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Synthesis of Hafnium and Zirconium Imino−Amido Complexes from Bis-imine Ligands. A New Family of Olefin Polymerization Catalysts

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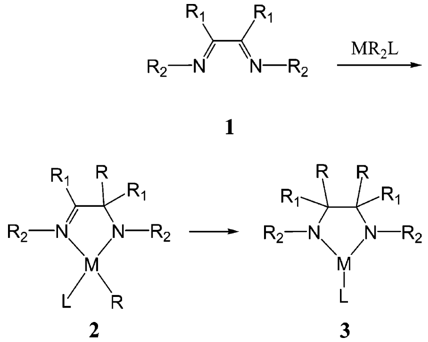
*Summary: The reaction of 2,6-diisopropylaniline-based bis-imine ligands (**4**, **9**) with M(CH$_2$Ph)$_4$ (M = Hf, Zr) led to formation of novel imino−amido tribenzyl complexes via migratory insertion of a benzyl group into a C═N bond. Imino−amido complexes were found to undergo unprecedented dibenzyl elimination to form ene−diamido complexes. Imino−amido complexes were found to be active ethylene polymerization catalysts.*

Metallocene-based catalysis dominated homogeneous olefin polymerization in the late 1980s and 1990s.[1] More recently, efforts have focused on the development of non-Cp-based catalysts,[2] giving rise to previously unknown polymerization behaviors[3] and new polymeric materials.[3a,4] Rapid synthesis and evaluation of novel non-Cp catalysts is, therefore, highly desired. We have previously shown[5] that the reaction between pyridyl−imine and tetrabenzylzirconium leads, after selective benzyl transfer, to the formation of novel catalysts for olefin polymerization reactions. Analogous reactions have also been reported by the groups of Scott[6] and Mashima,[7] which showed that reaction between bis(phenol−imine) and pyrrole−imine ligands with tetrabenzylzirconium leads, after selective benzyl transfer, to novel zirconium bis-phenoxy−amido and pyrrolo−amido complexes.[8] We wondered if an analogous reaction could occur between the neutral bis-imine ligands **1** and transition-metal alkyl precursors.[9,10,18] Such a transformation might lead to the rapid synthesis of a new family of either imino−amido (**2**) or/and bis-amido (**3**) complexes, as illustrated. Bis-imines have been extensively studied as supporting ligands in late-transition-metal olefin polymerization catalysts[3a,11] but have not been directly utilized as ligand precursors for early transition metal catalysts.



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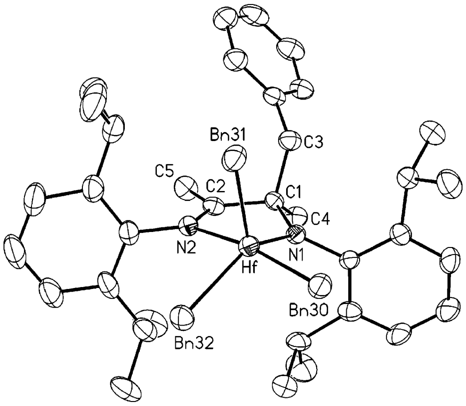
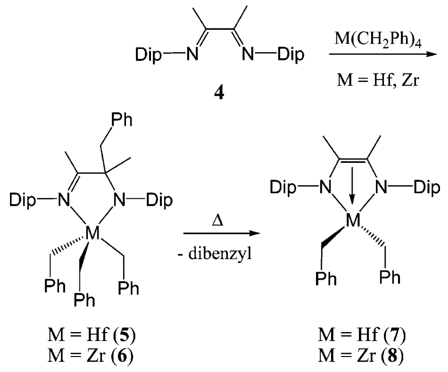


Figure 1. Molecular structure of **5**. Hydrogen atoms and phenyls of the Hf benzyl groups were removed for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bonds (Å) and angles (deg): Hf−N1 = 2.070(3), Hf−N2 = 2.423(3), C2−N2 = 1.278(5), C1−C2 = 1.527(5), C1−N1 = 1.503(4); N2−Hf−N1 = 70.8(1).

