Constrained geometry nitrogen-functionalised diphenylcyclopentadienyl chromium (III) complex: synthesis, structure and catalytic properties for ethylene polymerisation

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A bidentate ligand 1-[2-(*N*,*N*-dimethylaminophenyl)]-3, 4-biphenylcyclopentadiene **1**, as well as its corresponding constrained geometry chromium complex dichloro-η^5-[1-(2-*N*,*N*-dimethylaminophenyl)-3, 4-diphenylcyclopentadienyl] chromium (III) **2** have been synthesised and characterised. When activated with $Al(^iBu)_3$ and $Ph_3C[B(C_6F_5)_4]$, complex **2** exhibits reasonable catalytic activity for ethylene polymerisation, producing polyethylenes with moderate molecular weights and melting points. The effects of polymerisation temperature, ethylene pressure, B/Cr and Al/Cr ratios on catalytic activity were studied.

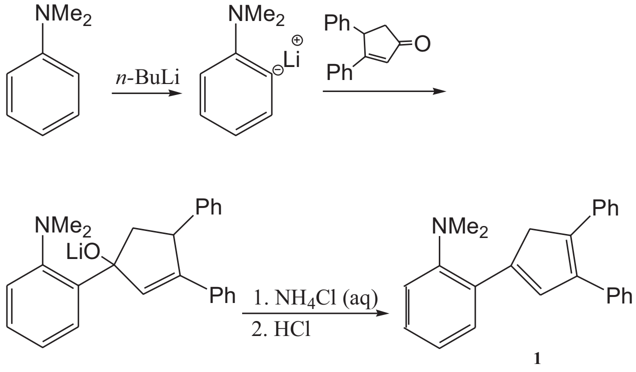
Keywords: constrained geometry catalyst, chromium complex, metallocene, ethylene polymerisation

In recent years, organometallic transition metal olefin polymerisation catalysts with a cyclopentadienyl ligand bearing a sidearm with a donor moiety have attracted extensive attention.[1] The constrained geometry catalysts of titanium and zirconium have been widely studied in industry and academic institutions for their good catalytic properties.[2,3] Recently, some of constrained geometry catalysts of chromium such as $[CrCl_2(\eta^1:\eta^5\text{-}Me_2NC_2H_4C_5Me_4)]$(**3**)[4] and $[CrCl_2(\eta^1:\eta^5\text{-}Me_2NC_6H_4C_5Me_4)]$(**4**)[5] have been developed. However, there have been limited reports on the synthesis and catalytic properties of this type of cyclopentadienylchromium (III) catalyst. We have focused on the synthesis and properties of constrained geometry olefin polymerisation catalysts in recent years[6,7] and have modified the *N*,*N*-dimethylanilinylcyclopentadienyl ligand by introducing two electron-withdrawing Ph groups to the Cp group to reduce the electron density of the Cp ring and its reactivity in the complex-forming reaction, and therefore increase the selectivity of forming the desired complex in its synthetic reaction.[6] With the new ligand precursor, we have synthesised a new constrained geometry chromium (III) complex in high yield (> 90%). We now report the synthesis and characterisation of the ligand precursor 1-[2-(*N*,*N*-dimethylaminophenyl)-3, 4-biphenylcyclopentadiene **1**, and the complex η^1: η^5-[1-(2-*N*,*N*-dimethylaminophenyl)-3, 4-diphenylcyclopentadienyl] chromium (III) dichloride **2**, as well as the catalytic performance of complex **2** for ethylene polymerisation.

Results and discussion

Synthesis of ligand precursor

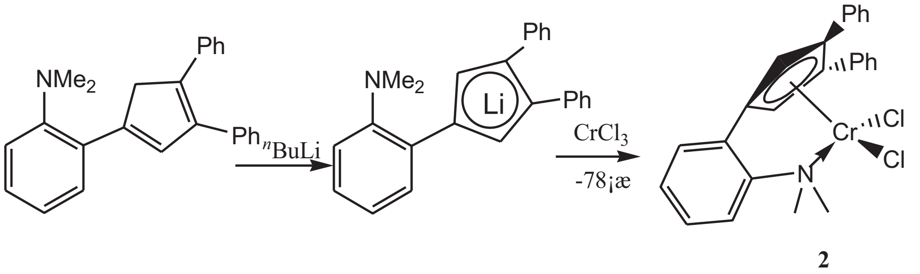
Ligand precursor **1** was synthesised by the reaction of 4-diphenyl-2-cyclopentenone with the lithium salt of *N*,*N*-dimethylaniline in toluene at room temperature followed by hydrolysation and dehydration (Scheme 1). The lithium salt of *N*,*N*-dimethylaniline was obtained by the reaction of *N*,*N*-dimethylaniline with *n*-BuLi without solvent at 80°C. The lithium salt of *N*,*N*-dimethylaniline could not be obtained when reactions were carried out in the presence of Et_2O or THF as solvent. Compound **1** was characterised by elemental analysis and NMR spectroscopy. The character of ligand **1** is different from 1-[2-(*N*,*N*-dimethylaminophenyl)-2, 3, 4, 5- tetramethylcyclopentadiene which has three isomers.[8]



