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Synthesis, crystal structure and catalysis for polyethylene of a paramagnetic chromium complex $[(\eta^5-Cp^{Si})Cr(\mu-Cl)Cl]_2 [Cp^{Si} = (C_5H_4)Si(CH_3)_2(C_6H_5)]$

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Abstract

The synthesis of the substituted silyl cyclopentadiene ligand $(C_5H_5)Si(CH_3)_2(C_6H_5)$ $(Cp^{Si}H)$ (1) is described. Deprotonation of (1) gives $(Cp^{Si}Li)$ (2) which reacts with CrCl₃ to produce the chloro-bridged complex $[(\eta^5-Cp^{Si})Cr(\mu-Cl)Cl]_2$ (3). Single-crystal X-ray structure analysis reveals that a centrosymmetric dimer exists in the solid state. When activated with methylaluminoxane (MAO), complex (3) exhibits several interesting features as a catalyst for ethylene polymerization. With the help of a semi-empirical MO calculation, a cationic sandwich intermediate structure in the catalytic process was proposed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Chromium; Crystal structures; Homogeneous catalyst; Electron spin resonance; Polyethylene

1. Introduction

The area of homogeneous metallocene-catalyzed olefin polymerization recently has received much attention, in part because ligand modification is an effective means of optimizing catalyst activity as well as polymer properties such as molecular weight, stereoregularity and microstructure, etc. [1-7]. Our most recent efforts were in this area [8,9].

Chromium has played a prominent role among the transition metals that catalyze the polymerization of olefins [10-12]. Recently, a class of chromium-based homogeneous catalysts has been synthesized [13-15], and some of them are cationic species, which are somewhat similar to the cationic Group 4 zirconocene complexes [16]. In some cationic zirconocene complexes, evidence for the coordination of a phenyl group to the zirconium center via agostic C–H–M interaction was

obtained by NMR spectroscopy [17]. It is also noticeable that the active centers in homogeneous Kaminsky catalyst systems are cationic [18–20], and chromium proved easy to coordinate phenyl [21,22]. Therefore, we prepared a novel chromium-based paramagnetic homogeneous catalyst that bears a phenyl ring bound to the Cp group via a silicon bridge in the hope that the cation produced by methylaluminoxane (MAO) might give higher activity of polyethylene, which could be regarded as evidence for phenyl–chromium interactions.

2. Results and discussion

2.1. Ligand synthesis

Grignard reaction of Mg with bromobenzene in Et_2O followed by addition to $(CH_3)_2SiCl_2$ gives $(CH_3)_2SiCl(C_6H_5)$ as a light yellow oil in near quantitative yield (Scheme 1). Its isolation is possible, but not necessary since in situ addition of either NaCp or LiCp in Et_2O produces a yellow solution. This yellow solution

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was hydrolyzed, extracted by Et₂O, and then purified by column chromatography. The major yellow oil is the desired substituted cyclopentadiene $(C_5H_5)Si(CH_3)_2$ - $(C_6H_5)(Cp^{Si}H)$ (1) as identified by ¹H NMR, IR spectra and MS (Scheme 1).

The ¹H NMR of (1) displays two broadened Cp ring resonances and we attribute this to rapid sigmatropic shifts of either the methine proton, the silyl group or both. Sigmatropic rearrangements are well known in related silyl substituted cyclopentadienyl systems [23,24]. Compound (1) is readily deprotonated by "BuLi in hexane to give the base-free lithium salt $Li(C_5H_4)Si(CH_3)_2(C_6H_5)$ (2) (Cp^{Si}Li) in good yield as an air sensitive white solid that is insoluble in aliphatic and aromatic hydrocarbons and soluble in ethers (Eq. (1)). Exposure of (2) to moisture produces (1) as observed by ¹H NMR.



2.2. Chromium complex synthesis

The reaction of 1 equiv. of (2) with 1 equiv. of $CrCl_3$ in Et₂O produces $[(\eta^5-Cp^{Si})Cr(\mu-Cl)Cl]_2$ (3) which is extracted and recrystallized in CH₂Cl₂ with high yield as an air sensitive dark blue crystal that is soluble in most common organic solvents (Eq. (2)). Complex (3) was identified by IR spectra, elemental analysis, MS, ESR and single-crystal X-ray analysis. Since complex (3) is paramagnetic, it cannot be identified by ¹H NMR.



