

Synthesis, Structures and Ethylene Polymerisation Behaviour of Low Valent β -Diketiminato Chromium Complexes

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Keywords: Chromium / N ligands / Ethylene / Polymerisation

The preparation, reaction chemistry and ethylene polymerisation behaviour of low valent β -diketiminato chromium complexes are described. $[(\text{DDP})\text{CrCl}(\mu\text{-Cl})_2]$ (**1**) [DDPH = 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene] is formed by treatment of $\text{CrCl}_3(\text{THF})_3$ with LiDDP. Alkylation of **1** with AlMe_3 results in the formation of the binuclear dimethyl complex $[(\text{DDP})\text{CrMe}(\mu\text{-Cl})_2]$ (**2**). In contrast, the attempted alkylation of **1** with benzylmagnesium chloride results in reduction to form the dichromium(II) complex $[(\text{DDP})\text{Cr}(\mu\text{-Cl})_2]$ (**3**). Depending on the conditions of crystallisation, **3** can be obtained as the THF adduct $[\text{3}(\text{THF})_2\cdot\text{THF}]$ or co-crystallised with a molecule of dibenzyl $[\text{3-Bz-Bz}]$. Cleavage of the dimeric unit in **1** can be achieved by the addition of carboxylates or β -diketonates to give $[(\text{DDP})\text{CrCl}(\text{O}_2\text{CR})(\text{THF})]$ ($\text{R} = \text{Me}$ **4a**, Ph **4b**) and $[(\text{DDP})\text{CrCl}\{\text{O}(\text{R})\text{C}_2\text{CH}\}]$ ($\text{R} = \text{Me}$ **5a**, Ph **5b**), respectively.

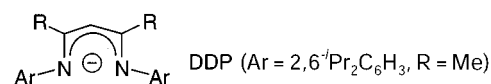
Single crystal X-ray diffraction studies have been performed on **1**, **2**, $[\text{3}(\text{THF})_2\cdot\text{THF}]$, **3-Bz-Bz**, **4a**, and **5b**. Complexes **1**, **2** and $[\text{3}(\text{THF})_2\cdot\text{THF}]$ are dimeric and have molecular C_{2h} symmetry. Complex **3-Bz-Bz** is also dimeric but has its potential C_{2h} symmetry removed by a significant tetrahedral distortion of the chromium coordination geometry. Compound **4a** has an octahedral chromium centre coordinated to a single bidentate diketiminato ligand, a bidentate acetate, a chloride and a THF molecule. Complex **5b** has a square pyramidal chromium with apical chloride and basal η^2 diketiminato and diketonate ligands. The complex contains strong intramolecular $\text{C-H}\cdots\pi$ stabilising interactions. All the complexes are active in ethylene polymerisation on treatment with suitable aluminium activators, affording high molecular weight polyethylene.

Introduction

Supported chromium catalysts play a key role in the worldwide production of polyethylene, and much effort has been directed towards developing an understanding of these systems from a surface science/heterogeneous catalysis point of view.^[1,2] A complementary approach is to develop homogeneous model systems, not only to gain understanding of the chromium-centred chemistry of the supported systems, but also to advance chromium olefin polymerisation catalysis into an era of well-defined, single-site catalysts. To date, the majority of reports of homogeneous chromium catalysts for olefin polymerisation have been on half-sandwich chromium systems.^[3–4] However, more recently there has been growing interest in non-cyclopentadienyl chromium catalysts.^[5,6]

In this paper we are concerned with chemistry of low-valent chromium compounds containing the monoanionic N,N -chelate β -diketiminato ligand, $[\text{ArNC}(\text{Me})\text{CHC}(\text{Me})\text{-NAr}]^-$ ($\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$, DDP). This ligand (DDP) and members of the general family, $[\text{ArNC}(\text{R})\text{CHC}(\text{R})\text{NAr}]^-$, have been the subject of intense interest in recent years and complexes incorporating early^[7] and late^[8] transition metals, main group metals^[9] and lanthanides have been reported.^[10] Their ease of preparation, facility for aryl (Ar)

and R group variation and variability in bonding mode,^[7c] are particularly attractive features.



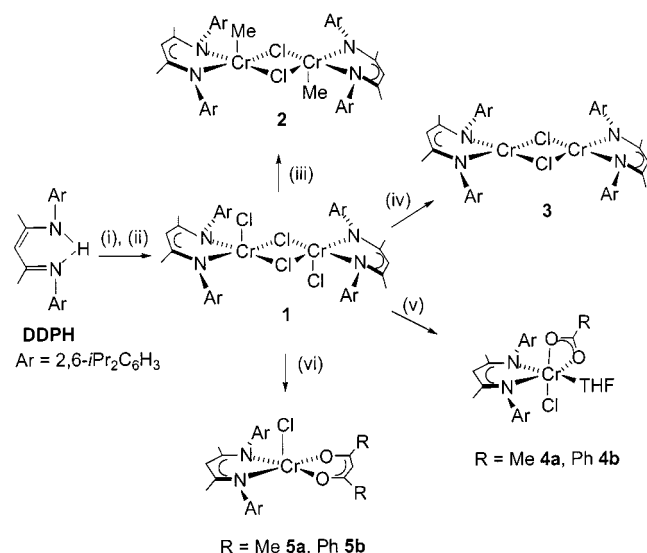
In independent studies, Theopold and this group have communicated chromium(III) (d^3) complexes supported by β -diketiminato ligands, albeit with different aryl groups, as olefin polymerisation catalysts.^[6b,6i] Herein we report, as part of a general study of the olefin polymerisation capability of non-cyclopentadienyl-containing chromium complexes,^[6b–6h] our findings on a range of DDP-supported chromium(II) and -(III) systems (Scheme 1).

Results and Discussion

The protonated β -diketiminato ligand, 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene (DDPH) was prepared using a method similar to that reported for related ligands^[11] and more recently by Feldman for DDPH itself.^[8b] The lithium salt of DDPH was prepared by addition of one equivalent of $n\text{BuLi}$ to a THF solution of DDPH at -78°C and used without isolation.

