

Chromium ethylene polymerisation catalysts bearing reduced Schiff-base N,O-chelate ligands

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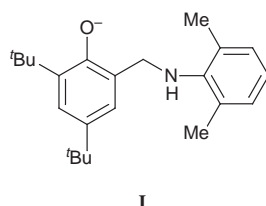
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Treatment of $\text{CrCl}_3(\text{THF})_3$ with the lithium and sodium salts of the reduced Schiff-base ligand 3,5-(^tBu) $_2$ -2-(OH) $\text{C}_6\text{H}_2\text{CH}_2\text{NH}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ affords bis-chelate chromium(II) and mono-chelate chromium(III) complexes respectively; both give active ethylene polymerisation catalysts upon treatment with alkylaluminium activators.

There is currently much academic and industrial interest in the development of highly efficient molecular α -olefin polymerisation catalysts.¹ In these systems, it is the steric and electronic properties of ancillary ligands that allow control over the molecular weight and microstructure of the resultant polymers.^{2,3} Industrially, chromium supported on silica plays an important role in the global production of polyethylene.⁴ Examples of molecular systems are, however, scarce^{5–10} and of those that have been reported, low valent half-sandwich chromium compounds predominate.^{7,8}

We have been investigating non-cyclopentadienyl chromium systems as potential well-defined catalysts for ethylene polymerisation. In recent reports, we⁵ and others⁶ have described new chromium catalysts bearing monoanionic N,N-chelate ligands. We now report new precatalysts based upon the bulky monoanionic N,O-chelating ligand **1** derived from reduction of the corresponding Schiff-base precursor; ethylene polymerisation tests reveal the highest activities to date for a non-cyclopentadienyl chromium system.



Treatment of $[\text{CrCl}_3(\text{THF})_3]$ with two equivalents of the lithium salt of 3,5-(^tBu) $_2$ -2-(OH) $\text{C}_6\text{H}_2\text{CH}_2\text{NH}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ **1** in THF at -78°C leads to reduction and formation of the bis-chelated red chromium(II) complex $\{\text{Cr}[3,5-(^t\text{Bu})_2-2-(\text{O})\text{C}_6\text{H}_2\text{CH}_2\text{NH}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]_2\}$ **1** in 45% yield (Scheme 1).[†] Use of only one equivalent of the lithium salt again affords **1**, albeit in reduced yield (23%).

The single crystal X-ray structure[‡] of **1** shows the ligands to have *cis*-coordinated oxygen and nitrogen atoms respectively (Fig. 1) and to have retained their amino hydrogen atoms, hence indicating a formal +2 oxidation state at the chromium centre. The molecule has crystallographic C_2 symmetry about an axis bisecting the $\text{O}-\text{Cr}-\text{O}'$ angle. The geometry at chromium is distorted square planar, there being a 14° twist about the C_2 axis between the $\text{O}-\text{Cr}-\text{O}'$ and $\text{N}-\text{Cr}-\text{N}'$ planes. The bite of the N,O-chelating ligand **1** appears to be near optimal, the angle subtended at chromium being $90.3(1)^\circ$. The six-membered chelate ring has a folded boat-like conformation with O and C(1) as "prow" and "stern" respectively; the out of plane fold angle about the $\text{O}\cdots\text{C}(1)$ vector is *ca.* 22° . The two 2,6-

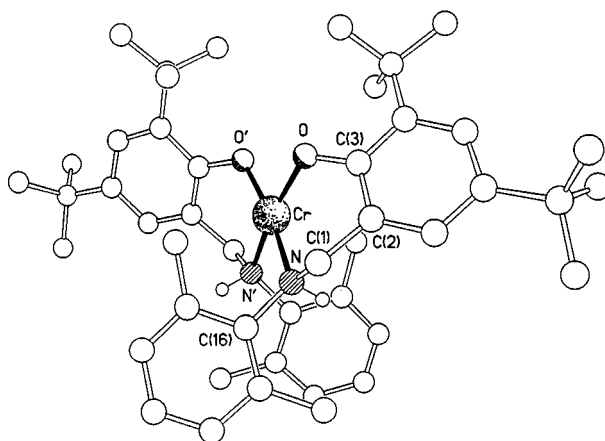
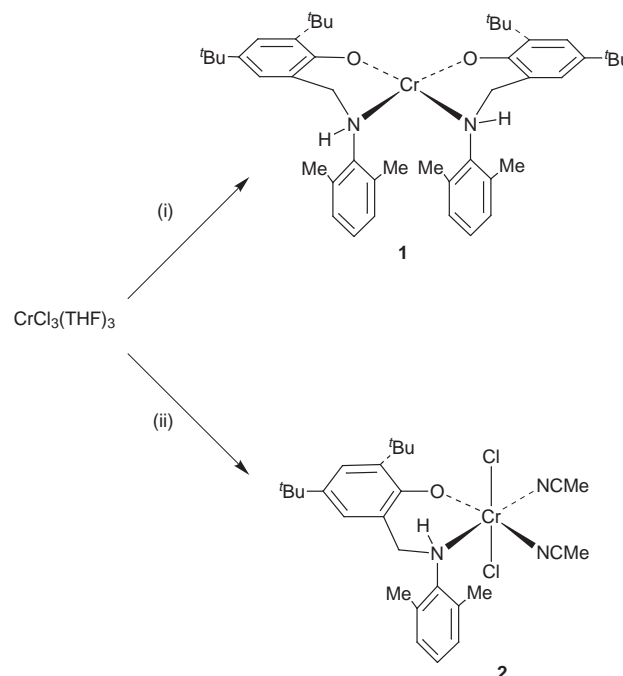


