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Pentamethylcyclopentadienyl imido compounds of chromium †

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The interaction of the pentamethylcyclopentadienylchromium(III) complex $[CrBr(\mu\text{-}Br)(\eta\text{-}C_5Me_5)]_2$ with alkyl- and aryl-lithium amido compounds, LiNHR, gave products whose nature depends on the reactants and on reaction conditions. For the aryl (R) $2,6\text{-}Pr^i{}_2C_6H_3$ both $[(\eta\text{-}C_5Me_5)Cr(\mu\text{-}NR)(\mu\text{-}NHR)(\mu\text{-}Br)Cr(\eta\text{-}C_5Me_5)]$ **1** and $[Cr(\eta\text{-}C_5Me_5)(\mu\text{-}NR)]_2$ **2** were obtained, whereas $LiNH(C_6H_{11})$ gave $[CrBr(\eta\text{-}C_5Me_5)(\mu\text{-}NC_6H_{11})]_2$ **5**. Use of R = $2,4,6\text{-}Bu^t{}_3C_6H_2$ gave $[Cr(\eta\text{-}C_5Me_5)(\mu\text{-}NR)]_2$ **3**. The unisolable chromium(III) intermediate can be trapped by interaction of $[CrBr_2(\eta\text{-}C_5Me_5)]_2$ and LiNHR (R = $2,6\text{-}Pr^i{}_2C_6H_3$) in the presence of diphenylacetylene to give $Cr(\eta\text{-}C_5Me_5)(NR)(PhC{\equiv}CPh)$ **6**. A comparable reaction but using $LiNHBu^t$ gave only the dimer $(\eta\text{-}C_5Me_5)BrCr(\mu\text{-}NHBu^t)_2Cr(NBu^t)(NHBu^t)$ **7**. Trapping by various other ligands failed but the interaction in the presence of 2,6-xylyl isocyanide gave a chromium(III) chelate **8** of a quinoline diamide where an isopropyl group has been removed from the original $C_6H_3Pr^i{}_2$ moiety. The crystal structures of **1**–**7** and **8** have been determined. The triply bridged complex **1**, which has a confacial bitetrahedral structure (assuming C_5Me_5 takes one co-ordination site) has a $Cr^{III}\cdots Cr^{III}$ distance of 2.649(5) Å (average over two molecules), whilst the doubly bridged $(Cr^{III})_2$ complexes **2** and **3**, each of which is centrosymmetric, have $Cr^{III}\cdots Cr^{III}$ distances of 2.591(1) and 2.564(1) Å. In compound **5**, also showing centrosymmetric bis(imido) bridging, the $Cr^{IV}\cdots Cr^{IV}$ distance is 2.974(5) Å. In **6** the acetylene is symmetrically bihapto and the imido function bonds in a linear manner. Compound **7** has dissimilar chromium atoms, formally assigned as Cr^{III}, Cr^{IV}, with bridging amido functions. The $Cr\cdots Cr$ distance is 2.936(2) Å.

Although both alkyl- and aryl-imido compounds of chromium in oxidation states IV–VI have been described[1–3] no mention of chromium(III) species was made in a recent extensive review,[3] although imido compounds in the III oxidation state for V, Nb, Ta, Re and Ir were noted. Since $[CrBr(\mu\text{-}Br)(\eta\text{-}C_5Me_5)]_2$[4] is a readily available starting material, interactions with LiNHR, R = $2,6\text{-}Pr^i{}_2C_6H_3$, $2,4,6\text{-}Bu^t{}_3C_6H_2$, Ph, Bu^t and C_6H_{11}, have been studied. Related reactions of $Cr^{III}(\eta\text{-}C_5Me_5)$ and $Cr^{II}(\eta\text{-}C_5Me_5)$ halides with lithium alkyls and hydrides have been reported.[5] Physical and analytical data for new compounds are given in Table 1.

Results and Discussion

The interactions of $[CrBr(\mu\text{-}Br)(\eta\text{-}C_5Me_5)]_2$ with the lithium amides proceed in different, unpredictable ways depending upon the nature of the reactants and the conditions. Using 4 equivalents of $LiNHBu^t$ or LiNHR (R = $2,6\text{-}Pr^i{}_2C_6H_3$) in tetrahydrofuran (thf) at −78 °C, the green-brown solutions became purple after warming to room temperature and stirring for *ca.* 8 h. Evaporation gives intractable solids and no crystalline products could be obtained from hexane and other solvents. Rapid work up (*ca.* 1 h) of the green-brown solution from the LiNHR reactions after reaching room temperature gave low yields of a brown, crystalline solid shown to be the chromium(III) complex $[(\eta\text{-}C_5Me_5)Cr(\mu\text{-}NR)(\mu\text{-}NHR)(\mu\text{-}Br)\text{-}Cr(\eta\text{-}C_5Me_5)]$ **1** by X-ray study.

The crystal structure of compound **1** contains two crystallographically independent dimers. The structure of one molecule is shown as Fig. 1; selected bond lengths and angles for both molecules are given in Table 2. The precision of the bond lengths and angles is lower than preferred due probably to the effect on the quality of the intensity data of the twin components present in the specimen (see Experimental section). Nevertheless the main features of the structure are consistently demonstrated. In each case the two 'NR' ligands bridge symmetrically within the limits of experimental error but give different Cr–N bond lengths; one group in each molecule gives values of 1.92–1.97(1) Å and is identified as a bridging imido group, whilst the other, which is identified as a bridging amido group, gives values of 2.02–2.10(1) Å. This difference is the basis of our assignment of the NHR groups, in spite of the fact that the respective nitrogens are nearly planar (angle sums of 351.2 and 353.1°, but *cf.* values of 357.1 and 356.6° for the imido

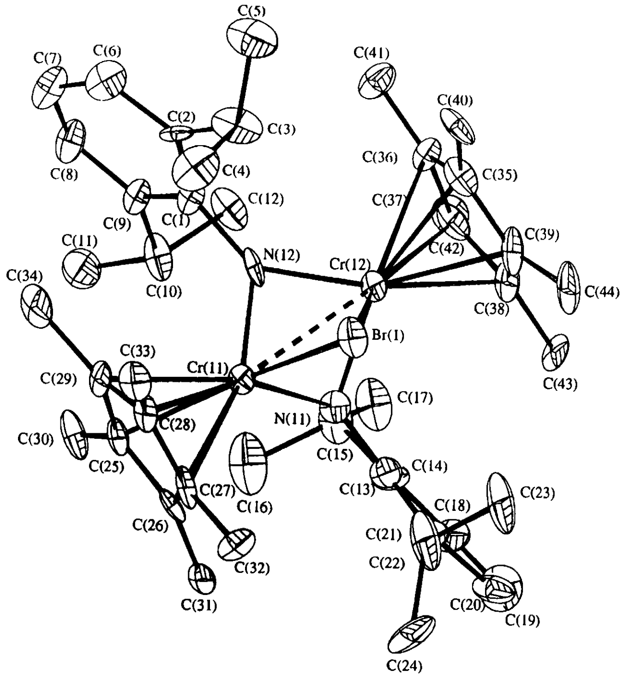

Fig. 1 The structure of $(\eta\text{-}C_5Me_5)Cr(\mu\text{-}NR)(\mu\text{-}NHR)(\mu\text{-}Br)Cr(\eta\text{-}C_5Me_5)$ **1** (R = $2,6\text{-}Pr^i{}_2C_6H_3$)

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† *Non-SI units employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

Table 1 Analytical and physical data for new compounds

Compound	Colour	M.p./°C	Analysis (%)* C	H	N
1 $[Cr(\eta\text{-}C_5Me_5)]_2(\mu\text{-}Br)(\mu\text{-}NC_6H_3Pr^i{}_2\text{-}2,6)(\mu\text{-}NHC_6H_3Pr^i{}_2\text{-}2,6)$	Green-brown	> 220	64.5 (65.5)	7.6 (7.9)	3.5 (3.5)
2 $[Cr(\eta\text{-}C_5Me_5)(\mu\text{-}NC_6H_3Pr^i{}_2\text{-}2,6)]_2$	Orange-brown	> 220	72.5 (72.9)	9.7 (9.1)	3.8 (3.8)
3 $[Cr(\eta\text{-}C_5Me_5)(\mu\text{-}NC_6H_2Bu_3{}^t\text{-}2,4,6)]_2$	Orange-brown	> 220	75.0 (75.3)	9.5 (9.9)	3.2 (3.1)
4 $[CrBr(\eta\text{-}C_5Me_5)(\mu\text{-}NPh)]_2$	Purple	> 220	53.8 (53.6)	5.7 (5.6)	3.9 (3.9)
5 $[CrBr(\eta\text{-}C_5Me_5)(\mu\text{-}NC_6H_{11})]_2$	Blue-purple	> 220	52.0 (52.6)	7.0 (7.1)	3.3 (3.8)
6 $Cr(\eta\text{-}C_5Me_5)(NC_6H_3Pr^i{}_2\text{-}2,6)(Ph_2C_2)$	Brown	130–135	79.2 (79.6)	7.5 (7.7)	2.6 (2.6)
7 $(\eta\text{-}C_5Me_5)BrCr(\mu\text{-}NHBu^t)_2Cr(NHBu^t)(NBu^t)$	Green-purple	167–169 (decomp.)	51.0 (51.5)	8.5 (8.9)	9.0 (9.2)
8 $Cr(\eta\text{-}C_5Me_5)(C_{36}H_{38}N_4)$	Red-purple	> 240	77.0 (77.4)	7.5 (7.4)	7.4 (7.8)

* Calculated values in parentheses. Mass spectral data are given in the Experimental section.

