

边臂修饰的水杨醛亚胺第四族金属配合物的合成、结构 及其乙烯聚合行为研究

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摘要 通过给电子基团取代的(*E*)-2,4-二-叔丁基-6-(苯基亚胺基甲基)苯酚与等当量的 $M(\text{CH}_2\text{Ph})_4$ 反应制备了一系列第四族金属的双苯基配合物. 反应经历了甲苯消除及分子内苯基从金属至亚胺碳的迁移反应, 中间体的分离和结构鉴定证实了该反应历程. 通过核磁、元素分析和 X-ray 单晶衍射表征了配合物的结构. 在甲基铝氧烷(MMAO)的活化下, 钛配合物可以高活性地催化乙烯的均聚合和乙烯/1-己烯的共聚合, 而相应的锆、铪的配合物在同样的条件下则几乎没有活性.

关键词 乙烯聚合; 乙烯/己烯共聚合; 第四族金属配合物; 水杨醛亚胺; 分子内迁移

Synthesis, Structure and Ethylene Polymerization Behavior of Group 4 Metal Complexes Bearing Salicylaldaminato Ligands with Appended Donor Functionality

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Abstract A series of group 4 metal complexes were synthesized by an equimolar reaction of $M(\text{CH}_2\text{Ph})_4$ with (*E*)-2,4-di-*tert*-butyl-6-[(phenylimino)methyl]phenol bearing donor functionality. This process involved toluene elimination followed by an intramolecular migration reaction of one benzyl group from metal to the imino carbon, which was supported by the isolation and structural characterization of the intermediate. These new complexes were fully characterized by multi-nuclear NMR spectroscopy, elemental analyses and X-ray analyses. The titanium complexes showed a very high activity in both ethylene polymerization and ethylene/1-hexene copolymerization upon activation with modified methylaluminoxane (MMAO), whereas the corresponding zirconium and hafnium complexes were almost inactive under the same reaction conditions.

Keywords ethylene polymerization; ethylene/1-hexene copolymerization; group 4 metal complex; salicylaldaminato; intramolecular migration

1 Introduction

Single-site catalysts based on the group 4 metallocenes have been extensively studied in the past decades.^[1,2] On the other hand, there has been a growing interest in developing new non-metallocene catalysts,^[3-9] in which complexes bearing phenoxyimine ligands are the promising examples.^[7,8] For instance, Fujita found that bis[*N*-(3-*tert*-

butylsalicylidene)-anilinato] titanium(IV) dichloride complexes were excellent precatalysts for ethylene polymerization,^[7a] and the corresponding bis[*N*-(3-*tert*-butylsalicylidene)-anilinato]zirconium(IV) dichloride displayed an ultra high ethylene polymerization activity of 5.50×10^8 g/(mol·atm·h) with a viscosity average molecular weight of 0.9×10^4 at 25 °C.^[7c] Recently, we disclosed a series of catalysts (Chart 1) in which a hard salicylaldiminato ligand

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was combined with a soft side-arm donor.^[9] Even at low Al/Ti ratio, these catalysts were highly active for ethylene homopolymerization and copolymerization with α -olefin or norbornene.^[9a-9d] Furthermore, some of them were also highly active in promoting the incorporation of 10-undecenol or 10-undecenoic acid into polyethylene backbone without the pretreatment of the comonomer with trialkylaluminum.^[9e] However, many attempts to synthesize its zirconium and hafnium analogues for comparison in polymerization/copolymerization activity failed, giving a mixture of inseparable products. It seemed that the salt metathesis method, which worked well for the preparation of the Ti complexes,^[9] could not be applied to the Zr and Hf analogues. We then tried to use alkane elimination method to prepare the corresponding group 4 metal alkyls. Unprecedentedly, a series of group 4 metal dibenzyls were isolated in high yields when treatment of salicylaldehydeimine with $M(\text{CH}_2\text{Ph})_4$. Their synthesis, structure and ethylene polymerization behaviors are reported in this article.