Fig. 1 The molecular structure of **1**. Selected bond lengths (Å) and angles ($^\circ$): Cr–O 1.913(3), Cr–N 2.100(3), N–C(1) 1.463(5), N–C(16) 1.444(5), O–C(3) 1.336(4); O–Cr–O' $90.9(2)$, O–Cr–N $90.3(1)$, O–Cr–N' $169.9(1)$, N–Cr–N' $90.3(2)$.



Scheme 1 Preparation of chromium complexes **1** and **2** featuring ligand **1**. Reagents and conditions: (i) 2LiI, -78°C , THF, 12 h; (ii) NaI, -78°C , THF, 12 h, followed by recrystallisation from heptane- CH_3CN .

dimethylphenyl rings are sheared, there being no $\pi\cdots\pi$ stacking interaction between them.

By contrast, reaction of one equivalent of the sodium salt

Table 1 Results of ethylene polymerisation runs using procatalysts **1** and **2**^a

Run	Procatalyst/ mmol	Activator ^b / mmol (equiv.)	Yield PE ^c /g	Activity/ g mmol ⁻¹ h ⁻¹ bar ⁻¹
1	1 (0.017)	MAO (12/700)	0.26	15
2	1 (0.017)	Et ₂ AlCl (0.6/35)	1.02	60
3	2 (0.025)	MAO (10/400)	0.11	4
4	2 (0.025)	Et ₂ AlCl (0.5/20)	3.26	130§

^a General conditions: 1 bar ethylene, Schlenk test carried out in toluene (40 cm³) at 25 °C, over 60 min, reaction quenched with dilute HCl and the solid washed with methanol (50 cm³) and dried in a vacuum oven at 40 °C. ^b MAO = Methylaluminoxane. ^c Solid polyethylene.

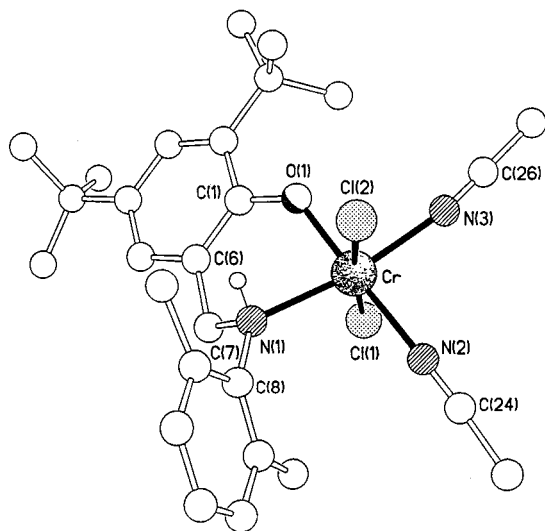


Fig. 2 The molecular structure of **2**. Selected bond lengths (Å) and angles (°): Cr–O(1) 1.865(3), Cr–N(1) 2.123(3), Cr–N(2) 2.102(4), Cr–N(3) 2.100(4), Cr–Cl(1) 2.311(2), Cr–Cl(2) 2.330(2), O(1)–C(1) 1.341(5), N(1)–C(7) 1.486(6), N(1)–C(8) 1.468(5); O(1)–Cr–N(3) 88.9(1), O(1)–Cr–N(2) 179.3(1), N(3)–Cr–N(2) 90.4(2), O(1)–Cr–N(1) 82.7(1), N(3)–Cr–N(1) 171.1(2), N(2)–Cr–N(1) 98.0(1), O(1)–Cr–Cl(1) 92.7(1), N(3)–Cr–Cl(1) 86.8(1), N(2)–Cr–Cl(1) 87.4(1), N(1)–Cr–Cl(1) 96.5(1), O(1)–Cr–Cl(2) 91.6(1), N(3)–Cr–Cl(2) 89.0(1), N(2)–Cr–Cl(2) 88.3(1), N(1)–Cr–Cl(2) 88.3(1), Cl(1)–Cr–Cl(2) 174.0(1).

