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Amido, imido and carbene complexes of chromium

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Abstract—Interaction of $CrCl_2$ with LiNHAr*, Ar* = 2,6-$Pr^i_2C_6H_3$, in thf gave the homoleptic amide Cr^{II} $(NHAr^*)_4$ $[Li(thf)]_2$ (**1**), which resisted further deprotonation by strong bases. Interaction of $Cr(Nmes)_2Cl_2$,mes = 2,4,6-$Me_3C_6H_2$, with LiNHmes gave the mesitylimido complex $[Cr^{VI}(Nmes)_3(NHmes)]Li(Et_2O)_2$ (**2**), which also resisted further deprotonation. Pentamethylcyclopentadienyl chromium(V) complexes $Cp^*Cr(NAr')X_2$, X = SC_6H_5, Ar′ = 2-$Pr^iC_6H_4$, (**3**); 4-Me-C_6H_4 (**4**); 2-$Bu^tC_6H_4$, (**5**), have been prepared by interaction of $(Cp^*CrBr_2)_2$ with Li(Ar′NSPh). Reaction of $(Cp^*CrBr_2)_2$ with mesitylnitrene, generated from $mesN_3$ *in situ*, gave the ionic Cr^{III} species $[Cp^*CrBr_3][mesNH_3]$, (**6**). (**3**) and (**5**) as well as the previously reported $Cp^*Cr(NBu^t)X_2$ can be transformed to the corresponding chlorides (**7**)–(**9**), by reaction with BCl_3. Finally, interactions of $Cr(mes)_2(thf)_3$ with the carbene $\overline{\text{CN(Pr}^i\text{)C}_2\text{Me}_2\text{N}}\text{Pr}^i$ = L gave $Cr(mes)_2L_2$ (**10**). The X-ray crystal structures of compounds (**1**)–(**3**), (**6**), (**7**), (**9**) and (**10**) have been determined. (**1**) is a molecular cluster with square planar Cr^{II} and with two $[Li(thf)]^+$ ions bridging the nitrogen atoms of pairs of amide ligands on opposite sides of the square. (**2**) has a distorted tetrahedral metal geometry with one $[Li(Et_2O)_2]^+$ ion bridging the nitrogen atoms of two imido ligands. (**3**) has a monomeric pseudo tetrahedral structure, as do (**7**) and (**9**) and the anion in (**6**). (**10**) has a *trans* square planar structure in which the Cr—C distances to the mesityl and carbene ligands are equal within error.

Keywords: amido; imido; carbene; chromium; crystal structure.

Although *t*-butylimido complexes of chromium have been known for some time [1], arylimido analogues have only recently been synthesised [2]. In the latter class there are no examples of homoleptic species, while cyclopentadienyl- and pentamethylcyclopentadienyl substituted compounds are rather rare and not well explored [2,3].

In this paper we describe attempts to prepare tetraarylimidochromates, analogous to the known $Cr(NBu^t)_4Li_2$ [4]. We also report on the synthesis of arylimido complexes of type $Cp^*Cr(NAr')(SPh)_2$, Ar′ = 4-MeC_6H_4, 2-$Pr^iC_6H_4$, 2-$Bu^tC_6H_4$, following the method used for the *t*-butylimido analogues [5] and their transformation to the chloride complexes.

Finally, the stable carbene $\overline{\text{CN(Pr}^i\text{)C}_2\text{Me}_2\text{N}}\text{Pr}^i$ = L has been used to obtain $Cr(mes)_2L_2$, mes = 2,4,6-trimethylphenyl, adducts. Analytical and physical data for new compounds are given in Table 1.

RESULTS AND DISCUSSION

Amido complexes

Attempts to prepare homoleptic arylimido complexes of chromium by interaction of known oxo-compounds, e.g. CrO_2Cl_2, $CrO_2(OSiPh_3)_2$, CrO_4^{2-} and CrO_3 and adducts thereof, with arylisocyanates, arylsilylanilines or phosphinimines under a variety of experimental conditions gave only intractable mixtures. Alternative routes were, therefore, inves-

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Table 1. Analytical and physical data for new compounds

Compound	Colour	M.p (°C)	Analysis (%)[a]		
			C	H	N
1 $Cr(HNC_6H_3Pr^i_2\text{-}2,6)_4Li_2(thf)_2$	Yellow–green	244 (decomp.)	73.2 (73.8)	9.7 (9.5)	6.3 (6.2)
2 $Cr(NC_6H_2Me_3\text{-}2,4,6)_3(NHC_6H_2Me_3\text{-}2,4,6)Li(Et_2O)_2$	Red–brown	190 (decomp.)	71.1 (71.7)	8.4 (8.8)	7.4 (7.6)
3 $Cr(\eta\text{-}C_5Me_5)(NC_6H_4Pr^i\text{-}2)(SC_6H_5)_2$	Green–brown	126–9	69.0 (69.1)	6.5 (6.7)	2.5 (2.6)
4 $Cr(\eta\text{-}C_5Me_5)(NC_6H_4Me\text{-}4)(SC_6H_5)_2$	Green–brown	123–5	68.5 (68.2)	6.1 (6.3)	2.5 (2.7)
5 $Cr(\eta\text{-}C_5Me_5)(NC_6H_4Bu^t\text{-}2)(SC_6H_5)_2$	Green–brown	124–7	69.2 (69.6)	6.5 (6.9)	2.5 (2.5)
7 $Cr(\eta\text{-}C_5Me_5)(NC_6H_4Pr^i\text{-}2)Cl_2$	Brown	221 (decomp.)	57.9 (58.3)	6.5 (6.6)	3.3 (3.6)
8 $Cr(\eta\text{-}C_5Me_5)(NC_6H_4Bu^t\text{-}2)Cl_2$	Brown	223 (decomp.)	58.8 (59.3)	6.5 (6.7)	3.4 (3.5)
9 $Cr(\eta\text{-}C_5Me_5)(NBu^t)Cl_2$	Yellow–green	148 (decomp.)	50.6 (51.0)	7.1 (7.3)	4.1 (4.2)
10 $Cr(mes)_2[\overline{CN(Pr^i)C(Me)C(Me)N}Pr^i]_2$	Yellow	180 (decomp.)	73.5 (73.8)	9.4 (9.7)	6.3 (6.2)

[a] Calculated values are in parentheses. Mass spectra data are given in Experimental section.

tigated; e.g. (i) synthesis of homoleptic amido complexes $\mathrm{Cr(NHAr)_4Li_x}$, $x = 1, 2$, Ar = substituted phenyl, which could provide an entry to imido complexes by subsequent deprotonation and/or oxidation and (ii) substitution of chloride in $\mathrm{(mesN)_2CrCl_2}$ [2a] by amido groups using lithium amide reagents, LiNHAr, followed by deprotonation of the resulting amido-imido species using a strong base.

Interaction of $\mathrm{CrCl_2(anh)}$ with four equivalents of $\mathrm{LiNH(2,6\text{-}Pr^i_2C_6H_3)}$ in thf gave after work-up the homoleptic paramagnetic tetraamido chromate, $\mathrm{Cr[NH(2,6\text{-}Pr^i_2C_6H_3)]_4[Li(thf)]_2}$ (**1**), as very air sensitive yellow–green crystals. (**1**) melts with decomposition and fails to give molecular ion in the mass spectrum. Its identity is deduced from analytical data and confirmed by X-ray diffraction methods. A diagram of the compound is shown in Fig. 1; selected bond lengths and angles are given in Table 2.

The compound is essentially a molecular cluster with the solvated lithium ions embedded in the $\mathrm{CrN_4}$ core. The chromium centre has the expected square planar geometry and $\mathrm{[Li(thf)]^+}$ units bridge pairs of amide nitrogen atoms on opposite sides of the square plane. The cluster has an overall conformation which is close to centrosymmetric. The Cr—N distances occur in pairs, with two mutually *trans* bonds [Cr—N(1), Cr—N(3)] slightly shorter [2.093(3), 2.097(3) Å] than the other two [Cr—N(2), Cr—N(4)–2.133(3), 2.123(3) Å]. These differences correlate with the Cr—N—C angles which are *ca* 140° for the shorter bonds and *ca* 120° for the longer ones (see Table 2). We presume that these features may be of steric origin. The $\mathrm{Li^+}$ ions are essentially three coordinate, with bonds to two nitrogen and the thf oxygen atoms and almost planar (angle sum around lithium atoms *ca* 355°). The structure is closely analogous to that of $\mathrm{Cr(NEt_2)_4(Lipy)_2}$ [6], which, however, shows no variation in the Cr—N bond lengths.