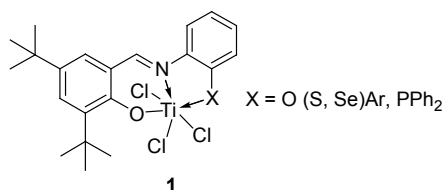
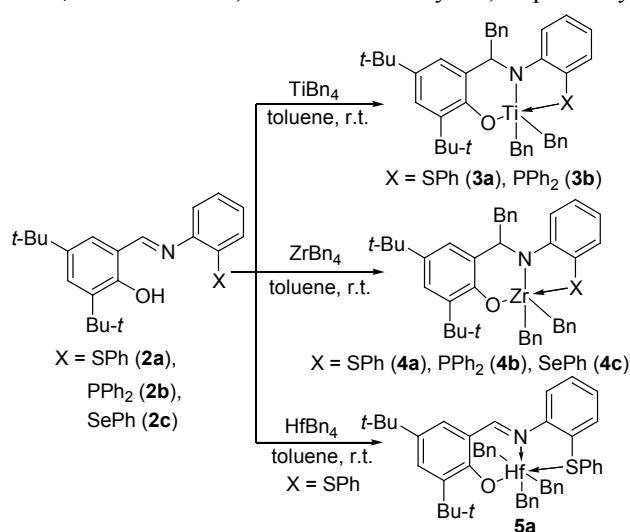


Chart 1 [ONX]TiCl₃ complexes

2 Results and discussion

2.1 Synthesis and characterization

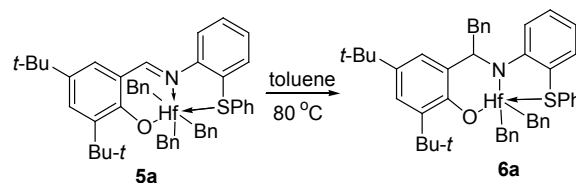
Alkane elimination reaction serves as an efficient method for the synthesis of group 4 metal alkyls.^[10] Treatment of ZrBn_4 ($\text{Bn}=\text{CH}_2\text{Ph}$) with 1 equiv. of salicylaldehydeimine **2a** at room temperature gave an unexpected zirconium dibenzyl complex **4a** in 85% yield, rather than the expected tribenzylzirconium species $[\text{NOS}]\text{ZrBn}_3$ (Scheme 1). Similar phenomenon was observed in other ligand systems.^[11-14] Accordingly, complexes **4b** and **4c** were synthesized in the same manner from the reaction of ZrBn_4 with **2b** and **2c**, in 81% and 78% yield, respectively.



Scheme 1 Synthesis of group 4 metal complexes 3–5

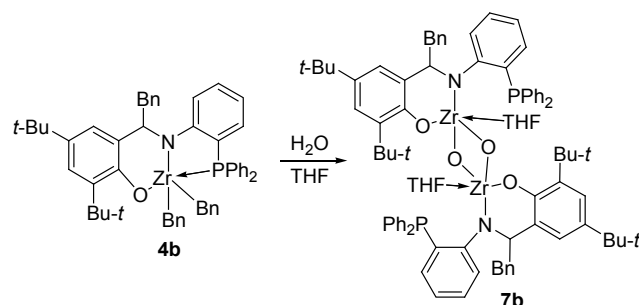
The ¹H NMR spectroscopy at $-30\text{ }^\circ\text{C}$ indicated the initial formation of a tribenzyl zirconium complex which was then converted to the product **4a**. Many attempts to isolate this intermediate were not successful.