Table 2 Selected bond lengths (Å) and angles (°) for $(\eta\text{-}C_5Me_5)Cr(\mu\text{-}NR)(\mu\text{-}NHR)(\mu\text{-}Br)Cr(\eta\text{-}C_5Me_5)$ **1** ($R = 2,6\text{-}Pr^i{}_2C_6H_3$) with estimated standard deviations (e.s.d.s) in parentheses

Cr(11)–Cr(12)	2.647(5)	Cr(21)–Cr(22)	2.651(5)
Cr(11)–Br(1)	2.543(4)	Cr(21)–Br(2)	2.541(4)
Cr(11)–N(11)	2.090(9)	Cr(21)–N(21)	2.023(10)
Cr(11)–N(12)	1.944(10)	Cr(21)–N(22)	1.969(9)
Cr(11)–Cp1	1.925	Cr(21)–Cp3	1.939
Cr(12)–Br(1)	2.573(3)	Cr(22)–Br(2)	2.586(3)
Cr(12)–N(11)	2.096(9)	Cr(22)–N(21)	2.086(10)
Cr(12)–N(12)	1.918(9)	Cr(22)–N(22)	1.967(9)
Cr(12)–Cp2	1.941	Cr(22)–Cp4	1.938
N(11)–C(13)	1.428(14)	N(21)–C(45)	1.41(1)
N(12)–C(1)	1.470(14)	N(22)–C(57)	1.43(2)
N(11)–Cr(11)–N(12)	79.2(4)	N(21)–Cr(21)–N(22)	80.4(4)
N(11)–Cr(11)–Br(1)	91.3(3)	N(22)–Cr(21)–Br(2)	90.1(3)
N(11)–Cr(11)–Cp1	130.19	N(22)–Cr(21)–Cp3	131.04
N(11)–Cr(12)–N(12)	79.9(4)	N(21)–Cr(22)–N(22)	78.9(4)
N(11)–Cr(12)–Br(1)	90.4(3)	N(22)–Cr(22)–Br(2)	88.8(3)
N(11)–Cr(12)–Cp2	131.26	N(22)–Cr(22)–Cp4	133.12
N(12)–Cr(11)–Br(1)	89.1(3)	N(21)–Cr(21)–Br(2)	91.4(3)
N(12)–Cr(11)–Cp1	132.99	N(21)–Cr(21)–Cp3	130.85
N(12)–Cr(12)–Br(1)	88.8(3)	N(21)–Cr(22)–Br(2)	88.7(3)
N(12)–Cr(12)–Cp2	134.16	N(21)–Cr(22)–Cp4	133.58
Br(1)–Cr(11)–Cp1	120.22	Br(2)–Cr(21)–Cp3	119.94
Br(1)–Cr(12)–Cp2	118.52	Br(2)–Cr(22)–Cp4	118.82
Cr(11)–Br(1)–Cr(12)	62.3(1)	Cr(21)–Br(2)–Cr(22)	62.3(1)
Cr(11)–N(11)–C(13)	144.3(8)	Cr(21)–N(22)–C(57)	133.4(8)
Cr(11)–N(12)–C(1)	129.4(7)	Cr(21)–N(21)–C(45)	146.5(7)
Cr(11)–N(11)–Cr(12)	78.4(3)	Cr(21)–N(22)–Cr(22)	84.7(4)
Cr(11)–N(12)–Cr(12)	86.5(4)	Cr(21)–N(21)–Cr(22)	80.3(4)
Cr(12)–N(11)–C(13)	128.5(7)	Cr(22)–N(22)–C(57)	138.5(8)
Cr(12)–N(12)–C(1)	141.2(7)	Cr(22)–N(21)–C(45)	126.3(7)

Cp1 represents the centroid of the C_5Me_5 ring C(25)–C(29), Cp2 that of C(35)–C(39), Cp3 that of C(69)–C(73) and Cp4 that of C(79)–C(83).

groups) and we were not able to locate the amido hydrogens. In contrast to the symmetry of the NR and NHR bridges, the Cr–Br–Cr bridges are asymmetric, with differences in Cr–Br distances of 0.03 and 0.04 Å. We presume that these differences are due to steric interactions involving the C_5Me_5 and Pr^i groups. The former show some degree of tilting since the individual Cr–C(C_5Me_5) distances vary by *ca.* 0.04–0.09 Å. The Cr ··· Cr′ distances of 2.647(5) and 2.651(5) Å indicate metal–metal interactions.

No N–H bands for bridging NHR groups could be found in the IR spectrum; a similar observation was reported by Tilley and co-workers[6] and in the case of compound **7**, structure **I** discussed later, only a single sharp band assigned to the terminal $NHBu^t$ group was observed. The magnetic moment in solution by Evans' NMR method gave a value of 1.12 μ_B per Cr atom.

The addition of solid $[CrBr_2(\eta\text{-}C_5Me_5)]_2$ to LiNHR ($R = 2,6\text{-}Pr^i{}_2C_6H_3$) in toluene at 0 °C produces a green-brown solution which on heating at 60 °C for 30 min turns orange-brown; on work-up orange crystals of $[Cr(\eta\text{-}C_5Me_5)(\mu\text{-}NR)]_2$ **2** are obtained. If heating is prolonged a purple solution is formed and no crystalline products could be isolated. Compound **2** is sparingly soluble in organic solvents and is unaffected by refluxing in thf or in toluene. It does not react with Na-Hg in thf at room temperature. It is weakly paramagnetic (0.2 μ_B per Cr in the solid state at room temperature) presumably due to electron coupling through the bridges or the short Cr–Cr bond (see below). A similar reaction using $LiNH(C_6H_2Bu^t{}_3\text{-}2,4,6)$ gives a similar orange compound **3**.

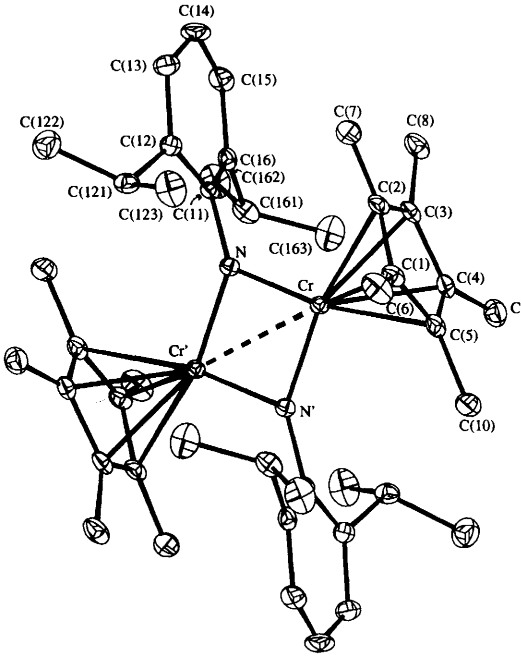


Fig. 2 The structure of $[Cr(\eta\text{-}C_5Me_5)(\mu\text{-}NR)]_2$ **2** ($R = 2,6\text{-}Pr^i{}_2C_6H_3$)

The structure of the molecule **2** is shown in Fig. 2; selected bond lengths and angles are given in Table 3. The structure contains two Cr^{III}, two bridging NR groups and two terminal C_5Me_5 ligands. The centrosymmetric dimer has two slightly asymmetric μ-NR ligands [Cr–N 1.861(2) and 1.886(2) Å]. The $\eta^5\text{-}C_5Me_5$ rings are equivalent, by symmetry, and the Cr–C bonds range from 2.253(2) to 2.288(2) Å. The isopropyl groups are in a distal arrangement. In the planar Cr_2N_2 dimer ring the angles at N are smaller than those at Cr [87.5(1) *vs.* 92.5(1)°] and are in keeping with the idea of some Cr ··· Cr′ bonding where the Cr ··· Cr′ distance of 2.591(1) Å indicates strong interaction.

The structure of the molecule **3** is shown in Fig. 3; selected bond lengths and angles are given in Table 3. This centrosymmetric dimer is analogous to **2** and contains two Cr^{III}, two bridging arylimido groups and two terminal C_5Me_5 ligands. The slight differences observed between **2** and **3** are due

Table 3 Selected bond lengths (Å) and angles (°) for [Cr(η-C_5Me_5)(μ-NR)]$_2$ (R = 2,6-$Pr^i{}_2C_6H_3$ **2** or 2,4,6-$Bu^t{}_3C_6H_2$ **3** with e.s.d.s in parentheses

	2	**3**
Cr–Cr′	2.591(1)	2.564(1)
Cr–N	1.886(2)	1.888(2)
Cr–N′	1.861(2)	1.905(2)
Cr–Cp1	1.915	1.939
N–C(11)	1.392(3)	1.428(3)
N–Cr–N′	92.5(1)	94.9(1)
Cr–N–Cr′	87.5(1)	85.1(1)
N–Cr–Cp1	135.41	131.95
N′–Cr–Cp1	132.06	133.10
Cr–N–C(11)	128.9(1)	136.7(2)
Cr′–N–C(11)	143.5(1)	138.2(2)

The primed atoms are related by the symmetry operations $-x$, $-y$, $z + 1$ for **2** and $-x + 1$, $-y$, $-z$ for **3**; Cp1 represents the centroid of the C_5Me_5 ring C(1)–C(5).

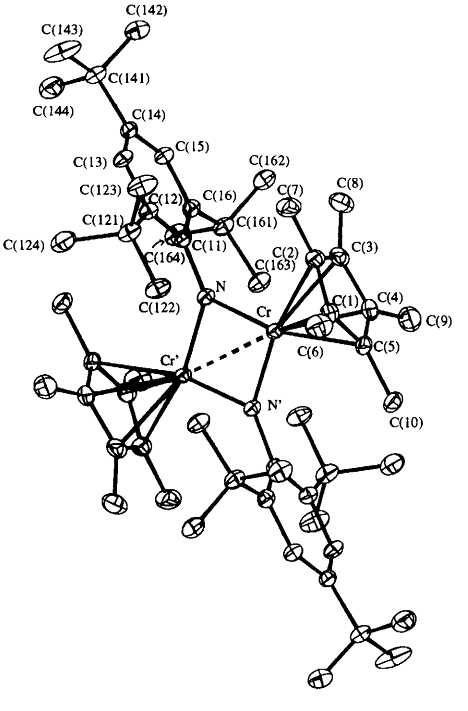


Fig. 3 The structure of [Cr(η-C_5Me_5)(μ-NR)]$_2$, **3** (R = 2,4,6-$Bu^t{}_3C_6H_2$)

to the nature of the substituents on the aryl rings possibly generating slightly differing steric and electronic effects. In comparison with **2**, the Cr • • • Cr′ distance is *ca.* 0.03 Å shorter in **3**. A corresponding trend is observed in the angles within the planar Cr_2N_2 dimer ring; the angles at Cr are more obtuse and those at N more acute [94.9(1) in **3** *vs.* 92.5(1) in **2**, and 85.1(1) in **3** *vs.* 87.5(1)° in **2**].

