Benzylation of α-Diimine Ligands Bound to Zirconium and Hafnium. A New Convenient Route to Olefin Polymerization Catalysts

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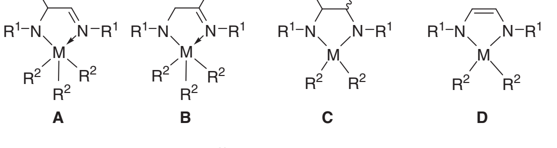
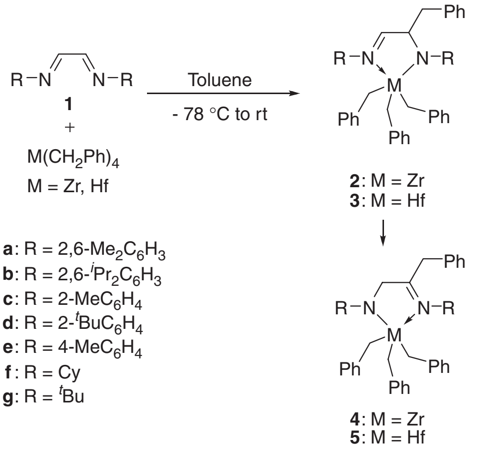
Reactions of $\mathrm{M(CH_2Ph)_4}$ (M = Zr and Hf) with α-diimine ligands **1** at −78 °C selectively afford tribenzyl amido–imino complexes of zirconium **4** and hafnium **5**, whose treatment with $\mathrm{B(C_6F_5)_3}$ gave the corresponding cationic dibenzyl complexes **6** and **7** capable of polymerizing 1-hexene.

In the last two decades, development of homogeneous olefin polymerization catalysts bearing metallocene fragments has been remarkable, and recent effort has aimed at developing the non-metallocene catalysts.[1] Among these non-metallocene catalysts, different types of imine-based ligands have attracted special interest because these nitrogen-based ligands have been flexibly designed and their complexes have exhibited unique catalytic performance for olefin polymerization.[2,3] We already reported the benzyl transfer reaction of tetrabenzylzirconium with iminopyrroles, giving amido–pyrrolyl zirconium catalysts for olefin polymerization.[4] Similar alkylation of the imine moiety of phenoxy–imine ligands was reported by Scott and his co-workers: the reaction of $\mathrm{Zr(CH_2Ph)_4}$ with phenoxy–imine ligands afforded the corresponding amido–phenoxy complexes.[5] In addition, reduction and alkylation of the imine group has been observed for imine-based olefin polymerization catalysts combined with any alkylaluminum cocataysts.[6–10] As our continuous interest in polymerization catalysts of early transition metals bearing such the imine-based ligands,[4,11] we focused our attention to the reaction between alkyl–metal compounds with α-diimine ligands, whose possible transformations (**A**–**D**) are illustrated in Scheme 1. Herein, we communicate our preliminary results on the systematic reaction of various α-diimine ligands with $\mathrm{M(CH_2Ph)_4}$ (M = Zr and Hf), selectively producing two complexes **A** and **B** as olefin polymerization catalysts, by varying the substituents on the nitrogen atoms of the α-diimine ligands and kind of metal center, though the benzylation reaction was independently reported by the group of Dow Chemical Company.[12]



Scheme 1.



Scheme 2.

Treatment of 1,4-dixylyl-1,4-diaza-1,3-butadiene (**1a**) with $\mathrm{Zr(CH_2Ph)_4}$ and $\mathrm{Hf(CH_2Ph)_4}$ at −78 °C selectively afforded the corresponding amido–imino complexes **4a** and **5a**,[13,14] which are products of benzyl transfer from metal to one of C=N bonds of the α-diimine ligand **1a**, respectively, giving intermediate species **2a** and **3a**, followed by the hydrogen transfer (Scheme 2). The ^{1}H NMR spectra of **4a** and **5a** display one set of signals attributable to the benzylated dissymmetric amido–imino ligand together with two singlets in a 3:1 ratio due to two kinds of methylene protons of the benzyl groups bound to the metal and the ligand, respectively. The observation of only one singlet signal for benzyl groups bound to the metal indicates a rapid exchange of three benzyl groups on the NMR time scale. Figure 1 shows the crystal structure of **4a**,[15] whose structure is essentially the same as that of the reported compound **4b**,[12] adopting a distorted trigonal bipyramidal with N1, C26, and C33 in trigonal planar (sum of the angles around the zirconium atom = 359.94°) and N2 and C40 at apical positions. Dissymmetric ligation is revealed by a significantly longer Zr–N (imino) bond (2.445(3) Å) than the Zr–N (amido) bond (2.121(3) Å) and a shorter C(1)=N (imino) bond (1.301(4) Å) compared to the C(2)–N (amido) (1.450(4) Å) bond. In solid state, one benzyl group coordinates in an η^2-fashion to the zirconium atom, having a rather short Zr–C(27) (2.651(3) Å) bond and an acute angle Zr–C26–C27 (87.06(18)°).