The corresponding titanium and hafnium dibenzyl complexes were also prepared by the same method aforementioned. Treatment of **2a–2b** with 1 equiv. of TiBn_4 in toluene at room temperature led to the formation of the dibenzyl titanium complexes **3a–3b** as dark red needle crystals in 83% and 88% yields. The reaction proceeded so fast that the tribenzyl titanium intermediate was not observed by ¹H NMR spectroscopy even at $-30\text{ }^\circ\text{C}$. On the other hand, reaction of **2a** with 1 equiv. of HfBn_4 in toluene at room temperature afforded the tribenzyl hafnium complex **5a** in 77% isolated yield as red crystals. Complex **5a** is stable at room temperature for several weeks, which could be attributed to the higher stability of the $\text{Hf}-\text{C}$ bond over the corresponding $\text{Zr}-\text{C}$ and $\text{Ti}-\text{C}$ ones.^[12c] Upon heating a toluene solution at $80\text{ }^\circ\text{C}$, **5a** was quantitatively converted into the dibenzyl hafnium complex **6a** (Scheme 2). During this process, the color of the solution was gradually changed from red to yellow.



Scheme 2 Intramolecular benzylation of salicylaldehydeimine ligated hafnium tribenzyls (**5a**)

Complexes **3** and **4** are thermally stable. No ligand redistribution was observed even if they were heated at $110\text{ }^\circ\text{C}$ in toluene for several hours. However, they are sensitive to moisture. A trace amount of H_2O in THF led to the partial hydrolysis of dibenzyl zirconium complex **4b**, producing crystals that were identified as **7b** by X-ray analyses (Figure 1).^[15] Its spectroscopic data were not obtained owing to insufficient amount of materials.



Scheme 3 Hydrolysis of the zirconium benzyl complex (**4b**)

Complexes **3a**, **3b**, **4a**, **4c**, **5a** and **6a** were fully characterized by spectroscopic techniques and elemental analyses. The ¹H NMR spectra of **3a**, **3b**, **4a**, **4c** and **6a** essentially displayed the same pattern, indicating clearly that the imino group was benzylated. The most informative spectroscopic data were the three sets of benzyl signals. Methylene protons of the benzyl group attached to the carbon adjacent to the nitrogen atom appeared as an ABX pattern,

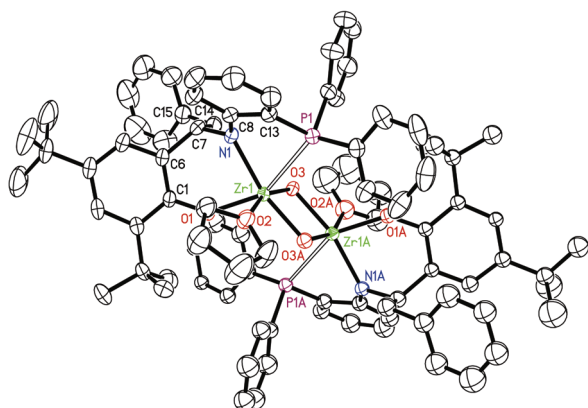


Figure 1 Molecular structure of $\{[NOP]ZrO(THF)\}_2$ (**7b**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)—O(1) 2.002(3), Zr(1)—N(1) 2.217(3), Zr(1)—O(2) 2.375(3), Zr(1)—O(3) 1.947(3), Zr(1)—O(3A) 2.036(3), Zr(1)—P(1) 2.8138(12), O(3)—Zr(1)—O(2) 159.07(11), O(1)—Zr(1)—P(1) 147.65(9), O(3)—Zr(1)—O(3A) 79.61(12), C(7)—N(1)—C(8) 117.0(3), C(7)—N(1)—Zr(1) 114.4(3), C(8)—N(1)—Zr(1) 123.6(3)

whereas the methylene protons of the other two non-equivalent benzyl groups were diastereotopic and an AA'BB' system was observed in the ^1H NMR spectra.