of 3,5-(^tBu)₂-2-(OH)C₆H₂CH₂NH(2,6-Me₂C₆H₃) in THF at –78 °C with CrCl₃(THF)₃ affords, upon recrystallisation from acetonitrile–heptane, green blocks of the mono-chelated octahedral chromium(III) complex {Cr[3,5-(^tBu)₂-2-(O)C₆H₂CH₂NH(2,6-Me₂C₆H₃)](η¹-NCCH₃)₂Cl₂} **2**[†] (51%) (Scheme 1). The crystal structure[‡] of **2** shows the geometry at chromium to be distorted octahedral with *trans*-chlorides and *cis*-acetonitriles (Fig. 2) and angles ranging from 82.7(1)–98.0(1)° and 171.1(2)–179.3(1)°. Interestingly, the bite of **1** is here reduced to 82.7(1)°, *cf.* 90.3(1)° in **1**. The geometry of the six-membered chelate ring is also different, adopting here a half-chair conformation with the N(1)–Cr–C(7) plane being folded by *ca.* 58° out of the Cr–O(1)–C(1)–C(6)–C(7) plane. The Cr–O(1) and Cr–N(1) distances are comparable to those observed in **1** and in other related systems.¹¹

The infrared spectra of complexes **1** and **2** both exhibit absorption bands between 3312 and 3222 cm⁻¹ consistent with ν(N–H) stretching modes while complex **2** shows, in addition, strong bands at 2319 and 2291 cm⁻¹ due to the symmetric and asymmetric nitrile stretches.¹² Both complexes are paramagnetic with the Cr(II) complex **1** displaying a magnetic moment of 2.6 μ_B (consistent with an *S* = 1 ground state) and the Cr(III) complex, **2**, 3.9 μ_B (Evans balance).

The results of the ethylene polymerisation runs are collected in Table 1. Compounds **1** and **2** are both active as procatalysts in ethylene polymerisation and afford polymers with high molecular weight and virtually no branching by NMR.[§]

The highest activity is observed using a combination of **2** and

Et₂AlCl (130 g mmol⁻¹ h⁻¹ bar⁻¹, run 4). Under related conditions, the chromium(II) species **1** results in an activity less than half that of **2** (60 g mmol⁻¹ h⁻¹ bar⁻¹, run 2). As we have reported elsewhere⁵ dialkylaluminium chlorides appear to be more compatible co-catalysts (runs 2, 4) than MAO (runs 1, 3) for chromium systems of this type.

In conclusion, two chromium complexes incorporating the bulky reduced-Schiff-base ligand **1** have been prepared and their role in ethylene polymerisation has been examined. The higher activity observed for **2** relative to **1** may be attributed to a more accessible chromium centre, possibly aided by the lability of the ancillary acetonitrile ligands. Further studies are in progress to obtain a greater understanding of the factors influencing the activity and selectivity of these and related molecular chromium polymerisation catalysts.

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Notes and references

[†] Synthesis of **1**: to a THF (20 cm³) solution of **HI** (1.62 g, 4.76 mmol) was added ^tBuLi (3.2 cm³, 5.0 mmol) at –78 °C. The solution was allowed to warm to room temperature and stirred for 1 h. On cooling to –78 °C, solid CrCl₃(THF)₃ (0.90 g, 2.38 mmol) was added. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. Following removal of the volatile components, the residue was extracted into pentane (50 cm³) and taken to dryness. Recrystallisation from heptane afforded, on prolonged standing (1–2 d) at ambient temperature, dark red prisms of **1** in 45% yield (0.62 g) (Found: C, 75.8; H, 8.2; N, 3.5. Calc. for C₄₆H₆₄N₂O₂Cr **1**: C, 75.8; H, 8.8; N, 3.8%).

Synthesis of **2**: **HI** (2.00 g, 5.89 mmol) and NaH (0.31 g, 12.96 mmol) were refluxed in THF (45 cm³) for 12 h. On cooling, the suspension was filtered into a solution of CrCl₃(THF)₃ (2.21 g, 5.89 mmol) in THF (25 cm³) at –78 °C. The solution was stirred at room temperature for 12 h. Following removal of the volatile components, the solid residue was extracted into toluene (75 cm³) and taken to dryness. Recrystallisation from acetonitrile–heptane (1:3) afforded **2** as green blocks on prolonged standing (3–4 d). Yield 51% (1.65 g) (Found: C, 59.4; H, 7.7; N, 7.0. Calc. for C₂₇H₃₈N₃OCl₂Cr **2**: C, 59.7; H, 7.0; N, 7.7%).

