

## Efficient ethylene polymerisation catalysis by a cationic benzyl hafnium complex containing pyrrolide-imine ligands †

Shigekazu Matsui,<sup>a,b</sup> Thomas P. Spaniol,<sup>b</sup> Yukihiro Takagi,<sup>a</sup> Yasunori Yoshida<sup>a</sup> and Jun Okuda<sup>\*b</sup><sup>a</sup> Catalysis Science Laboratory, Mitsui Chemicals, Inc., 580–32 Nagaura, Sodegaura, Chiba 299-0265, Japan. E-mail: SKMatsui@aol.com<sup>b</sup> Institut für Anorganische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55099, Mainz, Germany. E-mail: okuda@mail.uni-mainz.de

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A dibenzyl hafnium(IV) complex containing pyrrolide-imine chelate ligands was synthesized and investigated as an ethylene polymerisation catalyst.

Recent attempts to develop alternatives to metallocene-type single-site catalysts have resulted in the creation of numerous non-metallocene catalysts based on Group 4 transition metals, containing non-cyclopentadienyl ligands.<sup>1</sup> Among these, pyrrolide-imine catalyst systems exhibited intriguing catalytic performance in the preparation of new polymers, such as the living catalysis of ethylene–norbornene copolymerisation as well as the preparation of conventional polyolefins with high activity.<sup>2–6</sup> As part of our research aimed at investigating the utility of the pyrrolide-imine ligand in transition metal chemistry, we were interested in preparing dialkyl complexes as well as cationic alkyl complexes as catalyst precursors for olefin polymerisation. In this paper, we describe the synthesis and characterisation of benzyl complexes with pyrrolide-imine ligands and with hafnium(IV) as the central metal. This hafnium complex gave ethylene polymerisation results that demonstrate the high potential of pyrrolide-imine catalysts in olefin polymerisation.

Pyrrole-imine (HL<sup>1–3</sup>)† used in this study can be prepared from the reaction of pyrrole-2-carboxyaldehyde with a corresponding amine in dry ethanol (yield: HL<sup>1</sup>; 57%, HL<sup>2</sup>; 72%, HL<sup>3</sup>; 71%). Pyrrole-imine HL<sup>1</sup>, with an aromatic group attached at the imine position, reacted with 0.5 equiv. of Hf(CH<sub>2</sub>Ph)<sub>4</sub> at –78 °C in toluene to give an orange solid.<sup>7</sup> In the complicated <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of the reaction mixture at –30 °C, a singlet could be assigned to equivalent benzyl groups [2.73 ppm (<sup>1</sup>H), 82.70 ppm (<sup>13</sup>C)]. However, the typical AB quartet pattern due to *cis*-benzyl groups could not be found. Isolation of the complex failed, because its low stability resulted in its decomposition during the purification step.

The reaction of 2 equiv. of HL<sup>2</sup> with Hf(CH<sub>2</sub>Ph)<sub>4</sub> in toluene at –78 °C afforded an orange solution of (L<sup>2</sup>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)<sub>2</sub> (**2**).<sup>8</sup> According to the <sup>1</sup>H NMR spectra of the reaction mixture at –30 °C, a singlet was observed for the benzyl groups at 2.83 ppm. <sup>13</sup>C NMR spectra showed a methylene peak at 82.15 ppm. These results suggest that complex **2** possesses *trans*-benzyl groups, so that, of the five idealised octahedral structures A–E, shown in Scheme 1, configuration A or B is adopted in solution. The Hf complex **2** gradually decomposed at room temperature even in the solid state.

