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Preparation and characterization of iminopyrrolyl hafnium complexes as catalyst precursors for α-olefin polymerization

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Abstract

Amido, chloro, and benzyl hafnium complexes bearing 2-(*N*-aryliminomethyl)pyrrole [(R-pyr)H, **1a**: R = DIP = 2-{*N*-(2,6-diisopropylphenyl)-iminomethyl}, **1b**: R = XYL = 2-{*N*-(2,6-dimethylphenyl)iminomethyl}, **1c**: R = ANI = 2-{*N*-(4-methoxyphenyl)iminomethyl}, **1d**: R = TOL = 2-{*N*-(4-methylphenyl)iminomethyl}] were prepared and characterized. The coordination modes of $(R\text{-pyr})_2Hf(NMe_2)_2$ (**2a–d**) depend on the bulkiness of the aromatic substituent at the imine nitrogen of the ligands. In contrast, all $(R\text{-pyr})_2HfCl_2$ (**3a–d**) have a C_2-symmetric octahedral structure. These diamido- and dichloro-bis(iminopyrrolyl)hafnium complexes, when combined with MMAO, become active catalysts for ethylene polymerization. Two types of hafnium benzyl complexes, $(DIP\text{-pyr})Hf(CH_2Ph)_3$ (**4a**) and $(DIP\text{-pyr})_2Hf(CH_2Ph)_2$ (**5a**), were prepared by the alkane elimination reaction from reactions of $Hf(CH_2Ph)_4$ with controlled amounts of iminopyrrole (**1a**). The mono(iminopyrrolyl)hafnium tribenzyl complex (**4a**) exhibited a high catalytic activity for 1-hexene polymerization.

Keywords: Polymerization; Ethylene; 1-Hexene; Hafnium; Iminopyrrole

1. Introduction

Recently there has been increasing interest in the development of α-olefin polymerization using well-defined transition metal complexes. A promising candidate is the combination of an anionic non-Cp ligand and group 4 metals [1–3]. Studies of nitrogen-based ligand modification have led to the introduction of sterically and electronically demanding features on the ancillary ligand [4,5]. Monoanionic *N*-aryliminopyrrole ligands have attracted attention in the last 5 years [6,7], as a system comparable to phenoxyimine complexes of group 4 metals, complexes that contain a similar steric feature and have ultra-high catalytic activity and living characteristics for ethylene polymerization [8]. Our continuing efforts to generate group 4 metal complexes having iminopyrrolyl ligands have been extended to hafnium as the central metal. Here we report the preparation of hafnium complexes bearing mono- and bis(iminopyrrolyl) ligands and the catalyst performance for ethylene and 1-hexene polymerizations.

2. Experimental

2.1. General

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using the standard Schlenk techniques under argon. Hexane and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Benzene-d_6 and toluene-d_8 were distilled from P_2O_5 and thoroughly degassed by trap-to-trap distillation before use. 1-Hexene, bromobenzene, bromobenzene-d_5, and chloroform-d_3 were distilled from CaH_2 and deoxygenated. Tetrabenzyl complex $Hf(CH_2Ph)_4$ [9] and tetraamido complex $Hf(NMe_2)_4$ [10] were prepared according to the literature. 2-{*N*-(aryl)iminomethyl}pyrrole ligands **1a–d** were prepared by condensation of the 2-formylpyrrole with the corresponding aniline derivatives [11].

The ^1H NMR (400 and 300 MHz) and ^{13}C NMR (100 and 75 MHz) spectra were measured on a JEOL JNM-AL400 and a VARIAN Mercury-300 spectrometer. Elemental analyses were recorded by Perkin-Elmer 2400 at Faculty of Engineering Science, Osaka University. All melting points were measured in sealed tubes under argon atmosphere and were not corrected.

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The gel permeation chromatographic analyses were carried out at 40 °C by using a Shimadzu LC-10A liquid chromatograph system and a RID 10A refractive index detector, equipped with a Shodex KF-806L column which was calibrated versus commercially available polystyrene standards (Showa Denko).

2.2. Preparation of diamido complexes, $Hf(R\text{-}pyr)_2(NMe_2)_2$ (**2a–d**) [(R-pyr)H = **1a–d**]

To a solution of $Hf(NMe_2)_4$ (393 mg, 1.11 mmol) in toluene (6 mL) was added a toluene solution of **1c** (444 mg, 2.22 mmol) in toluene (8 mL) at room temperature. After the reaction mixture was heated at 50 °C for 4 h, all volatiles were removed under reduced pressure. The resulting yellow product was washed with three portions of hexane (4 mL), and then dried under reduced pressure. **2c**: 96% yield, mp 210–212 °C (dec). ^{1}H NMR ($CDCl_3$, 308 K): δ 3.13 (s, 12H, NMe_2), 3.74 (s, 6H, OMe), 6.22 (dd, 2H, $^3J_{H-H}$ = 2.0 and 3.4 Hz, 4-pyr), 6.58 (d, 2H, $^3J_{H-H}$ = 3.4 Hz, 3-pyr), 6.60 (s, 8H, *o*- and *m*-C_6H_4), 7.20 (br s, 2H, 5-pyr), 7.93 (s, 2H, N = C*H*). ^{13}C NMR ($CDCl_3$, 308 K): δ 44.6 (q, $^1J_{C-H}$ = 133 Hz, N*Me*$_2$), 55.5 (q, $^1J_{C-H}$ = 143 Hz, OMe), 113.2 (d, $^1J_{C-H}$ = 168 Hz, 4-pyr), 113.7 (d, $^1J_{C-H}$ = 160 Hz, *m*-C_6H_4), 119.8 (d, $^1J_{C-H}$ = 168 Hz, 3-pyr), 122.2 (d, $^1J_{C-H}$ = 160 Hz, *o*-C_6H_4), 137.7 (d, $^1J_{C-H}$ = 178 Hz, 5-pyr), 138.6 (s, 2-pyr), 143.1 (s, *ipso*-C_6H_4), 157.0 (s, *p*-C_6H_4), 157.8 (d, $^1J_{C-H}$ = 163 Hz, N = *C*H). Anal. Calcd for $C_{28}H_{34}HfN_6O_2$: C, 50.56; H, 5.15; N, 12.64. Found: C, 50.84; H, 5.24; N, 12.25.

