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Synthesis, crystal structure and catalytic activity of a novel zirconium complex bearing an unsymmetrical aliphatic benzamidinato ligand

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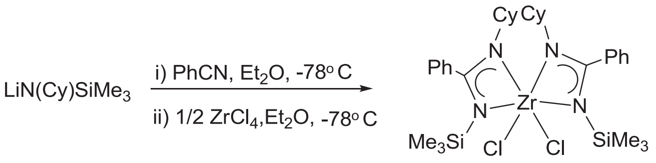
ABSTRACT

A novel non-symmetric aliphatic benzamidinato zirconium complex, $[\{CyNC(Ph)(NSiMe_3)\}_2ZrCl_2]$ (Cy = cyclohexyl) (**1**) has been readily prepared via the reaction of freshly prepared aliphatic lithium benzamidinate with zirconium tetrachloride. Complex **1** has been characterized by various spectroscopic techniques, elemental analysis, and single-crystal X-ray diffraction analysis. Complex **1** has a distorted pseudo-octahedral structure. Catalytic studies showed that the zirconium complex was active for ethylene polymerization with the activity of 6.66×10^4 g PE/mol Zr h. The influences of Al/Zr molar ratios, ethylene pressures and reaction temperature on the activities were investigated.

Nitrogen-centered donor amidinate and guanidinate group 4 complexes have been widely studied for the past decades, mainly due to the growing interest in the development of catalysts for the polymerization of olefins [1–7]. The amidinato and guanidinato ligands provide tunable systems for exploring the effects of making rational modifications to both the steric and electronic properties [8]. To date, group 4 amidinate and guanidinate complexes have been shown to be promising for these purposes. However, aliphatic amidinato ligands and group 4 metal complexes are rare [9]. In recent years, we have developed a series of guanidinato ligands. Their Zr and Hf complexes are useful catalysts for the polymerization of ethylene [10,11]. Metal complexes with silyl-linked bis(amidinate), silyl-linked amidinate-amidine, mixed silyl-linked bis(amidinate) and cyclopentadienyl ligand also showed good catalytic behaviors in the polymerization of olefins [12–15]. Other related zirconium complexes bearing [(*N*,*N*-dimethylamino)dimethylsilyl]-2,6-diisopropylanilido ligand exhibited good activity toward ethylene polymerization and gave polyethylenes with broad molecular weight distributions [16]. Very recently, we reported our ongoing investigation into the incorporation of aliphatic benzamidinato ligand and related metal complexes [17]. Included in this paper are the synthesis, characterization and catalytic behaviors toward ethylene of a novel bis(amidinate) zirconium complex **1** (Eq. (1)).(1)



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(1)

The crystalline, colorless unsymmetrical aliphatic benzamidinato zirconium complex **1** was prepared from $CyNH(SiMe_3)$ (Cy = cyclohexyl) after lithiation with n-BuLi and the concomitant reaction with benzonitrile [17], and further metathesis reaction of the freshly prepared solution of lithium amidinate with zirconium tetrachloride [18]. Complex **1** has been characterized by various spectroscopic techniques, elemental analysis, and X-ray diffraction analysis [19]. In the IR spectra, there is strong absorption of C═N stretch in the range of 1581 cm^{-1} for **1**, which indicates the existence of the delocalized double bond of the N–C–N linkage. The strong bands around 1448 cm^{-1} can be assigned to the C–N single bond stretching [20]. The UV–vis spectrum of **1** in a diluted tetrahydrofuran solution has maximum absorption at 230 nm, being thought to arise from the delocalized system of N–C–N backbone.

