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FULL PAPER

Chromium complexes bearing pyrrolide-imine *N*,*N*-chelate ligands: synthesis, structures and ethylene polymerisation behaviour†

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Chromium(II) and chromium(III) complexes bearing two bulky monoanionic *N,N*-chelating pyrrolide-imine ligands, $\{ArN{=}CH(C_4H_3N\text{-}2)\}_2Cr$ (**1**) and $\{ArN{=}CH(C_4H_3N\text{-}2)\}_2Cr(\mu\text{-}Cl)_2Li(THF)_2$ (**2**), have been prepared in high yield by treatment of the sodium and lithium salts of $ArN{=}CH(C_4H_3NH\text{-}2)$ ($Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$) with $CrCl_2(THF)$ and $CrCl_3(THF)_3$, respectively. The molecular structure of **1** reveals a square planar geometry about chromium with the pyrrolide-N units disposed mutually *trans*. Conversely, an octahedral geometry is exhibited by the chromium centre in **2** with mutually *cis*-oriented pyrrolide-N units and *cis*-chloride ligands which, in turn, link to a $Li(THF)_2$ unit. Complex **2** can be alkylated with AlR_3 to give the five-coordinate mono-alkyl species $\{ArN{=}CH(C_4H_3N\text{-}2)\}_2CrR$ (**3a** R = Me; **3b** R = Et), in which two pyrrolide-imine ligands occupy the square base of the square pyramidal chromium centre. Complexes **1**–**3** behave as ethylene polymerisation catalysts upon treatment with an excess of a range of aluminium activators including MAO, Et_2AlCl and Me_2AlCl, converting ethylene to high molecular weight polyethylene. In all cases the dialkylaluminium chlorides are superior co-catalysts to MAO, affording acitivities up to 120 g $mmol^{-1}$ h^{-1} bar^{-1}. The coordinatively unsaturated bis(pyrrolide-imine) chromium alkyl complexes **3a** and **3b** are inactive for the polymerisation of ethylene in the absence of activator.

Introduction

Recent years have seen growing interest in the development of new highly active, well-defined catalysts for olefin polymerisation based on both early and late transition metals.[1] Central to these developments has been the design of new ligand frames that can be readily tailored to influence the properties of the resultant polymers. Some notably successful ligands are those containing the unsaturated imino donor functionality. Examples include α-diimines (Ni, Pd),[2] bis(imino)pyridines (Fe, Co)[3] and phenolate-imines (Ni[4] and Group 4 metals.[5])

Notwithstanding the industrial significance of chromium in heterogeneous polymerisation catalysis,[6] the development of molecular-based chromium catalysts for olefin polymerisation has progressed more slowly than for other metals and is based principally on low valent half-sandwich chromium(III) species[7] along with a limited number of non-cyclopentadienyl chromium(VI)[8] and chromium(III) systems.[9–11] We have been interested in the use of sterically demanding mono-anionic bidentate ligands as supports for chromium catalysts in low oxidation states.[10] In an earlier communication we described chromium complexes containing two *N,N*-chelating pyrrolide-imine ligands as ethylene polymerisation catalysts.[11] Such ligands have more recently been reported to give rise to active polymerisation catalysts when attached to Group 4 metals.[12,13]

In this article we present full synthetic and characterisation details for chromium pre-catalysts containing pyrrolide-imine ligands, along with the results of ethylene polymerisation studies.

Results and discussion

The pyrrole-imine, $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CH(C_4H_3NH\text{-}2)$, was prepared in high yield as a white solid by the condensation reaction of pyrrole-2-carboxaldehyde with one equivalent of 2,6-diisopropylaniline in refluxing diethyl ether in the presence of a catalytic amount of glacial acetic acid (Scheme 1). Compound $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CH(C_4H_3NH\text{-}2)$ has been characterised by microanalysis, ^1H, ^{13}C NMR spectroscopy along with mass spectrometry (see Experimental section).

The ^1H NMR spectrum of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CH(C_4H_3NH\text{-}2)$ in $CDCl_3$ exhibits a resonance at δ 7.91 for the imine C*H* proton, with the corresponding ^{13}C NMR signal occurring at δ 153.2. Compound $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CH(C_4H_3NH\text{-}2)$ also displays three signals between δ 6.41 and 5.97 in the ^1H NMR spectrum characteristic of the pyrrole ring protons, whilst the N*H* proton of the pyrrole ring appears downfield at δ 11.59. The infrared absorption band of the imine is clearly visible at 1623 cm^{-1}, and a molecular ion peak is observed in the EI mass spectrum at 254 amu.

Reaction of two equivalents of the sodium salt of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CH(C_4H_3NH\text{-}2)$ (prepared by treatment with NaH) with $CrCl_2{\cdot}THF$ in THF at ambient temperature afforded, after work-up, air sensitive orange crystalline $\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CH(C_4H_3N\text{-}2)\}_2Cr$ (**1**) in high yield (Scheme 1). Crystals of **1** were grown from petroleum ether (bp 40–60 °C) at 253 K. The molecular structure is shown in Fig. 1; selected bond lengths and angles are listed in Table 1. The molecule is monomeric and has non-crystallographic C_2 symmetry. The geometry at chromium is distorted square planar with *cis* angles in the range 81.8(2) to 98.4(2)°, the coordination sphere being planar to within 0.002 Å; the five-membered chelate rings are co-planar to within 0.012 Å. The pyrrolide-N units of each ligand are

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† Electronic supplementary information (ESI) available: a plot of the molecular structure of **3a**. See http://www.rsc.org/suppdata/dt/b2/b204568k/

