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Synthesis, structure and catalytic properties of a novel zirconium guanidinato complex $[Zr\{ArNC(NMe_2)N(SiMe_3)\}(\mu_2\text{-}Cl)Cl_2]_2[Ar = 2, 6\text{-}{}^iPr_2\text{-}C_6H_3]$

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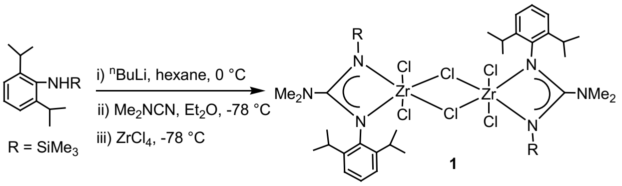
Abstract

A novel non-symmetric zirconium guanidinato complex, $[\{Zr\{ArNC(NMe_2)N(SiMe_3)\}(\mu_2\text{-}Cl)Cl_2\}_2]$ ($Ar = 2,6\text{-}{}^iPr_2\text{-}C_6H_3$), was synthesized and structurally characterized. Catalytic studies showed that the zirconium complex was active for ethylene polymerization with the activity of 4.98×10^5 g PE/mol Zr h. The influences of cocatalysts, Al/Zr molar ratios and ethylene pressures on the activities were investigated.

Keywords: Zirconium complex; Guanidinate; Catalysis; Ethylene polymerization

Major advances have been achieved in the polymerization of α-olefins by well-defined or single-site catalysis [1]. In searching for alternatives to cyclopentadienyl-based ligands in early transition metal chemistry, bidentate N-donor ligands have drawn increased attention in recent years [2,3] and have been studied as active catalysts for the polymerization of ethylene [4–6]. In this regard, we were attracted to *N*-substituted guanidinato ligands with a trigonal planar CN_3 unit, as potential bulky supporting ligands for group 4 metals. These ligands present a fine-tuned system for exploring the effects of making rational modifications to both the steric bulk and electronic properties [7], and play important roles in evaluating the activities of their complexes at the stages of the proceeding catalytic system in order to create the high active species. Our long term aim is to gain access to a range of nitrogen-based transition metal complexes as potential catalysts for ethylene polymerization. The focus was on developing diversified ligation modes with varied organic substituents and introducing varied functions in the conjugated NCN or NCCCN moieties. Herein, we report the synthesis, crystal structure and catalytic properties of a new complex, $[\{Zr\{ArNC(NMe_2)N(SiMe_3)\}(\mu_2\text{-}Cl)Cl_2\}_2]$ ($Ar = 2,6\text{-}{}^iPr_2\text{-}C_6H_3$) (**1**) [Eq. (1)]



1

(1)

The crystalline, colorless zirconium *N*, *N′* – disubstituted guanidinate **1** was prepared from $ArNH(SiMe_3)$ ($Ar = 2,6\text{-}{}^iPr_2\text{-}C_6H_3$) after lithiation with n-BuLi and the concomitant reaction with dimethylcyanmide, and further reaction with zirconium tetrachloride [8]. This involved insertion of $(CH_3)_2NCN$ into Li–N bond of $Li[N(SiMe_3)Ar]$ ($Ar = 2,6\text{-}{}^iPr_2\text{-}C_6H_3$) with a 1,3-$SiMe_3$ $N \rightarrow N'$

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rearrangement. When $ZrCl_4$ was added to the Et_2O solution of the corresponding ligand at low temperature, the color of the resulting solution changed from colorless to pale-yellow with the increase of the temperature. The mixture was stirred at room temperature for 24 h and gave a clear solution. The volatiles were removed *in vacuo* and the residue was extracted into dichloromethane. The extract was filtered. The filtrate was concentrated *in vacuo* yielding single crystals of **1** for X-ray analysis. Complex **1** was very soluble in polar solvents such as CH_2Cl_2, and slightly soluble in aliphatic hydrocarbons. **1** was not very sensitive, no perceptible change was observed after several hours when exposed to air.

