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Pyrrolide-imine benzyl complexes of zirconium and hafnium: synthesis, structures, and efficient ethylene polymerization catalysis

Shigekazu Matsui [a,b,*], Yasunori Yoshida [b], Yukihiro Takagi [b], Thomas P. Spaniol [a,1], Jun Okuda [a,*,1]

[a] *Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany*
[b] *Catalysis Science Laboratory, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba 299-0265, Japan*

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Abstract

A series of pyrrolyl-imines HL^{1-6} was prepared by the condensation of pyrrole-2-carboxyaldehyde with different amines. The reaction of 2 equiv of pyrrolyl-imine with tetrabenzyl complexes of hafnium and zirconium $M(CH_2Ph)_4$ (M = Hf or Zr) gave dibenzyl complexes $(L^{3-6})_2M(CH_2Ph)_2$, which were characterized by NMR spectroscopy and crystal structure analysis. NMR spectra of the complexes with secondary alkyl substituents at the imine nitrogen (isopropyl: **3a**, 4-*tert*-butylcyclohexyl: **4a** and **4b**) suggest that rapid racemization between Δ and Λ configurations occurs in solution on the NMR time scale. The complexes with pyrrolide-imine ligands with a tertiary alkyl group such as *tert*-butyl (**5a** and **5b**) or 1-adamantyl (**6a** and **6b**) at the imine nitrogen possess *cis*-configured benzyl groups. Hafnium complexes **5a** and **6a** react with $B(C_6F_5)_3$ in bromobenzene-d_5 to give the corresponding cationic benzyl complexes, which exhibit high activity for ethylene polymerization (**5a**: 2242 kg-polymer/ mol-Hf h bar, **6a**: 2096 kg-polymer/ mol-Hf h bar). Zirconium complexes **5b** and **6b** display a remarkably high ethylene polymerization activity when activated with methylaluminoxane (**5b**: 17,952 kg-polymer/mol-Zr h bar, **6b**: 22,944 kg-polymer/mol-Zr h bar).

Keywords: Pyrrolide-imine; Zirconium; Hafnium; Benzyl complex; Ethylene polymerization

1. Introduction

In the last two decades, remarkable advances have been made in the design and synthesis of well-defined olefin polymerization catalysts which allowed the synthesis of polyolefins with novel properties and applications. The vast majority of homogeneous catalysts are based on metallocene derivatives. Recently, transition metal complexes which do not contain cyclopentadienyl ligands have received considerable attention as new generations of polymerization catalyst precursors with improved catalytic performance, such as activity, selectivity, and stability [1]. Chelating non-cyclopentadienyl ligands which include diamido [2–6], diphenoxy [7–9], phenoxy-imine [10–15], pyrrolide-imine [16–21], indolido-imine [25], phosphine-imido [22], tris(pyrazolyl)borate ligands [23] are currently being explored for the design of olefin polymerization catalysts based on group 4 transition metal complexes. Some of these systems have proved to be more active, allowing high flexibility in the design of polymerization processes. For instance, methylaluminoxane-activated pyrrolide-imine dichloro titanium complexes allow the synthesis of conventional polyolefins with high activity [16] and promote a living copolymerization of ethylene with norbornene [16d]. Recently, we have reported the synthesis of dibenzyl hafnium complexes containing pyrrolide-imine ligands as highly active catalyst precursors for ethylene polymerization. In this article we describe the full details for the synthesis and structure of a series of dibenzyl

* Corresponding authors. Tel.: +0241-894-645; fax: +0241-892-644.
E-mail address: jun.okuda@ac.rwth-aachen.de (J. Okuda).
[1] New address: Institute of Inorganic Chemistry, Aachen University of Technology (RWTH), Prof.-Pirlet-Strasse 1, D-52056 Aachen, Germany.

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hafnium and zirconium pyrrolide-imine complexes. The reactions of these complexes with $B(C_6F_5)_3$ are examined along with the results of ethylene polymerization studies [24].

2. Results and discussion

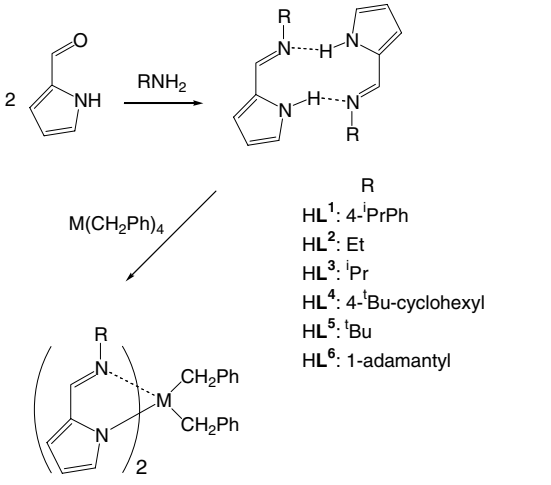
Pyrrole-imines (HL^{1-5}) used as ligand precursors in this study were prepared from the reaction of pyrrole-2-carboxyaldehyde with a corresponding primary amine (or aniline) derivatives using a standard condensation method [16c]. All pyrrole-imines were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. According to crystal structure analyses, the pyrrole-imines HL^1 and HL^4 exist as hydrogen-bridged dimers in the solid state (see Section 5).

The synthesis of bis(pyrrolide-imine) dibenzyl complexes is summarized in Scheme 1. Pyrrole-imine HL^1 with a 4-isopropylphenyl group as the imine substituent R reacted with 0.5 equiv. of $Hf(CH_2Ph)_4$ at −30 °C in toluene to give an orange solid as a complex mixture. In the complicated ^1H NMR spectra of the reaction mixture, a singlet at 2.73 ppm could be assigned to the equivalent protons of the benzylic methylene groups (^{13}C NMR: 82.70 ppm). Isolation of the complex failed because of its low stability; it decomposed during the purification step. Likewise, when HL^2 with a primary alkyl substituent was used, the corresponding complex could not be obtained under similar conditions; only an insoluble precipitate was obtained from toluene.

The preparation of bis(pyrrolide-imine) complexes with a secondary alkyl group at the imine position was then investigated. The introduction of an isopropyl group in the ligand L^3 gave the hafnium complex $(L^3)_2Hf(CH_2Ph)_2$ (**3a**). However, complex **3a** gradually decomposed at room temperature even in the solid state. Attachment of a 4-*tert*-butylcyclohexyl group which is sterically larger than an isopropyl group enhanced the thermal stability leading to $(L^4)_2Hf(CH_2Ph)_2$ (**4a**), which is stable at room temperature in the solid state as well as in benzene or bromobenzene solution. In a similar manner, the dibenzyl zirconium complex $(L^4)_2Zr(CH_2Ph)_2$ (**4b**) was isolated from the reaction of 2 equiv of HL^4 with $Zr(CH_2Ph)_4$ in toluene. **4b** is thermally less stable than the corresponding hafnium complex **4a**.