The molecular structures of **3a**, **3b**, **4a**, **4c**, **5a** and **6a** were further confirmed by single-crystal X-ray analyses and are shown in Figures 2—7, respectively. Key structural data of these complexes were listed in Table 1. The metal atom in complexes **3a**, **3b**, **4a**, **4c** and **6a** adopts a distorted trigonal-bipyramidal geometry, which can be further tested by the corresponding τ ratios (0.6—0.8).^[16] The hafnium complex **5a** possesses a distorted-octahedral geometry. In all structures, the heteroatoms of the side arms are coordinated to the central metal atoms, resulting in a tridentate ligating sphere. The distances of M—O and M—N bonds fall in the range often observed for group 4 metal-oxygen and -nitrogen bond distances.^[6f,17] All the nitrogen atoms are almost planar as judged by the sum of angles around the nitrogen atoms:^[12-14] 358.7° in **3a**, 359.3° in **3b**, 359.2° in **4a**, 358.1° in **4c**, and 359.3° in **6a**, suggesting that the alkylamino group serves as a strong electron donor to the central metal. The M—S bond

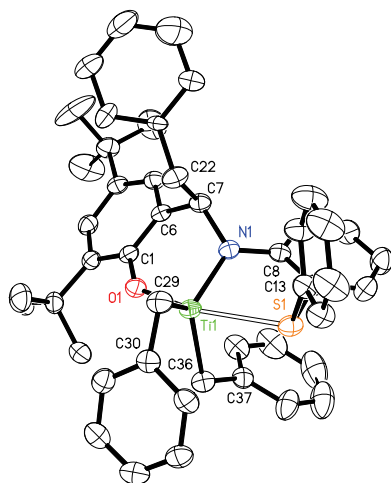


Figure 2 Molecular structure of $[NOS]TiBn_2$ (**3a**). Hydrogen atoms are omitted for clarity

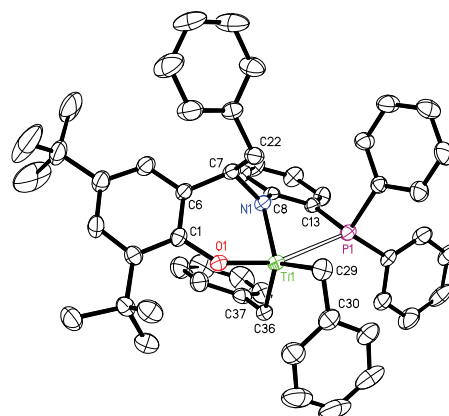


Figure 3 Molecular structure of $[NOP]TiBn_2$ (**3b**). Hydrogen atoms are omitted for clarity

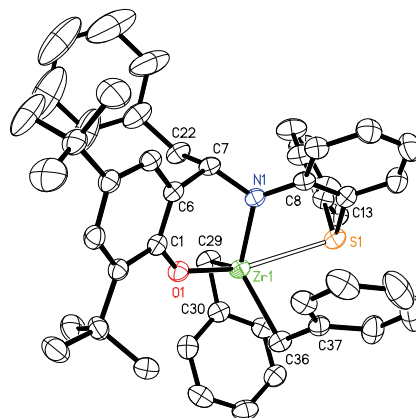


Figure 4 Molecular structure of $[NOS]ZrBn_2$ (**4a**). Hydrogen atoms are omitted for clarity

distances are 2.710(1) Å in **3a**, 2.792(1) Å in **4a**, and 2.771(2) Å in **6a**, which are significantly shorter than the Hf—S bond distance of 2.975(3) Å in **5a** due to the differences in coordination number.^[18]

Notably, the three heteroatoms and group 4 metal atom in all structures are co-planar, in which the ligand exhibits a “pincer” like system.^[19] For instance, the sum of the angles of O(1)—Ti(1)—N(1) [88.99(11)°] and N(1)—Ti(1)—S(1) [75.73(8)°] in complex **3a** is almost equal to that of O(1)—Ti(1)—S(1) [163.03(8)°]. As a result, the coordination sphere around the metal center is quite open, and the C—M—C angles [122.4(1)° in **3a**, 126.0(2)° in **3b**, 123.8(1)° in **4a**, 124.1(5)° in **4c**, and 123.2(2)° in **6a**] are very large.^[14,20]

