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# Diverse coordination behaviors of the silyl-linked bis(amidinate) ligand $[SiMe_2{NC(Ph)N(Ph)}_2]^{2-}$ to zirconium center

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#### ABSTRACT

The reactions between the silyl-linked bis(amidinate) ligand  $[SiMe_2{NC(Ph)N(Ph)Li(thf)_2}_2]$  and  $ZrCl_4$  in different stoichiometric chemistry, 2:1, 1:1, and 1:2, were explored. The resulting zirconium compounds, **1**, **2**, and **3**, showed different molecular structural features which were confirmed by X-ray crystallographic analysis. The metal center in **1** was located in a highly saturated coordination environment with four amidinate moieties. Compound **2** exhibited an unprecedented linked tris(amidinate) N–C–N–Si–N–C–N–Si–N–C–N–Si–N–C–N skeleton formed after the intermolecular rearrangement. In compound **3**, a novel silyl-linked imino-amidinate ligand via the intramolecular rearrangement was involved. The mechanism for the formation of compounds **2** and **3** was proposed. Compound **2** was found to be a highly active catalyst for ethylene polymerization in the presence of methylalumoxane (MAO).

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#### 1. Introduction

Amidinate ligands are four-electron, *mon*oanionic, and N-donor bidentate chelates. They demonstrate a great diversity by variation of substituents on the conjugated N–C–N backbone. Their steric and electronic properties are easily tunable to meet the requirements of different metal centers. The coordination chemistry of amidinates toward metals from across the periodic table was well established in the past few decades, and amidinate complexes proved to be productive [1,2]. They were found to be potential catalysts for the oligomerization and polymerization of olefins, for hydroamination, intramolecular hydroamination/cyclization, and hydrosilylation [2–8]. Moreover, some of them, such as the bis(amidinate) group IV metal complexes **I**, showed high performance in the activation and reduction of dinitrogen or other molecules [4,7].

In recent years, an increasing interest of metal complexes incorporated with the *bi*anionic-linked bis(amidinate) ligands [4f,4g,6h,7d,7h,9] arose. For example, a series of mononuclear and binuclear lanthanide compounds were capable of catalyzing the ring-opening polymerization of lactones and lactides efficiently [9j–9m]. Besides those examples reported in the literatures, a special class of linked bis(amidinate) ligands [SiMe<sub>2</sub>{NC(Ph)N(R)}<sub>2</sub>]<sup>2–</sup> were developed in our laboratory [10]. They displayed a close contact between the two amidinate moieties. These unique *bi*anionic ligands had the advantage of affording binuclear complexes and

mononuclear complexes analogous to the "ansa-metallocene", leading to intriguing geometric structures and properties. We next attempted to synthesize a series of compounds in the configuration of type **II**. By comparing **II** with **I** (shown in Scheme 1), the different properties resulting from bridging could be investigated. To our surprise, the seemingly easy pathway from the silyl-linked bis(amidinate) ligand [SiMe<sub>2</sub>{NC(Ph)N(Ph)Li(thf)<sub>2</sub>}<sub>2</sub>] and ZrCl<sub>4</sub> could not afford the expected product as **II**. It was found that the N–C–N–Si–N–C–N backbone of the ligand was both chelating and labile toward the Zr center. Herein, we report the special intra-and intermolecular rearrangements of the title linked bis(amidinate) ligand.

#### 2. Experimental

#### 2.1. General considerations

All manipulations and reactions were performed under a purified nitrogen atmosphere using the standard Schlenk techniques on a dual manifold Schlenk line. Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone under nitrogen. Dichloromethane was distilled from CaH<sub>2</sub> under nitrogen. The ligand transfer reagent was prepared according to the reported methods [10]. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker DRX-300 spectrometer. Elemental analyses were performed with a Vario EL-III instrument. Melting points were measured with a Sanyo Gallenkamp Variable Heater.