The reaction of [$CrBr_2$(η-C_5Me_5)]$_2$ in thf with LiNHPh is different again. If 4 equivalents per dimer are used no isolable product is formed, but with 2 equivalents [CrBr(η-C_5Me_5)(μ-NPh)]$_2$ **4** is obtained. This stoichiometry is proposed on the basis of analytical and IR data since X-ray quality crystals were not obtained. Support for this is provided by characterization by X-ray diffraction of [CrBr(η-C_5Me_5)(μ-NC_6H_{11})]$_2$ **5**, isolated from the reaction with 2 equivalents of LiNH(C_6H_{11}) in toluene; if thf was used as a solvent no product could be isolated. Compound **5** which is purple-blue and paramagnetic like **4** has chromium in the IV oxidation state. The formation presumably arises from some type of disproportionation 2 III $\longrightarrow$ II + IV as proposed for the synthesis of Cr(C_6H_{11})$_4$ in the reaction of $CrCl_3$(thf)$_3$ and MgBr(C_6H_{11}).[7]

Table 4 Selected bond lengths (Å) and angles (°) for the co-ordination sphere of [CrBr(η-C_5Me_5)(μ-NC_6H_{11})]$_2$·C_6H_5Me **5** with e.s.d.s in parentheses

Cr–Cr′	2.974(5)	Cr–N′	2.010(8)
Cr–Br	2.470(2)	Cr–Cp1	1.955
Cr–N	1.985(5)	N–C(11)	1.421(8)
N–Cr–N′	83.8(2)	Br–Cr–C(4)	144.7(2)
N–Cr–Br	97.0(2)	Br–Cr–C(5)	134.6(2)
N′–Cr–Br	94.2(2)	N–Cr–Cp1	125.23
Cr–N–Cr′	96.2(2)	N′–Cr–Cp1	130.06
Br–Cr–C(1)	100.1(2)	Br–Cr–Cp1	117.38
Br–Cr–C(2)	86.9(2)	Cr–N–C(11)	132.1(5)
Br–Cr–C(3)	109.6(2)	Cr′–N–C(11)	131.0(5)

The primed atoms are related by the symmetry operation $-x + 2$, $-y$, $-z + 2$; Cp1 represents the centroid of the C_5Me_5 ring C(1)–C(5).

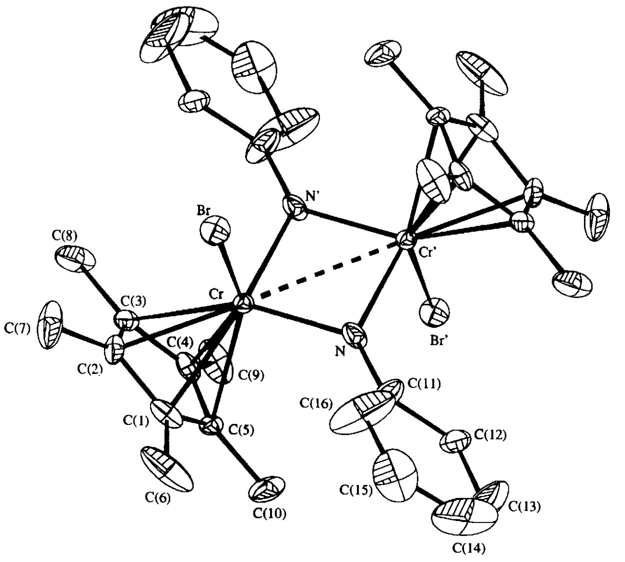


Fig. 4 The structure of [CrBr(η-C_5Me_5)(μ-NC_6H_{11})]$_2$ **5**

The structure of the complex **5** as its toluene solvate is shown in Fig. 4; selected bond lengths and angles are given in Table 4. This centrosymmetric dimer contains two Cr^{IV}, two bridging NC_6H_{11} groups, two terminal Br atoms and two terminal C_5Me_5 ligands. As previously observed in compounds **1**–**3** the μ-NR groups are slightly asymmetric [1.985(5) *vs.* 2.010(8) Å]. The thermal ellipsoids for the atoms of the cyclohexyl rings are generally large, indicating conformational disorder. The C_5Me_5 rings are related by symmetry and give Cr–C bonds of lengths ranging from 2.262 to 2.306(6) Å. This range indicates a slight tilting, probably due to the steric effect of the Br atoms. The Cr • • • Cr′ distance is longer than previously observed [2.974(5) Å], due probably to both an increase in the co-ordination number and steric crowding.

It is difficult to rationalize the processes by which the above compounds are formed. It is likely that [$CrBr_2$(η-C_5Me_5)]$_2$ behaves differently in different solvents; for example, thf cleavage could occur to give $CrBr_2$(η-C_5Me_5)(thf);[8] [$CrCl_2$(η-C_5Me_5)]$_2$ is readily cleaved quantitatively by tertiary phosphines.[9] It may also be noted that [CrX_2(η-C_5Me_5)]$_2$ species exhibit antiferromagnetic behaviour[8] so that single-temperature measurements such as those given above are not very meaningful.

To try to ascertain whether a Cr(η-C_5Me_5)(NR) species is an intermediate some trapping experiments were attempted. Such a species could be obtained by formation of Cr(η-C_5Me_5)(NHR)$_2$ and elimination of RNH_2 as proposed for the formation of Ir(η-C_5Me_5)(NR) (R = Bu^t or 2,6-$Pr^i{}_2C_6H_3$)[10a] and Zr(η-C_5Me_5)$_2$(NR).[10b] Dimerization of 'Cr(η-C_5Me_5)(NR)' *via* a [2 + 2] cycloaddition[11] could give rise to **2** and **3**.

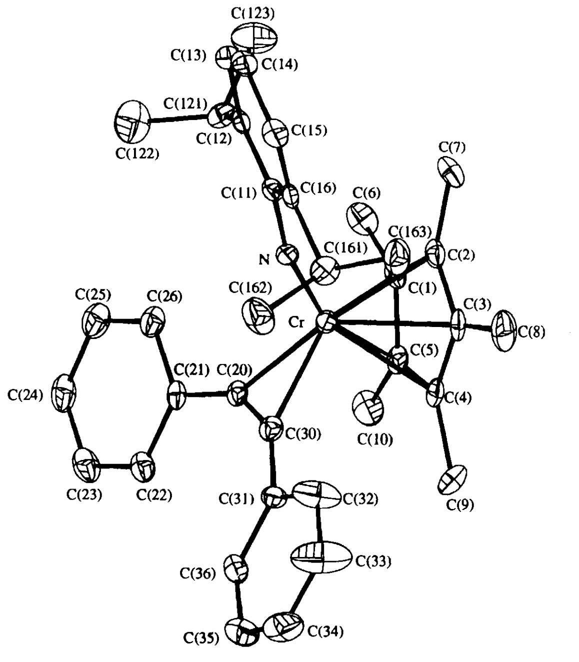


Fig. 5 The structure of Cr(η-C_5Me_5)(NR)(PhC≡CPh) **6** (R = 2,6-$Pr^i_2C_6H_3$)

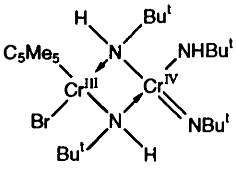
Interaction of [$CrBr_2$(η-C_5Me_5)]$_2$ with LiNHR (R = 2,6-$Pr^i_2C_6H_3$) in thf or toluene in the presence of CO, C_2H_4, cycloocta-1,5-diene, stilbene and PMe_3 led to intractable products and only the use of PhC≡CPh was successful. Four equivalents of LiNHR were added to a thf solution of [$CrBr_2$(η-C_5Me_5)]$_2$ at −78 °C containing an excess of diphenylacetylene. If the acetylene was not present before addition of LiNHR, a purple solution was obtained and no acetylene complex could be detected.

The structure of the adduct Cr(η-C_5Me_5)(NR)(PhC_2Ph) **6** which is formed in high yields is shown in Fig. 5; selected bond lengths and angles are given in Table 5. The monomer contains a Cr atom bonded to an η^5-C_5Me_5 ligand, an NR group and a diphenylacetylene PhC≡CPh. The Cr≡N bond is short [1.659(3) Å] and the Cr–N–C angle is almost linear [165.8(3)°] indicating 6e imido bonding, with parameters similar to those observed previously for $Cr(NR)_2(OR)_2$ (R = 2,4,6-$Me_3C_6H_2$) [1.655(3) Å and 165.1(3)°].[1] The isopropyl groups are in a distal arrangement, as previously observed for **2**. The C_5Me_5 ligand is slightly tilted, with the Cr–C bonds ranging from 2.216(4) to 2.272(3) Å; this is possibly due to the steric requirements of the acetylene ligand. Upon co-ordination the acetylene ligand C≡C triple bond is lengthened, as expected, to 1.295(5) Å, almost to a value which can formally be considered as a double bond. The compound could be formulated as having either Cr^{III} or Cr^{V}.

Compound **6** is paramagnetic (2.20 μ_B in solution at room temperature). The X-band EPR spectrum is temperature dependent. At *ca.* 25 °C there is a sharp singlet, peak-to-peak separation ΔH = 12.5 G centred at g = 2.007. Nitrogen isotopic hyperfine splitting, 3.75 G, can be detected under conditions controlled to avoid spin saturation. At low temperatures the spectrum becomes asymmetric, much weaker and no fine structure is observed.