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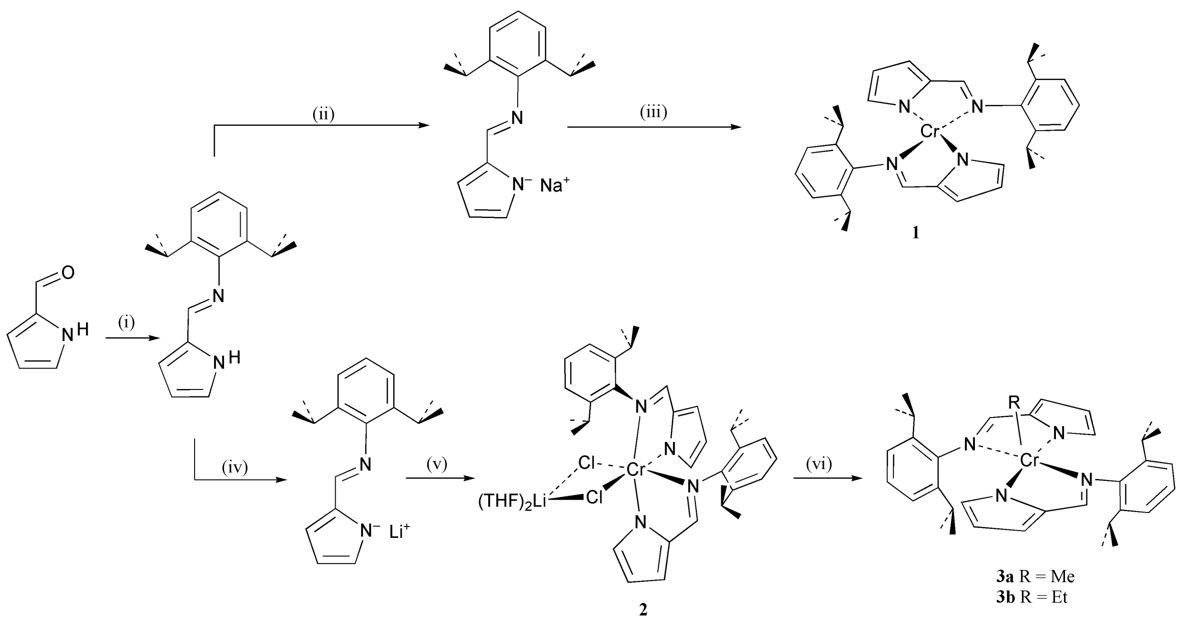

Scheme 1 Reagents and conditions: (i) 2,6-*i*-$Pr_2C_6H_3NH_2$, Et_2O, H^+, 308 K; (ii) NaH, THF; (iii) 1/2 $CrCl_2$·THF, THF, 293 K; (iv) *n*-BuLi, THF, 195 K; (v) 1/2 $CrCl_3$·3THF, THF, 195 K; (vi) AlR_3 (R = Me, Et), THF, 293 K.

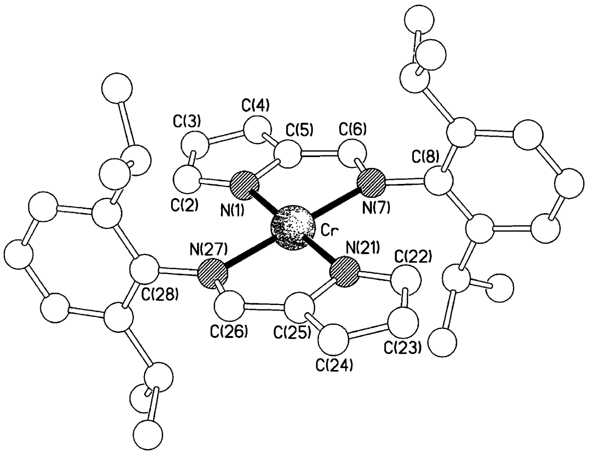

Fig. 1 The molecular structure of **1**.

Table 1 Selected bond lengths [Å] and angles [°] for complex **1**

Cr–N(27)	2.069(4)	Cr–N(1)	2.073(4)
Cr–N(21)	2.078(4)	Cr–N(7)	2.085(4)
N(21)–C(25)	1.389(6)	N(1)–C(5)	1.382(7)
C(6)–N(7)	1.291(7)	C(26)–N(27)	1.281(7)
C(5)–C(6)	1.413(7)	C(25)–C(26)	1.423(7)
N(27)–Cr–N(1)	98.4(2)	N(27)–Cr–N(21)	82.1(2)
N(27)–Cr–N(7)	179.7(2)	N(1)–Cr–N(7)	81.8(2)
N(1)–Cr–N(21)	179.5(2)	N(21)–Cr–N(7)	97.7(2)

oriented mutually *trans* and the Cr–N distances are comparable with those of related Cr(II) complexes containing chelating nitrogen donor ligands.[14] The imino linkages within the chelate rings retain their double bond character [C(6)–N(7) 1.291(7) Å, C(26)–N(27) 1.281(7) Å]. The 2,6-diisopropyl rings are oriented virtually orthogonally (*ca.* 86°) to the planes of their associated five-membered metallocyclic rings.

Complex **1** is paramagnetic with a magnetic moment of 4.81 μ_B (Evans Balance at ambient temperature) indicating a high spin d^4 electronic configuration for the divalent chromium centre. As with most divalent chromium compounds, **1** showed a poorly resolved and uninformative EPR spectrum. Although **1** is paramagnetic the ^1H NMR spectrum was recorded and broad unassignable resonances could be observed in the range δ 14 to −1. The infrared absorption for the imine C=N stretch is observed at 1591 cm^{-1}. Microanalysis and FAB mass spectrometry of **1** are consistent with its formulation.

The preparation of $\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CH(C_4H_3N\text{-}2)\}_2Cr(\mu\text{-}Cl)_2Li(THF)_2$ (**2**) was carried out in THF by reacting $CrCl_3$·3THF with the lithium salt of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CH(C_4H_3NH\text{-}2)$ in a 1 : 2 molar ratio at 195 K (Scheme 1). Complex **2** was isolated in good yield and in crystalline form as an air sensitive compound. Although elemental analyses on the bulk sample indicate some contamination by the monochloride species, orange/red crystals of **2**, suitable for X-ray diffraction, can be grown from a pentane solution at ambient temperature. The molecular structure is illustrated in Fig. 2; selected bond lengths and angles are listed in Table 2.

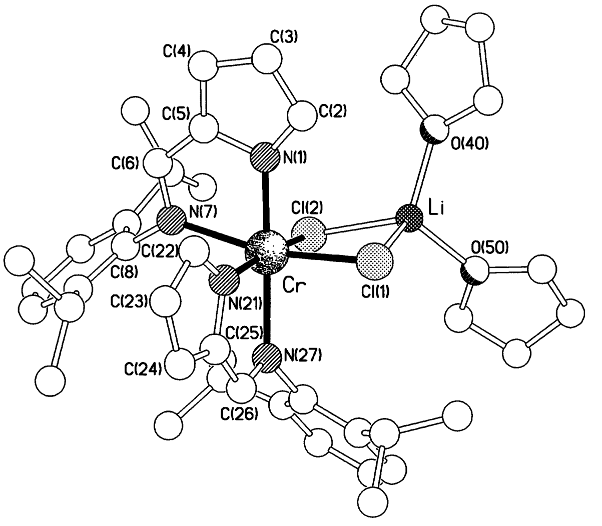

Fig. 2 The molecular structure of **2**. The transannular Cr ··· Li distance is 3.26(2) Å.

