Arylimido Complexes of Chromium-(VI), -(V) and -(IV)†

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The first arylimido compounds of chromium(VI), $CrCl_2(NR)_2$ (R = 2,4,6-$Me_3H_2C_6$ or 2,6-$Me_2H_3C_6$), have been made by interaction of $CrCl_2(NBu^t)_2$ with the aryl isocyanates. Similar interaction with 2,6-$Pr^i_2C_6H_3NCO$ gave a dimeric chromium(V) compound $[CrCl(\mu\text{-}NBu^t)(NC_6H_3Pr^i_2\text{-}2,6)]_2$. The chloride $CrCl_2(NC_6H_2Me_3\text{-}2,4,6)_2$ formed adducts with Lewis bases, *e.g.* $CrCl_2(NC_6H_2Me_3\text{-}2,4,6)_2(PMe_3)_2$ and $[Cr(NC_6H_2Me_3\text{-}2,4,6)_2(terpy)][BF_4]_2$ (terpy = 2,2′:6′,2″-terpyridine) was obtained with $AgBF_4$. Substitution of Cl atoms occurred with NaR′ (R′ = $OSiMe_3$, $OC_6H_2Me_3$-2,4,6, $SC_6H_2Me_3$-2,4,6, SC_6F_5 or $SC_6H_2Pr^i_3$-2,4,6) and with Grignard reagents, MgR″Br (R″ = CH_2CMe_3, CH_2CMe_2Ph or CH_2Ph) giving in all cases compounds of the type $Cr(NC_6H_2Me_3\text{-}2,4,6)_2R'_2$ or $Cr(NC_6H_2Me_3\text{-}2,4,6)_2R''_2$. The alkyl compounds underwent insertion with Bu^tNC, or 2,6-$Me_2H_3C_6NC$ to give η^2-iminoacyl compounds of Cr^{VI} and reduction by PMe_3 on heating to give the chromium(IV) dimer $[Cr(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)(NC_6H_2Me_3\text{-}2,4,6)(PMe_3)]_2$. The interaction of $CrCl_2(NC_6H_2Me_3\text{-}2,4,6)_2$ with the Grignard reagent derived from 4-*tert*-butylbenzyl chloride gave not a dialkyl but an amidochromium(IV) dimer $\{CrCl(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)[N(CH_2C_6H_4Bu^t\text{-}4)(C_6H_2Me_3\text{-}2,4,6)]\}_2$, while on interaction with MgEtBr in the presence of PMe_3 it gave the dichromium(V) compound $(2,4,6\text{-}Me_3H_2C_6N)BrCr(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)_2CrBr(NC_6H_2Me_3\text{-}2,4,6)(PMe_3)$. The crystal structures of seven compounds have been determined, in six of which the Cr atoms have slightly distorted tetrahedral geometry, while in the remaining compound one atom is tetrahedral and the other five-co-ordinate. The geometries of the Cr_2N_2 rings in four of the compounds are indicative of some direct Cr ··· Cr interaction.

There is a variety of *tert*-butylimido compounds of chromium in oxidation states VI and V such as $Cr(NBu^t)_2X_2$ (X = Cl, $OSiMe_3$ or $C_6H_2Me_3$-2,4,6) and $CrCl_3(NBu^t)L_2$ (L = tertiary phosphines and pyridines).[1–7] We have now synthesised the first arylimido compound, $CrCl_2(NC_6H_2Me_3\text{-}2,4,6)_2$ **1** and its 2,6-$Me_2C_6H_3N$ analogue **2**. A variety of reactions of the mesityl, **1**, have been studied and the principal ones are shown in Scheme 1. Analytical and physical data for the new compounds are given in Table 1.

Results and Discussion

Previous attempts in this laboratory, and elsewhere,[5] to make arylimidochromium compounds by routes analogous to those used for molybdenum and tungsten compounds[7] such as interaction of aryl isocyanates, arylsilylamines or arylphosphine imines with CrO_3 or CrO_2Cl_2 under a variety of conditions were unsuccessful, presumably due to reduction of the chromium(VI) starting materials.

Since the interaction of Bu^tNCO with $Cr(NBu^t)_2(NHBu^t)_2$ led to insertion into the Cr–N bond of a $Cr(NHBu^t)$ group[6] it seemed possible that by using $CrCl_2(NBu^t)_2$ or other compounds with ligands not susceptible to facile insertion reactions, the reaction with aryl isocyanates could give imido exchange, a reaction established in other cases.[8] The reaction (1) carried out in refluxing octane gives yields of 75–80% for

$$CrCl_2(NBu^t)_2 + 2RNCO \longrightarrow CrCl_2(NR)_2 + 2Bu^tNCO \quad (1)$$

R = $C_6H_2Me_3$-2,4,6 and $C_6H_3Me_2$-2,6 as compounds **1** and **2** respectively. The exchange reaction is an example of the Wittig-like [2 + 2] exchange of multiply bonded ligands (Scheme 2). This is the basis of the synthesis of M(NR) compounds from M=O species and RNCO.[9] It is interesting that reaction (1) is irreversible even when $CrCl_2(NR)_2$ is heated for 48 h in refluxing neat Bu^tNCO. The crystal structures of **1**, along with that of $CrCl_2(NBu^t)_2$ **1a** for comparison are shown in Figs. 1 and 2; bond lengths and angles are given in Tables 2 and 3 respectively. The structures exhibit distorted-tetrahedral chromium geometry, with angles ranging from 105.73(7) to 118.81(3)° for **1** and 103.2(3) to 121.0(1)° for the *tert*-butyl analogue. The molecular structures are very similar and contain normal, near-linear imido ligands with Cr–N bonds of 1.650(2) Å and Cr–N–C angles ranging from 157.8(2) to 159.4(2)° for **1** and 1.597(8) to 1.640(9) Å and 159.1(8) to 172.5(8)° for **1a**. The distribution of angles in the $CrCl_2N_2$ tetrahedra shows that the Cl–Cr–Cl angles [average 118.81(3) and 120.4(1)°] are *ca.* 8 and 7° larger, respectively, than the N–Cr–N angles [average 110.95(10)° for **1** and 113.3(4)° for **1a**]. Most structures containing two neighbouring multiply bonded functions, *e.g.* $M(NR)_2$, exhibit repulsion of the π-electron density of the two bonds, leading to an increase in the angle from idealised values. The small N–Cr–N angles in both compounds are consistent with that found in the previously determined structure[2] of $Cr(NBu^t)_2(C_6H_2Me_3\text{-}2,4,6)_2$, 114.5(3)°.

The interaction of $CrCl_2(NBu^t)_2$ with 2,6-$Pr^i_2C_6H_3NCO$ in xylene differs from the reaction (1) in giving a low yield (*ca.* 20%) of the only isolable product found to be the dimeric chromium(V) species $[CrCl(\mu\text{-}NBu^t)(NC_6H_3Pr^i_2\text{-}2,6)]_2$ **3**, even after prolonged reaction with an excess of the isocyanate. The compound is diamagnetic due to spin coupling *via* the imido bridge (or to a Cr–Cr bond). The structure of the molecule is shown in Fig. 3; selected bond lengths and angles are given in Table 4. The structure contains two crystallographically independent, centrosymmetric dimers, in which the Bu^tN groups are bridging and the $Pr^i_2C_6H_3N$ and chloride groups are terminal. The precision of the bond lengths and angles is lower than would be preferred due to the likely effect on the

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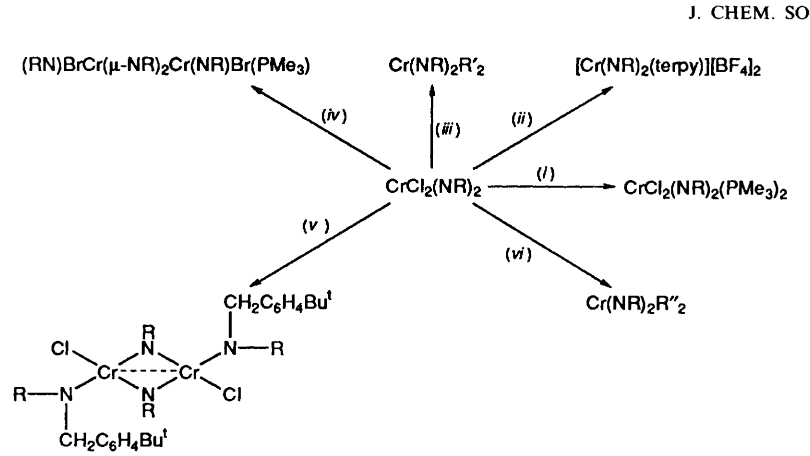
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 Principal reactions of $CrCl_2(NR)_2$, where R = 2,4,6-$Me_3C_6H_2$. (*i*) PMe_3; (*ii*) terpyridine, $AgBF_4$, MeCN; (*iii*) MgR′Cl, Et_2O, R′ = Me_3CCH_2, Me_2PhCCH_2 or $PhCH_2$; (*iv*) MgEtBr, PMe_3, Et_2O; (*v*) $Mg(CH_2C_6H_4Bu^t\text{-}4)Cl$, Et_2O; (*vi*) NaR″, Et_2O, R″ = $OSiMe_3$, OR, SR or SC_6F_5

Table 1 Analytical and physical data for new compounds

Compound	Colour	M.p./°C	Analysis (%)[a] C	H	N
1 $\mathrm{CrCl_2(NC_6H_2Me_3\text{-}2,4,6)_2}$	Red-brown	175–177	55.6 (55.5)	5.9 (5.7)	7.1 (7.2)
2 $\mathrm{CrCl_2(NC_6H_3Me_2\text{-}2,6)_2}$	Brown	165–168	51.8 (53.0)	5.1 (5.0)	7.3 (7.7)
3 $\mathrm{[CrCl(\mu\text{-}NBu^t)(NC_6H_3Pr^i{}_2\text{-}2,6)]_2}$	Red-brown	190–195	57.1 (57.6)	7.5 (7.8)	8.2 (8.4)
4 $\mathrm{CrCl_2(NC_6H_2Me_3\text{-}2,4,6)_2(PMe_3)_2}$	Orange	182–185	52.8 (53.3)	7.4 (7.4)	4.9 (5.2)
5 $\mathrm{[Cr(NC_6H_2Me_3\text{-}2,4,6)_2(terpy)][BF_4]_2}$	Orange	> 240	53.8 (54.4)	4.9 (5.1)	9.6 (9.6)
6 $\mathrm{Cr(NC_6H_2Me_3\text{-}2,4,6)_2(OSiMe_3)_2}$	Red-brown	86–87	57.5 (58.0)	8.0 (8.1)	5.4 (5.6)
7 $\mathrm{Cr(NC_6H_2Me_3\text{-}2,4,6)_2(OC_6H_2Me_3\text{-}2,4,6)_2}$	Red-brown	122–123	72.5 (73.5)	7.9 (7.5)	4.4 (4.8)
8 $\mathrm{Cr(NC_6H_2Me_3\text{-}2,4,6)_2(SC_6H_2Me_3\text{-}2,4,6)_2}$	Red	111–115	68.7 (69.7)	7.0 (7.0)	4.5 (4.7)
9 $\mathrm{Cr(NC_6H_2Me_3\text{-}2,4,6)_2(SC_6F_5)_2}$	Red	155–156	50.3 (50.6)	3.1 (3.1)	3.9 (3.9)
10 $\mathrm{Cr(NC_6H_2Me_3\text{-}2,4,6)_2(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2}$	Red	75–80	72.2 (73.0)	8.6 (8.6)	3.2 (3.5)
11 $\mathrm{Cr(NC_6H_2Me_3\text{-}2,4,6)_2(CH_2CMe_3)_2}$	Yellow	122–125 (decomp.)	71.5 (73.0)	9.4 (9.6)	6.0 (6.1)
12 $\mathrm{Cr(NC_6H_2Me_3\text{-}2,4,6)_2(CH_2CMe_2Ph)_2}$	Yellow	137–138 (decomp.)	77.2 (78.1)	8.0 (8.2)	4.6 (4.8)
13 $\mathrm{Cr(NC_6H_2Me_3\text{-}2,4,6)_2(CH_2Ph)_2}$	Yellow-orange	97–100 (decomp.)	76.3 (76.8)	7.2 (7.2)	5.7 (5.6)
14 $\mathrm{\{CrCl(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)[N(CH_2C_6H_4Bu^t\text{-}4)\text{-}(C_6H_2Me_3\text{-}2,4,6)]\}_2}$	Green-brown	185–190 (decomp.)	70.0 (69.5)	8.2 (7.4)	5.1 (5.6)
15 $\mathrm{Br(NC_6H_2Me_3\text{-}2,4,6)Cr(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)_2\text{-}CrBr(NC_6H_2Me_3\text{-}2,4,6)(PMe_3)}$	Red-brown	195–198 (decomp.)	58.0 (60.1)	6.2 (6.6)	7.0 (7.4)
16 $\mathrm{Cr(NC_6H_2Me_3\text{-}2,4,6)_2(CH_2CMe_2Ph)\text{-}[(2,6\text{-}Me_2H_3C_6)N{=}C(CH_2CMe_2Ph)]}$	Orange	164–166	78.0 (78.9)	7.9 (8.0)	5.9 (5.9)
17 $\mathrm{Cr(NC_6H_2Me_3\text{-}2,4,6)_2(CH_2CMe_2Ph)\text{-}[Bu^tN{=}C(CH_2CMe_2Ph)]}$	Orange	Oil[b]			
18 $\mathrm{[Cr(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)(NC_6H_2Me_3\text{-}2,4,6)(PMe_3)]_2}$	Green-brown	> 220	63.7 (63.9)	7.8 (7.9)	7.1 (7.1)

[a] Calculated values in parentheses; for mass spectra see Experimental section. [b] Mass spectrum only.

