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Isoselective Living Polymerization of 1-Hexene Catalyzed by Half-Metallocene Dimethyl Complexes of Hafnium with Bidentate N-Substituted (Iminomethyl)pyrrolyl Ligands

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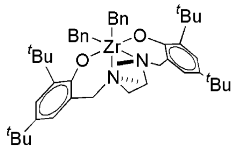
*Summary: The nonbridged half-metallocene dimethylhafnium complexes **3a−c** with N-substituted (iminomethyl)pyrrolyl ligands **2a−c** have been synthesized and characterized by NMR spectroscopy as well as X-ray analyses for **3a,b**. These complexes were found to be active catalysts for the isoselective living polymerization of 1-hexene upon treatment with [Ph$_3$C][B(C$_6$F$_5$)$_4$] below 0 °C.*



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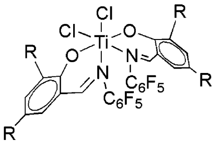

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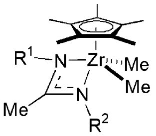

C

Living polymerization of α-olefins has attracted much interest, because it allows syntheses of precisely controlled polyolefins such as monodisperse polymers and blocking copolymers. Although the living polymerization of ethylene or α-olefin has been achieved by using various catalyst systems,[1−15] only a few catalysts can control the polymerization in both living and highly stereoselective manners. Soga et al.[11] reported the isoselective living polymerization of 1-hexene by C_2-*ansa*-zirconocene with B(C$_6$F$_5$)$_3$, though its catalytic activity was low. As post-metallocene catalysts, Kol et al.[12] reported that the tetradentate bis-phenolate zirconium complex **A** catalyzed the isoselective living polymerization of 1-hexene at room temperature, and Coates et al.[13] and Fujita et al.[14] independently reported that titanium complexes **B** bearing phenoxy-imine ligands became catalyst precursors for the syndioselec-

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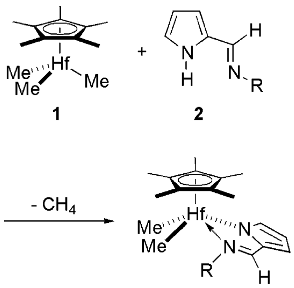
tive living polymerization of propylene. Another intriguing catalyst system is Sita's half-zirconocene complexes **C** with an unsymmetrical amidinate ligand ($R^1 \neq R^2$), which were found to be catalyst precursors for the highly isospecific living polymerization of 1-hexene.[15]

We have been interested in the application of iminopyrrolyl ligands as unique unsymmetrical monoanionic ligands for supporting nonmetallocene group 4 metal complexes.[16] As an extension of our continuous interest in the iminopyrrolyl ligand system, we here report the syntheses of half-metallocene-type hafnium dimethyl complexes with the iminopyrrolyl ligand and their catalytic performance for 1-hexene polymerization upon treatment with $[Ph_3C][B(C_6F_5)_4]$, giving monodispersed poly(1-hexene) with high isotacticity (up to [*mmmm*] = 90%).

Treatment of Cp^*HfMe_3 (**1**) with 1 equiv of iminopyrrolyl ligands **2a**−**c** in ether or toluene afforded the corresponding dimethyl complexes Cp^*HfMe_2(R-pyr) (**3a**−**c**), with the release of 1 equiv of methane (eq 1).



1 **2** **3**

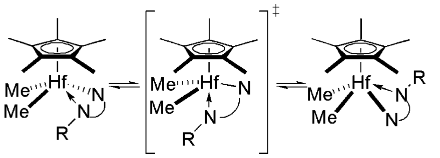
(1)

a: R = 4-MeOC$_6$H$_4$
b: R = 4-MeC$_6$H$_4$
c: R = cyclohexyl

Complexes **3a**−**c** were air and moisture sensitive and were characterized by combustion analysis and spectral data together with X-ray analysis of **3a**,**b**.