The structure of **2** consists of an octahedral Cr(III) centre coordinated to two *N*,*N*′-chelating pyrrolide-imine ligands and two *cis*-chloride groups. Unlike in **1**, here the pyrrolide functionalities of each ligand are oriented mutually *cis* with the *trans* sites occupied by an imine-N unit and a chloride ligand. The main distortions from octahedral geometry arise from the bite angles of the two chelating ligands [N(1)–Cr–N(7) 78.5(3), N(21)–Cr–N(27) 78.8(3)°], and a noticeable asymmetry in the

Table 2 Selected bond lengths [Å] and angles [°] for complex **2**

Cr–N(21)	2.005(7)	Cr–N(1)	2.011(7)
Cr–N(7)	2.188(6)	Cr–N(27)	2.149(6)
Cr–Cl(1)	2.349(2)	Cr–Cl(2)	2.354(3)
N(1)–C(5)	1.371(10)	C(5)–C(6)	1.394(11)
N(21)–C(25)	1.380(10)	C(25)–C(26)	1.425(11)
C(26)–N(27)	1.287(9)	C(6)–N(7)	1.286(9)
Li–O(40)	1.91(2)	Li–O(50)	1.92(2)
Li–Cl(1)	2.35(2)	Li–Cl(2)	2.31(2)
N(21)–Cr–N(1)	88.7(3)	N(21)–Cr–N(27)	78.8(3)
N(21)–Cr–N(7)	88.5(2)	N(1)–Cr–N(7)	78.5(3)
N(1)–Cr–N(27)	166.6(3)	N(27)–Cr–N(7)	105.5(2)
N(21)–Cr–Cl(1)	93.2(2)	N(1)–Cr–Cl(1)	88.4(2)
N(7)–Cr–Cl(1)	166.7(2)	N(21)–Cr–Cl(2)	172.2(2)
N(27)–Cr–Cl(2)	94.2(2)	N(7)–Cr–Cl(2)	90.2(2)
N(27)–Cr–Cl(1)	87.7(2)	N(1)–Cr–Cl(2)	98.6(2)
O(40)–Li–O(50)	108.6(8)	O(40)–Li–Cl(2)	112.2(8)
O(40)–Li–Cl(1)	119.0(8)	O(50)–Li–Cl(1)	110.9(8)
O(50)–Li–Cl(2)	114.7(8)	Cl(2)–Li–Cl(1)	90.7(6)
Cr–Cl(1)–Li	87.8(4)	Li–Cl(2)–Cr	88.6(4)
Cl(1)–Cr–Cl(2)	89.87(9)		

Cr–N distances with those to the pyrrolide nitrogen atoms being significantly shorter [Cr–N(1) 2.011(7), Cr–N(21) 2.005(7) Å], than those to the imino-nitrogens [Cr–N(27) 2.149(6), Cr–N(7) 2.188(6) Å]. The two five-membered chelate rings have different conformations with that containing N(1) having an envelope conformation and a *ca.* 11° fold about the N(1) ··· N(7) vector whereas that containing N(21) is essentially planar. The two chlorines are further coordinated to a solvated Li centre, the $CrLiCl_2$ ring having a slightly folded geometry with the Li atom lying 0.53 Å out of the $CrCl_2$ plane. The geometry at Li is distorted tetrahedral with angles ranging between 90.7(6) and 119.0(8)°, the most 'acute' angle being that subtended by the two Cl atoms. The only intermolecular packing contact of note is a C–H ··· π interaction (H ··· π 2.68 Å, C–H ··· π 155°) between C(23)–H in one molecule and the C(8)-containing 2,6-diisopropylphenyl ring of another.

It would appear that the steric congestion imposed by the bulky aryl substituents in the pyrrolide-imine ligands in **2** is responsible for preventing the binding of three ligands in a manner that has been observed in related complexes.[15] Surprisingly, the preferred octahedral geometry for Cr(III) is achieved by the inclusion of a molecule of lithium chloride (as a THF solvate).[16] Presumably, the bulky ligand substituents prevent dimerisation from occurring. It is worthy of note that, for the related titanium complexes $\{RN{=}CH(C_4H_3N\text{-}2)\}_2TiCl_2$ (R = Ph, Et, Cy), the only isomers isolated are those in which the pyrrolide moieties are mutually *trans*.[12] Indeed, for $\{PhN{=}CH(C_4H_3N\text{-}2)\}_2TiCl_2$ this configuration has been shown by calculations (DFT) to be more stable than the corresponding configuration adopted by **2**. It is likely that steric hindrance disfavours formation of a similar isomer for **2**.

The ^1H NMR spectrum of **2** displays broad and uninformative signals. The magnetic susceptibilty measurement reveals a magnetic moment of 4.11 μ_B (Evans Balance at ambient temperature) which is consistent with three unpaired electrons (d^3). This is further supported by the X-band EPR spectrum in toluene at room temperature which shows a sharp signal with a *g*-value of 2.0 which is typical of chromium(III), there is no observable hyperfine splitting. In the infrared spectrum of **2** an absorption band for the imine C=N stretch is observed at 1595 cm^{-1}, and noticeably lower in magnitude than that for the free ligand. In the FAB mass spectrum of **2** no molecular ion peak is observed but a fragmentation peak corresponding to the loss of $Li(THF)_2$ and two chloride ligands is seen.

With the intent of generating a well-defined single component chromium catalyst for olefin polymerisation we set out to explore the alkylation chemistry of complex **2**. We anticipated that a five-coordinate coordinatively unsaturated alkyl complex could be accessible. On treatment of **2** with $AlMe_3$ in THF at ambient temperature alkylation proceeded smoothly to afford $\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CH(C_4H_3N\text{-}2)\}_2CrMe$ (Scheme 1). Complex **3a** was isolated in moderate yield and in crystalline form as an air sensitive compound. Recrystallisation from petroleum ether (bp 40–60 °C) at 243 K gave green crystals of **3a**. The molecular structure of **3a** has been reported previously[11] and is illustrated in Fig. S1 (see ESI †); selected bond lengths and angles are listed in Table 3.