In the ^1H NMR spectra of the complexes **3a**, **4a**, and **4b**, a singlet assigned to the benzyl methylene group was observed at 2.83, 2.64, and 2.73 ppm, respectively. The ^{13}C NMR spectra of these complexes show one resonance for the methylene groups (**3a**, 82.15; **4a**, 81.98; **4b**, 76.46 ppm). 2D ^1H NMR (COSY) analysis of complex **4a** confirmed C_2-symmetry on the NMR time scale. Nuclear Overhauser experiments by irradiating the methylene protons led to the disappearance of the peak for the 5-proton in the pyrrole ring, suggesting a *cis*-configuration for the pyrrole groups in **4a**. The typical AB quartet pattern due to *cis*-benzyl groups was not found in the ^1H NMR spectra. These results suggest that epimerization between the Λ and Δ configuration occurs, probably caused by a rapid site exchange of the benzyl and pyrrole-imine groups in solution on the NMR time scale (Scheme 2).

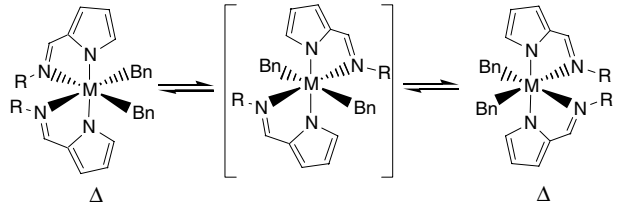
In contrast, thermally robust dibenzyl hafnium or zirconium complexes, *cis*-$(L^{5,6})_2M(CH_2Ph)_2$ (**5a**, R: *t*-Bu, M: Hf; **5b**, R: *t*-Bu, M: Zr; **6a**, R: 1-adamantyl, M: Hf; **6b**, R: 1-adamantyl, M: Zr), were successfully obtained from the reaction of 2 equiv of $HL^{5,6}$ with $Hf(CH_2Ph)_4$ or $Zr(CH_2Ph)_4$ in toluene. The ^1H NMR spectra of the hafnium (**5a** and **6a**) and zirconium complexes (**5b** and **6b**) with a tertiary alkyl group show mainly one isomer in solution (benzene-d_6 and bromobenzene-d_5). Within the temperature range of −30 and 75 °C, the spectra of these complexes in bromobenzene-d_5 solution practically show no change. The ^1H NMR resonances of the benzyl methylene moieties attached to the central metal are recorded as an AB quartet, indicating that no enantiomerization of the complex occurs



R
HL1: 4-iPrPh
HL2: Et
HL3: iPr
HL4: 4-tBu-cyclohexyl
HL5: tBu
HL6: 1-adamantyl

1a: R= 4-^{i}PrPh, M = Hf
3a: R=^{i}Pr, M = Hf
4a: R=4-^{t}Bu-cyclohexyl, M = Hf, **4b**: R=4-^{t}Bu-cyclohexyl, M = Zr
5a: R=^{t}Bu, M = Hf, **5b**: R= ^{t}Bu, M = Zr
6a: R= 1-adamantyl, M = Hf, **6b**: R= 1-adamantyl, M = Zr

Scheme 1.



Scheme 2.

in solution, probably due to the bulkiness of the R groups. Apparently, pyrrolide-imine complexes with a tertiary alkyl group adopt C_2-symmetric configurations with *cis*-benzyl groups.

We have previously reported that complex **5a** shows C_2-symmetry in solution, but not in the solid state [24]. In this work, we have crystallographically characterized the adamantyl substituted complexes of hafnium (**6a**) as well as of zirconium (**6b**). Both compounds crystallize isotypically and show crystallographic C_2-symmetry. In all of these compounds, the pyrrolide moieties are bound to the central metal in an η^1-fashion with σ-character of the M–N bond. The structures are similar to those of related dichloro titanium(IV) complexes with two pyrrolide-imine ligands [16b,16c], where the metal center is also octahedrally coordinated with *trans*-configuration of the anionic pyrrolide donors and *cis*-configuration of the neutral imine donors. The *cis* configuration of the two benzyl groups is evident from the C–M–C bond angles in **5a**: C(19)–Hf–C(26) = 96.4(4)°, **6a**: C(16)–Hf–C(16)′ = 91.4(2)°, and **6b**: C(16)–Zr–C(16)′ = 91.9(1)°. Both benzyl groups are bound in an η^1-fashion to the metal. Fig. 1 shows the ORTEP diagram of the hafnium complex **6a**. Table 1 summarizes the pertinent bond parameters of **6a** and **6b** as compared to those of **5a** [24].

Subsequently, the catalytic performances of the hafnium complexes **4a**–**6a** and of the zirconium complexes **4b**–**6b** were investigated. As for the hafnium complexes, complex **4a** with its secondary alkyl R substitutent displayed very low ethylene polymerization activities when the cocatalysts $B(C_6F_5)_3$/triisobutylaluminium ($^iBu_3Al$) or methylalumoxane (MAO) were used (Table 2, entries 1 and 2). In contrast, cationic complexes derived from in situ reaction of $B(C_6F_5)_3$ with complexes **5a** or **6a** which have tertiary alkyl substitutents polymerized ethylene with high activities of more than 2000 kg-polymer/mol-Hf h bar in the presence of $^iBu_3Al$ (entries 3 and 5). When MAO was used, the activities of **5a** and **6a** were 1273 and 616 kg-polymer/mol-Hf h bar (entries 4 and 6), which are comparable to those found for titanium complexes with pyrrolide-imine ligands under the same polymerization conditions [16]. The hafnium catalysts produced multimodal polyethylenes with broad molecular weight distributions, possibly caused by the gradual generation of the active species and/or isomerization of the active species in the polymerization conditions [10p].