A similar trapping attempt with PhC≡CPh but using $LiNHBu^t$ instead of LiNH($C_6H_3Pr^i_2$-2,6) leads on work-up to low yields of the green crystalline compound **7** the structure of which is shown in Fig. 6 and diagram **I**. Not only is there no co-ordinated acetylene but a C_5Me_5 group has been eliminated. The latter is uncommon but has been reported in the interaction of $ReCl(NBu^t)_3$ with Na(C_5H_5) and of Mn(η-C_5H_5)$_2$ with the lithium salt of a tripodal amine.[13]

An η^1-C_5Me_5 is possibly a better leaving group than is an η^5-C_5Me_5 and could be formed in the presence of strongly π-donating amido and imido ligands. The formation reaction which also involves oxidation to Cr^{IV} is doubtless complex and in view of the low yield of **7** other unidentifiable species are evidently also formed. It is unfortunate that as in earlier cases, monitoring of reaction progress by NMR spectra is not possible due to the paramagnetism of the reactants and products.



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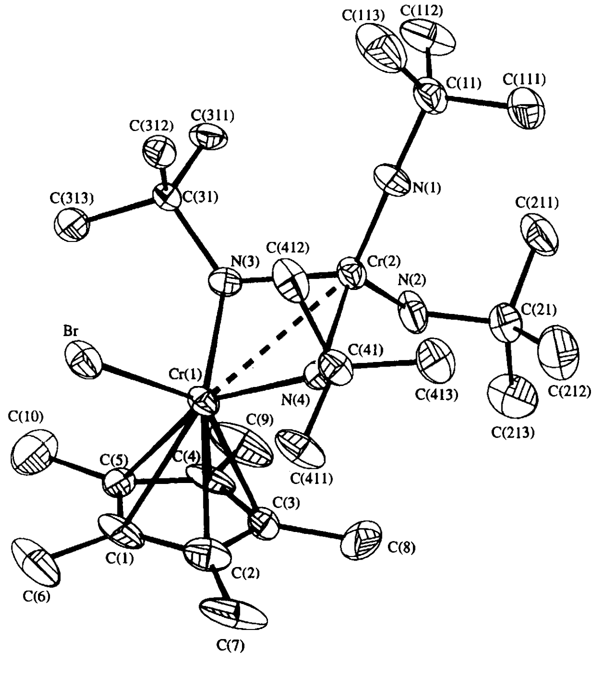


Fig. 6 The structure of (η-C_5Me_5)BrCr(μ-$NHBu^t$)$_2$Cr($NHBu^t$)(NBu^t) **7**

Table 5 Selected bond lengths (Å) and angles (°) for Cr(η-C_5Me_5)($NC_6H_3Pr^i_2$-2,6)(Ph_2C_2) **6** with e.s.d.s in parentheses

Cr–N	1.659(3)	N–C(11)	1.408(4)
Cr–C(20)	2.002(4)	C(20)–C(30)	1.295(5)
Cr–C(30)	2.011(4)	C(20)–C(21)	1.454(5)
Cr–Cp1	1.883	C(30)–C(31)	1.449(5)
C(20)–Cr–C(30)	37.6(1)	C(20)–Cr–Cp1	119.44
N–Cr–C(20)	108.4(1)	C(30)–Cr–Cp1	119.66
N–Cr–C(30)	108.0(1)	Cr–N–C(11)	165.8(3)
N–Cr–Cp1	129.34		

Cp1 represents the centroid of the C_5Me_5 ring C(1)–C(5).

The structure of compound **7** is shown in Fig. 6; selected bond lengths and angles are given in Table 6. The dimer contains two different Cr atoms, Cr(1) is bonded to an η^5-C_5Me_5 ligand, a terminal Br atom and two bridging $NHBu^t$ groups whereas Cr(2) is bonded to one terminal NBu^t, one terminal $NHBu^t$ and two bridging $NHBu^t$ groups. The oxidation states of the metal atoms can be considered as III and IV respectively. The C_5Me_5 ring is tilted and the Cr–C bond lengths range from 2.256(7) to 2.333(8) Å; this effect is due to the steric requirements of the neighbouring Br atom. The asymmetrically bridging amido nitrogens give Cr–N bonds of 2.053(6) and 2.069(6) Å with Cr(1), 2.062(6) and 2.047(6) Å with Cr(2). The terminal groups on Cr(2) are formally imido

Table 6 Selected bond lengths (Å) and angles (°) for (η-C_5Me_5)BrCr(μ-$\mathrm{NHBu^t}$)$_2$Cr($\mathrm{NHBu^t}$)($\mathrm{NBu^t}$) **7** with e.s.d.s in parentheses

Cr(1)–Cr(2)	2.936(2)	Cr(2)–N(3)	2.062(6)
Cr(1)–Br	2.464(2)	Cr(2)–N(4)	2.047(6)
Cr(1)–N(3)	2.053(6)	N(1)–C(11)	1.446(10)
Cr(1)–N(4)	2.069(6)	N(2)–C(21)	1.468(10)
Cr(1)–Cp1	1.956	N(3)–C(31)	1.534(8)
Cr(2)–N(1)	1.665(6)	N(4)–C(41)	1.510(10)
Cr(2)–N(2)	1.824(7)		
Cr(1)–N(3)–Cr(2)	91.0(2)	N(2)–Cr(2)–N(4)	114.8(3)
Cr(1)–N(4)–Cr(2)	91.0(2)	N(1)–Cr(2)–N(3)	123.0(3)
Br–Cr(1)–N(3)	103.0(2)	N(2)–Cr(2)–N(3)	98.4(3)
Br–Cr(1)–N(4)	102.4(2)	N(4)–Cr(2)–N(3)	87.8(2)
Br–Cr(1)–Cp1	114.66	Cr(1)–N(3)–C(31)	130.5(5)
N(3)–Cr(1)–Cp1	122.47	Cr(1)–N(4)–C(41)	131.8(5)
N(4)–Cr(1)–Cp1	122.01	Cr(2)–N(1)–C(11)	167.1(6)
N(3)–Cr(1)–N(4)	87.5(2)	Cr(2)–N(2)–C(21)	136.5(6)
N(1)–Cr(2)–N(2)	113.7(3)	Cr(2)–N(3)–C(31)	119.6(5)
N(1)–Cr(2)–N(4)	116.0(3)	Cr(2)–N(4)–C(41)	122.0(5)

Cp1 represents the centroid of the C_5Me_5 ring C(1)–C(5).

[Cr(2)≡N(1) 1.665(6) Å, Cr(2)–N(1)–C(11) 167.1(6)°] and amido [Cr(2)–N(2) 1.824(7) Å and Cr(2)–N(2)–C(21) 136.5(6)°] ligands. The long Cr(1)•••Cr(2) distance of 2.936(2) Å is consistent with the higher oxidation state of the Cr atoms, and indicates only a weak metal–metal interaction.

A potential trapping agent that could have given an isocyanide adduct, 2,6-xylyl isocyanide, showed quite unexpected behaviour giving high yields of the complex **8** shown in diagram **II**. The structure of complex **8** is shown in Fig. 7 (including experimentally located hydrogen atoms); selected bond lengths and angles are given in Table 7. The monomer contains chromium(III) η^5-bonded to a C_5Me_5 ligand and the two amide nitrogens of the unusual, substituted 2,3-dixylylaminoquinoline ligand. The nitrogen atoms are planar but the Cr–N bond lengths are long, indicative of single bonds, and are equivalent within experimental error [1.932(3) and 1.931(3) Å]. The Cr–C(C_5Me_5) bond lengths are very similar, ranging between 2.230(4) and 2.248(3) Å, and indicate symmetrical pentahapto bonding. The nitrogen atom [N(3)] in the pendant xylylamido group is also planar but does not appear to be involved in delocalization with either aromatic system since the C–N bond torsion angles are 59 (to the quinoline ring) and 19° to the xylyl ring. The two C–N distances are equal [1.41(1) Å]

There is a very extensive chemistry of isocyanides coordinated to transition metals as well as insertion reactions of isocyanides into M–X bonds, X = C, H, N, O or Cl, that may be single or multiple; a wide range of organic compounds, free or co-ordinated may be obtained.[14]

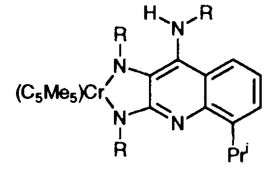
Coupling reactions between transition-metal imido compounds and isocyanides are restricted. The complex Ir(C_5Me_5)($\mathrm{NBu^t}$) and $\mathrm{Bu^tNC}$ give the η^2-N,C carbodiimide complex Ir(η-C_5Me_5)($\mathrm{CNBu^t}$)($\mathrm{Bu^tN{=}C{=}NBu^t}$);[10a] while Zr($\eta$-$C_5H_5$)$_2$($\mathrm{NBu^t}$)(thf) or the transient unsolvated species reacts similarly.[15] The Os(NR) complexes of *p*-cymene and C_6Me_6, R = $\mathrm{Bu^t}$ or 2,6-$\mathrm{Pr^i_2C_6H_3}$, were said to react with isocyanides giving complexes less stable than the iridium(III) ones noted above but no data were provided.[16]

Interaction of $\mathrm{Cr(NR)_2(SR)_2}$ (R = 2,4,6-$\mathrm{Me_3C_6H_2}$) with 2,6-xylyl isocyanide involves imido transfer to form $\mathrm{Cr(NR)(SR)_2}$(2,6-$\mathrm{Me_2C_6H_3NC)_2}$ and free $\mathrm{RN{=}C{=}NC_6H_3}$-$\mathrm{Me_2}$-2,6; an unstable intermediate with an η^2-carbodiimide was proposed.[17] Other similar chromium(VI) complexes,[18] *e.g.* $\mathrm{Cr(NBu^t)_2(C_6H_2Me_3}$-2,4,6)$_2$, were found to undergo insertion of $\mathrm{Bu^tNC}$ into one Cr–C bond to give η^2-iminoacyl complexes. Imido transfer to give carbodiimides catalytically has been reported for the reaction of PhNCO and V($\mathrm{NC_6H_4Me}$-4)-($\mathrm{OBu^t}$)$_3$.[19]