Attempts to oxidise (**1**) using controlled quantities of molecular oxygen, $\mathrm{Cp_2Fe^+}$, halogens or $\mathrm{PhICl_2}$ gave only intractable oils which could not be further characterised. Mixtures of products were also obtained when lithium anilides with less bulky aryls were used.

Interaction of $\mathrm{(mesN)_2CrCl_2}$ with 4 equiv. of LiNHmes in thf followed by work-up and crystallisation from ether afforded $\mathrm{[Cr(Nmes)_3(NHmes)][Li(Et_2O)_2]}$, (**2**), in moderate yields as red–brown air sensitive crystals. The identity of (**2**) was established from analytical and spectroscopic (NMR) data. The ^{1}H NMR spectrum at room temperature showed three equivalent imido and one amido groups. The molecule

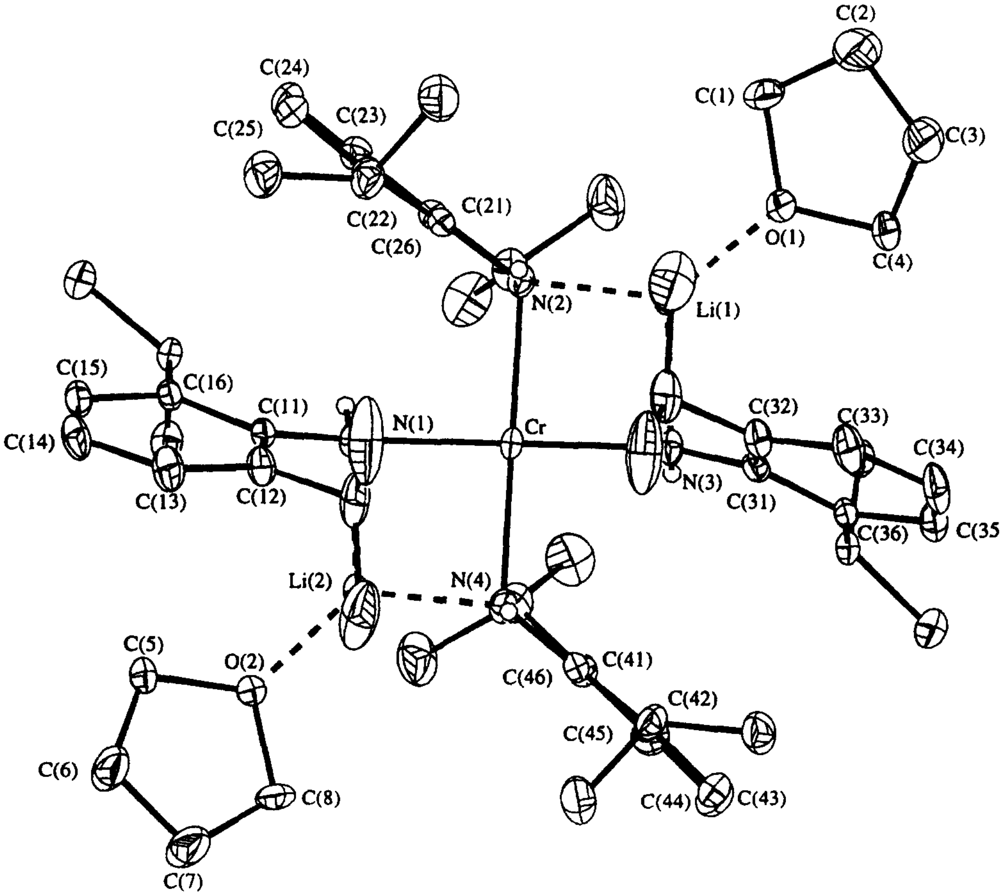


Fig. 1. The structure of $\mathrm{Cr[HN(2,6\text{-}Pr^i_2C_6H_3]_4Li_2(thf)_2}$ (**1**).

Table 2. Bond lengths (Å) and angles (°) for compound **1**

Cr—N(1)	2.097(3)	Cr—N(2)	2.133(3)
Cr—N(3)	2.093(3)	Cr—N(4)	2.123(3)
Li(1)—O(1)	1.931(7)	Li(2)—O(2)	1.894(7)
Li(1)—N(2)	1.964(7)	Li(2)—N(1)	2.009(8)
Li(1)—N(3)	1.986(8)	Li(2)—N(4)	1.962(7)
Li(1)—C(31)	2.725(8)	Li(2)—C(11)	2.642(8)
N(1)—C(11)	1.399(5)	N(2)—C(21)	1.405(5)
N(3)—C(31)	1.396(5)	N(4)—C(41)	1.397(5)
N(1)—Cr—N(2)	91.81(13)	N(1)—Cr—N(4)	88.26(13)
N(3)—Cr—N(1)	171.0(2)	N(3)—Cr—N(2)	88.17(13)
N(3)—Cr—N(4)	91.46(13)	N(4)—Cr—N(2)	178.0(2)
O(1)—Li(1)—N(2)	131.6(4)	O(1)—Li(1)—N(3)	125.3(4)
O(1)—Li(1)—C(31)	97.3(3)	N(2)—Li(1)—N(3)	96.2(3)
N(2)—Li(1)—C(31)	115.2(3)	N(3)—Li(1)—C(31)	29.5(2)
C(1)—O(1)—Li(1)	119.6(3)	C(4)—O(1)—Li(1)	128.5(3)
C(21)—N(2)—Li(1)	134.1(4)	C(31)—N(3)—Li(1)	106.1(3)
O(2)—Li(2)—N(1)	130.1(4)	O(2)—Li(2)—N(4)	129.8(4)
O(2)—Li(2)—C(11)	100.5(3)	N(1)—Li(2)—C(11)	31.4
N(4)—Li(2)—N(1)	95.4(3)	N(4)—Li(2)—C(11)	116.1(3)
C(5)—O(2)—Li(2)	128.5(3)	C(8)—O(2)—Li(2)	120.3(3)
C(11)—N(1)—Li(2)	100.1(3)	C(41)—N(4)—Li(2)	129.2(4)

was nonfluxional between −60 and +60°C in d^8 toluene.

The structure in the solid state was confirmed by X-ray diffraction study. The unit cell contains two independent molecules, one of which is shown in Fig. 2; selected bond lengths and angles for both are given in Table 3. The species is again a molecular cluster, with $[Li(Et_2O)_2]^+$ units strongly coordinated to, and symmetrically bridging, two imido nitrogens in each molecule. The CrN_4 geometry around the chromium atoms is distorted tetrahedral. In the two independent molecules the N—Cr—N angles involving the two imido nitrogens bridged by the lithium atoms are *ca* 103–104°; similar values are observed for the angles between the non-bridged imido/amido pairs. The Cr—N distances and Cr—N—C angles reflect the different characters and environments of the N atoms. Cr—N distances for the terminal imido function are 1.669(3) and 1.654(3) Å, for the bridged imido ligands, 1.711(3)–1.756(3) Å, and for the terminal amido 1.933(3) and 1.927(3) Å. The corresponding Cr—N—C angles are 165.6(3), 174.2(3)°; 132.0(3), 149.9(3)°; and 132.4(3), 126.8(3)°, respectively. Angles at the Li centres range from 80.6(3), 81.6(3) for N—Li—N, to 101.3(4), 106.7(3) for O—Li—O, and 113.5(4) to 134.1(4) for O—Li—N. Amido-imido compounds of type $[(mesN)_3Ta(NHmes)]Li_2(thf)_2$ have been reported by Wigley [7] and *t*-butyl analogues of the latter by our group [8].