It is noteworthy that the *ortho*-alkyl substituent on the phenyl ring played an important role for the formation of the desired zirconium complex. In the reaction of $ZrCl_4$ and other less bulky analogous guanidinano ligands (**L**) without alkyl substituent on the *ortho*-position of the phenyl ring, $\mathbf{L}_3$MCl-type rather than $\mathbf{L}MCl_3$-type complexes were formed with a seven-coordinate configuration around the zirconium atom [9]. The result may be due to the adjacent steric interference between the *ortho*–isopropyl and the R group (phenyl).

Single-crystal X-ray diffraction analysis [10] reveals that **1** crystallizes in the monoclinic $P2_1/n$ space group. The structure of **1** shows a centrosymmetric dinuclear zirconium center (Fig. 1). Each zirconium atom is coordinated by two nitrogen atoms (N(1) and N(2)) of the ligand, two terminal chloride atoms (Cl(1) and Cl(2)) and two bridging chloride atoms (Cl(3) and Cl(3′)). The bond lengths of Zr(1)–N(1), Zr(1)–N(2), Zr(1)–Cl(1), Zr(1)–Cl(2), Zr(1)–Cl(3) and Zr(1)–Cl(3′) are 2.131(5), 2.165(5), 2.382(2), 2.386(2), 2.593(2), 2.613(2) Å, respectively. The zirconium atom adopts a distorted octahedral geometry, in which the equatorial plane contains N(1), Cl(1), Cl(3) and Cl(3′) atoms (mean deviation 0.0023 Å) while the other two atoms (Cl(2) and N(2)) occupy the axial positions. The angle of N(2)–Zr(1)–Cl(2) is 147.82 (13)° (smaller than 180°), and the zirconium atom locates 0.109 Å above the equatorial plane toward Cl(2). The four-membered chelating ring N(1)–Zr(1)–N(2)–C(13) is planar (mean deviation 0.01 Å), where the bond angles N(1)–Zr(1)–N(2) and N(1)–C(13)–N(2) are 62.30(18) and 110.2(5)°, respectively. The ligand is nearly perpendicular to the N(1)–Cl(1)–Cl(3′)–Cl(3) plane with a dihedral angle of 94.3°.

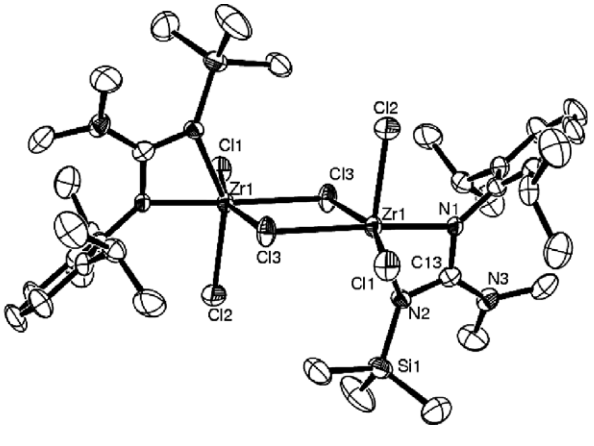

Fig. 1. Crystal structure of $[\{Zr\{ArNC(NMe_2)N(SiMe_3)\}(\mu_2\text{-}Cl)Cl_2\}_2]$. Thermal ellipsoids are plotted at 50% probability level. Hydrogen atoms are omitted for clarity.