Scheme 1 Synthesis of ligand 1

Synthesis of complex 2

Complex **2** was synthesised from the reaction of $CrCl_3$ with the lithium salt of ligand **1** (Scheme 2). The ligand precursor **1** was treated with one equivalent of *n*-BuLi, and then mixed with a solution of $CrCl_3$ in THF at –78°C. After filtration and concentration of the reaction mixture, complex **2** was obtained as a blue crystalline solid in a high yield (> 90%).



Scheme 2 Synthesis of complex **2**.

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Complex **2** is green in THF and blue in CH_2Cl_2. Compared to the synthesis of complex **4**, the yield of complex **2** is increased presumably due to the introduction of the two electron-withdrawing Ph groups to the Cp ring, which would reduce the electron density of the Cp and its reactivity, and increase the selectivity of forming the desired complex **2**.[6] The reaction was also tried in toluene and Et_2O, and complex **2** could not be obtained because of the low solubility of $CrCl_3$ in these solvents. It was found that complex **2** can be easily hydrolysed in solution but it is considerably stable in the solid state. Due to the paramagnetic nature of complex **2**, NMR study was not feasible. Elemental analysis of complex **2** fits the structure obtained by X-ray crystal structure study.

Crystal structure of complex **2**

The molecular structure of complex **2** was determined by X-ray crystal structure analysis. The ORTEP drawing of the molecule structure is shown in Fig. 1. The selected bond lengths and angles are summarised in Table 1. The general structure feature of **2** is comparable to that previously reported for **4** which adopt C_s-symmetry with pseudo-tetrahedral geometry. The chromium atom is bonded to the nitrogen donor and is η^5-coordinated by the cyclopentadienyl ring. The metal atom is not located exactly below the centre of the five-membered ring but is shifted slightly toward the tethered donor ligand. The distances of $Cr–C_3$ and $Cr–C_4$ in **2** are obviously longer than those of the Cr–C(Cp) bonds and the $Cr–Cp(cent)–C_1$ angle of **2** (85.2°) is less than 90°. The nitrogen–chromium distance in **2** (2.18 Å) is somewhat shorter than that in **4** (2.25 Å), and the Cl–Cr–Cl angle in complex **2** (97.98°) is slightly smaller than that in complex **4** (98.1°). The Cp(cent)–Cr–N angle is 117.4° and the dimethylaniline plane–Cp plane dihedral angle is 72.5° for **2** which is smaller than that of **4** (87.3°). The (dimethylaniline) $C_6–C_1$(Cp) vector is bent 10.9° in **2** from the Cp ring plane. The differences in solid state structures of complex **2** and **4** probably result from crystal packing forces since there is no other reasonable explanation for them.

Ethylene polymerisation studies

Complex **2** was studied as an ethylene polymerisation catalyst and the results are summarised in Table 2. Upon alkylation and activation with $Al(^iBu)_3$ and $Ph_3C[B(C_6F_5)_4]$, complex **2** turns green from blue, which indicates the catalytically active species is formed. The catalyst system shows reasonable catalytic activity for ethylene polymerisation, producing polyethylenes with moderate molecular weights and melting points. Compared with the catalytic activity of complex **3** (1.66×10^6 g PE (mol Cr)$^{-1}$ h^{-1})[4] and complex **4** (3.55×10^6 g PE (mol Cr)$^{-1}$ h^{-1}),[5] complex **2** shows somewhat lower catalytic activity ($0.128{\sim}1.159 \times 10^6$ g PE (mol Cr)$^{-1}$ h^{-1}) for ethylene polymerisation. Under similar conditions, the catalytic activity of complex **2** increases with the increase in Al/Cr ratio and reaches the highest catalytic activities with the Al/Cr ratio about 300. Further increase in the Al/Cr ratio results in a decrease in the catalytic activity. It is possible that excessive $Al(^iBu)_3$ would consume enough $Ph_3C[B(C_6F_5)_4]$, which makes the activation of the catalyst inefficient.[9] The catalytic activity of **2** was also found to increase with the increase in B/Cr ratio from 1.1 to 1.3. Further increase of the B/Cr ratio results in a decrease in the catalytic activity. It is understandable that excessive $Ph_3C[B(C_6F_5)_4]$ would abstract the R group of the catalytic active species and deactivate the catalyst. The catalytic activity of complex **2** is low at room temperature and increases at elevated temperatures due probably to tight interaction between the catalyst cation and the cocatalyst anion in the constrained geometry catalyst systems.[10] ^{13}C NMR analysis of typical polymer samples reveals that the obtained polyethylenes are linear and do not contain the ethyl branch that is usually observed in the polyethylenes produced by titanium constrained geometry catalysts.