The coordinative unsaturation around the metal center is thus compensated by the coordination of the ipso carbon of the benzyl group (all the M—C—C_{ipso} angles are listed in Table 1). Taking **3a** for example, one M—C—C_{ipso} angle is 89.1(2)° whereas the other is 112.7(2)°. The similar results are observed in **3b**, **4a** and **6a**, suggesting that one benzyl group may be involved in η^2 -binding interactions with the metal atom and the other is η^1 -bound to the metal.^[14,21] On the other hand, the two M—C—C_{ipso} angles in complex **4c** are 92.3(9)° and 108.5(9)°, indicating a weakened

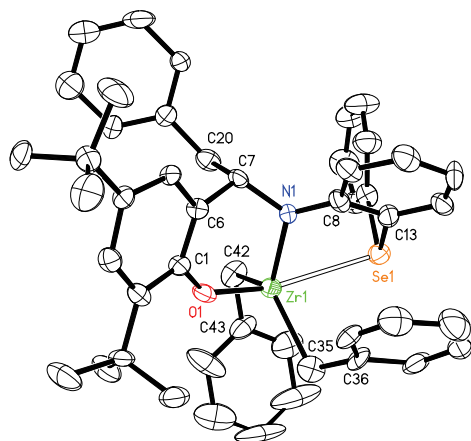


Figure 5 Molecular structure of [NOSe]ZrBn₂ (**4c**). Hydrogen atoms are omitted for clarity

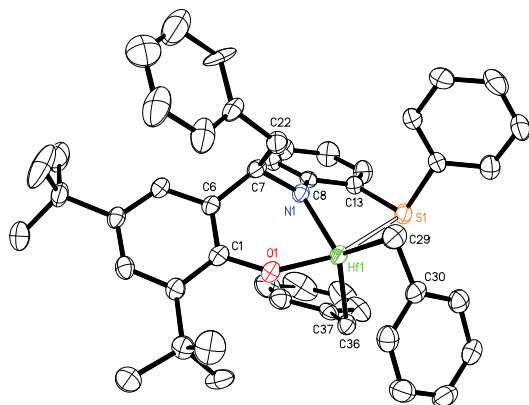


Figure 6 Molecular structure of [NOS]HfBn₃ (**5a**). Hydrogen atoms are omitted for clarity

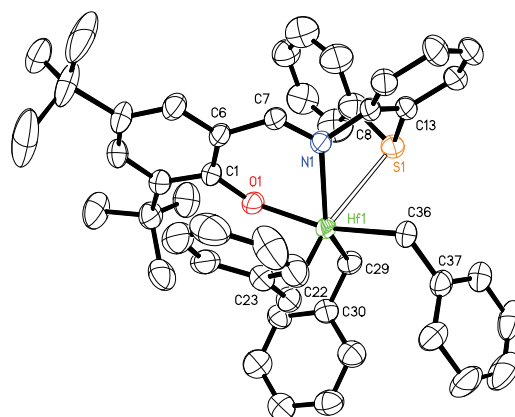


Figure 7 Molecular structure of [NOS]HfBn₂ (**6a**). Hydrogen atoms are omitted for clarity

η^2 -binding between zirconium atom and benzyl group.^[22] It is noted that all three benzyls in **5a** are η^1 -bound to the Hf atom as judged by Hf-Cipso distances (>3.08 Å) and Hf-C-Cipso angles ($>108^\circ$).^[23]

2.2 Olefin polymerization

The catalytic properties of complexes **3**–**6** in ethylene polymerization was examined in the presence of MMAO (MMAO=modified methylaluminumoxane). The results were compiled in Table 2. The titanium complexes **3a**, **3b** showed a very high activity at 30 °C (Entries 1–5).^[9] X group has great influence on the catalytic behavior. When X is SPh, an activity of 1.99×10^6 g/(mol·atm·h) was achieved. Replacing the SPh group with PPh₂ group reduced the activity to 0.82×10^6 g/(mol·atm·h). Increasing Al/Ti ratio from 500 to 2000 had a little impact on activity. However, decreasing the molecular weight of the polymer

Table 1 Selected bond distances (Å) and angles (°)