In this communication we report our preliminary results on the reaction between two different bis-imine ligands (**4**, **9**) and $M(CH_2Ph)_4$ (M = Hf, Zr). These transformations produce imino−amido tribenzyl complexes that display good activity as catalysts in ethylene/octene (EO) copolymerization reactions. Additionally, the unprecedented formation of ene−diamido complexes has been observed.

Reaction of the bis-imine **4** with tetrabenzylhafnium at ambient temperature quantitatively yields the chiral imino−amido complex **5** within 24 h, upon benzyl transfer from Hf to the bis-imine ligand.[12] The most notable feature in the ^{1}H NMR spectrum of **5** is the presence of two sets of two mutually coupled doublets in a 3:1 ratio, corresponding to the diastereotopic methylene protons of the benzyl groups. The observation of only one pair of doublets for the three Hf-bound benzyl groups indicates rapid benzyl group exchange on the NMR time scale. The X-ray crystal structure of **5** (Figure 1) reveals a significantly longer Hf−N(imino) bond (2.423(3) Å) as compared to the Hf−N(amido) (2.070(3) Å) bond. The two carbon and two nitrogen atoms of the metallacycle are almost planar, with the Hf atom located 0.64 Å above this plane. In an attempt to produce a bis-amido complex (such as **3**), by transfer of a second benzyl group, a toluene solution of **5** was heated to 70 °C overnight.

Scheme 1. Reactions of the Bis-imine 4 with $M(CH_2Ph)_4$ (M = Hf, Zr)



Dip = 2,6-*i*-$Pr_2C_6H_3$

Thermolysis of **5** did indeed produce a new diamido complex; however, its structure was different from that expected. Instead of a second benzyl transfer, elimination of dibenzyl from **5** was exclusively observed, yielding the ene−diamido[13] complex **7** (Scheme 1) quantitatively. While many ene−diamido complexes are known,[14] conversion of **5** to **7** via elimination of a dialkyl species is unprecedented. Decomposition of **5** follows first-order kinetics with a k_{obs} value of 1.1×10^{-4} s^{-1} at 70.5 °C ($t_{1/2}$ = 105 min) and with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of 33.3(6) kcal/mol and 20(2) eu, respectively. The X-ray crystal structure of **7** (Figure 2) shows the ene−diamido fragment coordinated to Hf via both nitrogen atoms and the double bond. The dihedral angle between planes defined by N1−Hf−N2 and N1−C1−C2−N2 is 122.9°. The Hf atom is positioned above the ene−diamido

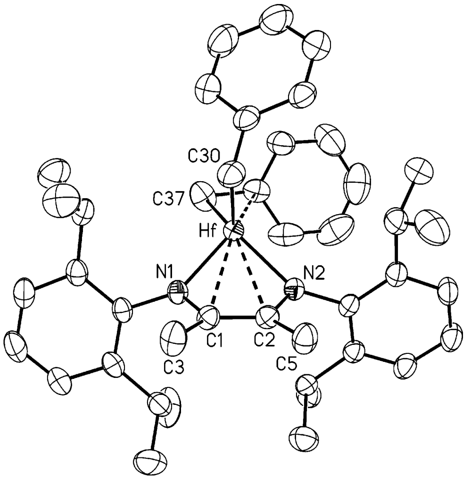


Figure 2. Molecular structure of **7**. Hydrogen atoms were removed for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bonds (Å) and angles (deg): Hf−N1 = 2.005(3), Hf−N2 = 2.028(3), Hf−C1 = 2.505(3), Hf−C2 = 2.533(3), C2−N2 = 1.417(4), C1−C2 = 1.368(5), C1−N1 = 1.422(4); N2−Hf−N1 = 87.2(1).

