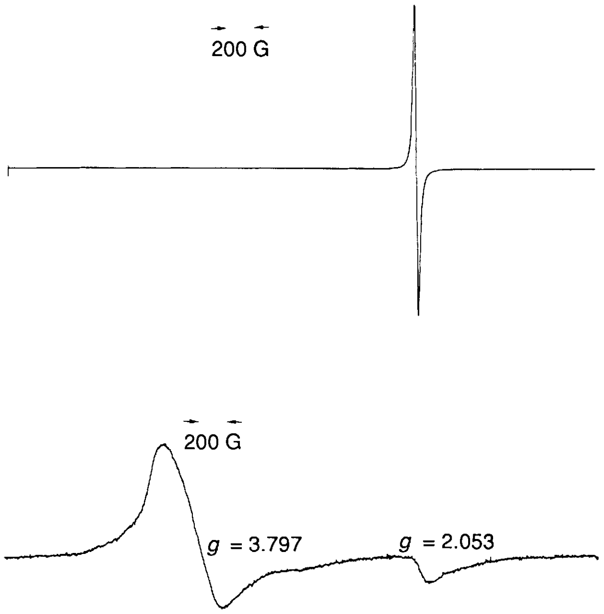


Fig. 2 X-Band EPR spectra in MeCN. Top: $\text{Cr(NBu}^t\text{)Cl}_3\text{(PMe}_2\text{Ph)}_2$ at 77 K. Bottom: spectrum at 77 K after photolysis at room temperature

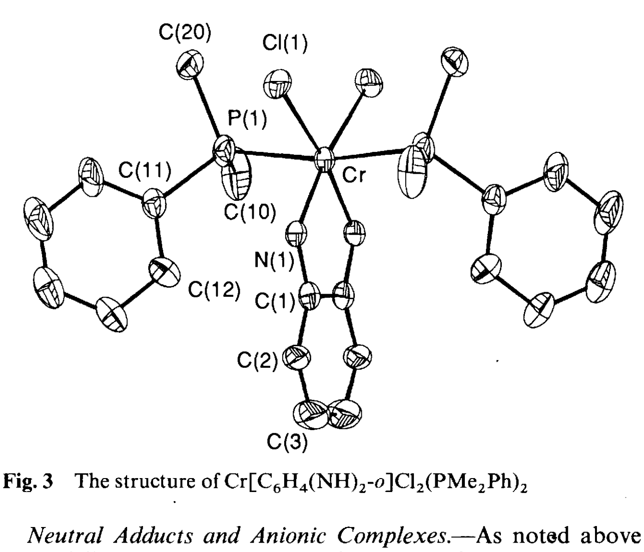


Fig. 3 The structure of $\text{Cr[C}_6\text{H}_4\text{(NH)}_2\text{-}o\text{]Cl}_2\text{(PMe}_2\text{Ph)}_2$

Neutral Adducts and Anionic Complexes.—As noted above neutral ligands give a variety of adducts of which the green $\text{Cr(NBu}^t\text{)Cl}_3\text{(thf)}_2$ **1** or $\text{Cr(NBu}^t\text{)Cl}_3\text{(dme)}$ **2** are easily obtained and provide useful starting materials. The bromide, $\text{Cr(NBu}^t\text{)Br}_3\text{(dme)}$ **3**, has also been made. The structure of **2** is shown in Fig. 1; bond lengths and angles are in Table 2.

The structure differs from that of the octahedral bis PEtPh_2 adduct **7**,[4] where the donor ligands are mutually *trans*, since the two co-ordinating atoms here belong to a bidentate chelate and must therefore occupy *cis* sites. Furthermore, whilst the three chlorines occupy three sites of the octahedral co-ordination geometry in a *mer* configuration, they are all mutually *cis* to the imido function; in the phosphine complex the central chlorine was *trans* to this group. In the present complex one of the dme oxygens is *trans* to the imido group and this leads to a considerable difference in Cr–O bond lengths, of 0.12 Å (see Table 2). The second oxygen of the dme is *trans* to the central chlorine of the *mer*-Cl_3 group, for which the Cr–Cl bond is the shortest of three. The other two, mutually *trans*, Cr–Cl bonds inexplicably show lengths differing by *ca.* 0.04 Å; a similar feature was noted for the bis(phosphine).[4] The Cr–NBu^t distance is similar to that in the phosphine complex also.

From **1** and **2** can readily be made the tertiary phosphine compounds $\text{Cr(NBu}^t\text{)Cl}_3\text{(PR}_3\text{)}_2$ (R_3 = Me_3, **4**; Et_3, **5**; Me_2Ph, **6**; or EtPh_2, **7**) and also $\text{Cr(NBu}^t\text{)Cl}_3\text{(NC}_7\text{H}_{13}\text{)}_2$ (NC_7H_{13} = quinuclidine) **8**. All of these adducts are slightly moisture sensitive and also light sensitive (see below). The adducts other than **2** and **7** were characterised by analysis and spectra. The IR spectra show $\nu(\text{CrNBu}^t)$ at *ca.* 1200 cm^{-1} while ν(CrCl) usually[9] appears in the region 300–450 cm^{-1} and the spectra indicate *mer* chlorines in the octahedral species as found in **1**. The EPR spectra are discussed later.

In addition to these neutral adducts, interaction of $\text{Cr(NBu}^t\text{)Cl}_3$ with $\text{(PPh}_4\text{)Cl}$ or $\text{[N(PPh}_3\text{)}_2\text{]Cl}$ in CH_2Cl_2 gives the air-stable salts **9** and **10** of the $\text{[Cr(NBu}^t\text{)Cl}_4\text{]}^-$ ion; the IR spectra have ν(Cr–Cl) at 373 cm^{-1} (*cf.* the value[10] for $\text{[CrOCl}_4\text{]}^-$ of 405 cm^{-1}).

In the presence of an excess of the phosphine, the phosphine adducts noted above are reduced to chromium(III) phosphine complexes and the phosphinimine either photochemically in toluene with a half-life of *ca.* 15 min or thermally in boiling toluene (*ca.* 24 h). For the dimethylphenylphosphine complex **6** the reaction is as in equation (2) where the products were

$$\text{Cr(NBu}^t\text{)Cl}_3\text{(PMe}_2\text{Ph)}_2 + 2\text{PMe}_2\text{Ph} \longrightarrow \text{CrCl}_3\text{(PMe}_2\text{Ph)}_3 + \text{Bu}^t\text{N=PMe}_2\text{Ph} \quad (2)$$

isolated and identified analytically and spectroscopically; $\text{CrCl}_3\text{(PMe}_2\text{Ph)}_3$ has not been previously reported. The EPR spectra of the initial and final products are shown in Fig. 2. Excited-state properties of complexes of the type $\text{Ta(NR)Cl}_3\text{L}_2$ (R = Ph, $\text{C}_6\text{H}_3\text{Pr}^i{}_2$-2,6, *etc.*; L = PMe_3, thf, *etc.*) have been briefly reported.[11] Although photochemical reduction occurs in the absence of excess of phosphine and the colour changes from the red-brown Cr^V to blue-green Cr^III, we could not cleanly separate the products.

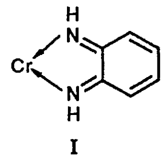
The compound $\text{Cr(NBu}^t\text{)Cl}_3\text{(PMe}_2\text{Ph)}_2$ **6** undergoes a reaction with 1 equivalent of *o*-phenylenediamine in toluene in the presence of NEt_3 as HCl acceptor. The NBu^t group is removed and the red *o*-phenylenediamido complex of chromium(IV), $\text{Cr[(C}_6\text{H}_4\text{(NH)}_2\text{-}o\text{]Cl}_2\text{(PMe}_2\text{Ph)}_2$ **11**, is obtained but in yield less than 50%. Further substitution of chloride does not occur under forcing conditions. It seems unlikely that reduction by a dissociated phosphine (see above) occurs since no chromium(III) species can be identified by isolation or EPR spectra. It is possible that reduction by the diamine occurs but, in view of a reaction discussed below and particularly the loss of a NBu^t group, it seems more likely that there is a disproportionation reaction: $2\text{Cr}^\text{V} \longrightarrow \text{Cr}^\text{IV} + \text{Cr}^\text{VI}$. The other products of the reaction have so far not been identified but presumably they are $\text{Cr}^\text{VI}\text{(NBu}^t\text{)}_2$ species.