Similar treatment of $Hf(NMe_2)_4$ with the corresponding ligand was operated for **2a**, **2b**, and **2d**.

2a: 97% yield, mp 162–164 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 308 K): δ 0.67 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 0.69 (d, 3H, $^3J_{H-H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 0.82 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.02 (d, 3H, $^3J_{H-H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.08 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.16 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.21 (d, 3H, $^3J_{H-H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.33 (d, 3H, $^3J_{H-H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.70 (m, 1H, C*H*(CH$_3$)$_2$), 2.28 (m, 1H, C*H*(CH$_3$)$_2$), 2.56 (s, 6H, N(C*H*$_3$)$_2$), 2.93 (s, 3H, N(C*H*$_3$)$_2$), 3.15 (m, 1H, C*H*(CH$_3$)$_2$), 3.32 (s, 3H, N(C*H*$_3$)$_2$), 3.59 (m, 1H, C*H*(CH$_3$)$_2$), 6.09 (br s, 1H, 4-pyr), 6.19 (br s, 1H, 4-pyr), 6.46 (br s, 1H, 5-pyr), 6.75 (d, 1H, $^3J_{H-H}$ = 3.2 Hz, 3-pyr), 6.80 (d, 1H, $^3J_{H-H}$ = 2.8 Hz, 3-pyr), 7.0–7.2 (m, 6H, C_6H_3), 7.34 (br s, 1H, 5-pyr), 7.80 (s, 1H, N = C*H*), 7.87 (s, 1H, N = C*H*). ^{13}C NMR (100 MHz, C_6D_6, 308 K): δ 22.7, 22.7, 23.0, 24.1, 26.5, 26.5, 26.5, and 26.7 (q, $^1J_{C-H}$ = 125–127 Hz, CH(*C*H$_3$)$_2$), 27.0, 27.2, 27.2, and 28.4 (d, $^1J_{C-H}$ = 125–128 Hz, *C*H(CH$_3$)$_2$), 40.5, 44.9, and 46.2 (q, $^1J_{C-H}$ = 131–134 Hz, N(*C*H$_3$)$_2$), 112.9 (d, $^1J_{C-H}$ = 168 Hz, 4-pyr), 114.3 (d, $^1J_{C-H}$ = 168 Hz, 4-pyr), 118.8 (d, $^1J_{C-H}$ = 168 Hz, 3-pyr), 121.7 (d, $^1J_{C-H}$ = 168 Hz, 3-pyr), 123.3, 123.4, 123.5, 123.6, 125.8, and 126.4 (d, $^1J_{C-H}$ = 156–160 Hz, *p*- and *m*-C_6H_3), 137.1 (s, 2-pyr), 137.3 (s, 2-pyr), 137.6 (d, $^1J_{C-H}$ = 181 Hz, 5-pyr), 140.2 (d, $^1J_{C-H}$ = 181 Hz, 5-pyr), 141.9 (s, *o*-C_6H_3), 141.9 (s, *o*-C_6H_3), 142.8 (s, *o*-C_6H_3), 143.1 (s, *o*-C_6H_3), 147.1 (s, *ipso*-C_6H_3), 149.4 (s, *ipso*-C_6H_3), 161.9 (d, $^1J_{C-H}$ = 163 Hz, N = *C*H), 163.9 (d, $^1J_{C-H}$ = 164 Hz, N = *C*H). Anal. Calcd for $C_{38}H_{54}HfN_6$: C, 59.02; H, 7.04; N, 10.87. Found: C, 58.76; H, 7.44; N, 10.52.

2b: 92% yield, mp 197–199 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 308 K): δ 1.23 (s, 3H, Ar-C*H*$_3$), 1.28 (s, 3H, Ar-C*H*$_3$), 2.47 (s, 6H, N(C*H*$_3$)$_2$), 2.96 (br s, 3H, N(C*H*$_3$)$_2$), 3.25 (br s, 3H, N(C*H*$_3$)$_2$), 6.14 (br s, 1H, 5-pyr), 6.16 (br s, 1H, 4-pyr), 6.47 (br s, 1H, 4-pyr), 6.73 (br s, 1H, 3-pyr), 6.83 (d, 1H, $^3J_{H-H}$ = 2.9 Hz, 3-pyr), 6.8–7.1 (m, 6H, C_6H_3), 7.39 (br s, 1H, 5-pyr), 7.80 (s, 1H, N = C*H*), 7.81 (s, 1H, N = C*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 308 K): δ 15.5 (q, $^1J_{C-H}$ = 126 Hz, Ar-*C*H$_3$), 17.1 (q, $^1J_{C-H}$ = 127 Hz, Ar-*C*H$_3$), 39.8 (q, $^1J_{C-H}$ = 133 Hz, N(*C*H$_3$)$_2$), 43.1 (br q, $^1J_{C-H}$ = 136 Hz, N(*C*H$_3$)$_2$), 46.0 (br q, $^1J_{C-H}$ = 136 Hz, N(*C*H$_3$)$_2$), 112.9 (d, $^1J_{C-H}$ = 168 Hz, 4-pyr), 114.4 (d, $^1J_{C-H}$ = 168 Hz, 4-pyr), 118.7 (d, $^1J_{C-H}$ = 168 Hz, 3-pyr), 120.8 (d, $^1J_{C-H}$ = 168 Hz, 3-pyr), 125.1 (d, $^1J_{C-H}$ = 160 Hz, *p*-C_6H_3), 125.5 (d, $^1J_{C-H}$ = 159 Hz, *p*-C_6H_3), 127.6 (d, $^1J_{C-H}$ = 158 Hz, *m*-C_6H_3), 127.8 (d, $^1J_{C-H}$ = 158 Hz, *m*-C_6H_3), 128.2 (d, $^1J_{C-H}$ = 158 Hz, *m*-C_6H_3), 128.3 (d, $^1J_{C-H}$ = 158 Hz, *m*-C_6H_3), 131.5 (s, *o*-C_6H_3), 131.6 (s, *o*-C_6H_3), 132.3 (s, *o*-C_6H_3), 132.5 (s, *o*-C_6H_3), 137.7 (d, $^1J_{C-H}$ = 181 Hz, 5-pyr), 137.9 (s, 2-pyr), 138.1 (s, 2-pyr), 139.9 (d, $^1J_{C-H}$ = 181 Hz, 5-pyr), 149.2 (s, *ipso*-C_6H_3), 150.0 (s, *ipso*-C_6H_3), 160.7 (d, $^1J_{C-H}$ = 163 Hz, N = *C*H), 163.8 (d, $^1J_{C-H}$ = 163 Hz, N = *C*H). Anal. Calcd for $C_{30}H_{38}HfN_6$: C, 54.50; H, 5.79; N, 12.71. Found: C, 54.79; H, 6.10; N, 12.39.