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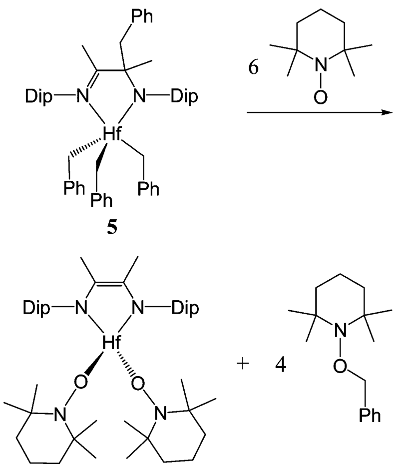
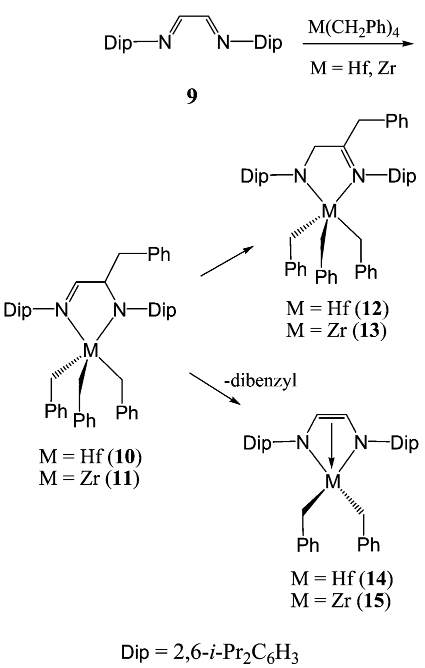
(12) Preparation of **5**. To a 40 mL vial was added 2.00 g (3.68 mmol) of $Hf(CH_2Ph)_4$ and 1.49 g (3.68 mmol) of *N*,*N*′-bis(2,6-diisopropylphenyl)-2,3-butanediimine followed by 8 mL of toluene to dissolve all reagents. The solution was stirred for 42 h at ambient temperature, yielding a dark orange solution. The solvent amount was reduced under reduced pressure to 4 mL. During solvent removal a yellow solid appeared. Hexane (25 mL) was added to this suspension to induce further precipitation. After the mixture was stirred for 10 min, the solid was collected on a frit, washed with 20 mL of hexanes, and dried under reduced pressure to give 2.55 g of product. The filtrate was stored overnight at −30 °C, causing the precipitation of additional solid. Upon workup (as above) a second crop of 0.3 g was isolated. Combined yield: 2.85 g, 82%. ^{1}H NMR (C_6D_6, 300 Hz, 23 °C): δ 7.29 (dd, 1H, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 2.1 Hz), 7.24 (t, 1H, $^3J_{H-H}$ = 7.5 Hz), 7.16 (dd, 1H, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.8 Hz), 6.80 (t, 3H, $^3J_{H-H}$ = 7.5 Hz, *p*-CH_2Ph), 6.94−7.14 (m, 14H), 6.62 (d, 6H, $^3J_{H-H}$ = 7.5 Hz, *o*-CH_2Ph), 3.83 (d, 1H, $^2J_{H-H}$ = 13.5 Hz, C−CH_2Ph), 3.75 (septet, 1H, $^3J_{H-H}$ = 6.6 Hz, C$H(CH_3)_3$), 3.53 (septet, 1H, $^3J_{H-H}$ = 6.6 Hz, C$H(CH_3)_3$), 3.42 (d, 1H, $^2J_{H-H}$ = 13.5 Hz, C−CH_2Ph), 3.04 (septet, 2H, $^3J_{H-H}$ = 6.6 Hz, C$H(CH_3)_2$), 2.34 (d, 3H, $^2J_{H-H}$ = 11.7 Hz, HfCH_2Ph), 2.21 (d, 3H, $^2J_{H-H}$ = 11.7 Hz, HfCH_2Ph), 1.33 (d, 3H, $^3J_{H-H}$ = 6.9 Hz, CH(C$H_3)_2$), 1.32 (d, 6H, $^3J_{H-H}$ = 6.9 Hz, CH(C$H_3)_2$), 1.23 (d, 3H, $^3J_{H-H}$ = 6.9 Hz, CH(C$H_3)_2$), 1.18 (d, 3H, $^3J_{H-H}$ = 6.6 Hz, CH(C$H_3)_2$), 1.11 (d, 3H, $^3J_{H-H}$ = 6.6 Hz, CH(C$H_3)_2$), 1.06 (d, 3H, $^3J_{H-H}$ = 6.9 Hz, CH(C$H_3)_2$), 1.01 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 0.84 (d, 3H, $^3J_{H-H}$ = 6.6 Hz, CH-(C$H_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75 Hz, 23 °C): δ 198.25 (N=*C*), 148.11 (quat), 148.04 (quat), 147.89 (quat), 146.11 (quat), 143.17 (quat), 140.64 (quat), 140.24 (quat), 138.13 (quat), 130.90 (*C*H), 128.54 (*C*H), 128.41 (*C*H), 127.83 (*C*H), 127.21 (*C*H), 126.48 (*C*H), 126.21 (*C*H), 125.60 (*C*H), 125.56 (*C*H), 124.73 (*C*H), 89.20 (br s, Hf(*C*H_2Ph)$_3$), 78.21 (quat), 54.45 (C−*C*H_2Ph), 29.92 (*C*H), 28.79 (2 carbons, *C*H), 28.02 (*C*H), 27.67 (*C*H_3), 26.51 (*C*H_3), 26.35 (*C*H_3), 26.14 (*C*H_3), 25.77 (*C*H_3), 24.99 (*C*H_3), 24.70 (*C*H_3), 24.23 (*C*H_3), 23.15 (*C*H_3), 22.62 (*C*H_3). NMR spectra are given in the Supporting Information. Anal. Calcd for $C_{56}H_{68}HfN_2$: C, 70.98; H, 7.23; N, 2.96. Found: C, 70.50; H, 7.14; N, 2.84.