In contrast, dibenzyl hafnium complex *cis*-(L<sup>3</sup>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)<sub>2</sub> (**3**) (R = *t*-Bu) was successfully obtained in 84% yield as an orange powder from the reaction of 2 equiv. of HL<sup>3</sup> with Hf(CH<sub>2</sub>Ph)<sub>4</sub> in toluene.<sup>9,10</sup> Single crystals of **3**, suitable for

an X-ray structure determination were obtained by cooling a toluene–pentane (1 : 10) solution of **3** to –78 °C. ‡

The <sup>1</sup>H NMR spectrum of **3** shows the presence of only one isomer in solution (benzene-d<sub>6</sub>, toluene-d<sub>8</sub> and bromobenzene-d<sub>5</sub>). Cooling or warming a bromobenzene-d<sub>5</sub> solution of **3** (–30 to 75 °C) does not result in changes in the spectra. The <sup>1</sup>H NMR resonances of the benzyl methylene moieties attached to the central hafnium atom are found as an AB quartet at 2.59 and 2.80 ppm, and the corresponding <sup>13</sup>C NMR resonance is recorded at 84.23 ppm. 2-D <sup>1</sup>H NMR (COSY) analysis confirmed that complex **3** possesses C<sub>2</sub>-symmetry on the NMR time scale. Irradiation of the methylene protons resulted in the disappearance of the peak for the 5-proton in the pyrrole ring (NOE). These results suggest that the Hf complex **3** adopts configuration C, with *cis*-benzyl groups, in solution. Complex **3** is stable at room temperature both in the solid state and in solution (benzene, toluene, bromobenzene, diethyl ether). Moreover, warming a bromobenzene-d<sub>5</sub> solution of **3** to 75 °C for 15 min and monitoring the solution by NMR spectroscopy showed that **3** has a relatively high thermal stability.

The crystal structure of the C<sub>2</sub>-symmetric hafnium complex **3** reveals that the pyrrolide-imines are bound to the central hafnium atom in an η<sup>2</sup> fashion and that the Hf–N<sup>(a)</sup> bond has σ-character, as shown in Fig. 1. The overall structure is similar to dichloro titanium(IV) complexes with pyrrolide-imine

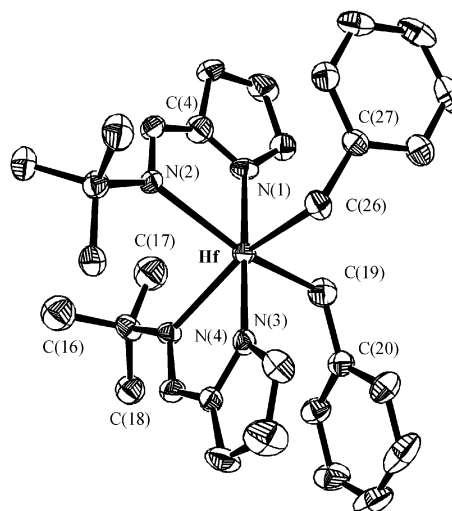


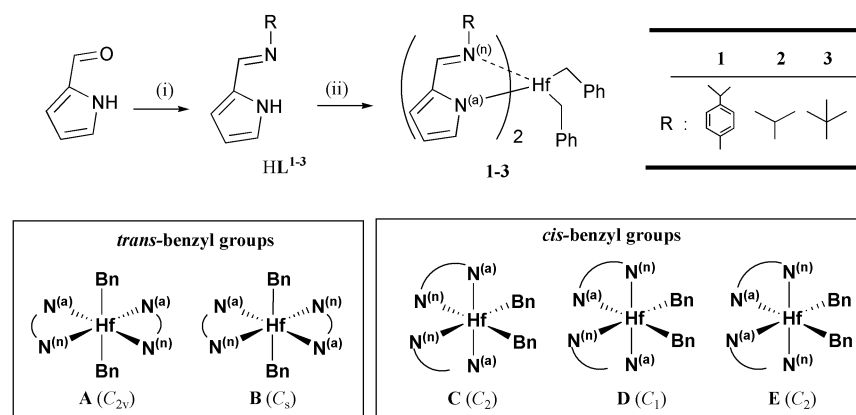
Fig. 1 Molecular structure of **3** (hydrogen atoms omitted for clarity, thermal ellipsoids drawn at the 30% probability level). Disordered carbon atoms of the *tert*-butyl group C(16)–(18) as well as the imine group C(4) are shown in one split position. Selected interatomic distances (Å) and angles (°): Hf–N(1) 2.201(6), Hf–N(3) 2.196(6), Hf–C(19) 2.25(1), Hf–C(26) 2.270(9), Hf–N(2) 2.354(6), Hf–N(4) 2.363(6); N(1)–Hf–N(3) 178.7(3), N(2)–Hf–N(4) 90.4(2), C(19)–Hf–C(26) 96.4(4), C(20)–C(19)–Hf 116.3(7), C(27)–C(26)–Hf 114.6(6).