The structure of the diamidochromium(IV) compound **11** has been confirmed by X-ray diffraction and a diagram of the molecule is shown in Fig. 3; bond distances and angles are in Table 3. The molecule has an octahedral geometry with a chelating diamido function, *cis* chlorines and *trans* phosphines, and occupies a site of crystallographic C_2 symmetry. The Cr–Cl

Table 3 Selected bond lengths (Å) and angles (°) for the complex Cr[$C_6H_4(NH)_2$-*o*]Cl_2(PMe_2Ph)$_2$

Cl(1)–Cr	2.343(5)	P(1)–Cr	2.454(5)
N(1)–Cr	1.943(10)	C(10)–P(1)	1.859(12)
C(20)–P(1)	1.853(14)	C(11)–P(1)	1.833(8)
C(1)–N(1)	1.350(13)	C(2)–C(1)	1.409(15)
C(1)–C(1B)	1.475(17)	C(3)–C(2)	1.364(18)
C(3)–C(3B)	1.440(24)		
P(1)–Cr–Cl(1)	88.9(2)	N(1)–Cr–Cl(1)	90.7(3)
N(1)–Cr–P(1)	97.5(3)	Cl(1)–Cr–Cl(1B)	98.6(2)
P(1)–Cr–P(1B)	170.4(1)	N(1)–Cr–N(1B)	80.2(5)
C(1)–Cr–P(1B)	84.8(3)	P(1)–Cr–N(1B)	89.9(6)
Cl(1)–Cr–N(1B)	170.5(4)	C(10)–P(1)–Cr	114.0(5)
C(20)–P(1)–Cr	113.0(5)	C(20)–P(1)–C(10)	104.4(7)
C(11)–P(1)–Cr	116.5(3)	C(11)–P(1)–C(10)	102.1(6)
C(11)–P(1)–C(20)	105.5(6)	C(1)–N(1)–Cr	117.5(7)
C(2)–C(1)–N(1)	127.9(10)	N(1)–C(1)–C(1B)	112.4(9)
C(2)–C(1)–C(1B)	119.7(10)	C(3)–C(2)–C(1)	118.6(11)
C(2)–C(3)–C(3B)	121.6(11)		

Key to symmetry operation relating designated atoms to reference atoms at (x,y,z): B $-x, y, 0.5 - z$.



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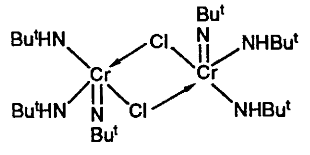

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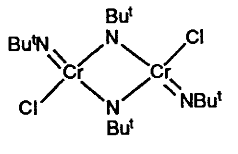

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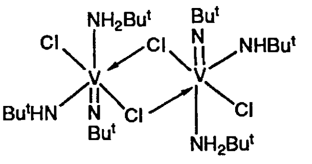

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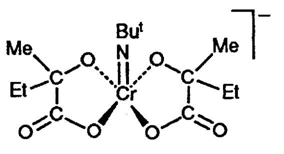
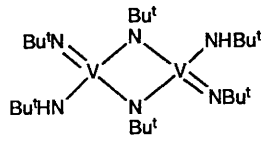
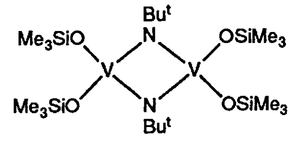


III



IV



V

bond lengths are just slightly longer than the average of those to the mutually *trans* chlorines in the chromium(v) complex above, as expected. The Cr–N distances are slightly shortened, indicating a small amount of multiple-bond character. Most interestingly, the bond lengths in the diamido ligand show a significant contribution from the form I, which would imply a formally chromium(II) state. On the other hand, the Cr–P distances are quite long and consistent with a higher oxidation state.[12a]

It may be noted that relatively few octahedral chromium(IV) complexes have been structurally characterised, an imido one being [Cr(NEt)(dmpe)$_2$Cl]CF_3SO_3[12b] [dmpe = 1,2-bis(dimethylphosphino)ethane].

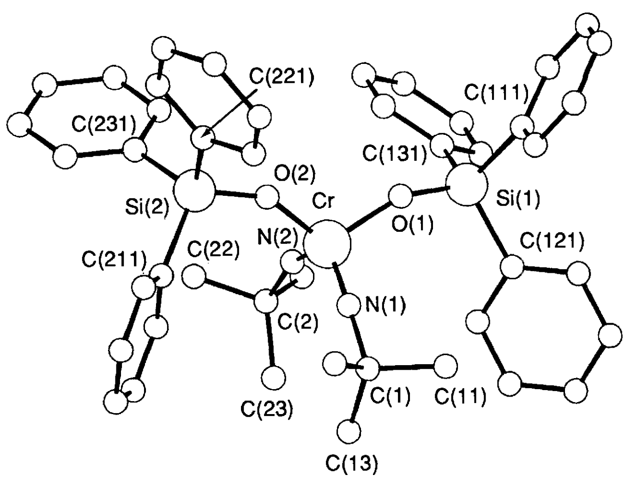


Fig. 4 The structure of Cr(NBu^t)$_2$(OSiPh$_3$)$_2$

Table 4 Selected bond lengths (Å) and angles (°) for the complex Cr(NBu^t)$_2$(OSiPh$_3$)$_2$

O(1)–Cr	1.776(13)	O(2)–Cr	1.798(13)
N(1)–Cr	1.548(15)	N(2)–Cr	1.629(16)
O(1)–Si(1)	1.615(13)	C(111)–Si(1)	1.884(12)
C(121)–Si(1)	1.870(12)	C(131)–Si(1)	1.883(13)
O(2)–Si(2)	1.610(13)	C(211)–Si(2)	1.885(13)
C(221)–Si(2)	1.871(13)	C(231)–Si(2)	1.885(11)
C(1)–N(1)	1.502(25)	C(2)–N(2)	1.477(26)
O(2)–Cr–O(1)	112.0(6)	N(1)–Cr–O(1)	107.7(7)
N(1)–Cr–O(2)	106.6(7)	N(2)–Cr–O(1)	107.7(8)
N(2)–Cr–O(2)	107.0(7)	N(2)–Cr–N(1)	116.0(8)
Si(1)–O(1)–Cr	149.0(7)	Si(2)–O(2)–Cr	150.6(7)
C(1)–N(1)–Cr	174.3(13)	C(2)–N(2)–Cr	160.7(13)

The dme adduct **2** reacts with SiMe$_3$(NHBu^t) to give the dimer [Cr(NBu^t)(NHBu^t)$_2$Cl]$_2$ **12**, which, on the basis of IR [ν(N–H) 3251 cm^{-1}] and NMR spectra we formulate as **IIa**. This chromium(v) dimer is diamagnetic [*cf.* the diamagnetic chromium(v) dimer **IIb** obtained by reduction of Cr(NBu^t)$_2$Cl$_2$[3b]]. It may be noted that interaction of V(NBu^t)Cl$_3$ with NH$_2$Bu^t gives the structurally characterised chloride-bridged dimer **IIc**.[13] The diamagnetism of dimer **12** could be due to superexchange interaction or the metal–metal bond formation but unfortunately X-ray-quality crystals could not be obtained due to persistent twinning.

The interaction of excess of 2,6-dichloroaniline with Cr(NBu^t)Cl$_3$(dme) gave a similar diamagnetic arylamido dimer, [Cr(NBu^t)(NHC$_6$H$_3$Cl$_2$-2,6)$_2$Cl]$_2$ **13**.

Halide Substitution Reactions.—Oxygen, O,N *and* N *ligands* The reaction of complex **2** with lithium triphenylsiloxide, LiOSiPh$_3$, leads to three crystalline products. An orange-brown chromium(v) complex is formulated as [Cr(μ-NBu^t)(OSiPh$_3$)$_3$]$_2$ **14** on the basis of analyses, IR and NMR spectra and as a dimer because of the diamagnetism. We were unable to obtain crystals of X-ray quality. A second diamagnetic complex as brown plates has been characterised by X-ray study as the chromium(VI) bis(imido) compound, Cr(NBu^t)$_2$(OSiPh$_3$)$_2$ **15**, while the third, red, crystalline product appears to be Cr(OSiPh$_3$)$_4$.