Scheme 2. Reactions of 5 with 6 equiv of TEMPO



Scheme 3. Reactions of the Bis-imine 9 with $M(CH_2Ph)_4$ (M = Hf, Zr)



plane. Complex **7** is fluxional at ambient temperature ($\Delta G^{\ddagger} =$ 14.1 kcal/mol at 51 °C), due to rapid dynamic equilibrium between two nonequivalent folded metallacycle conformations.

There are two potential pathways for dibenzyl elimination from **5**. One involves reductive elimination of dibenzyl groups from Hf with concomitant formation of a Hf(II) species, followed by benzyl group transfer from the ligand back to hafnium. The second possible mechanism involves homolytic cleavage and subsequent recombination of one benzyl group attached to Hf and the one bonded to the ligand. Preliminary results point to the homolytic, radical pathway for this decomposition, as heating of **5** at 70.5 °C in the presence of 6 equiv of TEMPO produced TEMPO-CH_2Ph nearly quantitatively, with only a trace of dibenzyl formation observed (Scheme 2). This reaction follows a first-order decomposition with a rate only slightly faster (1.4×10^{-4} s^{-1} at 70.5 °C) than that observed for the conversion of **5** to **7**. Ene–dienyl-based radicals have been proposed as intermediates in the formation of zinc imino–amido compounds.[9c]

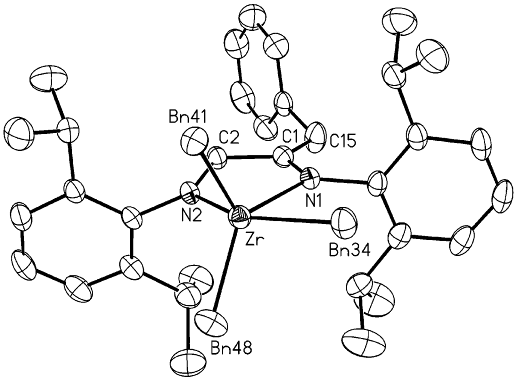


Figure 3. Molecular structure of **13**. Hydrogen atoms and phenyls of the Zr benzyl groups were removed for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bonds (Å) and angles (deg): Zr–N1 = 2.429(2), Zr–N2 = 2.121(2), C2–N2 = 1.453(2), C1–C2 = 1.488(2), C1–N1 = 1.286(2); N2–Zr–N1 = 70.05(5).