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2.2. Synthesis of metal complexes

2.2.1.  $[SiMe_2{NC(Ph)N(Ph)}_2]_2Zr(1)$ 

A solution of  $[SiMe_2{NC(Ph)N(Ph)Li(thf)_2}_2]$  (1.67 g, 2.24 mmol) in thf (ca. 10 mL) was added into a stirred slurry of ZrCl<sub>4</sub> (0.26 g, 1.12 mmol) in Et<sub>2</sub>O (ca. 15 mL) at 0 °C. The reaction mixture was warmed to room temperature and it continued to stir for 12 h. It was dried in vacuum to remove all volatiles and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL). The concentration of the filtrate under reduced pressure resulted in compound **1** as yellow crystals. Yield: 0.61 g (53%); m.p. 241–242 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.32–6.30 (m, 40H; phenyl), 5.32 (s, 1H; 0.5 CH<sub>2</sub>Cl<sub>2</sub>), 0.18– -0.90 (m, 12H; SiMe<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 191.6, 172.6 (N–C–N), 148.9–120.8 (phenyl), 53.5 (CH<sub>2</sub>Cl<sub>2</sub>), 2.1 (SiMe<sub>2</sub>) ppm. Anal. Calc. for C<sub>56</sub>H<sub>52</sub>N<sub>8</sub>Si<sub>2</sub>Zr·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.5</sub> (1026.92): C, 66.08; H, 5.20; N, 10.91. Found: C, 65.81; H, 5.20; N, 10.87%.

#### 2.2.2. [{N(Ph)C(Ph)N}SiMe<sub>2</sub>{NC(Ph)N(Ph)}SiMe<sub>2</sub>{NC(Ph)N(Ph)}]ZrCl<sub>2</sub> (**2**)

A solution of  $[SiMe_{2}{NC(Ph)N(Ph)Li(thf)_{2}_{2}]}(1.54 g, 2.05 mmol)$ in thf (ca. 10 mL) was added into a stirred slurry of ZrCl<sub>4</sub> (0.48 g, 2.05 mmol) in Et<sub>2</sub>O (ca. 20 mL) at -78 °C. The reaction mixture was warmed to room temperature and it continued to stir for 12 h. It was dried in vacuum to remove all volatiles and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL). CH<sub>2</sub>Cl<sub>2</sub> was removed and toluene was added. Concentrating the solution to about 3 mL and making it stand gave colorless crystals of compound **2**. Yield: 0.74 g (38%); m.p. 255–257 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.25–6.68 (m, 35H; phenyl), 2.35 (s, 3H; *Me* of toluene), 0.00, -0.06 (d, 12H; SiMe<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 178.1, 174.4, 173.8 (N–C–N), 145.3–123.6 (phenyl), 26.3, 22.2 (*Me* of toluene), 2.5, 1.3 (SiMe<sub>2</sub>) ppm. *Anal.* Calc. for C<sub>43</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>6</sub>Si<sub>2</sub>Zr·(C<sub>7</sub>H<sub>8</sub>) (953.26): C, 62.99; H, 5.29; N, 8.82. Found: C, 62.21; H, 5.17; N, 8.75%.