† Electronic supplementary information (ESI) available: experimental and spectroscopic details. See <http://www.rsc.org/suppdata/dt/b2/b209582c/>

**Table 1** Ethylene polymerisation with **3**

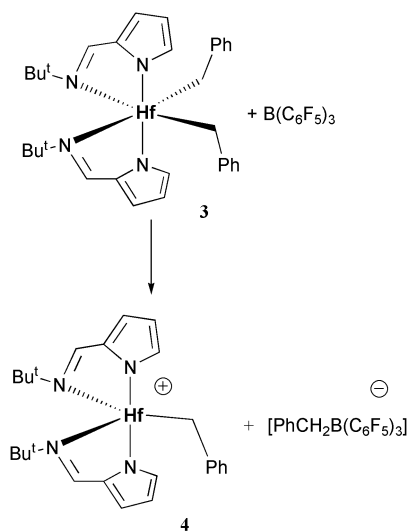
Entry	Cocatalyst	Yield/g	Activity <sup>a</sup>	$M_w^b/10^4$	$M_w/M_n^b$	$T_m/^\circ\text{C}$
1 <sup>c</sup>	Borane <sup>e</sup>	0.934	2242	8.8	9.19	132
2 <sup>c</sup>	Borate <sup>f</sup>	0.123	294	2.8	2.07	131
3 <sup>d</sup>	Borate <sup>f</sup>	1.277	3064	89.6	21.15	134
4 <sup>c</sup>	MAO <sup>g</sup>	0.530	1273	8.7	6.05	132

Conditions: 25 °C, 1 bar, polymerisation time; 5 min, **3**; 5 μmol.<sup>a</sup> In (g PE) (mmol Hf)<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>. <sup>b</sup> Determined by GPC using polystyrene standard. Solvent (250 mL).<sup>c</sup> Toluene. <sup>d</sup> *n*-Heptane. <sup>e</sup> B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>; 10 μmol/*i*-Bu<sub>3</sub>Al; 0.25 mmol. <sup>f</sup> [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]; 10 μmol/*i*-Bu<sub>3</sub>Al; 0.25 mmol. <sup>g</sup> MAO(A1); 1.25 mmol.

**Scheme 1** Reagents and conditions: (i) RNH<sub>2</sub>, ethanol; (ii) 0.5 equiv. Hf(CH<sub>2</sub>Ph)<sub>4</sub>, toluene.

ligands,<sup>2c</sup> displaying an octahedral structure with *trans*-pyrrolide nitrogens [anionic nitrogen: N<sup>(a)</sup>] [N(1)–Hf–N(3): 178.7(3)°] and *cis*-imine nitrogens [neutral nitrogen: N<sup>(n)</sup>] [N(2)–Hf–N(4): 90.4(2)°] to one another, respectively. The *cis* configuration of the two benzyl groups is evident from the C(19)–Hf–C(26) angle of 96.4(4)°. Both benzyl groups are bound in η<sup>1</sup> fashion to the metal. The Hf–C–C angles [116.3(7) and 114.6(6)°] of the benzyl groups in **3** are slightly smaller than the theoretical value of 120°, suggesting the partial flow of electron density from the benzyl moieties to the Hf centre.

