Well-defined Ethylene Polymerisation Catalysts derived from Bis(imido) Chromium(VI) Precursors

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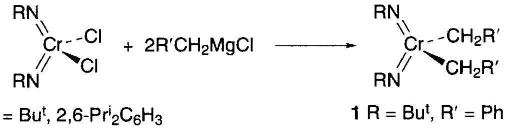
Well-defined, cationic alkyl chromium polymerisation catalysts are generated upon treatment of the chromium(VI) dialkyl complexes $Cr(NR)_2(CH_2R')_2$ (R = Bu^t, R′ = Ph; R = $2,6\text{-}Pr^i{}_2C_6H_3$, R′ = Ph, H) with the borate salts $[Ph_3C][B(C_6F_5)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$.

In recent years there has been a resurgence of interest in group 4 metallocene compounds as homogeneous alkene polymerisation catalysts (i) due to the spectacular rate enhancements afforded by methylaluminoxane (MAO) as a co-catalyst[1] and (ii) due to the subsequent development of well-defined, cationic alkyl derivatives[2] that have allowed unprecedented levels of control over the polymerisation process and much insight into how such catalysts function.

We have been exploring the isolobal relationship between η^5-C_5H_5 and imido ligands with a view to developing new reagents for organic synthesis and polymerisation catalysis.[3] The bis(imido)chromium system is of particular relevance to polymerisation catalysis since chromium catalysts play a central role in the worldwide production of polyolefins. The commercial catalyst formulations are heterogeneous, the Union Carbide 'Unipol' family of catalysts being prepared by treatment of silica with low-valent organometallic compounds such as chromocene,[4] while the Philips catalyst system involves the deposition of CrO_3 on silica, followed by reductive activation.[5] With the exception of Theopold's half-sandwich Cr^{III} system,[6] examples of homogeneous chromium polymerisation catalysts remain rare. Here, we describe the synthesis and characterisation† of some novel well-defined cationic alkyl chromium complexes that are surprisingly efficient homogeneous ethylene polymerisation catalysts.

The catalysts are derived from the chromium(VI) dialkyl compounds $Cr(NR)_2(CH_2R')_2$ [**1** R = Bu^t, R′ = Ph; **2**; R = $2,6\text{-}Pr^i{}_2C_6H_3$, R′ = Ph; **3** R = $2,6\text{-}Pr^i{}_2C_6H_3$, R′ = H] which may be synthesised in good yield according to Scheme 1. Schaverien[7] has previously found that the dialkyl derivatives of bis(*tert*-butylimido)chromium are invariably oils which presents considerable difficulties in their handling and purification. We have found, however, that the previously unreported dibenzyl derivative may be isolated as a deep-red crystalline solid. We have also recently described the first bis(arylimido)chromium complexes[8] and find that the 2,6-diisopropylphenylimido group affords a beneficial effect on crystallinity; for example, not only the dibenzyl complex **2** but also the dimethyl derivative **3** bearing 2,6-diisopropylphenylimido ligands may be isolated as crystalline green solids. Due to the close isolobal relationship of compounds **1**–**3** with metallocene dialkyl species that are commonly used as precursors to cationic metallocene alkyl catalysts, a crystal structure of a chromium precursor was of considerable interest. X-Ray quality crystals of **1** were grown from a saturated pentane solution at −30 °C and the molecular structure is shown in Fig. 1.‡

The most striking feature of the structure is the presence of η^1- and η^2-benzyl ligand coordination modes. The bond parameters for the η^2 ligand, a C(9)–C(10) bond length of 1.443(3) Å, a Cr–C(9)–C(10) angle of 82.16(11)° and elongated C_{ipso}–C_{ortho} distances [1.409(3) Å (av) *cf.* 1.395(3) Å (av.) for the η^1 CH_2Ph group] are within the ranges found for other η^2-benzyl ligands.[9] The interaction of the *ipso* carbon with the metal centre lies between the Cr–C(9) and Cr–C(16) bonds and is approximately in the plane defined by C(9)–Cr–C(16) (deviation 4.8°) consistent with the metallocene-like frontier orbitals of the $[Cr(NR)]_2$ fragment. The N–Cr–N angle of 116.09(8)° is comparable with the value found in $Cr(NBu^t)_2(2,4,6\text{-}Me_3C_6H_2)_2$ [114.5(3)°][10] as are the Cr=N distances of 1.625(2) and 1.632(2) Å.