Addition of one equivalent of $\text{CrCl}_3(\text{THF})_3$ to LiDDP in THF gave $[(\text{DDP})\text{CrCl}(\mu\text{-Cl})_2]$ (**1**) as a green solid in good yield upon workup (Scheme 1). Crystals of **1** suitable for an X-ray structure determination were grown from a concentrated pentane solution at -20°C . The structure is dimeric

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Scheme 1. Reagents and conditions: (i) *n*BuLi, THF, -78°C ; (ii) $\text{CrCl}_3(\text{THF})_3$, THF, -78°C ; (iii) AlMe_3 , THF, 20°C ; (iv) BzMgCl , THF, -78°C ; (v) NaO_2CR , THF, -78°C ; (vi) $\text{Li}[\text{O}(\text{R})\text{C}]_2\text{CH}$, THF, -78°C

(Figure 1) and has non-crystallographic C_{2h} symmetry about an axis passing through the two bridging chlorine atoms (the crystallographic symmetry is C_i). The geometry at chromium is distorted square pyramidal with the chromium atom being displaced by 0.35 Å out of the basal plane in the direction of Cl(1). Although the bridging Cr–Cl distances are identical within the errors of the structure determination, there is a marked asymmetry in the apical/basal Cr–Cl distances, with the apical bond being ca. 0.17 Å shorter than its basal counterparts (Table 1). The Cr–N distances are unexceptional. The nonbonded Cr...Cr separation (3.69 Å) is long, and extends outside the range found in a number of other chloride-bridged chromium(III) complexes.^[12–15] This distance may in part be due to the steric repulsion between the bulky aryl ligands. The six-membered chelate ring has a boat conformation with the chromium and C(5) atoms lying 0.60 and 0.13 Å, respectively, out of the N(3)–C(4)–C(6)–N(7) plane (which is coplanar to within 0.01 Å). There is a pronounced pattern of delocalisation in the bond lengths of the N(3) to N(7) linkages. All four 2,6-diisopropylphenyl rings are oriented essentially orthogonally (84 and 87°) to their respective chelate C–N–Cr planes, a geometry that is stabilised by pairs of C–H...N(p_{π}) interactions^[16] between N(3) and N(7) and their proximal isopropyl methine hydrogen atoms; the H...N distances are in the range 2.42 to 2.54 Å with associated C...N distances of between 2.89 and 3.00 Å. There are no intermolecular packing interactions of note.

It is noteworthy that substitution of the 2,6-diisopropylphenyl groups in DDP for phenyl groups results in a mononuclear six-coordinate chromium(III) dichloride complex in which the coordination sphere is completed by THF molecules.^[6] The preference of complexes coordinated by β -diketiminato ligands, with bulky groups on the 2,6-positions of the aryl substituents, to exhibit low coordination

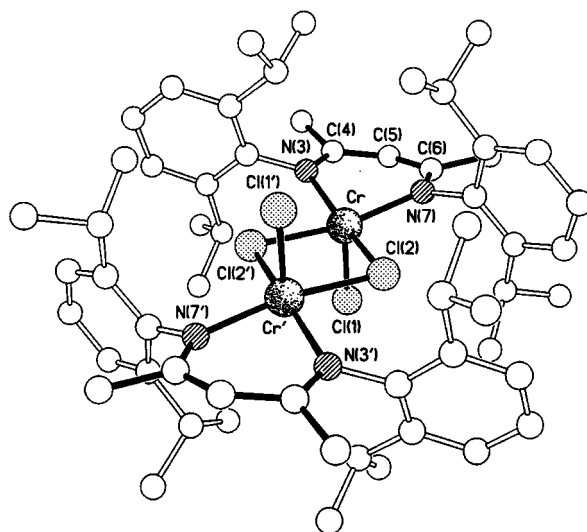


Figure 1. The molecular structure of **1**

Table 1. Selected bond lengths (Å) and angles ($^{\circ}$) for **1** (apical = Cl) and **2** (apical = Me)

	1	2 ^[a]	
Cr–apical	2.233(2)	2.037(7)	2.042(8)
Cr–Cl(2)	2.403(2)	2.3951(13)	2.3925(13)
Cr–Cl(2')	2.397(2)	2.3951(13)	2.3925(13)
Cr–N(3)	1.986(5)	2.028(4)	2.031(4)
Cr–N(7)	1.990(5)	2.028(4)	2.031(4)
N(3)–C(4)	1.349(8)	1.328(6)	1.324(7)
C(4)–C(5)	1.395(9)	1.400(6)	1.397(6)
C(5)–C(6)	1.379(9)	1.400(6)	1.397(6)
C(6)–N(7)	1.349(8)	1.328(6)	1.324(7)
N(3)–Cr–N(7)	91.4(2)	91.3(2)	90.8(2)
N(3)–Cr–Cl(1)	99.6(2)	95.4(2)	96.8(2)
N(7)–Cr–Cl(1)	99.5(2)	95.4(2)	96.8(2)
N(3)–Cr–Cl(2')	91.2(2)	92.68(11)	92.68(12)
N(7)–Cr–Cl(2')	160.1(2)	165.73(12)	165.41(12)
Cl(1)–Cr–Cl(2')	99.49(7)	97.8(2)	96.8(2)
N(3)–Cr–Cl(2)	160.34(14)	165.73(12)	165.41(12)
N(7)–Cr–Cl(2)	91.9(2)	92.68(11)	92.68(12)
Cl(1)–Cr–Cl(2)	98.91(7)	97.8(2)	96.8(2)
Cl(2)–Cr–Cl(2')	79.34(6)	80.31(7)	80.62(7)
Cr–Cl(2)–Cr'	100.66(6)	99.69(7)	99.38(7)

^[a] The two sets of values refer to the two crystallographically independent molecules.

numbers has also recently been observed by Budzelaar and co-workers.^[8a]

The *N,N*- β -diketiminato chromium derivatives **2–5** have been prepared by in situ formation of **1** followed by treatment with the reagents shown in Scheme 1. The reaction with AlMe_3 affords a dark oily residue. Extraction of this residue into pentane and cooling to -20°C gives crimson needles of $[(\text{DDP})\text{CrMe}(\mu\text{-Cl})]_2$ (**2**) in good yield. A crystal prepared in this manner was used for a single crystal X-ray diffraction study. Complex **2** crystallises with two independent molecules in the asymmetric unit. Both have crystallographic C_{2h} symmetry and essentially identical conforma-

tions — the maximum deviation of the best fit of the two molecules (excluding the isopropyl methyl groups) is 0.08 Å. Replacement of the apical chloride in **1** by a methyl group to give **2** has virtually no effect on the geometry of **2**, the central core (including the two chelate rings) fitting to within 0.1 Å of that in **1**, though the Cr–N distances are noticeably increased by ca. 0.04 Å (Table 1). The Cr–Me distances in the two independent molecules are 2.037(7) and 2.042(8) Å. The displacement of the chromium atom out of the basal plane in the direction of the apical methyl group (ca. 0.25 Å) is noticeably less than that towards the chloride in **1**. The nonbonded Cr...Cr separation is slightly reduced (ca. 3.66 Å). Within the chelate ring Cr and C(2) lie 0.52 and 0.14 Å out of the N(3)–C(4)–C(6)–N(7) plane (see Figure 1) in one independent molecule and 0.55 and 0.15 Å, respectively, in the other. Each of the 2,6-diisopropylphenyl rings are rotated by ca. 85° out of their respective chelate C–N–Cr planes, a conformation again stabilised by pairs of C–H...N(p_π) interactions; the C...N distances are in the range 2.87 to 3.00 Å with associated H...N distances of between 2.40 and 2.52 Å. As with **1**, there are no noteworthy intermolecular packing interactions.