Table 7 Selected bond lengths (Å) and angles (°) for the quinolineamido derivative **8** with e.s.d.s in parentheses

Cr–N(1)	1.932(3)	N(3)–C(47)	1.409(4)
Cr–N(2)	1.931(3)	N(4)–C(40)	1.331(4)
Cr–Cp1	1.886	N(4)–C(41)	1.369(4)
N(1)–C(11)	1.430(4)	C(40)–C(48)	1.446(5)
N(1)–C(48)	1.393(4)	C(47)–C(48)	1.392(5)
N(2)–C(21)	1.431(4)	C(41)–C(46)	1.412(5)
N(2)–C(40)	1.374(4)	C(46)–C(47)	1.430(4)
N(3)–C(31)	1.408(4)		
N(1)–Cr–N(2)	82.10(12)	C(48)–N(1)–C(11)	120.8(3)
N(1)–Cr–Cp1	140.0	C(40)–N(2)–C(21)	116.4(3)
N(2)–Cr–Cp1	137.87	C(31)–N(3)–C(47)	127.8(3)
N(1)–C(48)–C(47)	130.3(3)	C(40)–N(4)–C(41)	117.1(3)
N(1)–C(48)–C(40)	112.3(3)	C(48)–N(1)–Cr	115.8(2)
N(2)–C(40)–C(48)	114.1(3)	C(11)–N(1)–Cr	122.5(2)
N(2)–C(40)–N(4)	120.8(3)	C(40)–N(2)–Cr	115.7(2)
N(3)–C(47)–C(46)	119.0(3)	C(21)–N(2)–Cr	127.7(2)
N(3)–C(47)–C(48)	122.3(3)	C(48)–C(47)–C(46)	118.8(3)
N(4)–C(40)–C(48)	125.1(3)	C(47)–C(48)–C(40)	117.1(3)
N(4)–C(41)–C(46)	122.8(3)		

Cp1 represents the centroid of the C_5Me_5 ring C(1)–C(5).



II R = 2.6-xylyl

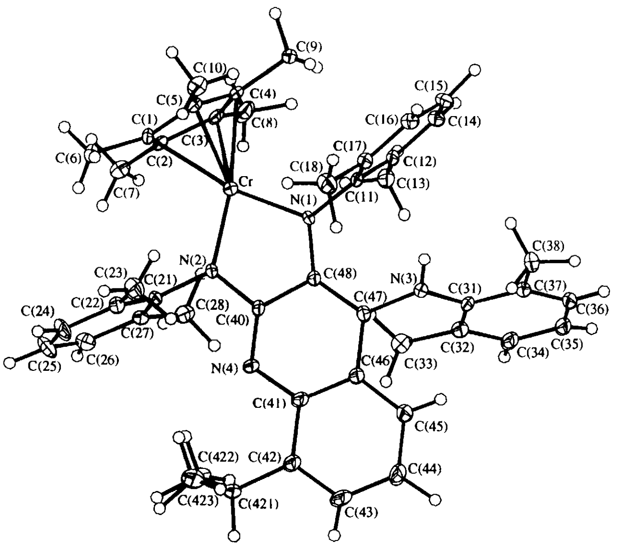
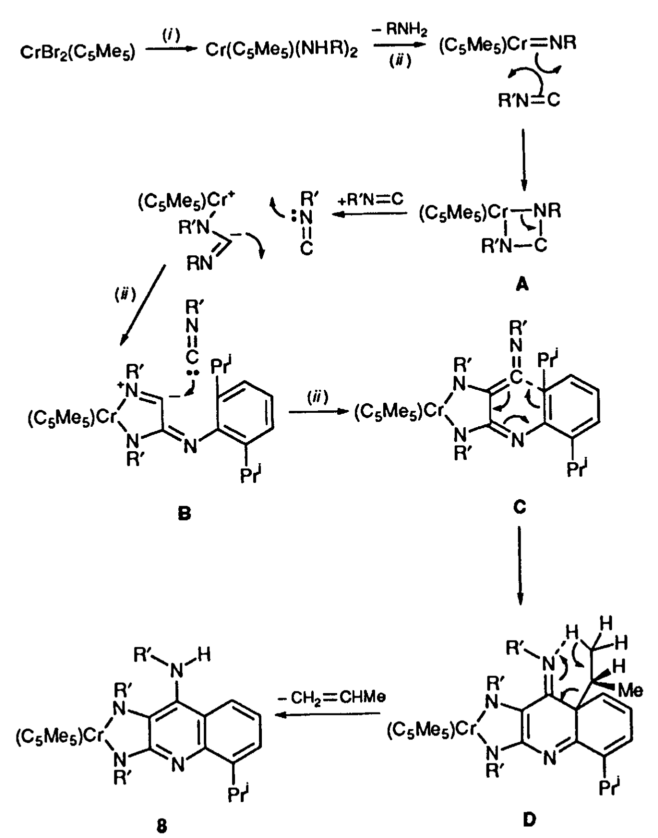
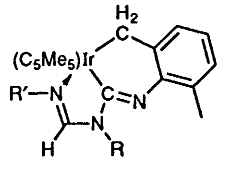


Fig. 7 The structure of the quinolineamido compound **8**

There is thus little precedent for the overall reaction giving compound **8**, although there are precedents for some of the intermediate steps; one of several possible routes is shown in Scheme 1. Since the interaction of $[\mathrm{CrBr_2(\eta\text{-}C_5Me_5)}]_2$ with LiNHR (R = $\mathrm{C_6H_3Pr^i_2}$-2,6) and 2,6-$\mathrm{Me_2C_6H_3NC}$ is evidently similar to the trapping reaction with PhC≡CPh, we can assume that the imido species (η-C_5Me_5)Cr=NR initially reacts with the isocyanide in a [2 + 2] cycloaddition to give the transient four-membered ring complex **A**. Successive reactions with two molecules of isocyanide and subsequent electron shifts lead to C–C bond formation in **B**. This is followed by ring closure and elimination of $\mathrm{CH_2{=}C(H)Me}$ to give the quinoline



Scheme 1 Interaction of $[CrBr(\mu\text{-}Br)(\eta\text{-}C_5Me_5)]_2$, $LiNH(C_6H_3Pr^i{}_2\text{-}2,6)$ and 2,6-xylyl isocyanide to give the quinoline derivative **8**; any tetrahydrofuran of solvation is omitted. R = $2,6\text{-}Pr^i{}_2C_6H_3$, R' = $2,6\text{-}Me_2C_6H_3$ (xylyl). (*i*) 2LiNHR; (*ii*) R'NC



III

R = $2,6\text{-}Pr^i{}_2C_6H_3$,
R' = $2,6\text{-}Me_2C_6H_3$

amido complex **8**. Although the removal of alkyl side chains from arenes as alkenes is known [20] the reaction usually requires much higher temperatures than in the present case. There is no change in the oxidation state of chromium in this overall sequence and although all the species are paramagnetic (Cr^{III}, d^3) it seems unnecessary to invoke radical reactions. It is appropriate to note here that although the iridium(III) analogue of $Cr(\eta\text{-}C_5Me_5)NR$ was made [10a] it was not treated with an isocyanide. Using $2,6\text{-}Me_2C_6H_3NC$ under conditions identical to those used for the chromium reaction, the iridium compound gives the very different product shown in diagram **III** and whose crystal structure has been determined.[21]

It is clear that it is far from easy to predict the outcome of any reactions between organic isocyanides and transition-metal imido complexes. Studies on different types of imido complexes and different metals now in progress may possibly provide some enlightenment.

Experimental

Analyses were by the 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 and instrumentation used have been described.[22] Commercial chemicals were from Aldrich. Light petroleum used had b.p. 40–60 °C. Lithium amides were made by interaction of the freshly distilled amine with $LiBu^n$ in light petroleum.

(μ-Bromo)(μ-2,6-diisopropylphenylamido)(μ-2,6-diisopropylphenylimido)bis(η-pentamethylcyclopentadienyl)dichromium(III) 1

To a solution of $[CrBr_2(\eta\text{-}C_5Me_5)]_2$ in thf (0.35 g, 0.5 mmol in 30 cm^3) at −78 °C was added a solution of $LiNH(C_6H_3Pr^i{}_2\text{-}2,6)$ in thf (0.35 g, 2.0 mmol in 20 cm^3). The green-brown reaction mixture was allowed to reach room temperature slowly and stirred for *ca.* 1 h. Removal of volatiles under vacuum, extraction of the brown residue with light petroleum, filtration, concentration of filtrates to *ca.* 20 cm^3 and cooling for 3 d (−20 °C) gave green-brown rhomboidal prisms. Yield: 0.14 g (*ca.* 35%).

Bis[(μ-2,6-diisopropylphenylimido)(η-pentamethylcyclopentadienyl)chromium(III)] 2

To a suspension of $LiNH(C_6H_3Pr^i{}_2\text{-}2,6)$ in toluene (0.74 g, 4 mmol in 30 cm^3) at 0 °C was added in small portions *via* a powder addition tube $[CrBr_2(\eta\text{-}C_5Me_5)]_2$ (0.7 g, 1 mmol). After completion of the addition the green-brown reaction mixture was allowed to reach room temperature and stirred at 60 °C until it became orange-brown. Longer heating times should be avoided. After filtering the hot reaction mixture, concentrating to *ca.* 10 cm^3 and cooling (−20 °C) the orange-brown crystals were isolated and washed with light petroleum. Yield: 0.29 g, *ca.* 40%. Mass spectrum (FAB): *m/z* 724, M^+; 362, $M^+ - (C_5Me_5)CrN(C_6H_3Pr^i{}_2)$ and 187, $(C_5Me_5)Cr^+$.

Bis[(η-pentamethylcyclopentadienyl)(μ-2,4,6-tri-*tert*-butylphenylimido)chromium(III)] 3

This compound was prepared as for **2** from $[CrBr_2(\eta\text{-}C_5Me_5)]_2$ (0.35 g, 0.5 mmol) and $LiNH(C_6H_2Bu^t{}_3\text{-}2,4,6)$ (0.53 g, 2 mmol). After evaporating the toluene solution to dryness the residue was extracted with light petroleum (30 cm^3), filtered, concentrated to *ca.* 5 cm^3 and cooled (4 °C) to give orange-brown prisms. Yield: 0.1 g, *ca.* 25%. Mass spectrum (FAB): *m/z* 892, M^+; 446, $M^+ - (C_5Me_5)CrN(C_6H_2Bu^t{}_3)$ and 187, $(C_5Me_5)Cr^+$.