R = Bu^t, $2,6\text{-}Pr^i{}_2C_6H_3$

1 R = Bu^t, R′ = Ph
2 R = $2,6\text{-}Pr^i{}_2C_6H_3$, R′ = Ph
3 R = $2,6\text{-}Pr^i{}_2C_6H_3$, R′ = H

Scheme 1

The presence of the η^2-benzyl ligand is not clearly evident in room temperature solution NMR spectra due to rapid averaging of the η^1- and η^2-environments, and furthermore a frozen structure is not observed to −80 °C in CD_2Cl_2. A solid state ^{13}C NMR spectrum, however, clearly shows the two coordination modes, with distinguishing shifts for the *ipso*-phenyl carbon atoms at δ 157.9 (η^1) and 124.4 (η^2).

Treatment of **1** with $[Ph_3C][B(C_6F_5)_4]$ in CH_2Cl_2 affords Ph_3CCH_2Ph and the red cationic mono-benzyl complex **4** which forms an immiscible oil in hydrocarbon solvents but is completely miscible in CH_2Cl_2. NMR data for **4** indicate that the remaining benzyl ligand is bound in η^2-fashion; for example, the *ipso* carbon resonance occurs at δ 128.8 with a small $^2J_{CH}$ coupling of 5.3 Hz to the benzyl methylene hydrogens (confirmed by selective decoupling of the methylene

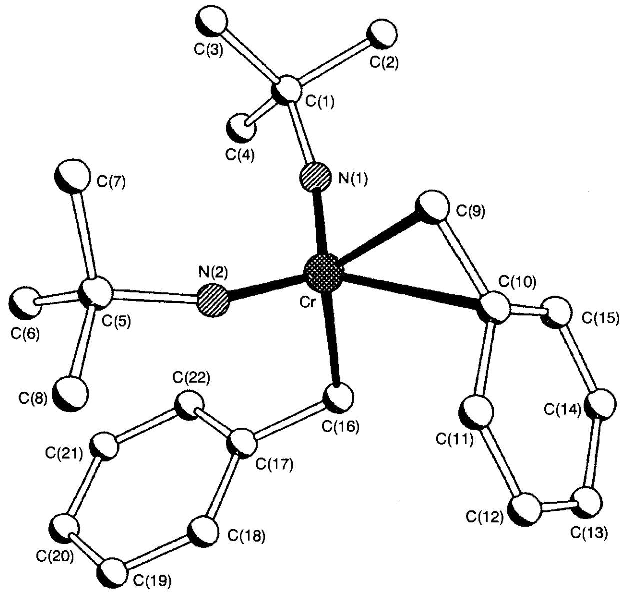
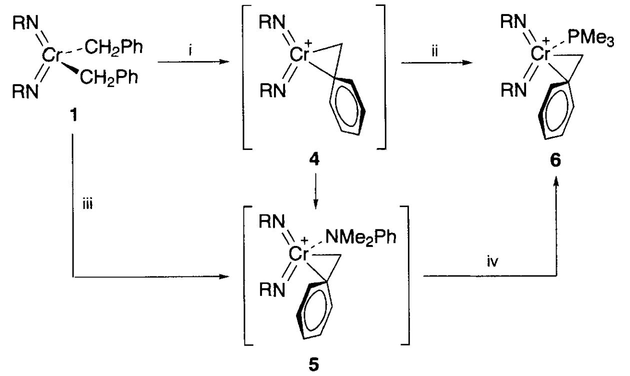


Fig. 1 Molecular structure of **1**, without H atoms and with atom labels. Selected dimensions (Å and °): Cr–N(1) 1.625(2), Cr–N(2) 1.632(2), Cr–C(9) 2.071(2), Cr–C(10) 2.357(2), Cr–C(16) 2.096(3), C(9)–C(10) 1.443(3), C(10)–C(11) 1.411(3), C(10)–C(15) 1.406(3), other C–C in this ligand in range 1.371(3)–1.384(3), C(16)–C(17) 1.475(3), other C–C in this ligand in range 1.375(3)–1.402(3); N(1)–Cr–N(2) 116.09(8), C(9)–Cr–C(10) 37.32(8), C(9)–Cr–C(16) 131.93(8), C(10)–Cr–C(16) 94.86(7), Cr–N(1)–C(1) 166.07(13), Cr–N(2)–C(5) 160.60(13), Cr–C(9)–C(10) 82.16(11), Cr–C(16)–C(17) 114.73(13).



Scheme 2 *Reagents and conditions*: i, $[Ph_3C][B(C_6F_5)_4]$ (1 equiv.), CH_2Cl_2, room temp. 30 min; ii, PMe_3 (1 equiv.), CH_2Cl_2, room temp. 10 min; iii, $[PhNMe_2H][B(C_6F_5)_4]$, CH_2Cl_2, room temp. 30 min; iv, PMe_3 (1 equiv.), CH_2Cl_2, room temp. 10 min