Attempted alkylation of **1** with benzyl Grignard reagent, however, results in the reduction of **1** to give [(DDP)Cr(μ -Cl)]₂ (**3**) as a green solid in high yield. Recrystallisation of this solid from THF gives **3**(THF)₂·THF while from pentane **3-Bz-Bz** is obtained. Single crystals of both forms of **3** were obtained by cooling the corresponding solutions to –20 °C overnight. The X-ray analysis showed **3**(THF)₂·THF to be structurally related to **2**, having crystallographic C_{2h} symmetry (Figure 2) but with the apical methyl ligand replaced by a weakly bound THF molecule [Cr–O(20) = 2.442(3) Å, Table 2] which is disordered about the mirror plane which passes through Cr, Cr', O(20) and O(20'). The geometry at chromium is still square pyramidal with the chromium atom lying 0.13 Å out of the basal plane. The Cr–N distance [2.071(2) Å] is increased relative to that in **2** [av. 2.030 Å], although it still lies within the range observed for Cr–N bonds in the literature. The chelate rings retain a boat conformation with Cr and C(2) lying 0.43 and 0.12 Å, respectively, out of the N–C(1)–N'–C(1') plane. The non-bonded Cr...Cr separation is 3.67 Å and lies at the top end of the range reported for chloride-bridged dichromium(II) complexes.^[17,18] The 2,6-diisopropylphenyl rings are rotated by ca. 85° out of their respective chelate C–N–Cr planes, a conformation again stabilised by pairs of C–H...N(p_π) interactions; the C...N distances are in the range 2.91 to 2.94 Å with associated H...N distances of between 2.41 and 2.50 Å. There are no significant intermolecular close contacts between the complexes or the included THF solvent molecule.

In the structure of **3-Bz-Bz**, where there is an absence of apical substituents on the chromium centres, the geometry at chromium is square planar (Figure 3), although with a marked tetrahedral distortion, the N–N–Cr and Cr–Cl–Cl planes being inclined by 18°. The complex has crystallographic C_i symmetry and symmetric Cr–Cl bridges (Table 3). The Cr–N bond lengths are the same as

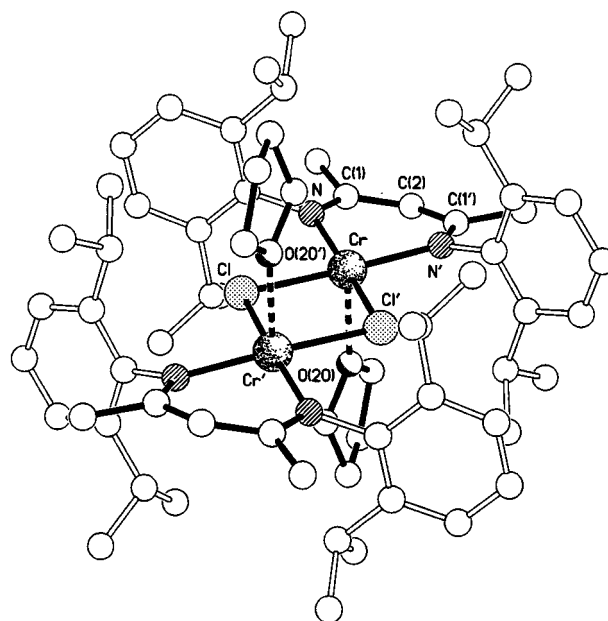


Figure 2. The molecular structure of the metal complex in **3**(THF)₂·THF

Table 2. Selected bond lengths (Å) and angles (°) for **3**(THF)₂·THF

Cr–Cl'	2.4182(6)	Cr–Cl	2.4182(6)
Cr–N	2.071(2)	Cr–N'	2.071(2)
Cr–O(20)	2.442(3)	N–C(1)	1.336(3)
N–Ar	1.450(3)	C(1)–C(2)	1.400(3)
C(2)–C(1')	1.400(3)		
N–Cr–N'	91.26(10)	N–Cr–Cl'	171.58(6)
N'–Cr–Cl'	93.37(5)	N–Cr–Cl	93.37(5)
N'–Cr–Cl	171.58(6)	Cl'–Cr–Cl	81.21(3)
N–Cr–O(20)	92.39(7)	N'–Cr–O(20)	92.39(7)
Cl'–Cr–O(20)	94.44(5)	Cl–Cr–O(20)	94.44(5)
Cr–Cl–Cr'	98.79(3)		

in **2**. The non-bonded Cr...Cr separation here is 3.60 Å, noticeably shorter than in **1**, **2** and **3**(THF)₂·THF. The chelate ring, whilst still having a boat conformation, is distinctly flattened in comparison to **1**, **2** and **3**(THF)₂·THF, with Cr and C(3) lying 0.30 and 0.09 Å, respectively, out of the N(1)–C(2)–C(4)–N(5) plane. The 2,6-diisopropylphenyl rings are rotated by 85 and 88° out of their respective chelate C–N–Cr planes, with associated C–H...N(p_π) interactions (C...N distances in the range 2.87 to 2.92 Å, H...N distances between 2.39 and 2.50 Å). There are no notable intermolecular packing interactions involving either the complex or the co-crystallised dibenzyl molecules.

It is noteworthy that complex **3**(THF)₂·THF can also be prepared more directly by treating CrCl₂·THF with one equivalent of LiDDP in THF.

The pathway by which **3** is formed from **1** is uncertain. However, it would seem possible that benzylation of the apical *trans* sites in **1** occurs initially to give the benzyl analogue of **2** in a manner similar to the benzylation of [Cp*CrCl(μ -Cl)]₂,^[13c] followed by isomerisation to the *cis* isomer and reductive coupling of benzyl groups to give **3** and di-

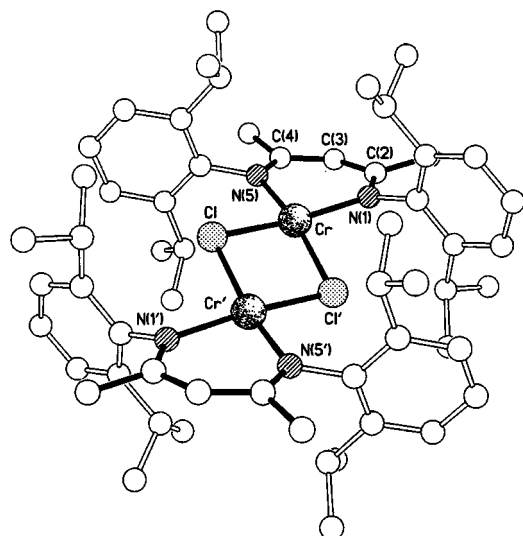


Figure 3. The molecular structure of the chromium-containing species in **3·Bz-Bz**