#### 2.2.3. $[{N(Ph)C(Ph)N}SiMe_2{N(Ph)C(Ph)NH}]ZrCl_3(thf) (3)$

A solution of  $[SiMe_{2}{NC(Ph)N(Ph)Li(thf)_{2}_{2}]} (0.96 g, 1.28 mmol)$ in thf (ca. 10 mL) was added into a stirred slurry of ZrCl<sub>4</sub> (0.60 g, 2.57 mmol) in Et<sub>2</sub>O (ca. 25 mL) at 0 °C. The reaction mixture was warmed to room temperature and it continued to stir for 12 h. It was dried in vacuum to remove all volatiles and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL). CH<sub>2</sub>Cl<sub>2</sub> was removed and toluene was added. Concentrating the solution to about 3 mL and making it stand gave pale yellow crystals of compound **3**. Yield: 0.78 g (75%); m.p. 165–166 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.58, 9.40 (d, 1H; NH), 7.52–6.63 (m, 25H; phenyl), 4.18 (br, 4H; OCH<sub>2</sub> of thf), 2.34 (s, 3H; *Me* of toluene), 1.58 (br, 4H; 3,4-2CH<sub>2</sub> of thf), 0.11 (d, 6H; SiMe<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 137.9– 123.2 (phenyl), 25.1, 21.4 (*Me* of toluene), -0.3 (SiMe<sub>2</sub>) ppm. *Anal.* Calc. for C<sub>28</sub>H<sub>27</sub>Cl<sub>3</sub>N<sub>4</sub>SiZr·(C<sub>4</sub>H<sub>8</sub>O, C<sub>7</sub>H<sub>8</sub>) (809.43): C, 57.87; H, 5.35; N, 6.92. Found: C, 57.53; H, 5.36; N, 6.89%. 2.2.4.  $[{N(Ph)C(Ph)N}SiMe_2{N(Ph)C(Ph)NH}]ZrCl_2[N(Ph)C(Ph)NH}](4)$ ZrCl<sub>4</sub> (0.49 g, 2.10 mmol) was slowly added into a solution of  $[SiMe_2[NC(Ph)N(Ph)Li(thf)_2]_2]$  (1.57 g, 2.10 mmol) in thf (ca. 30 mL) at -78 °C. The reaction mixture was stirred for half an hour and PhCN (0.44 mL, 4.20 mmol) was added with a syringe at 0 °C. It was warmed to room temperature and continued to stir overnight. The resultant solution was dried in vacuum to remove all volatiles and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL). Concentrating the filtrate to about 3 mL under reduced pressure and making it stand gave colorless crystals of compound **4**. Yield: 1.11 g (59%); m.p. 124–125 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.63, 9.46 (d, NH), 7.92-6.67 (m, 30H; phenyl), 5.32 (s, CH<sub>2</sub>Cl<sub>2</sub>), 3.78 (s, OCH<sub>2</sub> of thf), 1.88 (s, 3,4-2CH<sub>2</sub> of thf), 0.66--0.02 (m, 6H; SiMe<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 181.5, 178.4, 167.8 (N-C-N), 149.1–120.4 (phenyl), 56.1, 28.3 (thf), 4.2, 2.9, 2.4 (SiMe<sub>2</sub>) ppm. Anal. Calc. for C<sub>41</sub>H<sub>38</sub>Cl<sub>2</sub>N<sub>6</sub>SiZr·(CH<sub>2</sub>Cl<sub>2</sub>) (889.91): C, 56.68; H, 4.53; N, 9.44. Found: C, 56.88; H, 4.66; N, 9.28%.

#### 2.3. X-ray data collection and crystal structure determination

The single crystals of **1**, **2**, **3**, and **4** suitable for X-ray diffraction studies were obtained. X-ray diffraction data were collected with graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker Smart Apex CCD diffractometer, equipped with an Oxford Cryosystems CRYOSTREAM device. The collected frames were processed with the proprietary software SAINT and an absorption correction was applied (SADABS) to the collected reflections [11,12]. The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the software SHELXTL [13]. Structure refinements were made on  $F^2$  using the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized positions and allowed to ride on the respective parent atoms. Pertinent crystallographic data and other experimental details are summarized in Table 1.

#### 2.4. Ethylene polymerization

The polymerizations were performed in a 250 mL autoclave. Compound **2** was dissolved in toluene and transferred into an autoclave with a syringe. The solution of methylalumoxane (MAO) in toluene was added with a syringe for activation. While stirring, the ethylene gas was filled into the reactor. After stirring for a definite period of time, the reaction mixture was quenched with 5% HCI/EtOH. The polymer was filtered, washed with ethanol, and dried under vacuum.

#### 3. Results and discussion

#### 3.1. Analogous reactions about titanium

The short distance between two amidinate moieties is the most noted structural feature in this series of ligands. On the other hand, the presence of the shared silyl-bridge brings the seven-membered N–C–N–Si–N–C–N skeleton two labile N–Si bonds. N–Si bond exhibited a significant function in the reaction of  $[SiMe_2$ {NC(Ph)N(Ph)Li(thf)<sub>2</sub>]<sub>2</sub>] and TiCl<sub>4</sub> (shown in Scheme 2) [14]. Attempts of preparing a titanium linked bis(amidinate) compound were unsuccessful and the only isolated product was characterized as an imido titanium species, suggesting that the original tetradentate N–C–N–Si–N–C–N backbone was broken into small N–C–N fragments at the silyl-bridge. In addition to the vulnerable site of silyl-bridge, another factor of the ligand dissociation was supposed to be the high Lewis acidity of TiCl<sub>4</sub>. More recently, the reaction between [SiMe<sub>2</sub>{NC(Ph)N(Ph)Li(thf)<sub>2</sub>]<sub>2</sub>] and TiCl<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>) was investi-

Table	1
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Crystal data and refinement results for compounds 1, 2, 3, and 4.