In the process of the above reaction, we observed that the solution is firstly dark green, then gradually turns to green-blue, and finally becomes blue. Only this blue solution gives the dark blue crystals that can be identified as dimeric by X-ray diffraction. We also tried to isolate the green intermediate product, but it was easily lost Et_2O in vacuum so that it could not be obtained. A similar process was described by S. K. Noh [25], so we speculate that the following equilibrium may exist (Eq. (3)).



This hypothesis is further supported by the observation that if in the reaction there are other coordinatively stronger reagents such as PPh₃ or pyridine, the solution color is always green and we cannot obtain the dark blue crystals for X-ray diffraction.

2.3. Study of electron spin resonance

The ESR spectrum of (3) displayed in Fig. 1 shows that complex (3) has unpaired electrons and reveals that Cr (III) is located at a highly symmetric site.



Fig. 1. ESR spectrum of complex (3) in toluene solution at room temperature; g = 1.986; microwave frequency: 9.77 GHz; microwave power: 20 dB, 2 mW; cavity: TE 104.



Fig. 2. Molecular structure of (3) with the atom-numbering scheme.

2.4. X-ray crystal structure analysis

The molecular structure of (3) is shown in Fig. 2. Selected bond distances and angles are given in Table 1. The complex (3) is a dimer located at a crystallographic inversion center. Each chromium atom is bonded to one Cp^{Si} ligand, one terminal chlorine atom and two bridging chlorine atoms, thus completing the familiar pseudooctahedral coordination environment of a threelegged piano stool. The Cp ring is bonded to the Cr atom in the η^5 manner and can be thought of as a tridentate ligand occupying one of the trigonal faces of the octahedron. This view is certainly consistent with its ESR behavior. Each chromium center has a 15-electron configuration, so it is slightly electronic unsaturated. The Cr–Cr (1A) distance of 3.336 Å is too long to form a metal-metal bond [25-27]. There are no short intermolecular contacts between dimers. The distance from the chromium to the Cp ring center is 1.861 Å. The angle between the Cp ring plane and the phenyl ring plane is 78.7°

2.5. Polymerization

In order to further our understanding of the structure of complex (3), it was tested for catalytic activity in

Table 1 Selected bond lengths (Å) and angles (°) for complex (3)

Bond lenghts			
Cr-C(4)	2.209(3)	Cr-C (2)	2.222(3)
Cr-C (3)	2.212(3)	Cr-Cl(2)	2.273(1)
Cr-C(1)	2.217(3)	Cr-Cl(1)	2.3679(9)
Cr-C(5)	2.218(3)	Si-C (8)	1.871(3)
Si-C (7)	1.852(3)	Si-C (3)	1.881(3)
Si-C (6)	1.851(3)		
Bond angles			
Cl (2)-Cr-Cl (1A)	96.56(4)	Cl (1A)-Cr-Cl (1)	90.40(4)
Cl (2)–Cr–Cl (1)	95.79(4)	C (7)-Si-C (6)	111.3(2)
C (7)-Si-C (8)	111.2(2)	C (8)-Si-C (6)	110.5(2)
C (8)-Si-C (3)	105.19(13)	C (7)-Si-C (3)	108.93(14)
C (6)-Si-C (3)	109.56(14)		

ethylene polymerization. Upon activation with MAO, (3) shows moderate catalytic activity. The polymerization results are summarized in Table 2. As can be seen from the results, (3) shows several interesting features as a catalyst for ethylene polymerization. First, a low Al: Cr ratio (500:1) is needed to obtain full activity in contrast to the value of approximately 10^4 :1 (Al:Zr) reported for the MAO-activated ansa-zirconocene catalysts, and this is similar to the amino-substituted cyclopentadienyl chromium catalyst [28]. Second, the catalytic activity of (3) does not decrease very much when the Al: Cr ratio changes from 500 to 1000. Third, the catalytic activity of (3) and the molecular weights of polyethylene are much higher than the reported chromium-based cationic half-sandwich catalysts [13]. It is obvious that these observed features could be explained on the basis of phenyl-chromium interactions, which could weaken the interaction between the cationic chromium center and the anionic cocatalyst and, therefore, efficiently prevent the active catalyst from bimolecular deactivation. On the other hand, this interaction could effectively lower the rate of chain termination by β -H elimination. So less MAO is required to keep the catalyst in an active state and a relatively long polyethylene chain can be formed. As a result, the catalytic activity and lifetime of the catalyst increase, and the

Table 2							
Ethylene	polymerization	results	obtained	with	complex	(3)	activated
by MAO	а						

Number	Al:Cr	Activity $^{b} \times 10^{-5}$	$M_{\eta}^{c} \times 10^{-5}$	$T_{\rm m}$ (°C) ^d
1	80:1	0.279	0.66	133.77
2	300:1	0.976	1.4	134.32
3	500:1	3.81	1.47	134.03
4	1000:1	3.40	0.93	134.43
5	2000:1	1.11	0.699	132.77

^a Polymerization conditions: 50 ml of toluene, catalyst 1.5 μ mol, time 2 h, temp. 16 °C, $P_i(C_2H_4) = 1.5$ atm. MAO: methylaluminox-ane.