[‡] Crystal data for **1**: C₄₆H₆₄N₂O₂Cr, *M* = 729.0, monoclinic, *I*2/a (no. 15), *a* = 13.645(5), *b* = 18.382(4), *c* = 17.243(8) Å, β = 102.73(2)°, *V* = 4219(3) Å³, *Z* = 4 (the molecule has *C*₂ symmetry), *D*_c = 1.148 g cm⁻³, μ(Mo–Kα) = 3.08 cm⁻¹, *F*(000) = 1576, *T* = 203 K; red blocks, 0.50 × 0.43 × 0.37 mm, Siemens P4/PC diffractometer, ω-scans, 3669 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on *F*² to give *R*₁ = 0.060, *wR*₂ = 0.125 for 2158 independent observed reflections [*|F_o|* > 4σ(*|F_o|*), 2θ ≤ 50°] and 235 parameters.

Crystal data for **2**: C₂₇H₃₈N₃OCl₂Cr, *M* = 543.5, monoclinic, *P*2₁/*n* (no. 14), *a* = 9.566(1), *b* = 13.048(2), *c* = 23.432(4) Å, β = 95.83(1)°, *V* = 2909.7(8) Å³, *Z* = 4, *D*_c = 1.241 g cm⁻³, μ(Cu–Kα) = 50.9 cm⁻¹, *F*(000) = 1148, *T* = 293 K; green plates, 0.27 × 0.27 × 0.10 mm, Siemens P4/PC diffractometer, ω-scans, 4438 independent reflections. The structure was solved by direct methods and the major occupancy non-hydrogen atoms were refined anisotropically using full matrix least-squares based on *F*² to give *R*₁ = 0.057, *wR*₂ = 0.127 for 3139 independent observed absorption corrected reflections [*|F_o|* > 4σ(*|F_o|*), 2θ ≤ 128°] and 324 parameters. CCDC reference number 186/1346. See <http://www.rsc.org/suppdata/dt/1999/827> for crystallographic files in .cif format.

[§] As a representative example, GPC analysis of the polyethylene obtained from run 4 afforded *M*_w 827000, *M*_n 84000, *M*_w/*M*_n 9.8; ¹³C NMR (C₂D₂Cl₄–1,2,4-trichlorobenzene at 130 °C) gave 0.6 Me per 1000 C atoms.

- W. Kaminsky, *J. Chem. Soc., Dalton Trans.*, 1998, 1413; K. Soga and T. Shiono, *Prog. Polym. Sci.*, 1997, **22**, 1503; R. G. Harvan, *Chem. Ind.*, 1997, 212; R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325; G. P. J. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.
- G. P. J. 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. L. Small, M. Brookhart and A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049.

- 3 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; L. K. Johnson, C. M. Killian, S. D. Arthur, J. Feldman, E. F. McCord, S. J. McLain, K. A. Kreutzer, M. A. Bennett, E. B. Coughlin, S. D. Ittel, A. Parthasarathy, D. J. Tempel and M. S. Brookhart (DuPont), *Pat.* WO 96/23010, 1996; *Chem Abstr.*, 1996, **125**, 222773t.
- 4 F. J. Karol, G. L. Karapinka, C. Wu, A. W. Dow, R. N. Johnson and W. I. Carrick, *J. Polym. Sci., Part A*, 1972, **10**, 2621; J. P. Hogan, *J. Polym. Sci., Part A*, 1972, **8**, 2637.
- 5 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.
- 6 W.-K. Kim, M. J. Fevola, L. M. Liable-Sands, A. L. Rheingold and K. H. Theopold, *Organometallics*, 1998, **17**, 4541.
- 7 For recent reviews see, K. H. Theopold, *Eur. J. Inorg. Chem.*, 1998, **1**, 15; K. H. Theopold, *CHEMTECH*, 1997, **27**, 26.
- 8 R. Emrich, O. Heinemann, P. W. Jolly, C. Krüger and G. P. J. Verhovnik, *Organometallics*, 1997, **16**, 1511.
- 9 M. P. Coles, C. I. Dalby, V. C. Gibson, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc., Chem. Commun.*, 1995, 1709.
- 10 F. J. Feher and R. L. Blanski, *J. Chem. Soc., Chem. Commun.*, 1990, 1614.
- 11 G. Wilkinson, C. Redshaw, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1992, 1803.
- 12 S. J. Anderson, F. J. Wells, G. Wilkinson, B. Hussain and M. B. Hursthouse, *Polyhedron*, 1988, **7**, 2615.

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