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Communications to the Editor

Synthesis of β-Iminoaminate Zirconium Complexes and Their Application in Ethylene Polymerization

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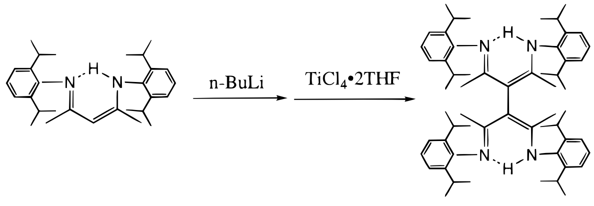
Introduction. Since Sinn and Kaminsky's first report of highly active metallocene catalysts for olefin polymerization,[1,2] considerable research has focused on the design and synthesis of well-defined homogeneous catalysts. The vast majority of reported catalysts are based on complexes with either cyclopentadienyl (Cp) or indenyl (In) ligands. Spurred by the success of these systems, and by their associated and formidable patent fences, recent efforts have shifted to alternative ligands with the hope of yielding catalysts with differentiated reactivities. The largest subset of non-Cp alternatives that have shown promising results appears to be dinitrogen chelates that include benzamidine,[3,4] diimine,[5] and diamine[6−8] ligands. Examples of nonchelating ligands showing extraordinary activities also have been reported.[9]

Herein we report the synthesis and polymerization activity of a new class of homogeneous catalysts based on the non-Cp ligands, β-iminoamines (β-IAMs). The successful zirconium catalyst series includes β-iminoamine compounds possessing different aromatic or aliphatic substituents. When activated by methylaluminoxane (MAO), we found that the β-iminoaminate zirconium complexes are highly active catalysts for the polymerization of ethylene.

Results and Discussion. a. Preparation of (β-IAM) Ligands. The aliphatic β-IAM derivative, dimethyl-β-IAM (**1a**), was prepared as described in the literature.[10] Using synthetic routes analogous to the synthesis of bis(2,6-diisopropylphenyl)-β-IAM (**1e**),[11] the aromatic β-IAM compounds (**1b**−**1d**) were prepared from acetylacetone and the corresponding aromatic amine.

b. Explorations into Titanium (β-IAM) Complexes. The titanium β-IAM complexes were the first targeted, but unfortunately, less than satisfactory results were obtained using $TiCl_4$ as the titanium source. When the deprotonated β-IAM (**1a**) was allowed to react with $TiCl_4$·2THF, nonspecific decomposition was observed. Under the same conditions, however, deprotonated **2e** proved to be far more interesting. No titanium adducts were isolated; instead, **1e** was nearly quantitatively dimerized to **1f** (eq 1).



(1)

The structure of **1f** is consistent with a mechanistic path involving radical coupling. ESR studies on the reaction mixture showed strong Ti(III) signals which lends support to an electron-transfer, radical coupling process. The use of **1f** as a bimetallic ligand is currently under investigation. Recently, we have succeeded in making the β-IAM analogues by using $Ti(NMe_2)_4$ as the precursor source, and these results will be reported elsewhere.

c. Synthesis of the Zirconium β-IAM Complexes. All of the ligands were metalated using the same procedure. Deprotoned with BuLi at low temperature, the anionic β-IAMs were allowed to react with $ZrCl_4$·2THF to afford yellow to orange β-IAM-$ZrCl_3$·THF complexes (Scheme 1). These complexes can be further purified by recrystallization from the toluene/hexane

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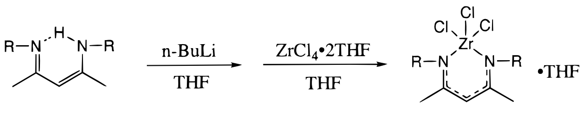
Scheme 1



2a: R=Me
2b: R=Ph
2c: R=2-methylphenyl
2d: R=2,6-dimethylphenyl
2e: R=2,6-diisopropylphenyl

mixtures. The NMR and elemental analysis of complexes **2a**−**e** were all consistent with the proposed 1 to 1 adducts. This structure was later confirmed by single-crystal X-ray analysis of complex **2e**.

Full structure analysis was important for the characterization of these complexes because the anionic β-IAM ligands can act as either four- or six-electron donors depending on the interaction between the metal and the two nitrogens and central α-carbon atom. Complex **2e** crystallizes with one THF molecule coordinated to the zirconium center. The ORTEP diagram of the β-IAM-ZrCl$_3$•THF complex **2e** is shown in Figure 1. There are two asymmetric molecules in the unit cell. The bonding positions of Cl1 and THF on the two molecules are switched relative to each other. In addition, there are slight differences in the bond lengths and angles of other atoms.