^b g PE (mol Cr)⁻¹ h⁻¹.

^c Measured in decahydronaphthalene at 135 °C.

^d Determined with DSC at a heating rate of 10 $^{\circ}$ C min⁻¹.

molecular weight of polyethylene increases correspondingly. In a word, there must be a sterically crowded environment around the metal center [8,9].

For understanding the catalytic process we calculated the cationic intermediate structure by a semi-empirical ZINDO/1 MO method. Two stable structures were obtained by geometry optimization (Fig. 3). The energy of the sandwich structure was 80.4 kcal mol⁻¹ lower than that of the half-sandwich structure, which means the sandwich is so stable that it is the only possible structure in the catalytic process.

So we speculate that in the process of polymerization the dimer (3) first depolymerizes and then loses a chlorine to form a cationic sandwich complex in which the phenyl coordinates to the Cr(III) in the presence of MAO. This proposed structure is consistent with the experimental results. This process is illustrated in Scheme 2.

3. Experimental

3.1. General procedures and material

All reactions with moisture- and air-sensitive compounds were carried out under dry argon atmosphere (ultra-high purity) using standard Schlenk techniques. All reagents are commercially available and were used as received unless otherwise stated.



Fig. 3. Geometrically optimized structures of the cationic intermediate in the catalytic process by semi-empirical ZINDO/1 MO method. A: half-sandwich structure; B: sandwich structure.

Tetrahydrofuran (THF), diethyl ether (Et₂O) and toluene were refluxed over sodium benzophenone ketyl and distilled before use under nitrogen. Hexane and dichloromethane (CH₂Cl₂) were refluxed and distilled from CaH₂ under nitrogen. CrCl₃ was prepared according to a published route [29,30]. Polymerization grade ethylene was further purified by passage through columns of 10 Å molecular sieves and MnO. Methylaluminoxane (MAO, 10 wt.% solution in toluene, $M_n =$ 800 g mol^{-1} , Al = 5.3 wt.%) was purchased from Witco. ^{*n*}BuLi (1.6 M in hexanes) was purchased from Aldrich. Elemental analyses were performed on American PE-240 C elemental analyzer at the Center of Analysis and Test of Jilin University. The MS was obtained by Finningan GC-MS-DS MAT4510. The ESR spectrum was acquired by Bruker ER2000 EPR. NMR spectra were recorded on a Varian Unity-400 spectrometer and the X-ray structure on a Siemens P4 diffractometer. Viscosity-average molecular weights of the polyethylene were determined in decahydronaphthalene at 135 °C using a Schott Gerate model AVS/T2 Ubbelohde viscosimeter. Melting transition temperatures (T_m) of the polyethylene were determined by DSC (Du Pont 910 differential scanning calorimeter) at a heating rate of 10 °C min⁻¹.

3.2. Synthesis of $Cp^{Si}H(1)$

To a solution of Me₂SiCl₂ (8ml, 66.33 mmol) in Et₂O (40 ml) was added dropwise a solution of PhMgBr (50 ml, 1.00 N, 50.03 mmol) in Et₂O (10 ml) at -50 °C and stirred for 1 h at room temperature (r.t.). Then solvent and excess Me2SiCl2 were removed in vacuo. The residue was redissolved in Et₂O (40 ml), and CpNa (26 ml, 1.1919 N, 49.9 mmol) in THF was added dropwise slowly to the above solution at -78 °C over 40 min, and stirred at r.t. for 5-6 h to give a pale yellow solution. The reaction was hydrolyzed and was extracted with Et₂O. The Et₂O layer was dried with MgSO₄. After filtration, the solvent was evaporated under vacuum and left behind a yellow oil. The product was purified by column chromatogram over silica gel (hexane-CH₂Cl₂, 3:1). Yield 83%. ¹H NMR (CDCl₃): δ 0.255 (s, 6H, Si (CH₃)₂); 3.135(s, 1/3H, methine); 3.676(br, 2/3H, methine); 6.580-6.696(br, 4H, Cp 7.425-7.645(m, 5H, phenyl). ring); IR (KBr): 3070.12(m), 2960.20(m), 1625.70(m), 1427.07(w), 1253.50(s). 1114.65(m), 1062.59(w), 975.80(m), 9530.85(m), 829.24(s), 802.24(s), 732.82(s), 700.03(s). spectrum (m/e): $400.6[(Me_2PhSiCpH)_2^+],$ Mass $200.3(M^+).$