Table 3 Selected bond lengths [Å] and angles [°] for complexes **3a** and **3b**

3a			
Cr–C	2.037(9)	Cr–N(1)	2.026(5)
Cr–N(7)	2.073(4)	C(6)–N(7)	1.318(7)
N(1)–C(5)	1.382(7)	C(5)–C(6)	1.410(8)
N(1)–Cr–N(1′)	173.2(4)	N(1)–Cr–C	93.4(2)
N(1)–Cr–N(7′)	97.9(2)	N(7)–Cr–N(7′)	159.2(3)
N(1)–Cr–N(7)	80.9(2)	C–Cr–N(7)	100.39(14)
3b			
Cr–C(20)	2.02(2)	Cr–N(1)	2.054(10)
Cr–N(7)	2.059(10)	C(6)–N(7)	1.27(2)
N(1)–C(5)	1.42(2)	C(5)–C(6)	1.42(2)
C(20)–Cr–N(1)	92.9(4)	N(1)–Cr–N(1′)	174.1(8)
N(1)–Cr–N(7′)	98.0(5)	N(7)–Cr–N(7′)	160.6(6)
C(20)–Cr–N(7)	99.7(3)	N(1)–Cr–N(7)	81.0(5)

The structure of **3a** reveals a distorted square pyramidal Cr(III) centre, coordinated basally to two chelating pyrrolide-imine ligands and apically to a terminal methyl group at 2.037(9) Å. The complex has crystallographic C_2 symmetry about an axis passing through the Cr–Me bond, and the two independent Cr–N distances differ significantly, with that to the pyrrolide [Cr–N(1) 2.026(5) Å] being shorter than that to the imine [Cr–N(7) 2.073(4) Å], a pattern of bonding that is also observed in **2** but not in **1** where all four Cr–N distances are essentially the same (av. 2.076 Å). Although the reason for the absence of any difference between the Cr–N(pyrrolide) and Cr–N(imino) distances in **1** is not immediately apparent, it may be a consequence of the degree of Cr–pyrrolide π-bonding which is maximised in **2** and **3** due to the higher oxidation state of the metal centres, *i.e.* Cr(II) *vs.* Cr(III).

Throughout the three structures discussed (**1**, **2** and **3a**) and also in structure **3b** (*vide infra*) the conformation of, and the pattern of bonding within, the pyrrolide-imine ligand is remarkably consistent. For example, the double bond character of the imino C=N linkage is retained and ranges between 1.27(2) Å (in **3b**) and 1.318(7) Å (in **3a**) as does the single bond imine-pyrrolide linkage with a range between 1.394(11) Å (in **2**) and 1.423(7) Å (in **1**). Similarly, the pyrrolide and imine units are coplanar to within 0.13 Å. In all cases the 2,6-diisopropylphenyl ring plane is steeply inclined to the pyrrolide-imine plane, with interplanar angles ranging between *ca.* 70 and 86°. This orthogonal conformation has been observed previously and has been attributed to a stabilisation by weak C–H ··· N(pπ) interactions between the isopropyl methine hydrogen atoms and the non-bonding p orbitals of the ring nitrogen atom.[10c,17]

The alkylation of **2** with trimethylaluminium is readily extendable to other alkylaluminium reagents, and we have synthesised the ethyl derivative $\{(2,6\text{-}i\text{-}Pr_2C_6H_3)ArN{=}CH(C_4H_3N\text{-}2)\}_2CrEt$ (**3b**) from the reaction of **2** with triethylaluminium in THF at ambient temperature (Scheme 1). Crystals of **3b** were of poor quality, but sufficient to establish that the complex adopts a structure that is isomorphous and virtually identical to that of **3a**[11] with an ethyl group occupying the axial site but with the terminal methyl group disordered about the crystallographic 2-fold axis (Fig. 3). Bond lengths and angles for **3b** are listed in Table 3 for comparison with **3a**. It is noteworthy that

Table 4 Results of ethylene polymerisation runs with pre-catalysts **1**–**3**[a]

Run	Pre-catalyst/mmol	Cocatalyst[b] (mmol/ equiv.)	Yield[c]/g	Activity/g mmol^{-1} h^{-1} bar^{-1}	M_n	M_w	M_w/M_n
1	**1** (0.015)	$ClAlEt_2$ (0.45/30)	0.20	13	22 000	1 043 000	47.4
2	**1** (0.015)	$ClAlMe_2$ (0.45/30)	1.20	80	336 000	1 377 000	4.1
3	**1** (0.015)	MAO (6.0/400)	0.06	4	–	–	–
4	**2** (0.015)	$ClAlEt_2$ (0.45/30)	1.04	69	133 000[d]	293 000[d]	2.2[d]
5	**2** (0.015)	$ClAlMe_2$ (0.45/30)	3.00	113	500 000	1 742 000	3.5
6	**2** (0.015)	MAO (6.0/400)	0.08	5	–	–	–
7	**3a** (0.015)	$ClAlEt_2$ (0.45/30)	1.05	70	79 000	1 306 000	16.6
8	**3a** (0.015)	$ClAlMe_2$ (0.45/30)	1.31	87	610 000	1 958 000	3.2
9	**3a** (0.015)	MAO (6.0/400)	0.05	3	–	–	–
10	**3b** (0.010)	$ClAlEt_2$ (0.30/30)	0.55	55	22 000	1 168 000	53.1
11	**3b** (0.010)	$ClAlMe_2$ (0.30/30)	1.20	119	[e]	[e]	[e]
12	**3b** (0.010)	MAO (4.0/400)	0.02	2	–	–	–

[a] General conditions: Schlenk tests carried out at 1 bar ethylene in toluene (40 mL) at ambient temperature, over 60 min, reaction quenched with dil. HCl and the solid PE washed with methanol (50 mL) and dried in a vacuum oven at 323 K. [b] MAO = methylaluminoxane. [c] Solid polyethylene. [d] Care should be taken in the interpretation of this result as the polymer derived is not fully soluble in the 1,2,4-trichlorobenzene GPC solvent even upon heating at 433 K for several hours. [e] Insoluble in 1,2,4-trichlorobenzene GPC solvent even upon heating at 433 K for several hours.