The structure of compound **15** is shown in Fig. 4; bond lengths and angles are listed in Table 4. The molecule has a distorted-tetrahedral geometry with an approximate (*i.e.* non-crystallographic) mirror plane of symmetry containing the metal and the imido functions. The angles around chromium vary from 106.6(7) to 116.0(8)° with the two larger angles being O–Cr–O [112.0(6)°] and N–Cr–N [116.0(8)°]. The rather small

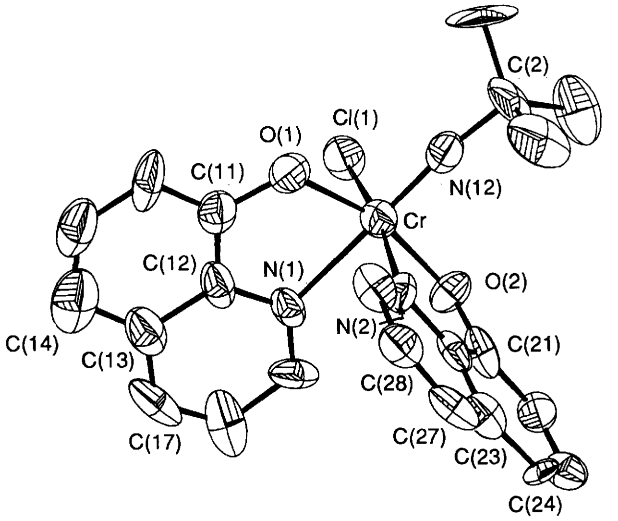


Fig. 5 The structure of Cr(NBu^t)Cl(OC$_9$H$_6$N)$_2$

Table 5 Selected bond lengths (Å) and angles (°) for the complex Cr(NBu^t)Cl(OC$_9$H$_6$N)$_2$

Cl–Cr	2.303(5)	O(1)–Cr	1.920(9)
N(1)–Cr	2.169(11)	N(2)–Cr	2.067(10)
O(2)–Cr	1.922(8)	N(12)–Cr	1.621(10)
O(1)–Cr–Cl	93.5(3)	N(1)–Cr–Cl	86.2(3)
N(1)–Cr–O(1)	79.8(4)	N(2)–Cr–Cl	169.1(3)
N(2)–Cr–O(1)	89.8(4)	N(2)–Cr–N(1)	84.2(4)
O(2)–Cr–Cl	91.8(3)	O(2)–Cr–O(1)	163.2(3)
O(2)–Cr–N(1)	84.7(4)	O(2)–Cr–N(2)	82.2(4)
N(12)–Cr–Cl	96.9(4)	N(12)–Cr–O(1)	97.6(5)
N(12)–Cr–N(1)	176.1(4)	N(12)–Cr–N(2)	92.9(4)
N(12)–Cr–O(2)	97.6(5)	C(11)–O(1)–Cr	116.2(8)
C(12)–N(1)–Cr	110.0(8)	C(19)–N(1)–Cr	130.8(9)
C(19)–N(1)–C(12)	119.1(12)	C(22)–N(2)–Cr	109.8(7)
C(29)–N(2)–Cr	130.0(9)	C(21)–O(2)–Cr	114.7(7)
C(2)–N(12)–Cr	171.6(7)		

Table 6 Selected bond lengths (Å) and angles (°) for the complex [N(PPh$_3$)$_2$][Cr(NBu^t)(mnt)$_2$]

S(1)–Cr	2.293(6)	S(2)–Cr	2.295(8)
S(3)–Cr	2.299(8)	S(4)–Cr	2.302(6)
N(11)–Cr	1.583(14)		
S(2)–Cr–S(1)	84.3(3)	S(3)–Cr–S(1)	87.4(3)
S(3)–Cr–S(2)	151.3(2)	S(4)–Cr–S(1)	147.4(2)
S(4)–Cr–S(2)	87.2(3)	S(4)–Cr–S(3)	85.2(3)
N(11)–Cr–S(1)	101.8(5)	N(11)–Cr–S(2)	106.9(6)
N(11)–Cr–S(3)	101.6(5)	N(11)–Cr–S(4)	110.8(5)
C(3)–S(1)–Cr	99.8(6)	C(2)–S(2)–Cr	104.3(7)
C(4)–S(3)–Cr)	99.4(8)	C(1)–S(4)–Cr	103.1(6)
C(10)–N(11)–Cr	173.8(14)		

opening of the L–Cr–L angles for these bulky ligands (and strongly multiply bonded in the imido case) is similar to results found previously [1,3b] for other chromium(VI) species. The Cr–N distances are typically short and the Cr–O distances of 1.79(1) Å indicate substantial π bonding. The large Cr–O–Si angle of *ca.* 150° is consistent with this.

The formation of the chromium(VI) siloxide we suggest arises *via* a thermal disproportionation reaction [(Ph$_3$SiO)$_3$Cr(μ-NBu^t)]$_2$ $\longrightarrow$ Cr^{VI}(NBu^t)$_2$(OSiPh$_3$)$_2$ + Cr^{IV}(OSiPh$_3$)$_4$ that probably proceeds *via* an intermediate (Ph$_3$SiO)$_2$Cr(μ-NBu^t)$_2$(μ-OSiPh$_3$)Cr(OSiPh$_3$)$_3$.

Further evidence for disproportionation comes from a study of the reaction of Cr(NBu^t)Cl$_3$(dme) with 3 equivalents of potassium *tert*-butoxide. The brown oil obtained after evaporation, extraction of the residue with hexane, and evaporation of the latter was characterised as Cr^{V}(NBu^t)(OBu^t)$_3$ by its IR and EPR spectra (isotropic signal with g_{iso} *ca.* 1.97 and ^{14}N hyperfine structure, *cf.* discussion below). On heating the brown oil in vacuum a blue-green oil distils at *ca.* 140 °C and 10^{-2} mmHg (*ca.* 1.33 Pa); this is EPR silent. The mass spectrum indicates that it is a *ca.* 1:1 mixture of Cr(OBu^t)$_4$[14] (parent ion, m/z = 344 with appropriate fragmentation pattern) and Cr(NBu^t)$_2$(OBu^t)$_2$ [parent ion m/z = 340 and other ions at 325 (M – Me), 269 (M – NBu^t), 267 (M – OBu^t), 198 (M – 2NBu^t), 196 (M – NBu^t– OBu^t), 194 (M – 2OBu^t), *etc.*]. Although we have not been able to separate these *tert*-butoxides due to their similar boiling points, air and moisture sensitivity, we consider the evidence is sufficient to establish the reaction (3). Disproportionation reactions probably account for the

$$2\mathrm{Cr(NBu^t)(OBu^t)_3} \xrightarrow{\text{heat}} \mathrm{Cr(NBu^t)_2(OBu^t)_2} + \mathrm{Cr(OBu^t)_4} \quad (3)$$

difficulties we experienced in isolating products in attempted alkylations of Cr(NBu^t)Cl$_3$(dme) with LiCH$_2$SiMe$_3$ and other alkylating agents where clean products could not be readily obtained.

The reaction of either complex **1** or **2** with 8-hydroxyquinoline in the presence of NEt$_3$ gives air-stable green prisms of *cis*-Cr(NBu^t)Cl(OC$_9$H$_6$N)$_2$ **16**, which has ν(Cr–Cl) at *ca.* 350 cm^{-1}, CrNBu^t at 1106 cm^{-1} in the IR spectrum and a characteristic chromium(V) EPR spectrum. The structure has been confirmed by X-ray study; a diagram of the molecule is shown in Fig. 5 and bond lengths and angles are given in Table 5.

In the octahedral co-ordination the two chelating hydroxyquinolinato groups are arranged to give mutually *trans* Cr–O bonds and *cis* Cr–N bonds. The latter are then *trans* to the imido function and the chloride. The former Cr–N (quinoline) bond is *ca.* 0.1 Å longer than the latter, as expected. The Cr–Cl bond is similar to the average Cr–Cl bond in the dme complex **2** described above, but the two Cr–O distances are much shorter than either of those in **2**.

Interaction of the [N(PPh$_3$)$_2$]$^+$ salt **10** with 2-hydroxy-2-methylbutyric acid in presence of NEt$_3$ affords the air-stable complex anion **III** as its [N(PPh$_3$)$_2$]$^+$ salt **17**. The IR and magnetic moment (μ_B = 1.8) are similar to values for the well known oxo analogues.[8,15]

Interaction of complex **2** with the sodium salt of ethylenebis(salicylideneimine), Na$_2$(salen), in MeCN leads to the Schiff-base complex Cr(NBu^t)Cl(salen) which is slightly soluble in MeCN or thf but readily soluble in CH$_2$Cl$_2$ in which it is a non-conductor. Oxochromium(V) Schiff-base complexes are known.[8]

Interaction of complex **2** with 4 equivalents of NaCN in MeOH gave an orange solution from which orange crystals of Na[Cr(NBu^t)(CN)$_4$] **19** could be isolated on recrystallisation from MeCN. The complex is insoluble in CH$_2$Cl$_2$ or thf but very soluble in MeCN. The IR spectrum has cyanide bands at 2165 and 2265 cm^{-1} while the EPR spectrum is characteristic of Cr^{V}.