Addition of strong Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to **3** in toluene-d<sub>8</sub> at –25 °C resulted in the formation of a yellow solution from which some red–brown oil precipitated immediately. The corresponding cationic species was not observed in the toluene-soluble part by <sup>1</sup>H NMR analysis. Alternatively, activation of **3** in bromobenzene-d<sub>5</sub> at –25 °C with 1 equiv. of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> yielded a homogeneous red–brown solution containing the ion pair [(L<sup>3</sup>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)][B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>2</sub>Ph)] (**4**) (Scheme 2).<sup>11</sup> The <sup>1</sup>H NMR spectrum (–25 °C, bromobenzene-d<sub>5</sub>) for **4** shows the resonances for the methylene groups

**Scheme 2**

attached to the Hf atom and the B atom at 2.54 and 3.66 ppm, respectively. The anion shows  $\Delta\delta(m,p-F) = 2.78$  ppm; this is indicative of a solvent-separated ion pair.<sup>12</sup> It is noteworthy that the cationic hafnium complex **4** possesses high thermal stability in bromobenzene-d<sub>5</sub>, showing almost no decomposition, even at 75 °C over a period of at least 15 min.

Subsequently, the catalytic performance of the cationic complex derived from complex **3** was investigated. Cationic complex **4**, which was prepared *in situ*, resulted in ethylene polymerisation with the high activity of 2242 (g PE) (mmol Hf)<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup> and with an  $M_w$  value of  $8.8 \times 10^4$  in the presence of triisobutylaluminium (*i*-Bu<sub>3</sub>Al) in toluene (entry 1). When [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was used as a cocatalyst in the presence of *i*-Bu<sub>3</sub>Al, rapid heat generation was observed at the beginning of the reaction; however, deactivation was observed immediately in toluene (entry 2). The molecular weight distribution ( $M_w/M_n$ ) of the polymer thus obtained is 2.07, as expected for a polymer produced by a single-site catalyst, with an  $M_w$  of  $2.8 \times 10^4$ . Interestingly, in *n*-heptane solvent (entry 3), the catalyst system complex **3**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/*i*-Bu<sub>3</sub>Al resulted in a continuous exothermic reaction for at least 5 min and a high activity [3064 (g PE) (mmol Hf)<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>] with a high  $M_w$  value of  $89.6 \times 10^4$ . In the case of association with methylaluminumoxane (MAO) in toluene (entry 4), the activity of complex **3** was 1273 (g PE) (mmol Hf)<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>, (Table 1) which is the same order of magnitude as that found with titanium complexes with pyrrolide-imine ligands under the same polymerisation conditions.<sup>2a–c</sup> The results reported here, along with those reported recently for titanium complexes with chelating pyrrolide-imine ligands, suggest that pyrrolide-imine catalyst systems based on Group 4 transition metals are promising post-metallocene catalysts.

In conclusion, we could show that a thermally robust dibenzyl hafnium complex containing a pyrrolide-imine ligand can be made accessible by the proper choice of the imine substituent. Moreover, the complex can be converted into the benzyl cation, which shows high ethylene polymerisation activity. Detailed investigation of the polymerisation catalysis of the pyrrolide-imine Group 4 metal complexes and mechanistic studies are now in progress.

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## Notes and references

‡ Crystal data for **3**:  $C_{32}H_{40}N_4Hf$ ;  $M = 659.19$ , monoclinic,  $P2_1/c$ ,  $a = 13.602(1)$ ,  $b = 9.7110(5)$ ,  $c = 22.397(2)$  Å,  $\beta = 95.228(7)^\circ$ ,  $U = 2946.1(4)$  Å<sup>3</sup>,  $T = 293(2)$  K,  $Z = 4$ ,  $D_c = 1.486$  Mg m<sup>-3</sup>,  $\mu = 3.567$  mm<sup>-1</sup>,  $2\theta_{max} = 54^\circ$ , 12320 collected reflections, 6401 unique ( $R_{int} = 0.0736$ ), 427 parameters,  $R_1 = 0.0525$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.0772$ . CCDC reference number 194574. See <http://www.rsc.org/suppdata/dt/b2/b209582c/> for crystallographic data in CIF or other electronic format.