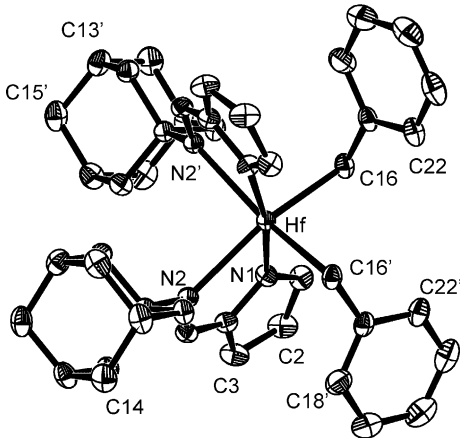


Fig. 1. Molecular structure of complex **6a** in the Λ configuration. Thermal ellipsoids are given with 30% probability. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances and bond angles of **6a** and **6b** as compared to those of **5a** [24]

Complex	5a	6a	6b
Bond distances (Å)			
M–N(a)	2.201(6)	2.197(4)	2.220(2)
	2.196(6)		
M–N(n)	2.354(6)	2.386(3)	2.403(2)
	2.363(6)		
M–C(benzyl)	2.25(1)	2.264(4)	2.287(2)
	2.270(9)		
Bond angles (°)			
N(a)–M–N(a)	178.7(3)	170.1(2)	169.94(9)
N(n)–M–N(n)	90.4(2)	92.9(2)	92.07(8)
C–M–C	96.4(4)	91.4(2)	91.9(1)
N(a)–M–N(n)	73.1(3)	72.5(1)	72.37(6)
	73.3(2)	100.5(1)	99.73(6)
	106.4(2)		
	107.8(2)		
N(a)–M–C	83.8(3)	87.4(2)	85.24(7)
	82.8(3)	99.6(2)	102.53(8)
	96.9(3)		
	96.0(3)		
N(n)–M–C	93.6(3)	91.4(2)	92.32(7)
	89.5(3)	159.8(2)	157.61(7)
	155.6(3)		
	156.0(3)		
M–C–C	116.3(7)	112.0(3)	107.8(2)
	114.6(6)		

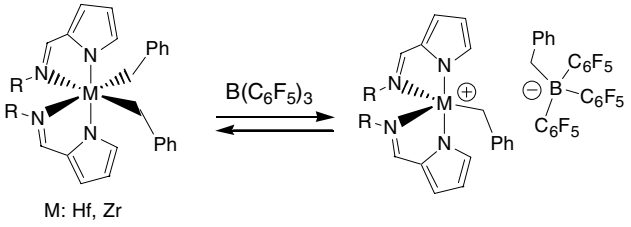
For the zirconium complexes, the ethylene polymerization follows similar trends as the hafnium complexes. Complex **4b** with its secondary alkyl substituent practically displayed no activity. Although the zirconium complexes **5b** and **6b** have the same ligands as the hafnium complexes **5a** and **6a**, they produced polyethylenes with activities of 746 and 1760 kg-polymer/mol-Zr h, respectively. The molecular weight distribution (M_w/M_n) values of the polymer obtained are 2.25 (**5b**) and 2.05 (**6b**), as expected for a polymer produced by a single-site catalyst, with values for M_w of 2.4×10^4 and 6.3×10^4, respectively. It is noteworthy that the complexes **5b** and **6b** exhibited activties that are one order of magnitude larger (**5b**, 17,952 kg-polymer/mol-Zr h bar; **6b**, 22,944 kg-polymer/mol-Zr h bar) and gave polymers with narrow molecular weight distribution values (M_w/M_n ca. 2), when MAO was used as a cocatalyst.

Table 2
Ethylene polymerization results with Hf complexes **4a**–**6a** or Zr complexes **4b**–**6b**

Entry	Complex (μmol)		$B(C_6F_5)$ (μmol)	$^iBu_3Al$ (mmol)	MAO (mmol)	Yield (g)	Activity[a]	M_w[b] (10^4)	M_w/M_n[b]	T_m (°C)
1	**4a**	5.0	10.0	0.25	–	Trace	–	–	–	–
2	**4a**	5.0	–	–	1.25	Trace	–	–	–	–
3	**5a**	5.0	10.0	0.25	–	0.934	2242	8.8	9.19	132
4	**5a**	5.0	–	–	1.25	0.530	1273	8.7	6.05	132
5	**6a**	5.0	10.0	0.25	–	0.874	2096	9.6	12.15	132
6	**6a**	5.0	–	–	1.25	0.257	616	3.6	6.66	130
7	**4b**	5.0	10.0	0.25	–	Trace	–	–	–	–
8	**4b**	5.0	–	–	1.25	Trace	–	–	–	–
9	**5b**	5.0	10.0	0.25	–	0.311	746	2.4	2.25	130
10	**5b**	5.0	–	–	1.25	3.368	(8083)[c]	2.9	2.25	130
11	**5b**	0.5	–	–	1.25	1.496	17,952	2.6	2.09	131
12	**6b**	5.0	10.0	0.25	–	0.733	1760	6.3	2.05	134
13	**6b**	5.0	–	–	1.25	3.671	(8810)[c]	8.7	2.08	134
14	**6b**	0.5	–	–	1.25	1.912	22,944	7.1	2.17	133

Conditions: 25 °C, 0.1 MPa ethylene pressure, solvent: toluene (250 ml), polymerization time: 5 min.
[a] kg-polymer/mol-M h bar.
[b] Determined by GPC using polystyrene standard.
[c] Stirring difficulty was encountered because of excessive polymer production.

For the detailed investigation of the polymerization catalysis using the above complexes, the structures of the cationic species were studied by ^1H NMR spectroscopy. With the hafnium complexes, homogeneous red-brown solutions containing the ion pair $[(L^5)_2Hf(CH_2Ph)][B(C_6F_5)_3(CH_2P\ h)]$ (**5a***) and $[(L^6)_2Hf(CH_2Ph)][B(C_6F_5)_3(CH_2P\ h)]$ (**6a***) were successfully obtained by the reaction **5a** and **6a** with 1 equiv of $B(C_6F_5)_3$ in bromobenzene-d_5. The cationic hafnium complexes **5a*** or **6a*** are stable in bromobenzene-d_5 even at room temperature. The ^1H NMR spectra (−25 °C, bromobenzene-d_5) for the hafnium cationic complexes show the resonances for the methylene groups attached to the hafnium atom (**5a***: 3.66 ppm, **6a***: 3.67 ppm) and the boron atom (**5a***: 2.54 ppm, **6a***: 2.61 ppm). The anion shows $\Delta\delta(m,p\text{-F})$ values (**5a***: 2.78 ppm, **6a***: 2.85 ppm) indicative of a solvent-separated ion pair [25]. In contrast, the ^1H NMR spectra of the corresponding cationic zirconium complexes **5b*** and **6b*** showed one singlet (**5b***: 3.55 ppm, **6b***: 3.56 ppm) assigned to the methylene protons of the equivalent benzyl groups (Scheme 3). Values for $\Delta\delta(m,p\text{-F})$ of the anion of the zirconium complexes (**5b***: 2.96 ppm, **6b***: 2.97 ppm) were slightly larger than those of the corresponding hafnium complexes **5a*** and **6a***. This suggests that the hafnium complexes have a higher ion pair character than the zirconium analogues.