For the guanidine moiety, the bond lengths of N(1)–C(13), N(2)–C(13) and N(3)–C(13) are 1.358(7), 1.352(7) and 1.346(7) Å, respectively. Thus the CN_3 fragment can be rendered as a π-electron delocalized system. In addition, the dihedral angle formed by the planar NMe_2 function and the Zr(1)–N(1)–C(13)–N(2) plane offers a means of evaluating the possibility of π overlap between these two moieties. The torsion angle between these two planes is 23.6°, which is much smaller than the value of 88.2° observed in N-substituted zirconium guanidinate $[(^iPrNC\text{-}[N(SiMe_3)_2]N^iPr)_2ZrCl_2]$ [11], suggest that the steric interaction between the phenyl or trimethylsilyl functions and the dimethylamido group is somewhat limited and is not big enough to eliminate the π conjugation. In fact, the sum of 359.9° for the three bond angles about N atom in dimethylamido group is consistent with the sp^2 hybridization necessary for conjugation.

To demonstrate what factors, and how they may affect the polymerization of ethylene, the activities of catalyst precursor **1** were investigated at varied Al/Zr molar ratios, cocatalysts and ethylene pressures. Table 1 summarized the catalyst activities obtained for ethylene polymerization catalyzed by complex **1**.

The influences of various cocatalysts on the ethylene activation were evaluated with the catalytic systems formed from **1** in the presence of methylaluminoxane (MAO), modified methylaluminoxane (MMAO) or Et_2AlCl. The catalytic system with methylaluminoxane (MAO) showed higher catalytic activities for ethylene polymerization. When activated with methylaluminoxane (MAO) under 1 atm of ethylene, complex **1** showed lower activity (4.48×10^3 g PE/mol Zr h), therefore, 10 atm pressure of ethylene was employed in the remaining experiments, in which other reaction parameters were changed.

MAO has been known to play roles in initiating the polymerization reactions, most likely by creating an empty site on the catalyst for the insertion of an ethylene monomer. Indeed, we observed that the amount of MAO used in the complex **1**-catalyzed ethylene polymerization reaction was critical for the catalyst to exhibit high activity, and the optimal Al/Zr ratio was 2000. The activity reached as high as 4.98×10^5 g PE/mol Zr h with a 2000 Al/Zr ratio. However, further increase of the Al/Zr ratio impaired the activity of the catalyst. The explanation for this observation is that, with the proper ratio of MAO to the zirconium complex, the formation and stabilization of the active species is achieved.

The properties of the resulted polymer were affected by the Al/Zr molar ratio. With the increase of the Al/Zr molar ratio from 1000 to 4000, the T_m of the resultant polyethylene changed from 133.6 to 136.7 °C. Meanwhile, the

Table 1
Ethylene polymerization catalyzed by complex **1**/cocat system

Entry	Cocat	P (atm)	T (°C)	Al/Zr	Yield (mg)	Activity g mol^{-1} h^{-1}	T_m/°C[a]	M_η[b] (10^4)	M_w[c] (10^4)	M_w/M_n[c]
1	MAO	1	20	1000	11.2	4.48×10^3	132.0	20.6	–	–
2	MAO	10	20	1000	538.4	2.15×10^5	136.7	42.0	–	–
3	MMAO	10	20	1000	228.1	9.16×10^4	133.8	2.5	–	–
4	Et_2AlCl	10	20	500	–	No	–	–	–	–
5	MAO	10	20	2000	1245	4.98×10^5	133.6	4.4	–	–
6	MAO	10	20	3000	815.8	3.26×10^5	134.3	2.3	–	–
7	MAO	10	20	4000	584.0	2.34×10^5	136.0	18.8	–	–
8	MAO	10	40	2000	610	2.40×10^5	135.7	6.6	72.3	13
9	MAO	10	60	2000	1100	4.40×10^5	134.7	2.7	23.5	4.9
10	MAO	10	80	2000	1620	6.48×10^5	134.3	1.5	9.53	2.5

Conditions: 5 μmol catalyst, 30 ml toluene for 1 atm ethylene pressure, 100 ml toluene for 10 atm ethylene pressure, 0.5 h.

[a] Determined by DSC.

[b] Measured in decahydronaphthalene at 135 °C using an Ubbelohde viscometer according to $[\eta] = 62 \times 10^{-3} M_\eta^{0.7}$.