Sulphur ligands. Few complexes of chromium(V) with sulphur ligands are known. Homoleptic tris(dithiolene) complexes have been well characterised,[16] a species obtained from sodium chromate and glutathione[17] has an approximate formula Na$_4$[CrC$_{40}$H$_{75}$N$_{12}$S$_4$O$_{32}$], while EPR spectra of CrOCl$_2$(S$_2$CNEt$_2$) and CrOCl(S$_2$CNEt$_2$)$_2$ have recently been reported.[18] Interaction of the [Cr(NBu^t)Cl$_4$]$^-$ salts with sodium diethyldithiocarbamate in methanol leads to the air-stable complex Cr(NBu^t)Cl(S$_2$CNEt$_2$)$_2$ **20**, which is non-conducting in CH$_2$Cl$_2$. In addition to the CrNBu^t and CrCl bands the IR spectrum shows a high value for the ν(C=N) stretch, 1506 cm^{-1}, consistent with a bidentate dithiocarbamate group (ref. 9*a*, p. 348).

A similar reaction using the sodium salt of maleonitriledithiolate Na$_2$(mnt) gives [N(PPh$_3$)$_2$][Cr(NBu^t)(mnt)$_2$] **21**

Table 7 Electron paramagnetic resonance spectral data at 293 K[a]

Compound	Solvent	g_{iso}	α_{Cr}/G	α_N/G	α_P/G
2 $\mathrm{Cr(NBu^t)Cl_3(dme)}$	thf	1.9864	22.3	8.5	
4 $\mathrm{Cr(NBu^t)Cl_3(PMe_3)_2}$	Toluene	2.0032	19.5	7.8	36
5 $\mathrm{Cr(NBu^t)Cl_3(PEt_3)_2}$	Toluene	2.0035	19.5	7.5	35
6 $\mathrm{Cr(NBu^t)Cl_3(PMe_2Ph)_2}$	Toluene	2.0035	19.5	7.2	36
7 $\mathrm{Cr(NBu^t)Cl_3(PEtPh_2)_2}$	Toluene	2.0033	19.2	7.3	35
9 $\mathrm{[PPh_4][Cr(NBu^t)Cl_4]}$	$\mathrm{CH_2Cl_2}$–thf	1.9890	22.0	8.8	
20 $\mathrm{Cr(NBu^t)Cl(S_2CNEt_2)_2}$[b]	thf	1.9739	18.2	9.2	
21 $\mathrm{[N(PPh_3)_2][Cr(NBu^t)(mnt)_2]}$	thf	1.9946	16.4[c]	5.6[c]	

[a] Varian X-12, X-band; for other compounds at 77 K see Experimental section. [b] For $\mathrm{CrClO(S_2CNEt_2)_2}$, $g = 1.9863$; for $\mathrm{CrCl_2O(S_2CNEt_2)}$, $g = 1.9887$, $\alpha_{Cr} = 19.4$ (see ref. 18). [c] These low values may indicate some delocalisation of electron density onto the mnt ligands.

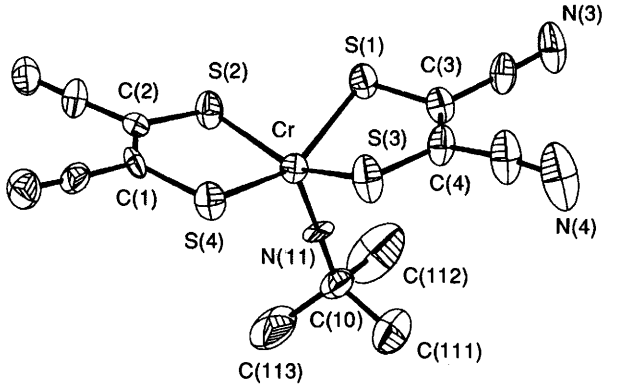


Fig. 6 The structure of the anion in $\mathrm{[N(PPh_3)_2][Cr(NBu^t)(mnt)_2]}$

Fig. 7 X-Band EPR spectrum at 295 K of $\mathrm{Cr(NBu^t)Cl_3(PMe_2Ph)_2}$ in toluene showing ^{53}Cr, ^{14}N and ^{31}P hyperfine splittings

that is sparingly soluble in MeOH but very soluble in $\mathrm{CH_2Cl_2}$ in which it is a 1:1 electrolyte. The structure of this complex has been determined by X-ray crystallography. A diagram of the anion is given in Fig. 6, selected bond lengths and angles in Table 6. In the anion the chromium geometry is square pyramidal, with an axial imido group. The Cr–N distance is typically short and the four Cr–S distances are equal within experimental error. The N–Cr–S angles are 101.6(6)–110.8(5)° (Table 6).

The cyclic voltammogram of complex **21** in 0.1 mol dm^{-3} $\mathrm{NBu_4PF_6}$ in $\mathrm{CH_2Cl_2}$ at a platinum electrode shows one-electron oxidation and reduction couples at 0.45 and −0.7 V *vs.* the ferrocene–ferrocenium couple respectively. The peak-to-peak separation (ΔE_p) and current ratios (i_{p_c}/i_{p_a} *ca.* 1:1) of both couples which are scan-rate independent are characteristic of a reversible one-electron process. Attempts to isolate the oxidised species by chemical oxidation using $\mathrm{AgO_3SCF_3}$ in $\mathrm{CH_2Cl_2}$ gave a paramagnetic dark green solid which decomposed on recrystallisation from MeCN to give highly insoluble yellow material. The corresponding cyclic voltammogram for the dithiocarbamate complex **20** shows irreversible oxidation and reduction waves at 1.10 and −1.26 V, respectively.

Reduction Reactions.—Attempts to reduce $\mathrm{Cr(NBu^t)Cl_3(dme)}$ in presence of neutral donors were generally not successful. However, interaction of the dme adduct **2** in thf with 1 equivalent of Na/Hg in presence of dmpe gave the diamagnetic, $(d_{xy})^2$ configuration, chromium(IV) complex *trans*-$\mathrm{[Cr(NBu^t)(dmpe)_2Cl]Cl}$ **22**. The similar ethylimido complex *trans*-$\mathrm{[Cr(NEt)(dmpe)_2Cl]O_3SCF_3}$, obtained by interaction of methanol on $\mathrm{[Cr(dmpe)_2(MeCN)Cl]^+}$, has been structurally characterised.[12b] The salt **22** is sparingly soluble in $\mathrm{CH_2Cl_2}$ but very soluble in MeCN in which it is a 1:1 electrolyte.

Electron Paramagnetic Resonance Spectra.—The X-band EPR spectra of oxochromium(V), d^1, species in frozen solution have been well studied.[13,16–19] The imido complexes with oxygen or N,O ligands are all paramagnetic with values for μ_B between 1.6 and 1.7; EPR spectra in frozen solutions show sharp singlets with g values close to 2.00. No ^{53}Cr hyperfine or ^{14}N superhyperfine structure is observed, probably due to anisotropy. At 293 K, however, the data given in Table 7 show that both α_{Cr} (^{53}Cr, $I = \frac{3}{2}$, 9.55%) and ^{14}N hyperfine structures are resolved. The values for the chromium splittings agree closely with literature values. The $\mathrm{Bu^tN}$ coupling constant in the range 5–7 G is two to three times greater than known values for $\mathrm{Cr^V}$–N single bonds, indicating stronger interaction between the unpaired electron on Cr with the nitrogen nucleus in the imido group. In the room-temperature EPR spectrum of $\mathrm{Cr(NBu^t)Cl(OC_9H_6N)}$ **16**, nitrogen coupling constants of *ca.* 2.3 G were observed, although complete analysis of the spectrum proved impossible.

For the tertiary phosphine complexes the EPR signal is additionally split by the two magnetically equivalent ^{31}P($I = \frac{1}{2}$) nuclei and $\alpha_P \approx$ 30–35 G (Table 7 and Fig. 7).