	3a (Ti)	3b (Ti)	4a (Zr)	4c (Zr)	5a (Hf)	6a (Hf)
M—O(1)	1.828(2)	1.839(2)	1.949(2)	1.964(8)	1.988(7)	1.938(3)
M—N(1)	1.958(3)	1.943(3)	2.111(2)	2.100(9)	2.321(9)	2.089(4)
M—C(29)	2.140(3)	2.149(4)	2.284(3)	2.243(12)	2.283(12)	2.254(5)
M—C(36)	2.141(3)	2.123(3)	2.271(3)	2.263(14)	2.328(11)	2.249(5)
M—X(S, P, Se)	2.710(1)	2.718(1)	2.792(1)	2.919(2)	2.975(3)	2.771(2)
N(1)—C(7)	1.492(4)	1.478(4)	1.482(3)	1.511(13)	1.288(14)	1.486(6)
O(1)—M—N(1)	89.0(1)	89.7(1)	84.8(1)	85.0(3)	76.6(3)	85.8(1)
N(1)—M—X	75.7(1)	71.0(1)	72.7(1)	72.9(2)	65.7(2)	73.4(1)
O(1)—M—X	163.0(1)	160.28(8)	155.7(1)	155.7(2)	102.6(2)	157.6(1)
O(1)—M—C(29)	102.6(1)	99.0(1)	103.8(1)	101.6(4)	101.3(4)	103.4(2)
O(1)—M—C(36)	99.1(1)	99.8(1)	99.0(1)	97.1(5)	154.9(4)	98.7(2)
C(29)—M—C(36)	122.4(1)	126.0(2)	123.8(1)	124.1(5)	—	123.2(2)
C(8)—N(1)—C(7)	117.3(3)	117.6(3)	117.5(2)	116.9(9)	114.8(9)	118.0(4)
C(8)—N(1)—M	123.3(2)	122.6(2)	124.4(2)	124.0(7)	121.3(7)	124.2(3)
C(7)—N(1)—M	118.1(2)	118.1(2)	117.2(2)	117.2(6)	123.9(7)	117.1(3)
C(30)—C(29)—M	89.1(2)	88.0(2)	85.2(2)	92.3(9)	109.8(9)	86.7(3)
C(37)—C(36)—M	112.7(2)	115.2(2)	106.2(2)	108.5(9)	112.1(8)	109.2(3)

was observed with the increase of Al/Ti ratio, indicating that the chain transfer mainly to aluminum occurred during the chain propagation. **3a** showed a very good thermal stability since the activity remained almost the same when the ethylene polymerization was performed at an elevated temperature (Entries 7 and 8). Bochmann and coworkers reported that zirconium complexes derived from $\text{HOC}_6\text{H}_3\text{-2-Bu-}t\text{-6-CH=NC}_6\text{H}_4\text{PPh}_2\text{-3}$ were highly active to polymerize ethylene.^[24] In sharp contrast, the corresponding Zr and Hf complexes **4–6** exhibited no catalytic activity (Entries 9–13).

Table 2 Ethylene polymerization catalyzed by group 4 metal dibenzyls^a

Entry	Cat./M	Cocat. ^b /equiv.	Temp./°C	Yield/g	M_w^c	PDI ^c	Activity ^e
1	3a /Ti	500	30	1.31	36 ^d	—	1.31
2	3a /Ti	1000	30	1.52	28.6	2.24	1.52
3	3a /Ti	1500	30	1.99	11.6	3.10	1.99
4	3a /Ti	2000	30	1.83	9.6	3.31	1.83
5	3b /Ti	1500	30	0.82	51.8	2.29	0.82
6	3a /Ti	1500	0	0.98	82 ^d	—	0.98
7	3a /Ti	1500	50	1.74	7.2	3.26	1.74
8	3a /Ti	1500	70	1.63	5.6	2.76	1.63
9	4a /Zr	1500	30	0	—	—	0
10	4b /Zr	1500	30	0	—	—	0
11	4c /Zr	1500	30	0	—	—	0
12	5a /Hf	1500	30	0	—	—	0
13	6a /Hf	1500	30	0	—	—	0

^a Conditions: 1 atm of ethylene; toluene, 50 mL; catalyst, 4.0 μmol ; reaction time, 15 min. ^b MMAO, 1.88 mmol/mL in heptane. ^c Determined by gel permeation chromatography, 10^4 g/mol. ^d 10^6 g/(mol \cdot atm \cdot h) M_w , determined by high temperature viscometer. ^e 10^6 g/(mol \cdot atm \cdot h).