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- 7 NMR data for **1** (mixture): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.05–1.28 (m, CH<sub>3</sub>), 2.61–2.80 (m, CH), 2.73 (s, CH<sub>2</sub>), 6.35–7.49 (m, Ar–H + pyrrole–H), 7.72–7.73 (m, CH=N).
- 8 NMR data for **2**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.63 (d,  $J = 6.8$  Hz, 12H, CH<sub>3</sub>), 2.83 (s, 4H, CH), 3.17 (q,  $J = 6.8$  Hz, 2H, CH<sub>2</sub>), 6.46 (m, 2H, pyrrole–4–H), 6.69 (m, 2H, pyrrole–3–H), 6.80–7.24 (m, 20H, Ar–H), 7.51 (s, 2H, pyrrole–5–H), 7.57 (s, 2H, CH=N). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  22.47, 54.50, 82.15, 113.48, 119.48, 121.43, 125.23, 128.87, 138.99, 140.01, 146.28, 158.30.
- 9 NMR data for **3**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.83 (s, 18H, *t*-Bu), 2.59, 2.80 (AB q,  $J = 12.0$  Hz, 4H, CH<sub>2</sub>), 6.49 (dd,  $J = 3.3$  and 1.2 Hz, 2H, pyrrole–4–H), 6.72 (dd,  $J = 3.3$  and 1.0 Hz, 2H, pyrrole–3–H), 6.85 (t, 2H,  $J = 7.6$  Hz, Ar–H(*p*)), 6.94 (d, 4H,  $J = 7.2$  Hz, Ar–H(*o*)), 7.22 (t, 4H,  $J = 7.6$  Hz, Ar–H(*m*)), 7.71 (br s, 2H, pyrrole–5–H), 7.84 (s, 2H, CH=N). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  29.90, 58.38, 84.23 (t,  $J_{C-H} = 114$  Hz, CH<sub>2</sub>), 113.91, 120.92, 121.46, 126.48, 127.84, 138.66, 139.98, 149.98, 158.44.
- 10 (L<sup>3</sup>)<sub>2</sub>Zr(CH<sub>2</sub>Ph)<sub>2</sub> (**5**) can be prepared from the reaction of Zr(CH<sub>2</sub>Ph)<sub>4</sub> and 2 equiv. of ligand HL<sup>3</sup> in a manner analogous to that used to prepare complex **3**. The configuration of **5** was similar to that of **3**, with C<sub>2</sub>-symmetry and two *cis*-benzyl groups, as determined by <sup>1</sup>H and <sup>13</sup>C NMR. (see ESI).
- 11 NMR data for **4**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Br, –25 °C):  $\delta$  0.90 (s, 18H, *t*-Bu), 2.54 (s, 2H, CH<sub>2</sub>Hf), 3.66 (s, 2H, CH<sub>2</sub>B), 6.45–6.48 (d,  $J = 7.2$  Hz, 2H, pyrrole–4–H), 6.58 (br s, 2H, pyrrole–3–H), 6.97–7.46 (m, 10H), 7.50 (br s, 2H, pyrrole–5–H), 8.27 (s, 2H, CH=N). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>5</sub>Br, –25 °C):  $\delta$  29.86, 61.11, 83.12, 117.48, 134.86, 141.87, 149.70, 159.42, (145–150). <sup>19</sup>F-NMR (C<sub>6</sub>D<sub>5</sub>Br, –25 °C):  $\delta$  –130.25 (*o*-F), –162.93 (*p*-F), –165.71 (*m*-F).
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