Vanadium Compounds.—For comparison with studies on $\mathrm{Cr(NBu^t)Cl_3}$ we have treated $\mathrm{V(NBu^t)X_3}$ (X = Cl or $\mathrm{MeCO_2}$)[20] with 3 equivalents of $\mathrm{LiNBu^t}$, which gives the dimer **IV**, **23**. It is evident that the third equivalent of $\mathrm{LiNHBu^t}$ acts as a base and not as a nucleophile. The dimer is extremely soluble in non-polar solvents which makes recovery in high yield very difficult. It is rapidly decomposed by moisture or moist air giving an orange-yellow powder. The ^{1}H NMR spectrum in $\mathrm{C_6D_6}$ at room temperature consists of two superimposed spectra, presumably due to different conformers, in a 1:3 ratio. The major component shows $\mathrm{Bu^t}$ resonances in a 1:1:1 ratio at δ 1.51, 1.47 and 1.42, corresponding respectively to terminal $\mathrm{NHBu^t}$, μ-$\mathrm{NBu^t}$ and terminal $\mathrm{NBu^t}$, while the minor one shows the corresponding resonances at δ 1.54, 1.42 and 1.41. At temperatures between +30 and +70 °C more peaks appear, but due to second-order effects the spectrum cannot be easily interpreted. These effects could arise from long-range, through-space coupling of the $\mathrm{Bu^t}$ groups. At +80 °C the spectrum simplifies to a 1:1:1 triplet for one conformation, probably the symmetrical one. A similar phenomenon was observed for the analogous chromium(V) dimer.[3b]

Interaction of $\mathrm{VOBr_2}$[21] with the $\mathrm{SiMe_3(NHBu^t)}$ leads to the formation of the dimer **24**, shown in diagram **V**. This compound is moderately air sensitive in solution but its air-stable in the solid state. Although containing V^{IV}, d^1, it is diamagnetic due either to the presence of a metal–metal bond or to super-exchange interaction *via* the NBu^t bridges. The bridged imido structure is indicated by the presence of single NBu^t and $OSiMe_3$ resonances in the ^1H NMR spectrum. The compound, for which regrettably X-ray-quality crystals could not be obtained, provides a rare example of vanadium(IV) imido species.[22] The dimer **24** reacts with BCl_3 in CH_2Cl_2, the solution immediately becoming bright orange and leading on work-up to a crystalline mixture according to mass and NMR spectra consisting of $V_2(\mu\text{-}NBu^t)_2Cl_n(OSiMe_3)_{4-n}$ (n = 3 or 4), which we have not studied further. The difficulty and low yields of the preparation of $VOBr_2$ make the method inconvenient as a general entry to vanadium(IV) species.

Experimental

Microanalyses were by Pascher, Imperial College and University College, London laboratories. General techniques and the instrumentation used have been described.[23]

CAUTION: chromium compounds are potentially carcinogenic[24] and should be handled appropriately, avoiding skin contact and inhalation.

The starting material $Cr(NBu^t)_2Cl_2$ was prepared by interaction of BCl_3 and $Cr(NBu^t)_2(OSiMe_3)_2$;[3b] Na_2(mnt) was prepared as described[25] and Na_2(salen) obtained from H_2salen and NaH in Et_2O. Commercial samples were from Aldrich. NMR spectra (δ values, ppm) in C_6D_6 unless otherwise stated, IR spectra (cm^{-1}) in Nujol mulls; mass spectra [*m/z* (%)] by electron impact and EPR (X-band, g_{iso}) spectra at 77 K in CH_2Cl_2) unless otherwise specified. Magnetic susceptibilities were obtained by Evans' NMR method.

All operations were carried out under N_2 or Ar or in vacuum; solvents were dried by standard methods.

tert-*Butylimidotrichlorobis*(*tetrahydrofuran*)*chromium*(V) **1**.—Through a solution of $Cr(NBu^t)_2Cl_2$[3] (3 g, 10 mmol) in CH_2Cl_2 (70 cm^3) in a round-bottom flask (250 cm^3) was passed chlorine for 1 min at room temperature when the colour of the solution changed from red-brown to orange-red (5–10 s) and brown-green (1–3 min). After stirring for 30 min the volatiles were removed under vacuum and the residue dissolved in CH_2Cl_2 (50 cm^3). After filtration, thf (5 cm^3) was added when the brown-green solution became emerald green. After *ca.* 15 min the solvent was removed and the residue crystallised from thf-hexane (1:1) as green needles. Yield: 2.9 g, 70%. IR: 1201 ($CrNBu^t$); 380, 365 and 327 cm^{-1} (CrCl). EPR: *g* 1.998.

tert-*Butylimidotrichloro*(1,2-*dimethoxyethane*)*chromium*(V) **2**.—As above from $Cr(NBu^t)_2Cl_2$ (3.5 g, 13.2 mmol) except that dme (10 cm^3) was added and the green solution stirred for 1 h, concentrated (to 15 cm^3) and Et_2O added. The green precipitate was collected and recrystallised from CH_2Cl_2–Et_2O (1:1). Yield: 3.8 g, 92%. IR: 1185 ($CrNBu^t$); 350 and 300 cm^{-1} (CrCl). EPR: *g* 2.035. The corresponding *tribromide* **3** was obtained from the trichloride (0.32 g, 1 mmol) in CH_2Cl_2 (20 cm^3) by addition of $SiBrMe_3$ (0.55 g, 0.45 cm^3, 3.5 mmol) when the green solution became yellow-brown after stirring for 8 h. Removal of volatiles, extraction of the residue into toluene (3 × 15 cm^3), concentration of filtered extracts (to *ca.* 5 cm^3) and cooling (−20 °C) gave dark red crystals. Yield: 0.3 g (65%).

tert-*Butylimidotrichlorobis*(*tertiary phosphine*)*chromium*(V).—For $Cr(NBu^t)Cl_3L_2$ (L = PMe_3, **4**; PEt_3, **5**; PMe_2Ph, **6**; or $PEtPh_2$, **7**) an excess of the neat phosphine (2.5 mmol) was added to a solution of $Cr(NBu^t)Cl_3(thf)_2$ (0.37 g, 1 mmol) in CH_2Cl_2 (20 cm^3) when the colour changed to orange-red (**4**, **5**) or brown-red (**6**, **7**). After stirring for 0.5 h volatiles were removed and the residue extracted with toluene until the extracts were colourless (3 × 10 cm^3 for **4** and **5**, 5 × 10 cm^3 for **6** and **7**). Evaporation and crystallisation of the residue from CH_2Cl_2–Et_2O (**5**–**7**) or toluene-hexane containing a few drops of PMe_3 (**4**) afforded orange-red crystals in 85–95% yield. The dme adduct **2** can equally well be used. IR: **4** 1200 ($CrNBu^t$); 344 and 295 (CrCl); **5** 1210 ($CrNBu^t$); 345 and 295 (Cr–Cl); **6** 1202 ($CrNBu^t$); 348, 325 and 310 (CrCl); **7** 205 ($CrNBu^t$); 345, 327 and 310 cm^{-1} (CrCl). EPR: see Table 2.

tert-*Butylimidotrichlorobis*(*quinuclidine*)*chromium*(V) **8**.—This compound was prepared as for the PR_3 species from **1** (0.35 g, 0.95 mmol) and quinuclidine (0.21 g, 19 mmol) in CH_2Cl_2, when the product precipitates as a microcrystalline powder essentially quantitatively. IR: 1202 ($CrNBu^t$); 350 and 317 (CrCl). EPR (MeCN): *g* 2.001.

Tetraphenylphosphonium tert-*butylimidotetrachlorochromate*-(V) **9**.—To a solution of $Cr(NBu^t)Cl_3$ from $Cr(NBu^t)_2Cl_2$ (3.5 g, 13.2 mmol) in CH_2Cl_2 (30 cm^3) was added a solution of PPh_4Cl (*ca.* 4.9 g, 13.2 mmol) in CH_2Cl_2 (10 cm^3). After stirring for 15 min the volume was reduced to *ca.* 15 cm^3 and the minimum amount of Et_2O added to precipitate an olive-green solid which was collected and recrystallised from CH_2Cl_2–Et_2O. Yield: 6.4 g, 80%. Conductivity (CH_2Cl_2, 25 °C): Λ_M = 35.9 ohm^{-1} cm^2 mol^{-1}. IR: 1191 ($CrNBu^t$), 373 (CrCl). EPR: *g* 1.998. The $[N(PPh_3)_2]^+$ salt **10** was obtained similarly. Yield: 8.7 g (83%). EPR: see Table 2.