2d: 89% yield, mp 145–150 °C (dec). ^{1}H NMR (toluene-d_8, 308 K): δ 2.09 (s, 6H, Ar-Me), 3.23 (s, 12H, NMe_2), 6.34 (dd, 2H, $^3J_{H-H}$ = 3.6 and 1.9 Hz, 4-pyr), 6.57 (d, 2H, $^3J_{H-H}$ = 3.6 Hz, 3-pyr), 6.62 (d, 4H, $^3J_{H-H}$ = 8.0 Hz, C_6H_4), 6.82 (d, 4H, C_6H_4), 7.34 (br s, 2H, 5-pyr), 7.63 (s, 2H, N = C*H*). ^{13}C NMR (toluene-d_8, 308 K): δ 20.8 (q, $^1J_{C-H}$ = 125 Hz, Ar-Me), 41.1 (q, $^1J_{C-H}$ = 130 Hz, N*Me*$_2$), 114.0 (d, $^1J_{C-H}$ = 168 Hz, 4-pyr), 120.9 (d, $^1J_{C-H}$ = 169 Hz, 3-pyr), 121.8 (d, $^1J_{C-H}$ = 160 Hz, *o*-C_6H_4), 129.3 (d, $^1J_{C-H}$ = 161 Hz, *m*-C_6H_4), 134.6 (s, *p*-C_6H_4), 138.6 (d, $^1J_{C-H}$ = 173 Hz, 5-pyr), 139.2 (s, 2-pyr), 147.9 (s, *ipso*-C_6H_4), 158.6 (d, $^1J_{C-H}$ = 163 Hz, N = *C*H). Anal. Calcd for $C_{28}H_{34}HfN_6$: C, 53.12; H, 5.41; N, 13.27. Found: C, 53.03; H, 5.73; N, 13.21.

2.3. Preparation of dichloro complexes $Hf(R\text{-}pyr)_2Cl_2$ (**3a–d**) [(R-pyr)H = **1a–d**]

To **2c** (300 mg, 0.451 mmol) suspended in hexane (5.0 mL) was added trimethylsilyl chloride (0.57 mL, 4.5 mmol) via syringe. After the reaction mixture was stirred for 4 h at 40 °C. Removal of all volatile afforded orange microcrystals, which were washed with hexane (4× 5 mL) and dried in vacuo, giving **3c** (265 mg, 0.409 mmol, 91% yield), mp 120–121 °C (dec). ^{1}H NMR ($CDCl_3$, 308 K): δ 3.76 (s, 6H, OMe), 6.24 (dd, $^3J_{H-H}$ = 2.0 and 3.4 Hz, 2H, 4-pyr), 6.67 (2H, 3-pyr), 6.69 (d, 4H, $^3J_{H-H}$ = 8.9 Hz, *m*-C_6H_4), 6.84 (d, 4H, *o*-C_6H_4), 7.43 (br s, 2H, 5-pyr), 7.94 (s, 2H, N = C*H*). ^{13}C NMR ($CDCl_3$, 308 K): δ 55.5 (q, $^1J_{C-H}$ = 143 Hz, OMe), 113.9 (d, $^1J_{C-H}$ = 161 Hz, *m*-C_6H_4), 115.1 (d, $^1J_{C-H}$ = 172 Hz, 4-pyr), 123.0 (d, $^1J_{C-H}$ = 162 Hz, *o*-C_6H_4), 123.5 (d, $^1J_{C-H}$ = 171 Hz, 3-pyr), 138.2 (s, 2-pyr), 141.6 (s, *ipso*-C_6H_4), 143.0 (d, $^1J_{C-H}$ = 185 Hz, 5-pyr), 157.9 (s, *p*-C_6H_4), 160.2 (d, $^1J_{C-H}$ = 168 Hz, N = *C*H). Anal. Calcd for $C_{24}H_{22}Cl_2HfN_4O_2$: C, 44.49; H, 3.42; N, 8.65. Found: C, 44.21; H, 3.71; N, 8.70.

Similar treatment with Me_3SiCl afforded the corresponding dichloro complexes.