(**2**) could not be further deprotonated even when using strongly basic alkyl lithiums, a behaviour also observed for both tantalum complexes mentioned above. This is to be contrasted with $Cr(NBu^t)_2(NHBu^t)_2$ which can be deprotonated to $Cr(NBu^t)_4Li_2$ [4], in analogy with $W(NBu^t)_4Li_2$ and $Mo(NBu^t)_4Li_2$ [9].

Pentamethylcyclopentadienyl complexes

Interaction of $(Cp^*CrBr_2)_2$ with 4 equiv. of Li(Ar′N–SPh) in thf followed by work-up and crystallisation from toluene or ether gave good yields of $Cp^*Cr(NAr')(SPh)_2$. Ar′ = $2\text{-}Pr^iC_6H_4$, (**3**); $4\text{-}MeC_6H_4$, (**4**); $2\text{-}Bu^tC_6H_4$, (**5**). Best yields are obtained for (**3**). (**3**)–(**5**) are air and thermally stable compounds, monomeric in the gas phase as evidenced by the observation of intense molecular ion under EI ionisation conditions. In view of their electron count ($17e^-$), their monomeric nature could be ascribed to steric factors, although the less sterically congested chloride (*vide infra*), is also monomeric. The structure of (**3**) in the solid state is established by X-ray diffraction study, and is shown in Fig. 3; selected bond lengths and angles are given in Table 4.

The metal configuration is pseudo-tetrahedral and the structure is closely analogous to that of the *tert*-butylimido analogue previously reported [5]. Bond lengths and angles in the coordination sphere of (**3**) show small differences compared with those in the *t*-butylimido compound. Thus the Cr—N distance in (**3**) is *ca* 0.04 Å longer than in the *t*-butylimido and the Cr—C distances range from 2.222(5) to 2.310(4) Å, whereas in the *t*-butylimido the range is smaller, at 2.244(5)–2.286(5) Å. The Cr—S distances are significantly different in both complexes, but the differ-

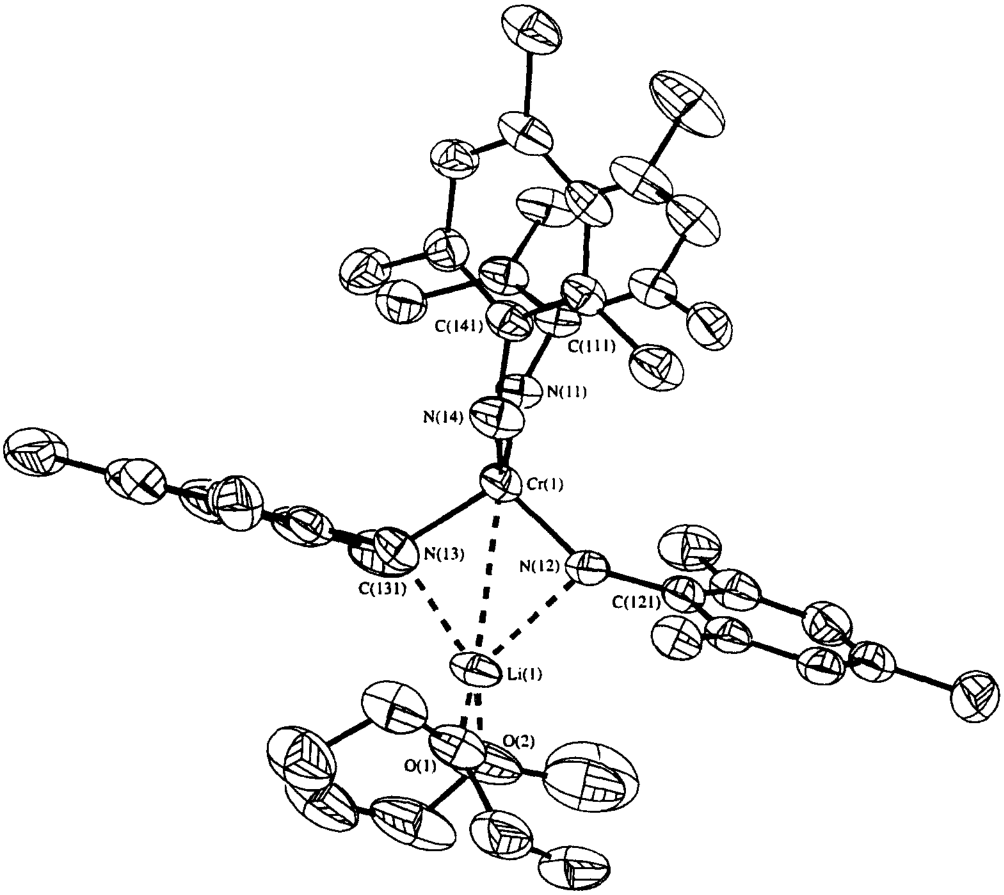


Fig. 2. The structure of $[\mathrm{Cr(Nmes)_3(NHmes)Li(Et_2O)_2}]$ (**2**).

ence in (**3**), 0.045 Å, is greater than that in the *t*-butylimido, 0.026 Å. We ascribe these differences to steric effects in the coordination sphere, arising from the substitution of the *t*-butylimido with the arylimido, and the different arrangements of the bend Cr—S—Ph functions.

As mentioned before [5] the mechanism of this reaction is not clear. GC/MS studies of the reaction mixtures showed the presence of $(\mathrm{PhS})_2$ and anilines in varying ratios. In order to exclude the possibility of intermediate formation of free nitrene Ar′N, which could add to a chromium(III) complex giving arylimido chromium species, we generated mesitylnitrene from $\mathrm{mesN_3}$ under photochemical or thermal conditions. In the former case we isolated after work-up low yields of $[\mathrm{Cp^*CrBr_3}]^-[\mathrm{mesNH_3}]^+$ (**6**) as intense blue crystalline material which was characterised by X-ray diffraction. No other products analogous to (**7**)–(**9**) (*vide infra*) could be detected. We therefore think that the most likely mechanism for the formation of (**3**)–(**5**) involves free radicals, a fact which could also account for the moderate yields observed. A diagram of the ion-pair (**6**) is shown in Fig. 4 and selected bond lengths and angles are given in Table 5. The anion geometry in this $\mathrm{Cr^{III}}$ complex may also be described as pseudo tetrahedral, with the Cp* ligand occupying one site. The Br—Cr—Br angles, lie in the range 93.48(5)–95.72(5)°. The Cr—C distances to the Cp* carbons show the variation found in the compounds discussed above, with values of 2.211(7)–2.248(7) Å. These differences presumably result from steric interactions in the coordination sphere. Cyclopentadienyl *t*-butylimido complexes of chromium have been prepared by interaction of $(\mathrm{Bu^tN})\mathrm{Cr^VCl_3(dme)}$ with TlCp [3]. This method does not work when TlCp* is used, the only product identified being $\mathrm{Cp^*_2}$. Arylimido complexes of type (ArN) $\mathrm{Cr^VCl_3L}_n$, L = donor, are not known and could not be prepared by chlorination of $\mathrm{(ArN)_2CrCl_2}$ as described for the *t*-butylimido analogues. Therefore, the transformation of sulfenanilide to arylimido complexes, although subjected to the limitations of stability of sulfenanilide starting materials is a useful entry to arylimido complexes of chromium(V).