Table 1. Polymerization Data for Complexes 5, 7, and 12[a]

cat. (amt, μmol)	polymer yield (g)	cat. activity[b]	M_w (K)/PDI[c]	octene content (mol %)
5 (0.25)	29.5	661 000	238/7.4	13.1
7 (10)	3.3	3 617	175/25	9.2
12 (5)	26.8	30 030	362/8	10.2

[a] Polymerization conditions: 533 mL of Isopar-E; 250 g of octene; temperature 120 °C; ethylene pressure 460 psi; procatalyst:activator = 1:1.1; activator $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$; 10 μmol of MMAO; reaction time 15 min. [b] Activity in units of g of polymer/g of metal. [c] Polydispersity index (M_w/M_n).

Reaction of the bis-imine **4** with $Zr(CH_2Ph)_4$ proceeds more slowly than that observed with $Hf(CH_2Ph)_4$ and is only 57% complete after 4 d at ambient temperature, yielding a 1:1 mixture of **6** and **8** (Scheme 1). Complex **8** can be obtained in pure form when the reaction is conducted at higher temperature (*e.g.* 65 °C), to allow for complete decomposition of **6**. Complex **8** is also fluxional, but the barrier for this process ($\Delta G^{\ddagger} = 16.9$ kcal/mol at 71 °C) is higher by about 3 kcal/mol compared to that for **7**. The X-ray crystal structure of **8** is analogous to that of **7**.[15]

Reaction of the bis-imine **9** with either $Hf(CH_2Ph)_4$ or $Zr(CH_2Ph)_4$ at ambient temperature gave mixtures of the imino–amido and ene–diamido complexes **12**/**14** (3:1 ratio) and **13**/**15** (1:1.5 ratio), respectively (Scheme 3). In this case, however, the derived imino–amido complexes are achiral, as indicated by the appearance of only two singlets for the benzyl group methylene protons in the ^1H NMR spectra. Inspection of the reaction mixtures in the early stages of the reactions revealed the presence of the chiral intermediate **10**/**11**, which within minutes underwent competitive transformation into **12**/**13** and **14**/**15**, presumably by a 1,2-hydrogen shift and dibenzyl elimination, respectively. Significant solubility differences between imino–amido and ene–diamido complexes allowed for their easy separation. In addition to characterization by NMR and EA, the identity of **13** was confirmed by X-ray analysis (Figure 3).

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(13) Formally, these ligands are called diazabutadienes. For early-TM complexes, however, these ligands coordinate in their dianionic (ene–diamido) form (σ^2-N,N′,π).

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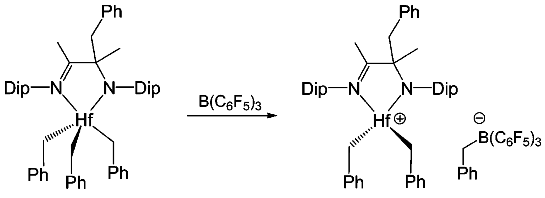
(15) See the Supporting Information for details.