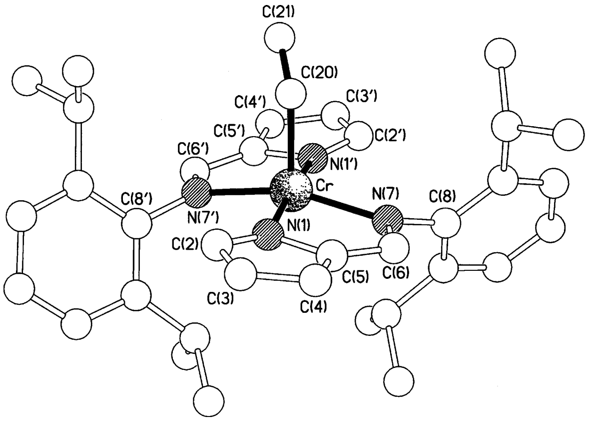

Fig. 3 The molecular structure of **3b**.

the stability of these alkyl complexes (**3a** and **3b**) lies in contrast to the related β-diketimininato complexes, $[(Ph)_2nacnac]_2CrR$ (R = alkyl), where $(Ph)_2nacnac$ is the *N*,*N*'-diphenyl-2,4-pentanediiminato anion, which are unstable and decompose *via* orthometallation.[9c] Furthermore, **3a** and **3b** provide rare examples of structurally characterised mononuclear five-coordinate trivalent chromium alkyl complexes.[18]

As with the precursor Cr(III) complex **2** the ^1H NMR spectra of **3a**–**3b** are broad and uninformative. Compounds **3a** and **3b** exhibit magnetic moments of 3.61 and 3.67 μ_B consistent with the complexes being mononuclear and possessing d^3 electronic configurations. The X-band EPR spectrum of **3a** recorded at ambient temperature in toluene displays broad features at low field at *ca.* $g = 4.4$ and 3.3 along with several weaker features at higher field at *ca.* $g = 1.2$; no hyperfine structure is evident. Similar features have been observed for the rhombically distorted d^3 species $(dmpe)_2VX_2$ (X = Cl, Me) reported by Wilkinson and Girolami.[19] It is noteworthy that for **3b** these features are only observed at 140 K. In the infrared spectra of **3a** and **3b** the imine C=N stretches are observed at *ca.* 1595 cm^{-1}. In addition, the microanalytical and FAB mass spectrometric data are in accord with the structures of **3a** and **3b**.

All the new complexes, **1**–**3**, have been screened as pre-catalysts or catalysts for the polymerisation and oligomerisation of ethylene at 1 bar ethylene and room temperature. Three types of aluminium co-catalyst have been employed to activate pre-catalysts **1**–**3** namely, methylaluminoxane (MAO), Et_2AlCl and Me_2AlCl (see Table 4; runs 1–12).

All the dual-component systems are active, converting ethylene to high molecular weight linear polyethylene. In no case has high molecular weight polyethylene been obtained using the bis(pyrrolide-imine) chromium complexes as single component systems, nor has there been any evidence for low molecular weight oligomers.

On analysis of the data contained within Table 4, several points emerge. The Cr(III) complexes **2** and **3b** are the most active of all the pyrrolide-imine containing chromium complexes, with activities of 113 and 119 g mmol^{-1} h^{-1} bar^{-1} (Table 2, see runs 5 and 11), respectively. The bis(pyrrolide-imine) chromium alkyl complexes **3a** and **3b** are inactive as single component catalysts despite the availability of a vacant coordination site. This may be due to ethylene binding *trans* to the alkyl group or, alternatively, it is possible that *cis* binding occurs but the enhanced stability of the resultant octahedral Cr(III) species may lead to an energetically prohibitive barrier to ethylene insertion. In almost all cases, the most compatible co-catalysts are the dialkylaluminium chlorides, Me_2AlCl and Et_2AlCl, rather than MAO which affords in all cases only trace amounts of polyethylene.

The polyethylene generated by catalysts **1**–**3** has very little branching (by ^{13}C NMR) and, in its general properties, resembles the polyethylene generated by heterogeneous chromium catalysts.[6] For example, gel permeation chromatography (GPC) analysis (in 1,2,4-trichlorobenzene) of the polyethylene formed shows the M_w's ranging from 293 000 (run 4) to 1 958 000 (run 8), with polydispersities (M_w/M_n) in the range 2.2–53.1. Indeed, in some cases (see run 11), the molecular weight was too high to be determined, even upon heating at 433 K in 1,2,4-trichlorobenzene for several days. It is noteworthy that control polymerisation tests undertaken using the low valent chromium precursors, $CrCl_3\cdot3THF$ and $CrCl_2\cdot THF$, gave only trace amounts of polyethylene.

In conclusion, chromium complexes in oxidation states (II) and (III) supported by two pyrrolide-imine ligands, $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CH(C_4H_3N\text{-}2)]$, have been prepared and evaluated as ethylene polymerisation catalysts. All of the complexes give active catalysts on treatment with alkylaluminium activators. While MAO behaves as a poor activator, dialkylaluminium chloride activators perform significantly better leading to more productive systems. The coordinatively unsaturated bis(pyrrolide-imine) chromium alkyl complexes **3a** and **3b** are inactive catalysts by themselves in the presence of ethylene.

Experimental

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 (^{13}C) at 293 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. IR spectra (Nujol mulls) were recorded on Perkin-Elmer 577 and 457 grating spectrophotometers. Mass spectra were obtained using either fast atom bombardment (FAB), electron impact (EI) or chemical ionisation (CI). Gel permeatation chromatographs (GPCs) were obtained using a Waters 150CV (columns are supplied by Shodex (807, 806 & 804) (BP Chemicals Ltd)). Analysis for oligomeric products was performed using GCMS, employing a 25 m BPX-5 column, injector temperature 513 K and a Micromass Autospec-Q mass spectrometer. Magnetic susceptibility studies were performed using an Evans Balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods[20] and corrections for underlying diamagnetism were applied to the data.[21]