Compound	1	2	3	4
Empirical formula	C56.50H53ClN8Si2Zr	C50H50Cl2N6Si2Zr	C <sub>39</sub> H <sub>43</sub> Cl <sub>3</sub> N <sub>4</sub> OSiZr	C42H40Cl4N6SiZr
Molecular mass	1026.92	953.26	809.43	889.91
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	ΡĪ	ΡĪ	ΡĪ	ΡĪ
a [Å]	10.7678(17)	13.8382(8)	11.658(2)	12.7709(17)
b [Å]	10.9464(18)	14.0886(8)	12.535(2)	13.5973(18)
c [Å]	21.668(4)	14.2529(8)	14.725(3)	14.5664(19)
α [°]	90.337(2)	87.8280(10)	95.924(3)	88.071(2)
β [°]	90.605(2)	67.4630(10)	105.488(3)	69.612(2)
γ [°]	90.305(2)	74.3530(10)	108.075(3)	68.647(2)
$V(\hat{A}^3)$	2553.8(7)	2464.7(2)	1930.3(6)	2195.6(5)
Ζ	2	2	2	2
F(0 0 0)	1066	988	836	912
$D_{\text{calcd}} [\text{g cm}^{-3}]$	1.335	1.284	1.393	1.346
$M(Mo K\alpha) [mm^{-1}]$	0.361	0.420	0.560	0.557
Reflections collected	12 490	16 708	8002	9123
Unique reflections	8808	11 681	6649	7590
Observed reflections	6772	6745	4223	6045
Goodness-of-fit (GOF) on F <sup>2</sup>	1.033	0.935	0.870	1.031
$R_1, wR_2 [I > 2\sigma(I)]$	0.0601, 0.1391	0.0530, 0.1170	0.0513, 0.0998	0.0445, 0.1300
$R_1$ , $wR_2$ (all data)	0.0776, 0.1478	0.1067, 0.1389	0.0804, 0.1078	0.0551, 0.1360
Largest difference in peak and hole [e Å $^{-3}$ ]	1.036 and -0.739	0.751 and -0.588	0.838 and -0.451	0.892 and -0.410





gated for comparison [15]. The ligand was found to undergo a rearrangement process from the linked bis(amidinate) configuration to the linked imido-amidinate configuration though N–C–N–Si–N–C– N backbone was maintained. Furthermore,  $[SiMe_2(NC(Ph)N(Ph)-Li(thf)_2]_2]$  was treated with  $TiCl_2(C_5H_5)_2$  and it gave a titanium compound with original ligand [16]. Comparing the analogous reactions, the same ligand tended to be "stable" as the Lewis acid-ity of titanium salts decreased with coordination of cyclopentadienyl. Consequently, it was believed that the acid–base balance between the metal salt and the linked bis(amidinate) ligand is a crucial factor in the corresponding reactions.

## 3.2. Synthesis of zirconium complexes and crystal structure descriptions

The reactions between  $[SiMe_2{NC(Ph)N(Ph)Li(thf)_2}]$  and  $ZrCl_4$  were supposed to be mild because the Lewis acidity of  $ZrCl_4$  is also lower than that of TiCl\_4. Scheme 3 shows the synthetic routes for a series of zirconium compounds. Lithium compound was treated with half an equivalent of zirconium tetrachloride in tetrahydrofuran. It gave compound **1** as yellow crystals after extraction with  $CH_2Cl_2$  and crystallization. The molecular structure of **1** is shown in Fig. 1. The zirconium center is wrapped by two ligands with eight Zr–N bonds in a tetradentate fashion, and the bond lengths of Zr–N bonds are in the range of 2.25–2.37 Å, demonstrating the half cycle configuration and affording three adjacent N–Zr–N bond







Fig. 1. ORTEP drawing (30% probability level) of the molecular structure of compound 1, and hydrogen atoms were omitted for clarity.

ferred through the crowded coordination environment of the metal center.