Interaction of (**3**), (**5**) and the previously reported *t*-butylimido analogue with $\mathrm{BCl_3}$ results in substitution of the thiophenolato ligands with chlorides. The best solvent for this reaction is petroleum

Table 3. Bond lengths (Å) and angles (°) for compound **2**

Cr(1)—N(11)	1.669(3)	Cr(2)—N(21)	1.654(3)
Cr(1)—N(12)	1.711(3)	Cr(2)—N(23)	1.735(3)
Cr(1)—N(13)	1.756(3)	Cr(2)—N(22)	1.745(3)
Cr(1)—N(14)	1.933(4)	Cr(2)—N(24)	1.927(3)
Li(1)—O(1)	2.022(7)	Li(1)—O(2)	1.968(7)
Li(2)—O(3)	2.008(7)	Li(2)—O(4)	1.995(7)
Li(1)—N(12)	2.126(8)	Li(1)—N(13)	2.050(8)
Li(2)—N(22)	2.071(8)	Li(2)—N(23)	2.166(8)

N(11)—Cr(1)—N(12)	118.2(2)	N(21)—Cr(2)—N(22)	115.8(2)
N(11)—Cr(1)—N(13)	115.6(2)	N(21)—Cr(2)—N(23)	116.2(2)
N(11)—Cr(1)—N(14)	103.0(2)	N(21)—Cr(2)—N(24)	103.5(2)
N(12)—Cr(1)—N(13)	103.9(2)	N(22)—Cr(2)—N(23)	104.0(2)
N(12)—Cr(1)—N(14)	105.3(2)	N(22)—Cr(2)—N(24)	106.7(2)
N(13)—Cr(1)—N(14)	110.5(2)	N(23)—Cr(2)—N(24)	110.3(2)
O(1)—Li(1)—N(12)	113.5(4)	O(3)—Li(2)—N(22)	115.1(4)
O(1)—Li(1)—N(13)	118.9(4)	O(3)—Li(2)—N(23)	134.1(4)
O(2)—Li(1)—N(12)	116.9(4)	O(4)—Li(2)—N(22)	120.8(4)
O(2)—Li(1)—N(13)	117.9(4)	O(4)—Li(2)—N(23)	106.2(3)
O(2)—Li(1)—L(1)	106.7(3)	O(4)—Li(2)—O(3)	101.3(4)
N(13)—Li(1)—N(12)	81.6(3)	N(22)—Li(2)—N(23)	80.6(3)
Cr(1)—N(12)—Li(1)	86.5(2)	Cr(2)—N(22)—Li(2)	88.4(2)
Cr(1)—N(13)—Li(1)	87.8(3)	Cr(2)—N(23)—Li(2)	85.6(2)
C(111)—N(11)—Cr(1)	165.6(3)	C(211)—N(21)—Cr(2)	174.2(3)
C(121)—N(12)—Cr(1)	149.9(3)	C(221)—N(22)—Cr(2)	137.8(3)
C(131)—N(13)—Cr(1)	132.0(3)	C(231)—N(23)—Cr(2)	146.5(3)
C(141)—N(14)—Cr(1)	132.4(3)	C(241)—N(24)—Cr(2)	126.8(3)
C(121)—N(12)—Li(1)	121.6(3)	C(221)—N(22)—Li(2)	130.6(3)
C(131)—N(13)—Li(1)	136.6(3)	C(231)—N(23)—Li(2)	124.3(3)

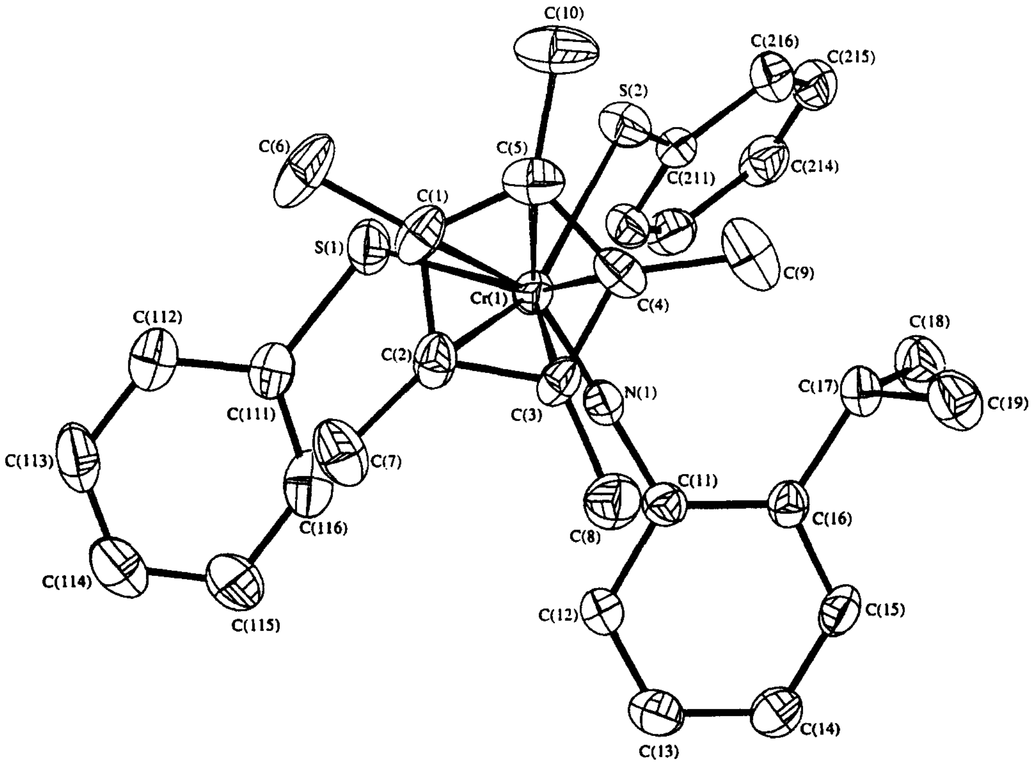


Fig. 3. The structure of Cp*Cr[N(2-Pr^{i}C$_6$H$_4$)](SC$_6$H$_5$)$_2$ (**3**).

Table 4. Bond lengths (Å) and angles (°) for compound **3**

Cr—N(1)	1.663(3)	Cr—C(3)	2.222(5)
Cr—C(4)	2.225(4)	Cr—C(2)	2.237(5)
Cr—S(2)	2.300(2)	Cr—C(5)	2.303(5)
Cr—C(1)	2.310(4)	Cr—S(1)	2.345(2)
S(1)—C(111)	1.773(5)	S(2)—C(211)	1.759(5)
N(1)—Cr—C(1)	146.6(2)	N(1)—Cr—C(2)	110.5(2)
N(1)—Cr—C(3)	89.8(2)	N(1)—Cr—C(4)	105.6(2)
N(1)—Cr—C(5)	142.0(2)	N(1)—Cr—S(1)	106.56(13)
N(1)—Cr—S(2)	103.53(12)	S(2)—Cr—S(1)	88.31(7)
C(1)—Cr—S(1)	87.79(12)	C(2)—Cr—S(1)	98.61(12)
C(3)—Cr—S(1)	135.73(11)	C(4)—Cr—S(1)	146.86(13)
C(5)—Cr—S(1)	111.23(13)	C(1)—Cr—S(2)	106.94(14)
C(2)—Cr—S(2)	141.39(13)	C(3)—Cr—S(2)	128.25(13)
C(4)—Cr—S(2)	91.95(13)	C(5)—Cr—S(2)	81.36(12)
C(111)—S(1)—Cr	107.5(2)	C(211)—S(2)—Cr	110.8(2)
C(11)—N(1)—Cr	165.9(3)		

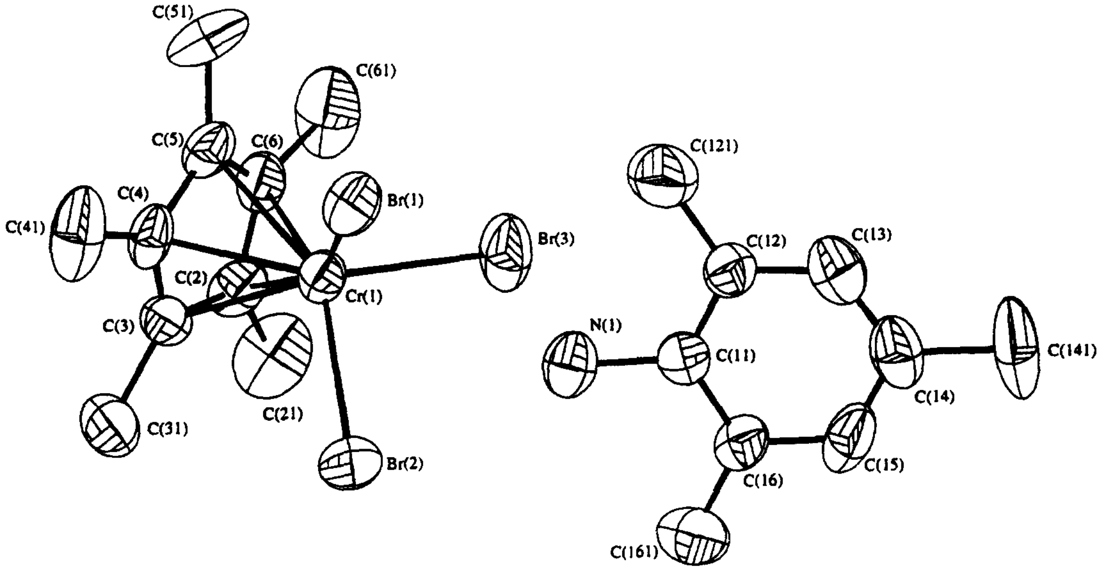


Fig. 4. The structure of $[Cp^*CrBr_3]^-[mesNH_3]^+$ (**6**).

especially when arylimido groups are present. Excess of BCl_3 gives $(Cp^*CrCl_2)_2$ as an impurity. The chlorides (**7**)–(**9**) are thermally unstable crystalline or microcrystalline compounds, which give low intensity molecular ions in the mass spectrum (EI ionisation). They were characterised by analytical methods.