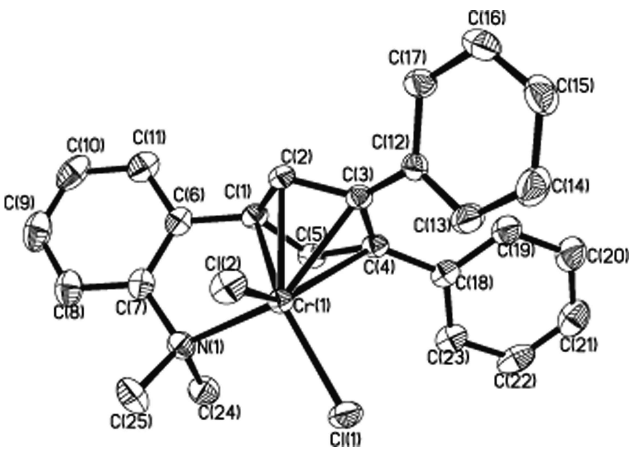

Fig. 1 Structure of complex **2** (Thermal ellipsoids are drawn at the 30% probability level).

Table 1 Selected bond lengths (Å) and angles (deg)

Complex **2**			
Cr(1)–C(1)	2.155(2)	Cr(1)–Cl(1)	2.2689(9)
Cr(1)–C(2)	2.209(2)	Cr(1)–Cl(2)	2.2942(9)
Cr(1)–C(3)	2.285(2)	Cr(1)–N(1)	2.184(2)
Cr(1)–C(4)	2.318(2)	N(1)–C(7)	1.465(3)
Cr(1)–C(5)	2.209(2)	C(4)–C(18)	1.478(3)
Cr–Cp(cent)–C(1)	85.2	Cr–Cp(cent)	1.882
Cp(cent)–Cr(1)–N(1)	111.7	Cl(1)–Cr(1)–Cl(2)	97.98(2)
C(7)–N(1)–Cr(1)	108.01(14)	C(25)–N(1)–C(24)	106.6(2)

Experimental

General comments

Reactions with organometallic reagents were carried out under an argon atmosphere (ultra-high purity) using standard Schlenk techniques.[11] Solvents were dried and distilled prior to use.[12] Polymerisation grade ethylene was further purified by passage through columns of 10 A molecular sieves and MnO. $Al(^iBu)_3$, *n*-BuLi and $CrCl_3$ were purchased from Aldrich. 3, 4-diphenyl-2-cyclopentenone,[13] and $Ph_3[CB(C_6F_5)4]$[14] were prepared according to literature procedures. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer.

Table 2 Summary of ethylene polymerisation catalysed by complex 2 (activated by $Ph_3C[B(C_6F_5)_4]$[a]

No.	Al: Cr	B[b]: Cr	T/°C	Yield/g	Activity[c]	$M\eta^d \times 10^{-4}$	T_m/°C[e]
1	300	1.3: 1	40	0.536	0.536	8.75	127.9
2	300	1.3: 1	60	1.159	1.159	9.85	131.9
3	300	1.3: 1	80	0.827	0.827	8.51	129.5
4	200	1.3: 1	60	0.229	0.229	7.54	128.3
5	400	1.3: 1	60	0.954	0.954	9.22	129.4
6	300	1.1: 1	60	0.842	0.842	8.23	128.7
7	300	1.5: 1	60	1.064	1.064	8.87	129.2
8[f]	300	1.3: 1	60	0.128	0.128	8.12	128.7

[a]Polymerisation conditions: solvent 50 ml of toluene, time 30 min, ethylene pressure 8 bar. [b]B means $Ph_3C[B(C_6F_5)_4]$. [c]10^6g PE (mol Cr)$^{-1}$ h^{-1}. [d]Mη means viscosity-average molecular weight of the polymers which measured in decahydro- naphthalene at 135°C. [e]T_m, Melting temperature of the polymers which determined by DSC at a heating rate of 10°C min^{-1}. [f]ethylene pressure 4 bar.