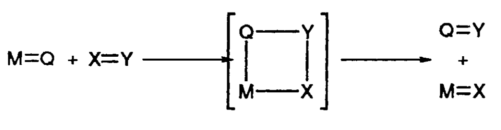
Table 2 Selected bond lengths (Å) and angles (°) for $CrCl_2(NC_6H_2Me_3\text{-}2,4,6)_2$ **1**, with estimated standard deviations (e.s.d.s) in parentheses

Cr–N(1)	1.650(2)	Cr–Cl(2)	2.1908(8)
Cr–N(2)	1.650(2)	N(1)–C(11)	1.375(3)
Cr–Cl(1)	2.1964(8)	N(2)–C(21)	1.370(3)
N(1)–Cr–Cl(1)	107.32(7)	N(2)–Cr–Cl(2)	107.17(7)
N(1)–Cr–Cl(2)	106.85(7)	Cl(1)–Cr–Cl(2)	118.81(3)
N(1)–Cr–N(2)	110.95(10)	C(11)–N(1)–Cr	157.8(2)
N(2)–Cr–Cl(1)	105.73(7)	C(21)–N(2)–Cr	159.4(2)

Table 3 Selected bond lengths (Å) and angles (°) for $CrCl_2(NBu^t)_2$ **1a**, with e.s.d.s in parentheses

	Molecule 1, *n* = 1	Molecule 2, *n* = 2
Cr(*n*)–N(*n*1)	1.640(9)	1.630(8)
Cr(*n*)–N(*n*2)	1.623(8)	1.597(8)
Cr(*n*)–Cl(*n*1)	2.187(3)	2.186(3)
Cr(*n*)–Cl(*n*2)	2.187(3)	2.188(3)
N(*n*1)–C(*n*1)	1.453(13)	1.486(11)
N(*n*2)–C(*n*2)	1.472(11)	1.484(12)
N(*n*1)–Cr(*n*)–Cl(*n*1)	104.7(3)	106.5(3)
N(*n*1)–Cr(*n*)–Cl(*n*2)	106.9(4)	107.0(3)
N(*n*1)–Cr(*n*)–N(*n*2)	113.6(4)	113.0(5)
N(*n*2)–Cr(*n*)–Cl(*n*1)	104.4(4)	103.2(3)
N(*n*2)–Cr(*n*)–Cl(*n*2)	106.5(3)	107.7(3)
Cl(*n*1)–Cr(*n*)–Cl(*n*2)	121.0(1)	119.7(1)
C(*n*1)–N(*n*1)–Cr(*n*)	165.3(8)	159.1(8)
C(*n*2)–N(*n*2)–Cr(*n*)	160.3(7)	172.5(8)

intensity data of diffraction from the twin components present in the specimen (see Experimental section). Nevertheless, the main features are clear, and the two molecules show reasonably consistent results. Thus the bridges are symmetrical, with Cr–N distances of *ca.* 1.80 Å, and the bond lengths to the terminal imidos are *ca.* 1.64 Å. The Cr–Cl distances of 2.179(6) and 2.186(6) Å are very similar to those in **1** and **1a** and are consistent with the high oxidation states of the chromium atoms. In the Cr_2N_2 dimer ring, the angles at N are smaller than those at Cr [85.6(5), 87.8(7) *vs.* 94.4(5), 92.2(7)°] and are in keeping with the idea of some Cr ⋯ Cr bonding. The Cr ⋯ Cr distances average 2.487(7) Å.



Scheme 2

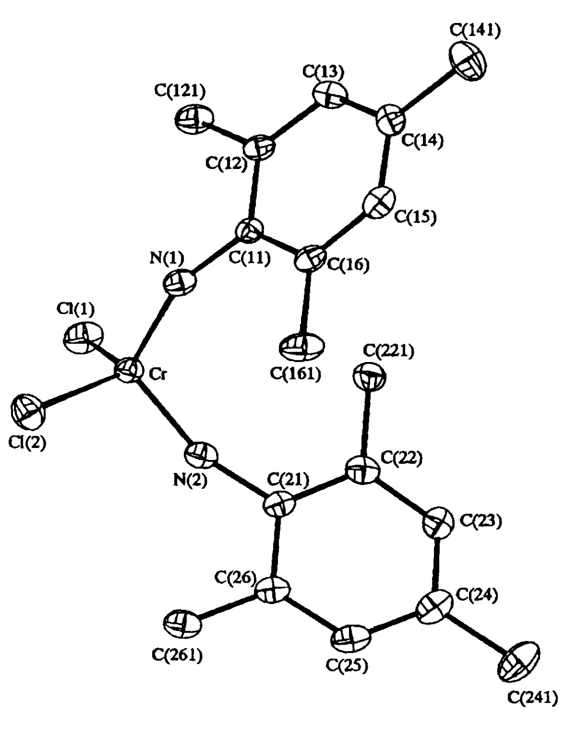


Fig. 1 Structure of $CrCl_2(NC_6H_2Me_3\text{-}2,4,6)_2$ **1**

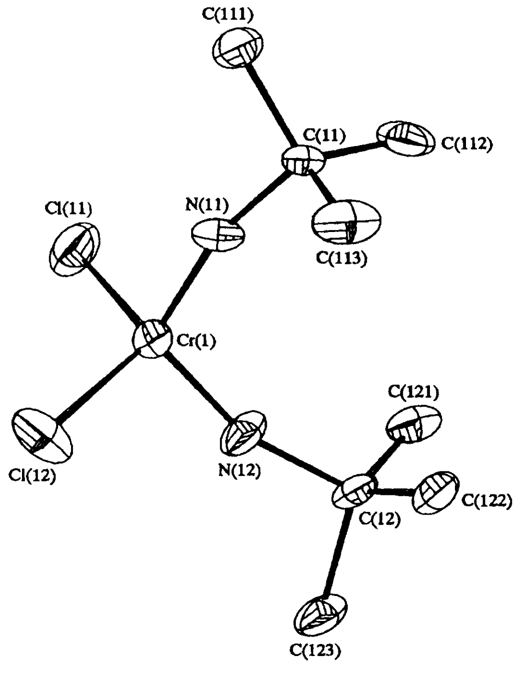


Fig. 2 Structure of $CrCl_2(NBu^t)_2$ **1a**

Reactions of the Mesitylimido Compound **1**.—*Adducts.* Like $CrCl_2(NBu^t)_2$,[3] compound **1** forms adducts with Lewis bases; the addition of PMe_3 or pyridine (py) to solutions in $CDCl_3$ causes an immediate change from orange-brown to light orange or red-orange, respectively. The PMe_3 compound **4** was isolated. The ^1H NMR spectra show a shift of mesityl resonances from δ 2.25 (o-CH_3) and 1.85 (p-CH_3) to 2.60 and 2.40 (t, J_{P-H} = 3.3 Hz) with the p-CH_3 showing ^{31}P coupling. From these data, integrations and analytical data **4** can be formulated as $CrCl_2(NC_6H_2Me_3\text{-}2,4,6)_2(PMe_3)_2$. The equivalence of the mesityl groups in the ^1H NMR spectra and of the PMe_3 groups in the $^{31}P\text{-}\{^1H\}$ spectrum indicates a symmetrical geometry or fast interconversions in solution. Analogous behaviour observed with pyridine in solution is consistent with the structure $CrCl_2(NC_6H_2Me_3\text{-}2,4,6)_2(py)_2$.

Table 4 Selected bond lengths (Å) and angles (°) for $[CrCl(\mu\text{-}NBu^t)(NC_6H_3Pr^i_2\text{-}2,6)]_2$ **3** with e.s.d.s in parentheses

	Molecule 1, *n* = 1	Molecule 2, *n* = 2
Cr(*n*1)···Cr(*n*1′)	2.486(6)	2.488(7)
Cr(*n*1′)–N(*n*1)	1.838(13)	1.80(2)
Cr(*n*1)–N(*n*1)	1.820(14)	1.785(14)
Cr(*n*1)–N(*n*1′)	1.838(13)	1.80(2)
Cr(*n*1)–N(*n*2)	1.64(2)	1.638(13)
Cr(*n*1)–Cl(*n*1)	2.179(6)	2.186(6)
N(*n*1)–C(*n*1)	1.47(2)	1.53(2)
N(*n*2)–C(*n*2)	1.41(2)	1.39(2)
N(*n*1)–Cr(*n*1)–N(*n*1′)	94.4(5)	92.2(7)
N(*n*1)–Cr(*n*1)–N(*n*2)	113.7(6)	116.4(7)
N(*n*1)–Cr(*n*1)–Cl(*n*1)	112.5(5)	111.1(5)
N(*n*1′)–Cr(*n*1)–N(*n*2)	111.8(7)	111.8(7)
N(*n*1′)–Cr(*n*1)–Cl(*n*1)	113.6(5)	115.9(5)
N(*n*2)–Cr(*n*1)–Cl(*n*1)	110.1(5)	109.0(7)
Cr(*n*1)–N(*n*1)–Cr(*n*1′)	85.6(5)	87.8(7)
C(*n*1)–N(*n*1)–Cr(*n*1)	139(1)	136(1)
C(*n*1)–N(*n*1)–Cr(*n*1′)	135(1)	136(1)
C(*n*2)–N(*n*2)–Cr(*n*1)	172(1)	171(2)

Primed atoms are related by the symmetry transformations: for dimer 1, $-x + 1, -y + 1, -z + 2$; for dimer 2, $-x, -y, -z + 1$.

Chloride substitution reactions. The interaction of compound **1** with 2,2′:6′,2″-terpyridine (terpy) and 2 equivalents of $AgBF_4$ in refluxing acetonitrile leads, on work-up, to the orange-brown crystalline salt $[Cr(NC_6H_2Me_3\text{-}2,4,6)_2(terpy)][BF_4]_2$ **5**. X-Ray-quality crystals could not be obtained even with other anions but the analytical and spectroscopic data are adequate to formulate the compound as in **I**. It is diamagnetic and five-co-ordinate with the $NC_6H_2Me_3\text{-}2,4,6$ groups equivalent on the NMR time-scale; it is a 2:1 electrolyte in acetonitrile.

Nucleophilic substitution of the Cl atoms of compound **1** is facile but sodium reagents rather than lithium ones are preferred since the latter tend to give products more difficult to obtain pure. The dialkoxides with $OSiMe_3$ **6** and $OC_6H_2Me_3\text{-}2,4,6$ **7**, dithiolates with $SC_6H_2Me_3\text{-}2,4,6$ **8**, SC_6F_5 **9** and $SC_6H_2Pr^i_3\text{-}2,4,6$ **10** have been made by interaction of the appropriate sodium salt in Et_2O. On the basis of ^1H NMR data all of these compounds appear to be tetrahedral in solution. Only one type of $NC_6H_2Me_3\text{-}2,4,6$ group is observed even at low temperature which indicates these groups to be equivalent on the NMR time-scale.

The crystal structure of the compound $Cr(NC_6H_2Me_3\text{-}2,4,6)_2(OC_6H_2Me_3\text{-}2,4,6)_2$ **7** was determined. The asymmetric unit was shown to contain two crystallographically independent molecules, and a diagram of molecule 1 is shown in Fig. 4; bond lengths and angles are given in Table 5. The positioning of the O and N atoms was clearly indicated by their thermal parameters in the refinement and their geometry. Thus the Cr$\overset{\text{—}}{=}$N bonds are shorter [average 1.655(3) Å] and more nearly linear [156.2(3)–165.1(3)°] than the corresponding values for the $Cr\text{–}OC_6H_2Me_3\text{-}2,4,6$ functions [average Cr–O 1.819(3) Å, Cr–O–C 125.0(2)–133.2(2)°]. Of particular note are the similarities in the N–Cr–N, O–Cr–O and N–Cr–O angles, which are all within a few degrees of tetrahedral, 106.2(2)–114.9(1)°, and do not show the large differences found in the dichlorides.