Dichlorobis(*dimethylphenylphosphine*)(o-*phenylenediamido*)-*chromium*(IV) **11**.—To a solution of the PMe_2Ph complex **7** (0.5 g, 1 mmol) in toluene (30 cm^3) was added 1,2-diaminobenzene (0.11 g, 1 mmol) and triethylamine (0.5 cm^3, excess). The brown reaction mixture was stirred for 12 h in the dark; removal of volatiles, washing of the residue with Et_2O (2 × 20 cm^3) and extraction into toluene (3 × 10 cm^3) gave a solution which on concentration (to *ca.* 5 cm^3) and cooling (−20 °C, 12 h) afforded red prisms. Yield: 0.25 g, 48%. IR: 334 and 264 cm^{-1} (CrCl). EPR: silent.

Tetrakis(tert-*butylamido*)*bis*(tert-*butylimido*)-*di*-μ-*chloro*-*di*-*chromium*(V) **12**.—To a solution of complex **2** (0.25 g, 0.78 mmol) in CH_2Cl_2 (20 cm^3) was added excess of $SiMe_3(NHBu^t)$ (0.5 cm^3). After stirring the dark red solution (4 h) the solvent was recovered and the residue extracted with hexane (15 cm^3) which on concentration (5 cm^3) and cooling (−20 °C) gave dark orange crystals. Yield: 0.1 g, 45%. IR: 3251 cm^{-1} (ν_{N-H}). ^1H NMR ($CDCl_3$): δ 1.40 (s, 9 H, NBu^t) and 1.48 (s, 18 H, $NHBu^t$).

Bis(tert-*butylimido*)*dichlorotetrakis*(2,6-*dichlorophenyl*-*amido*)*dichromium*(V) **13**.—This was prepared as for complex **12** but from **2** (0.25 g, 0.78 mmol) in CH_2Cl_2 (20 cm^3) and 2,6-$Cl_2C_6H_3NH_2$ (0.15 g, excess) in CH_2Cl_2 (10 cm^3). Extraction of the hexane-washed residue with toluene, concentration and cooling gave dark purple crystals. Yield: 0.18 g, 50%. IR: 3270 cm^{-1} (ν_{N-H}). ^1H NMR ($CDCl_3$): δ 1.35 (s, NBu^t) + aromatic protons.

(tert-*Butylimido*)*tris*(*triphenylsiloxo*)*chromium*(V) *dimer* **14** *and Bis*(tert-*butylimido*)*bis*(*triphenylsiloxo*)*chromium*(VI) **15**.—To a mixture of complex **2** (0.32 g, 1 mmol) and $LiOSiPh_3$ (0.56 g, 2 mmol) was added dme (30 cm^3). After stirring (2 h) the orange-red solution was refluxed (2 h) then evaporated in vacuum and the residue extracted with hexamethyldisiloxane (30 cm^3) at 60 °C. Concentration of the extracts (to *ca.* 15 cm^3) and standing at room temperature (12 h) gave orange needles of complex **14** in *ca.* 40% yield contaminated with red prisms $[Cr(OSiPh_3)_4]$ which were removed manually. From the supernatant on further concentration and cooling (−20 °C) were obtained brown plates of **15** in *ca.* 20% yield. Mass spectrum: **15**, *m/z* 744 (M^+). IR: **14**, 1114 ($CrNBu^t$) and 716

Table 8 Crystal data, details of intensity measurements and structure refinement

Molecular formula	$C_8H_{19}Cl_3CrNO_2$	$C_{22}H_{28}Cl_2CrN_2P_2$	$C_{44}H_{48}CrO_2Si_2$	$C_{22}H_{21}ClCrN_2O_2\cdot 0.5(C_2H_5)_2O$	$C_{48}H_{39}CrN_6P_2S_4$
M	319.60	505.327	717.013	469.931	942.086
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
a/Å	7.052(1)	14.511(1)	10.262(3)	8.878(2)	9.132(3)
b/Å	12.990(1)	15.502(5)	15.719(2)	15.260(1)	34.776(12)
c/Å	15.638(2)	12.869(4)	26.237(8)	17.073(2)	15.731(2)
α/°	90	90	90	90	90
β/°	90	119.51(1)	100.51(2)	90	103.65(2)
γ/°	90	90	90	90	90
U/Å^3	1420.27	2519.36	4160.24	2313.02	4854.66
Space group	$P2_12_12_1$	$C2/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/n$
Z	4	4	4	4	4
D_c/g cm^{-3}	1.495	1.332	1.145	1.350	1.289
μ/cm^{-1}	16.36	7.93	6.233	6.220	7.710
F(000)	660	1048	1528	980	1948
Total no. of reflections	7470	9125	18 718	6968	22 098
No. of unique reflections	2521	3409	7295	2336	10 574
No. of reflections	1843	991	2223	2169	2556
Significance test	$F > 6\sigma(F)$	$F > 6\sigma(F)$	$F > 3\sigma(F)$	$F > 6\sigma(F)$	$F > 5\sigma(F)$
No. of parameters	135	120	389	298	479
Weighting scheme parameter g in $w = 1[\sigma^2(F) + gF^2]^{-1}$	0.003	0.0005	Unit weights	0.0031	0.0002
Final R	0.0597	0.0581	0.0952	0.0404	0.0799
Final R'	0.0660	0.0609	0.0952	0.0391	0.0722

Table 9 Fractional atomic coordinates ($\times 10^4$) for the complex $Cr(NBu^t)Cl_3(dme)$

Atom	x	y	z
Cr	5 782(2)	9 882(1)	8 693(1)
Cl(2)	7 500	8 982(2)	9 728(2)
Cl(1)	7 578(4)	11 292(2)	8 903(2)
O(1)	3 795(9)	8 701(4)	8 756(4)
O(2)	3 855(8)	10 391(4)	9 724(4)
C(1)	2 128(13)	9 786(8)	9 725(8)
C(2)	2 748(13)	8 684(7)	9 559(8)
C(11)	3 391(16)	11 415(8)	9 904(8)
C(12)	4 216(18)	7 689(7)	8 453(8)
Cl(3)	3 736(4)	10 755(2)	7 811(2)
N	6 988(10)	9 433(5)	7 909(4)
C(10)	8 029(13)	9 156(7)	7 153(6)
C(101)	9 128(15)	10 134(9)	6 891(7)
C(102)	6 585(18)	8 853(12)	6 460(7)
C(103)	9 376(19)	8 283(11)	7 390(8)

Table 10 Fractional atomic coordinates ($\times 10^4$) for the complex $Cr[C_6H_4(NH)_2\text{-}o]Cl_2(PMe_2Ph)_2$

Atom	x	y	z
Cr	0	156(1)	2500
Cl(1)	252(2)	1142(2)	1282(2)
P(1)	1887(2)	289(2)	3975(2)
N(1)	122(6)	−803(5)	1602(5)
C(1)	67(7)	−1608(7)	1968(7)
C(2)	88(9)	−2397(7)	1436(9)
C(3)	50(12)	−3146(9)	1971(11)
C(10)	2216(9)	−13(10)	5517(8)
C(20)	2393(9)	1404(8)	4116(10)
C(11)	2800(4)	−388(4)	3734(5)
C(12)	2646(4)	−1279(4)	3662(5)
C(13)	3336(4)	−1818(4)	3502(5)
C(14)	4180(4)	−1466(4)	3414(5)
C(15)	4334(4)	−575(4)	3486(5)
C(16)	3644(4)	−36(4)	3646(5)

cm^{-1} (CrOSi). ^{1}H NMR: **14**, δ 0.92 (s, NBu^t) + phenyl resonances; **15**, 0.99 (s, NBu^t).

tert-*Butylimidochlorobis*(*quinolin*-8-*olato*)*chromium*(V) **16**.—To a solution of complex **2** (0.32 g, 1 mmol) in CH_2Cl_2 (20 cm^3) was added 8-hydroxyquinoline (0.29 g, 2 mmol) and after 5 min NEt_3 (0.5 cm^3, excess). After stirring the red-brown solution (12 h), removal of volatiles, and extraction of the Et_2O-washed (2 × 20 cm^3) residue with hot toluene (3 × 30 cm^3) followed by vacuum evaporation and recrystallisation of the residue from Et_2O–CH_2Cl_2 gave green crystals. Yield: 0.32 g, 72%. IR: 1106 (CrNBu^t); 361 and 347 cm^{-1} (CrCl). EPR (thf): g 1.9913.