Scheme 3.

3. Conclusion

We could show that thermally robust dibenzyl hafnium and zirconium complexes with two pyrrolide-imine ligands are accessible by the proper choice of the imine substituent. The dibenzyl hafnium complexes can be converted into the benzyl cations by the reaction of $B(C_6F_5)_3$ which polymerize ethylene with very high activity. Similar to titanium pyrrolide-imine complexes [16], hafnium and zirconium complexes containing specifically substituted pyrrolide-imine ligands promise to be highly efficient olefin polymerization catalysts.

4. Experimental

4.1. General procedures

All manipulations were performed under exclusion of oxygen and moisture in an argon or nitrogen atmosphere using standard Schlenk techniques in oven-dried glassware. Toluene and *n*-pentane used for complex syntheses were distilled from sodium/benzophenone ketyl. Toluene used for polymerizations was dried over Al_2O_3 and degassed by bubbling nitrogen gas. Starting materials for the synthesis of ligand precursors HL[1–6], 2-carboxypyrolaldehyde (98%), 4-isopropylaniline (99%),

ethylamine (70% aq.), isopropylamine (99.5%), *tert*-butylamine (97%), 4-*tert*-butylcyclohexylamine (97%), and 1-adamantylamine (97%) were purchased from commercial sources and used without further purification. $M(CH_2Ph)_4$ (M = Zr, Hf) [26] and $B(C_6F_5)_3$ [27] were prepared according to literature procedures. Ethylene was obtained from Sumitomo Seika Co. Methylalumoxane (MAO) was purchased from Albemarle as a 1.2 M of a toluene solution, and remaining trimethylaluminum was evaporated in vacuo prior to use. ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were recorded on a Bruker DRX-400 spectrometer at 25 °C (unless stated otherwise). Chemical shifts were measured relative to residual ^1H and ^{13}C resonances in the deuterated solvents. NMR solvents (benzene-d_6 and bromobenzene-d_5) were distilled from sodium and stored under argon. NOESY experiments were performed at 25 °C. Elemental analyses were carried out in this department. M_w values and molecular weight distribution (M_w/M_n) values of the polymers were determined using a Waters 150-C gel permeation chromatograph at 145 °C using polyethylene calibration and equipped with three TSKgel columns (two sets of TSKgelGMH_{HR}-H(S)HT and TSKgelGMH_6-HTL). *ortho*-Dichlorobenzene was employed as solvent at a flow rate of 1.0 ml/min. Transition melting temperatures (T_m) of the polymers were determined by DSC with a Perkin Elmer DSC-7 differential-scanning calorimeter in the following manner: First, the sample was heated to 200 °C at 20 °C/min, maintained at 200 °C for 10 min, and then cooled to 30 °C at 10 °C/min for crystallization followed by reheating at 10 °C/min. The thermogram of the sample was recorded in the second heating run to remove the thermal history. The instrument was calibrated by the melting points of indium and lead.

4.2. Preparation of HL^1

To a solution of pyrrole-2-carboxyaldehyde (4.83 g, 49.78 mmol) in ethanol (100 ml) were added 4-isopropylaniline (7.44 g, 54.73 mmol) and catalytic amount of *p*-toluenesulfonic acid. The reaction mixture was stirred for 12 h at 50 °C. After the evaporation of the ethanol, the resulting mixture was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (19/1) as eluent, and recrystallization was attempted from ethanol to give *N*-(2-pyrrolidene)-4-isopropylaniline (HL^1) as white crystals in 58.2% yield (7.32 g, 28.99 mmol). ^1H NMR (C_6D_6) δ: 1.26 (d, $J = 6.8$ Hz, 6H, CH_3), 2.83 (q, $J = 6.8$ Hz, 1H, CH), 6.24 (dd, $J = 3.2$ and 2.8 Hz, 1H, pyrrole-4-H), 6.43 (br s, 1H, pyrrole-3-H), 6.58 (d, $J = 3.2$ Hz, 1H, pyrrole-5-H), 7.17–7.26 (m, 2H, Ar–H), 8.15 (s, 1H, CH=N), 10.09 (br s, 1H, NH). ^{13}C NMR (C_6D_6) δ: 23.81, 33.60, 109.99, 116.45, 121.00, 123.08, 127.01, 130.92, 145.79, 149.28, 149.93. Anal Calc. for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 79.19; H, 7.67; N, 13.26%.

4.3. Preparation of HL^2

Pyrrole-2-carboxyaldehyde (1.01 g, 10.30 mmol) was dissolved in ethanol (5 ml). To this solution, ethylamine (70% aqueous, 1.29 g, 20.00 mmol) was added. The reaction mixture was stirred for 12 h at room temperature. After the evaporation of the ethanol, the resulting mixture was distilled under reduced pressure to give *N*-(2-pyrrolidene)-ethylamine (HL^2) as a colorless liquid in 48.4% yield (0.61 g, 4.99 mmol), b.p. 65 °C/2.0 mbar. ^1H NMR (C_6D_6) δ:1.18 (t, $J = 7.2$ Hz, 3H, CH_3), 3.38 (q, $J = 7.2$ Hz, 2H, CH_2), 6.33 (dd, $J = 3.2$ and 2.4 Hz, 1H, pyrrole-4-H), 6.48 (br s, 1H, pyrrole-3-H), 6.53 (d, $J = 3.2$ Hz, 1H, pyrrole-5-H), 7.83 (s, 1H, CH=N), 10.48 (br s, 1H, NH). ^{13}C NMR (C_6D_6) δ: 16.30, 54.67, 109.34, 114.21, 121.73, 130.37, 151.37. Anal. Calc. for $C_8H_{12}N_2$: C, 68.82; H, 8.25; N, 22.93. Found: C, 68.66; H, 7.88; N, 22.87%.