Compounds $CrCl_2\cdot THF$[22] and $CrCl_3\cdot 3THF$[23] were prepared according to established procedures. The reagents $AlMe_3$ (2.0 M solution in toluene), $AlEt_3$ (1.9 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 pyrrole-2-carboxaldehyde were purchased from Aldrich Chemical Co. All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparation of (2,6-*i*-$Pr_2C_6H_3$)N=CH(C_4H_3NH-2)

To a solution of pyrrole-2-carboxaldehyde (1.50 g, 15.8 mmol) in diethyl ether (30 mL) was added 2,6-diisopropylaniline (2.98 mL, 15.8 mmol). After addition of a few drops of glacial acetic acid the solution was heated to reflux for 6 h. Upon cooling to room temperature the product crystallised. After filtration the white solid was washed with cold diethyl ether (3 x 20 mL) and dried overnight to give 3.25 g (81%) of (2,6-*i*-$Pr_2C_6H_3$)N=CH(C_4H_3NH-2). ^1H NMR ($CDCl_3$): δ 11.59 (s, 1H, C_4H_3N–*H*), 7.91 (s, 1H, NC*H*Ar), 7.2–7.1 (m, 3H, Ar–*H*), 6.41 (s, br 1H, C_4H_3NH), 6.00 (s, br 1H, C_4H_3NH), 5.97 (s, br, 1H, C_4H_3NH), 3.07 (sept, 2H, ^3J(HH) 6.9, C*H*Me_2), 1.08 (d, 12H, CH*Me*$_2$). ^{13}C NMR ($CDCl_3$, ^1H gated decoupled): δ 153.2 (s, N=*C*), 148.9 (s, pyrrole *C*–N), 139.5 (s, pyrrole *C*–N), 130.3 (s, Ar), 125.0 (s, Ar), 124.8 (s, Ar), 123.7 (s, Ar), 117.3 (s, pyrrole), 110.3 (s, pyrrole), 28.4 (s, *C*HMe_2) and 24.0 (s, CH*Me*$_2$). EI mass spectrum, *m*/*z* 254 [M^+]. IR (cm^{-1}) ν(N–H) 3453, ν(C=N) 1623. Anal. Calcd. for $C_{17}H_{22}N_2$: C, 80.31; H, 8.66; N, 11.02. Found: C, 80.56; H, 8.91; N, 10.91%.

Preparation of {(2,6-*i*-$Pr_2C_6H_3$)N=CH(C_4H_3N-2)}$_2$Cr (1)

The sodium salt of (2,6-*i*-$Pr_2C_6H_3$)N=CH(C_4H_3NH-2) was prepared by addition of NaH (0.129 g, 5.34 mmol) to (2,6-*i*-$Pr_2C_6H_3$)N=CH(C_4H_3NH-2) (1.356 g, 5.34 mmol) in THF (40 mL) at room temperature. The solution was left to stir overnight and then filtered, at room temperature, into a second flask containing $CrCl_2\cdot THF$ (0.521 g, 2.67 mmol) in THF (10 mL). The resulting red/brown solution was allowed to stir overnight at room temperature. The volatiles were removed under reduced pressure and petroleum ether (bp 40–60 °C) (60 mL) introduced. The solution was then stirred, filtered and the filtrate concentrated to half volume. Orange air-sensitive crystals of **1** were obtained upon standing of the solution at 253 K overnight (1.14 g, 77%). FAB mass spectrum, *m*/*z* 558 [M+], 303 [M^+ − ArN=CHC_4H_3N-2]. IR (cm^{-1}) ν(C=N) 1591. Anal. Calcd. for $C_{34}H_{42}N_4Cr$: C, 73.12; H, 7.53; N, 10.03. Found: C, 72.91; H, 7.41; N, 9.91%. μ_{eff} 4.81 μ_B.

Preparation of {(2,6-*i*-$Pr_2C_6H_3$)N=CH(C_4H_3N-2)}$_2$Cr(μ-Cl)$_2$-Li(THF)$_2$ (2)

The lithium salt of (2,6-*i*-$Pr_2C_6H_3$)N=CH(C_4H_3NH-2) was prepared by addition of *n*-BuLi (3.34 mL, 5.34 mmol) to (2,6-*i*-$Pr_2C_6H_3$)N=CH(C_4H_3NH-2) (1.356 g, 5.34 mmol) in THF (40 mL) at 195 K. The solution was allowed to warm to room temperature and stirred for a further hour. The pale yellow solution was re-cooled to 195 K and filtered into a second reaction vessel containing $CrCl_3\cdot 3THF$ (1.00 g, 2.67 mmol) in THF (10 mL) at 195 K. The solution was allowed to warm to room temperature and stirred overnight. The volatiles were removed under reduced pressure to give an orange/green residue which was extracted into pentane (60 mL). The solution was filtered and the filtrate concentrated to *ca.* half volume and left to stand overnight a room temperature to give **2** as orange/red crystals (1.56 g, 75%). FAB mass spectrum, *m*/*z* 558 [M^+ − 2Cl − Li(THF)$_2$]. IR (cm^{-1}) ν(C=N) 1595. Anal. Calcd. for $C_{34}H_{42}N_4CrCl\cdot 0.4LiCl(THF)_2$: C, 66.82; H, 7.24; N, 8.38. Found: C, 66.71; H, 7.16; N, 8.59%. μ_{eff} 4.11 μ_B.

Preparation of {(2,6-*i*-$Pr_2C_6H_3$)N=CH(C_4H_3N-2)}$_2$CrR (R = Me 3a, Et 3b)

3a R = Me. The lithium salt of **1** was prepared by addition of *n*-BuLi (3.34 mL, 5.34 mmol) to **1** (1.356 g, 5.34 mmol) in THF (40 mL) at 195 K. The solution was allowed to warm to room temperature and stirred for a further hour. The pale yellow solution was re-cooled to 195 K and added dropwise to a solution of $CrCl_3\cdot 3THF$ (1.00 g, 2.67 mmol) in THF (10 ml) at 195 K. The solution was allowed to warm to room temperature and stirred for 1 h. $AlMe_3$ (2.7 ml, 5.34 mmol) was then added at room temperature and the resulting solution left to stir. After one night at room temperature the volatiles were removed under reduced pressure to give a green residue. Extraction of the residue into petroleum ether (bp 40–60 °C) (60 ml) gave an olive green solution which, on concentration to half volume and cooling to 253 K overnight, afforded green crystals of **3a** (0.78 g, 51%). FAB mass spectrum, *m*/*z* 574 [M^+], 558 [M^+ − CH_3], 303 [M^+ − CH_3 − ArN=CHC_4H_3N-2]. IR (cm^{-1}) ν(C=N) 1594. Anal. Calcd. for $C_{35}H_{45}N_4Cr$: C, 73.30; H, 7.85; N, 9.77. Found: C, 73.01; H, 7.67; N, 9.51%. μ_{eff} 3.61 μ_B.