Bis(*triphenylphosphoranylidene*)*ammonium* tert-*Butylimidobis*(2-*methyl*-2-*hydroxobutanoato*)*chromate*(V) **17**.—A solution of the $[N(PPh_3)_2]^+$ salt **10** (0.6 g, 0.75 mmol), 2-methyl-2-hydroxybutyric acid (0.18 g, 1.5 mmol) and NEt_3 (0.3 g, 3 mmol) in MeOH (20 cm^3) was stirred (3 h), evaporated and the Et_2O-washed residue recrystallised from CH_2Cl_2–Et_2O. Yield: 0.26 g, 38%. IR: 1194 (CrNBu^t); 1669 and 1665 cm^{-1} [C(O)O]. EPR: g 2.001. Conductivity (acetone, 25 °C): Λ_M = 86.3 ohm^{-1} cm^2 mol^{-1}.

tert-*Butylimidochloro*[*ethylenebis*(*salicylideneiminato*)] *chromium*(V) **18**.—To a slurry of Na_2(salen) (0.27 g, 0.78 mmol) in MeCN (10 cm^3) was added the dme adduct **2** (0.25 g, 0.78 mmol) in MeCN (10 cm^3) and the mixture stirred for 12 h. After solvent removal the residue was twice crystallised from CH_2Cl_2–Et_2O and the brown product washed with Et_2O and dried. Yield: 0.15 g, 45%. Conductivity (CH_2Cl_2, 25 °C): Λ_M = 2.9 ohm^{-1} cm^2 mol^{-1}. EPR (CH_2Cl_2): g 1.984.

Sodium tert-*Butylimidotetracyanochromate*(V) **19**.—To a suspension of NaCN (0.15 g, 3.1 mmol) in MeOH (10 cm^3) was added the dme adduct **2** (0.25 g, 0.78 mmol) in MeOH (10 cm^3) and the mixture stirred for *ca.* 12 h. Removal of MeOH and crystallisation of the residue from MeCN gave orange crystals. Yield: *ca.* 50%. IR: 2265 and 2165 cm^{-1} (CN). EPR (MeCN): g 1.992.

tert-*Butylimidochlorobis*(*diethyldithiocarbamato*)*chromium*(V) **20**.—A mixture of the $[N(PPh_3)_2]^+$ salt **10** (0.6 g, 0.75 mmol) and $Na(S_2CNEt_2)$ (0.23 g, 1.5 mmol) in MeOH (20 cm^3) was stirred (3 h), the solvent removed and the residue extracted with CH_2Cl_2 (3 × 10 cm^3). The green extract was filtered,

Table 11 Fractional atomic coordinates (× 10^4) for the complex $\mathrm{Cr(NBu^t)_2(OSiPh_3)_2}$

Atom	*x*	*y*	*z*
Cr	1346(3)	814(2)	2514(1)
Si(1)	1650(4)	76(3)	3694(2)
Si(2)	496(4)	147(3)	1308(2)
O(1)	1578(11)	162(7)	3076(4)
O(2)	918(11)	201(7)	1929(4)
C(111)	2530(11)	−956(6)	3893(4)
C(112)	2007(11)	−1577(6)	4178(4)
C(113)	2685(11)	−2340(6)	4301(4)
C(114)	3887(11)	−2483(6)	4138(4)
C(115)	4410(11)	−1863(6)	3853(4)
C(116)	3732(11)	−1099(6)	3731(4)
C(121)	2652(10)	961(6)	4046(4)
C(122)	3758(10)	781(6)	4426(4)
C(123)	4548(10)	1442(6)	4665(4)
C(124)	4233(10)	2283(6)	4524(4)
C(125)	3127(10)	2463(6)	4145(4)
C(126)	2337(10)	1802(6)	3906(4)
C(131)	−84(9)	86(7)	3835(5)
C(132)	−343(9)	356(7)	4313(5)
C(133)	−1635(9)	339(7)	4409(5)
C(134)	−2669(9)	52(7)	4028(5)
C(135)	−2411(9)	−219(7)	3549(5)
C(136)	−1119(9)	−202(7)	3453(5)
C(211)	1150(10)	1079(6)	979(4)
C(212)	1954(10)	943(6)	611(4)
C(213)	2468(10)	1634(6)	379(4)
C(214)	2178(10)	2462(6)	515(4)
C(215)	1374(10)	2598(6)	882(4)
C(216)	860(10)	1907(6)	1114(4)
C(221)	1231(10)	−844(6)	1084(4)
C(222)	472(10)	−1395(6)	732(4)
C(223)	1056(10)	−2111(6)	554(4)
C(224)	2399(10)	−2276(6)	728(4)
C(225)	3158(10)	−1725(6)	1079(4)
C(226)	2574(10)	−1009(6)	1257(4)
C(231)	−1368(8)	121(7)	1134(4)
C(232)	−1999(8)	339(7)	634(4)
C(233)	−3377(8)	293(7)	500(4)
C(234)	−4123(8)	29(7)	865(4)
C(235)	−3492(8)	−189(7)	1365(4)
C(236)	−2115(8)	−143(7)	1499(4)
N(1)	2686(12)	1253(9)	2491(5)
N(2)	103(13)	1447(9)	2540(5)
C(1)	3923(17)	1758(13)	2481(8)
C(2)	−669(18)	2233(13)	2567(7)
C(11)	4901(19)	1500(18)	2984(9)
C(12)	4412(21)	1468(16)	2008(9)
C(13)	3654(25)	2716(14)	2495(13)
C(21)	−1288(22)	2152(15)	3043(8)
C(22)	−1804(20)	2165(16)	2104(9)
C(23)	223(25)	3032(13)	2565(11)

Table 12 Fractional atomic coordinates (× 10^4) for the complex $\mathrm{Cr(NBu^t)Cl(OC_9H_6N)_2}$

Atom	*x*	*y*	*z*
Cr	−9 722(2)	−179(1)	−7 786(1)
Cl	−10 749(3)	−172(2)	−6 547(1)
O(1)	−8 921(8)	984(4)	−7 686(4)
N(1)	−7 594(10)	−463(6)	−7 215(5)
N(2)	−8 506(8)	−349(6)	−8 807(4)
O(2)	−9 910(7)	−1 431(4)	−7 861(3)
C(11)	−7 559(11)	1 059(8)	−7 300(6)
C(12)	−6 864(12)	277(10)	−7 065(5)
C(13)	−5 475(11)	313(11)	−6 666(5)
C(14)	−4 842(16)	1 116(13)	−6 527(7)
C(15)	−5 548(17)	1 870(11)	−6 770(8)
C(16)	−6 912(14)	1 852(8)	−7 155(7)
C(17)	−4 907(13)	−520(10)	−6 465(7)
C(18)	−5 671(14)	−1 253(10)	−6 607(6)
C(19)	−7 022(13)	−1 189(9)	−6 990(6)
C(21)	−9 253(11)	−1 787(7)	−8 495(6)
C(22)	−8 494(9)	−1 218(7)	−9 010(5)
C(23)	−7 744(10)	−1 504(8)	−9 701(5)
C(24)	−7 821(12)	−2 404(9)	−9 856(6)
C(25)	−8 539(13)	−2 964(8)	−9 358(6)
C(26)	−9 261(11)	−2 667(7)	−8 667(6)
C(27)	−7 054(11)	−861(8)	−10 135(6)
C(28)	−7 093(10)	−30(8)	−9 936(5)
C(29)	−7 828(10)	222(9)	−9 241(6)
N(12)	−11 250(8)	75(6)	−8 254(4)
C(2)	−12 544(11)	205(10)	−8 753(5)
C(212)	−13 569(16)	−569(10)	−8 597(8)
C(211)	−12 040(13)	161(10)	−9 580(5)
C(213)	−13 243(21)	1 052(10)	−8 535(9)

evaporated and the residue recrystallised from $\mathrm{CH_2Cl_2}$–$\mathrm{Et_2O}$–hexane (1:1:1). Yield: 0.13 g, 41%. Mass spectrum: *m*/*z* 419 (*M* − Cl), 363 (*M* − $\mathrm{CH_2{=}CMe_2}$) and 348 (*M* − $\mathrm{NBu^t}$). IR: 1002 ($\mathrm{CrNBu^t}$), 351 (CrCl) and 1506 $\mathrm{cm^{-1}}$ (CN). EPR: *g* 2.002.