The monomeric **1** crystallizes in the monoclinic $P2_1/c$ space group. The metal center is in a distorted pseudooctahedral environment consisting of the four nitrogen atoms of two bidentate amidinate anions with *cis* chloride ligands completing the coordination sphere (Fig. 1). The equatorial plane contains N(1), N(2), N(4) and Cl(2)

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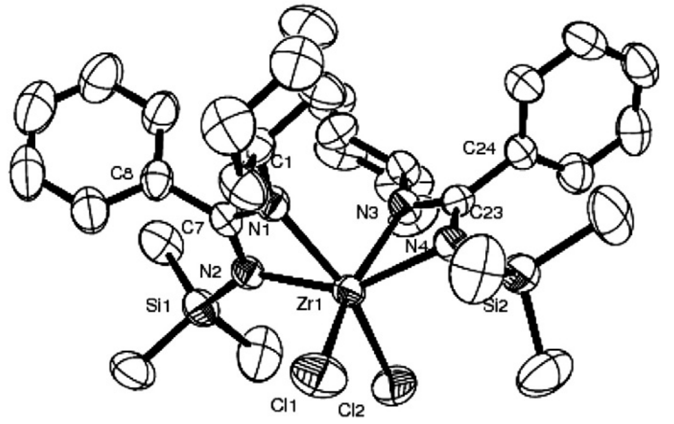

Fig. 1. Molecular structure of [{CyNC(Ph)N(SiMe$_3$)}$_2$ZrCl$_2$] (Cy = cyclohexyl). Thermal ellipsoids are plotted at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr(1)–N(1) 2.231(2), Zr(1)–N(2) 2.199(2), Zr(1)–N(3) 2.242(2), Zr(1)–N(4) 2.194(2), Zr(1)–Cl(1) 2.4123(9), Zr(1)–Cl(2) 2.4124(9); N(1)–Zr(1)–N(2) 60.81(9), N(3)–Zr(1)–N(4) 60.72(8), Zr(1)–N(1)–C(7) 92.35(18), Zr(1)–N(3)–C(23) 92.17(17), Cl(1)–Zr(1)–Cl(2) 93.38(4).

atoms while the other two atoms (Cl(1) and N(3)) occupy the axial position. The Zr atom lies on an approximate 2-fold axis which bisects the Cl(1)–Zr(1)–Cl(2) angle [93.38(4)°] with two planar bidentate amidinate anions. The four-membered chelating rings N(1)–Zr(1)–N(2)–C(7) and N(3)–Zr(1)–N(4)–C(23) are planar with mean deviations of 0.0088 and 0.0093 Å, respectively. The bond angle C(7)–Zr(1)–C(23) is 109.85 (9)°, much smaller than those of [^{i}PrNC[N(SiMe$_3$)$_2$]N^{i}Pr]$_2$ZrCl$_2$ [131.6(2)°] [21] and Cp(centroid)–Zr–Cp(centroid) (134°) in Cp$_2$ZrCl$_2$ [22]. The bond distances of Zr–Cl [2.4123(9), 2.4124(9)Å] in **1** are comparable to those in other bis(amidinate) zirconium complexes such as [CyNC(Me)NCy]$_2$ZrCl$_2$ [2.426(3)–2.436(3) Å] [23] and [Me$_3$SiNC(C$_6$H$_5$) NSiMe$_3$]$_2$ZrCl$_2$ [2.401 Å] [24], but slightly shorter than those in Cp$_2$ZrCl$_2$ [2.44 Å]. The bond angle of Cl–Zr–Cl [93.38(4)°] in **1** is smaller than the corresponding values in Cp$_2$ZrCl$_2$ [97.1°], much smaller than in [Me$_3$SiNC(C$_6$H$_5$)NSiMe$_3$]$_2$ZrCl$_2$ [103.71°], but comparable to that in [CyNC(Me)NCy]$_2$ZrCl$_2$ [93.1(1)°].

A further comparison of the structures of **1**, bis(amidinate) zirconium complex [CyNC(Me)NCy]$_2$ZrCl$_2$ (**I**) [23] and bis(guanidinate) zirconium complex [CyNC(N–^{i}Pr$_2$)NCy]$_2$ZrCl$_2$ (**II**) [25] featured C_2 symmetric structure with a κ^2-bonded ligand is made in Fig. 2. The bond angle N–C–N of the planar four-membered chelating ring N–C–N–Zr in **1** is slightly wider than those in **I** and **II**. The C–N and N–Zr bond distances, and N–Zr–N bond angle in **1** are comparable to those in **I** and **II**. The larger C$_{bridge}$–N–SiMe$_3$ than C$_{bridge}$–N–Cy angle and the smaller Zr–N–SiMe$_3$ than Zr–N–Cy angle in **1** suggest the steric interactions of the SiMe$_3$ and Ph substituents.