Attempts to grow good single crystals of (**7**) were not very successful, the specimens generally depositing as small multiple clusters. However, it was possible, using one fragment in which a reasonably sized single crystal component was present, to obtain sufficient data in order to determine an approximate structure (see experimental), and confirm the proposed identity (Fig. 5). Good crystals of (**9**) were obtained from ether, and a full structural analysis was completed. A diagram of the structure of one of two independent molecules in the unit cell is given in Fig. 6, and selected bond lengths and angles for both are in Table 6. We presume that the reason for the monomeric nature of these $17e^-$ species is the steric crowding in the coordination sphere. In the dimeric Cp*Cr imido complexes previously described [2c], the formal metal coordination number for the related monomers would be lower than here. Detailed inspection of the structure of (**9**) shows close approach of the chlorine atoms and atoms C(13), C(14) of the Cp* ligand, $Cl(11)\cdots C(13) = 3.15$ Å, $Cl(12)\cdots C(14) = 3.16$ Å. These carbons also show the longest Cr—C(cp) distances in molecule 1. Similar features occur for molecule 2.

Table 5. Bond lengths (Å) and angles (°) for compound **6**

Cr(1)—C(2)	2.211(7)	Cr(1)—C(3)	2.248(7)
Cr(1)—C(4)	2.217(8)	Cr(1)—C(5)	2.231(8)
Cr(1)—C(6)	2.247(7)	Cr(1)—Br(1)	2.4963(14)
Cr(1)—Br(2)	2.486(2)	Cr(1)—Br(3)	2.498(2)
N(1)—C(11)	1.459(9)		
C(2)—Cr(1)—Br(1)	154.0(2)	C(3)—Cr(1)—Br(1)	127.4(3)
C(4)—Cr(1)—Br(1)	94.9(2)	C(5)—Cr(1)—Br(1)	93.9(2)
C(6)—Cr(1)—Br(1)	124.4(3)	C(2)—Cr(1)—Br(2)	103.9(2)
C(3)—Cr(1)—Br(2)	90.2(2)	C(4)—Cr(1)—Br(2)	111.8(3)
C(5)—Cr(1)—Br(2)	148.3(2)	C(6)—Cr(1)—Br(2)	139.8(3)
C(2)—Cr(1)—Br(3)	100.9(2)	C(3)—Cr(1)—Br(3)	136.3(2)
C(4)—Cr(1)—Br(3)	151.6(2)	C(5)—Cr(1)—Br(3)	115.9(3)
C(6)—Cr(1)—Br(3)	90.9(2)	Br(1)—Cr(1)—Br(3)	95.72(5)
Br(2)—Cr(1)—Br(1)	94.86(5)	Br(2)—Cr(1)—Br(3)	93.48(5)

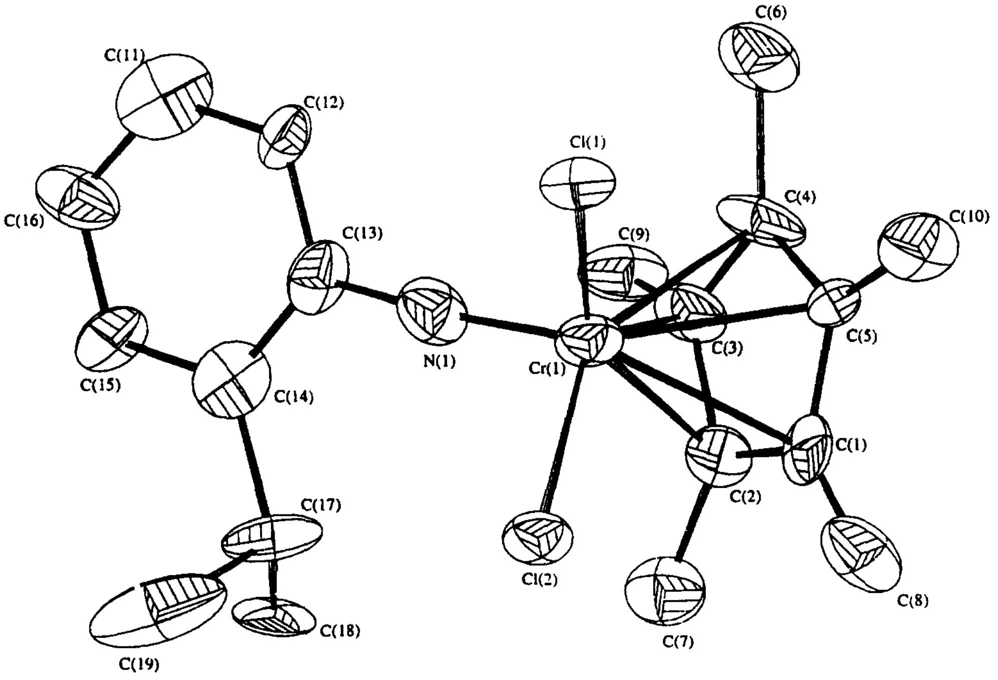
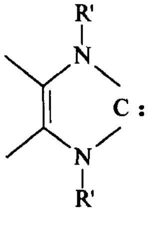


Fig. 5. The structure of $\mathrm{Cr(\eta\text{-}C_5Me_5)(NC_6H_4Pr^{i}\text{-}2)Cl_2}$ (7).

Carbene complex

Recently, Arduengo [10a] has used extensively stable 'carbenes' of type



where, R′ = bulky alkyl or aryl groups, for the preparation of carbene complexes of late transition metals e.g. Pd, Ni, Pt etc. Numerous examples of similar complexes with a variety of metals across the periodic table have now been reported [10b]. In order to directly compare the metal-'carbene' bond with other metal carbon bonds on the same metal centre we obtained $\mathrm{Cr(mes)_2L_2}$, (**10**), $\mathrm{L = \overline{CN(Pr^{i})C_2Me_2N}Pr^{i}}$, by interaction of L with $\mathrm{Cr(mes)_2(thf)_3}$, as an air sensitive, moderately thermally stable crystalline material. Its mass spectrum (EI ionisation) does not give any useful information for its identity, which was established by analytical methods. A single crystal X-

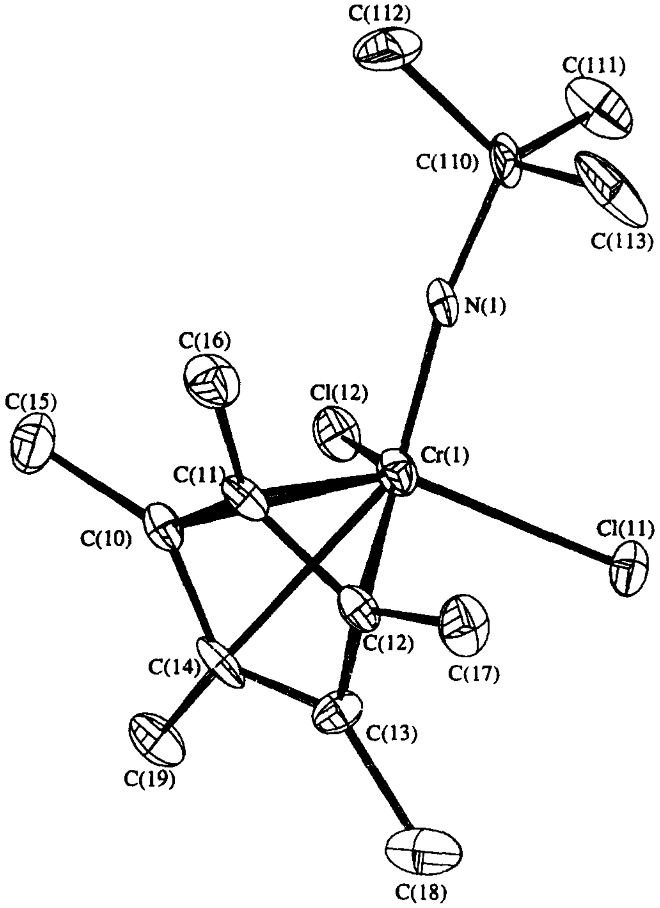


Fig. 6. The structure of $Cr(\eta\text{-}C_5Me_5)(NBu^t)Cl_2$ (**9**).

ray diffraction study revealed the structure in the solid state and is shown Fig. 7; important bond lengths and angles are given in Table 7.