Bis[bromo(η-pentamethylcyclopentadienyl)(μ-phenylimido)chromium(IV)] 4

To a solution of $[CrBr_2(\eta\text{-}C_5Me_5)]_2$ in thf (0.35 g, 0.5 mmol in 30 cm^3) at −78 °C was added a solution of LiNHPh in thf (0.1 g, 1 mmol). The purple reaction mixture was allowed to warm to room temperature and stirred for 2 h. After removal of thf under vacuum, extraction of the residue with toluene, filtration, concentration of the extracts to *ca.* 10 cm^3 and addition of light petroleum gave a purple microcystalline powder. Yield: 0.16 g, *ca.* 45%.

Bis[bromo(μ-cyclohexylimido)(η-pentamethylcyclopentadienyl)chromium(IV)] 5

To a suspension of $[CrBr_2(\eta\text{-}C_5Me_5)]_2$ in toluene (0.35 g, 0.5 mmol in 30 cm^3) at −78 °C was added a solution of $LiNH(C_6H_{11})$ in the same solvent (0.1 g, 1 mmol in 20 cm^3). The reaction mixture was allowed to reach room temperature, stirred overnight (green-blue) and refluxed for 1 h (blue-purple). After filtration, concentration to *ca.* 10 cm^3 and cooling, blue-purple crystals of compound **5** were isolated. Yield: *ca.* 30%.

(2,6-Diisopropylimido)(diphenylacetylene)(η-pentamethylcyclopentadienyl)chromium(III) 6

To a solution of $[CrBr_2(\eta\text{-}C_5Me_5)]_2$ (0.35 g, 0.5 mmol) and Ph_2C_2 (0.35 g, 2.0 mmol) in thf (50 cm^3) at −78 °C was added

Table 8 Crystal data and structure refinement details for compounds **1**–**3** and **5**–**8**

Compound	**1**	**2**	**3**	**5**	**6**	**7**	**8**
Formula	$C_{44}H_{65}BrCr_2N_2$	$C_{44}H_{64}Cr_2N_2$	$C_{56}H_8Cr_2N_2$	$C_{32}H_{52}Br_2Cr_2N_2 \cdot C_7H_8$	$C_{36}H_{42}CrN$	$C_{26}H_{54}BrCr_2N_4$	$C_{46}H_{53}CrN_4$
M_r	805.910	724.98	893.28	820.72	540.71	606.64	713.92
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_12_12$	$P2_1/c$	$P\bar{1}$
a/Å	18.67(2)	10.179(13)	10.964(4)	11.87(4)	14.140(4)	11.318(3)	12.448(7)
b/Å	22.64(3)	16.538(4)	11.806(3)	9.31(1)	20.442(5)	15.709(1)	13.157(5)
c/Å	20.91(4)	11.737(4)	19.547(4)	18.23(1)	10.412(3)	18.031(10)	14.452(8)
α/°							107.71(4)
β/°	114.06(6)	97.76(2)	99.57(4)	105.92(8)		104.99(1)	100.16(5)
γ/°							113.29(2)
U/Å^3	8068(19)	1958(3)	2495(1)	1938(6)	3010(1)	3097(2)	1948(2)
Z	8	2	2	2	4	4	2
D_c/Mg m^{-3}	1.327	1.230	1.189	1.407	1.193	1.301	1.217
F(000)	3 408	780	972	852	1156	1284	762
Crystal size/mm	0.21 × 0.20 × 0.18	0.33 × 0.30 × 0.21	0.30 × 0.14 × 0.13	0.24 × 0.24 × 0.18	0.42 × 0.15 × 0.12	0.18 × 0.18 × 0.06	0.25 × 0.16 × 0.12
μ(Mo-Kα)/mm^{-1}	1.561	0.587	0.473	2.651	0.404	2.011	0.331
Collection temperature/K	150	150	140	140	150	150	150
Reflections collected	25 984	7853	10 431	7496	7794	12 072	8243
Independent reflections (R_{int})	12 160 (0.1732)	3028 (0.0614)	3772 (0.0539)	2910 (0.0527)	4046 (0.0479)	4420 (0.0773)	5387 (0.0531)
Maximum, minimum correction factors	—	1.131, 0.909	1.043, 0.899	1.277, 0.867	1.166, 0.879	1.081, 0.810	1.068, 0.866
Data, restraints parameters	12 158, 0, 939	3 026, 0, 246	3 771, 0, 285	2 910, 0, 231	4 046, 0, 412	4 419, 0, 315	5 385, 0, 672
Goodness of fit on F^2, S	0.757	1.100	0.973	0.832	0.939	0.526	0.718
Final $R1$, $wR2$							
[$I > 2\sigma(I)$]	0.0805, 0.1806	0.0459, 0.1200	0.0451, 0.1103	0.0472, 0.1051	0.0395, 0.0920	0.0492, 0.1132	0.0434, 0.0893
(all data)	0.2009, 0.2184	0.0546, 0.1321	0.0616, 0.1146	0.0934, 0.1137	0.0457, 0.0936	0.1079, 0.1693	0.0776, 0.0992
Peak and hole/e Å^{-3}	2.632, −0.744	1.185, −0.325	0.670, −0.289	0.432, −0.318	0.389, −0.307	0.864, −0.344	0.286, −0.289

$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{\frac{1}{2}}$, $R_1 = \Sigma[(F_o - F_c)]/\Sigma F_o$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $P = [\max(F_o^2) + 2(F_c^2)]/3$, $w = 1/[\sigma^2(F_o)^2 + (xP)^2]$, where n = number of reflections and p = total number of parameters, x = 0.0839, 0.0859, 0.0659, 0.0544, 0.0437, 0.0000 and 0.0240 for compounds **1**, **2**, **3**, **5**, **6**, **7** and **8** respectively.

Table 9 Fractional atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr(11)	−1 998(1)	−1 299(1)	6 404(1)	Cr(21)	1 906(1)	600(1)	8 542(1)
Cr(12)	−2 248(1)	−1 308(1)	7 562(1)	Cr(22)	2 124(1)	608(1)	7 366(1)
Br(1)	−1 039(1)	−800(1)	7 512(1)	Br(2)	917(1)	108(1)	7 445(1)
N(11)	−2 955(5)	−972(4)	6 570(4)	N(21)	2 813(6)	274(4)	8 358(5)
N(12)	−2 142(5)	−1 924(4)	6 977(4)	N(22)	2 038(5)	1 246(4)	7 969(5)
C(1)	−1 961(7)	−2 557(5)	6 991(5)	C(45)	3 388(7)	−172(5)	8 514(6)
C(2)	−1 192(6)	−2 799(5)	7 423(5)	C(46)	4 170(7)	−4(6)	8 655(6)
C(3)	−589(6)	−2 425(5)	7 978(5)	C(47)	4 430(7)	624(6)	8 751(6)
C(4)	−1(7)	−2 196(6)	7 674(7)	C(48)	4 581(9)	824(7)	9 496(7)
C(5)	−174(8)	−2 781(7)	8 625(7)	C(49)	5 134(7)	744(7)	8 609(7)
C(6)	−1 046(8)	−3 402(6)	7 324(7)	C(50)	4 734(7)	−449(5)	8 746(6)
C(7)	−1 627(8)	−3 759(5)	6 802(7)	C(51)	4 553(7)	−1 042(6)	8 702(7)
C(8)	−2 343(7)	−3 522(6)	6 457(7)	C(52)	3 800(7)	−1 226(5)	8 589(6)
C(9)	−2 561(6)	−2 953(5)	6 515(6)	C(53)	3 203(6)	−789(5)	8 523(5)
C(10)	−3 389(7)	−2 731(6)	6 137(6)	C(54)	2 408(7)	−1 022(6)	8 418(6)
C(11)	−3 872(8)	−3 130(6)	5 498(6)	C(55)	1 976(8)	−1 262(6)	7 696(7)
C(12)	−3 782(6)	−2 785(6)	6 677(6)	C(56)	2 477(8)	−1 529(6)	8 979(7)
C(13)	−3 522(7)	−508(5)	6 394(6)	C(57)	1 862(7)	1 863(6)	7 921(7)
C(14)	−4 330(6)	−668(5)	6 187(6)	C(58)	1 099(8)	2 092(6)	7 483(7)
C(15)	−4 591(7)	−1 311(6)	6 077(6)	C(59)	496(7)	1 702(5)	6 989(6)
C(16)	−4 754(8)	−1 491(7)	5 308(7)	C(60)	−88(8)	1 501(7)	7 292(7)
C(17)	−5 359(7)	−1 432(6)	6 175(6)	C(61)	−9(9)	2 044(6)	6 313(7)
C(18)	−4 875(7)	−208(5)	6 122(6)	C(62)	931(8)	2 691(5)	7 551(8)
C(19)	−4 665(7)	377(6)	6 212(7)	C(63)	1 474(9)	3 071(6)	7 984(9)
C(20)	−3 893(7)	551(6)	6 369(6)	C(64)	2 242(9)	2 849(6)	8 412(8)
C(21)	−3 326(6)	101(5)	6 426(6)	C(65)	2 442(8)	2 253(6)	8 392(7)
C(22)	−2 492(7)	325(4)	6 571(6)	C(66)	3 300(8)	2 108(5)	8 768(7)
C(23)	−2 061(8)	556(7)	7 310(6)	C(67)	3 714(8)	2 131(6)	8 291(7)
C(24)	−2 553(8)	798(5)	6 010(7)	C(68)	3 774(10)	2 460(6)	9 443(7)
C(25)	−2 372(6)	−1 609(5)	5 297(5)	C(79)	1 890(7)	128(5)	6 330(6)
C(26)	−2 365(7)	−972(5)	5 289(5)	C(80)	1 529(7)	701(5)	6 177(5)
C(27)	−1 575(6)	−809(5)	5 665(5)	C(81)	2 123(7)	1 136(5)	6 446(6)
C(28)	−1 108(6)	−1 300(5)	5 911(5)	C(82)	2 851(6)	835(5)	6 747(5)
C(29)	−1 575(6)	−1 820(5)	5 685(5)	C(83)	2 713(7)	207(5)	6 689(6)
C(30)	−3 058(7)	−1 993(6)	4 865(6)	C(84)	1 479(8)	−451(5)	6 051(6)
C(31)	−3 048(6)	−592(5)	4 924(5)	C(85)	660(7)	787(6)	5 710(6)
C(32)	−1 273(7)	−183(5)	5 763(6)	C(86)	2 004(8)	1 786(6)	6 336(7)
C(33)	−227(6)	−1 306(5)	6 234(6)	C(87)	3 622(7)	1 105(6)	6 956(6)
C(34)	−1 295(7)	−2 450(5)	5 734(6)	C(88)	3 310(7)	−277(6)	6 877(6)
C(35)	−1 679(6)	−1 397(6)	8 748(6)	C(69)	2 278(6)	285(5)	9 661(5)
C(36)	−2 283(7)	−1 837(5)	8 499(6)	C(70)	1 496(6)	98(5)	9 268(6)
C(37)	−3 012(6)	−1 513(6)	8 135(5)	C(71)	1 030(6)	637(5)	9 079(5)
C(38)	−2 862(7)	−899(5)	8 210(6)	C(72)	1 511(7)	1 137(5)	9 295(5)
C(39)	−2 029(7)	−830(5)	8 603(6)	C(73)	2 295(7)	919(5)	9 651(5)
C(40)	−828(6)	−1 498(6)	9 206(5)	C(74)	2 981(6)	−118(5)	10 032(6)
C(41)	−2 184(7)	−2 487(5)	8 612(7)	C(75)	1 159(7)	−507(5)	9 208(6)
C(42)	−3 812(6)	−1 776(5)	7 942(6)	C(76)	144(6)	616(6)	8 757(7)
C(43)	−3 487(7)	−431(5)	7 996(6)	C(77)	1 262(7)	1 764(5)	9 247(6)
C(44)	−1 608(8)	−255(5)	8 876(6)	C(78)	2 989(6)	1 293(5)	10 116(6)

