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Zirconium Complexes with the New Ancillary Diamido Ligand 2,2′-Ethylenebis(*N*,*N*′-(triisopropylsilyl)anilinido)$^{2-}$: Syntheses, Structures, and Living α-Olefin Polymerization Activities

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Summary: Using the new ancillary ligand 2,2′-ethylenebis(N,N′-(triisopropylsilyl)anilinido) (EBT^{i}P, **1***), the zirconium complexes (EBT^{i}P)ZrCl$_2$ (***2***) and (EBT^{i}P)ZrMe$_2$ (***3***) have been prepared. X-ray crystal structures and ^{1}H NMR spectra of* **2** *and* **3** *reveal that they both have a C$_2$-symmetric conformation. Complexes* **2***, activated by MAO, and* **3***, activated by either MAO or B(C$_6$F$_5$)$_3$, are good catalysts for the polymerization of terminal olefins. In particular, the polymerization of 1-hexene catalyzed by* **3***/B(C$_6$F$_5$)$_3$ at low temperature is living.*

The search for well-defined or single-site catalysts for the polymerization of terminal olefins has been the subject of intensive research in the past decade.[1−3] Most of these catalysts are metallocene derivatives[2,3] or metal complexes with one cyclopentadienyl ring[4] and a pendant amido ligand.[5] Recently, complexes containing only a chelating diphenoxide[6] or a chelating diamido ligand[7] have received much attention as potential α-olefin polymerization catalysts. One advantage of such ligands over cyclopentadienyl ligands is their easier accessibility. Moreover, the metal complexes derived therefrom often exhibit new types of polymerization activities. For example, McConville and coworkers showed propylene-bridged aryl-substituted diamido titanium complexes promote the living polymerization of terminal olefins.[7k] Schrock and co-workers also reported that zirconium complexes of ether-bridged dianiline derivatives are good catalysts for the living polymerization of terminal olefins.[7l]

As a part of our effort to discover new polymerization catalysts with noncyclopentadienyl ligands we have synthesized zirconium complexes of the new diamido ancillary ligand 2,2′-ethylenebis(*N*,*N*′-(triisopropylsilyl)anilinido) (EBT^{i}P). Preliminary results show that when activated by either methylaluminoxane (MAO) or B(C$_6$F$_5$)$_3$, these complexes catalyze the polymerization of olefins. The catalytic activity for the polymerization of ethylene and propylene is much higher than with any other d^0 metal complexes with noncyclopentadienyl ancillary ligands and is almost comparable to that of zirconocene or its derivatives. Furthermore, the polymerization of 1-hexene catalyzed by these complexes at low temperature is living. Here, we present the syntheses and X-ray crystal structures of these complexes and preliminary results on the polymerization of α-olefins by activated dichloro- and dimethylzirconium complexes.

The free-base ligand H$_2$(EBT^{i}P) (**1**) was synthesized by the reaction of lithiated 2,2′-ethylenedianiline and 2 equiv of triisopropylsilyl chloride in THF (Scheme 1).

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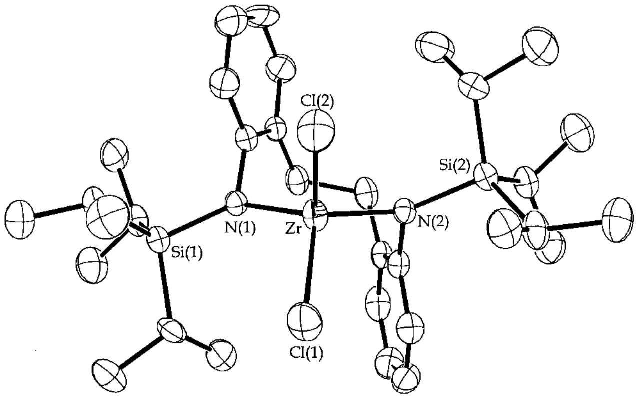
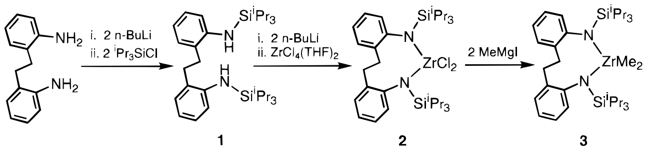


Figure 1. X-ray crystal structure of **2**. Selected bond distances (Å) and angles (deg): Zr−Cl(1) 2.374(2), Zr−Cl(2) 2.362(2), Zr−N(1) 2.028(5), Zr−N(2) 2.030(5), Cl(1)−Zr−Cl(2) 98.36(8), N(1)−Zr−N(2) 115.0(2).

