Chromium(III) complexes bearing N,N-chelate ligands as ethene polymerization catalysts

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Novel chromium(III) ethene polymerization catalysts bearing bulky monoanionic N,N-chelate ligands are described.

Chromium supported on silica plays a central role in the world-wide production of polyethylene.[1] As heterogeneous catalysts they have not proved amenable to intimate study, and even to this day there remains an on-going debate about the oxidation state of the active chromium centres.[2] The development of homogeneous molecular chromium catalysts is therefore an important objective, since these offer the potential for understanding the *modus operandi* of supported chromium catalysts and may provide new opportunities for tuning activity and selectivity. A number of reports of molecular chromium catalysts have appeared in the recent literature,[3–6] the majority on half-sandwich chromium species as models for the active sites of chromocene-derived systems.[3,4]

Here we describe a series of coordinatively unsaturated chromium(III) ethene polymerization procatalysts bearing either β-diketimate or pyrrolide-imine ligands. A general feature of these ligands is the presence of bulky aryl substituents which offer protection to the active centre, a strategy that has proved successful for the stabilisation of new N,N-chelate catalysts based on early[7] and late transition metal systems.[8] A similar strategy has also recently been applied to a new catalyst system based on iron and cobalt.[9]

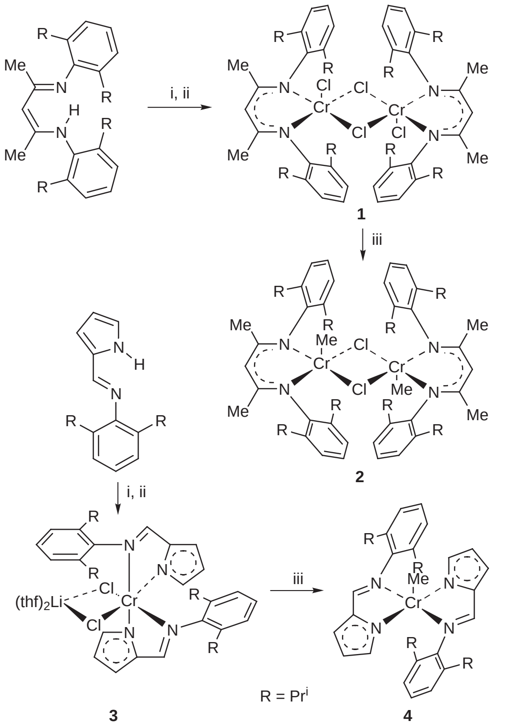
The chromium chloride complexes, **1** and **3**, were prepared in high yield by the treatment of [$CrCl_3(thf)_3$] with the lithium salts of the β-diketimate ligand or the pyrrolide-imine ligand, respectively (Scheme 1).‡ The structures of **1** and **3** were confirmed by X-ray structure determinations.[10] Interestingly, only one β-diketimate ligand can be coordinated to chromium in **1**, while in **3** the less sterically demanding pyrrolide-imine ligand allows bis-chelation. It is also of note that the vacant sixth coordination site in **3** is unexpectedly occupied by a molecule of lithium chloride (as a thf solvate).

Complex **2**, the dimethyl derivative of **1**, has been prepared in good yield by treatment of **1** with trimethylaluminium (TMA). Crystals of **2** suitable for an X-ray structure determination§ were grown from a concentrated pentane solution. The structure is dimeric, the two crystallographically independent molecules both having C_{2h} symmetry and comprising in each case two slightly distorted square pyramidal Cr^{III} centres linked by chloride bridges, the remaining basal sites being occupied by bidentate β-diketimate ligands (Fig. 1). The apical position on each chromium centre is filled by a terminal methyl group with Cr–C distances of 2.037(7) and 2.042(8) Å for the two independent molecules. The 2,6-diisopropylphenyl rings are oriented almost orthogonally (*ca.* 87°) with respect to the basal plane.