Polymerization reactions were carried out with complex **1** using methylalumoxane (MAO) as a cocatalyst. The polymerization data

Table 1
Data for ethylene polymerization catalyzed by complex **1**/cocat system[a].

Entry	P/atm	T/°C	Al/Zr	Yield (mg)	Activity[b]
1	1	30	1000	Trace	–
2	1	50	1000	13.6	5.44×10^3
3	1	70	1000	Trace	–
4	10	50	500	33.2	1.33×10^4
5	10	50	1000	116	4.62×10^4
6	10	50	1500	120	4.82×10^4
7	10	50	2000	155	6.19×10^4
8	10	30	2500	20.1	8.00×10^3
9	10	40	2500	86.1	3.44×10^4
10	10	50	2500	166	6.66×10^4
11	10	60	2500	62.7	2.51×10^4
12	10	70	2500	37.1	1.48×10^4
13	10	50	3000	130	5.20×10^4

[a] Polymerization conditions: 5 μmol of Zr, Cocat: MAO, 100 ml toluene, 0.5 h.
[b] g mol^{-1} h^{-1}.

show that **1** can catalyze the polymerization of ethylene [26] under mild conditions (Table 1). When activated with MAO under 1 atm of ethylene, complex **1** showed lower activity (5.44×10^3 g PE/mol Zr h) (Entry 2), therefore, 10 atm pressure of ethylene was employed in the remaining experiments, in which other reaction parameters were changed.

At the temperature of 50 °C, with the increase of the Al/Zr molar ratio from 500 to 3000 (Entries 4–7, 10, 13), complex **1** reached its highest activity of 6.66×10^4 g PE/mol Zr h with an optimal Al/Zr ratio of 2500. However, further increase of the temperature impaired the activity of the catalyst (Entries 11–12).

Comparing with other six-coordination bis(amidinate) zirconium dichloride complex such as [Me$_3$SiNC(C$_6$H$_5$)NSiMe$_3$]$_2$ZrCl$_2$ [24b], complex **1** showed lower activity. However, both systems are substantially lower than those of the analogous metallocene systems for the polymerization of ethylene (6×10^6 g PE (mol Zr)$^{-1}$ h^{-1} atm^{-1}) [27], probably due to the smaller angle tilted to the back of the molecule that prevented the approach of the olefin [24b].

In conclusion, a new bis(amidinate) zirconium complex [{CyNC(Ph)(NSiMe$_3$)}$_2$ZrCl$_2$] (Cy = cyclohexyl) has been readily prepared via the reaction of freshly prepared lithium amidinate with zirconium tetrachloride. Structural studies confirm the C_2 symmetric feature of complex **1**. Complex **1** represents a novel potential precursor of group 4 free of Cp ligands. Upon treatment with MAO, complex **1** showed moderate activity of 6.66×10^4 g PE/mol Zr h in the polymerization of ethylene.

Acknowledgments

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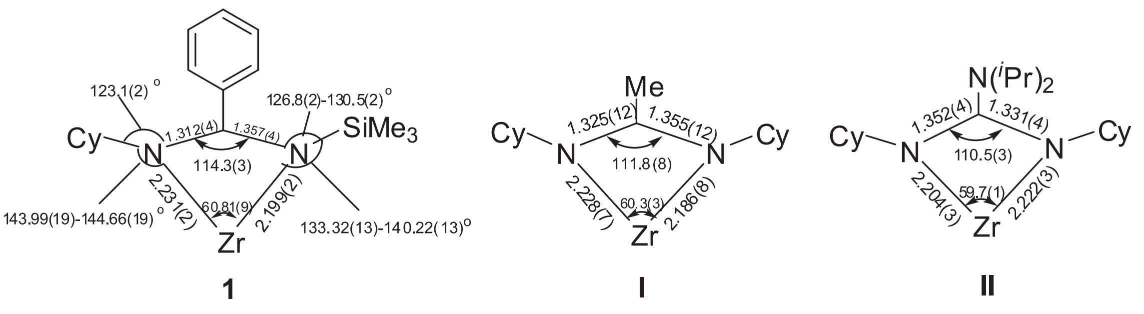

Fig. 2. Structural comparison of **1** and its four electron-donating analogs.