via cannula a solution of $LiNH(C_6H_3Pr^i_2\text{-}2,6)$ (0.36 g, 2.0 mmol). The reaction mixture was allowed to reach room temperature and stirred for 3 h (green-brown). Removal of volatiles under vacuum, extraction of the residue with light petroleum, filtration, concentration and cooling of the organic extracts (−20 °C) gave yellow-brown crystals. Yield: 0.45 g, *ca.* 85%. Mass spectrum (electron impact, EI): *m*/*z* 362, $M^+ - Ph_2C_2$; 178, $Ph_2C_2^+$ and 187, $(C_5Me_5)Cr^+$. IR (Nujol): 1261 (Cr=NR), 794, 754 and 733 cm^{-1} (aromatic).

Reactions of $[CrBr_2(\eta\text{-}C_5Me_5)]_2$

With $LiNHBu^t$ in the presence of Ph_2C_2. To a solution of $[CrBr_2(\eta\text{-}C_5Me_5)]_2$ and diphenylacetylene in thf (0.3 g, 0.4 mmol of Cr compound and 0.28 g, 1.6 mmol of acetylene in 30 cm^3) at −78 °C was added a solution of $LiNHBu^t$ in thf (0.13 g, 1.6 mmol in 30 cm^3). The blue reaction mixture turned green-brown at −60 °C and green at *ca.* −50 °C. It was allowed to reach room temperature over 8 h. After removal of the volatiles under reduced pressure, the residue was extracted into light petroleum (4 x 30 cm^3), filtered (green), concentrated and cooled to −20 °C for 24 h to give green crystals of compound **7**. Yield: 0.045 g, *ca.* 18%. IR (Nujol): 3239 (N–H) and 1260 cm^{-1} ($Cr{=}NBu^t$).

With $LiNH(C_6H_3Pr^i_2\text{-}2,6)$ in the presence of 2,6-xylyl isocyanide. To a solution of $[CrBr_2(\eta\text{-}C_5Me_5)]_2$ in thf (0.7 g, 1.0 mmol, in 40 cm^3) at −78 °C was added *via* cannula a solution of $LiNH(C_6H_3Pr^i_2\text{-}2,6)$ in the same solvent (0.77 g, 4.2 mmol in 40 cm^3). The mixture was allowed to warm to −50 °C when it changed from blue to green. At this temperature a solution of 2,6-xylyl isocyanide in thf (0.55 g, 4.2 mmol in 10 cm^3) was added dropwise over 2 min when the colour changed from green to orange-brown. After warming to room temperature over 8 h the brown reaction mixture was refluxed for *ca.* 1 h when it became red-purple. After cooling, evaporation of volatiles under vacuum, extraction of the residue with light petroleum (3 x 40 cm^3), filtration and concentration of the filtrates, cooling (−20 °C) for 24 h gave red-purple crystals. Yield: 0.5 g, *ca.* 35% based on chromium. Mass spectrum (EI): *m*/*z* 713, M^+; 698, M^+ − Me; 593, $M^+ - Me_2C_6H_3N$ and 528,

Table 10 Fractional atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Cr	436(1)	699(1)	5382(1)
N	−82(2)	266(1)	3902(1)
C(1)	89(2)	1843(1)	6347(2)
C(2)	408(2)	2079(1)	5241(2)
C(3)	1703(2)	1807(1)	5160(2)
C(4)	2205(2)	1409(1)	6199(2)
C(5)	1204(2)	1436(1)	6945(2)
C(6)	−1132(2)	2107(1)	6840(2)
C(7)	−363(2)	2641(1)	4411(2)
C(8)	2458(2)	2044(1)	4191(2)
C(9)	3608(2)	1118(1)	6516(2)
C(10)	1343(3)	1138(1)	8166(2)
C(11)	−114(2)	640(1)	2837(2)
C(12)	−1253(2)	1066(1)	2348(2)
C(13)	−1155(2)	1576(1)	1415(2)
C(14)	1(3)	1626(2)	926(2)
C(15)	1035(2)	1101(1)	1291(2)
C(16)	996(2)	587(1)	2222(2)
C(121)	−2589(2)	899(1)	2754(2)
C(122)	−3700(3)	848(2)	1738(2)
C(123)	−2987(3)	1482(2)	3653(2)
C(161)	2034(2)	−64(2)	2535(2)
C(162)	2594(3)	−404(2)	1486(2)
C(163)	3156(2)	167(2)	3464(2)

Table 11 Fractional atomic coordinates (× 10^4) for compound **3**

Atom	*x*	*y*	*z*
Cr	5 848(1)	724(1)	217(1)
N	5 868(2)	−651(2)	−274(1)
C(1)	6 687(3)	2 462(2)	80(2)
C(2)	7 608(3)	1 620(2)	34(2)
C(3)	7 868(3)	1 061(2)	676(2)
C(4)	7 118(3)	1 543(2)	1 131(2)
C(5)	6 389(3)	2 415(2)	761(2)
C(6)	6 345(3)	3 352(2)	−470(2)
C(7)	8 366(3)	1 489(3)	−532(2)
C(8)	8 942(3)	265(3)	862(2)
C(9)	7 305(3)	1 297(3)	1 897(2)
C(10)	5 547(3)	3 229(2)	1 056(2)
C(11)	6 771(2)	−1 328(2)	−532(1)
C(12)	7 016(2)	−1 211(2)	−1 232(1)
C(13)	7 833(2)	−1 969(2)	−1 474(1)
C(14)	8 451(2)	−2 828(2)	−1 086(1)
C(15)	8 255(2)	−2 897(2)	−412(1)
C(16)	7 464(2)	−2 200(2)	−109(1)
C(121)	6 431(3)	−387(2)	−1 834(2)
C(122)	5 592(3)	548(2)	−1 627(2)
C(123)	7 459(3)	207(3)	−2 163(2)
C(124)	5 658(3)	−1 099(3)	−2 407(2)
C(141)	9 248(3)	−3 719(2)	−1 384(1)
C(142)	10 513(3)	−3 831(3)	−932(2)
C(143)	9 421(4)	−3 453(3)	−2 122(2)
C(144)	8 596(3)	−4 872(3)	−1 390(2)
C(161)	7 392(3)	−2 599(2)	651(1)
C(162)	8 687(3)	−2 710(2)	1 098(2)
C(163)	6 638(3)	−1 847(2)	1 062(1)
C(164)	6 811(3)	−3 791(2)	607(2)

$M^+ - (C_5Me_5)Cr + 2H$. IR (Nujol): 3396 (N–H), 768 and 749 cm^{-1} (aromatic).