Table 3. Selected bond lengths (Å) and angles (°) for **3·Bz-Bz**

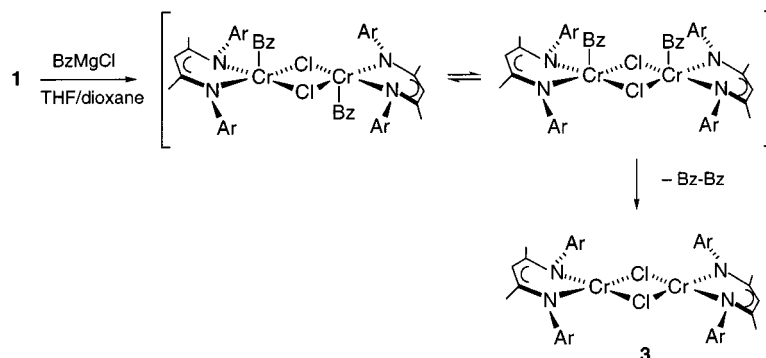
Cr–Cl	2.3877(9)	Cr–Cl'	2.3851(9)
Cr–N(1)	2.036(2)	Cr–N(5)	2.031(2)
N(1)–C(2)	1.331(4)	C(2)–C(3)	1.393(4)
C(3)–C(4)	1.400(4)	C(4)–N(5)	1.335(4)
N(5)–Cr–N(1)	90.93(10)	N(5)–Cr–Cl'	168.04(8)
N(1)–Cr–Cl'	94.54(7)	N(5)–Cr–Cl	95.21(7)
N(1)–Cr–Cl	165.75(8)	Cl–Cr–Cl'	81.95(3)
Cr–Cl–Cr'	98.05(3)		

benzyl (Scheme 2). It is noteworthy that Theopold has recently postulated a related *trans-cis* isomerisation of the related complex $[\text{Cp}^*\text{CrMe}(\mu\text{-Cl})_2]_2$.^[13a] However, we cannot rule out Wurtz coupling occurring independently of the transition metal centre in a way that is often observed during the preparation of benzylic Grignard reagents.^[19,20]

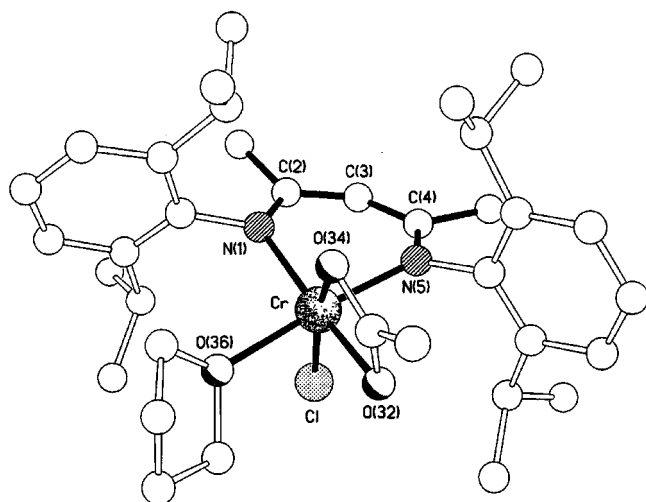
Whilst reaction of **1** with either AlMe_3 or BzMgCl results in preservation of the dimeric core, interaction with carboxylates or β -diketonates results in cleavage of the dimer to give discrete mononuclear chromium(III) complexes.

For example, treatment of **1** with NaO_2CR ($\text{R} = \text{Me}, \text{Ph}$) at -78°C gives the complexes $[(\text{DDP})\text{CrCl}(\text{O}_2\text{CR})(\text{THF})]$ ($\text{R} = \text{Me}$ **4a**, Ph **4b**) in high yield. Both **4a** and **4b** can be recrystallised from a concentrated pentane solution at -20°C . A single crystal of **4a** was subjected to an X-ray diffraction study. The structure of **4a** consists of an octahedral chromium centre with the oxygen atom of the THF ligand and one of the oxygen atoms of the acetate ligand in the same plane as the nitrogen atoms of the bidentate ligand; the remaining oxygen atom of the η^2 -chelating acetate group occupies a site *trans* to the chloride ligand (Figure 4). The structure of **4a** thus resembles that of the less sterically demanding diphenyl β -diketiminato complex $[\{\text{PhNC}(\text{Me})\text{CHC}(\text{Me})\text{NPh}\}\text{CrCl}_2(\text{THF})_2]$,^[61] with a THF and a chloride ligand effectively replaced by an acetate group. In **4a** the geometry at chromium is distorted with *cis* angles in the range $63.7(1)$ to $101.9(1)^\circ$, the acute angle being associated with the bite of the acetate ligand. The Cr–N distances (Table 4) are the same as in **2** and **3·BzBz**, and the Cr–Cl distance [$2.295(1)$ Å] is similar to that to the terminal chloride in **1**. The Cr–O(THF) distance [$2.119(3)$ Å] is consistent with the presence of a formal σ -bond, similar to that to the loosely associated apical ligand in $3(\text{THF})_2\cdot\text{THF}$ [$2.442(3)$ Å]. The six-membered chelate ring has a distinctive boat conformation with the chromium and C(3) lying 0.60 and 0.11 Å, respectively, out of the N(1)–C(2)–C(4)–N(5) plane. There are characteristic orthogonal orientations (83 and 87°) of the 2,6-diisopropylphenyl ring systems to the chelate ring. Stabilisation of this conformation is again by weak $\text{C}\cdots\text{H}\cdots\text{N}(\text{p}_\pi)$ interactions ($\text{C}\cdots\text{N}$ distances in the range 2.89 to 2.98 Å, $\text{H}\cdots\text{N}$ distances between 2.41 and 2.50 Å). The packing is normal van der Waals.

Compound **4b** is presumed to possess a similar structure to **4a**. Unlike the reactions of **1** with carboxylates, treatment of **1** with the more sterically demanding β -diketonates, $\{\text{CH}[\text{C}(\text{R})\text{O}]_2\}^-$ [$\text{R} = \text{Me}$ (acac), Ph (dbm)], results in the five-coordinate complexes $[(\text{DDP})\text{CrCl}\{\text{O}(\text{R})\text{C}_2\text{CH}\}]$ ($\text{R} = \text{Me}$ **5a**, Ph **5b**). Both **5a** and **5b** can be recrystallised from pentane at -20°C . Compound **5b** has been the subject of a single crystal X-ray diffraction study. This study shows **5b** to have a square pyramidal coordination geometry at chromium (Figure 5), with the basal sites occupied