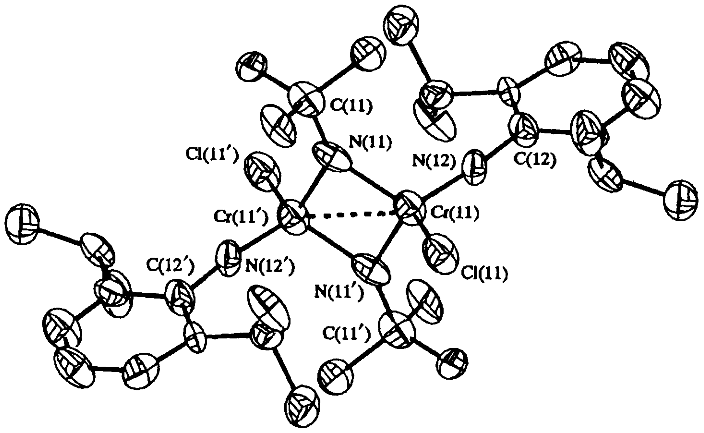
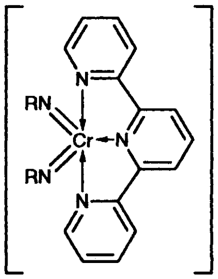


Fig. 3 Structure of the chromium(v) dimer $[CrCl(\mu\text{-}NBu^t)(NC_6H_3Pr^i_2\text{-}2,6)]_2$ **3**



I R = $C_6H_2Me_3$-2, 4, 6

Table 5 Selected bond lengths (Å) and angles (°) for $Cr(NC_6H_2Me_3\text{-}2,4,6)_2(OC_6H_2Me_3\text{-}2,4,6)_2\cdot0.25Et_2O$ **7** with e.s.d.s in parentheses

	Molecule 1, *n* = 1	Molecule 2, *n* = 2
Cr(*n*)–N(*n*1)	1.649(4)	1.664(3)
Cr(*n*)–N(*n*2)	1.655(3)	1.652(3)
Cr(*n*)–O(*n*1)	1.816(3)	1.826(3)
Cr(*n*)–O(*n*2)	1.818(3)	1.815(3)
N(*n*1)–C(*n*11)	1.367(5)	1.367(4)
N(*n*2)–C(*n*21)	1.376(5)	1.374(4)
O(*n*1)–C(*n*31)	1.357(5)	1.363(4)
O(*n*2)–C(*n*41)	1.363(5)	1.364(5)
O(*n*1)–Cr(*n*)–O(*n*2)	114.3(1)	114.9(1)
O(*n*1)–Cr(*n*)–N(*n*1)	108.7(2)	107.7(1)
O(*n*1)–Cr(*n*)–N(*n*2)	106.2(2)	106.9(1)
O(*n*2)–Cr(*n*)–N(*n*1)	106.9(2)	109.4(1)
O(*n*2)–Cr(*n*)–N(*n*2)	110.1(1)	106.8(1)
N(*n*1)–Cr(*n*)–N(*n*2)	110.7(2)	111.2(1)
Cr(*n*)–N(*n*1)–C(*n*11)	163.9(3)	156.2(3)
Cr(*n*)–N(*n*2)–C(*n*21)	157.3(3)	165.1(3)
Cr(*n*)–O(*n*1)–C(*n*31)	130.4(2)	129.2(2)
Cr(*n*)–O(*n*2)–C(*n*41)	125.0(2)	133.2(2)

The unit cell also contains four diethyl ether molecules disordered about centres of symmetry.

Attempts to obtain X-ray-quality crystals of a thiolate were unsuccessful.

It may be noted that while compound **1** and $NaOSiMe_3$ in Et_2O gave **6**, this compound could not be obtained by interaction of $Cr(NBu^t)_2(OSiMe_3)_2$ with $2,4,6\text{-}Me_3C_6H_2NCO$ in refluxing octane; only intractable mixtures result.

Alkyl substitution in compound **1** is easy using Grignard reagents MgRCl (R = CH_2CMe_3, CH_2CMe_2Ph or CH_2Ph) in Et_2O; the crystalline alkyls $Cr(NC_6H_2Me_3\text{-}2,4,6)_2R_2$ **11**, **12** and **13**, respectively, are all orange-yellow and thermally stable up to the melting point, although **11** and **12** failed to give the molecular ion in electron impact (EI) or chemical ionisation (CI) mass spectra. The only structurally characterised compounds of this type are $Cr(NBu^t)_2(C_6H_2Me_3\text{-}2,4,6)_2$[2] and $Cr(NBu^t)_2[o\text{-}(CHSiMe_3)_2C_6H_4]$.[5] Similar alkyls that were oils were characterised spectroscopically.[5] The ^1H NMR spectra and analytical data for **11**–**13** are all consistent with the formulation but crystals of X-ray quality could not be obtained.

The interaction of compound **1** with the Grignard reagent from 4-*tert*-butylbenzyl chloride in Et_2O did not give the expected dialkyl but the green-brown crystalline compound **14** shown in **II** in which the oxidation state of both Cr atoms is IV. The structure of the molecule, as determined by X-ray diffraction, is shown in Fig. 5; bond lengths and angles are in Table 6. The molecule lies on a centre of symmetry and there are two disordered diethyl ether molecules per dimer. The bridging imido groups are again symmetrically disposed with bridging Cr–N distances of 1.820(4) and 1.814(4) Å. The Cr–Cl distances, 2.211(2) Å, are slightly longer than the analogous distances in compound **3** and this is consistent with the change in oxidation state from V in **3** to IV here. The Cr–N (amido) distance is almost equal to the distances to the bridging imido groups and this implies a similar degree of multiple-bonding character. The Cr ··· Cr distance is 2.512(2) Å, again somewhat longer than that in the chromium(v) complex **3**, in which some Cr ··· Cr bonding interaction is envisaged. We presume there to be similar Cr ··· Cr interaction here, and this is consistent with the Cr–N–Cr and N–Cr–N angles in the Cr_2N_2 ring, where the former, 87.4(2)°, is smaller than the latter, 92.6(2)°.

It is difficult to prove the method of formation of compound **14** but initial substitution to give a monobenzyl species could then be followed by reductive rearrangement of the alkyl **III** to give the amido intermediate **IV** that dimerises to produce **14** (Scheme 3). The compound **14** is a rare example of a chromium(IV) dimer though the common tetrahedral co-ordination about Cr^{IV} found in paramagnetic alkyls,[10] aryls,[11] dialkylamides and alkoxides[12] is retained. It is of interest that unisolable amido intermediates of the type **IV** have been proposed in modelling studies for C–N bond formation in acrylonitrile synthesis (ammoxidation) where benzyl radicals were trapped by NR groups in, *e.g.*, $Cr(NBu^t)_2(OSiMe_3)_2$.[13]

The interaction of compound **1** with MgEtBr in the presence of PMe_3 leads to **15**, as shown in **V**. In reactions that involve reduction, dimerisation and halogen exchange, reductions using MgEtBr are, of course, well established. The structure of **15** has been confirmed by X-ray diffraction and is shown in Fig. 6; bond lengths and angles are in Table 7. The unsymmetrical configuration and substitution pattern for this formally dichromium(v) compound produces some interesting geometry differences, some of them not surprising in view of the different

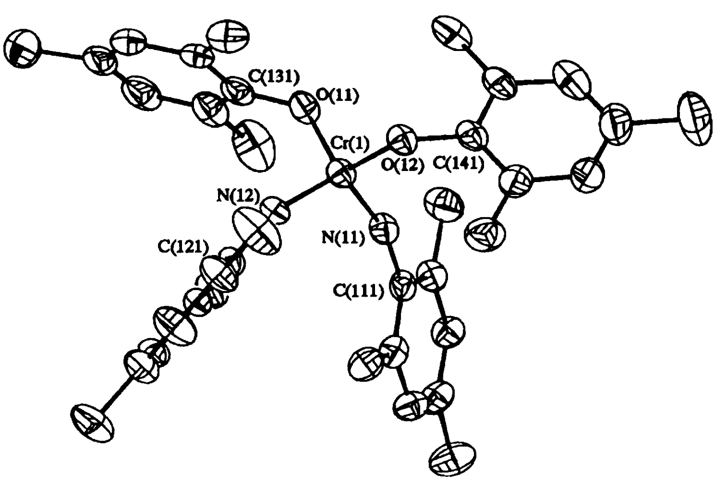
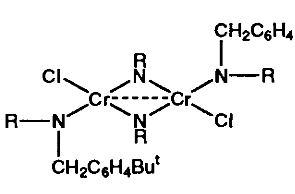


Fig. 4 Co-ordination sphere of $Cr(NC_6H_2Me_3\text{-}2,4,6)_2(OC_6H_2Me_3\text{-}2,4,6)_2\cdot 0.25Et_2O$ **7**

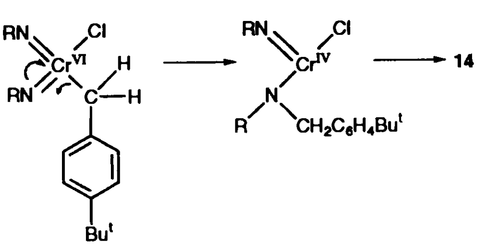


II R = $C_6H_2Me_3$-2, 4, 6

co-ordination numbers. Thus the Cr–Br distances show a difference of 0.08 Å, the larger one, as expected, involving the five-co-ordinate chromium. Both Cr–N–Cr bridges are unsymmetrical, with longer distances to the five-co-ordinate chromium. Most noteworthy is the very significant *trans* influence exerted by the phosphine–chromium bond on the Cr(2)–N(2) bond, which is 0.07 Å longer than Cr(2)–N(4). Even more surprising, however, is the near equivalence of the terminal Cr–N (imido) bond lengths, which differ by only 0.007 Å, and which seem to be normal triple Cr≡N bonds when compared with the structures above. The Cr···Cr distance, 2.530(2) Å, and the angles within the Cr_2N_2 ring (see Table 7) are consistent with some weak Cr···Cr bonding. The crystal structure also contains disordered diethyl ether molecules. Other similar chromium(V) dimers, *e.g.* $[CrCl(\mu\text{-}NBu^t)(NBu^t)]_2$, though not structurally characterised by X-ray diffraction are known.[3,4b] There are also the species $[Cr(\eta\text{-}C_5Me_5)(\mu\text{-}O)O_2]_2$[14a] and $[Cr(\eta\text{-}C_5H_5)(\mu\text{-}NSiMe_3)(NSiMe_3)]_2$.[14b]

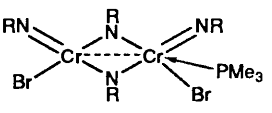
Insertion Reactions of the Alkyl Compounds.—Reactions have been described for $M(NBu^t)_2(C_6H_2Me_3\text{-}2,4,6)_2$,[2] M = Cr, Mo or W, with Bu^tNC; the products have a single η^2-iminoacyl group as in $Cr(NBu^t)_2(C_6H_2Me_3\text{-}2,4,6)[(2,4,6\text{-}Me_3\text{-}C_6H_2)C{=}NBu^t)]$ whose structure was determined by X-ray diffraction.

The alkyl compound **12** behaves similarly with both Bu^tNC and 2,6-xylyl isocyanide to give the iminoacyls $Cr(NC_6H_2Me_3\text{-}2,4,6)_2(CH_2CMe_2Ph)[RN{=}C(CH_2CMe_2Ph)]$ (R = $C_6H_3Me_2$-2,6 **16** or Bu^t **17**). Although crystals of X-ray quality could not be obtained, using **11** and **13**, which react similarly to **12**, the identities of the compounds were unequivocally confirmed by (NMR, IR and mass) spectroscopic data. Interaction of the alkyls with CS_2 and isocyanates RNCO (R = Bu^t or Ph) and with CO under pressure at 70 °C for 2 d led to unidentifiable decomposition products.



III IV

Scheme 3 R = $C_6H_2Me_3$-2,4,6



V R = $C_6H_2Me_3$-2, 4, 6

Reduction of Alkyl Compounds.—On heating in aromatic solvents at 60–70 °C in the presence of PMe_3 for *ca.* 8 h reduction of compounds **11–13** occurs to give the chromium(IV) compound $[Cr(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)(NC_6H_2Me_3\text{-}2,4,6)(PMe_3)]_2$ **18**. The yields are *ca.* 20–40% and are highest using **13** in benzene. The chromium(IV) dimer is diamagnetic and sufficiently soluble to give NMR spectra. In CD_2Cl_2 the ^1H spectrum shows two types of $NC_6H_2Me_3$-2,4,6 groups and the broad ^{31}P signal is at δ *ca.* 19. In $[^2H_8]$tetrahydrofuran there is only one $NC_6H_2Me_3$-2,4,6 proton resonance; the ^{31}P chemical shift is at δ 36 with a strong signal due to free PMe_3 at δ −58, while some solid decomposition product appears after *ca.* 0.5 h. These results are probably due to partial displacement of PMe_3 by tetrahydrofuran (thf) and/or breaking of the μ-$NC_6H_2Me_3$-2,4,6 bridge since the peak at δ +36 corresponds to a type of monomer $Cr(NC_6H_2Me_3\text{-}2,4,6)_2(PMe_3)_x(thf)_{3-x}$ (x = 1 or 2). These findings are reminiscent of the recently reported dynamic behaviour of $Mo(NC_6H_2Me_3\text{-}2,4,6)_2(PMe_3)_3$,[15] but for the chromium case detailed study is difficult due to the dimerisation and decomposition.