protons in the ^{13}C NMR spectrum); the methylene carbon resonance appears at δ 59.3. It has not proved possible to establish the precise structure of **4**, for example by X-ray crystallography, due to its oily nature; a higher nuclearity species is a possibility, though a single resonance for the *tert*-butylimido methyl groups appears to rule out a static structure involving both bridging and terminal imido groups. Treatment of **4** with trimethylphosphine gives a PMe_3 adduct **6** whose NMR data are consistent with the four coordinate, pseudo-tetrahedral structure shown in Scheme 2. The methylene hydrogens of the η^2-benzyl ligand show a coupling of 2 Hz to the adjacent phosphorus, while the methylene carbon appears as a doublet resonance at δ 52.9 ($^2J_{CP}$ = 4.5 Hz) in the proton decoupled spectrum. The *ipso* carbon resonance at δ 128.8, by contrast, shows no coupling to phosphorus, though a small triplet splitting (5.3 Hz) due to the methylenic hydrogens is observable in the proton coupled spectrum. These observations are consistent with the benzyl methylene group lying adjacent to the PMe_3 ligand by comparison with the spectral features of other $[M(NBu^t)_2(L)(PMe_3)]$ complexes,[11] where L is an alkene or alkyne. The reaction of **1** with $[PhNMe_2H][B(C_6F_5)_4]$ gives a more complicated product mixture that contains both bound and free $PhNMe_2$, plus an additional minor species that remains unidentified. The spectral features of the major component are consistent with the mono-amine adduct **5**. This same mixture results upon treatment of the base-free cation **4** with 1 equiv. of $PhNMe_2$, while the mixture containing **5** is cleanly converted to **6** upon treatment with PMe_3.

Solutions of both **4** and **5** in either CH_2Cl_2 or toluene are highly active for the polymerisation of ethylene, with figures of merit considerably higher than for conventional dual component systems of the type $Cr(NBu^t)_2Cl_2$–Et_2AlCl and $Cr(NBu^t)_2Cl_2$–MAO.[12] For example, exposure of the solutions of **4** or **5** to 10 bar of ethylene for 60 min periods produces polyethylene§ with activities in the range 25 000 to 66 000 $g\,mol^{-1}\,h^{-1}\,bar^{-1}$.

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Footnotes

† *Crystal data* for **1**: $C_{22}H_{32}CrN_2$, M = 376.5, orthorhombic, space group $P2_12_12_1$, a = 9.785(8), b = 14.75(2), c = 14.794(10) Å, U = 2135(3) Å^3, Z = 4, D_c = 1.171 g cm^{-3}, $F(000)$ = 808. 11 235 reflections were measured on a Stoe-Siemens diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, $2\theta < 50°$, μ = 0.542 mm^{-1}) with ω/θ scans and on-line profile fitting.[13] Data were corrected for absorption by a semi-empirical method from Ψ-scan data.[14] Structure solution was by direct methods,[14] refinement by full-matrix least-squares analysis on F^2 for all 3769 independent reflections (R_{int} = 0.0571).[14] $Rw = \{\Sigma[w(F_o2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.0678 for all data, conventional R [on F values of 3651 reflections with $F_o^2 > 2\sigma(F_o^2)$] = 0.0259, goodness of fit S = 1.062 on F^2 for 246 refined parameters. All non-H atoms were refined with anisotropic displacement parameters, H-atoms were constrained. Refinement of an enantiopole parameter indicates probable racemic twinning.[15] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ *Selected spectroscopic data* for **1**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 6.99 (m, 10 H, C_6H_5), 2.49 (s, 4 H, CH_2Ph) and 1.20 [s, 18 H, $NC(CH_3)_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ 140.34 (s, C_6H_5-C_{ipso}), 131.60 (d, $^1J_{CH}$ 157.1 Hz, C_6H_5-C_{ortho}), 128.94 (d*, C_6H_5–C_{meta}), 125.65 (d, $^1J_{CH}$ 160.5 Hz, C_6H_5–C_{para}), 71.97 [s, $C(CH_3)_3$], 44.50 (t, $^1J_{CH}$ 141.9 Hz, CH_2Ph), 31.63 [q, $^1J_{CH}$ 127.0 Hz, $C(CH_3)_3$]. For **2**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 7.17–6.88 (m, 16 H, CH_2Ph and C_6H_3), 3.85 (sept, $^3J_{HH}$ 6.6 Hz, 4 H, $CHMe_2$), 3.41 (s, 4 H, CH_2Ph), and 1.12 (d, $^3J_{HH}$ 7.2 Hz, 24 H, $CHMe_2$). ^{13}C NMR (C_6D_6, 125 MHz, 298 K): δ 158.00 (s, C_6H_3–C_{ipso}), 146.03 (s, C_6H_3–C_{ortho}), 140.15 (s, C_6H_5–C_{ipso}), 132.69 (d, $^1J_{CH}$ 158.3 Hz, C_6H_5–C_{ortho}), 128.78 (d*, C_6H_5–C_{meta}), 127.12 (d*, C_6H_3–C_{para}), 126.24 (d, $^1J_{CH}$ 160.2 Hz, C_6H_5–C_{para}), 122.79 (d, $^1J_{CH}$ 156.4 Hz, C_6H_3–C_{meta}), 59.88 (t, $^1J_{CH}$ 139.6 Hz, CH_2Ph), 28.48 (d, $^1J_{CH}$ 129.3 Hz, $CHMe_2$), 23.87 (q, $^1J_{CH}$ 125.9 Hz, $CHMe_2$). For **3**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 6.91 (m, 6 H, C_6H_3), 3.73 (sept, $^3J_{HH}$ 6.9 Hz, 4 H, $CHMe_2$), 1.83 (s, 6 H, CH_3) and 1.12 (d, $^3J_{HH}$ 6.8 Hz, 6 H, $CHMe_2$). ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ 157.81 (s, C_6H_3–C_{ipso}), 145.24 (s, C_6H_3–C_{ortho}), 127.60 (d*, C_6H_3–C_{para}), 122.74 (d, $^1J_{CH}$ 156.4 Hz, C_6H_3–C_{meta}), 49.73 (q, $^1J_{CH}$ 130.5 Hz, CH_3), 28.80 (d, $^1J_{CH}$ 128.9 Hz, $CHMe_2$), 23.52 (q, $^1J_{CH}$ 126.0 Hz, $CHMe_2$). (* $^1J_{CH}$ value obscured by overlap with solvent resonance.)