3a: 85% yield, mp 115–117 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 308 K): δ 0.88 (d, 12H, $^3J_{H-H}$ = 6.7 Hz, $CH(CH_3)_2$), 0.90 (br s, 6H, $CH(CH_3)_2$), 1.13 (br s, 6H, $CH(CH_3)_2$), 2.66 (m, 2H, $CH(CH_3)_2$), 2.88 (br s, 2H, $CH(CH_3)_2$), 6.38 (br s, 2H, 4-pyr), 6.92 (br s, 2H, 5-pyr), 6.96 (d, 2H, $^3J_{H-H}$ = 3.5 Hz, 3-pyr), 7.13–7.26 (6H, 2 C_6H_3), 8.00 (s, 2H, N = C*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 308 K): δ 26.7 (q, $^1J_{C-H}$ = 128 Hz, $CH(CH_3)_2$), 28.0 (d, $^1J_{C-H}$ = 126 Hz, $CH(CH_3)_2$), 115.3 (d, $^1J_{C-H}$ = 168 Hz, 4-pyr), 124.1 (d, $^1J_{C-H}$ = 171 Hz, 3-pyr), 124.3 (d, $^1J_{C-H}$ = 158 Hz, *m*-C_6H_3), 127.4 (d, $^1J_{C-H}$ = 160 Hz, *p*-C_6H_3), 137.6 (s, *o*-C_6H_3), 142.4 (s, 2-pyr), 144.2 (d, $^1J_{C-H}$ = 177 Hz, 5-pyr), 145.4 (s, *ipso*-C_6H_3), 168 (d, $^1J_{C-H}$ = 164 Hz, N = *C*H). Anal. Calcd for $C_{34}H_{42}Cl_2HfN_4$: C, 54.01; H, 5.60; N, 7.41. Found: C, 53.61; H, 5.99; N, 7.48.

3b: 80% yield, mp 110–112 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 308 K): δ 1.98 (s, 12H, Ar-C*H*$_3$), 6.33 (m, 2H, 4-pyr), 6.93 (m, 4H, 3-pyr and 5-pyr), 7.00 (m, 6H, C_6H_3), 8.01 (s, 2H, N = C*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 308 K): δ 18.5 (q, $^1J_{C-H}$ = 127 Hz, Ar-*C*H$_3$), 115.5 (d, $^1J_{C-H}$ = 172 Hz, 4-pyr), 124.3 (d, $^1J_{C-H}$ = 171 Hz, 3-pyr), 126.5 (d, $^1J_{C-H}$ = 159 Hz, *p*-C_6H_3), 128.5 (d, $^1J_{C-H}$ = 157 Hz, *m*-C_6H_3), 132.2 (s, 2-pyr), 138.2 (s, *o*-C_6H_3), 144.5 (d, $^1J_{C-H}$ = 186 Hz, 5-pyr), 147.7 (s, *ipso*-C_6H_3), 164.5(d, $^1J_{C-H}$ = 168 Hz, N = *C*H). Anal. Calcd for $C_{26}H_{26}Cl_2HfN_4$: C, 48.50; H, 4.07; N, 8.70. Found: C, 48.24; H, 4.16; N, 9.02.

3d: 80% yield, mp 93–95 °C (dec). ^{1}H NMR ($CDCl_3$, 308 K): δ 2.26 (s, 6H, Ar-Me), 6.24 (dd, $^3J_{H-H}$ = 1.6 and 4.0 Hz, 2H, 4-pyr), 6.68 (d, 2H, 3-pyr), 6.79 (d, 4H, $^3J_{H-H}$ = 8.3 Hz, *o*-C_6H_4), 6.97 (d, 4H, *m*-C_6H_4), 7.42 (br s, 2H, 5-pyr), 7.95 (s, 2H, N = C*H*). ^{13}C NMR ($CDCl_3$, 308 K): δ 21.0 (q, $^1J_{C-H}$ = 127 Hz, Ar-Me), 115.1 (d, $^1J_{C-H}$ = 172 Hz, 4-pyr), 121.8 (d, $^1J_{C-H}$ = 161 Hz, *o*-C_6H_4), 123.7 (d, $^1J_{C-H}$ = 170 Hz, 3-pyr), 129.2 (d, $^1J_{C-H}$ = 160 Hz, *m*-C_6H_4), 136.0 (s, *p*-C_6H_4), 138.3 (s, 2-pyr), 143.8 (d, $^1J_{C-H}$ = 184 Hz, 5-pyr), 145.8 (s, *ipso*-C_6H_4), 160.5 (d, $^1J_{C-H}$ = 168 Hz, N = *C*H). Anal. Calcd for $C_{24}H_{22}Cl_2HfN_4$: C, 46.81; H, 3.60; N, 9.10. Found: C, 47.06; H, 3.47; N, 9.32.

2.4. Preparation of tribenzyl complex (R-pyr)Hf(CH_2Ph)$_3$ (**4a**)

In a schlenk, $Hf(Ch_2Ph)_4$ (1.631 g, 3.00 mmol) was dissolved in toluene (20 mL) at room temperature. To the solution, cooled to −78 °C, was added a solid of **1a** (0.695 g, 2.73 mmol). The reaction mixture was allowed to warm to room temperature and then stirred overnight. The color of the solution turned to yellow–brown. After removal of insoluble products by centrifugation, most of volatiles were removed in vacuo. The resulting yellow–brown solution was added hexane (2 mL) and stored at −20 °C, giving **4a** as yellow microcrystals in 61% yield, mp 80–94 °C (dec). ^{1}H NMR (300 MHz, $C_6D_5CD_3$, 308 K): δ 0.92 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.12 (d, $^3J_{H-H}$ = 6.8, 6H, $CH(CH_3)_2$), 1.98 (s, 6H, $HfCH_2Ph$), 2.61 (sep, $^3J_{H-H}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 6.25 (dd, $^3J_{H-H}$ = 1.9 Hz and 3.6 Hz, 1H, 4-pyr), 6.61 (3-pyr overrapped with other resonance), 6.63 (d, $^3J_{H-H}$ = 7.1 Hz, 6H, *o*-Ph of $HfCH_2$*Ph*), 6.83 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, *p*-Ph of $HfCH_2$*Ph*), 6.95–7.10 (aromatic protons and 5-pyr), 7.57 (s, 1H, N = CH). ^{13}C NMR (75 MHz, $C_6D_5CD_3$, 308 K) δ 22.9 (q, $^1J_{C-H}$ = 126 Hz, $CHMe_2$), 25.5 (q, $^1J_{C-H}$ = 126 Hz, $CHMe_2$), 28.7 (d, $^1J_{C-H}$ = 127 Hz, $CHMe_2$), 85.6 (t, $^1J_{C-H}$ = 122 Hz, $HfCH_2Ph$), 115.3 (d, $^1J_{C-H}$ = 170 Hz, 4-pyr), 122.5 (d, $^1J_{C-H}$ = 169 Hz, 3-pyr), 122.8 (d, $^1J_{C-H}$ = 161 Hz, *p*-Ph of $HfCH_2Ph$), 123.6, 125.2, 127.1, 128.1, 128.8, 129.0 (d, $^1J_{C-H}$ = 154 Hz, *o*-Ph of $HfCH_2Ph$), 138.3, 141.5, 142.5 (d, $^1J_{C-H}$ = 181 Hz, 5-pyr), 147.5, 164.9 (d, $^1J_{C-H}$ = 167 Hz, N = CH). Anal. Calcd for $C_{38}H_{42}N_2Hf_1$: C, 64.72; H, 6.00; N, 3.97. Found: C, 65.31; H, 6.18; N, 3.76.