4.4. Preparation of HL^3

Pyrrole-2-carboxyaldehyde (1.06 g, 10.81 mmol) was dissolved in ethanol (5 ml). To this solution, isopropylamine (1.18 g, 19.90 mmol) was added. The reaction mixture was stirred for 17 h at room temperature. After the evaporation of the ethanol, the resulting mixture was distilled under reduced pressure to give *N*-(2-pyrrolidene)-isopropylamine (HL^3) as a colorless liquid in 73.6% yield (1.08 g, 7.96 mmol), b.p. 67 °C/2.3 mbar. ^1H NMR (C_6D_6) δ: 1.21 (d, $J = 6.4$ Hz, 6H, CH_3), 3.29 (q, $J = 6.4$ Hz, 1H, CH), 6.29 (dd, $J = 3.2$ and 2.8 Hz, 1H, pyrrole-4-H), 6.51 (d, $J = 3.6$ Hz, 1H, pyrrole-3-H), 6.55 (br s, 1H, pyrrole-5-H), 7.90 (s, 1H, CH=N), 10.42 (br s, 1H, NH). ^{13}C NMR (C_6D_6) δ: 24.13, 60.62, 109.29, 113.73, 121.39, 130.43, 149.22. Anal. Calc. for $C_8H_{12}N_2$: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.43; H, 8.74; N, 20.67%.

4.5. Preparation of HL^4

Pyrrole-2-carboxyaldehyde (1.15 g, 11.86 mmol) was dissolved in ethanol (5 ml). To this solution, 4-*tert*-butylcyclohexylamine (2.25 g, 14.05 mmol) was added. The reaction mixture was stirred for 15 h at room temperature. After the evaporation of the ethanol, the resulting mixture was recrystallized in ethanol to give *N*-(2-pyrrolidene)-4′-*t*-butylcyclohexylamine (HL^4) as colorless crystals in 50.8% yield (1.40 g, 6.02 mmol). ^1H NMR (C_6D_6) δ: 0.93 (s, 9H, *t*-Bu), 1.03–1.18 (m, 3H, CH + CH_2), 1.67–1.96 (m, 6H, CH_2), 2.91–2.99 (m, 1H, N–CH), 6.30 (dd, $J = 3.2$ and 2.8 Hz, 1H, pyrrole-4-H), 6.42 (d, $J = 1.2$ Hz, 1H, pyrrole-3-H), 6.51–6.52 (m, 1H, pyrrole-5-H), 8.01 (s, 1H, CH=N). ^{13}C NMR (C_6D_6) δ: 25.75, 27.30, 31.95, 35.08, 46.99, 69.42, 109.30, 113.47,

121.15, 128.87, 149.32. Anal. Calc. for $C_{14}H_{16}N_2$: C, 77.53; H, 10.41; N, 12.06. Found: C, 77.48; H, 10.48; N, 11.99%.

4.6. Preparation of HL^5

Pyrrole-2-carboxyaldehyde (3.12 g, 32.10 mmol) was dissolved in ethanol (50 ml). To this solution, *tert*-butylamine (3.66 g, 48.50 mmol) was added. The reaction mixture was stirred for 24 h at room temperature. After the evaporation of the ethanol, the resulting mixture was distilled under reduced pressure to give *N*-(2-pyrrolidene)-*tert*-butylamine (HL^5) as yellow crystals in 72.1% yield (3.97 g, 23.17 mmol), b.p. 66–68 °C/1.8 mbar. ^{1}H NMR (C_6D_6) δ: 1.26 (s, 9H, *t*-Bu), 6.31 (dd, 3.2 and 2.8 Hz, 1H, pyrrole-4-H), 6.49 (br s, 1H, pyrrole-3-H), 6.52 (d, $J = 3.6$ Hz, 1H, pyrrole-5-H), 8.05 (s, 1H, CH = N), 9.71 (br s, 1H, NH). ^{13}C NMR (C_6D_6) δ: 29.49, 56.06, 109.30, 113.16, 120.80, 131.20, 145.77. Anal. Calc. for $C_9H_{14}N_2$: C, 71.96; H, 9.39; N, 18.65. Found: C, 71.83; H, 9.19; N, 18.62%.

4.7. Preparation of HL^6

Pyrrole-2-carboxyaldehyde (2.365 g, 24.37 mmol) was dissolved in ethanol (50 ml). To this solution, 1-adamantylamine (4.51 g, 28.92 mmol) was added. The reaction mixture was stirred for 24 h at 50 °C. After evaporating the ethanol, the resulting mixture was recrystallized from ethyl acetate to give *N*-(2-pyrrolidene)-1-adamantylamine (HL^6) as a white powder in 92.9% yield (5.17 g, 22.64 mmol). ^{1}H NMR (C_6D_6) δ: 1.66–1.71 (m, 6H, CH_2), 1.86 (d, 6H, $J = 2.4$ Hz, N–CH_2), 2.12 (br s, 3H, CH), 6.22 (dd, $J = 3.2$ and 2.8 Hz, 1H, pyrrole-4-H), 6.44 (d, $J = 1.6$ Hz, 1H, pyrrole-3-H), 6.55 (d, $J = 3.2$ Hz, 1H, pyrrole-5-H), 8.07 (s, 1H, CH=N), 9.10 (brs, 1H, NH). ^{13}C NMR (C_6D_6) δ: 29.62, 36.46, 43.27, 56.39, 109.31, 112.88, 120.49, 131.50, 145.09. Anal. Calc. for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.73; H, 8.78; N, 12.36%.

4.8. Preparation of $(L^1)_2Hf(CH_2Ph)_2$ (**1a**) (mixture)

To a stirred solution of $Hf(CH_2Ph)_4$ (127 mg, 0.234 mmol) in toluene (8 ml) at −78 °C with shielded light, a solution of HL^1 (99 mg, 0.468 mmol) in toluene (4 ml) was added dropwise over a 5 min period under an argon atmosphere and stirred for 3h. The reaction mixture was allowed to warm to −30 °C and stored overnight. The resulting mixture was evaporated at 0 °C to obtain 150 mg of an orange solid as a crude mixture. ^{1}H NMR (C_6D_6) δ: 1.05–1.28 (m, CH_3), 2.61–2.80 (m, CH), 2.73 (s, CH_2), 6.35–7.49 (m, Ar–H + pyrrole-H), 7.72–7.73 (m, CH=N). ^{13}C NMR (C_6D_6) δ: 23.51, 23.60, 23.73, 33.44, 33.63, 82.70, 113.69, 114.64, 121.68, 121.85, 121.94, 122.33, 122.39, 125.81, 126.12, 126.24, 126.36, 128.11, 128.23, 128.87, 138.84, 139.87, 141.30, 146.05, 146.43, 158.43, 158.92.