Bis(*triphenylphosphoranylidene*)*ammonium* tert-*Butylimidobis*(*maleonitriledithiolato*)*chromate*(V) **21**.—This was prepared as for the dithiocarbamate **20** but with $\mathrm{Na_2(mnt)}$ (0.28 g, 1.5 mmol), when bluish green crystals were deposited from the methanol solution. These were collected, washed with a little MeOH and recrystallised from $\mathrm{CH_2Cl_2}$–$\mathrm{Et_2O}$. Yield: 0.35 g, 49%. IR: 1209 ($\mathrm{CrNBu^t}$) and 2222 $\mathrm{cm^{-1}}$ (CN). EPR: see Table 2. Conductivity ($\mathrm{CH_2Cl_2}$, 25 °C): Λ_M = 38.6 $\mathrm{ohm^{-1}\ cm^2\ mol^{-1}}$.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*] tert-*butylimidochlorochromium*(IV) *Chloride* **22**.—The dme adduct **2** (0.25 g, 0.78 mmol), dmpe (0.3 $\mathrm{cm^3}$) and Na/Hg (0.5%, 18 mg Na, 0.78 mmol) in thf (25 $\mathrm{cm^3}$) were stirred (24 h) and then the solvent removed. Extraction of the residue with MeCN (2 × 15 $\mathrm{cm^3}$) followed by concentration (to 5 $\mathrm{cm^3}$) and addition of $\mathrm{Et_2O}$ gave a green precipitate which was collected, washed with $\mathrm{Et_2O}$ and recrystallised from MeCN–$\mathrm{Et_2O}$. Yield: 0.25 g, 52%. Conductivity (MeCN, 25 °C): Λ_M = 130 $\mathrm{ohm^{-1}\ cm^2\ mol^{-1}}$. NMR ($\mathrm{CD_3CN}$): ^{1}H, δ 1.24 (s, $\mathrm{NBu^t}$), 1.48 (m, $\mathrm{Me_2P}$) and 1.71 (m, $\mathrm{PC}H_2\mathrm{C}H_2$); ^{31}P-{^{1}H}, δ 29.79.

Bis[(tert-*butylamido*)(μ-tert-*butylimido*)(tert-*butylimido*)-*vanadium*(V)] **23**.—To a solution of $\mathrm{V(NBu^t)(O_2CMe)_3}$ (0.52 g, 1.74 mmol) in thf (30 $\mathrm{cm^3}$) was added, at −78 °C, a cooled (−78 °C) solution of $\mathrm{LiNHBu^t}$ (0.44 g, 5.5 mmol) in $\mathrm{Et_2O}$ (30 $\mathrm{cm^3}$) when the colour changed to red-brown. After warming slowly with stirring (12 h) and removal of solvent the residue was extracted with $\mathrm{(Me_3Si)_2O}$ (3 × 10 $\mathrm{cm^3}$), concentrated (2 $\mathrm{cm^3}$) and cooled (−20 °C, 12 h) to give red-black crystals which were collected and washed with cold (−78 °C) hexane. Yield: 0.2 g, *ca.* 48%. Use of $\mathrm{V(NBu^t)Cl_3}$ instead of the acetate gives a somewhat lower yield. Mass spectrum: *m*/*z* 530 (*M*), 515 (*M* − Me) and 459 (*M* − $\mathrm{NBu^t}$). IR: 3324, 3255 ($\nu_{\mathrm{N-H}}$); 1207 $\mathrm{cm^{-1}}$ ($\mathrm{VNBu^t}$). ^{1}H NMR: superimposition of spectra of two conformers (see Discussion), δ 9.1 (s, br, NH); 1.54 (s), 1.42 (s), 1.41 (s), 1.51 (s), 1.47 (s) and 1.42 (s).

Bis[(μ-tert-*butylimido*)*bis*(*trimethylsiloxo*)*vanadium*(IV)] **24**.—The compound $\mathrm{VOBr_2}$ (0.5 g, 2.2 mol) and $\mathrm{SiMe_3(NHBu^t)}$ (15 $\mathrm{cm^3}$) were refluxed (8 h) when the bromide slowly dissolved to give a yellow-brown solution. Removal of volatiles under vacuum and extraction of the residue in hexane, filtration, concentration and cooling (−20 °C) gave yellow-green plates. Yield: 0.15 g, 35%. Mass spectrum: *m*/*z* 600 (*M*), 585 (*M* − Me), 544 (*M* − $\mathrm{CH_2{=}CMe_2}$) and 528 (*M* − $\mathrm{NBu^t}$).

Table 13 Fractional atomic coordinates (× 10^4) for the complex $[N(PPh_3)_2][Cr(NBu^t)(mnt)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr	222(3)	678(1)	1731(2)	C(201)	3739(12)	1125(2)	7529(7)
S(1)	557(5)	1272(1)	2385(3)	C(202)	4191(12)	769(2)	7274(7)
S(2)	−632(5)	505(1)	2938(3)	C(203)	3862(12)	434(2)	7679(7)
S(3)	2140(6)	834(1)	1074(3)	C(204)	3080(12)	455(2)	8340(7)
S(4)	1078(5)	57(1)	1707(3)	C(205)	2627(12)	811(2)	8595(7)
C(1)	517(16)	−161(3)	2591(11)	C(206)	2957(12)	1146(2)	8190(7)
C(2)	−163(17)	35(4)	3092(10)	C(301)	2714(11)	1877(3)	6848(7)
C(3)	1357(18)	1513(4)	1651(10)	C(302)	1222(11)	1754(3)	6707(7)
C(4)	2023(19)	1331(4)	1104(12)	C(303)	47(11)	2017(3)	6451(7)
C(11)	882(20)	−557(4)	2693(11)	C(304)	365(11)	2404(3)	6335(7)
C(21)	−663(19)	−155(4)	3769(12)	C(305)	1856(11)	2527(3)	6475(7)
C(41)	2766(24)	1544(5)	554(14)	C(306)	3031(11)	2263(3)	6732(7)
C(31)	1357(19)	1932(4)	1682(11)	C(401)	2209(8)	1469(2)	4816(6)
N(1)	1155(18)	−880(4)	2820(10)	C(402)	1290(8)	1164(2)	4945(6)
N(2)	−1093(18)	−296(4)	4330(11)	C(403)	−274(8)	1204(2)	4712(6)
N(3)	1407(18)	2256(4)	1731(10)	C(404)	−919(8)	1549(2)	4351(6)
N(4)	3222(24)	1722(4)	31(16)	C(405)	−1(8)	1853(2)	4222(6)
N(11)	−1217(15)	748(3)	960(8)	C(406)	1563(8)	1813(2)	4455(6)
C(10)	−2600(25)	821(5)	336(13)	C(501)	5028(10)	1773(2)	4610(6)
C(111)	−2110(33)	914(6)	−571(15)	C(502)	5883(10)	2073(2)	5067(6)
C(112)	−3308(33)	1166(9)	539(19)	C(503)	6475(10)	2355(2)	4615(6)
C(113)	−3544(36)	446(8)	219(21)	C(504)	6212(10)	2338(2)	3705(6)
P(1)	4252(5)	1551(1)	7031(3)	C(505)	5357(10)	2039(2)	3248(6)
N(10)	4847(13)	1455(3)	6202(7)	C(506)	4765(10)	1756(2)	3701(6)
P(2)	4206(4)	1417(1)	5184(3)	C(601)	4707(10)	962(2)	4825(6)
C(101)	5739(11)	1763(2)	7836(5)	C(602)	6078(10)	802(2)	5262(6)
C(102)	5416(11)	1955(2)	8549(5)	C(603)	6574(10)	460(2)	4961(6)
C(103)	6584(11)	2109(2)	9196(5)	C(604)	5699(10)	278(2)	4223(6)
C(104)	8073(11)	2071(2)	9130(5)	C(605)	4328(10)	439(2)	3786(6)
C(105)	8396(11)	1879(2)	8416(5)	C(606)	3832(10)	781(2)	4087(6)
C(106)	7229(11)	1725(2)	7769(5)				

X-Ray Crystallography.—Crystals used for the X-ray work were sealed in thin-walled glass capillaries except for the mnt complex **21** which was mounted in air on a glass fibre. Intensity data for all compounds were recorded using a Delft Instruments (formerly Enraf-Nonius) FAST TV area detector and monochromatic Mo-Kα radiation from a rotating anode generator. Following procedures previously outlined,[26] slightly more than one hemisphere of data was recorded in each case. Crystals of the siloxide **15** and dithiolate **21** were very small and of poor quality, and did not diffract at all well. The structures were solved *via* the Patterson method and developed normally. Refinement was by full-matrix least squares. Hydrogens were included in idealised positions for compound **16** only. Experimental details are summarised in Table 8. Final atomic coordinates are listed in Tables 9–13.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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