Regarding an organometallic compound with good catalytic properties, the corresponding metal center should be in low coordination saturation and be electronically deficient. Obviously, compound **1** could not meet the need. The model of **II** may be qualified. Therefore, the ligand transfer reagent was treated with one equivalent of zirconium tetrachloride. However, the attempt to obtain compound as II was unsuccessful in this way. After being worked up in toluene, it gave a colorless crystalline compound 2. The Xray crystallography determination revealed 2 as an interesting structure (shown in Fig. 2). An unprecedented linked tris(amidinate) ligand was formed, and it coordinated to Zr. The original N-C-N-Si-N-C-N backbone is prolonged, resulting in an 11-membered chain N-C-N-Si-N-C-N-Si-N-C-N. It bends around the metal center nearly to be a cycle and provides five nitrogen atoms as donor sites. The two open ends of the chain bind the metal center with an angle of 95.04(9)°. Two terminal amidinate moieties coordinate to Zr in a chelating mode. The related bite angles are over 57°, being 2° bigger than the corresponding values in compound 1. The linked tris(amidinate) ligand and the two remaining chlorine atoms form a pentagon bipyramid environment for Zr.

Regarding the ease for the linked bis(amidinate) ligands to support the binuclear species, the ligand transfer reagent was treated with two equivalents of zirconium tetrachloride. In this case, a pale yellow crystalline compound **3** was obtained. The structure of **3** (shown in Fig. 3) demonstrates a mononuclear species. Though the ligand around the Zr has the same N–C–N–Si–N–C–N backbone as the lithium precursor, **3** has been converted as a linked imino-amidinate complex. On both sides of the silyl-bridge, two N–C–N moieties exhibit different coordination styles to the metal center: one is ionic chelating and the other is neutral mono-dentate. The

three Zr–N bonds are in the range of 2.20–2.25 Å. Three chlorine atoms are maintained. Atoms Cl(1), Zr(1), and Cl(2) are closely linear. This line is perpendicular to Zr(1)–Cl(3). In the presence of a tetrahydrofuran molecule, the Zr adopts a similar coordination configuration of pentagon bipyramid as that in compound **2**. It should be pointed out that only 20% excess of zirconium tetrachloride could also yield the same result as compound **3**. Therefore, the excessive zirconium salt beyond one equivalent was supposed to be playing the catalytic function rather than the synthetic function.

#### 3.3. Rearrangement reactions and proposed mechanism

As is apparent from the above-mentioned reactions, different stoichiometries of the ligand to metal salt lead to different products. Moreover, it is noteworthy that compounds 2 and 3 are not coordinated with the starting linked-bis(amidinate) ligand and they are not consistent with the stoichiometries of their parent reactants. It is convincing that rearrangement reactions occur. The proposed mechanism for the formation of 2 and 3 is outlined in Scheme 4: (1) It forms the "normal" compound, a transition state a in the same configuration as II after combination of the parent reactants. (2) The linked bis(amidinate) species a transforms into the linked imido-amidinate species **b**, which is another transition state (the intramolecular rearrangement process is induced by the active metal center and has been reported in previous work [15]). (3) The ligand in **b** is polarized and the terminal imido nitrogen is more nucleophilic in the absence of hindrance of the phenyl; then intermolecular rearrangement is initiated with nucleophilic attack of the imido nitrogen toward the bridging silicon atom of another molecule, which leads to the breakage of N-Zr and N-Si bonds, formation of N-Zr and N-Si bonds as well as displacement of N–C double bonds. (4) It gives compound **2** and **c** (**c** is presumed



Fig. 2. ORTEP drawing (30% probability level) of the molecular structure of compound 2, and hydrogen atoms were omitted for clarity.