4.9. Preparation of $(L^3)_2Hf(CH_2Ph)_2$ (**3a**)

To a stirred solution of $Hf(CH_2Ph)_4$ (203 mg, 0.374 mmol) in toluene (10 ml) at −78 °C with shielded light, a solution of HL^3 (102 mg, 0.748 mmol) in toluene (5 ml) was added dropwise over a 5 min period under an argon atmosphere and stirred for 3 h. The reaction mixture was allowed to warm to −30 °C and stored overnight. The resulting mixture was evaporated at 0 °C. The solid was washed with toluene (0.5 ml)/*n*-pentane (5 ml) at −30 °C to give an orange solid (38 mg, 0.061 mmol) in 16.3% yield. ^{1}H NMR (C_6D_6) δ: 0.64 (d, $J = 6.8$ Hz, 12H, CH_3), 2.83 (s, 4H, CH_2Ph), 3.17 (q, $J = 6.8$ Hz, 2H, CH), 6.47 (dd, $J = 3.6$ and 2.0 Hz, 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). ^{13}C NMR (C_6D_6) δ: 22.47, 54.50, 82.15, 113.48, 119.48, 121.43, 125.23, 128.87, 138.99, 140.01, 146.28, 158.30.

4.10. Preparation of $(L^4)_2Hf(CH_2Ph)_2$ (**4a**)

To a stirred solution of $Hf(CH_2Ph)_4$ (310 mg, 0.571 mmol) in toluene (10 ml) at −78 °C with shielded light, a solution of HL^4 (266 mg, 1.145 mmol) in toluene (10 ml) was added dropwise over a 5 min period under an argon atmosphere and stirred for 3 h. The reaction mixture was allowed to warm to −30 °C and stored for 4 days. The resulting mixture was evaporated at 0 °C. The solid was recrystallized with a mixture of toluene (0.5 ml) and *n*-pentane (5 ml) at −30 °C to give a red-orange powder (285 mg, 0.346 mmol) in 60.7% yield. ^{1}H NMR (C_6D_6) δ: 0.69–1.09 (m, 28H, $CH_3 + CH_2 + CH$ (0.85: s (CH_3)), 1.48–1.51 (m, 4H, CH_2), 1.61–1.64 (m, 4H, CH_2), 2.64 (s, 4H, CH_2-Ph), 2.69–2.76 (m, 2H, N–CH), 6.45 (dd, $J = 2.0$ and 1.0 Hz, 2H, pyrrole-4-H), 6.72 (d, $J = 2.4$ Hz, 2H, pyrrole-3-H), 6.87 (t, 2H, $J = 7.2$ Hz, Ar-H(*p*)), 7.05-7.25 (m, 8H, Ar–H(*o*) + Ar–H(*m*)), 7.51 (br s, 2H, pyrrole-3-H), 7.66 (s, 2H, CH=N). ^{13}C NMR (C_6D_6) δ: 26.38, 27.18, 31.72, 33.53, 47.12, 63.22, 81.98 (t, $J_{C-H} = 118$ Hz), 113.37, 119.24, 121.56, 125.23, 128.87, 139.01,140.22, 146.09, 158.60. Anal. Calc. for $C_{44}H_{60}N_{24}Hf$: C, 64.15; H, 7.34; N, 6.80. Found: C, 63.02; H, 7.29; N, 6.94%.

4.11. Preparation of $(L^4)_2Zr(CH_2Ph)_2$ (**4b**)

To a stirred solution of $Zr(CH_2Ph)_4$ (234 mg, 0.513 mmol) in toluene (8 ml) at −78 °C with shielded light, a solution of HL^4 (239 mg, 1.028 mmol) in toluene (7 ml) was added dropwise over a 5 min period under an argon atmosphere and stirred for 3 h. The reaction mixture was allowed to warm to −30 °C and stored overnight. The resulting mixture was evaporated at 0 °C to obtain a

crude orange solid. ^{1}H NMR (C_6D_6) δ: 0.71–1.03, (m, 28H, $CH_3 + CH_2 + CH$ (0.87: s (CH_3)), 1.54–1.70 (m, 8H, CH_2), 2.73 (s, 4H, CH_2–Ph), 2.69–2.76 (m, 2H, N–CH), 6.45 (d, $J = 1.2$ Hz, 2H, pyrrole-4-H), 6.76 (d, $J = 1.2$ Hz, 2H, pyrrole-3-H), 6.83 (t, 2H, $J = 7.2$ Hz, Ar–H(p)), 7.04–7.25 (m, 8H, Ar–H(o) + Ar-H(m)), 7.38 (d, $J = 8.0$ Hz, 2H, pyrrole-3-H), 7.59 (s, 2H, CH=N). ^{13}C NMR (C_6D_6) δ: 26.46, 27.21, 31.75, 33.88, 47.17, 62.68, 76.46 (t, $J_{C-H} = 121$ Hz), 112.83, 118.21, 123.43, 125.23, 126.06, 137.43, 138.56, 139.73, 142.73, 157.22.

4.12. Preparation of $(L^5)_2Hf(CH_2Ph)_2$ (**5a**)

To a stirred solution of $Hf(CH_2Ph)_4$ (0.545 g, 1.00 mmol) in toluene (15 ml) at −78 °C with shielded light, a solution of HL^5 (0.300 g, 2.00 mmol) in toluene (5 ml) was added dropwise over a 5 min period under an argon atmosphere and stirred for 3 h. The reaction mixture was allowed to warm to −30 °C and stored overnight. The resulting mixture was evaporated at 0 °C. The solid was recrystallized from toluene (0.5 ml)/*n*-pentane (5 ml) at −78 °C to give orange crystals (0.458 g, 0.694 mmol) in 69.4% yield. Single crystals of **5a**, suitable for an X-ray structure determination were obtained by cooling a toluene/pentane (1/10) solution of **5a** to −78 °C. ^{1}H NMR (C_6D_6) δ: 0.83 (s, 18H, *t*-Bu), 2.59, 2.80 (AB q, $J = 12.0$ Hz, 4H, CH_2Ph), 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-3-H), 7.84 (s, 2H, CH=N). ^{13}C NMR (C_6D_6) δ: 29.90, 58.38, 84.23, 113.91, 120.92, 121.46, 126.48, 127.84, 138.66, 139.98, 149.98, 158.44. Anal. Calc. for $C_{32}H_{40}N_4Hf$: C, 58.27; H, 6.11; N, 8.49. Found: C, 57.75; H, 6.20; N, 8.22%.