Complexes **5**, **7**, and **12** were evaluated as catalysts in an ethylene/octene copolymerization process at 120 °C and 460 psi of ethylene pressure. The data presented in Table 1 show that the imino−amido complexes (**5** and **12**) led to active catalysts upon activation, with **5** demonstrating especially high activity (661 000 g of EO/g of Hf). Complex **5** also is a good octene incorporator, leading to an octene content of 13.1 mol %. Substantially different polymerization activities between **5** and **7** suggest that the activated complex $\mathbf{5}^+$ is not converted (at least not entirely) into $\mathbf{7}^+$ in the polymerization reactor. The observed broad polydispersities of the polymer samples are indicative of multicenter behavior during catalysis. The ene−diamido complex **7** exhibited polymerization activity significantly lower than that of the imino−amido complexes. It is interesting to note that subtle changes in ligand structure led to catalysts with very different activities and polymer molecular weight capabilities (**5** vs **12**, Table 1). This offers a promise that examination of other bis-imine ligands with transition-metal alkyl complexes may lead to catalysts with diverse catalytic behavior.

Observation of multicenter behavior suggests that perhaps the activation chemistry leads to multiple different catalytically active species. To probe this possibility, **5** was reacted with 1 equiv of $B(C_6F_5)_3$ in C_6D_5Cl. This reaction leads to a single room-temperature-stable ion pair, as shown by multinuclear and multidimensional NMR spectroscopy.[15] Unlike **5**, which exhibits only one type of Hf-bound benzyl groups in the ^{1}H NMR spectrum (two mutually coupled doublets), the ion pair **16** shows two distinct Hf-bound benzyl groups (two sets of two mutually coupled doublets) at ambient temperature. These two benzyl groups, however, undergo slow chemical exchange (2.8 s^{-1} at 28 °C), as shown by magnetization transfer using the DPFGSE-NOE method. This exchange most likely occurs by dissociation of the N(imine) donor from the Hf center, rotation along the Hf−N(amido) bond, and recoordination of the N(imine) fragment to the metal center. The ^{19}F NMR shows clean formation of a single borate anion with a chemical shift difference between *meta* and *para* fluorine resonances of 2.54 ppm. This indicates that the benzyl group of the PhCH$_2$−B(C$_6$F$_5$)$_3$ anion does not coordinate to the Hf cationic center,[16] presumably due to steric congestion at the metal center.[17] The high stability of **16** at ambient temperature suggests that multi-sited behavior of imino−amido catalysts is most likely derived from their decomposition at high temperature or side reactions with alkylaluminum species present during polymerization reactions.



5 **16**

In summary, we have demonstrated that reactions between bis-imine ligands and tetrabenzylhafnium and -zirconium led to formation of new imino−amido complexes in good yields. These complexes were found to be good precatalysts for ethylene/octene copolymerization at high polymerization temperatures. One-step synthesis of a variety of bis-imine ligands from commercially available diones and amines offers the possibility of easy access to diverse families of imino−amido complexes. We are currently investigating the reactivity of other bis-imines with transition-metal alkyls, and our research in this area will be the subject of future reports.

Supporting Information Available: Synthetic procedures, NMR spectra, kinetic data, polymerization protocol, and X-ray data including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672−2674.

(17) For examples of a metal-bound PhCH$_2$−B(C$_6$F$_5$)$_3$ anion, see: (a) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424−5436. (b) Thorn, M. G.; Etheridge, Z. C.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1998**, *17*, 3636−3638. (c) Pindado, G. J.; Thornton-Pett, M.; Hursthouse, M. B.; Coles, S. J.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1999**, 1663−1668. (d) Shafir, A.; Arnold, J. *Organometallics* **2003**, *22*, 567−575. For examples of a metal-unbound PhCH$_2$−B(C$_6$F$_5$)$_3$ anion, see: (e) Pellecchia, C.; Immirzi, A.; Pappalardo, D.; Peluso, A. *Organometallics* **1994**, *13*, 3773−3775. (f) Reference 17c. (g) Axenov, K. V.; Kilpelainen, I.; Klinga, M.; Leskela, M.; Repo, T. *Organometallics* **2006**, *25*, 463−471.

(18) Some of this work has appeared in the patent literature: Murray, R. E. U.S. Patent 6,096,676 (Union Carbide Corp.), 2000.