The ^1H NMR spectra of **3a**−**c** essentially displayed the same pattern. The resonance due to the imine proton of the complexes **3a**−**c** is shifted upfield from that of the free ligand, indicating the coordination of the imine nitrogen atom to the hafnium atom in solution. The diastereotopic two methyl groups bound to the hafnium atom exchanged, and the activation parameters (**3a**, $T_c = 268$ K, $\Delta G_c^\ddagger = 13.0$ kcal/mol, $\Delta H^\ddagger = 12.4(0.7)$ kcal/mol, $\Delta S^\ddagger = -3.4(2.6)$ cal/(mol K); **3b**, $T_c = 266$ K, $\Delta G_c^\ddagger = 12.9$ kcal/mol, $\Delta H^\ddagger = 12.8(0.7)$ kcal/mol, $\Delta S^\ddagger = -0.3(2.7)$ cal/(mol K); **3c**, $T_c = 313$ K, $\Delta G_c^\ddagger = 15.1$ kcal/mol, $\Delta H^\ddagger = 15.2(0.4)$ kcal/mol, $\Delta S^\ddagger = 0.7(1.4)$ cal/(mol K)) were able to be estimated by NMR shape analysis at variable temperature. Two mechanisms are plausibly proposed: one is a "ring-flipping" process of the iminopyrrolyl ligand bound to the hafnium atom through a distorted-trigonal-bipyramidal transition state (Scheme 1), and the other is a dissociative mechanism, for which a positive value of $\Delta S^\ddagger$ has been reported,[17] through a three-legged piano-stool intermediate after the dissociation of the imino moiety (Scheme 2). The small negative $\Delta S^\ddagger$ values observed for **3** suggest that the fluxional behavior of **3** involves the "ring-flipping" process. A similar "ring-flipping" process has already been observed for the half-metallocene amidinate complex of titanium $Cp^*TiMe_2[N(R^1)C(Me)N(R^2)]$.[18]

Scheme 1



Scheme 2

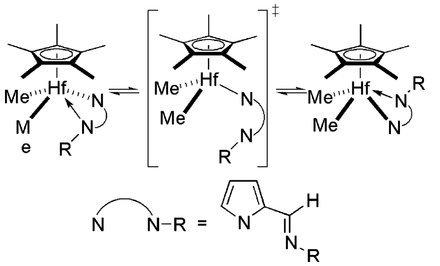


Figure 1 shows the four-legged piano-stool geometry of **3a**, in which the imine nitrogen atom and the pyrrolyl nitrogen atom coordinate in an η^1 fashion to the hafnium atom and two methyl groups occupy a cis position. The structure of **3b** was found to be essentially the same as **3a**.[19] The bond distances of Hf−N(1) and Hf−N(2) in **3a** are similar to those of a nonmetallocene type hafnium complex, $[2\text{-}(^tBuNCH)C_4H_3N]_2Hf(CH_2Ph)_2$.[16f] The averaged Hf−C(methyl) bond distance (2.26 Å) of Hf−C(11) and Hf−C(12) is the same as that (2.27−

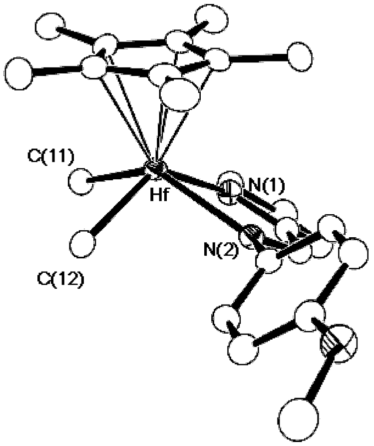


Figure 1. View of **3a** showing the 50% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Hf−N(1) = 2.225(3), Hf−N(2) = 2.365(3), Hf−C(11) = 2.251(4), Hf−C(12) = 2.259(4); N(1)−Hf−N(2) = 71.45(11), C(11)−Hf−C(12) = 87.48(14).

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Table 1. Results of 1-Hexene Polymerization by Using 3a−c[a]

run	cat.	R	temp (°C)	time (h)	activity[b]	M_n[c] ($\times 10^3$)	M_w[c] ($\times 10^3$)	M_w/M_n[c]	[*mmmm*] (%)
1	**3a**	4-MeOC_6H_4	25	1.5	5300	14.1	18.1	1.28	66
2	**3a**	4-MeOC_6H_4	25	3	5700	13.0	19.0	1.45	65
3	**3a**	4-MeOC_6H_4	0	3	2000	33.1	36.1	1.09	76
4	**3a**	4-MeOC_6H_4	−10	3	1400	13.6	14.7	1.08	89
5	**3a**	4-MeOC_6H_4	−20	6	1600	23.5	25.1	1.07	89
6	**3b**	4-MeC_6H_4	25	3	7000[d]	9.1	12.7	1.40	43
						0.6	0.7	1.14	
7	**3b**	4-MeC_6H_4	0	3	4200	29.4	31.9	1.08	84
8	**3b**	4-MeC_6H_4	−20	6	1200	22.5	24.1	1.07	90
9	**3c**	cyclohexyl	25	3	3000	5.9	8.4	1.42	39
10	**3c**	cyclohexyl	0	3	1300	12.6	13.0	1.12	73
11	**3c**	cyclohexyl	−20	6	480	9.0	9.7	1.08	75

[a] Conditions: cat. 20 μmol, [Ph_3C][$B(C_6F_5)_4$] 20 μmol, 1-hexene 1.25 mL (10 mmol), chlorobenzene 2.75 mL. [b] In units of g of polymer/((mol of cat.) h). [c] M_n, M_w, and M_w/M_n were determined by GPC analysis at 40 °C using polystyrene standards and THF as the eluant. [d] Bimodal molecular weight distribution.