Scheme 1



Lithiation of **1** using 2 equiv of n-BuLi followed by reaction with $ZrCl_4(THF)_2$ in refluxing toluene yields colorless $(EBT^iP)ZrCl_2$ (**2**).[8] The X-ray structure of **2** (Figure 1) reveals that the complex possesses overall C_2 symmetry and the zirconium has a distorted tetrahedral coordination geometry.[9] The average Zr−Cl distance is 2.368(2) Å, which is slightly shorter than that in Cp_2ZrCl_2 (2.441(5) Å). The Cl−Zr−Cl bond angle (98.36(8)°) is larger than that in Cp_2ZrCl_2 (97.1(2)°) but much smaller than those in any other crystallographically characterized dichloro zirconium complexes with ancillary diamido ligands.[10]

Alkylation of **2** with excess MeMgI affords $(EBT^iP)ZrMe_2$ (**3**) in quantitative yield.[8] The structure of **3** was also determined by X-ray crystallography (Figure 2).[9] Complex **3** is isostructural to **2**. The Me−Zr−Me angle (97.48(13)°) is considerably larger than that in Cp_2ZrMe_2 (95.6(12)°), while the average Zr−Me length (2.249(3) Å) is slightly shorter than that in Cp_2ZrMe_2 (2.277(5) Å).[11]

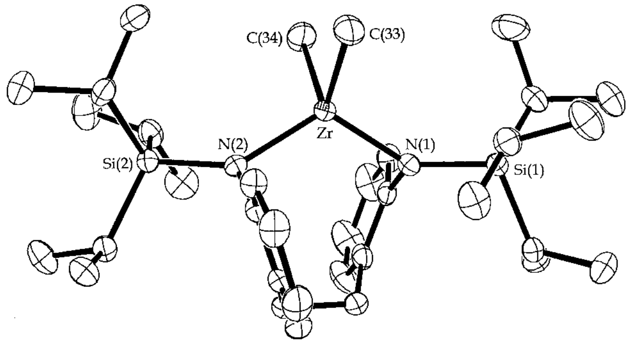


Figure 2. X-ray crystal structure of **3**. Selected bond distances (Å) and angles (deg): Zr−C(33) 2.256(3), Zr−C(34) 2.242(3), Zr−N(1) 2.070(2), Zr−N(2) 2.069(2), C(33)−Zr−C(34) 97.48(13), N(1)−Zr−N(2) 117.26(8).

Complexes **2** and **3** appear to sustain a C_2-symmetric conformation in solution. In their ^1H NMR spectra taken in benzene-d_6 or toluene-d_8, however, only a singlet signal is observed for the protons of the ethylene bridge at room temperature, which indicates a fast fluxional behavior of the ethylene bridge on the NMR time scale. The decoalescence occurs around −50 °C. The activation barrier is estimated to be 46 kJ mol^{-1}. A similar fluxional behavior has been observed in titanium complexes containing an ethylene-bridged bisphenolato ligand with a higher activation barrier.[6d] In chloroform-d solution, however, a characteristic AB spin pattern is observed for the ethylene protons at room temperature; no coalescence is observed up to 60 °C. This solvent dependence of the fluxional behavior has not been fully understood. The isopropyl methyl groups are diastereotopic, which we interpret as a consequence of restricted rotation about the N−Si bond, presumably due to the conjugation between the filled p orbital of nitrogen and an empty d orbital of silicon. The sum of the bond angles around the coordinating nitrogen atoms in **2** and **3** are 356.9° and 358.0°, respectively, which indicates that the four atoms Zr, N(1), C(1), and Si(1) constitute a common plane.[12] The amide nitrogens can be, therefore, considered as a four-electron donor to the zirconium metal center.

Complexes **2**, activated by MAO, and **3**, activated by either MAO or $B(C_6F_5)_3$, are good catalysts for the polymerization of olefins such as ethylene, propylene, and 1-hexene, although the angles of Cl−Zr−Cl and Me−Zr−Me are very small.[7] A summary of the polymerization results is shown in Table 1.[13] These catalytic systems generate high molecular weight polymers with narrow polydispersities (PDI). The catalytic activities of these complexes for the polymerization of ethylene and propylene are almost comparable to that of the Cp_2ZrCl_2/MAO system.[14] For example, **2** (7.31 μmol_{cat} in 10 mL of toluene, 500 equiv of MAO, ~1 atm of ethylene, 22 °C, and 5 min) affords 3.21 g (5.27×10^6 g mol_{cat}^{-1}