4.13. Preparation of the cationic complex **5a***

One equivalent of $B(C_6F_5)_3$ was added to **5a** in bromobenzene-d_5 at −30 °C under an argon atmosphere. ^{1}H NMR (C_6D_5Br, −25 °C) δ: 0.90 (s, 18H, *t*-Bu), 2.54 (s, 2H, BCH_2), 3.66 (s, 2H, $HfCH_2$), 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). ^{13}C NMR (C_6D_5Br, −25 °C) δ: 29.86, 61.11, 83.12, 117.48, 134.86, 141.87, 143.55, 147.53, 149.70, 159.42. ^{19}F NMR (C_6D_5Br, −25 °C) δ: −130.25 (*o*-F), −162.93 (*p*-F), −165.71 (*m*-F).

4.14. Preparation of $(L^5)_2Zr(CH_2Ph)_2)_2$ (**5b**)

To a stirred solution of $Zr(CH_2Ph)_4$ (456 mg, 1.00 mmol) in toluene (15 ml) at −78 °C with shielded light, a solution of HL^5 (0.300 g, 2.00 mmol) in toluene (5 ml) was added dropwise over a 5 min period under an argon atmosphere and stirred for 3 h. The reaction mixture was allowed to warm to −30 °C and stored overnight. The resulting mixture was evaporated at 0 °C. The solid was recrystallized from toluene (0.5 ml)/*n*-pentane (5 ml) at −78 °C to give a red powder (265 mg, 0.463 mmol) in 46.3% yield. ^{1}H NMR (C_6D_6) δ: 0.85 (s, 18H, *t*-Bu), 2.92, 3.10 (AB q, $J = 11.6$ Hz, 4H, CH_2Ph), 6.51 (dd, $J = 2.0$ and 1.2 Hz, 2H, pyrrole-4-H), 6.77 (dd, $J = 3.2$ and 1.6 Hz, 2H, pyrrole-3-H), 6.86–7.20 (m, 10H, Ar–H), 7.73 (br s, 2H, pyrrole-5-H), 7.76 (s, 2H, CH=N). (Additional complicated multiplets were observed at 0.87–1.30 ppm.) ^{13}C NMR (C_6D_6) δ: 29.97, 57.82, 81.98 (t, $J_{C-H} = 121$ Hz), 113.42, 121.32, 125.23, 126.88, 128.87, 138.73, 139.64, 147.83, 157.89. Anal. Calc. for $C_{32}H_{40}N_4Zr$: C, 67.20; H, 7.05; N, 9.80. Found: C, 65.75; H, 6.90; N, 9.91%.

4.15. Preparation of cationic complex **5b***

One equivalent of $B(C_6F_5)_3$ was added to **5b** in bromobenzene-d_5 at −30 °C under an atmosphere of argon. ^{1}H NMR (C_6D_5Br, −25 °C) δ: 0.82–1.42 (m), 3.55 (br s), 6.27–7.48 (m), 7.99–8.31 (m). ^{13}C NMR (C_6D_5Br, −25 °C, selected peaks) δ: 29.84, 61.85, 65.05, 116.32, 135.44, 137.83, 141.87, 147.28, 148.86, 149.76, 158.07. ^{19}F NMR (C_6D_5Br, −25 °C) δ: −130.41 (*o*-F), −162.59 (*p*-F), −165.55 (*m*-F).

4.16. Preparation of $(L^6)_2Hf(CH_2Ph)_2$ (**6a**)

To a stirred solution of $Hf(CH_2Ph)_4$ (1.082 g, 1.99 mmol) in toluene (20 ml) at −78 °C with shielded light, a solution of HL^6 (0.910 g, 3.99 mmol) in toluene (20 ml) was added dropwise over a 5 min period under an argon atmosphere and stirred for 2 h. The reaction mixture was allowed to warm to −30 °C and stored for 2 days. The resulting mixture was evaporated at 0 °C. The solid was recrystallized from toluene (0.5 ml)/*n*-pentane (5 ml) at −30 °C to give orange crystals (0.884 g, 1.08 mmol) in 54.2% yield. Single crystals of **6a**, suitable for a crystal structure determination were obtained from a toluene solution of **6a**. ^{1}H NMR (C_6D_6) δ: 1.34–1.97 (m, 30H, adamantyl), 2.65, 2.89 (AB q, $J = 12.0$ Hz, 4H, CH_2Ph), 6.49 (dd, $J = 3.2$ and 2.4 Hz, 2H, pyrrole-4-H), 6.78 (d, $J = 2.4$ Hz, 2H, pyrrole-3-H), 6.88 (t, $J = 7.2$ Hz, 2H, Ar–H(p)), 7.03, 7.09 (d, $J = 7.2$ Hz, 4H, Ar–H(o)), 7.10-7.18 (m, 4H, Ar–H(m)), 7.70 (br s, 2H, pyrrole-3-H), 7.92 (s, 2H, CH=N). ^{13}C NMR (C_6D_6) δ: 20.96, 29.57, 35.59, 42.70, 59.26, 84.67 (t, $J_{C-H} = 116$ Hz), 113.78, 120.82, 125.23, 126.59, 128.87, 139.09, 139.62, 149.28, 157.26. Anal. Calc. for $C_{44}H_{52}N_4Hf$: C, 64.78; H, 6.42; N, 6.87. Found: C, 64.21; H, 6.78; N, 6.91%.

4.17. Preparation of cationic complex **6a***

One equivalent of $B(C_6F_5)_3$ was added to **6a** in bromobenzene-d_5 at −30 °C under an argon atmosphere.

^{1}H NMR (C_6D_5Br, −25 °C) δ: 1.27–2.10 (m, 30H, adamantyl), 2.61 (s, 2H, BCH_2), 3.67 (s, 2H, $HfCH_2$), 6.41–7.78 (m, 16H, Ar–H), 8.27 (br s, 2H, CH=N). ^{13}C NMR (C_6D_5Br, −25 °C) δ: 21.69, 29.49, 35.13, 42.67, 61.04, 83.84, 116.82, 135.51, 137.69, 138.89, 147.38, 148.95, 149.81, 159.37. ^{19}F NMR (C_6D_5Br, −25 °C) δ: −130.27 (*o*-F), −163.00 (*p*-F), −165.85 (*m*-F).