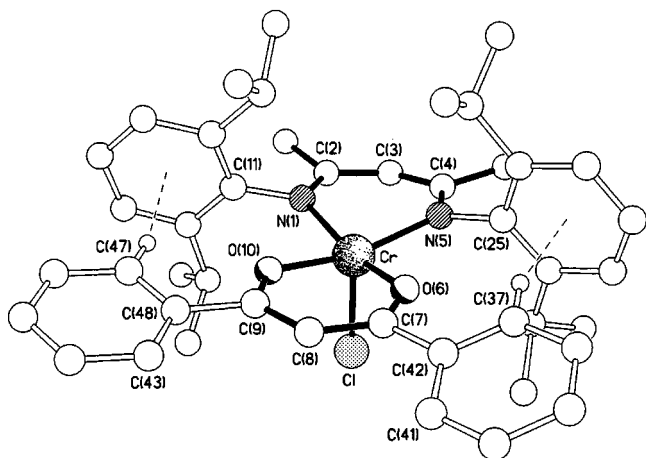


Scheme 2. Plausible pathway for the formation of **3** from **1**

Figure 4. The molecular structure of **4a**Table 4. Selected bond lengths (Å) and angles (°) for **4a**

Cr–Cl	2.2947(12)	Cr–N(1)	2.029(3)
Cr–N(5)	2.023(3)	Cr–O(32)	2.059(3)
Cr–O(34)	2.043(3)	Cr–O(36)	2.119(3)
N(1)–C(2)	1.330(5)	C(2)–C(3)	1.409(5)
C(3)–C(4)	1.383(5)	C(4)–N(5)	1.323(5)
N(5)–Cr–N(1)	90.37(12)	N(5)–Cr–O(34)	90.70(12)
N(1)–Cr–O(34)	101.90(12)	N(5)–Cr–O(32)	91.06(12)
N(1)–Cr–O(32)	165.52(12)	O(34)–Cr–O(32)	63.67(12)
N(5)–Cr–O(36)	174.12(12)	N(1)–Cr–O(36)	95.14(11)
O(34)–Cr–O(36)	86.16(12)	O(32)–Cr–O(36)	83.10(11)
N(5)–Cr–Cl	93.10(9)	N(1)–Cr–Cl	93.23(9)
O(34)–Cr–Cl	164.38(9)	O(32)–Cr–Cl	101.08(10)
O(36)–Cr–Cl	88.65(9)		

by the two η^2 ligands and the apical site by a chloride ligand. The metal atom lies 0.32 Å out of the basal plane (which is planar to within 0.002 Å) in the direction of the chloride ligand [Cr–Cl 2.229(1) Å]. The Cr–N distances (Table 5) are the same as in **2**, **3-Bz-Bz** and **4a**. The diketim-

Figure 5. The molecular structure of **5b**, showing also the weak intramolecular C–H... π stabilising interactionsTable 5. Selected bond lengths (Å) and angles (°) for **5b**

Cr–Cl	2.2294(14)	Cr–N(1)	2.020(3)
Cr–N(5)	2.032(3)	Cr–O(6)	1.958(3)
Cr–O(10)	1.961(3)	N(1)–C(2)	1.341(5)
C(2)–C(3)	1.387(6)	C(3)–C(4)	1.391(6)
C(4)–N(5)	1.329(5)		
O(6)–Cr–O(10)	86.89(11)	O(6)–Cr–N(1)	161.27(13)
O(10)–Cr–N(1)	87.83(12)	O(6)–Cr–N(5)	88.85(13)
O(10)–Cr–N(5)	161.63(13)	N(1)–Cr–N(5)	90.54(13)
O(6)–Cr–Cl	96.18(10)	O(10)–Cr–Cl	96.02(10)
N(1)–Cr–Cl	102.25(11)	N(5)–Cr–Cl	102.20(10)

inate chelate ring has, as in all the other complexes, a boat conformation with the chromium and C(3) lying 0.43 and 0.11 Å, respectively, out of the N(1)–C(2)–C(4)–N(5) plane. The Cr(dbm) chelate ring is much flatter, with the chromium and C(8) lying 0.23 and 0.02 Å, respectively, out of the O(6)–C(7)–C(9)–O(10) plane. The 2,6-diisopropylphenyl ring systems are, as usual, oriented orthogonally (83 and 86°) to the chelate ring, with C–H...N(p_π) stabilisation (C...N distances in the range 2.90 to 2.98 Å, H...N distances between 2.38 and 2.49 Å). In contrast, the planes of the two phenyl rings of the dbm ligand lie close to that of their chelate ring (twists of ca. 10 and 20°) and as a consequence direct one of their *ortho* C–H hydrogen atoms into the faces of their proximal 2,6-diisopropylphenyl rings of the diketiminate ligand; the H... π distances are short at 2.40 and 2.53 Å and have associated C–H... π angles of 168 and 160°, respectively. Accompanying this interaction is a noticeable contraction of both the O(6)–C(7)–C(42) and O(10)–C(9)–C(48) angles [115.8(3) and 116.2(3)°, respectively], and to a lesser extent also those for C(7)–C(42)–C(37) and C(9)–C(48)–C(47) [117.3(2) and 118.0(2)°, respectively], from normal trigonal values. These interactions are directly analogous to those present between the *ortho* hydrogen atoms of a dbm ligand coordinated to iridium and the phenyl rings of a pair of triphenylphosphane ligands coordinated to the same metal centre.^[21] There are no packing interactions of note.

Examples of mononuclear five-coordinate Cr^{III} complexes are rare, due to the significant ligand-field stabilisation of the d^3 configuration in an octahedral geometry.^[20] **5a** is presumed to possess a similar structure to **5b**.

All the complexes are paramagnetic, affording broad uninformative ¹H NMR spectra. The mononuclear complexes **4** and **5** exhibit magnetic moments between 3.8 and 4.1 BM (Evans Balance at ambient temperature) consistent with three unpaired electrons (d^3) while the dimeric chromium(III) complexes **1** and **2** display magnetic moments of 3.5 and 3.6 BM characteristic of antiferromagnetically coupled $S = 3/2$ chromium(III) centres.^[7f,23] In addition, the X-band EPR spectra of all the Cr^{III} complexes in toluene at ambient temperature all support the complexes being assigned Cr^{III} with sharp signals corresponding to g values of ca. 1.98 with no observable hyperfine coupling.^[24]

The FAB mass spectra of the mononuclear complexes **4** and **5** give molecular ion peaks and/or peaks corresponding

to fragmentation peaks. For the dimeric complexes **1–3** fragmentation of the dinuclear unit must readily occur in the instrument as only peaks attributable to mononuclear fragments are observed. This observation is consistent with the ready cleavage of the dimeric assembly in the presence of carboxylates or β -diketonates (see complexes **4** and **5**) leading to the prospect that **1–3** can be regarded as loosely associated monomers.

The results of Schlenk-scale ethylene polymerisation screening tests at 1 bar/25 °C using dual-component catalyst systems (**1–5** + cocatalyst) are collected in Table 6. Three types of aluminium co-catalyst have been employed to activate pre-catalysts **1–5**, namely methylaluminoxane (MAO), diethylaluminium chloride (DEAC) and dimethylaluminium chloride (DMAC) (see Table 6; runs 1–19). The results reported in Table 6 were reproduced several times, though not optimised beyond the conditions reported.