2.5. Preparation of dibenzyl complex (R-pyr)$_2$Hf(CH_2Ph)$_2$ (**5a**)

To a solution of $Hf(Ch_2Ph)_4$ (142 mg, 0.261 mmol) in toluene (10 mL), cooled to −78 °C, was added a solid of **1a** (123 mg, 0.482 mmol). The reaction mixture was stirred overnight at room temperature. The color of the solution turned to yellow–brown. After removal of insoluble products by centrifugation, all volatiles were removed in vacuo. The resulting yellow–brown oil was dissolved in small amount of hexane and stored at −20 °C. Complex **5a** was obtained as yellow microcrystals in 76% yield (mp 115–119 °C). ^{1}H NMR (300 MHz, $C_6D_5CD_3$, 308 K): δ 0.90 (d, $^3J_{H-H}$ = 6.6 Hz, 12H, $CH(CH_3)_2$), 0.96 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 2.15 (s, 4H, Hf-CH_2Ph), 2.93 (br m, 4H, $CH(CH_3)_2$), 6.13 (dd, $^3J_{H-H}$ = 2.2 and 3.6 Hz, 2H, 4-pyr), 6.47 (d, $^3J_{H-H}$ = 7.4 Hz, 4H, *o*-Ph of Hf-CH_2Ph), 6.70 (d, $^3J_{H-H}$ = 3.6 Hz, 2H, 5-pyr), 6.72 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, *p*-Ph of Hf-CH_2Ph), 6.78 (br, 2H, 3-pyr), 6.97 (t, $^3J_{H-H}$ = 8.0 Hz, 6H, *m*-Ph of Hf-CH_2Ph), 7.05–7.15 (m, 6H, Ph), 7.85 (s, 2H, N = CH). ^{13}C NMR (75 MHz, $C_6D_5CD_3$, 308 K) δ 23.2 (q, $^1J_{C-H}$ = 125 Hz, $CHMe_2$), 27.6 (q, $^1J_{C-H}$ = 126 Hz, $CHMe_2$), 29.3 (d, $^1J_{C-H}$ = 134 Hz, $CHMe_2$), 90.3 (t, $^1J_{C-H}$ = 118 Hz, $HfCH_2Ph$), 115.7, 122.9, 123.6, 124.8, 127.8, 128.5, 128.6, 139.4, 143.0, 143.4, 147.5, 148.5, 164.4 (d, $^1J_{C-H}$ = 165 Hz, N = CH). Anal. Calcd for $C_{48}H_{56}N_4Hf_1$: C, 66.46; H, 6.51; N, 6.46. Found: C, 66.59; H, 6.59; N, 6.40.

2.6. Polymerization of ethylene

The precatalyst (1.0–3.0 mg) was dissolved in toluene and then 1000 equiv. of methylaluminoxane (MAO) in toluene was added at 25 °C. The orange solution (1.0 mmol/L) was magnetically stirred and maintained under ethylene (1 atm). The polymerization was carefully terminated by the addition of methanol and aqueous hydrogen chloride. The resulting white polymer was collected by filtration and dried in vacuo at 60 °C.

2.7. Polymerization of 1-hexene

A solution of precatalyst (20 μmol) in C_6H_5Br (1.5 mL) was added to a solution of $[Ph_3C][B(C_6F_5)_4]$ (20 μmol) in C_6H_5Br (1.0 mL) at 0 °C. After 1-hexene (2.5 mL) was added, the reaction mixture was stirred. The polymerization was quenched by

adding 1N HCl in MeOH. The polymer was extracted by hexane and washed by MeOH. The hexane solution was filtered through silica gel, and then dried under vacuum.

2.8. Crystallographic data collection and structure determination of *4a*

Crystals of **4a** suitable for the X-ray diffraction study were mounted on glass fibers. All measurements were made on a Rigaku R-AXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71095). Indexing was performed from three oscillations. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. A symmetry-related absorption correction using the program ABSCOR was applied. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods (SIR92) [12] and refined on F^2 by full-matrix least-squares methods, using SHELXL-97 [13]. The non-hydrogen atoms were refined anisotropically by the full-matrix least squares method. All hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function $R1$ and $wR2$ were $\sum||Fo|-|Fc||/\sum|Fo|$ and $\left[\sum w(Fo^2-Fc^2)^2/\sum w(Fo^2)^2\right]^{1/2}$. All calculations of least-squares refinements were performed with SHELXL-97 programs on an Origin 3400 computer of Silicon Graphics Inc., at the Research Center for Structural Biology Institute for Protein Research, Osaka University. Structural parameters and X-ray structure analysis are summarized in Table 1.