The structure of the dimer **18** was determined by X-ray diffraction and is shown in Fig. 7; bond distances and angles are given in Table 8. The dimeric molecule lies on a two-fold axis through the centre of, and perpendicular to, the Cr_2N_2 ring. The Cr–N–Cr bridges show only minor (0.01 Å) asymmetry. The Cr–N (imido) distance is slightly longer than in compounds **3** and **15**, as would be expected for the lower oxidation state here (IV), but the Cr–P distance is 0.091 Å shorter than in **15**, reflecting, perhaps, some Cr→P π-back bonding. The angles at chromium [94.6(1)°] and at the nitrogen [85.3(1)°] in the

Cr_2N_2 ring, together with the Cr $\cdots$ Cr distance of 2.496(1) Å, are consistent with some Cr $\cdots$ Cr interaction.

It may be noted that other phosphines [PMe_2Ph, $PMePh_2$ and $(Ph_2PCH_2)_2$] give only intractable products. The reduction of the alkyls **11**–**13** in toluene containing an excess of PMe_3 by Na/Hg yields after *ca.* 8 h an olive-green, very air-sensitive solution but no crystalline product could be isolated. Attempts to follow the reduction in $C_6D_5CD_3$ by ^{31}P NMR spectra showed at room temperature a peak at δ *ca.* 20 assignable to **18** and a very broad peak at δ *ca.* 54. The latter sharpens on cooling to −80 °C and this process is reversible and possibly attributable to a fluxional, monomeric species such as $Cr(NC_6H_2Me_3\text{-}2,4,6)_2(PMe_3)_3$ but isolation is not possible. By contrast to the above, reduction of **1** with Na/Hg in toluene and thf in the presence of PMe_3 gives a brown mixture possibly of chromium(V) dimers that we have been unable to isolate.

Experimental

Analyses were by the Imperial College and Medac analytical laboratories. General techniques have been described.[16] The NMR data were obtained on a JEOL-EX-270 spectrometer at 270 MHz (^1H) and referenced to residual H impurity in the solvent (δ 7.15, C_6D_6; 7.26, $CDCl_3$). Mass spectra (EI) were taken on a VG-7070E spectrometer. Commercial chemicals were from Aldrich, Avocado, Fluka and Janssen. Aryl isocyanates were made by the interaction of a toluene solution of $COCl_2$ with the amine in the presence of NEt_3.[17] Literature

Table 6 Selected bond lengths (Å) and angles (°) for $\{CrCl(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)[N(CH_2C_6H_4Bu^t\text{-}4)(C_6H_2Me_3\text{-}2,4,6)]\}_2\cdot 2Et_2O$ **14** with e.s.d.s in parentheses

Cr $\cdots$ Cr′	2.512(2)	Cr–N(2)	1.820(4)
Cr–Cl	2.211(2)	N(1)–C(11)	1.433(6)
Cr–N(1)	1.820(4)	N(2)–C(21)	1.425(5)
Cr–N(1′)	1.814(4)	N(2)–C(2)	1.473(8)
Cr′–N(1)	1.814(4)	C(2)–C(3)	1.510(9)
N(1)–Cr–Cl	111.5(1)	Cr–N(1)–Cr′	87.4(2)
N(1)–Cr–N(2)	114.6(2)	Cr–N(1)–C(11)	134.9(4)
N(1)–Cr–N(1′)	92.6(2)	Cr′–N(1)–C(11)	137.6(3)
Cl–Cr–N(2)	110.3(1)	C(21)–N(2)–C(2)	116.8(5)
Cl–Cr–N(1′)	114.9(2)	C(21)–N(2)–Cr	129.9(4)
N(2)–Cr–N(1′)	112.1(2)	C(2)–N(2)–Cr	113.3(4)
		N(2)–C(2)–C(3)	114.2(5)

Primed atoms are related by the symmetry transformation $-x, -y + 1, -z$.

Table 7 Selected bond lengths (Å) and angles (°) for $(2,4,6\text{-}Me_3C_6H_2N)BrCr(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)_2CrBr(NC_6H_2Me_3\text{-}2,4,6)(PMe_3)\cdot Et_2O$ **15** with e.s.d.s in parentheses

Cr(1) $\cdots$ Cr(2)	2.530(2)	Cr(2)–N(2)	1.963(4)
Cr(1)–Br(1)	2.372(2)	Cr(2)–N(3)	1.648(5)
Cr(1)–N(1)	1.655(5)	Cr(2)–N(4)	1.894(5)
Cr(1)–N(2)	1.756(5)	N(1)–C(10)	1.397(7)
Cr(1)–N(4)	1.793(5)	N(2)–C(20)	1.407(7)
Cr(2)–Br(2)	2.451(2)	N(3)–C(30)	1.373(7)
Cr(2)–P	2.413(2)	N(4)–C(40)	1.403(7)
N(1)–Cr(1)–N(2)	116.8(2)	N(3)–Cr(2)–P	86.1(2)
N(1)–Cr(1)–N(4)	114.5(2)	N(4)–Cr(2)–Br(2)	132.6(2)
N(1)–Cr(1)–Br(1)	104.5(2)	N(4)–Cr(2)–P	92.7(1)
N(2)–Cr(1)–N(4)	97.8(2)	Br(2)–Cr(2)–P	87.5(1)
N(2)–Cr(1)–Br(1)	108.6(2)	Cr(1)–N(1)–C(10)	177.1(5)
N(4)–Cr(1)–Br(1)	115.0(2)	Cr(1)–N(2)–C(20)	137.6(4)
N(2)–Cr(2)–N(3)	105.1(2)	Cr(1)–N(4)–C(40)	132.1(4)
N(2)–Cr(2)–N(4)	87.8(2)	Cr(2)–N(2)–C(20)	136.5(4)
N(2)–Cr(2)–Br(2)	88.9(1)	Cr(2)–N(3)–C(30)	176.0(4)
N(2)–Cr(2)–P	167.4(2)	Cr(2)–N(4)–C(40)	138.0(4)
N(3)–Cr(2)–N(4)	115.4(2)	Cr(1)–N(2)–Cr(2)	85.5(2)
N(3)–Cr(2)–Br(2)	111.0(2)	Cr(1)–N(4)–Cr(2)	86.6(2)

Table 8 Selected bond lengths (Å) and angles (°) for $[Cr(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)(NC_6H_2Me_3\text{-}2,4,6)(PMe_3)]_2$ **18** with e.s.d.s in parentheses

Cr $\cdots$ Cr′	2.496(1)	Cr–P	2.322(1)
Cr–N(1)	1.680(2)	N(1)–C(11)	1.375(4)
Cr–N(2)	1.848(2)	N(2)–C(21)	1.410(4)
Cr–N(2′)	1.836(2)		
N(1)–Cr–N(2)	125.4(1)	N(2′)–Cr–P	114.4(1)
N(1)–Cr–N(2′)	122.8(1)	Cr–N(1)–C(11)	177.0(2)
N(1)–Cr–P	90.3(1)	Cr–N(2)–C(21)	135.7(2)
N(2)–Cr–N(2′)	94.6(1)	Cr′–N(2)–C(21)	135.2(2)
N(2)–Cr–P	110.2(1)	Cr–N(2)–Cr′	85.3(1)

Primed atoms are related by the symmetry transformation $-x + \frac{3}{2}, y, -z + \frac{3}{2}$.

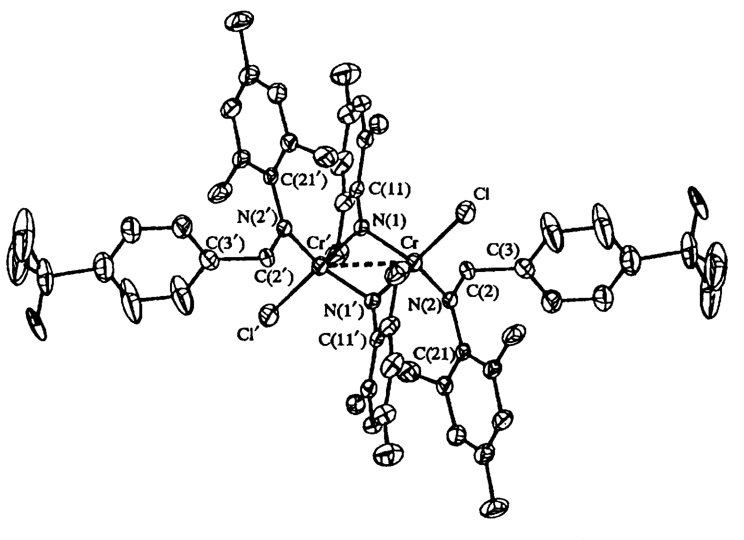


Fig. 5 Co-ordination sphere of $\{CrCl(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)[N(CH_2C_6H_4Bu^t\text{-}4)(C_6H_2Me_3\text{-}2,4,6)]\}_2\cdot 2Et_2O$ **14**. One conformation of the disordered *tert*-butyl group is shown

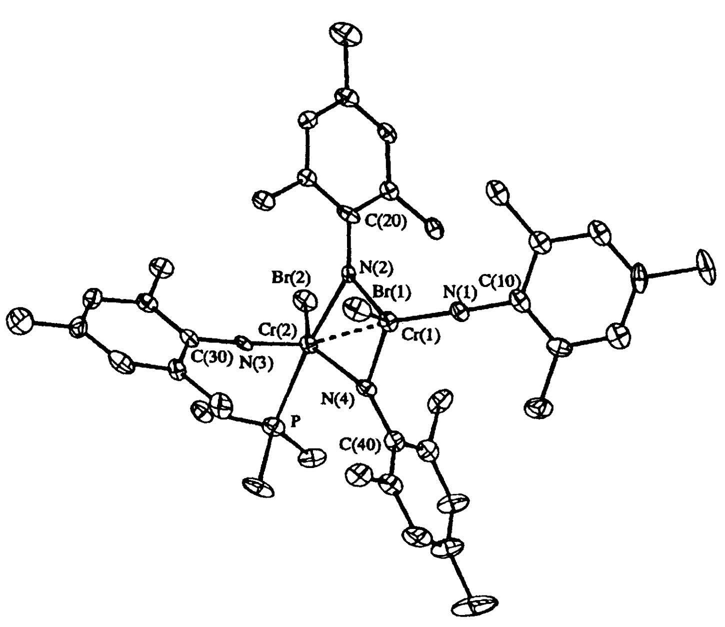


Fig. 6 Co-ordination sphere of $(2,4,6\text{-}Me_3C_6H_2N)BrCr(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)_2CrBr(NC_6H_2Me_3\text{-}2,4,6)(PMe_3)\cdot Et_2O$ **15**

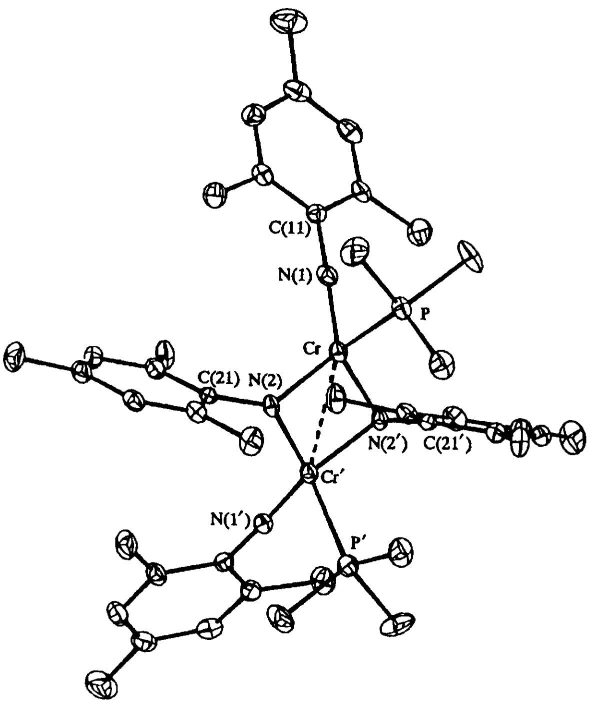


Fig. 7 Structure of $[Cr(\mu\text{-}NC_6H_2Me_3\text{-}2,4,6)(NC_6H_2Me_3\text{-}2,4,6)(PMe_3)]_2$ **18**

procedures were used for $CrCl_2(NBu^t)_2$,[3] $NaOSiMe_3$[18] and $2,4,6\text{-}Pr^i{}_3C_6H_2SH$.[19] Sodium salts of alkoxides and thiols were made in diethyl ether by interaction with Na. Solvents were dried and degassed by standard methods. The light petroleum used had b.p. 40–60 °C. All operations were carried out under purified N_2 or Ar, under vacuum or in a Vacuum Atmospheres box.