In the solid state, **2e** adopts a distorted, octahedral geometry at the zirconium center. The Zr−Cl1−N1−N2−O are almost coplanar ($\sum$Zr = 361°). As the Collins group reported in their β-IAM complexes,[12] the five atoms in the β-IAM ligand, N1−C2−C3−C4−N2, are coplanar, and these short bond lengths among those atoms show strong delocalization of the double bonds of the ligand. The Zr atom is bent above the ligand plane. However, the distances of Zr−C2 (3.1707(19)), Zr−C3 (3.4408(19)), and Zr−C4 (3.1594(20)) are too long to form real Zr−C bonds. Different from a η^5-coordinated β-IAM to the metal, claimed by Lappert and co-workers,[13] the β-IAM ligand in our complex is more close to the η^2-coordination mode. In addition, the bond lengths of Zr−N1 (2.2427(15)) and Zr−N2 (2.2134(16)) indicate there is no strong π-donation from the nitrogen atoms to the zirconium. Hence, the β-IAM zirconium compound **2e** is best described as a 12-electron, electron-deficient complex.

d. Ethylene Polymerization with Zirconium Complexes 2a−e. Activated by MAO, all of the five β-IAM zirconium complexes are active catalysts for ethylene polymerization. The zirconium complexes were dissolved in toluene and mixed with MAO in 200 mL Fisher-Porter bottles. The mixtures were aged for 30 min at polymerization temperature before ethylene was induced. Afterward, ethylene was pressurized to 100 psi and maintained constant during the duration of the polymerization. White polymer precipitated out quickly. After a predetermined reaction time, ethylene was vented, and the polymerization was quenched by the addition of methanol. The white polymer was filtered out, washed consecutively with methanol/HCl solution and methanol, and dried under vacuum. The polyethylene obtained was characterized by high-temperature NMR and DSC. The polymerization results are summarized in Table 1.

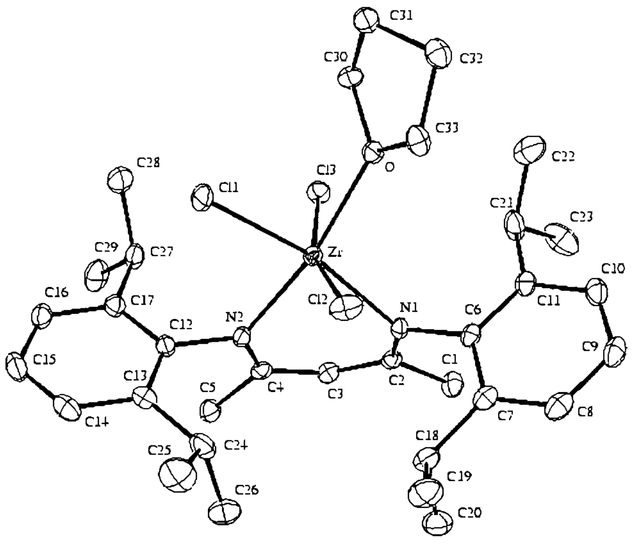


Figure 1. ORTEP drawing of compound **2e**.

Table 1. Ethylene Polymerizations with β-IAM-ZrCl$_3$·THF Complexes[a]

entry	catalyst	temp (°C)	time (h)	polymer yield (g)	activity (kg/(mol h))	melting point[b] (°C)
1	**2a**	r.t.	1	0.56	280	138.1
2	**2b**	r.t.	1	0.27	135	134.7
3	**2c**	r.t.	1	0.23	115	132.2
4	**2d**	r.t.	1	0.12	60	137.2
5	**2e**	r.t.	1	0.21	105	131.2
6	**2e**	r.t.	4	1.37	171	136.6
7	**2e**	r.t.	16	5.44	170	141.3
8	**2e**	40	1	0.1	50	134.5
9	**2e**	80	1	0.005	2.5	137.0
10	**2a**	r.t.	4	2.2	275	137.4
11	**2a**	40	1	0.64	320	132.7
12	**2a**	80	1	0.018	9	133.8

[a] Polymerization conditions: β-IAM-ZrCl$_3$·THF, 2.0 μmol; MAO, 2.0 mmol; toluene, 50 mL; ethylene pressure, 100 psi; toluene solution of catalyst and MAO is aged for 30 min at reaction temperature before ethylene is induced. [b] Endothermic peak temperatures from DSC.