4.18. Preparation of $(L^6)_2Zr(CH_2Ph)_2$ (**6b**)

To a stirred solution of $Zr(CH_2Ph)_4$ (460 mg, 1.01 mmol) in toluene (10 ml) at −78 °C with shielded light, a solution of HL^6 (461 mg, 2.02 mmol) in toluene (10 ml) was added dropwise over a 5 min period under an argon atmosphere and stirred for 2 h. The reaction mixture was allowed to warm to −30 °C and stored overnight. The resulting mixture was evaporated at 0 °C. The solid was recrystallized from toluene (0.5 ml)/*n*-pentane (5 ml) at −30 °C to give a red-orange powder (0.531 g, 0.729 mmol) in 72.2% yield. Single crystals of **6b**, suitable for a crystal structure determination were obtained from a benzene solution of **6b**. ^{1}H NMR (C_6D_6) δ: 1.39–1.70 (m, 30H, adamantyl), 2.99, 3.20 (AB q, $J = 11.2$ Hz, 4H, CH_2Ph), 6.51 (dd, $J = 2.8$ and 2.0 Hz, 2H, pyrrole-4-H), 6.78 (d, $J = 2.8$ Hz, 2H, pyrrole-3-H), 6.89-6.91 (m, 2H, Ar–H(*p*)), 7.09-7.37 (m, 8H, Ar–H(*o*) and Ar–H(*m*)), 7.76 (br s, 2H, pyrrole-3-H), 7.83 (s, 2H, CH=N). ^{13}C NMR (C_6D_6) δ: 20.96, 29.60, 35.63, 42.85, 58.76, 82.93 (t, $J_{C-H} = 116$ Hz), 113.33, 120.81, 121.34, 125.23, 128.87, 139.05, 139.31, 147.96, 156.66. Anal. Calc. for $C_{44}H_{52}N_4Zr$: C, 72.58; H, 7.20; N, 7.69. Found: C, 72.73; H, 7.05; N, 7.98%.

4.19. Preparation of cationic complex **6b***

One equivalent of $B(C_6F_5)_3$ was added to **6b** in bromobenzene-d_5 at −30 °C under an argon atmosphere. ^{1}H NMR (C_6D_5Br, −25 °C) δ: 1.00–2.30 (m), 3.56 (br s), 6.15–7.80 (m), 7.90–8.55 (m). ^{13}C NMR (C_6D_5Br, −25 °C, selected peaks) δ: 21.69, 28.97, 29.51, 35.17, 42.14, 61.58, 115.94, 137.70, 137.83, 138.91, 147.33, 148.86, 149.70. ^{19}F NMR (C_6D_5Br, −25 °C) δ: −130.51 (*o*-F), −162.54 (*p*-F), −165.54 (*m*-F).

Table 3
Summary of crystallographic data for complexes **6a** and **6b**

Complex	**6a**	**6b**
Crystal data		
Empirical formula	$C_{44}H_{52}N_4Hf \cdot 2C_6H_6$	$C_{44}H_{52}N_4Zr \cdot 2C_6H_6$
Formula weight	971.60	884.33
Crystal color, habit	Orange, plate	Red, prism
Crystal dimensions (mm)	$0.1 \times 0.3 \times 0.3$	$0.9 \times 0.9 \times 0.9$
Crystal system	Monoclinic	Monoclinic
a (Å)	13.307(1)	13.070(1)
b (Å)	9.5690(7)	9.6256(5)
c (Å)	19.271(1)	19.255(1)
β (°)	99.905(1)	101.742(8)
U (Å^3)	2417.3(3)	2371.8(3)
Space group	$P2/c$ (no. 13)	$P2/c$ (no. 13)
Z	4/2	4/2
D_{calc} (mg/m^3)	1.335	1.238
$F(000)$	1000	936
μ (Mo Kα) (mm^{-1})	2.198	0.273
Data collection		
λ (Mo Kα radiation) (Å)	0.71073	0.71073
Temperature (K)	203(2)	293(2)
$2\theta_{max}$	56.7	56.0
Number of total reflections	14,236	9456
Number of unique reflections	5492 ($R_{int} = 0.0862$)	5712 ($R_{int} = 0.0172$)
Structure solution and refinement		
Number of observations ($I > 2\sigma(I)$)	4766	4519
Number of variables	271	270
Reflection/parameter ratio	20	21
Final R indices ($I > 2\sigma(I)$); R_1, wR_2	0.0419, 0.1024	0.0409, 0.1068
Final R indices (all data) R_1, wR_2	0.0528, 0.1140	0.0599, 0.1158
Goodness-of-fit	1.101	1.061
Maximum peak in final difference map (e/Å^3)	2.129	0.425
Minimum peak in final difference map (e/Å^3)	–0.969	–0.625

4.20. Polymerization procedure

The ethylene polymerization was carried out at 25 °C under atmospheric pressure in a 500-ml glass reactor equipped with a propeller-like stirrer. The solvent (250 ml: toluene or *n*-heptane) was introduced into the nitrogen-purged reactor and stirred (600 rpm). The solvent was thermostated to a prescribed polymerization temperature, and then the monomer gas feed (100 l/h) was started. After 15 min, polymerization was initiated by adding a toluene solution of the cocatalyst followed by catalyst solution in toluene into the reactor with vigorous stirring (600 rpm). After 5 min, isobutanol (10 ml) was added to terminate the polymerization and the ethylene gas feed was stopped. To the resulting mixture, methanol (1000 ml) and conc. HCl (2 ml) were added. The polymer was collected by filtration, washed with methanol (200 ml) and dried in vacuo at 80 °C for 10 h.

4.21. Crystal structure analysis of **6a** and **6b**

For **6a**, the dataset was obtained with a Bruker AXS diffractometer at 203 K in the ω-scan mode. The data correction was carried out using the program system SAINT [28]. The structure was solved by direct methods and difference Fourier syntheses using the program system SHELXS-86 [29a]. The crystal contains two independent solvent molecules of benzene, which is partially disordered. The refinement based on F^2 was carried out using the program SHELXL-97 [29b]. Anisotropic thermal parameters were refined for the non-hydrogen atoms (except for the disordered groups). Hydrogen atoms were included into calculated positions, except for the hydrogen atoms of the benzyl groups which were refined in their position with isotropic thermal parameters. For **6b**, the dataset was obtained with an Enraf-Nonius diffactometer at 293 K in the ω-scan mode. The data correction was carried out using the program system WINGX [30]. The structure was solved by isotypic replacement using the coordinates of **6a**. Only the hydrogen atoms of the benzyl groups are refined in their position; the remaining hydrogen atoms were included into calculated positions. Results of the structure determination are given in Table 3.

5. Supporting information

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-220522 (HL^1) CCDC-220523 (HL^4), CCDC-220524 (**6a**), CCDC-220525 (**6b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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