In a similar way, complex **4** was obtained by treatment of **3** with TMA (Scheme 1). Crystals of **4** suitable for X-ray analysis were grown from a concentrated light petroleum (bp 40–60 °C) solution. The structure again reveals a five-coordinate square pyramidal Cr^{III} centre, this time coordinated basally to two chelating pyrrolide-imine ligands and apically to a terminal methyl group at 2.037(9) Å (Fig. 2). 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 [2.026(5) Å] markedly shorter than that to the imine [2.073(4) Å] reflecting the formal anionic nature of N(1). The double bond character of the imine has been retained [1.318(7) Å] though there is some evidence for delocalisation between the imine and pyrrolide systems, C(5)–C(6) being short at 1.410(8) Å. As in **2**, the 2,6-diisopropylphenyl rings are steeply inclined (*ca.* 65°) to the basal plane. It is noteworthy that both of these structures provide rare examples of five-coordinate chromium(III) alkyls, only two other examples having been found on the CCDC database [to March 1998, 175 093 entries].[11]

A summary of the ethene polymerization tests for **1**–**4** is shown in Table 1. Solid polyethylene is obtained in all cases with samples displaying high molecular weights¶ and virtually no branching (by NMR). A comparison of the polymerisation runs 1–12 shows that similar activities are found for procatalysts bearing either β-diketimate (**1** and **2**) or pyrrolide-imine ligands (**3** and **4**), the highest activity being 75 g mmol^{-1} h^{-1} bar^{-1} using **1** and diethylaluminium chloride (Et_2AlCl) activator (see run 2).

The nature of the activator is seen to have an important influence on activity; for example, alkylaluminium chloride activators are found to be more compatible with these



Scheme 1 Preparation of chromium complexes **1**–**4**. *Reagents and conditions*: i, Bu^{n}Li, −78 °C, thf; ii, [$CrCl_3(thf)_3$], −78 °C, thf; iii, $AlMe_3$, thf.

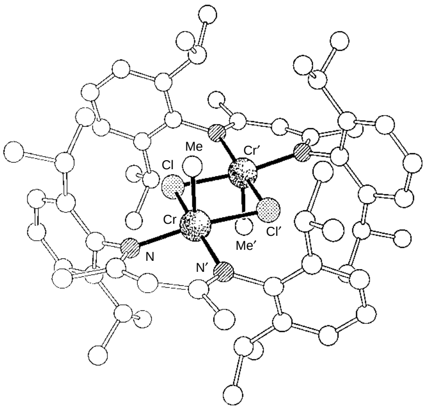


Fig. 1 The molecular structure of **2**. Selected bond lengths (Å) and angles (°) (values for the second independent molecule are in square brackets); Cr–Me 2.037(7) [2.042(8)], Cr–N 2.028(4) [2.031(4)], Cr–Cl 2.395(1) [2.393(1)]; Me–Cr–N 95.4(2) [96.8(2)], Me–Cr–Cl 97.8(2) [96.8(2)], N–Cr–N′ 91.3(2) [90.8(2)], Cl–Cr–Cl′ 80.3(1) [80.6(1)], N–Cr–Cl 92.7(1) [92.7(1)], N–Cr–Cl′ 165.7(1) [165.4(1)], Cr–Cl–Cr′ 99.7(1) [99.4(1)]. The transannular Cr···Cr distance is 3.66 Å [3.65 Å] and the chromium atom lies 0.25 Å [0.26 Å] out of its basal plane.

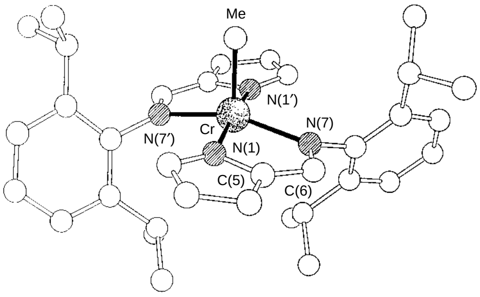


Fig. 2 The molecular structure of **4**. Selected bond lengths (Å) and angles (°); Cr–Me 2.037(9), Cr–N(1) 2.026(5), Cr–N(7) 2.073(4), C(5)–C(6) 1.410(8), C(6)–N(7) 1.318(7); Me–Cr–N(1) 93.4(2), Me–Cr–N(7) 100.4(1), N(1)–Cr–N(7) 80.9(2), N(1)–Cr–N(7′) 97.9(2), N(1)–Cr–N(1′) 173.2(4), N(7)–Cr–N(7′) 159.2(3).