Fig. 3. ORTEP drawing (30% probability level) of the molecular structure of compound 3, and hydrogen atoms were omitted for clarity.



according to titanium species in scheme 2). (5) In case  $ZrCl_4$  is excessive, **b** will strongly incline to be protonated at the imino nitrogen to form compound **3** instead of intermolecular attacking because a high Lewis acidic environment is provided.

An interesting question has arisen. What is the driving force for intra- and intermolecular rearrangement? It is believed that the combination of the following factors, including Lewis basicity of the ligand, Lewis acidity of the Zr, and lability of the N-Si bond, forces the transformation process. For example, when treating the ligand and  $ZrCl_4$  in the ratio of 2:1 to prepare compound 1, the Lewis basicity of the ligand is predominant and the metal center is tightly wrapped, losing the catalyzing ability. On the contrary, when the ratio of the ligand to  $ZrCl_4$  is not more than 1:1, the Lewis acidity is not "neutralized" completely. The electron deficient Zr will "catalyze" the breakage of the N-Si bond and rearrangement of the ligand to give **b**. The degree of Lewis acidity in the reaction mixture will determine the intermolecular rearrangement reaction or addition reaction for **b**. Consequently, compounds **2** and **3** were obtained, respectively.

As for the transition state **b**, its linked imido-amidinate ligand contains an active imido nitrogen atom. In order to trap this transition compound, the reaction route shown in Scheme 5 was contrived. One equivalent of ligand and one equivalent of zirconium

tetrachloride were combined. Half an hour later, two equivalents of benzonitrile was added. It was proposed that the imido nitrogen atom could attack the benzonitrile instead of another molecule. On the other hand, benzonitrile could increase the Lewis basicity of the system as neutral ligand coordinating to Zr. However, the obtained compound named **4** was not the expected product. Compound **4** displays the pentagon bipyramid configuration as **2** and **3**. Its molecular structure is illustrated in Fig. 4 and is nearly similar to that of **2**, except that it lacks a silyl-bridge. The tridentate ligand in **4** is identical to that in **3**. Additionally, the separate N–C–N moiety in **4** is related to the titanium compound shown in Scheme 2, and both are substantial proofs for the proposed byproduct **c**.



Scheme 5.



Fig. 4. ORTEP drawing (30% probability level) of the molecular structure of compound 4, and hydrogen atoms were omitted for clarity.

The formation of **4** especially for the separate N–C–N moiety is not clear and is under investigation. Nevertheless, it reflects the high accordance with **2** and **3**, obeying the rule of different conditions leading to different products. The selected structural data of this series of zirconium compounds are listed in Table 2.

#### 3.4. Catalytic activity for ethylene polymerization of compound 2

The catalytic activity of compound 2 for ethylene polymerization was examined under a variety of conditions. The preliminary results are listed in Table 3. It shows that the activity of compound **2** is highly dependent on pressure. At normal pressure, compound **2** was found to be an inactive catalyst for ethylene polymerization

Table 3 Ethylene polymerization by the 2/MAO system.<sup>a</sup>

Entry	T [°C]	<i>P</i> [atm]	Productivity <sup>b</sup>
1	30	1	no
2	50	1	trace
3	70	1	trace
4	30	10	438
5	50	10	1043

<sup>a</sup> Reaction conditions: 5 µmol catalyst, MAO/catalyst = 1000, time = 30 min, toluene solvent (100 mL). <sup>b</sup> kg(PE) mol<sup>-1</sup>(Zr) h<sup>-1</sup>.

at 30 °C. Only trace amount of polymer formation was observed even when heating the reaction system to 70 °C. The reaction

Гable	2

Selected bond lengths (Å) and bond angles (°) for compounds 1, 2, 3, and 4.