Preparation of 1-[2-(N,N-dimethylaminophenyl)-3, 4-biphenylcyclopentadiene **(1)**

N,N-dimethylaniline (5.0 ml, 0.04 mol) was added dropwise to 1.5 M *n*-BuLi (26.3 ml, 0.04 mol), in which the *n*-hexane has been moved, and then the mixture was heated to 80°C for 48 h. The lithium salt of *N,N*-dimethylaniline was washed with *n*-hexane and then dissolved in toluene. 4-Diphenyl-2-cyclopentenone (9.2 g, 0.04 mol) was added at room temperature. The reaction mixture was hydrolysed with saturated NH_4Cl (20 ml, aq) and then dehydrated with concentrated HCl (20 ml). The organic layer was separated, dried over $MgSO_4$, filtered and concentrated by distillation under reduced pressure. Pure product (6.3 g, 47.2%) was obtained by column chromatography over silica (Hexane/CH_2Cl_2, 4: 1) as a yellowish powder. Calcd for $C_{25}H_{23}N$ (337.18): C, 89.0, H, 6.9, N, 4.15. Found: C, 88.95, H, 6.9, N, 4.1. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 6.98–7.43(m, 14H, Ph), 7.14 (s, 1H, Cp), 4.06(s, H, Cp), 4.05(s, H, Cp), 2.72(s, 6H, N–Me_2). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 151.6, 145.1, 141.8, 139.0, 137.4, 137.0, 134.5, 130.2, 129.4, 128.4, 128.4, 128.2, 127.8, 127.6, 127.0, 126.3, 122.2, 118.5, 46.3, 44.0.

Preparation of dichloro-η^5-[1-(2-N,N-dimethylaminophenyl)-3, 4-diphenylcyclopentadienyl] chromium (III)

To a solution of ligand (0.51 g, 1.5 mmol) **1** in THF (15 ml) was added dropwise a solution of *n*-BuLi (1.5 mmol) at room temperature. After 30 min the orange solution was added dropwise to a suspension of $CrCl_3$ (0.24 g, 1.5 mmol) in THF (45 ml) at –78°C. The reaction mixture was warmed slowly to room temperature and stirred overnight. The colour of the reaction mixture turned from purple to dark green. The precipitate was filtered off and the solvent was removed to leave a blue solid. Recrystallisation from CH_2Cl_2: hexane (2: 1) gave pure **2** as blue crystals (0.64 g, 92.9%). Anal. Calcd for $C_{25}H_{22}Cl_2CrN$ (458.05): C, 65.4, H, 4.8, N, 3.05. Found: C, 65.3, H, 4.8, N, 3.0.

X-ray structure determinations of **2**

Single crystals of **2** suitable for X-ray structural analysis were obtained from solutions in mixed CH_2Cl_2/hexane (V/V = 2/1). The data were collected at 293(K) on a Bruker SMART-CCD diffractometer for **2** (graphite-monochromated Mo-K_α-radiation; λ = 0.71073Å). Details of the crystal data, data collections, and structure refinements are summarised in Table 3. Structure was solved by direct method[15] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealised position. All calculations were performed using the SHELXTL[16] crystallographic software packages.

Table 3 Crystal data and structural refinements details for 2

	2
Mol formula	$C_{25}H_{22}Cl_2CrN$
Mol wt	459.34
Cryst system	Orthorhombic
Space group	Pbca
a/Å	13.320(3)
b/Å	15.365(4)
c/Å	21.283(5)
α/deg	90
β/deg	90
γdeg	90
V/Å^3	4355.9(19)
Z	8
D_c/g cm^{-3}	1.401
F(000)	1896
Abs coeff/mm^{-1}	0.782
Scan type	ω-2θ
Collect range,deg	1.91≤2θ≤26.35
No. of reflns	23909
No. of indep reflns	4454
R_{int}	0.0549
No. of data/restraints/params	4454/0/350
R(I>2 sigma(I))	0.0392
R_w(I>2 sigma(I))	0.0961
Goodness of fit	1.031
Largest diff peak	0.439
And hole/e Å^{-3}	–0.209