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[8] For **2**: ^1H NMR ($CDCl_3$) δ 0.73 (d, 18H), 0.86 (d, 18H), 1.13 (m, 6H), 2.86 (d, 2H), 3.15 (d, 2H), 7.18−7.47 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.27, 19.49, 19.66, 34.36, 128.04, 130.36, 132.31, 135.09, 136.32, 148.40. Anal. Calcd for $C_{32}H_{54}N_2Si_2Cl_2Zr$: C, 56.14; H, 7.89; N, 4.09. Found: C, 56.28; H, 8.08; N, 4.08. For **3**: ^1H NMR ($CDCl_3$) δ 0.59 (s, 6H), 0.73 (d, 18H), 0.85 (d, 18H), 1.00 (m, 6H), 2.78 (d, 2H), 3.01 (d, 2H), 7.01−7.28 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.45, 19.52, 19.69, 33.86, 50.58, 127.19, 127.66, 131.78, 134.62, 137.33, 146.99. Anal. Calcd for $C_{34}H_{60}N_2Si_2Zr$: C, 63.43; H, 9.32; N, 4.35. Found: C, 62.96; H, 9.27; N, 4.16.

[9] Crystal data for **2**: $C_{32}H_{54}N_2Si_2Cl_2Zr$, $M = 684.61$, monoclinic, $P2_1/c$, $a = 15.646(4)$ Å, $b = 10.918(1)$ Å, $c = 21.248(2)$ Å, $\beta = 91.56(1)°$, $V = 3628.3(10)$ Å^3, $Z = 4$, $T = 293$ K, Enraf-Nonius CAD4 diffractometer, Mo Kα ($\lambda = 0.710\ 73$ Å), anisotropic refinement for all non-hydrogen atoms, final cycle of full-matrix least-squares refinement on F^2 with 4441 independent reflections and 352 variables (SHELXL-93), R1 ($I > 2\sigma(I)$) = 0.0545, wR2 (all data) = 0.1249, GOF = 1.027. For **3**: $C_{34}H_{60}N_2Si_2Zr$, $M = 643.72$, monoclinic, $P2_1/c$, $a = 15.5271(1)$ Å, $b = 11.0031(2)$ Å, $c = 21.2717(3)$ Å, $\beta = 91.493(1)°$, $V = 3632.96(9)$ Å^3, $Z = 4$, $T = 293$ K, Siemens SMART CCD diffractometer, anisotropic refinement for all non-hydrogen atoms, final cycle of refinement on F^2 with 5200 independent reflections and 352 variables, R1 ($I > 2\sigma(I)$) = 0.0310, wR2 (all data) = 0.0875, GOF = 1.068.

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Table 1. Polymerization of α-Olefins[a]

entry	cat. (μmol)	cocat. (equiv)	monomer	T (°C)	M_n[b]	M_w[b]	M_w/M_n	activity[c]
1	**2** (7.31)	MAO (500)	ethylene	22	5776	13 591	2.35	52.74
2	**2** (7.31)	MAO (500)	propylene	22	8508	17 863	2.09	7.86
3	**2** (7.31)	MAO (500)	1-hexene	22	6659	15 349	2.30	2.20
4	**3** (7.77)	MAO (500)	ethylene	0	75 296	161 341	2.82	12.58
5	**3** (7.77)	MAO (500)	propylene	0	16 513	41 672	2.52	18.67
6	**3** (7.77)	MAO (500)	1-hexene	0	10 983	26 517	2.41	5.40
7	**3** (7.77)	$B(C_6F_5)_3$ (1)	ethylene	0	84 000	165 241	1.96	1.78
8	**3** (7.77)	$B(C_6F_5)_3$ (1)	propylene	0	229 614	304 205	1.32	2.85
9	**3** (7.77)	$B(C_6F_5)_3$ (1)	1-hexene	0	118 300	146 088	1.23	3.94

[a] General conditions: See ref 13. [b] By GPC in 1,2,4-trichlorobenzene vs polystyrene standards. [c] 10^5 g of polymer/(mol of catalyst·h).

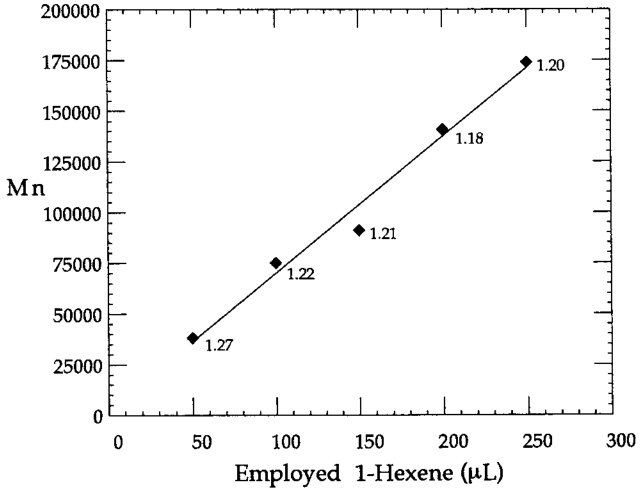

Figure 3. Number average molecular weight (M_n) vs amount of monomer employed for 1-hexene polymerization using **3**/$B(C_6F_5)_3$ at −10 °C.