1		2		3		4	
Zr(1)-N(1)	2.370(3)	Zr(1)-N(1)	2.316(3)	Zr(1)-N(1)	2.255(3)	Zr(1)-N(1)	2.223(3)
Zr(1)-N(2)	2.273(3)	Zr(1)-N(2)	2.172(3)	Zr(1)-N(2)	2.203(3)	Zr(1)-N(2)	2.225(2)
Zr(1)-N(3)	2.253(3)	Zr(1)-N(3)	2.336(3)	Zr(1)-N(4)	2.246(3)	Zr(1)-N(4)	2.266(2)
Zr(1)-N(4)	2.342(3)	Zr(1)-Cl(1)	2.4847(11)	Zr(1)-O(1)	2.284(3)	Zr(1)-Cl(1)	2.4857(9)
N(1)-C(7)	1.333(5)	N(1)-C(7)	1.326(4)	Zr(1)-Cl(1)	2.4776(12)	N(1)-C(7)	1.321(4)
N(2)-C(7)	1.333(5)	N(2)-C(7)	1.336(4)	N(1)-C(7)	1.312(5)	N(2)-C(7)	1.335(4)
Si(1)-N(2)	1.717(3)	Si(2)-N(4)	1.797(3)	N(2)-C(7)	1.331(5)	Si(1)-N(2)	1.710(3)
N(2)-Zr(1)-N(1)	57.08(11)	Si(2)-N(5)	1.694(3)	Si(1)-N(2)	1.715(3)	Si(1)-N(3)	1.800(3)
N(3)-Zr(1)-N(2)	65.00(11)	N(2)-Zr(1)-N(1)	59.08(10)	Si(1)-N(3)	1.790(3)	N(1)-Zr(1)-N(2)	59.39(9)
N(4)-Zr(1)-N(1)	175.67(11)	N(3)-Zr(1)-N(2)	66.99(10)	N(2)-Zr(1)-N(1)	59.09(12)	N(4)-Zr(1)-N(2)	79.60(9)
N(5)-Zr(1)-N(1)	89.10(11)	N(5)-Zr(1)-N(6)	59.56(10)	N(4)-Zr(1)-N(2)	76.15(12)	N(4)-Zr(1)-N(5)	79.90(9)
N(8)-Zr(1)-N(1)	90.38(11)	Cl(2)-Zr(1)-Cl(1)	171.66(4)	Cl(2)-Zr(1)-Cl(1)	178.98(5)	N(6)-Zr(1)-N(1)	81.99(10)
N(4)-Zr(1)-N(5)	88.88(11)	N(6)-Zr(1)-N(1)	95.04(9)	Cl(1)-Zr(1)-Cl(3)	90.95(5)	Cl(2)-Zr(1)-Cl(1)	174.30(3)
N(8)-Zr(1)-N(4)	91.93(11)	N(1)-C(7)-N(2)	112.7(3)	Cl(2)-Zr(1)-Cl(3)	89.96(5)	N(1)-Zr(1)-Cl(1)	91.37(8)
N(3)-Zr(1)-N(4)	57.23(11)	N(3)-Si(1)-N(2)	91.34(13)	N(1)-Zr(1)-Cl(1)	91.70(9)	N(6)-Zr(1)-Cl(1)	93.62(9)
N(1)-C(7)-N(2)	112.8(3)	N(3)-C(16)-N(4)	122.2(3)	N(1)-C(7)-N(2)	112.6(4)	N(1)-C(7)-N(2)	112.1(3)
N(3)-Si(1)-N(2)	90.64(15)	N(5)-Si(2)-N(4)	103.62(13)	N(2)-Si(1)-N(3)	103.26(16)	N(3)-Si(1)-N(2)	104.34(12)

was then performed at 10 atm. It resulted in an abrupt increase of the polymerization activity, which reached 438 kg(PE) mol<sup>-1</sup>(Zr) h<sup>-1</sup> at 30 °C. The amount of polymer was far doubled at 50 °C, which suggested that compound **2** was also a temperature-promoted catalyst.

#### 4. Conclusions

Four zirconium compounds derived from a linked bis(amidinate) ligand were obtained. These compounds are in high coordination state to meet the need of Zr. They were found to be closely related to the Lewis acidic/basic environment resulting from the reactants. In the cases of the linked bis(amidinate) ligand being deficient, rearrangement reactions will take place to compensate the coordination number of metal center. The transformations could happen because of the ligand containing labile N–Si bond. The group IV metal complexes with this series of linked bis(amidinate) ligands are potential catalysts for olefin polymerization.

#### Supplementary data

CCDC Nos. 623283, 623284, 623285, and 623286 contain the supplementary crystallographic data for **1**, **2**, **3**, and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/con-ts/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.

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