The formally chromium(II) centre has the expected square planar geometry. The molecule lies on a two-fold rotation axis of the unit cell and has a 4-bladed propellor conformation. The dihedral angles made by the two independent ligand planes with the CrC_4 coordination plane are 63.5° (aryl) and 55.2° (carbene). The two independent aryl and carbene Cr—C distances are equal within experimental limits and this suggests that the 'carbene' ligand acts as a strong σ-donor; π-back donation is minimal. The ring geometry around the carbene carbon [C—N distances, N—C—N angle are 1.360(4) Å and 103.6(3)°, respectively] is very similar to that found for L_2M systems where no form of M—L π-bonding is proposed [10a].

EXPERIMENTAL

Analyses were done by Imperial College microanalytical laboratory. All operations were carried out under purified N_2 or Ar, under vacuum or in a Vacuum Atmospheres box. General techniques have been described [11] NMR data were obtained on a JEOL-EX-270 spectrometer at 270 MHz (^1H) and referenced to residual H impurity in the solvent (δ7.15, C_6D_6). Mass spectra were taken on a VG Autospec spectrometer. Observed isotopic envelopes were compared with calculated ones to good agreement. Commercial chemicals were from Aldrich and Avocado Chemicals. The petroleum used had a b.p. 40–60°C. Literature procedures were followed for $Cr(Nmes)_2Cl_2$ [2a], $(Cp^*CrBr_2)_2$ [12], $Cr(mes)_2(thf)_3$ [13], 1,3-di-isopropyl-4,5-dimethylimidazol-2-ylidene [14], $Li(o\text{-}Pr^iC_6H_4NSPh)$ and $Li(p\text{-}MeC_6H_4NSPh)$ [15].

The compound $o\text{-}Bu^tC_6H_4N(H)SPh$ is readily made in multigram quantities as follows: To a mechanically stirred solution of $o\text{-}Bu^tC_6H_4NH_2$ (7.5 g, 0.05 mol) and Et_3N (7 cm^3, 0.05 mol) in Et_2O (200 cm^3) at −40°C was added dropwise, in air, a solution of PhSCl (7.2 g, 0.05 mol) in Et_2O (100 cm^3). After 30 min the solution was allowed to warm to room temperature, stirred for a further 2 h, and the solvent was removed under vacuum. The residue was extracted with light petroleum, the extracts filtered and evaporated under reduced pressure, to give the product as an orange oil which was used without further purification. Yield: *ca* 10 g, 80%. Mass spectrum (EI):

Table 6. Bond lengths (Å) and angles (°) for compound **9**

Cr(1)—C(10)	2.229(7)	Cr(2)—C(20)	2.212(6)
Cr(1)—C(11)	2.218(7)	Cr(2)—C(21)	2.224(6)
Cr(1)—C(12)	2.223(6)	Cr(2)—C(22)	2.215(7)
Cr(1)—C(13)	2.351(7)	Cr(2)—C(23)	2.354(7)
Cr(1)—C(14)	2.343(7)	Cr(2)—C(24)	2.338(5)
Cr(1)—N(1)	1.623(6)	Cr(2)—N(2)	1.613(5)
Cr(1)—Cl(11)	2.295(2)	Cr(2)—Cl(21)	2.277(2)
Cr(1)—Cl(12)	2.273(2)	Cr(2)—Cl(22)	2.272(2)
N(1)—Cr(1)—C(10)	112.5(3)	N(2)—Cr(2)—C(20)	110.3(3)
N(1)—Cr(1)—C(11)	92.9(3)	N(2)—Cr(2)—C(21)	93.4(3)
N(1)—Cr(1)—C(12)	109.9(3)	N(2)—Cr(2)—C(22)	112.2(3)
N(1)—Cr(1)—C(13)	146.3(3)	N(2)—Cr(2)—C(23)	148.9(3)
N(1)—Cr(1)—C(14)	148.7(3)	N(2)—Cr(2)—C(24)	146.3(3)
N(1)—Cr(1)—Cl(11)	99.1(2)	N(2)—Cr(2)—Cl(21)	98.4(2)
N(1)—Cr(1)—Cl(12)	99.6(2)	N(2)—Cr(2)—Cl(22)	101.2(2)
C(110)—N(1)—Cr(1)	171.7(5)	C(210)—N(2)—Cr(2)	172.7(5)
C(10)—Cr(1)—Cl(11)	145.2(2)	C(20)—Cr(2)—Cl(21)	146.6(2)
C(10)—Cr(1)—Cl(12)	91.5(2)	C(20)—Cr(2)—Cl(22)	93.8(2)
C(11)—Cr(1)—Cl(11)	130.5(2)	C(21)—Cr(2)—Cl(21)	127.4(2)
C(11)—Cr(1)—Cl(12)	127.5(2)	C(21)—Cr(2)—Cl(22)	130.4(2)
C(12)—Cr(1)—Cl(11)	93.7(2)	C(22)—Cr(2)—Cl(21)	91.3(2)
C(12)—Cr(1)—Cl(12)	146.3(2)	C(22)—Cr(2)—Cl(22)	143.8(2)
Cl(11)—Cr(1)—C(13)	85.3(2)	Cl(21)—Cr(2)—C(23)	86.4(2)
Cl(12)—Cr(1)—C(13)	113.0(2)	Cl(22)—Cr(2)—C(23)	108.7(2)
Cl(11)—Cr(1)—C(14)	110.5(2)	Cl(21)—Cr(2)—C(24)	114.0(2)
Cl(12)—Cr(1)—C(14)	86.3(2)	Cl(22)—Cr(2)—C(24)	84.3(2)
Cl(12)—Cr(1)—Cl(11)	97.53(8)	Cl(22)—Cr(2)—Cl(21)	97.25(8)

Table 7. Bond lengths (Å) and angles (°) for compound **10**

Cr(1)—C(1)	2.175(3)	Cr—C(11)	2.178(3)
N(1)—C(1)	1.360(4)	N(1)—C(3)	1.403(4)
N(2)—C(1)	1.359(4)	N(2)—C(2)	1.388(4)
C(2)—C(3)	1.342(5)		
C(18)—C(11)—Cr	122.9(2)	C(12)—C(11)—Cr	122.5(3)
C(1)—Cr—C(11)	89.67(11)	N(1)—C(1)—Cr	128.4(2)
N(2)—C(1)—Cr	128.0(2)	N(2)—C(1)—N(1)	103.6(3)
C(1)—N(1)—C(3)	111.1(3)	C(1)—N(1)—C(6)	121.1(3)
C(3)—N(1)—C(6)	127.8(3)	C(1)—N(2)—C(2)	112.2(3)
C(1)—N(2)—C(7)	121.6(3)	C(2)—N(2)—C(7)	126.1(3)

m/z 257 (M^+), 148 (M^+-PhS). NMR(C_6D_6) : ^1H, δ1.1 (s, 9H, Bu^t), 5.3 (s, 1H, NH), 6.8–7.7 (m, 4H, aromatic).