Polymerisation reactions

A dry 250 ml steel autoclave was charged with toluene (50 ml), thermostated at the desired temperature and saturated with ethylene (1.0 bar). The polymerisation reaction was started by injection of a mixture of catalyst and $Al(^iBu)_3$ in toluene (5 ml) and a solution of $Ph_3C[B(C_6F_5)_4]$ in toluene (5 ml) at the same time. The vessel was repressurised to the required pressure with ethylene immediately and the pressure was maintained by continuously feeding monomer. After 30 minutes, the polymerisation was quenched by injecting acidified methanol [HCl(3 M): methanol = 1: 1]. The mixture was stirred overnight and the polymer was collected by filtration, washed with water, methanol, and dried in vacuo at 60°C to a constant weight.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number: 292291 (**2**). Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http: //wwwccd.cam.ac.uk).

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References

1 Review articles: (a) J. Okuda, *Commun. Inorg. Chem.*, 1994, **16**, 185; (b) P. Jutzi and U. Siemeling *J. Organomet. Chem.*, 1995, **500**, 175; (c) P. Jutzi and T. Redeker, *Eur. J. Inorg. Chem.*, 1998, **6**, 663; (d) C. Muller, D. Vos and P. Jutzi, *J. Organomet. Chem.*, 2000, **600**, 127; (e) H. Butenschön, *Chem. Rev.*, 2000, **100**, 1527; (f) U. Siemeling, *Chem. Rev.*, 2000, **100**, 1495; (g) A.L. McKnight and R.M. Waymouth, *Chem. Rev.*, 1998, **96**, 2587.

2 Y.X. Chen and T.J. Marks, *Organometallics*, 1997, **16**, 5958.

3 (a) E.E. Bunnel, B.J. Burger and J.E. Bercaw, *J. Am. Chem. Soc.*, 1988, **110**, 976; (b) W.E. Piers, P.J. Shapiro, E.E. Bunel and J.E Bercaw, *Synlett,* 1990, **2**, 74; (c) P.J. Shapiro, E.E. Bunel, W.P. Schaefer and J.E. Bercaw, *Organometallics*, 1990, **9**, 867; (d) P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger and J.E. Bercaw, *J. Am. Chem. Soc.*, 1994, **116**, 4623; (e) J. Okuda, *Chem. Ber*., 1990, **123**, 1649; (f) Y.X. Chen, C.L. Stern, S. Yang and T.J. Marks, *J. Am. Chem. Soc.*, 1996, **118**, 12451; (g) H.G. Alt, A. Reb, W. Milins and A. Weis, *J. Organomet. Chem.*, 2001, **628**, 169.

4 A. Döhring, J. Göhre, P.W. Jolly, B. Kryger, J. Rust and G.P. Verhovnik, *J. Organometallics*, 2000, **19**, 38.

5 M. Enders, P. Fernandez, G. Ludwig and H. Pritzkow, *Organometallics*, 2001, **20**, 5005.

6 Y. Zhang, J. Wang, Y. Mu, Z. Shi, C. Lü, Y. Zhang, L. Qiao and S. Feng, *Organometallics*, 2003, **22**, 3877.

7 Y. Zhang, Y. Mu, C. Lu, G. Li, J. Xu, Y. Zhang, D. Zhu and S. Feng, *Organometallics*, 2004, **23**, 540.

8 M. Enders, G. Fernandez and H. Pritzkow, *Organometallics*, 2001, **20**, 827.

9 M. Bochmann and M. Sarsfield, *J. Organometallics*, 1998, **17**, 5908.

10 Y. Mu, W.E. Piers, M.A. MacDonald and M. Zaworotko, *J. Can. J. Chem.*, 1995, **73**, 2233.

11 D.F. Shriver, *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

12 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *The Purification of Laboratory Chemicals*, Pergamon: New York, 1980.

13 F.X. Kohl and P. Jutzi, *J. Organomet. Chem.*, 1983, **243**, 119.

14 (a) A.G. Massey and A.J. Park, *J. Org. Chem.*, 1962, **2**, 245; (b) A.G. Massey and A.J. Park, *J. Organomet. Chem.*, 1966, **5**, 218; (c) J.C.W. Chien, W.M. Tsai and M.D. Rasch, *J. Am. Chem. Soc.*, 1991, **113**, 8570.

15 SHELXTL; PC Siemens Analytical X-ray Instruments: Madison WI, 1993.

16 G.M. Sheldrick, *SHELXTL Structure Determination Programs*, Version 5.0; PC Siemens Analytical Systems: Madison, WI, 1994.