Dichlorobis(2,4,6-*trimethylphenylimido*)*chromium*(VI) **1**.—A mixture of $CrCl_2(NBu^t)_2$ (7.35 g, 0.028 mol) and 2,4,6-trimethylphenyl isocyanate (9.8 g, 0.061 mol) in octane (*ca.* 70 cm^3) was refluxed for 12 h. After cooling, the precipitated microcrystalline solid was collected, washed with light petroleum (2 × 10 cm^3) and extracted (Soxhlet) with diethyl ether (100 cm^3) until the extracts were colourless. After concentration and cooling (−20 °C) of the extracts, red-brown prisms were obtained. Yield: 8.2 g (*ca.* 75%). Mass spectrum (EI): *m*/*z* 388 (M^+), 353 (M^+ − Cl) and 318 (M^+ − 2 Cl). IR (cm^{-1}): 1280, 1265 ($Cr{=}NC_6H_2Me_3$); 851, 725 (aromatic); 391 (Cr–Cl). NMR (C_6D_6): ^{1}H, δ 6.23 (s, 4 H, $NC_6\mathit{H}_2Me_3$), 2.25 (s, 12 H, *o*-Me of $C_6H_2Me_3$) and 1.85 (s, 6 H, *p*-Me of $C_6H_2Me_3$); ^{13}C-{^{1}H}, δ 165.0 (*ipso*-C of $C_6H_2Me_3$), 142.9, 138.5, 129.4 (aromatic), 22.0 (*p*-Me) and 19.0 (*o*-Me).

Dichlorobis(2,6-*dimethylphenylimido*)*chromium*(VI) **2**.—The procedure was similar to that described for the mesityl analogue. A mixture of $CrCl_2(NBu^t)_2$ (2 g, 7.5 mmol) and 2,6-dimethylphenyl isocyanate (2.22 g, 15 mmol) was refluxed in octane (30 cm^3) for *ca.* 8 h. After cooling to room temperature the supernatant was discarded and the residue extracted with Et_2O until the extracts were almost colourless. Concentration of the extracts and cooling (−20 °C) gave red-brown crystals. Yield: 2.0 g (*ca.* 80%). Mass spectrum (EI): *m*/*z* 360 (M^+), 325 (M^+ − Cl) and 290 (M^+ − 2 Cl). NMR (C_6D_6): ^{1}H, δ 6.8–7.0 (m, 6 H, aromatic) and 2.19 (s, 12 H, *o*-Me); ^{13}C-{^{1}H}, δ 139.5 (*ipso*-C of $C_6H_3Me_2$), 132.7, 131.9, 130.9, 128.9 (aromatic) and 19.0 (*o*-Me). IR (cm^{-1}): 1285, 1250 ($Cr{=}NC_6H_3Me_2$); 900, 920 (aromatic C–H); 400 (Cr–Cl).

Bis[(μ-tert-*butylimido*)*chloro*(2,6-*diisopropylphenylimido*)-*chromium*(V)] **3**.—A mixture of $CrCl_2(NBu^t)_2$ (1 g, 3.78 mmol) and 2,6-diisopropylphenyl isocyanate (0.79 g, 3.9 mmol) in xylene (20 cm^3) was refluxed for 12 h. After cooling the reaction mixture to room temperature, addition of light petroleum (70 cm^3) and cooling (−78 °C) gave rhomboidal prisms. Yield: 0.25 g, *ca.* 20%. NMR (C_6D_6): ^{1}H, δ 7.1–6.8 (m, 6 H, aromatic), 3.5 (spt, 4 H, $C\mathit{H}Me_2$), 1.70 (s, 18 H, Bu^t) and 1.25 (d, 24 H, $CH\mathit{Me}_2$); ^{13}C-{^{1}H}, δ 148.0 (*ipso*-C of $C_6H_3Pr^i{}_2$), 129.0, 124.2 (aromatic, not all observed), 79.8 ($N\mathit{C}Me_3$), 34.5 (Me_3CN), 29.5 ($Me_2\mathit{C}H$) and 24.5 (Me_2CH).

Dichlorobis(2,4,6-*trimethylphenylimido*)*bis*(*trimethylphosphine*)*chromium*(VI) **4**.—To a solution of compound **1** in CH_2Cl_2 (0.2 g, 0.5 mmol in 10 cm^3) was added PMe_3 (0.2 cm^3, excess). The solution changed immediately to orange. After stirring for 5 min the volatiles were removed under reduced pressure, the residue was washed with diethyl ether (2 × 5 cm^3) dissolved in CH_2Cl_2 and reprecipitated as an orange microcrystalline powder after addition of ether. Yield: 0.2 g, *ca.* 80%. NMR ($CDCl_3$): ^{1}H, δ 6.9 (s, 4 H, aromatic), 2.58

(s, 12 H, *o*-Me), 2.40 (t, 6 H, *p*-Me) and 1.60 (filled-in triplet, 18 H, PMe_3); ^{31}P-{^1H}, δ 26.8.

(2,2′:6′,2″-*Terpyridine*)*bis*(2,4,6-*trimethylphenylimido*)*chromium*(VI) *Bis*(*tetrafluoroborate*) **5**.—A mixture of compound **1** (0.5 g, 1.3 mmol), $AgBF_4$ (0.51 g, 2.6 mmol) and terpy (0.3 g, 1.3 mmol) in acetonitrile (40 cm^3) was refluxed for 1 h. After cooling to room temperature, filtration and removal of volatiles under reduced pressure, the red-brown residue was washed with ether, extracted into CH_2Cl_2 (30 cm^3) and layered with ether. After 1 week red-brown needles of **5** appeared. Yield: 0.65 g, *ca.* 70%. NMR (CD_2Cl_2): ^1H, δ 8.9–7.5 (m, 11 H, terpy), 6.82 (s, 4 H, $NC_6H_2Me_3$), 2.4 (s, 6 H, *p*-Me) and 2.3 (s, 12 H, *o*-Me); ^{19}F, δ 178; ^{13}C-{^1H}, δ 164.2, 155.0, 154.8, 153.7, 149.9, 148.2, 145.5, 144.8, 130.7, 129.8, 127.3, 126.0 (aromatic, not assigned), 22.9 (*p*-Me) and 19.6 (*o*-Me).

Bis(2,4,6-*trimethylphenylimido*)*bis*(*trimethylsiloxo*)*chromium*(VI) **6**.—To a solution of compound **1** (0.3 g, 0.8 mmol) in ether (30 cm^3) at −78 °C was added a solution of $NaOSiMe_3$ (0.18 g, 1.6 mmol) in ether (20 cm^3). After warming to room temperature the reaction mixture was stirred for 12 h. Evaporation of volatiles under vacuum, extraction of the residue with light petroleum (2 × 20 cm^3), filtration and evaporation of the petroleum extracts under vacuum gave a red-brown oil which crystallised on standing at room temperature for 12 h. Yield: 0.25 g, *ca.* 62%. Mass spectrum (EI): *m*/*z* 496 (M^+), 406 (M^+ − $OSiMe_3$) and 316 (M^+ − 2 $OSiMe_3$). NMR (C_6D_6): ^1H, δ 6.46 (s, 4 H, $C_6H_2Me_3$), 2.35 (s, 12 H, *o*-Me), 1.98 (s, 6 H, *p*-Me) and 0.37 (s, 18 H, $OSiMe_3$); ^{13}C-{^1H}, δ 162.7 (*ipso*-C of $C_6H_2Me_3$), 136.9, 136.2, 133.5 (aromatic), 21.4 (*p*-Me), 19.0 (*o*-Me) and 3.2 ($OSiMe_3$).

Bis(2,4,6-*trimethylphenoxo*)*bis*(2,4,6-*trimethylphenylimido*)-*chromium*(VI)–*Diethyl Ether* (1/0.25) **7**.—To a solution of compound **1** (0.3 g, 0.8 mmol) in ether (30 cm^3) at −78 °C was added a solution of $NaOC_6H_2Me_3$-2,4,6 (0.27 g, 1.7 mmol) in ether (20 cm^3). After warming to room temperature the reaction mixture was stirred for 12 h. Evaporation of volatiles under vacuum, extraction of the residue with light petroleum (3 × 20 cm^3), filtration, concentration to *ca.* 10 cm^3 and cooling (−20 °C) gave red-brown prisms. Yield: 0.29 g, *ca.* 67%. Mass spectrum (EI): *m*/*z* 588 (M^+), 453 (M^+ − $Me_3H_2C_6O$) and 318 (M^+ − 2 $Me_3H_2C_6O$). NMR (C_6D_6): ^1H, δ 6.79 (s, 4 H, $Me_3OC_6H_2$), 6.35 (s, 4 H, $NC_6H_2Me_3$), 2.63 (s, 12 H, *o*-Me), 2.29 (s, 12 H, *o*-Me) and 2.16 and 1.90 (s, 12 H, *p*-Me); ^{13}C-{^1H}, δ 162.8 and 164.2 (*ipso*-C of $C_6H_2Me_3$, not assigned), 139.6, 137.3, 131.9, 129.9 (aromatic), 21.8 and 21.6 (*p*-Me, not assigned), 19.0 and 18.8 (*o*-Me).

Bis(2,4,6-*trimethylbenzenethiolato*)*bis*(2,4,6-*trimethylphenylimido*)*chromium*(VI) **8**.—To a solution of compound **1** (0.3 g, 0.8 mmol) in ether (30 cm^3) at −78 °C was added *via* cannula a suspension of $NaSC_6H_2Me_3$-2,4,6 (0.29 g, 1.7 mmol) in ether (50 cm^3). After warming to room temperature the red-purple reaction mixture was stirred for 12 h when the volatiles were removed under reduced pressure. The residue was extracted with light petroleum (2 × 20 cm^3) and the extracts evaporated leaving a red oil which was crystallised on standing for 2–3 d. Yield: 0.16 g, *ca.* 35%. Mass spectrum (EI): *m*/*z* 620 (M^+), 469 (M^+ − $SC_6H_2Me_3$), 334 (M^+ − $SC_6H_2Me_3$ − $H_2NC_6H_2Me_3$) and 302 (M^+ − $SC_6H_2Me_3$ − $H_2NC_6H_2Me_3$ − S). ^1H, NMR (C_6D_6): δ 6.79 (s, 4 H, $C_6H_2Me_3$), 6.38 (s, 4 H, $NC_6H_2Me_3$), 2.72 (s, 12 H, *o*-Me of $SC_6H_2Me_3$), 2.24 (s, 12 H, *o*-Me of $NC_6H_2Me_3$), 2.07 (s, 6 H, *p*-Me of $SC_6H_2Me_3$), 1.88 (s, 6 H, *p*-Me of $NC_6H_2Me_3$).

Bis(*pentafluorobenzenethiolato*)*bis*(2,4,6-*trimethylphenylimido*)*chromium*(VI) **9**.—To a solution of compound **1** (0.3 g, 0.8 mmol) in ether (30 cm^3) at −78 °C was added *via* cannula a suspension of $NaSC_6F_5$ (0.38 g, 1.7 mmol) in ether (50 cm^3). After warming to room temperature the red-purple reaction mixture was stirred for 12 h. Removal of volatiles under reduced pressure, extraction of the residue with light petroleum (3 × 20 cm^3), filtration, concentration of the extracts to *ca.* 40 cm^3 when crystallisation started, and cooling (−20 °C) for 8 h gave red-brown crystals. Yield: 0.67 g, *ca.* 85%. Mass spectrum (EI): *m*/*z* 716 (M^+), 517 (M^+ − SC_6F_5) and 317 (M^+ − 2 SC_6F_5). NMR (C_6D_6): ^1H, δ 6.26 (s, 4 H, $NC_6H_2Me_3$), 2.21 (s, 12 H, *o*-Me of $NC_6H_2Me_3$), and 1.82 (s, 6 H, *p*-Me of $NC_6H_2Me_3$); ^{13}C-{^1H}, δ 162.0, 142.0, 138.5, 130.1, 129.6 (aromatic), 22.0 (*p*-Me) and 19.0 (*o*-Me); ^{19}F, δ −130 (d), −156 (t) and −163 (t).