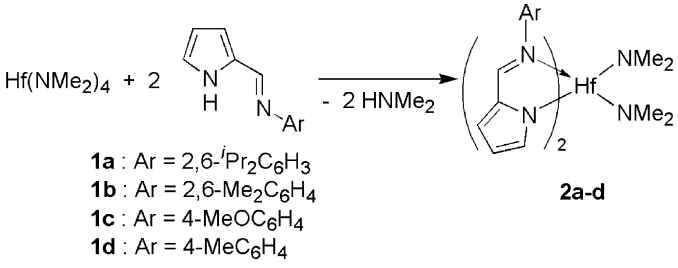
Table 1
Crystal data and data collection parameters of (DIP-pyr)Hf(CH_2Ph)$_3$ ($C_6H_5CH_3$) (**4a**)

Formula	$C_{45}H_{50}N_2Hf$
Formula weight	797.39
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	10.835(2)
b (Å)	11.013(3)
c (Å)	15.988(4)
α (°)	108.584(9)
β (°)	100.329(8)
γ (°)	95.738(9)
V (Å^3)	1753.6(7)
No. of reflections for cell det. (2θ range)	47425 (6.0–55.2°)
Z, D_{calcd} (g/cm^{-3})	2, 1.510
F(0 0 0)	812.00
μ [Mo Kα] (cm^{-1})	30.04
T (K)	120
Crystal size (mm)	0.35 × 0.10 × 0.20
$2\theta_{max}$ (°)	55.0
No. of reflections measured	55841
Unique data (R_{int})	8019 (0.074)
No. of observations ($I > 2.0\sigma(I)$)	7285
No. of variables	433
$R1$, $wR2$ ($I > 2.0\sigma(I)$)	0.0357, 0.0809
$R1$, $wR2$ (all data)	0.0401, 0.0830
GOF on F^2	1.11
$\Delta\rho$ (e Å^{-3})	1.36, −1.48

3. Results and discussion

3.1. Diamido- and dichloro-bis(iminopyrrolyl) complexes of hafnium

Bis(iminopyrrolyl) hafnium complexes, (R-pyr)$_2$Hf(NMe$_2$)$_2$ (**2a–d**), were prepared by treating Hf(NMe$_2$)$_4$ with the corresponding iminopyrroles **1a–d** in toluene (Eq. (1)). Two equiv. of dimethylamine were released. The geometry of the products highly depended on the bulkiness of the aromatic substituent at the imine nitrogen of the ligands. Treatments of Hf(NMe$_2$)$_4$ with bulky ligands **1a** and **1b** afforded bis(iminopyrrolyl)hafnium complexes **2a** and **2b** with dissymmetric structures, respectively, while reactions with the less bulky ligands **1c** and **1d** produced the corresponding six coordinated C_2-symmetric *cis*-diamido complexes **2c** and **2d**.



(1)

The ^{1}H NMR spectra of complexes **2a** and **2b** displayed two sets of resonances due to the two magnetically nonequivalent iminopyrrolyl ligands together with signals of two nonequivalent two NMe$_2$ ligands. Two imino protons appeared separately at δ_H 7.80 and 7.87 for **2a**, and δ_H 7.80 and 7.81 for **2b**. Because the chemical shift differences for each complex are small, two iminopyrrolyl ligands coordinated in a bidentate fashion to the hafnium atom. In the ^{13}C NMR spectra of complexes **2a** and **2b**, two imino carbons were observed at δ_C 161.9 and 163.9 for **2a** and δ_C 160.7 and 163.8 for **2b**. The downfield shift of two imino carbons, compared to the corresponding free ligands, also indicated that both imino groups coordinated to the metal. The 2D NOESY analyses of **2a** and **2b** confirmed that they possessed the *cis*-diamido moiety. These results indicated that the hafnium complexes **2a** and **2b** adopt structure **C** shown in Fig. 1. On the other hand, the ^{1}H NMR spectra of complexes **2c** and **2d** displayed rather simple signals due to a C_2-symmetric configuration (**A** or **B**).

Two amido moieties of complexes **2a–d** were able to be replaced by two chloride atoms. Treatments of complexes **2a–d** with trimethylsilyl chloride in hexane for 4 h at 40 °C resulted in quantitative formations of the corresponding dichloro complexes (R-pyr)$_2$HfCl$_2$ (**3a–d**) (Eq. (2)). The ^{1}H NMR spectra of all dichloro complexes **3a–d** exhibited sharp signals due to the C_2-symmetric octahedral structure. We previously reported that the zirconium analogue (ANI-pyr)$_2$ZrCl$_2$ has an octahedral geometry where the two chloride atoms are located in a *cis*-fashion [7f]. This observation suggested that the two chloride atoms of bis(iminopyrrolyl)hafnium complexes have a *cis*-

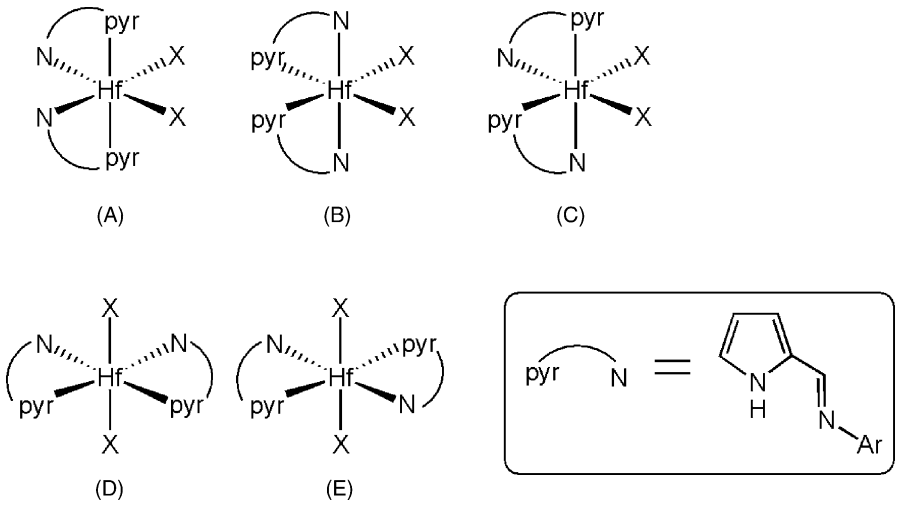
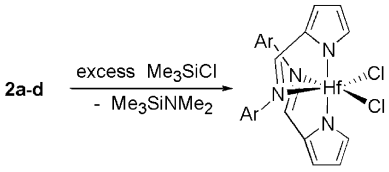


Fig. 1. Five isomeric octahedral structures (**A**–**E**) [**A**–**C**: *cis*-X geometry; **D** and **E**: *trans*-X geometry].

configuration.