3b R = Et. Complex **3b** was prepared in moderate yield (0.71 g, 45%) by employing a procedure similar to that outlined above but with $AlEt_3$ (2.8 ml, 5.34 mmol) in place of $AlMe_3$. FAB mass spectrum, *m*/*z* 558 [M^+ − $_2H_5$], 303 [M^+ − C_2H_5 − ArN=CHC_4H_3N-2]. IR (cm^{-1}) ν(C=N) 1594. Anal. Calcd. for $C_{36}H_{47}N_4Cr$: C, 73.60; H, 8.01; N, 9.54. Found: C, 73.47; H, 8.18; N, 9.41%. μ_{eff} 3.67 μ_B.

Polymerisation procedure

Results of Schlenk-line tests (1 bar) are listed in Table 4; polymerisation procedure is described as follows. The pre-catalyst was dissolved in toluene (40 mL) and the co-catalyst (MAO, Et_2AlCl or Me_2AlCl) 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 323 K). The presence of lower molecular weight polyethylene was screened using GCMS of the separated organic layer.

X-Ray crystal structure determinations

Table 5 provides a summary of the crystal data, data collection and refinement parameters for compounds **1**, **2**, **3a** and **3b**. All four structures were solved by direct methods and refined by full matrix least-squares based on F^2.

CCDC refernce numbers 185874–185877.

See http://www.rsc.org/suppdata/dt/b2/b204568k/ for crystallographic data in CIF or other electronic format.

In **2** the carbon atoms in the 3 and 4 positions of both of the THF units were found to be disordered; in each case two partial

Table 5 Crystal data, data collection and refinement parameters for complexes **1**, **2**, **3a** and **3b**[a]

	1	**2**	**3a**	**3b**
Formula	$C_{34}H_{42}N_4Cr$	$C_{42}H_{58}N_4O_2Cl_2LiCr$	$C_{35}H_{45}N_4Cr$	$C_{36}H_{47}N_4Cr$
Solvent	—	0.5 C_5H_{12}	—	—
M	558.7	816.8	573.8	587.8
Colour, habit	Orange prisms	Orange/red prisms	Green blocks	Dark green prisms
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$Fdd2$ (no. 43)	$Fdd2$ (no. 43)
a/Å	17.249(2)	17.598(4)	20.280(2)	19.820(4)
b/Å	10.570(1)	17.638(4)	34.103(4)	34.304(9)
c/Å	17.731(2)	15.151(4)	9.420(1)	9.969(3)
β/°	107.93(1)	102.06(1)	—	—
V/Å^3	3075.5(5)	4599(2)	6515(2)	6778(3)
Z	4	4	8[b]	8[b]
D_c/g cm^{-3}	1.207	1.180	1.170	1.152
$F(000)$	1192	1744	2456	2520
Radiation used	Cu-Kα[c]	Mo-Kα	Mo-Kα	Mo-Kα
μ/mm^{-1}	3.26	0.40	0.38	0.37
Unique reflections measured	4533	5949	1530	1576
observed, $\lvert F_o \rvert > 4\sigma(\lvert F_o \rvert)$	3427	2736	1193	1064
R_1[d]	0.086	0.074	0.049	0.099
wR_2[e]	0.254	0.133	0.094	0.256
Weighting factors$a$, b[f]	0.201, 2.237	0.058, 0.000	0.036, 0.000	0.214, 0.000
Largest diff. peak, hole/e Å^{-3}	0.84, –1.58	0.33, –0.31	0.23, –0.27	0.95, –0.64

[a] Details in common: graphite monochromated radiation, ω-scans, Siemens P4 diffractometer, 203 K, refinement based on F^2. [b] The molecule has crystallographic C_2 symmetry. [c] Rotating anode source. [d] $R_1 = \Sigma \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \Sigma \lvert F_o \rvert$. [e] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. [f] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

occupancy orientations were identified with only the major occupancy carbon atoms being refined anisotropically (the others were refined isotropically). In **3b** the metal-bonded ethyl moiety was found to be disordered about the crystallographic C_2 axis; two 50% occupancy orientations related by the twofold axis were identified and refined isotropically. The remaining non-hydrogen atoms in all four structures were refined anisotropically. The C–H hydrogen atoms for all of the structures were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, $[U(H) = 1.5U_{eq}(C\text{–Me})]$, and allowed to ride on their parent atoms. The polarity of **3a** was determined by a combination of R-factor tests $[R_1^+ = 0.0488, R_1^- = 0.0497]$ and by use of the Flack parameter $[x^+ = 0.10(13), x^- = 0.90(13)]$. The polarity of **3b** could not be reliably determined. All computations were carried out using the SHELXTL PC program system.[24]

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References and notes

1 (*a*) G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428; (*b*) S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169; (*c*) S. Mecking, *Angew. Chem., Int. Ed.*, 2001, **40**, 534.

2 (*a*) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; (*b*) D. P. Gates, S. A. Svejda, E. Onate, C. M. Killian, L. K. Johnson and M. Brookhart, *Macromolecules*, 2000, **33**, 2320.

3 (*a*) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 849; (*b*) B. L. Small, M. Brookhart and A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049.

4 (*a*) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben and M. W. Day, *Organometallics*, 1998, **17**, 3149; (*b*) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs and D. A. Bansleben, *Science*, 2000, **287**, 460.

5 (*a*) S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, M. Nitabaru, T. Nakano and T. Fujita, *Chem. Lett.*, 1999, 1065; (*b*) S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847.

6 For background to Phillips catalyst see: (*a*) J. P. Hogan and R. L. Banks, *US Pat.* 2,825,721, 1958; (*b*) E. A. Benham, P. D. Smith, E. T. Hsieh and M. P. McDaniel, *J. Macromol. Sci., Chem.*, 1988, **A25**, 259; (*c*) M. P. McDaniel, *Adv. Catal.*, 1985, **33**, 47; (*d*) H. L. Kraus, *J. Mol. Catal.*, 1988, **46**, 97; (*e*) G. Ghiotti, E. Garrone and A. Zecchini, *J. Mol. Catal.*, 1988, **46**, 61; (*f*) A. Clark, *Catal. Rev.*, 1969, **31**, 123.