Bis(2,4,6-*triisopropylbenzenethiolato*)*bis*(2,4,6-*trimethylphenylimido*)*chromium*(VI) **10**.—This was prepared as for compound **8** from **1** (0.6 g, 1.6 mmol) and $NaSC_6H_2Pr^i_3$-2,4,6 (0.82 g, 3.2 mmol). After evaporating the light petroleum extracts to dryness a red microcrystalline powder, pure according to NMR spectroscopy, was obtained. Yield: 0.9 g, 75%. Mass spectrum (FAB): *m*/*z* 789 (M^+) and 554 (M^+ − $SC_6H_2Pr^i_3$). ^1H NMR (C_6D_6): δ 7.11 and 6.52 (s, 4 H each, aromatic), 4.50 and 2.80 (spt, 4 H and 2 H, *o*- and *p*-$CHMe_2$, respectively), 2.31 (s, 12 H, *o*-Me), 2.01 (s, 6 H, *p*-Me), 1.50 and 1.35 (d, 24 H and 12 H, *o*- and *p*-$CHMe_2$).

Bis(*neopentyl*)*bis*(2,4,6-*trimethylphenylimido*)*chromium*(VI) **11**.—To a solution of compound **1** (0.25 g, 0.65 mmol) in ether (30 cm^3) at −78 °C was added neopentylmagnesium chloride in ether (1.5 cm^3 of a 0.9 mol dm^{-3} solution, 1.3 mmol). The red-brown colour immediately changed to green-brown and after warming to room temperature to yellow-brown. Stirring at room temperature for 2 h followed by evaporation under vacuum, extraction of the residue with light petroleum (2 × 20 cm^3), filtration and evaporation left a yellow-brown oil. This oil was pure according to NMR spectroscopy and crystallised on standing at room temperature for 2–3 d. Yield: 0.15 g, *ca.* 50%. Mass spectrum (EI): *m*/*z* 388 (M^+ − CMe_4) and 255 (M^+ − CMe_4 − $NC_6H_2Me_3$-2,4,6). NMR (C_6D_6): ^1H, δ 6.6 (s, 4 H, $NC_6H_2Me_3$), 2.45 (s, 4 H, CH_2CMe_3), 2.31 (s, 12 H, *o*-Me), 2.01 (s, 6 H, *p*-Me) and 1.30 (s, 18 H, CH_2CMe_3); ^{13}C-{^1H}, δ 145.0 (*ipso*-C of $NC_6H_2Me_3$), 136.4, 135.3, 129.4 (aromatic), 93.5 (CH_2CMe_3), 35.7 (CH_2CMe_3), 33.9 (CH_2CMe_3), 21.8 (*p*-Me) and 19.6 (*o*-Me).

Bis(2-*methyl*-2-*phenylpropyl*)*bis*(2,4,6-*trimethylphenylimido*)-*chromium*(VI) **12**.—To a solution of compound **1** (0.7 g, 1.8 mmol) in ether (50 cm^3) at −78 °C was added (2-methyl-2-phenylpropyl)magnesium chloride (7.7 cm^3 of a 0.48 mol dm^{-3} solution, 3.7 mmol) in ether. The reaction mixture was allowed to warm to room temperature and stirred for 2 h when the volatiles were removed under reduced pressure. Extraction of the residue with light petroleum (3 × 30 cm^3), filtration, concentration and cooling of the extracts (−20 °C) gave yellow crystals. Yield: 0.53 g, *ca.* 50% in two crops. NMR (C_6D_6): ^1H, δ 7.44 and 7.17 (m, 10 H, $CH_2CMe_2C_6H_5$), 6.57 (s, 4 H, $NC_6H_2Me_3$), 2.17 (s, 4 H, $CH_2CMe_2C_6H_5$), 2.15 (s, 12 H, *o*-Me), 2.03 (s, 6 H, *p*-Me) and 1.58 (s, 12 H, $CH_2CMe_2C_6H_5$); ^{13}C-{^1H}, δ 163.9 (*ipso*-C of $NC_6H_2Me_3$), 152.2, (*ipso*-C of CH_2CMe_2Ph), 136.4, 136.3, 129.3, 127.3, 126.4 (aromatic), 92.8 ($CH_2CMe_2C_6H_5$), 42.0 ($CH_2CMe_2C_6H_5$), 32.7 ($CH_2CMe_2C_6H_5$), 21.8 (*p*-Me) and 19.5 (*o*-Me).

Bis(*benzyl*)*bis*(2,4,6-*trimethylphenylimido*)*chromium*(VI) **13**.—To a solution of compound **1** (0.4 g, 1 mmol) in ether (50 cm^3) at −78 °C was added freshly prepared benzylmagnesium chloride in ether (5.4 cm^3 of a 0.38 mol dm^{-3} solution, 2.1 mmol). The red-brown solution was stirred at −78 °C for 10 min and then allowed to warm. After stirring at room temperature for 2 h the volatiles were evaporated under reduced

Table 9 Crystal data and structure refinement details for compounds **1**, **1a**, **3**, **7**, **14**, **15** and **18**

Compound	**1**	**1a**	**3**	**7**	**14**	**15**	**18**
Formula	$C_{18}H_{22}Cl_2CrN_2$	$C_{16}H_{36}Cl_4Cr_2N_4$	$C_{32}H_{52}Cl_2Cr_2N_4$	$C_{36}H_{44}CrN_2O_2\cdot 0.25(C_2H_5)_2O$	$C_{29}H_{37}ClCrN_2\cdot (C_2H_5)_2O$	$C_{36}H_{53}Br_2Cr_2N_4P\cdot (C_2H_5)_2O$	$C_{21}H_{31}CrN_2P$
M_r	389.28	530.29	667.68	607.28	575.18	910.74	394.45
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	Pc	$P\bar{1}$	$Pbca$	$P\bar{1}$	$C2/c$	$P2/n$
a/Å	8.691(1)	10.839(8)	9.353(9)	24.224(8)	10.447(2)	28.529(10)	13.778(8)
b/Å	14.004(1)	11.564(7)	11.709(9)	19.237(8)	11.921(1)	19.455(8)	8.733(6)
c/Å	15.776(1)	11.860(5)	16.96(2)	30.032(8)	14.891(4)	18.799(7)	18.445(4)
α/°	90	90	83.55(8)	90	98.23(3)	90	90
β/°	103.91(1)	111.83(4)	87.14(9)	90	102.08(2)	115.28(6)	99.02(4)
γ/°	90	90	72.42(5)	90	107.87(1)	90	90
U/Å^3	1863.8(3)	1380(1)	1759(3)	13995(8)	1682.6(6)	9435(6)	2192(2)
Z	4	2	2	16	2	8	4
D_c/Mg m^{-3}	1.387	1.276	1.261	1.153	1.135	1.282	1.195
$F(000)$	808	552	708	5192	616	3776	840
Crystal size/mm	0.24 × 0.21 × 0.15	0.26 × 0.12 × 0.09	0.15 × 0.12 × 0.09	0.36 × 0.18 × 0.15	0.225 × 0.09 × 0.03	0.84 × 0.18 × 0.15	0.36 × 0.12 × 0.12
μ(Mo-Kα)/mm^{-1}	0.901	1.182	0.795	0.360	0.444	2.19	0.600
Reflections collected	7689	4431	4494	43 157	6879	12 129	8923
Independent reflections (R_{int})	2793 (0.0687)	3320 (0.0449)	3976 (0.0901)	10 997 (0.0708)	4540 (0.0582)	6437 (0.0456)	3258 (0.0448)
Maximum, minimum absorption correction factors	1.166, 0.836	1.123, 0.885	1.186, 0.738	1.097, 0.862	1.064, 0.808	1.050, 0.867	1.127, 0.877
Data, restraints, parameters	2789, 0, 214	3318, 2, 247	3976, 0, 375	10 996, 0, 848	4536, 0, 387	6434, 0, 494	3255, 0, 251
Goodness of fit, F^2	0.994	0.665	0.442	0.850	0.773	0.794	0.921
Final R indices R_1, wR_2							
[$I > 2\sigma(I)$]	0.0369, 0.0871	0.0411, 0.0811	0.0594, 0.1342	0.0496, 0.1074	0.0535, 0.1079	0.0499, 0.1213	0.0400, 0.0948
(all data)	0.0492, 0.0932	0.0722, 0.0933	0.2210, 0.3295	0.1132, 0.1156	0.1164, 0.1329	0.0855, 0.1351	0.0610, 0.1016
Largest difference peak and hole/e Å^{-3}	0.410, −0.292	0.315, −0.281	0.287, −0.220	0.482, −0.504	0.294, −0.252	1.029, −0.437	0.495, −0.261

Goodness of fit, $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$ where n = number of reflections and p = total number of parameters; $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ where $w = 1/[\sigma^2(F_o)^2 + (xP)^2]$ with x = 0.0506, 0.0204, 0.0000, 0.0533, 0.0288, 0.0622 and 0.0515 for **1**, **1a**, **3**, **7**, **14**, **15** and **18** and $P = [\max(F_o^2) + 2(F_c^2)]/3$.

pressure. Extraction of the residue with light petroleum (3 × 30 cm^3), filtration, concentration to *ca.* 10 cm^3 and cooling (−20 °C) gave orange-brown crystals. Yield: 0.27 g, *ca.* 55%. Mass spectrum (EI): *m*/*z* 500 (M^+), 408 ($M^+ - CH_2Ph$) and 316 ($M^+ - 2\ CH_2Ph$). NMR (C_6D_6): ^1H, δ 7.08–6.95 (m, 10 H, $C_6\mathit{H}_5CH_2$), 6.58 (s, 4 H, $NC_6\mathit{H}_2Me_3$), 3.04 (s, 4 H, $C_6H_5C\mathit{H}_2$), 2.29 (s, 12 H, *o*-Me of $NC_6H_2Me_3$) and 2.03 (s, 6 H, *p*-Me of $NC_6H_2Me_3$); $^{13}C\text{-}\{^1H\}$, δ 158.5 (*ipso*-C of $NC_6H_2Me_3$), 139.4 (*ipso*-C of $CH_2C_6H_5$), 135.8, 135.3, 131.5, 128.7, 128.4, 127.3, 126.0 (aromatic, not assigned), 52.1 ($\mathit{C}H_2C_6H_5$), 21.0 (*p*-Me of $NC_6H_2Me_3$) and 18.8 (*o*-Me of $NC_6H_2Me_3$).

Bis{[(4-tert-*butylbenzyl*)(2,4,6-*trimethylphenyl*)*amido*]*chloro*(μ-2,4,6-*trimethylphenylimido*)*chromium*(IV)}–*DiethylEther*(1/2) **14**.—To a solution of compound **1** in ether (0.35 g, 0.9 mmol in 50 cm^3) was added a solution of 4-*tert*-butylbenzylmagnesium chloride (5.2 cm^3 of a 0.35 mol dm^{-3} solution, 1.8 mmol) at −78 °C. The reaction mixture was stirred for 15 min and then allowed to reach room temperature and stirred for 2 h. After removal of the volatiles under vacuum, the residue was extracted with light petroleum (3 × 50 cm^3) and the filtered extracts were concentrated to *ca.* 10 cm^3 and cooled (−20 °C) to give green-brown prisms. X-Ray-quality crystals were obtained by slowly cooling saturated light petroleum solutions. Yield: 0.18 g, *ca.* 40%. ^1H NMR (C_6D_6): δ 7.1–6.4 (m, 6 H, aromatic), 3.9 (s, 4 H, $C\mathit{H}_2C_6H_4Bu^t$), 2.20 (s, 6 H, *p*-Me in μ-$NC_6H_2Me_3$), 2.1 (s, 12 H, *o*-Me in μ-$NC_6H_2Me_3$), 1.60 (s, 12 H, *o*-Me in $Me_3H_2C_6NCH_2C_6H_4Bu^t$), 1.80 (s, 6 H, *p*-Me in $Me_3H_2C_6NCH_2C_6H_4Bu^t$) and 1.05 (s, 18 H, Bu^t).