[c] Determined by GPC.

molecular weight of the polymers varied. Increasing the reaction temperature from 20 to 80 °C, the activity initially decreased and then increased and the T_m of the resultant polymer decreased from 136.7 to 134.3 °C, which indicated that the molecular weights of resultant polyethylenes decreases along with elevated reaction temperature. Such results are consistent to the molecular weights determined by both viscosity and GPC (Entries 8–10). In addition, NMR data showed the formation of linear polyethylenes [12].

In summary, a novel zirconium guanidinato complex, $[\{Zr\{ArNC(NMe_2)N(SiMe_3)\}(\mu_2\text{-}Cl)Cl_2\}_2]$ (Ar = 2,6-^{i}Pr$_2$-C_6H_3), was synthesized and fully characterized. Upon treatment with MAO, the complex showed moderate activity of 4.98×10^5 g (mol of cat.)$^{-1}$ h^{-1} in polymerization of ethylene. Further detailed investigation, including varying reaction conditions, modifying the coordinational ligand and synthesizing hafnium and titanium metal complex analogues, is under way.

Acknowledgements

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Appendix A. Supplementary material

CCDC 644379 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 Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007. 08.001.

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[8] $(CH_3)_2NCN$ (0.17 ml, 2.07 mmol) was added to a solution of (C_6H_3-2,6-^{i}Pr$_2$)N(Li)SiMe$_3$ (0.53 g, 2.07 mmol) in Et_2O (30 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for 12 h. $ZrCl_4$ (0.48 g, 2.07 mmol) was added at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for 24 h. The volatiles were removed in vacuo, and the residue was extracted with dichloromethane and filtered. The filtrate was concentrated to give colorless crystals (0.42 g, 39%). Anal. calcd. for $C_{36}H_{64}Cl_6N_6Si_2Zr_2$(%): C, 41.89; H, 6.25; N, 8.14. Found: C, 42.05; H, 6.11; N, 8.01. ^{1}H NMR ($CDCl_3$): δ 0.05–0.48(m, 9H, SiMe$_3$), δ 1.13–1.23 (m, 12H, CH(CH$_3$)$_2$), δ 2.5 (m, 6H, N(CH$_3$)$_2$), δ 3.1 (s, C*H*Me$_2$), δ 7.0–7.2 (m, 3H, Ph). ^{13}C NMR ($CDCl_3$): δ 4.02, 5.03, 5.93 (t, SiMe$_3$), δ 25.2 (s, CH(*C*H$_3$)$_2$), δ 28.5 (s, *C*H(CH$_3$)$_2$), δ 42.2 (s, N(*C*H$_3$)$_2$), δ 126.6, 128.4, 129.3, 141.9, 145.7 (s, Ph), δ 158.5 (s, *C*(C$_5$H$_5$)), δ 166 (s, N*C*(NMe$_2$)N).

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[10] *Crystal data for* **1**: $C_{36}H_{64}Cl_6N_6Si_2Zr_2$, $M = 1032.25$, Monoclinic, space group $P2_1/n$, $T = 213$ K, $a = 10.041(6)$ Å, $b = 17.247(13)$ Å, $c = 13.727(8)$ Å, $\beta = 91.99(2)°$, $V = 2376(3)$ Å^3, $Z = 2$, $F_{000} = 1064$, GOF = 1.067, $\rho_{calcd.} = 1.443$ g cm^{-3}, crystal size = 0.20 × 0.15 × 0.10 mm. Data were collected on a Bruker SMART APEX diffractometer/CCD area detector, using mono-chromated Mo–Kα radiation, $\lambda = 0.71073$ Å at 213 K. A total 9698 reflections were collected, of which 4169 unique reflections (3012 with $I > 2\sigma(I)$) were for structure elucidation. The final R_1 was 0.691 for $I > 2\sigma(I)$ and 0.1035 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 F^2 using the SHELXTL-97 program package.

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