(2)

Because the diamido and dichloro moieties of hafnium complexes **2a–d** and **3a–d** have the *cis*-diamido and *cis*-dichloro geometry suitable for olefin polymerization activity, these complexes, upon activation by excess amounts of methylaluminoxane, were tested as catalysts for ethylene polymerization (Table 2). Although these complexes exhibited catalytic activity, their activities were lower than that found for other group 4 metal bis(iminopyrrolyl) complexes [7b,7h,7i].

3.2. Hafnium benzyl complexes bearing iminopyrrolyl ligands

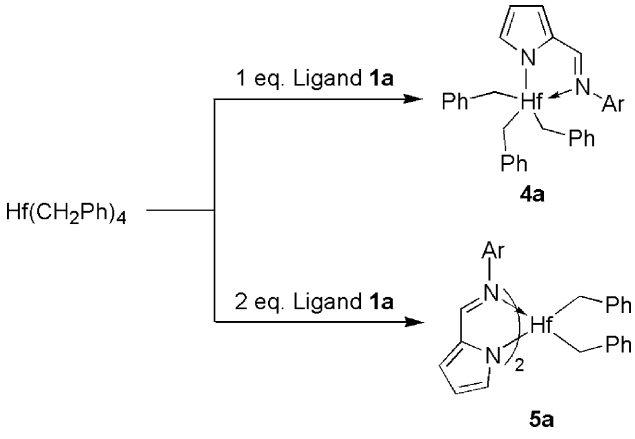
Scheme 1 shows the preparation of mono- and bis(iminopyrrolyl) hafnium benzyl complexes, **4a** and **5a**, starting from $Hf(CH_2Ph)_4$. These two hafnium complexes were isolated by the reactions of $Hf(CH_2Ph)_4$ with controlled amounts of iminopyrrole (**1a**). On the other hand, a reaction of $Hf(CH_2Ph)_4$ with 1 equiv. of a less sterically hindered iminopyrrole (**1b**) only afforded a mixture of mono- and bis(iminopyrrolyl) hafnium benzyl complexes. In the case of iminopyrrole ligands with *para*-aromatic substituents (**1c**, **d**), bis(iminopyrrolyl)hafnium dibenzyl complexes were the only products after treatment of $Hf(CH_2Ph)_4$ with 1 equiv. of the iminopyrrole ligands. Preparations of bis(iminopyrrolyl)hafnium dibenzyl complexes in which aromatic or alkyl substituents are located at the imino-nitrogen of the ligands were reported by Okuda and co-workers [7h,7i].

The complex **4a** was characterized by spectral data, combustion analysis, and X-ray analysis. The ^{1}H NMR spectrum of **4a** displayed one singlet signal due to benzyl protons and one set of signals due to the iminopyrrolyl ligand in an expected integral ratio. The benzyl proton resonance could be frozen to become a broad signal by cooling the sample solution to approximately −60 °C. In the ^{13}C NMR spectrum, the three-benzyl carbons were equal and the value of $^1J_{C-H}$ for the benzyl methylene carbons was 122 Hz, consistent with the typical η^1-coordination mode of the benzyl ligand [14].

Table 2
Polymerization of ethylene catalyzed by **2a–d** and **3a–d**

Catalyst	Temperature (°C)	Time (h)	μmol-cat (μmol)	PE (mg)	Activity (kg-PE/mol-cat h)
2a	20	9	12.2	42.0	3.4
2b	20	9	16.8	65.5	3.9
2c	20	9	17.6	53.7	3.1
2d	20	2	6.3	8.8	1.4
3a	0	9	10.7	141.5	13.2
3b	0	9	16.9	257.2	15.2
3c	0	9	19.4	218.2	11.2
3d	0	2	10.6	89.2	8.4

In toluene: [Hf] = 1.0 mM; MMAO 1000 eq.; ethylene 1 atm.



Scheme 1.

Table 3
Selected bond distances and angles in complex **4a**

Bond distances (Å)	
Hf—N1	2.214(3)
Hf—C18	2.222(4)
Hf—C25	2.252(4)
N1—C1	1.365(5)
C1—C2	1.388(7)
C3—C4	1.381(6)
N2—C5	1.302(5)
Hf—N2	2.289(3)
Hf—C19	2.663(4)
Hf—C32	2.261(3)
N1—C4	1.382(6)
C2—C3	1.390(7)
C4—C5	1.408(5)
Bond angles (°)	
N1—Hf—N2	72.0(1)
N1—Hf—C25	88.6(1)
N2—Hf—C18	109.0(2)
C18—Hf—C25	123.0(2)
Hf—C25—C26	107.3(3)
N1—Hf—C18	101.6(1)
N1—Hf—C32	149.8(1)
N2—Hf—C25	127.2(1)
Hf—C18—C19	89.8(3)
Hf—C32—C33	110.7(2)