Within this series of complexes, steric factors appear to be the overriding criteria in determining their activities. The dimethyl-β-IAM-ZrCl$_3$·THF, **2a**, is much more active than all of the catalysts with aromatic ligands (entry 1 vs entries 2−5). Moreover, the polyethylene from **2a** has the highest melting temperature under the identical polymerization condition, which may indicate higher molecular weight. High-temperature ^{13}C NMR analysis shows no evidence of long chain branching present. The activities of the aromatic β-IAM-ZrCl$_3$·THF complexes all fall within a very narrow range (entries 2−5). The substituent groups on the 2,6-positions of the phenyl ring of the aromatic β-IAM do not affect the polymerization activity to any great extent, although it seems the smaller the substituents on the phenyl ring, the higher the polymerization activities, except **2d**, which is less active than **2e**.

Both catalysts **2a** and **2e** maintain high activities in an ethylene environment for long periods of time. The polymerization activity of catalyst **2a** remains nearly constant over 4 h (entries 1 and 10). For catalyst **2e**, the polymer yields increase almost linearly with polymerization time up to 16 h (entries 5−7). It is very interesting that its average activities in 4 or 16 h are even higher than in 1 h. A polymer sample from a 1 h polymerization with **2e** shows a large shoulder in the melt transition peak around 100 °C (measured by DSC), which indicates a low molecular weight component is present. The shoulder becomes much smaller in the product from the 4 h polymerization and totally disappears after 16 h polymerization. These results are consistent with more than one active catalyst site formed at the beginning of the polymerization with complex **2e**. We hypothesize that while the polymerization proceeds, the less active site, which produces low molecular weight polymer, is either deactivated or converted into the more active form. Compared with normal high-density polyethylene, the melting point of the polyethylene produced by complex **2e** in 16 h polymerization is very high (entry 7).

The activity of catalyst **2a** first increases a small amount when the polymerization temperature increases from room temperature to 40 °C and then drops to a very low value at 80 °C (entries 11 and 12). Similarly, increasing polymerization temperature decreases the activity of catalyst **2e** sharply (entries 8 and 9). The activity drops more than 50% at 40 °C and becomes almost inactive at 80 °C. The reason for activity decreasing is very possible due to thermal decomposition of the catalysts. Catalyst **2a**, with the aliphatic β-IAM ligand, is more temperature tolerant than catalyst **2e**.

Conclusions. In summary, these β-IAM zirconium complexes are active catalyst precursors for ethylene polymerization. The MAO activated catalysts are very stable and keep constant activities during polymerization for long time periods. The dimethyl-β-IAM complex is more active and thermal stable than those aromatic β-IAM complexes. Polymerization of other olefins with these catalysts and synthesis of the β-IAM complexes with other transition metals will be reported shortly.

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References and Notes

(1) Andresen, A.; Cordes, H. G.; Herwig, J.; Keminsky, W.; Merck, A.; Mottweiler, R.; Pein, J.; Sinn, H.; Vollmer, H. J. *Angew. Chem.* **1976**, *88*, 689.

(2) Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem.* **1980**, *92*, 396.

(3) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 2106.

(4) Herskovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307.

(5) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6415.

(6) John, D. Scollard, D. H. M. *J. Am. Chem. Soc.* **1996**, *118*, 10008.

(7) Scollard, J.; McConville, D.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241.

(8) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830.

(9) (a) Stephan, D. W.; Stewart, J. C.; Guerin, F.; Spence, R. E. v. H.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *18*, 1116. (b) Stephan, D. W.; Guerin, F.; Spence, R. E. v. H.; Koch, L.; Gao, X.; Brown, S. J.; Swabey, J. W.; Wang, Q. Xu, W.; Zoricak, P.; Harrison, D. G. *Organometallics* **1999**, *18*, 2046.

(10) Minkin, V. I.; Olekhnovich, L. P.; Zhdanov, Y. A.; Kiselev, V. V.; Voronov, M. A.; Budarina, Z. N. *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 1347.

(11) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514.

(12) Rahim, M.; Taylor, N. J.; Xin, S.; Collins, S. *Organometallics* **1998**, *17*, 1315.

(13) Hitchcock, P. B.; Lappert, M. F.; Liu, d.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 2637.

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