LiNHmes was prepared by interaction of freshly distilled aniline with $LiBu^n$ in light petroleum.

Dilithiumtetrakis(2,6-*diisopropylphenylamido*)*chromium*(*II*)-*bis-tetrahydrofuran* (**1**)

To a suspension of $CrCl_2$ in thf (0.31 g, 2.5 mmol in 30 cm^3) at −78°C was added a solution of $LiNH(C_6H_3Pr^i_2$-2,6) in the same solvent (1.83 g, 10 mmol in 30 cm^3). The yellow–brown reaction mixture was allowed to reach room temperature and was stirred for 12 h. Removal of volatiles under vacuum, extraction of the residue with petroleum (3 × 50 cm^3), filtration, concentration of filtrates until crystallisation started and cooling (−20°C) gave yellow–green crystals. Yield : 1.60 g (70%).

Lithium[*tris*(2,4,6-*trimethylphenylimido*)](2,4,6-*trimethylphenylamido*)*chromate*(*VI*)*bis*(*diethyletherate*) (**2**)

To a solution of $Cr(Nmes)_2Cl_2$ in thf (0.39 g, 1 mmol in 20 cm^3) at −78°C was added a solution of $LiNH(C_6H_2Me_3$-2,4,6) in the same solvent (0.73 g, 4 mmol in 20 cm^3). The red–brown solution was allowed

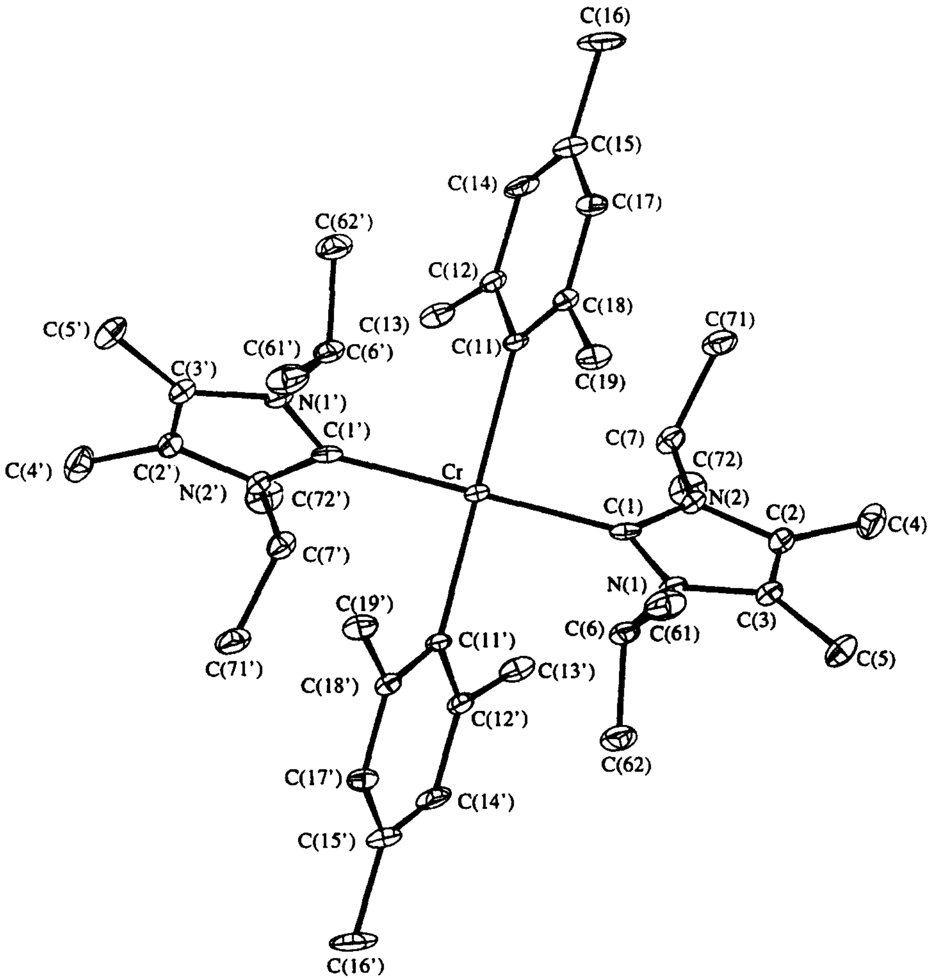


Fig. 7. The structure of $Crmes_2[\overline{CN(Pr^i)C(Me)C(Me)NPr^i}]_2$ (**10**).

to reach room temperature and stirred for 15 h. Removal of volatiles *in vacuo*, washing of the oily residue with cold petroleum (3×10 cm^3), extraction in toluene, filtration and evaporation to dryness gave a red–brown solid. This was dissolved in ether, concentration of this solution to *ca* 20 cm^3, addition of petroleum and cooling (-20°C) gave red–brown crystals. Yield: 0.40 g (*ca* 55%). ^1H NMR (C_6D_6): δ6.92 (s, 2*H*, $C_6H_2Me_3NH$), 6.80 (s, 6H, $C_6H_2Me_3N$), 6.05 (s, br, 1H, $C_6H_2Me_3NH$), 3.22 [q, 8H, $(CH_3CH_2)_2O$], 2.62 [s, 3H, $C_6H_2(p\text{-}Me)Me_2NH$], 2.38 (s, 27H, C_6H_2, Me_2N), 2.25 [s, 6H, $C_6H_2(o\text{-}Me_2)MeNH$], 1.00 [t, 12H, $(CH_3CH_2)_2O$].

(*η-Pentamethylcyclopentadienyl*)[*N-(2-isopropylphenyl)imido*]*bis*(*thiophenolato*)*chromium*(*V*) (**3**)

To a suspension of $(Cp^*CrBr_2)_2$ (0.35 g, 0.5 mmol) in toluene (30 cm^3) at -78°C was added dropwise with stirring a suspension of $Li(o\text{-}Pr^iC_6H_4NSPh)$ (0.52 g, 20.5 mmol) in toluene (30 cm^3). After warming to room temperature the mixture was stirred for 12 h. Filtration through Celite, followed by removal of the volatiles *in vacuo* extraction into Et_2O (3×20 cm^3), filtration, concentration to *ca* 15 cm^3 and cooling to -20°C gave the product as a dark green–brown micro-crystalline material. Yield: 0.32 g, 59%. Mass spectrum (EI): *m/z* 538 (M^+), 429 (M^+-SPh), 296 [M^+-(SPh-$Pr^iC_6H_4N$)].

(*η-Pentamethylcyclopentadienyl*)[*N-(4-methylphenyl) imido*]*bis*(*thiophenolato*)*chromium*(*V*) (**4**)

As for (**3**) but using $(Cp^*CrBr_2)_2$ (0.35 g, 0.5 mmol) and $Li(4\text{-}MeC_6H_4NSPh)$ (0.46 g, 2.05 mmol) to give the product as a green–brown powder. Yield: 0.2 g, 30%. Mass spectrum (EI): *m/z* 510 (M^+), 401 (M^+-SPh), 292 [M^+-(2-SPh).

*(η-Pentamethylcyclopentadienyl)[N-(2-*tert*-butylphenyl)imido]bis(thiophenolato)chromium(V)* **(5)**

To a solution of $(Cp^*CrBr_2)_2$ (0.35 g, 0.5 mmol) in thf (30 cm^3) at -78°C was added dropwise with stirring a solution of $Li(o\text{-}Bu^tC_6H_4NSPh)$ (0.54 g, 2.05 mmol) in thf (30 cm^3). After warming to room temperature the mixture was stirred for 12 h. Removal of the volatiles under vacuum followed by extraction of the residue into petroleum (4×30 cm^3), filtration through Celite, concentration to *ca* 20 cm^3 and cooling to -20°C gave the product as a green–brown solid. Yield: 0.25 g, 45%. Mass spectrum (FAB): *m/z* 552 (M^+), 443 (M^+-SPh), 334 [M^+-(2xSPh)].