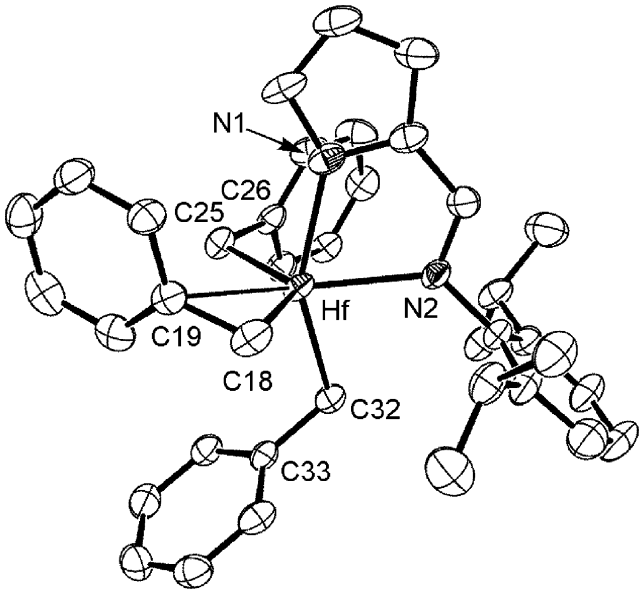


Fig. 2. The molecular structure of complex **4a**. All hydrogen atoms and a solvent molecule (toluene) were omitted for clarity.

The structure of **4a** is shown in Fig. 2 and selected bond distances and angles are summarized in Table 3. The hafnium atom of **4a** adopts a distorted trigonal bipyramidal geometry, in which a pyrrolyl nitrogen atom (N1) and one benzyl carbon (C32) occupy apical positions. The short distance (2.663(4) A) of Hf-C19 and the acute angle (89.8(3)°) of Hf-C18-C19 clearly indicate that one benzyl ligand is in an η^2-coordination mode to the hafnium atom, while the other two benzyl ligands are normal η^1-coordination ligands, which is in sharp contrast to the structure depicted by the NMR spectral data, presumably due to the rapid interconversion process of the three benzyl ligands in solution.

The ^{1}H NMR spectrum of **5a** displayed signals assignable to one set of iminopyrrolyl and that of benzyl in an expected 1:1 ratio. In the ^{1}H NMR spectrum, the two-iminopyrrolyl ligands were magnetically equivalent within the temperature range of −50 to 35 °C. Benzyl methylene protons were observed as a singlet at room temperature, and then became broad as the temperature was cooled below −40 °C, presumably due to the restricted rotation around the hafnium–carbon bond. It is assumed that complex **5a** possesses a C_2-symmetric geometry (**A** in Fig. 1). This structure is in contrast to our previous report that (DIP-pyr)$_2$Zr(CH$_2$Ph)$_2$ possessed a dissymmetric structure [7g] (**C** in Fig. 1), but consistent with a dibenzyl complex of bis{2-*N*-(adamantly)iminomethylpyrrolyl}hafnium, which adopts a C_2-symmetric structure (**A** in Fig. 1) [7i].

We examined the catalytic activity of **4a** and **5a**, upon combination with MMAO, for ethylene polymerization. Their catalytic activities were negligible. On the other hand, complex **4a**, when [Ph$_3$C][B(C$_6$F$_5$)$_4$] was used as a cocatalyst, became a catalyst for the polymerization of 1-hexene. The results conducted at room temperature and 60 °C are summarized in Table 4. The tri(benzyl) complex **4a** at room temperature had high catalytic activity for 1-hexene polymerization; however, the catalyst system afforded a mixture of polymers and oligomers, strongly suggesting that the chain transfer reaction, including β-hydrogen elimination, proceeded readily. At an elevated temperature (60 °C), the catalytic activity increased and the molecular weights of both polymers and oligomers decreased. The ^{1}H NMR spectra of these products displayed olefinic resonances around 4.7 and 5.4 ppm. The resonances around 4.7 ppm are due to 1,1-disubstituted olefins that result from β-elimination in a 1,2-insertion product, and the resonances around 5.4 ppm

Table 4
1-Hexene polymerization catalyzed by **2a**/[Ph$_3$C][B(C$_6$F$_5$)$_4$]

Run	Temperature (°C)	Time (min)	Yield (%)	Activity (kg-polymer/mol-cat h)	Mw	Mw/Mn
1	r.t.[a]	15	78	262	313800[b] 2900[b]	2.12[b] 2.41[b]
2	60	3	86	1446	92200[b] 1300[b]	1.90[b] 1.49[b]

Conditions: [cat] = 5.0 mM; solvent = C$_6$H$_5$Br; catalyst = 20 μmol; [1-hexene]/[cat] = 1000.
[a] The reaction mixture was boiling in 10 min.
[b] Bimodal molecular weight distribution.

are due to internal olefins that result from β-elimination in a 2,1-insertion product [15]. The sterically less demanding catalyst could not control the 1,2 versus 2,1-insertion and, moreover, facilitated β-elimination. When bis(iminopyrrolyl) complex **5a** was used as a catalyst precursor, the catalyst system was far less active than the tri(benzyl) complex **4a**/$[Ph_3C][B(C_6F_5)_4]$ catalyst.

4. Conclusions

We demonstrated the preparation and characterization of mono- and bis(iminopyrrolyl) hafnium complexes. From $Hf(NMe_2)_4$, amine elimination reaction was used to prepare bis(amido)-bis(iminopyrrolyl) hafnium complexes (**2a**–**d**). Simple treatment with Me_3SiCl led to the quantitative formation of dichloro derivatives (**3a**–**d**). On the other hand, from $Hf(CH_2Ph)_4$, mono(iminopyrrolyl) hafnium complex **4a** was isolated by a 1:1 reaction with sterically demanding iminopyrrole **1a**. The activity of bis(iminopyrrolyl) hafnium complexes **2a**–**d** and **3a**–**d** for ethylene polymerization was very low (0.7–15.2 kg-PE/mol-cat h); however, complex **4a** became a highly active catalyst for 1-hexene polymerization (262–1446 kg-polymer/mol-cat h), upon activation with $[Ph_3C][B(C_6F_5)_4]$.

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