7 See for example and refs. therein: (*a*) K. H. Theopold, *Chem. Eur. J.*, 1998, 15; (*b*) K. H. Theopold, *CHEMTECH*, 1997, **27**, 26–32; (*c*) R. Emrich, O. Heinemann, P. W. Jolly, C. Krüger and G. P. J. Verhovnik, *Organometallics*, 1997, **16**, 1511; (*d*) D. A. Gohre, P. W. Jolly, B. Kryger, J. Rust and G. P. J. Verhovnik, *Organometallics*, 2000, **19**, 388; (*e*) V. R. Jensen, K. Angermund, P. W. Jolly and K. J. Borve, *Organometallics*, 2000, **19**, 403.

8 (*a*) M. P. Coles, C. I. Dalby, V. C. Gibson, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc., Chem Commun.*, 1995, 1709; (*b*) F. J. Feher and R. L. Blanski, *J. Chem. Soc., Chem Commun.*, 1990, 1614; (*c*) M. P. Coles and V. C. Gibson, *Polym. Bull.*, 1994, **33**, 529.

9 (*a*) R. D. Köhn, M. Haufe, S. Mihan and D. Lilge, *Chem. Commun.*, 2000, 1927; (*b*) W.-K. Kim, M. J. Fevola, L. M. Liable-Sands, A. L. Rheingold and K. H. Theopold, *Organometallics*, 1998, **17**, 4541; (*c*) L. A. MacAdams, W. K. Lin, L. M. Liable-Sands, I. A. Guzei, A. L. Rheingold and K. H. Theopold, *Organometallics*, 2002, **21**, 952; (*d*) T. Ruther, N. Braussaud and K. J. Cavell, *Organometallics*, 2001, **20**, 1247–1250; (*e*) H. Ikeda, T. Monoi, Y. Nakayama and H. Yasuda, *J. Organomet. Chem.*, 2002, **642**, 156–162; (*f*) H. Ikeda, T. Monoi, K. Ogata and H. Yasuda, *Macromol. Chem. Phys.*, 2001, **202**, 1806–1811; (*g*) P. Wei and D. W. Stephan, *Organometallics*, 2002, **21**, 1308–1310.

10 (*a*) V. C. Gibson, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1999, 827; (*b*) V. C. Gibson, S. Mastroianni, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2000, 1969; (*c*) V. C. Gibson, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Eur. J. Inorg. Chem.*, 2001, 1895; (*d*) V. C. Gibson, C. Newton, G. A. Solan, (BP Chemicals Ltd.), *WO* 99/19335, 1999 [*Chem. Abstr.*, 1999, **130**, 297099p].

11 V. C. Gibson, P. J. Maddox, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 1651.

12 Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *Organometallics*, 2001, **20**, 4793.

13 D. M. Dawson, D. A. Walker, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 2000, 459.

14 (*a*) F. A. Cotton, L. M. Daniels, C. A. Murillo and P. Schooler, *J. Chem. Soc., Dalton Trans.*, 2000, 2001; (*b*) M. Dionne, J. Jubb, H. Jenkins, S. Wong and S. Gambarotta, *Inorg. Chem.*, 1996, **35**,

1874; (*c*) S. Hao, S. Gambarotta, C. Bensimon and J. J. H. Edema, *Inorg. Chim. Acta*, 1993, **213**, 65; (*d*) J. K. Buijinl, M. Noltemeyer and F. T. Edelmann, *Z. Naturforsch., Teil B*, 1991, **46**, 1328.

15 See for example: (*a*) J. A. Castro, J. Romero, J. A. Garcia-Vasquez, M. C. Duran, A. Sousa, E. E. Castellano and J. Zukerman-Schpector, *Polyhedron*, 1992, **11**, 235; (*b*) J. A. Garcia-Vasquez, M. C. Duran, A. Sousa and A. Castineiras, *Acta Crystallogr., Sect. C*, 1996, **52**, 2734.

16 For related complexes containing a Cr(μ-Cl)$_2$Li(THF)$_2$ unit see: (*a*) A. Kasani, R. McDonold and R. G. Cavell, *Chem. Commun.*, 1999, 1993; (*b*) G. W. Rabe, A. L. Rheingold and C. D. Incarvito, *Z. Kristallogr.*, 2000, **215**, 181.

17 See for example: (*a*) P. N. Jagg, P. F. Kelly, H. S. Rzepa, D. J. Williams, J. D. Woollins and W. Wylie, *J. Chem. Soc., Chem. Commun.*, 1991, 942; (*b*) P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, G. A. Solan, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2001, 1472.

18 For examples of five-coordinate Cr(III) alkyl complexes see: (*a*) M. D. Fryzuk, B. B. Leznoff and S. J. Rettig, *Organometallics*, 1997, **16**, 5116; (*b*) Y. Liang, G. P. A. Rheingold, A. L. Rheingold and K. H. Theopold, *Organometallics*, 1996, **15**, 5284; (*c*) E. Müller, J. Krause and K. Schmedeknecht, *J. Organomet. Chem.*, 1972, **44**, 127; (*d*) F. A. Cotton, J. Czuchajowska, L. R. Falvello and X. Feng, *Inorg. Chim. Acta*, 1990, **172**, 135.

19 (*a*) G. S. Girolami, G. Wilkinson, A. M. R. Galas, M. Thornton-Pett and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 1339; (*b*) R. J. Morris, S. R. Wilson and G. S. Girolami, *J. Organomet. Chem.*, 1994, **480**, 1.

20 M. B. Mabbs and D. J. Machin, *Magnetism and Transition Metal Complexes*, Chapman and Hall, London, 1973.

21 (*a*) C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 203; (*b*) *Handbook of Chemistry and Physics*, ed. R. C. Weast, CRC Press, Boca Raton, FL, 70th edn., 1990, p. E134.

22 L. F. Larkworthy and M. H. O. Nelson-Richardson, *Chem. Ind.*, 1974, 164.

23 J. Shamir, *Inorg. Chim. Acta*, 1989, **156**, 163.

24 SHELXTL, PC version 5.03, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1994.