Interaction of (Cp^*CrBr_2) *mesitylnitrene generated* in situ

A solution of $(Cp^*CrBr_2)_2$ (0.1 g, 0.15 mmol) and $mesN_3$ (0.08 g, 0.5 mmol) in thf (10 cm^3) was photolysed in a quartz apparatus (medium pressure Hg lamp, 125 W), at room temperature for 12 h. Removal of volatiles *in vacuo* and crystallisation of residue from toluene : petroleum gave low yields of **(6)**.

(η-Pentamethylcyclopentadienyl)[N-(2-isopropylphenyl)imido]dichlorochromium(V) **(7)**

To a solution of **(3)** (0.16 g, 0.3 mmol) in petroleum (30 cm^3) at 0°C was added a solution of BCl_3 in heptane (0.3 cm^3 of 1 molar solution, 0.3 mmol). The colour of the reaction mixture changed from brown to green–brown. After warming to room temperature over 1 h and stirring for 2 h, the volatiles were removed under vacuum. The residue was washed with hot petroleum (60×80°C) (5×20 cm^3) and extracted into toluene (2×20 cm^3). Filtration and evaporation to dryness gave the product as green–brown microcrystalline powder. Yield: *ca* 0.09 g, 75%. Mass spectrum (EI) : *m/z* 390 (M^+), 355 (M^+-Cl), 319 (M^+-2Cl).

*(η-Pentamethylcyclopentadienyl)[N-(2-*tert*-butylphenyl)imido]dichlorochromium(V)* **(8)**

This was prepared following the same method as for **(7)** using **(5)** (0.15 g, 0.27 mmol) and BCl_3 (0.3 cm^3 of 1 molar solution, 0.3 mmol) to give the product as green–brown microcrystalline powder. Yield: *ca* 0.08 g, 73%. Mass spectrum (EI) : *m/z* 404 (M^+), 369 (M^+-Cl), 257 (M^+-$Bu^tC_6H_4N$).

*(η-Pentamethylcyclopentadienyl)(*tert*-butylimido) dichlorochromium(V)* **(9)**

To a solution of $Cp^*Cr(NBu^t)(SC_6H_5)_2$ in petroleum (0.2 g, 0.42 mmol in 10 mm^3) at 0°C was added dropwise a solution of BCl_3 in heptane (0.45 cm^3 of 1 molar solution, 0.45 mmol). The colour of the reaction mixture changed from red–brown to yellow–brown. After warming to room temperature over 1 h and stirring for 0.5 h, the volatiles were removed under reduced pressure. The residue was extracted in petroleum (3×30 cm^3) or ether (2×10 cm^3) the extracts filtered, concentrated until crystallisation began and cooled (-20°C) for 12 h to afford yellow–green crystals. Yield : 0.05 g, *ca* 40%. Mass spectrum (EI) : *m/z* 328 (M^+) ; 293 $(M\text{-}Cl)^+$; 272 (M-isobutylene)$^+$; 257 $(M\text{-}Bu^tN)^+$.

Bis(2,4,6-trimethylphenyl)bis(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)chromium(II) **(10)**

To a solution of $Cr(mes)_2(thf)_3$ in thf (0.5 g, 1 mmol in 30 cm_3) at -78°C was added a solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene in the same solvent (0.36 g, 2 mmol in 40 cm^3). The colour of the solution changed immediately from purple to yellow. The mixture was allowed to reach room temperature and stirred for 1 h. Evaporation of volatiles under vacuum, extraction of the residue with petroleum (3×30 cm^3), filtration, concentration of extracts until crystallisation began and cooling (-20°C) gave yellow crystals. Yield: 0.38 g, *ca* 60%.

X-ray crystallography

X-ray data for compounds **(1)**–**(3)**, **(6)**, **(7)**, **(9)** and **(10)** were collected at low temperature using a FAST TV area-detector diffractometer with Mo-$K\alpha$ radiation ($\lambda = 0.71069$ Å), as previously described [16]. Crystal data and other experimental details are given in Table 8.

The structures were solved using direct methods in the program SHELXS-86 [17] and refined by full matrix least squares on a Fo^2 using SHELX93 [18]. Corrections for absorption were applied in most cases using the DIFABS program [19] (see Table 8).

For **(7)** it proved impossible to obtain an acceptable single crystal specimen, and some data were collected using a multiply-twinned specimen which showed one region of apparent single crystal characteristics, and which gave a diffraction pattern with some discernible maxima. By storing the frame data from the diffractometer and working with a set of 'found' reflections and our manual procedures for decoding twin diffraction patterns, we were able to identify the unit cell and orientation matrix, and extract the relevant intensity data. The structure was solved and refined, but the resulting quality is affected by deficiencies in the data due to arbitrary super-positions of reflections from other twin components. The results are included in Table 8, but no data have been deposited, nor geometry parameters reported in this paper.

Acknowledgements—We thank EPSRC for partial support

Table 8. Crystal data and structure refinement details for compounds (**1**)–(**3**), (**6**), (**7**), (**9**) and (**10**)

	(**1**)	(**2**)	(**3**)	(**6**)	(**7**)	(**9**)	(**10**)
Formula	$C_{56}H_{50}CrLi_2N_4O_2$	$C_{44}H_{65}CrLiN_4O_2$	$C_{31}H_{36}CrNS_2$	$C_{19}H_{29}Br_3CrN$	$C_{19}H_{26}Cl_2CrN$	$C_{14}H_{24}Cl_2CrN$	$C_{46}H_{62}CrN_4$
M_r	876.88	740.94	538.73	563.16	391.31	329.24	361.50
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2(1)/a$	$P2(1)/n$	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$	$P2(1)/a$	$C2/c$
a (Å)	17.555(4)	21.427	13.741(5)	11.4170(10)	6.933(3)	8.786(4)	20.754
b (Å)	16.272(11)	17.711	9.320(8)	12.408(2)	9.643(8)	27.047(9)	13.350
c (Å)	19.5170(10)	24.194	21.186(9)	17.184(5)	15.31(2)	14.590(9)	16.688
α (°)					81.75(10)		
β (°)	98.65(2)	108.29	95.88(3)	107.834(13)	86.64(10)	105.02(4)	108.23
γ (°)					78.88(4)		
U (Å^3)	5512	8717.6	2699(3)	2317.3(8)	993(2)	3349(3)	4391.5
Z	4	8	4	4	2	8	4
D_c/Mgm^{-3}	1.057	1.129	1.326	1.614	1.308	1.306	1.094
F(000)	1840	3200	1140	116	410	1384	1560
Crystal size/mm	0.27 × 0.24 × 0.15	0.54 × 0.27 × 0.21	0.22 × 0.2 × 0.18	0.13 × 0.36 × 0.2	0.18 × 0.25 × 0.10	0.21 × 0.18 × 0.24	0.39 × 0.18 × 0.18
μ(Mo-K$_\alpha$)/mm^{-1}	0.241	0.300	0.599	5.653	0.844	0.967	0.286
Collection temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Reflections collected	22376	34898	10240	8620	3398	12601	8819
Independent reflections (R_{int})	8273 (0.0883)	12976 (0.0628)	4021 (0.0650)	3434 (0.0786)	2407 (0.1222)	4985 (0.1170)	3295 (0.1547)
Maximum, minimum correction factors	0.789, 1.122	0.824, 1.078	0.875, 1.140	0.672, 1.218		0.822, 1.045	
Data, restraints, parameters	8273, 0, 698	12976, 0, 973	4021, 0, 323	3434, 0, 226	2407, 24, 188	4976, 0, 341	3292, 0, 240
Goodness of fit, F^2	0.854	0.593	0.759	0.440	1.031	0.438	0.891
Final $R1$, $wR2$							
[$I > 2\sigma(I)$]	0.0644, 0.1658	0.0528, 0.1225	0.0422, 0.0864	0.0309, 0.0543	0.1700, 0.4594	0.0410, 0.0669	0.0612, 0.1476
(all data)	0.1082, 0.1759	0.1077, 0.1613	0.0913, 0.0925	0.1225, 0.0691	0.2414, 0.4778	0.1696, 0.1591	0.0911, 0.1677
Largest difference peak and hole (eÅ^{-3})	0.856, −0.479	0.520, −0.338	0.426, −0.304	0.348, −0.278	1.390, −0.643	0.301, −0.276	0.637, −0.455

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