The reaction pattern of such the benzylation of the ligand highly depends on the substitutents on the nitrogen atoms of the ligand as well as the kind of metal.[13] Hafnium complexes **5b**–**5e** were obtained by the reactions of **1b**–**1e** with $\mathrm{Hf(CH_2Ph)_4}$. When cyclohexyl group was introduced as the substituents of the α-diimine ligand, the benzylation of **1f** by $\mathrm{Hf(CH_2Ph)_4}$ resulted in the selective formation of an amido–imino complex **3f**, in which a simple benzylation of the C=N bond of **1f** proceeded and no intramolecular hydrogen transfer occurred. Similarly, *tert*-butyl ligand **1g** reacted with $\mathrm{Hf(CH_2Ph)_4}$ to give **3g**. At room temperature, complex **3f** is thermally stable, while **3g** decomposes gradually. Notable spectral feature of **3f** and **3g** is that benzyl methylene protons are observed as an ABX pattern coupled with the methin proton. The reactions of $\mathrm{Zr(CH_2Ph)_4}$ with **1b** and **1d**, respectively, afforded **4b** and **4d**,

Table 1. Polymerization of 1-hexene by complexes **3**–**5**[a]

Entry	Cat.	Activity[b]	M_w[c] (10^3)	M_w/M_n[c]	Tacticity[d]
1	**4a**	3.6	bimodal	—	—
2	**4b**	2.9	2.29	1.99	atactic
3	**5a**	3.4	7.84	2.27	atactic
4	**5b**	5.6	4.39	2.03	atactic
5	**3f**	trace	—	—	—

[a] Polymerization conditions: cat. 10 µmol; $B(C_6F_5)_3$ 10 µmol; [1-Hexene] = 2.5 M; [Cat.] = 5.0 mM in chlorobenzene, time 6 h; temperature 25 °C. [b] Kg-polymer/mol-cat·h. [c] Determined by GPC. [d] Determined by ^{13}C NMR spectroscopic data.[17]

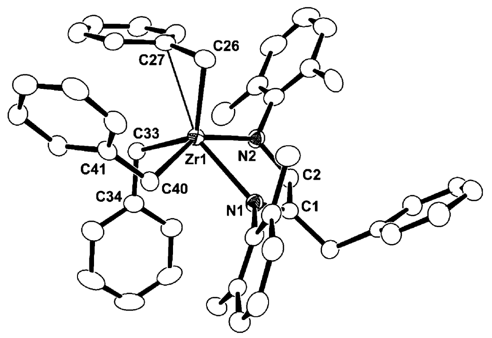
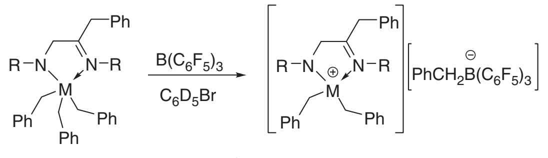


Figure 1. Drawing of the molecular structure of **4a**. Solvent molecule and all hydrogen atoms are omitted for clarity.

while the reaction with less bulky substituted ligands **1c**, **1e**, **1f**, and **1g** resulted in the decomposition, in consistent with the less stable Zr–C bond compared with Hf–C bond.[2a]

Zirconium and hafnium amido–imino complexes **4a**, **4b** and **5a**, **5b** together with **3f** were tested as catalyst precursors for 1-hexene polymerization upon treated with $B(C_6F_5)_3$ as cocatalyst, and results are shown in Table 1.[13] Complexes **4a**, **4b** and **5a**, **5b** showed moderate catalytic activity, and the polymerization proceeded through cationic dibenzyl species; the reactions of these tribenzyl complexes with $B(C_6F_5)_3$ in bromobenzene-d_5 afforded the corresponding zwitterionic dibenzyl complexes **6a**, **6b** and **7a**, **7b**, whose ^{19}F NMR data for $\Delta\delta$(m, p-F) indicated the formation of the separated anion of $[PhCH_2B(C_6F_5)_3]^-$.[16] In contrast, complex **3f** showed no activity because of thermal unstability of cationic species derived by **3f** and $B(C_6F_5)_3$.



(1)

4: M = Zr **a**: R = 2,6-$Me_2C_6H_3$ **6**: M = Zr
5: M = Hf **b**: R = 2,6-$^iPr_2C_6H_3$ **7**: M = Hf

In conclusion, we demonstrated that the substituent of the nitrogen atom of the α-diimine ligand controls the reaction pattern with $M(CH_2Ph)_4$ (M = Zr and Hf): (1) benzylation of 1,4-diaryl-1,4-diaza-1,3-butadienes followed by the hydrogen transfer within the ligands, giving amido–imino complexes **4** and **5** (Type B) through the intermediate complexes **2** and **3** and (2) benzylation of the dialkyl-substituted α-diimine ligands by $Hf(CH_2Ph)_4$, giving another amido–imino hafnium complexes **3** (Type A). Complexes **4a**, **4b** and **5a**, **5b** serve as catalyst precursors for 1-hexene polymerization upon activated by $B(C_6F_5)_3$. Thus, the convenient one-pot synthesis of catalyst precursors for olefin polymerization not only extends the flexibility in the design of precatalysts for olefin polymerization but also provides a new insight into possible side reaction of the catalysts bearing imine-based ligands because of easy alkylation of the imino moiety upon coordinated to early transition metals.

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13 Experimental details are given in Supporting Information, which is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.

14 On monitoring the reaction, we observed the formation **2** and **3** as transient species, which gradually disappeared. In contrast, the same reaction carried out at room temperature afforded ene–amido dibenzyl complexes (Type D) as by-roducts, whose formation was in consistent to the observation reported in Ref. 12.

15 Crystal data for **4a** is given in CIF format.

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