X-Ray crystallography

X-Ray data for compounds **1**–**3** and **5**–**8** were collected at low temperature (see Table 8) using a FAST TV area-detector diffractometer with Mo-Kα radiation (λ = 0.710 69 Å), as previously described.[23] Compound **7** was solved using the Patterson instruction of SHELXS 86[24] and the other structures *via* direct methods of the same program. The structures were refined using full-matrix least squares on F_o^2,[25] using all unique data corrected for Lorentz and polarization factors. The data for compounds **2**, **3**, **5**–**7** and **8** were corrected for absorption using the program DIFABS[26] with maximum and minimum

Table 12 Fractional atomic coordinates (× 10^4) for compound **5**

Atom	*x*	*y*	*z*
Br	8 132(1)	2 065(1)	9 111(1)
Cr	9 062(1)	−329(1)	9 292(1)
N	9 298(5)	−453(6)	10 412(3)
C(1)	7 478(6)	−1 735(7)	8 737(4)
C(2)	7 762(8)	−960(6)	8 147(4)
C(3)	8 866(7)	−1 389(8)	8 120(3)
C(4)	9 289(6)	−2 407(6)	8 706(4)
C(5)	8 388(6)	−2 633(6)	9 072(3)
C(6)	6 287(7)	−1 748(10)	8 911(6)
C(7)	6 928(10)	−16(8)	7 588(4)
C(8)	9 458(9)	−1 033(10)	7 494(4)
C(9)	10 408(7)	−3 273(9)	8 837(5)
C(10)	8 497(8)	−3 808(7)	9 644(4)
C(11)	8 519(7)	−768(10)	10 859(4)
C(12)	8 991(7)	−1 790(7)	11 515(4)
C(13)	8 228(12)	−2 240(22)	11 931(8)
C(14)	7 184(16)	−1 550(16)	11 866(10)
C(15)	6 687(9)	−595(16)	11 210(7)
C(16)	7 475(10)	−217(12)	
Disordered toluene molecule			
C(111)	6 373(31)	3 769(43)	695(14)
C(112)	5 603(19)	4 460(21)	217(15)
C(113)	6 041(29)	3 671(24)	7(34)
C(114)	4 813(11)	5 645(10)	536(7)
C(115)	3 509(58)	6 281(71)	−1 023(22)
C(116)	4 379(19)	5 051(30)	−1 033(14)

Occupancy factors for C(111)–C(116) are 0.6, 0.6, 0.4, 1.0, 0.4, 0.5 respectively.

Table 13 Fractional atomic coordinates (× 10^4) for compound **6**

Atom	*x*	*y*	*z*
Cr	4 946(1)	2 270(1)	8 691(1)
N	4 392(2)	2 963(1)	9 042(3)
C(1)	5 930(2)	2 303(2)	7 016(3)
C(2)	6 275(2)	2 730(2)	8 013(4)
C(3)	6 481(2)	2 341(2)	9 098(3)
C(4)	6 287(2)	1 672(2)	8 796(4)
C(5)	5 962(2)	1 655(2)	7 509(4)
C(6)	5 642(3)	2 496(2)	5 695(4)
C(7)	6 419(3)	3 461(2)	7 909(4)
C(8)	6 905(3)	2 587(2)	10 346(4)
C(9)	6 468(3)	1 092(2)	9 629(5)
C(10)	5 728(3)	1 047(2)	6 753(4)
C(11)	4 145(2)	3 619(2)	9 286(3)
C(12)	3 836(2)	4 022(2)	8 267(3)
C(13)	3 599(3)	4 668(2)	8 554(4)
C(14)	3 658(3)	4 911(2)	9 786(4)
C(15)	3 964(3)	4 508(2)	10 776(4)
C(16)	4 215(2)	3 864(2)	10 560(3)
C(20)	3 973(2)	1 572(2)	8 418(4)
C(21)	3 355(2)	1 318(2)	7 419(3)
C(22)	3 004(3)	678(2)	7 433(4)
C(23)	2 447(3)	449(2)	6 413(4)
C(24)	2 238(3)	849(2)	5 392(4)
C(25)	2 575(3)	1 482(2)	5 358(4)
C(26)	3 133(3)	1 714(2)	6 371(4)
C(30)	4 268(2)	1 537(2)	9 593(4)
C(31)	4 209(3)	1 219(2)	10 834(3)
C(32)	4 588(4)	1 502(2)	11 927(4)
C(33)	4 555(5)	1 211(3)	13 094(5)
C(34)	4 140(3)	603(2)	13 243(5)
C(35)	3 774(3)	303(3)	12 183(5)
C(36)	3 789(3)	605(2)	10 997(4)
C(121)	3 749(3)	3 760(2)	6 914(4)
C(122)	2 726(3)	3 608(2)	6 550(4)
C(123)	4 197(4)	4 220(2)	5 924(4)
C(161)	4 553(3)	3 436(2)	11 651(4)
C(162)	3 702(3)	3 225(2)	12 505(4)
C(163)	5 315(3)	3 758(2)	12 466(4)

Table 14 Fractional atomic coordinates (× 10^4) for compound **7**

Atom	x	y	z	Atom	x	y	z
Cr(1)	647(1)	1242(1)	3227(1)	C(11)	3773(8)	232(6)	1318(4)
Cr(2)	2408(1)	303(1)	2597(1)	C(21)	3619(8)	−1289(5)	3441(4)
Br	−194(1)	2556(1)	2546(1)	C(31)	−227(7)	414(5)	1512(4)
N(1)	3179(6)	372(4)	1928(3)	C(41)	3284(7)	2106(5)	3235(4)
N(2)	2599(6)	−716(5)	3100(3)	C(111)	5145(8)	133(7)	1664(5)
N(3)	528(6)	386(4)	2351(3)	C(112)	3264(9)	−552(7)	862(5)
N(4)	2492(5)	1347(4)	3288(3)	C(113)	3593(10)	995(7)	770(5)
C(1)	−472(9)	1628(6)	4095(4)	C(211)	3830(9)	−1884(6)	2841(5)
C(2)	709(9)	1516(6)	4499(4)	C(212)	4740(9)	−763(7)	3789(6)
C(3)	1019(7)	668(6)	4412(4)	C(213)	3276(10)	−1828(6)	4077(5)
C(4)	−16(9)	242(5)	3932(4)	C(311)	−99(8)	−415(5)	1140(4)
C(5)	−961(7)	869(6)	3715(4)	C(312)	206(8)	1135(5)	1086(4)
C(6)	−1223(10)	2441(6)	4120(5)	C(313)	−1573(7)	558(6)	1511(4)
C(7)	1493(10)	2184(7)	5029(4)	C(411)	3113(8)	2791(6)	3789(4)
C(8)	2188(9)	222(7)	4811(4)	C(412)	2932(8)	2451(5)	2409(4)
C(9)	−132(10)	−673(6)	3760(5)	C(413)	4624(8)	1826(6)	3440(5)
C(10)	−2281(9)	733(9)	3268(5)				

Table 15 Fractional atomic coordinates (× 10^4) for compound **8**

Atom	x	y	z	Atom	x	y	z
Cr	1 560(1)	8 533(1)	7 492(1)	C(24)	−329(4)	5 781(4)	9 221(3)
N(1)	3 169(2)	8 791(2)	7 398(2)	C(25)	−1 215(4)	4 708(4)	8 407(4)
N(2)	1 635(3)	7 281(2)	7 889(2)	C(26)	−1 149(4)	4 458(4)	7 436(4)
N(3)	5 495(3)	8 613(3)	7 209(2)	C(27)	−197(3)	5 287(3)	7 252(3)
N(4)	2 799(3)	6 278(3)	8 096(2)	C(28)	−87(5)	4 989(4)	6 196(3)
C(1)	83(3)	8 903(3)	7 952(3)	C(31)	5 857(3)	8 220(3)	6 356(3)
C(2)	−427(3)	8 113(3)	6 896(3)	C(32)	5 121(3)	7 063(3)	5 504(3)
C(3)	268(3)	8 732(3)	6 366(3)	C(33)	3 847(4)	6 140(4)	5 398(4)
C(4)	1 181(3)	9 913(3)	7 098(3)	C(34)	5 585(4)	6 784(4)	4 712(3)
C(5)	1 072(3)	10 014(3)	8 082(3)	C(35)	6 692(4)	7 597(4)	4 712(3)
C(6)	−438(5)	8 657(5)	8 774(4)	C(36)	7 388(4)	8 716(4)	5 527(3)
C(7)	−1 547(4)	6 890(4)	6 428(4)	C(37)	6 986(3)	9 035(3)	6 356(3)
C(8)	10(5)	8 241(5)	5 226(3)	C(38)	7 772(4)	10 273(4)	7 251(3)
C(9)	2 026(5)	10 901(4)	6 864(4)	C(40)	2 685(3)	7 162(3)	7 900(2)
C(10)	1 834(5)	11 140(4)	9 087(4)	C(41)	3 851(3)	6 192(3)	8 051(2)
C(11)	3 996(3)	9 831(3)	7 281(3)	C(42)	3 959(4)	5 212(3)	8 235(3)
C(12)	3 955(3)	9 810(3)	6 296(3)	C(43)	5 017(4)	5 117(4)	8 197(3)
C(13)	3 146(4)	8 659(4)	5 336(3)	C(44)	5 991(4)	5 943(4)	8 006(3)
C(14)	4 712(4)	10 866(4)	6 223(3)	C(45)	5 866(4)	6 865(4)	7 815(3)
C(15)	5 489(4)	11 931(4)	7 094(3)	C(46)	4 792(3)	6 992(3)	7 810(2)
C(16)	5 534(4)	11 953(4)	8 060(3)	C(47)	4 615(3)	7 892(3)	7 546(2)
C(17)	4 787(3)	10 913(3)	8 177(3)	C(48)	3 573(3)	8 020(3)	7 626(2)
C(18)	4 841(5)	10 953(4)	9 235(3)	C(421)	2 981(4)	4 335(3)	8 499(3)
C(21)	683(3)	6 395(3)	8 076(3)	C(422)	1 677(4)	3 631(4)	7 689(4)
C(22)	636(3)	6 640(3)	9 078(3)	C(423)	2 942(5)	4 947(5)	9 566(4)
C(23)	1 637(5)	7 781(5)	9 981(3)				

correction factors listed in Table 8. An absorption correction could not be applied to **1** because of the weakness of the data (possibly due to the crystal containing a twinned component). The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions for compounds **1**, **3**, **5** and **7**. Within the unit cell, each independent half of the dimer **5** is accompanied by half a molecule of toluene which is disordered about a centre of symmetry. The carbon atoms are represented by six fractionally occupied positions totalling 3.5, listed in Table 12. The hydrogens of the solvent were ignored. For compounds **2** and **6** the methyl hydrogens were calculated, but the tertiary hydrogens (and aromatic hydrogens of **6**) were experimentally located. The excellent quality of the data for **8** allowed experimental location of all of the hydrogens from the difference map (see Fig. 7). The equations used in the refinement, the weighting scheme and parameters employed for each compound are included in Table 8. Fractional atomic coordinates are given in Tables 9–15.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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