h^{-1}) of polyethylene (entry 1), and **3** (0 °C, 7.77 μmol_{cat} otherwise the same conditions as above) affords 1.21 g (1.87×10^6 g mol_{cat}^{-1} h^{-1}) of polypropylene (entry 5). These metal complexes are also good catalysts for the polymerization of 1-hexene. For example, **3**/$B(C_6F_5)_3$ (7.77 μmol in 8 mL of toluene, 2 mL of 1-hexene, 0 °C, and 5 min) affords 0.24 g (3.94×10^5 g mol_{cat}^{-1} h^{-1}) of poly(1-hexene) with M_n of 118 300 and PDI of 1.23 (entry 9). No olefinic resonances were observed in the $^{13}C/^{1}H$ NMR spectra of the polymers or oligomers prepared with these catalytic systems, which suggests the polymerization might be living. To examine whether the polymerization is living, the number average molecular weight (M_n) is plotted vs the amount of monomer employed for the 1-hexene polymerization using **3**/$B(C_6F_5)_3$ at −10 °C (Figure 3). The complete consumption of the employed monomer, small PDI, and a linear relationship between M_n and the amount of monomer employed suggest that the polymerization is indeed living under these conditions.[15] The living nature of the polymerization is further confirmed by formation of a block copolymer poly(1-hexene)-*block*-poly(1-octene) with a small PDI (M_n 108 730; M_w 130 088; PDI 1.21) in a quantitative yield upon sequential addition of the monomers.

For 1-hexene polymerization, **3**/$B(C_6F_5)_3$ exhibits a higher activity and narrower PDI of the polymer produced than **2**/MAO does. However, the activity of **3**/$B(C_6F_5)_3$ for polymerization of ethylene and propylene is much lower than that of the **2**/MAO and **3**/MAO systems, presumably due to some deactivation of the catalytic species by small impurities in ethylene and propylene gases.[16] Nevertheless, the PDI of the polymers produced with the borane cocatalyst are much narrower than those with MAO. The resulting polypropylene and poly(1-hexene) are atactic in all cases.

In summary, we report zirconium complexes with the new ancillary diamido ligand EBT^{i}P that are fully characterized by X-ray crystallography. These diamido zirconium complexes are easily accessible, robust, and serve as precursors for highly active catalysts for the living polymerization of terminal olefins. Successful polymerization and block copolymerization of other olefins with narrow polydispersities and mechanistic study will be reported shortly.

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Supporting Information Available: Experimental details of the synthesis, characterization, polymerization and X-ray crystal structure determination of **2** and **3**, including ORTEP diagrams with full atom labeling as well as crystallographic tables including atomic coordinates, thermal parameters, and bond distances and angles (20 pages). Ordering information is given on any current masthead page.

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(13) Typical polymerization procedure: **3** (1.00 mL of 7.77 mM stock solution) and MAO (225 mg, 3.88 mmol) were added to toluene to make the volume of the solution 10 mL. After the solution was stirred for 30 min, ethylene or propylene gas was bubbled into the solution for 5 min with vigorous stirring at 0 °C before the polymerization was quenched with 1.0 M HCl in ether. In the case of 1-hexene polymerization, 2 mL of 1-hexene was added to the solution. After 5 min of stirring, the reaction was quenched with 1.0 M HCl in ether solution. Polymers were isolated by the usual workup procedure and dried under vacuum. When **2** was used as catalyst, the polymerization was carried out at room temperature under the same conditions. See Supporting Information for complete details.

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(15) Considering the molecular weights of the resulting polymers, we suspect that only ~$^1/_3$ of the catalyst added is active in this experiment, which may be due to incomplete activation of the precatalyst. Once generated, nevertheless, the activated catalyst species seems stable and has living characteristics. Further study of the catalyst activation is underway.

(16) The bright yellow color of the solution containing **3** and the borane cocatalyst disappeared within 2 min after introduction of ethylene or propylene, while no color change was observed during 1-hexene polymerization. At the moment, we suspect that the catalyst deactivation in the ethylene and propylene polymerization is due to the presence of a small amount of unknown impurities in the monomers, which we have not been able to eliminate.