Table 6. Results of ethylene polymerisation runs using precatalysts **1–5**^[a]

Run	Precatalyst (mmol)	Activator ^[b] (mmol/ equiv.)	Yield PE (g) ^[c]	Activity (g/mmol·h·bar)
1	1 (0.015)	MAO (6.0/400)	0.12	4 ^[d]
2	1 (0.015)	DEAC (0.45/30)	2.25	75 ^[d]
3	2 (0.015)	MAO (6.0/400)	0.30	10 ^[d]
4	2 (0.015)	DEAC (0.45/30)	1.60	54 ^[d]
5	3 (0.015)	MAO (6.0/400)	0.24	8 ^[d]
6	3 (0.015)	DEAC (0.45/30)	2.16	72 ^[d]
7	3 (0.015)	DMAC (0.45/30)	2.37	79 ^[d]
8	4a (0.015)	MAO (6.0/400)	0.05	3
9	4a (0.015)	DEAC (0.45/30)	1.77	118 ^[e]
10	4a (0.015)	DMAC (0.45/30)	1.05	70
11	4b (0.01)	MAO (4.0/400)	0.13	13
12	4b (0.01)	DEAC (0.3/30)	0.85	85
13	4b (0.01)	DMAC (0.3/30)	0.93	93
14	5a (0.015)	MAO (6.0/400)	0.30	20
15	5a (0.015)	DEAC (0.45/30)	1.48	49
16	5a (0.015)	DMAC (0.45/30)	1.61	54
17	5b (0.015)	MAO (6.0/400)	0.15	10
18	5b (0.015)	DEAC (0.45/30)	0.84	56
19	5b (0.015)	DMAC (0.45/30)	1.20	80

^[a] General conditions: 1 bar ethylene Schlenk test carried out in toluene (40 mL) at 25 °C, over 60 min., reaction quenched with dil HCl and the solid washed with methanol (50 cm³) and dried in a vacuum oven at 40 °C. – ^[b] MAO = methylaluminoxane. – ^[c] Solid polyethylene. – ^[d] Activity reported per chromium centre. – ^[e] As a representative example, GPC analysis of the polyethylene afforded $M_w = 925000$, $M_n = 110000$, $M_w/M_n = 8.4$. Care should be taken in the interpretation of these values, however, since, in general, the polymers derived from these polymerizations are not fully soluble in the 1,2,4-trichlorobenzene GPC solvent, even upon heating at 160 °C for several hours.

On analysis of Table 6 several points emerge. Firstly, all DDP-supported chromium complexes are active in the presence of alkylaluminum activator, converting ethylene to high molecular weight polyethylene. In no case has polyethylene been obtained using **1–5** in the absence of an aluminium activator, nor has there been any evidence for low molecular weight oligomers (by GCMS). Secondly, the

most active systems (runs 9 and 13) comprise a combination of one equivalent of chromium complex to thirty equivalents of alkylaluminum chloride activator. We have found that activities start to fall with a greater or lower concentration of activator. Notably, MAO (400 equiv.) results in lower activities (runs 1, 3, 5, 8, 11, 14, 17). Thirdly, the similar activities [*cf.* 75 (run 2), 72 g/mmol·h·bar (run 6)] observed employing the DDP-supported Cr^{III}- and Cr^{II}-chloride complexes **1** and **3**, and the purple colour of the active catalyst (in both cases), suggest a common active species.

The mechanism by which these dual component systems operate is uncertain. The fact that the most active systems combine an alkylaluminum chloride rather than MAO rather suggests that alkyl abstraction to form a cationic species is not occurring here. This may account for the generally lower activities observed by comparison with the Cp-amine systems reported by Jolly where a cationic active centre is believed to operate. The identity of the active oxidation state is uncertain but the similarity in productivities and reactivity involving the Cr^{II} and Cr^{III} complexes **1** and **3**, coupled with the ready reduction of **1** on benzylation, lends some support for a Cr^{II} species.

Conclusions

The chemistry of the sterically demanding β -diketiminato ligand DDP on low valent chromium has been explored. Complexation of DDP with CrCl₃(THF)₃ leads to a readily derivatisable coordinatively unsaturated dimeric species **1**. Preservation of the dimeric core occurs on alkylation or reduction of **1**, while addition of chelating carboxylate or β -diketonate ligands to **1** causes fragmentation to give discrete mononuclear complexes. Notably, only in the case of **4** is the more common octahedral geometry of Cr^{III} achieved. All the complexes polymerise ethylene on addition of aluminium activators to give high molecular weight polyethylene.

Experimental Section

General: All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Imperial College and Medac Ltd. NMR spectra were recorded on a Bruker spectrometer at 250 MHz (¹H) and 62.9 MHz (¹³C) at room temperature; chemical shifts are referenced to the residual protonated impurity of the deuterated solvent. IR spectra (nujol mulls, KBr/CsI windows) were recorded on Perkin–Elmer 577 and 457 grating spectrophotometers. Mass spectra were obtained using fast atom bombardment (FAB). Gel permeation chromatographs (GPC) were obtained using a Waters 150CV [columns are supplied by Shodex (807, 806 & 804) BP Chemicals Ltd.]. Magnetic Susceptibility studies were performed using an Evans Balance at room temperature. Diamagnetic corrections for the samples were determined from Pascal's constants and literature values.^[25]

$\text{CrCl}_3(\text{THF})_3$ [26] and $\text{DDPH}^{[8b]}$ were prepared according to the established procedures. The reagents AlMe_3 (2.0 M solution in toluene), Et_2AlCl (1.8 M solution in toluene), Me_2AlCl (1.0 M solution in hexane), MAO (10% solution in toluene) and BzMgCl (2.0 M solution in THF) were purchased from Aldrich Chemical Co. All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparation of $[(\text{DDP})\text{CrCl}(\mu\text{-Cl})_2]$ (1): $\text{CrCl}_3(\text{THF})_3$ (1.00 g, 2.67 mmol) was loaded into a Schlenk flask containing one equivalent of the lithium salt of DDPH (1.13 g, 2.67 mol) in THF (40 mL) at -78°C . The solution was stirred overnight at room temperature giving an olive green solution. The volatiles were removed under reduced pressure and pentane (50 mL) added. Filtration of the lithium salts gave the crude product which was recrystallised by standing at -20°C overnight to give **1** (1.08 g, 75%). FAB-MS: $m/z = 504$ [$\text{M}^+ / 2$]. $-\text{C}_{58}\text{H}_{82}\text{Cl}_4\text{Cr}_2\text{N}_4$ (1081.1): calcd. C 64.44, H 7.59, N 5.19; found C 64.65, H 7.81, N 5.41. $-\mu_{\text{eff}} = 3.60$ BM.