Table 1 Results of ethene polymerisation runs using procatalysts **1**–**4**[a]

Run	Proctalyst (0.015 mmol)	Activator[b] (mmol/equiv.)	Yield PE[c]/g	Activity[d]/ g mmol^{-1} h^{-1} bar^{-1}
1	1	MAO (6.0/400)	0.12	4
2	1	Et_2AlCl (0.45/30)	2.25	75
3	1	$Et_2AlCl{\cdot}EtAlCl_2$ (0.3/20)	0.69	23
4	2	MAO (6.0/400)	0.15	10
5	2	Et_2AlCl (0.45/30)	0.80	54
6	2	$Et_2AlCl{\cdot}EtAlCl_2$ (0.3/20)	0.48	32
7	3	MAO (6.0/400)	0.08	5
8	3	Et_2AlCl (0.45/30)	1.04	69
9	3	$Et_2AlCl{\cdot}EtAlCl_2$ (0.45/30)	0.40	27
10	4	MAO (6.0/400)	0.04	3
11	4	Et_2AlCl (0.45/30)	1.05	70
12	4	$Et_2AlCl{\cdot}EtAlCl_2$ (0.45/30)	0.23	15

[a] *General conditions*: 1 bar ethene Schlenk test carried out in toluene (40 cm^3) at 25 °C, over 60 min, reaction quenched with dil. HCl and the solid PE washed with methanol (50 cm^3) and dried in a vacuum oven at 40 °C. [b] MAO = methylaluminoxane. [c] Solid polyethylene. [d] Activity reported per chromium centre.

procatalysts than methylaluminoxane (MAO). Moreover, diethylaluminium chloride (Et_2AlCl) is superior to aluminium sesquichloride ($Et_2AlCl{\cdot}EtAlCl_2$). Notably, the alkyl procatalysts **2** and **4** are inactive in the absence of activator.

The new catalyst types described herein represent a notable addition to the limited list of non-cyclopentadienyl chromium ethene polymerization catalysts[5,6] and highlight the importance of the choice of co-catalyst for optimal catalyst performance.

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Notes and References

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‡ Satisfactory elemental analyses have been obtained.

¶ As a representative example, GPC analysis of the polyethylene obtained from run 8 afforded M_w = 293,000, M_n = 113,000; M_w/M_n 2.2. Care should be taken in the interpretation of these values, however, since in general the polymers derived from these polymerisations are not fully soluble in the 1,2,4-trichlorobenzene GPC solvent, even upon heating at 160 °C for several hours.

§ *Crystal data*: for **2**: $C_{60}H_{88}Cl_2Cr_2N_4{\cdot}0.5C_5H_{12}$, M = 1076.3, monoclinic, space group $C2/m$ (no. 12), a = 19.434(3), b = 21.764(2), c = 15.098(2) Å, β = 90.58(1)°, U = 6386(1) Å^3, Z = 4 (there are two crystallographically independent C_{2h} symmetric molecules in the asymmetric unit), D_c = 1.120 g cm^{-3}, μ(Cu-Kα) = 38.5 cm^{-1}, $F(000)$ = 2316. A crimson prismatic needle of dimensions 0.33 × 0.17 × 0.13 mm was used. For **4**: $C_{35}H_{45}CrN_4$, M = 573.8, orthorhombic, space group $Fdd2$ (no. 43), a = 20.280(2), b = 34.103(4), c = 9.420(1) Å, U = 6515(2) Å^3, Z = 8 (the molecule has crystallographic C_2 symmetry), D_c = 1.170 g cm^{-3}, μ(Mo-Kα) = 3.79 cm^{-1}, $F(000)$ = 2456. A green block of dimensions 0.37 × 0.37 × 0.10 mm was used. 4866 (1530) independent reflections were measured at 203 K on Siemens P4(PC) diffractometers with Cu-Kα—rotating anode source—(Mo-Kα) radiation using ω-scans for **2** (**4**), respectively. The structures were solved by direct methods and all of the major occupancy non-hydrogen atoms were refined anisotropically using full matrix least squares based on F^2 to give R_1 = 0.065 (0.049), wR_2 = 0.164 (0.094) for 3370 (1193) independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120(50°)$] and 340 (182) parameters for **2** (**4**), respectively. The polarity of **4** was determined by a combination of R-factor tests [R_1^+ = 0.048, R_1^- = 0.050] and by use of the Flack parameter [x^+ = 0.10(1), x^- = 0.90(1)]. CCDC 182/903.

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10 X-Ray data for **1** and **3** will be published elsewhere.

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