For **4**: ^1H NMR (CD_2Cl_2, 250 MHz, 298 K): δ 6.67–7.90 (m, 25 H, $C_2H_2Ph_4$ and CH_2Ph), 4.22 (s, 2 H, $CH_2C_6H_5$), 4.00 (s, 2 H, $C_2H_2Ph_4$) and 1.59 (s, 18 H, CMe_3). ^{13}C NMR (CD_2Cl_2, 100.6 MHz, 298 K): δ 128.65 (d, $^1J_{CH}$ 159.9 Hz, $CH_2C_6H_5$–$C_{o/m}$), 129.70 (d*, $CH_2C_6H_5$–$C_{o/m}$), 128.78 (t, $^2J_{CH}$ 5.3 Hz, $CH_2C_6H_5$–C_{ipso}), 126.65 (d, $^1J_{CH}$ 161.9 Hz, $CH_2C_6H_5$–C_{para}), 79.56 (s, CMe_3), 59.34 (t, $^1J_{CH}$ 160.9 Hz, $CH_2C_6H_5$) and 31.07 [q, $^1J_{CH}$ 128.8 Hz, $C(CH_3)_3$]. (* $^1J_{CH}$ value obscured by overlap with 1,1,1,2-tetraphenylethane resonances.) For **5**: ^1H NMR (CD_2Cl_2, 250 MHz, 298 K): δ 6.87–7.39 (m, aryl H), 3.84 (s, 2 H, $CH_2C_6H_5$), 2.88 (s, 6 H, $C_6H_5NMe_2$), 1.67 (s, 18 H, CMe_3). For **6**: ^1H NMR (CD_2Cl_2, 400 MHz, 298 K): δ 6.67–7.90 (m, aryl H), 3.94 (d, $^3J_{PH}$ 2.0 Hz, 2 H, $CH_2C_6H_5$), 1.51 (s, 18 H, CMe_3) and 1.28 (d, $^2J_{PH}$ 10.4 Hz, 9 H, PMe_3). ^{13}C NMR (CD_2Cl_2, 100.6 MHz, 298 K): δ 128.64 (d, $^1J_{CH}$ 160.9 Hz, CH_2C_6H–$C_{o/m}$), 129.69 (d*, $CH_2C_6H_5$–$C_{o/m}$), 128.77 (t, $^2J_{CH}$ 5.3 Hz, $CH_2C_6H_5$–C_{ipso}), 126.63 (d, $^1J_{CH}$ 161.0 Hz, $CH_2C_6H_5$–C_{para}), 76.96 (d, $^3J_{CP}$ 2.3 Hz, CMe_3), 52.86 (td, $^1J_{CH}$ 159.1 Hz, $^2J_{CP}$ 4.5 Hz, $CH_2C_6H_5$), 31.45 (q, $^1J_{CH}$ 128.4 Hz, CMe_3) and 17.53 (qd, $^1J_{CP}$ 29.8 Hz, $^1J_{CH}$ 131.6 Hz, PMe_3). (* $^1J_{CH}$ value obscured by overlap with 1,1,1,2-tetraphenylethane resonances.) ^{31}P NMR (CD_2Cl_2, 101.26 MHz, 298 K): δ 12.4 (s, PMe_3). Satisfactory analyses has been obtained for compounds **1**–**3**.

§ Details of the polyethylene products will be published at a later date.

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