Preparation of $[(\text{DDP})\text{CrMe}(\mu\text{-Cl})_2]$ (2): A THF (40 mL) solution of **1** was formed as above by stirring $\text{CrCl}_3(\text{THF})_3$ (1.00 g, 2.67 mmol) and LiDDP (1.13 g, 2.67 mol) together overnight. AlMe_3 (2.5 mL, 5.0 mmol) was introduced to the green solution with a syringe at room temperature. After stirring overnight the solution was taken to dryness to give a dark oily residue. Extraction with pentane (60 mL) followed by filtration gave a dark purple solution. Concentration of the solution to half volume and standing at -20°C gave **2** as crimson needles (0.94 g, 68%). FAB-MS: $m/z = 469$ [$\text{M}^+ / 2 - \text{Me} - \text{Cl}$]. $-\text{C}_{60}\text{H}_{88}\text{Cl}_2\text{Cr}_2\text{N}_4$ (1040.3): calcd. C 69.30, H 8.47, N 5.39; found C 69.41, H 8.81, N 5.82. $-\mu_{\text{eff}} = 3.50$ BM.

Preparation of $[(\text{DDP})\text{Cr}(\mu\text{-Cl})_2]$ (3): A THF (40 mL) solution of **1** was formed as above by stirring $\text{CrCl}_3(\text{THF})_3$ (1.00 g, 2.67 mmol) and LiDDP (1.13 g, 2.67 mol) together overnight. Benzylmagnesium chloride (2.67 mL, 5.34 mmol) was added to the green solution at -78°C with a syringe and the solution allowed to warm to room temperature to give an apple green solution. Dioxane (2 mL) was added to the solution after 12 h, stirred for a further 2 h and filtered to give an apple green solution. The complex $3(\text{THF})_2\cdot\text{THF}$ (1.09 g, 71%) could be isolated as lime green crystals by cooling the apple green THF/dioxane solution to -20°C . Alternatively, **3-Bz-Bz** (1.03 g, 65%) could be isolated as green crystals by stripping the volatiles from the reaction mixture and extracting the residue with pentane and cooling the solution to -20°C .

$3(\text{THF})_2\cdot\text{THF}$: $\text{C}_{66}\text{H}_{98}\text{Cl}_2\text{Cr}_2\text{N}_4\text{O}_2$ (1154.4): calcd. C 68.69, H 8.50, N 4.86; found C 68.81, H 8.70, N 4.69. $-\text{FAB-MS: } m/z = 469$ [$\text{M}^+ / 2 - \text{Cl} - \text{THF}$].

****3-Bz-Bz**:** $\text{C}_{72}\text{H}_{96}\text{Cl}_2\text{Cr}_2\text{N}_4$ (1192.5): calcd. C 72.54, H 8.06, N 4.70; found C 72.71, H 8.34, N 4.69. $-\text{FAB-MS: } m/z = 469$ [$\text{M}^+ / 2 - \text{Cl} - \text{C}_6\text{H}_5\text{CH}_2$].

Preparation of $[(\text{DDP})\text{CrCl}(\text{O}_2\text{CR})(\text{THF})]$ (R = Me **4a, Ph **4b**):** To a THF (40 mL) solution of the lithium salt of DDPH (1.13 g, 2.67 mmol) at -78°C was added $\text{CrCl}_3(\text{THF})_3$ (1.00 g, 2.67 mmol). The solution was allowed to warm to room temperature and stirred for 3 h before the addition of sodium acetate (0.22 g, 2.67 mmol) or sodium benzoate (0.38 g, 2.67 mmol) at -78°C . The solutions were allowed to warm to room temperature and stirred for a further 12 h. After removal of the solvent under reduced pressure, pentane (60 mL) was introduced and the lithium salts filtered. Concentration of the filtrates to half volume and cooling to -20°C overnight gave **4a** (0.68 g, 45%) and **4b** (0.85 g, 49%) as green crystals.

4a: FAB-MS: $m/z = 563$ [$\text{M}^+ - \text{THF}$], 528 [$\text{M}^+ - \text{Cl} - \text{THF}$], 467 [$\text{M}^+ - \text{Cl} - \text{THF} - \text{O}_2\text{CMe}$]. $-\text{C}_{35}\text{H}_{52}\text{ClN}_2\text{O}_2$ (568.26): calcd. C

66.09, H 8.18, N 4.41; found C 66.12, H 8.41, N 4.29. $-\mu_{\text{eff}} = 3.80$ BM.

4b: FAB-MS: $m/z = 696$ [M^+], 590 [$\text{M}^+ - \text{Cl} - \text{THF}$], 467 [$\text{M}^+ - \text{Cl} - \text{THF} - \text{O}_2\text{CPh}$]. $-\text{C}_{40}\text{H}_{54}\text{ClCrN}_2$ (650.33): calcd. C 68.82, H 7.74, N 4.01; found C 68.91, H 7.89, N 3.98. $-\mu_{\text{eff}} = 3.74$ BM.

Preparation of $[(\text{DDP})\text{CrCl}\{\text{O}(\text{R})\text{C}_2\text{CH}\}]$ (R = Me **5a**, Ph **5b**):

To a THF (40 mL) solution of the lithium salt of DDPH (1.13 g, 2.67 mmol) at -78°C was added $\text{CrCl}_3(\text{THF})_3$ (1.00 g, 2.67 mmol). The solution was allowed to warm to room temperature and stirred for 3 h before the addition of the lithium salts of either 2,4-pentanedione (0.28 g, 2.67 mmol) or dibenzoylmethane (0.61 g, 2.67 mmol) at -78°C . The solutions were allowed to warm to room temperature and stirred for a further 12 h. After removal of the solvent under reduced pressure pentane (60 mL) was introduced and the lithium salts filtered. Concentration of the filtrates to half volume and cooling to -20°C overnight gave **5a** (0.72 g, 45%) and **5b** (0.99 g, 51%) as red crystals.

5a: FAB-MS: $m/z = 568$ [$\text{M}^+ - \text{Cl}$], 419 [$\text{M}^+ - \text{Cl} - \{\text{O}(\text{Me})\text{C}_2\text{CH} - \text{Cr}\}$]. $-\text{C}_{34}\text{H}_{48}\text{ClCrN}_2\text{O}_2$ (604.21): calcd. C 67.61, H 7.95, N 4.64; found C 67.30, H 8.01, N 4.44. $-\mu_{\text{eff}} = 4.06$ BM.

5b: FAB-MS: $m/z = 692$ [$\text{M}^+ - \text{Cl}$], 419 [$\text{M}^+ - \text{Cl} - \{\text{O}(\text{Ph})\text{C}_2\text{CH} - \text{Cr}\}$]. $-\text{C}_{44}\text{H}_{52}\text{ClCrN}_2\text{O}_2$ (728.36): calcd. C 72.58, H 7.15, N 3.85; found C 73.71, H 6.99, N 3.78. $-\mu_{\text{eff}} = 3.80$ BM.