2.29 Å)[15d,20] found for half-metallocene Zr complexes bearing amidinate ligands, taking the difference of covalent radii into account.

Upon activation with [Ph_3C][$B(C_6F_5)_4$] in chlorobenzene, the dimethyl complexes **3a**−**c** became catalysts for the polymerization of 1-hexene, and the results are summarized in Table 1. Under the same polymerization conditions, the substituent on the imine nitrogen atom affected the catalytic performance; an increased bulkiness resulted in a decreased catalytic activity and tacticity[21] of the polymer.

Although the molecular weight distribution of poly(1-hexene) produced by **3**/[Ph_3C][$B(C_6F_5)_4$] at 25 °C was narrow enough as a single-site catalyst, the chain transfer reaction via β-H elimination proceeded, as was evident from ^{1}H NMR spectral data due to olefinic protons of poly(1-hexene).[22] The chemical shifts of olefinic protons were found at 5.1 and 5.4 ppm, which are assigned as internal olefinic protons. In sharp contrast, polymers obtained below 0 °C have no olefinic protons in ^{1}H NMR spectra and much narrower molecular weight distribution, indicating that the polymerization proceeded in a living manner. Furthermore, a linear relationship[23] between M_n and polymerization time and narrow M_w/M_n values (1.07−1.08) were observed for the polymerizations by using **3a** at 0 and −20 °C (Figure 2), suggesting the living polymerization below 0 °C.

In the ^{13}C NMR spectra of the polymer, we observed no peak in the region of 35−40 ppm, which was assigned as regioerrors.[24] Furthermore, all catalyst systems were found to afford iso-rich polymer. As the polymerization temperature was lowered, poly(1-hexene) had higher isotacticity. When the polymerization reaction was carried out at −20 °C by using **3b**/[Ph_3C][$B(C_6F_5)_4$], the isotacticity ([*mmmm*] pentad) increased up to 90%.

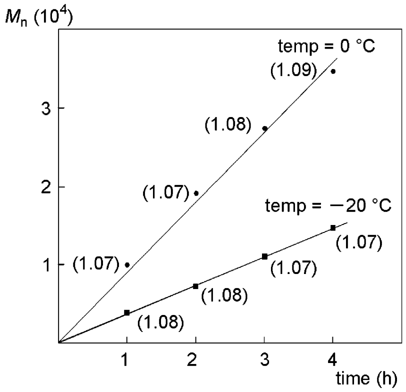

Figure 2. Plot of M_n as a function of polymerization time for 1-hexene polymerization with complex **3a**/[Ph_3C][$B(C_6F_5)_4$].

The tacticity of poly(1-hexene) generated by **3b** at 25 °C was lower than that of **3a**, though the structure of **3a** is almost the same as that of **3b** in the solid state. In the case of the polymerization by the complex **3b** at 25 °C (run 6), the color of the polymerization solution turned gradually from yellow-orange to red-orange, resulting in the bimodal molecular weight distribution of poly(1-hexene) because of the gradual decomposition of the active cationic species derived from **3b** at 25 °C.

It is necessary to obtain highly isotactic polymer so that the rate of propagation is significantly faster than that of the epimerization through the ligand flipping. Although complexes **3** have a barrier for the ligand flipping that is higher than that of a half-metallocene amidinate complex of zirconium, Cp*$ZrMe_2[N(^tBu)C(Me)N(Et)]$ (**4**; $\Delta G_c^\ddagger = 10.9$ kcal/mol),[20] the isotacticity of the polymer obtained from **3** was lower than that from **4**,[14a] presumably due to the slower propagation rate of **3**. The isotacticity of the polymer produced by **3c** was found to be low, though the $\Delta G_c^\ddagger$ value for the ligand flipping of **3c** was higher than that of **3a**,**b**. The bulkiness of **3c** might prevent the coordination of the monomer to the catalytically active center.

In conclusion, we have demonstrated that the nonbridged half-metallocene dimethylhafnium complexes **3a**−**c** with N-substituted (iminomethyl)pyrrolyl ligands became unique single-site catalyst precursors for the isoselective living polymerization of 1-hexene (up to [*mmmm*] = 90%). The catalytic performance of these hafnium complexes for the homo- and copolymerization of α-olefins as well as their mechanism is of current interest to us.

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Supporting Information Available: Text giving details of the syntheses of complexes **3** and experimental details of 1-hexene polymerization and CIF files giving X-ray crystallographic data for **3a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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