Dibromo-1κBr,2κBr-*bis*(μ-2,4,6-*trimethylphenylimido*)*bis*(2,4,6-*trimethylphenylimido*)-1κN,2κN-(*trimethylphosphine*-1κP)-*dichromium*(V)–*Diethyl Ether* (1/1) **15**.—To a solution of compound **1** (0.2 g, 0.5 mmol) and PMe_3 (0.3 cm^3) in Et_2O (30 cm^3) at −78 °C was added MgEtBr (0.8 cm^3 of a 1.3 mol dm^{-3} solution in ether, *ca.* 1 mmol). After warming to room temperature the mixture was stirred for 3 h when it changed

Table 10 Fractional atomic coordinates (× 10^4) for compound **1** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cr	1 535(1)	7 447(1)	3 044(1)
Cl(1)	3 280(1)	7 685(1)	2 264(1)
Cl(2)	−921(1)	7 126(1)	2 369(1)
N(1)	1 490(2)	8 421(1)	3 626(1)
N(2)	2 203(2)	6 528(1)	3 682(1)
C(11)	1 755(3)	8 994(2)	4 355(2)
C(12)	2 604(3)	9 851(2)	4 338(2)
C(13)	2 889(3)	10 426(2)	5 072(2)
C(14)	2 346(3)	10 194(2)	5 808(2)
C(15)	1 506(3)	9 344(2)	5 803(2)
C(16)	1 198(3)	8 732(2)	5 099(2)
C(21)	2 686(3)	5 999(2)	4 430(2)
C(22)	3 935(3)	6 306(2)	5 123(2)
C(23)	4 352(3)	5 727(2)	5 852(2)
C(24)	3 577(3)	4 873(2)	5 921(2)
C(25)	2 357(3)	4 587(2)	5 220(2)
C(26)	1 884(3)	5 124(2)	4 469(2)
C(121)	3 197(3)	10 111(2)	3 546(2)
C(141)	2 670(3)	10 834(2)	6 600(2)
C(161)	322(3)	7 810(2)	5 129(2)
C(221)	4 789(3)	7 235(2)	5 077(2)
C(241)	4 063(3)	4 269(2)	6 731(2)
C(261)	592(3)	4 809(2)	3 713(2)

Table 11 Fractional atomic coordinates (× 10^4) for compound **1a** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cr(1)	3 493(2)	1 627(1)	5 699(2)
Cr(2)	8 434(2)	−3 337(1)	5 833(2)
Cl(11)	3 671(3)	2 438(3)	7 417(2)
Cl(12)	3 158(3)	2 666(3)	4 071(2)
Cl(21)	9 251(2)	−2 201(2)	7 411(2)
Cl(22)	7 970(3)	−2 635(3)	4 008(2)
N(11)	2 224(8)	745(8)	5 385(8)
N(12)	4 902(8)	970(7)	5 997(8)
N(21)	7 057(8)	−3 865(8)	5 874(8)
N(22)	9 567(8)	−4 292(7)	6 063(8)
C(11)	1 357(11)	−260(9)	5 134(10)
C(12)	5 876(9)	30(7)	6 192(9)
C(21)	6 116(10)	−4 723(8)	6 036(9)
C(22)	10 535(10)	−5 259(9)	6 373(10)
C(111)	63(11)	165(10)	5 217(10)
C(112)	2 013(11)	−1 166(11)	6 103(11)
C(113)	1 151(11)	−727(12)	3 849(10)
C(121)	6 155(9)	−510(7)	7 425(7)
C(122)	5 259(11)	−887(10)	5 166(11)
C(123)	7 127(10)	590(10)	6 115(10)
C(211)	4 767(11)	−4 439(10)	5 145(10)
C(212)	6 209(11)	−4 520(9)	7 397(9)
C(213)	6 616(12)	−5 928(11)	5 940(11)
C(221)	10 783(10)	−5 649(10)	7 666(10)
C(222)	9 964(13)	−6 258(10)	5 441(12)
C(223)	1 1827(11)	−4 789(10)	6 284(10)

Table 12 Fractional atomic coordinates (× 10^4) for compound **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr(11)	4 615(3)	4 339(3)	9 583(2)	C(24)	−2 802(30)	5 496(23)	5 009(15)
Cr(21)	94(4)	982(3)	4 674(2)	C(25)	−3 556(30)	5 533(22)	5 735(13)
Cl(11)	4 851(6)	4 403(4)	8 296(3)	C(26)	−3 375(23)	4 416(19)	6 210(12)
Cl(21)	1 646(6)	1 197(5)	3 702(3)	C(27)	−2 555(20)	3 306(17)	5 953(14)
N(12)	3 879(16)	3 275(11)	9 927(8)	C(21)	2 323(21)	−96(17)	6 031(11)
N(11)	3 633(14)	5 803(12)	9 915(8)	C(211)	3 710(22)	−981(19)	5 692(14)
N(22)	−920(18)	2 316(12)	4 897(9)	C(212)	1 889(25)	−558(19)	6 846(12)
N(21)	1 055(15)	−38(11)	5 475(9)	C(213)	2 560(22)	1 121(14)	6 000(14)
C(12)	3 238(21)	2 424(15)	10 330(11)	C(131)	3 417(19)	1 667(14)	8 963(10)
C(13)	3 017(18)	1 569(16)	9 829(11)	C(132)	3 758(23)	479(16)	8 572(12)
C(14)	2 389(22)	744(19)	10 183(11)	C(133)	2 120(25)	2 637(17)	8 480(12)
C(15)	2 003(22)	682(19)	10 935(11)	C(171)	3 253(19)	3 234(15)	11 639(11)
C(16)	2 242(19)	1 482(17)	11 433(10)	C(172)	4 271(22)	2 601(17)	12 303(10)
C(17)	2 839(18)	2 391(14)	11 129(11)	C(173)	1 795(21)	4 128(17)	11 958(12)
C(11)	2 199(19)	6 754(16)	9 797(11)	C(231)	−1 206(22)	4 449(16)	3 911(10)
C(111)	1 013(19)	6 131(16)	9 668(11)	C(232)	−2 063(20)	4 143(14)	3 301(11)
C(112)	2 360(22)	7 575(14)	9 045(12)	C(233)	−867(23)	5 624(18)	3 620(12)
C(113)	1 875(20)	7 430(17)	10 501(11)	C(271)	−2 397(24)	2 136(16)	6 466(11)
C(22)	−1 861(23)	3 352(19)	5 183(11)	C(272)	−3 969(26)	2 000(20)	6 636(15)
C(23)	−1 989(26)	4 443(19)	4 727(10)	C(273)	−1 635(27)	2 132(21)	7 238(12)

Table 13 Fractional atomic coordinates (× 10^4) for compound **7** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr(1)	249(1)	7 888(1)	899(1)	Cr(2)	2 275(1)	9 019(1)	3 424(1)
O(11)	179(1)	7 090(1)	1 216(1)	O(21)	2 479(1)	9 610(1)	3 871(1)
O(12)	−351(1)	8 107(1)	563(1)	O(22)	2 806(1)	8 852(1)	3 011(1)
N(11)	775(1)	7 806(1)	554(1)	N(21)	1 723(1)	9 357(1)	3 175(1)
N(12)	370(1)	8 511(1)	1 267(1)	N(22)	2 127(1)	8 265(1)	3 659(1)
C(111)	1 280(1)	7 853(2)	354(1)	C(211)	1 183(1)	9 389(2)	3 045(1)
C(112)	1 519(1)	7 230(2)	182(1)	C(212)	868(2)	9 985(2)	3 134(1)
C(113)	1 192(2)	6 561(2)	202(1)	C(213)	1 119(2)	10 594(2)	3 377(2)
C(114)	2 035(2)	7 260(2)	0(1)	C(214)	325(2)	9 996(2)	2 998(2)
C(115)	2 336(2)	7 869(2)	−18(1)	C(215)	77(2)	9 451(2)	2 776(1)
C(116)	2 915(2)	7 877(2)	−202(2)	C(216)	−524(2)	9 480(2)	2 632(2)
C(117)	2 091(2)	8 469(2)	137(1)	C(217)	397(2)	8 873(2)	2 688(1)
C(118)	1 568(1)	8 488(2)	321(1)	C(218)	940(1)	8 823(2)	2 815(1)
C(119)	1 325(2)	9 162(2)	483(1)	C(219)	1 277(1)	8 188(2)	2 708(1)
C(121)	659(1)	9 032(2)	1 476(1)	C(221)	1 882(1)	7 655(2)	3 791(1)
C(122)	1 204(1)	8 930(2)	1 625(1)	C(222)	1 350(1)	7 654(2)	3 977(1)
C(123)	1 487(1)	8 247(2)	1 552(1)	C(223)	1 018(2)	8 311(2)	4 009(1)
C(124)	1 466(2)	9 479(2)	1 834(1)	C(224)	1 143(2)	7 018(2)	4 123(1)
C(125)	1 217(2)	10 119(2)	1 892(1)	C(225)	1 435(2)	6 404(2)	4 089(1)
C(126)	1 525(2)	10 712(2)	2 125(2)	C(226)	1 197(2)	5 730(2)	4 260(1)
C(127)	687(2)	10 201(2)	1 743(2)	C(227)	1 956(2)	6 416(2)	3 898(1)
C(128)	397(2)	9 675(2)	1 535(1)	C(228)	2 187(1)	7 032(2)	3 750(1)
C(129)	−182(2)	9 773(2)	1 359(2)	C(229)	2 761(2)	7 027(2)	3 548(1)
C(131)	229(2)	6 971(2)	1 660(1)	C(231)	2 621(1)	9 461(2)	4 299(1)
C(132)	701(2)	6 608(2)	1 806(1)	C(232)	3 102(1)	9 082(2)	4 392(1)
C(133)	1 125(2)	6 371(2)	1 477(2)	C(233)	3 474(1)	8 821(2)	4 021(1)
C(134)	759(2)	6 493(2)	2 260(2)	C(234)	3 233(2)	8 961(2)	4 837(2)
C(135)	378(2)	6 705(2)	2 564(2)	C(235)	2 910(2)	9 192(2)	5 186(1)
C(136)	480(2)	6 609(3)	3 062(2)	C(236)	3 055(2)	9 033(2)	5 670(2)
C(137)	−89(2)	7 045(2)	2 412(2)	C(237)	2 445(2)	9 581(2)	5 075(1)
C(138)	−176(2)	7 184(2)	1 965(1)	C(238)	2 295(2)	9 720(2)	4 645(1)
C(139)	−685(2)	7 562(2)	1 802(1)	C(239)	1 784(2)	10 130(2)	4 535(1)
C(141)	−425(1)	7 920(2)	130(1)	C(241)	2 861(1)	9 026(2)	2 573(1)
C(142)	−573(2)	7 233(2)	25(1)	C(242)	2 890(1)	8 487(2)	2 257(1)
C(143)	−659(2)	6 712(2)	391(1)	C(243)	2 846(2)	7 743(2)	2 396(1)
C(144)	−659(2)	7 073(2)	−425(2)	C(244)	2 965(2)	8 695(3)	1 813(2)
C(145)	−607(2)	7 547(3)	−761(2)	C(245)	3 010(2)	9 367(3)	1 683(2)
C(146)	−697(2)	7 344(3)	−1 250(2)	C(246)	3 069(2)	9 533(3)	1 182(2)
C(147)	−462(2)	8 221(2)	−652(2)	C(247)	2 985(2)	9 879(3)	1 998(2)
C(148)	−375(1)	8 415(2)	−208(1)	C(248)	2 919(2)	9 721(2)	2 447(1)
C(149)	−244(2)	9 161(2)	−85(2)	C(249)	2 913(2)	10 297(2)	2 798(2)
The disordered diethyl ether molecule[a]							
O	5 000[b]	10 000[b]	0[b]	C(3)	4 774(7)	9 949(7)	769(6)
C(1)	5 120(4)	9 767(4)	345(3)	C(4)	4 423(13)	9 894(15)	549(11)
C(2)	4 677(4)	10 037(5)	532(4)	C(5)	4 848(5)	9 693(6)	943(4)

[a] The occupancies for atoms O, C(1)–C(5) are 0.5, 0.6, 0.41, 0.4, 0.14 and 0.45. [b] Invariant parameter.

from orange-brown to yellow-brown. Evaporation under vacuum, extraction of the residue with light petroleum (3 × 20 cm^3), filtration, concentration of the petroleum extracts to *ca.* 5 cm^3 and cooling (−20 °C) for 12 h gave brown crystals. Yield: 0.05 g, *ca.* 23%. NMR (C_6D_6): ^{1}H, δ 6.9–6.2 (m, 8 H, aromatic), 2.65 and 2.20 (s, 12 H and 6 H, *o*- and *p*-Me in μ-$NC_6H_2Me_3$), 2.4–2.2 (filled-in triplet, 9 H, PMe_3), 1.90 and 1.82 (s, 6 H and 12 H, *p*- and *o*-Me in $NC_6H_2Me_3$); ^{31}P-{^{1}H}, δ 3.22.