Appendix A. Supplementary data

CCDC 907112 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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[18] Preparation of **1**: PhCN (0.44 ml, 4.23 mmol) was added to a solution of CyN(Li) SiMe$_3$ (0.75 g, 4.23 mmol) in Et$_2$O (30 cm^3) at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred overnight. The above solution was added to a solution of ZrCl$_4$ (0.49 g, 2.12 mmol) in Et$_2$O (10 cm^3) at −78 °C. The mixture was warmed to *ca.* 25 °C and stirred for 24 h, then filtered. The filtrate was concentrated *in vacuo* and stored at −25 °C for several days, yielding colorless crystals of **1** (1.17 g, 77.8%). Mp 240–242 °C. *Anal. calcd.* for C$_{32}$H$_{50}$Cl$_2$N$_4$Si$_2$Zr (%): C, 54.20; H, 7.11; N, 7.90. Found: C, 53.96; H, 7.01; N, 8.12. ^{1}H NMR (C$_6$D$_6$): δ 0.27 (s, 18 H, SiMe$_3$), 0.94–0.98 (m, 4 H, Cy), 1.17–1.24 (m, 2 H, Cy), 1.28–1.33 (m, 2 H, Cy), 1.70 (s, 4 H, Cy), 2.01–2.05 (m, 4 H, Cy), 2.34–2.47 (m, 4 H, Cy), 3.27 (m,2 H, Cy), 7.08–7.25 (m, 10 H, Ph). ^{13}C NMR (C$_6$D$_6$): δ 2.03 (SiMe$_3$), 25.55, 25.71, 34.28, 34.54 (CH$_2$/Cy), 58.78 (CH/Cy), 126.14 (*m*-*C*Ph), 128.64 (*p*-*C*Ph), 129.46 (*o*-*C*Ph), 135.1 (*C*ipso-Ph), 180.84 (N*C*N). IR (KBr, cm^{-1}): 3211, 3180, 3062, 2937, 2858, 1666, 1622, 1581, 1494, 1448, 1402, 1371, 1244, 933, 894, 837, 781, 750, 698. UV–vis (THF): $\lambda_{\mathrm{max,\ nm}} = 230$.

[19] Crystal data for 1: C32H50Cl2N4Si2Zr, M = 709.06, Monoclinic, space group P21/c, T = 200 K, a = 18.4197(14) Å, b = 9.1091(7) Å, c = 22.0430(17) Å, β = 96.142(2) ° V = 3677.3(5) Å^3, Z = 4, Fooo = 1488, GOF = 1.068, ρcalcd. = 1.281 g cm^{-3}, crystal size = 0.31 × 0.22 × 0.22 mm. Data were collected on a Bruker SMART APEX diffractometer/CCD area detector, using mono-chromated Mo-Kα radiation, λ = 0.71073 Å at 200 K. A total 20080 reflections were collected, of which 6508 unique reflections (4642 with I > 2σ(I)) were for structure elucidation. The final R1 was 0.0389 for I > 2σ(I) and 0.0646 for all reflections. Absorption correction was performed using the multi-scan method. The structures were solved by direct methods and refined by full-matrix least squares on F2 using the SHELXTL-97 program package.

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[26] *General procedure for polymerization of ethylene*. Ethylene polymerization was carried out in a 500 mL autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. Briefly, toluene, the desired amount of cocatalyst, and a toluene solution of the catalytic precursor (the total volume was 100 mL) were added to the reactor in this order under an ethylene atmosphere. When the desired reaction temperature was reached, ethylene at 10 atm pressure was introduced to start the reaction, and the ethylene pressure was maintained by constant feeding of ethylene. After 45 min, the reaction was stopped. The solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was filtered, washed with ethanol, and dried in vacuum at 60 °C to constant weight.

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