3.3. Synthesis of $Cp^{Si}Li(2)$

^{*n*}BuLi (14.5 ml) (1.6 M, 23.2 mmol) was injected slowly into a solution of $Cp^{Si}H$ (4.5043 g, 22.48 mmol)



Scheme 2.

in hexane (30 ml) at -78 °C. The reaction was allowed to warm to r.t. and left stirring for 5 h. A white precipitate was observed. The precipitate was cannula filtered, washed with 2×30 ml of hexane and dried under vacuum. Yield 70%.

3.4. Synthesis of $[(\eta^5 - Cp^{Si})Cr(\mu - Cl)Cl]_2$ (3)

Cp^{Si}Li powder (0.6367 g, 3.1 mmol), CrCl₃ powder (0.4946 g, 3.1 mmol) and 30 ml Et₂O was added to a dry 100 ml Schlenk flask under argon. The suspension was stirred at r.t. for 15 days. In this process the colorless solution gradually turns into green, then green-blue, and finally blue. The precipitate was filtered off and the solvent was removed in vacuo. The residue was extracted three times with CH₂Cl₂. The combined fractions were filtered and the solution was concentrated in vacuo. Recrystallization at -10 °C afforded (3) as a dark blue crystal. Yield 67.4%. IR: 3093.26(w), 3014.19(w), 2960.20(w), 2915.84(w), 1635.34(m), 1425.14(w), 1402.00(w), 1249.65(m), 1172.51(m), 1110.80(m), 1014.37(m), 833.10(s), 784.89(m), 736.67(m), 700.03(m). MS (m/e): 644.5 (M^+) . Anal. Calc. for (Me₂PhSiCpCrCl₂)₂: C, 48.46; H, 4.69; Found: C, 45.01; H, 4.42%.

3.5. X-ray structure determination

Data of (3) were collected on a Siemens P4 diffractometer with a graphite monochromator using Mo K α radiation. The structure was solved by direct methods and refined by full-matrix least-squares methods on F². All calculations were performed using SHELX-93 [31]. Hydrogen atoms were treated as idealized contributions. Crystallographic data and parameters are summarized in Table 3.

3.6. Polymerizations

A dry 250 ml steel reactor equipped with a magnetic stirrer was evacuated and pressurized with ethylene to 1.5 atm. Toluene and an appropriate amount of MAO were added to reactor through a septum port via syringe. After the solution was saturated with ethylene for 30 min, a solution of catalyst (1.5 μ mol) in toluene

Table 3 Crystal data and structure refinement for complex (3)

Empirical formula	C13H15Cl2CrSi
Formula weight	322.24
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	12.242(2)
b (Å)	9.621(2)
c (Å)	12.811(3)
β (°)	101.60(3)
V (Å ³)	1478.1(5)
Ζ	4
Absorption coefficient (mm^{-1})	1.192
Crystal size (mm)	0.50 imes 0.42 imes 0.28
θ Range for data collection (°)	2.67 to 25.01
Scan type	ω –2 θ
Reflections collected	3481
Independent reflections	2594 ($R_{\rm int} = 0.0238$)
Max./min. transmission	0.35464, 0.24856
Data/restraints/parameters	2594/0/154
Goodness-of-fit on F^2	0.705
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0369, wR_2 = 0.0949$
R indices (all data)	$R_1 = 0.0504, wR_2 = 0.1023$
Largest difference peak and hole (e ${\rm \AA}^{-3})$	0.396 and -0.646

was injected (total volume of the polymerization solution is 50 ml after the addition of catalyst). The vessel was repressurized to the required pressure with ethylene as soon as the catalyst was injected and the pressure was maintained by continuously feeding monomer. After the mixture was stirred for the desired reaction time, the reactor was vented and the polymerization was terminated by injecting acidified methanol [HCl (3 M)– methanol = 1:1]. The polymer was stirred in acidified methanol, dried in vacuo at 60 °C.

3.7. Semi-empirical MO calculation

The cationic intermediate structure in the catalytic process was calculated by a semi-empirical ZINDO/1 MO method of the HYPERCHEM 6.0 program [32]. The parameters are the following, Total charge: 1; spin multiplicity: 4; convergence limit: 0.01; RMS gradient of: 0.01 kcal mol⁻¹.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 163491. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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