[1-(2,6-*Dimethylphenylimino*)-3-*methyl*-3-*phenylbutyl*](2-*methyl*-2-*phenylpropyl*)*bis*(2,4,6-*trimethylphenylimido*)*chromium*(VI) **16**.—To a solution of compound **12** in light petroleum (0.1 g, 0.19 mmol, in 10 cm^3) at room temperature was added a solution of 2,6-dimethylphenyl isocyanide (0.03 g, *ca.* 0.2 mmol). The colour changed immediately from yellow to orange. After stirring at room temperature for 0.5 h the solution was filtered, concentrated to *ca.* 2 cm^3 and cooled (−20 °C) for 12 h to give orange prisms. Yield: 0.11 g, *ca.* 85%. Mass spectrum (EI): *m*/*z* 715 (M^+), 596 ($M^+ - NC_6H_3Me_2$), 582 ($M^+ - CH_2NC_6H_3Me_2$) and 449 ($M^+ - Me_3H_2C_6NCH_2NC_6H_3Me_2$). IR (cm^{-1}): 1658, 1602 (C=N); 1588, 1285 (Cr=N); 851, 776 and 698 (aromatic). NMR (C_6D_6): ^{1}H, δ 7.48–6.6 (m, 17 H, aromatic), 3.52 (s, 2 H, $Me_2H_3C_6NCC\mathit{H}_2CMe_2Ph$), 3.22 (s, 2 H, $\mathit{C}H_2CMe_2Ph$), 2.44 (s, 12 H, *o*-Me of $NC_6H_2Me_3$), 2.1 (s, 6 H, $NC_6H_3Me_2$), 1.97 (s, 6 H, *p*-Me of $NC_6H_2Me_3$), 1.45 and 1.44 (s, 6 H each, $CH_2C\mathit{Me}_2Ph$); ^{13}C-{^{1}H}, δ 159.0 (*ipso*-C of $NC_6H_2Me_3$), 156.2 (*ipso*-C of $NC_6H_3Me_2$), 149.0, 143.0, 136.1, 135.2, 131.6, 129.4, 129.3, 126.7, 126.4, 125.5 (aromatic, not assigned), 60.9 ($\mathit{C}H_2CMe_2Ph$), 51.4 ($CN\mathit{C}H_2CMe_2Ph$), 42.9, 39.1 ($CH_2\mathit{C}Me_2Ph$), 32.6, 30.3 ($CH_2C\mathit{Me}_2Ph$), 21.9, 20.0 and 19.2 (aromatic Me).

(1-tert-*Butylimino*-3-*methyl*-3-*phenylbutyl*)(2-*methyl*-2-*phenylpropyl*)*bis*(2,4,6-*trimethylphenylimido*)*chromium*(VI) **17**.—This was prepared as for compound **16** from **12** (0.1 g, 0.19 mmol) and *tert*-butyl isocyanide (0.1 g, excess) in light petroleum (10 cm^3). Cooling at −78 °C for 48 h gave an orange oil which could not be crystallised. Yield: 0.1 g, *ca.* 80%. Mass spectrum (EI): *m*/*z* 667 (M^+) and 596 ($M^+ - NBu^t$). IR (cm^{-1}): 1683, 1602 (C=N); 1286, 1261 (Cr=N); 852, 802 and 764 (C–H aromatic). ^{1}H NMR (C_6D_6): δ 7.8–6.6 (m, 14 H, aromatic), 3.8 (s, 2 H, $Bu^tNCC\mathit{H}_2CMe_2Ph$), 3.2 (s, 2 H,

Table 14 Fractional atomic coordinates (× 10^4) for compound **14** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr	0(1)	4 527(1)	702(1)	C(15)	41(8)	8 676(6)	2 089(4)
Cl	−1 830(2)	3 866(1)	1 258(1)	C(16)	−383(7)	7 551(5)	1 464(4)
N(1)	300(5)	6 065(4)	546(3)	C(21)	2 147(6)	3 436(5)	1 214(4)
N(2)	1 508(4)	4 306(4)	1 413(3)	C(22)	1 364(6)	2 211(5)	1 041(4)
C(2)	2 111(9)	5 151(6)	2 342(5)	C(23)	1 976(7)	1 361(5)	784(4)
C(3)	2 060(7)	4 548(5)	3 166(4)	C(24)	3 321(7)	1 687(6)	685(5)
C(4)	3 121(7)	4 261(6)	3 604(4)	C(25)	4 078(6)	2 904(6)	885(4)
C(5)	3 138(9)	3 789(6)	4 399(5)	C(26)	3 550(6)	3 798(5)	1 128(4)
C(6)	1 984(10)	3 547(6)	4 757(5)	C(61)	1 798(16)	2 970(10)	5 668(6)
C(7)	891(10)	3 853(9)	4 287(6)	C(121)	3 228(6)	7 659(5)	1 149(5)
C(8)	898(9)	4 291(8)	3 485(5)	C(141)	1 774(7)	10 663(5)	3 066(5)
C(11)	695(7)	7 222(5)	1 167(4)	C(161)	−1 878(6)	6 767(5)	1 181(4)
C(12)	2 093(7)	7 999(5)	1 472(5)	C(221)	−95(6)	1 764(5)	1 139(5)
C(13)	2 401(7)	9 105(5)	2 089(5)	C(241)	3 932(7)	751(5)	373(5)
C(14)	1 405(8)	9 469(6)	2 409(5)	C(261)	4 407(6)	5 086(5)	1 192(4)
Disordered Bu^t group attached to C(61)[a]							
C(611)	803(11)	1 681(10)	5 366(7)	C(614)	672(26)	3 482(23)	6 173(14)
C(612)	3 300(13)	2 769(10)	6 059(7)	C(615)	2 566(27)	4 483(21)	6 551(17)
C(613)	2 566(38)	3 597(32)	6 317(26)	C(616)	1 616(45)	3 801(32)	6 387(27)
Disordered diethyl ether molecule							
O	6 565(20)	1 960(17)	4 758(27)	C(34)	6 639(17)	1 045(19)	3 905(18)
C(31)	6 868(33)	1 765(24)	5 807(15)	C(35)	7 089(26)	1 258(24)	2 882(28)
C(32)	6 072(39)	2 346(29)	4 867(22)	C(36)	7 248(33)	392(25)	2 734(24)
C(33)	6 223(15)	2 719(17)	3 303(13)				

[a] Occupancies for C(611)–C(616) are 0.9, 0.8, 0.4, 0.4, 0.25 and 0.25. [b] Occupancies for O and C(31)–C(36) are 1.0, 0.4, 0.4, 0.9, 0.9, 0.8 and 0.6.

Table 15 Fractional atomic coordinates (× 10^4) for compound **15** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr(1)	2016(1)	2947(1)	1617(1)	C(23)	1755(3)	4532(3)	3922(4)
Cr(2)	2134(1)	2007(1)	2610(1)	C(24)	1348(3)	4206(3)	3325(3)
Br(1)	2792(1)	3448(1)	1685(1)	C(25)	1409(2)	3702(3)	2863(3)
Br(2)	1585(1)	1899(1)	3311(1)	C(26)	2893(2)	3652(3)	3767(4)
P	2082(1)	770(1)	2623(1)	C(27)	1662(3)	5065(3)	4430(4)
N(1)	1548(2)	3360(2)	889(3)	C(28)	952(2)	3365(3)	2213(4)
N(2)	2015(2)	3004(2)	2549(3)	C(30)	3260(2)	1862(3)	3753(4)
N(3)	2751(2)	1910(2)	3214(3)	C(31)	3652(2)	1771(3)	3485(3)
N(4)	1984(2)	2029(2)	1526(3)	C(32)	4158(3)	1729(3)	4054(4)
C(1)	1478(3)	308(3)	2215(4)	C(33)	4289(3)	1753(3)	4858(4)
C(2)	2459(3)	341(3)	2189(4)	C(34)	3895(2)	1830(3)	5092(4)
C(3)	2374(3)	452(3)	3629(4)	C(35)	3382(2)	1883(3)	4557(4)
C(10)	1142(2)	3716(3)	300(4)	C(36)	3532(3)	1757(3)	2635(4)
C(11)	1005(2)	4378(3)	467(4)	C(37)	4840(3)	1718(4)	5439(5)
C(12)	593(3)	4709(3)	−121(4)	C(38)	2962(3)	1999(3)	4839(4)
C(13)	321(3)	4426(4)	−852(4)	C(40)	1767(3)	1593(3)	871(4)
C(14)	480(3)	3792(4)	−1020(4)	C(41)	1247(3)	1369(3)	632(4)
C(15)	885(3)	3432(3)	−452(4)	C(42)	1042(3)	916(3)	8(4)
C(16)	1330(3)	4727(3)	1236(4)	C(43)	1323(3)	665(4)	−385(4)
C(17)	−121(3)	4811(4)	−1505(4)	C(44)	1810(3)	910(3)	−159(4)
C(18)	1062(3)	2759(3)	−659(4)	C(45)	2046(3)	1373(3)	454(4)
C(20)	1919(2)	3507(3)	3008(3)	C(46)	912(3)	1687(3)	991(4)
C(21)	2348(2)	3835(3)	3609(3)	C(47)	1089(4)	160(4)	−1067(5)
C(22)	2249(2)	4339(3)	4043(3)	C(48)	2577(3)	1628(3)	651(4)
Disordered diethyl ether molecules							
O(1)	0*	1216(17)	2500*	C(101)	244(10)	1325(22)	3711(33)
O(2)	0*	1512(13)	7500*	C(202)	612(9)	1354(11)	6263(28)
C(102)	593(7)	1239(14)	4892(22)	C(201)	414(13)	1781(12)	7073(15)

* Invariant parameter; occupancies for O(1) and O(2) = 0.5.

$C\mathit{H}_2CMe_2Ph$), 2.5 (s, 12 H, *o*-Me), 2.12 (s, 6 H, *p*-Me), 1.72 (s, 6 H, $CH_2C\mathit{Me}_2Ph$), 1.43 (s, 6 H, $CH_2C\mathit{Me}_2Ph$) and 1.21 (s, 9 H, Bu^t). The air sensitivity of the sticky oil precluded microanalysis.

Bis[(μ-2,4,6-*trimethylphenylimido*)(2,4,6-*trimethylphenylimido*)(*trimethylphosphine*)*chromium*(IV)] **18**.—Compound **11** (0.7 g, 1.4 mmol) was dissolved in benzene (*ca.* 10 cm^3) and PMe_3 (0.5 cm^3, excess) added. The reaction mixture was heated without stirring at 70 °C for 10 h. The green crystals formed were isolated after removal of solvent with a cannula, washed with light petroleum (2 × 5 cm^3) and dried for *ca.* 30 s under

Table 16 Fractional atomic coordinates (× 10^4) for compound **18** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cr	7594(1)	565(1)	6838(1)
P	7618(1)	2681(1)	6079(1)
N(1)	7724(2)	−605(3)	6137(1)
N(2)	6510(2)	646(3)	7313(1)
C(11)	7842(2)	−1623(3)	5589(2)
C(12)	8801(2)	−2097(3)	5496(2)
C(13)	9693(2)	−1517(4)	5997(2)
C(14)	8895(3)	−3113(4)	4933(2)
C(15)	8097(3)	−3671(4)	4456(2)
C(16)	8242(3)	−4701(4)	3819(2)
C(17)	7171(3)	−3202(4)	4563(2)
C(18)	7022(2)	−2183(3)	5105(2)
C(19)	5995(2)	−1670(4)	5166(2)
C(21)	5499(2)	329(3)	7123(1)
C(22)	4792(2)	1504(3)	7077(2)
C(23)	5096(2)	3133(4)	7219(2)
C(24)	3804(2)	1130(4)	6887(2)
C(25)	3484(2)	−345(4)	6719(2)
C(26)	2399(2)	−662(4)	6473(2)
C(27)	4181(2)	−1486(4)	6780(2)
C(28)	5183(2)	−1205(3)	6986(2)
C(29)	5908(2)	−2478(4)	7074(2)
C(31)	7614(2)	4588(4)	6470(2)
C(32)	8681(3)	2716(4)	5618(2)
C(33)	6605(3)	2752(4)	5327(2)

vacuum. Yield: 0.2 g, *ca.* 40%. NMR (CD_2Cl_2): ^1H, δ 6.7 and 6.6 (s, 4 H each, $NC_6H_2Me_3$), 2.16 and 2.04 (s, 6 H each, *p*-Me), 2.11 and 1.99 (s, 12 H each, *o*-Me) and 1.12 (pseudo-triplet, 18 H, PMe_3); $^{31}P-\{^1H\}$, δ 19.0.

X-Ray Crystallography.—The X-ray data were collected at either 120 (**3**, **7**, **15** and **18**) or 150 K (**1**, **1a** and **14**) using a FAST TV area detector diffractometer with Mo-Kα radiation (λ = 0.710 69 Å), as previously described.[20] The structures were solved *via* applications of direct methods in SHELXS 86.[21] Refinement was by full-matrix least squares on F^2 using the program SHELXL 93.[22] The data for all of the compounds were corrected for absorption using the program DIFABS[23] with maximum and minimum correction factors quoted in Table 9. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions, except for the tertiary hydrogens of the mesityl groups of compounds **7** and **18**, and the methylene protons of **14**, which were experimentally located from the difference map.

The crystals of compound **3** were very small, platey, rhombohedrons. That used for data collection contained a twinned component, as initially found on indexing the reciprocal lattice. However, the cell adopted refined satisfactorily and a weak data set was obtained (25% observed reflections). The structure refined without any problems, however the final wR_2 value is relatively high (0.329 on all data) due to the high proportion of weak reflections. Compounds **7**, **14** and **15** additionally contain disordered diethyl ether molecules within the crystal structure. The carbon atoms of **7** and **14** have been modelled with fractionally occupied sites, as listed in Tables 13 and 14. A complete listing of crystal data and structure refinement details for compounds **1**, **1a**, **3**, **7**, **14**, **15** and **18** is given in Table 9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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