Polymerisation Procedure: Results of Schlenk-line tests (1 bar) are listed in Table 6; the polymerisation procedure is as follows: The precatalyst (0.01–0.015 mmol of **1–5**) was dissolved in toluene (40 mL) and the co-catalyst (MAO, DEAC or DMAC) added. The Schlenk tube was purged with ethylene and the contents magnetically stirred and maintained under ethylene (1 bar) for the duration of the polymerisation. After 1 h the polymerisation was terminated by the addition of dil. HCl/MeOH . The solid polyethylene was recovered by filtration, washed with methanol (50 mL) and dried (vacuum oven at 50°C).

X-ray Crystal Structure Determinations of **1, **2**, $3(\text{THF})_2\cdot\text{THF}$, **3-Bz-Bz**, **4a**, and **5b**:** Table 7 provides a summary of the crystal data, data collection, and refinement parameters for compounds **1**, **2**, $3(\text{THF})_2\cdot\text{THF}$, **3-Bz-Bz**, **4a** and **5b**.

The structures were solved by direct methods, and the major occupancy non-hydrogen atoms were refined anisotropically using full-matrix, least-squares based on F^2 . In **1**, **2**, $3(\text{THF})_2\cdot\text{THF}$ and **4a** disorder was found in the solvent molecules; in each case two partial occupancy orientations were identified with, in **1**, $3(\text{THF})_2\cdot\text{THF}$ and **4a**, the major occupancy non-hydrogen atoms refined anisotropically and the minor occupancy non-hydrogen atoms refined isotropically, and in **2** all the disordered non-hydrogen atoms refined anisotropically. Throughout all six structures the C–H hydrogen atoms of methyl groups bound to sp^2 centres were located from ΔF maps, idealised, assigned isotropic thermal parameters [$U(\text{H}) = 1.5U_{\text{eq}}(\text{C})$] and allowed to ride on their parent atoms. The remaining hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters [$U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$; $U(\text{H}) = 1.5U_{\text{eq}}(\text{C-Me})$], and allowed to ride on their parent atoms. All computations were carried out using the SHELXTL PC program system.^[27]

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no's: CCDC-150447–150452 for structures **1–5b**, respectively (Table 7). Copies of the data can be obtained free of charge on application to CCCD, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 7. Crystal data, data collection and refinement parameters for compounds **1**, **2**, **3(THF)₂·THF**, **3-Bz-Bz**, **4a** and **5b**^[a]

	1	2	3(THF)₂·THF	3-Bz-Bz	4a	5b
Formula	C ₅₈ H ₈₂ N ₄ Cl ₄ Cr ₂	C ₆₀ H ₈₈ N ₄ Cl ₂ Cr ₂	C ₅₈ H ₈₂ N ₄ Cl ₂ Cr ₂	C ₅₈ H ₈₂ N ₄ Cl ₂ Cr ₂	C ₃₅ H ₅₂ N ₂ O ₃ ClCr	C ₄₄ H ₅₂ N ₂ O ₂ ClCr
Solvent	C ₅ H ₁₂	0.5C ₅ H ₁₂	3C ₄ H ₈ O	PhCH ₂ CH ₂ Ph	—	—
Molecular weight	1153.2	1076.3	1226.5	1192.4	636.2	728.3
Colour, habit	black blocks	crimson prismatic needles	green octahedra	green blocks	red prismatic needles	orange/red prisms
Crystal size/mm	0.23 × 0.10 × 0.07	0.33 × 0.17 × 0.13	0.73 × 0.67 × 0.67	0.67 × 0.50 × 0.33	0.90 × 0.27 × 0.27	0.57 × 0.40 × 0.23
Crystal system	monoclinic	monoclinic	tetragonal	triclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>C</i> 2/ <i>m</i> (no. 12)	<i>P</i> 4 ₂ / <i>m</i> (no. 84)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 1̄ (no. 2)
<i>T</i> /K	203	203	203	183	203	203
<i>a</i> /Å	13.581(3)	19.434(3)	13.036(2)	12.034(1)	8.935(2)	11.140(1)
<i>b</i> /Å	13.547(3)	21.764(2)	—	12.564(1)	17.001(2)	12.780(2)
<i>c</i> /Å	17.553(2)	15.098(2)	20.134(2)	13.637(1)	23.258(2)	14.712(3)
<i>a</i> /deg	—	—	—	97.37(1)	—	76.52(1)
<i>β</i> /deg	104.28(2)	90.58(1)	—	114.72(1)	97.66(1)	84.97(1)
<i>γ</i> /deg	—	—	—	110.28(1)	—	80.50(1)
<i>V</i> /Å ³	3130(1)	6386(1)	3421.3(7)	1663.9(1)	3501.2(8)	2006.2(5)
<i>Z</i>	2 ^[b]	4 ^[c]	2 ^[d]	1 ^[b]	4	2
<i>D_c</i> /g cm ^{−3}	1.224	1.120	1.191	1.190	1.207	1.206
<i>F</i> (000)	1232	2316	1320	638	1364	774
Radiation used	Cu- <i>K</i> _α ^[e]	Cu- <i>K</i> _α ^[e]	Mo- <i>K</i> _α	Cu- <i>K</i> _α ^[e]	Mo- <i>K</i> _α	Mo- <i>K</i> _α
μ/mm ^{−1}	4.73	3.85	0.44	3.75	0.44	0.39
θ range/deg	3.4–58.0	2.9–60.0	1.9–30.0	6.3–63.0	1.8–25.0	1.9–25.0
No. of unique reflections measured	4293	4866	5101	5228	6111	6954
observed, $ F_o > 4σ(F_o)$	2823	3370	3603	4547	3963	4296
Absorption correction	semi-empirical	—	—	semi-empirical	semi-empirical	—
Max., min. transmission	0.58, 0.41	—	—	0.35, 0.21	0.90, 0.83	—
No. of variables	353	340	245	350	383	427
<i>R</i> ₁ , <i>wR</i> ₂ ^[f]	0.067, 0.153	0.065, 0.164	0.056, 0.128	0.056, 0.142	0.054, 0.109	0.058, 0.112

^[a] Details in common: graphite monochromated radiation, ω-scans, Siemens P4 diffractometer, refinement based on *F*². — ^[b] The molecule has crystallographic *C_i* symmetry. — ^[c] There are two crystallographically independent *C_{2h}* symmetric molecules in the asymmetric unit. — ^[d] The molecule has crystallographic *C_{2h}* symmetry. — ^[e] Rotating anode source. — ^[f] *R*₁ = Σ||*F*_o| − |*F*_c||/Σ|*F*_o|; *wR*₂ = [Σ *w*(*F*_o² − *F*_c²)/Σ *w*(*F*_o²)]^{1/2}; *w*^{−1} = σ²(*F*_o²) + (*aP*)² + *bP*.

Acknowledgments

BP-Amoco Chemicals Ltd is thanked for financial support. Drs. J. Boyle and G. Audley are thanked for NMR and GPC measurements, respectively.

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Received November 20, 2000
[I00438]