Since complex **3a** proved to be a very good catalyst for ethylene polymerization, its activity in copolymerization of ethylene with 1-hexene was also investigated. The results were summarized in Table 3. The comonomer incorporation^[25] rose from 14.6 mol% to 33.3 mol% with the increasing of initial concentration of 1-hexene from 0.2 mol/L to 1.6 mol/L.^[9] But the catalytic activity and the

Table 3 Copolymerization of ethylene with 1-hexene catalyzed by titanium complex **3a**^a

Entry	1-Hexene/ mmol	Temp/ °C	Yield/ g	Activ- ity ^b	$M_w^c/(10^4$ g \cdot mol ⁻¹)	PDI ^c	Incorporation ^d /mol%
1	10	25	0.82	8.2	17.6	2.17	14.6
2	20	25	0.81	8.1	10.7	2.14	21.4
3	40	25	0.85	8.5	10.6	1.99	29.0
4	80	25	0.86	8.6	9.5	2.05	33.3
5	10	0	0.60	6.0	25.2	1.95	14.4
6	10	50	0.86	8.6	4.5	1.85	15.3

^a Conditions: 1 atm of ethylene; toluene, 50 mL; Al/Ti=1500; catalyst, 4.0 μmol ; reaction time, 15 min; MMAO, 1.88 mmol/mL in heptane. ^b 10^5 g/(mol \cdot atm \cdot h). ^c Determined by gel permeation chromatography. ^d Determined by ¹³C NMR.

comonomer incorporation ratio were almost independent of the reaction temperatures (Entries 1, 5 and 6).

Significant differences in catalytic activities among group 4 metal complexes could be ascribed to the size effect. After activation with MMAO, the resultant Zr and Hf cationic complexes might be much less stable than the corresponding Ti one, which might subsequently undergo ligand redistribution to form inactive bisligated species.^[5-9]

3 Conclusion

Several group 4 metal dibenzyl complexes were directly synthesized from the reaction of MBn_4 with (*E*)-2,4-di-*tert*-butyl-6-[(phenylimino)methyl]phenol bearing donor functionalities via an intramolecular migration of a benzyl group from the metal center to the imine unit. The rate of such a migration was closely related to the size of group 4 metals, and the following order was observed: Ti > Zr > Hf. The Hf tribenzyl complex was stable at room temperature, which was converted to the corresponding Hf dibenzyl species upon heating. Accordingly, a benzyl migration mechanism was proposed. The titanium complexes exhibited a very high catalytic activity in both ethylene polymerization and copolymerization of ethylene with 1-hexene upon activation with MMAO. In contrast, the corresponding zirconium and hafnium complexes were inert toward ethylene polymerization under the same reaction conditions, probably due to the formation of bisligated species.

4 Experimental section

4.1 Preparation of [ONS]TiBn₂ (**3a**)

To a solution of TiBn_4 (418 mg, 1.0 mmol) in toluene (10 mL) was added dropwise **2a** (415 mg, 1.0 mmol) in toluene (5 mL) at room temperature, and the mixture was stirred for 4 h at room temperature. Concentration of the solution gave a crude product, which was recrystallized from toluene at -30 °C, affording **3a** as a dark red solid (615 mg, 83%). Crystals suitable for X-ray analyses were grown from a saturated toluene/hexane solution. ¹H NMR (400 MHz, C_6D_6) δ : 7.56–7.50 (m, 3H), 7.44 (t, $J=7.6$ Hz, 2H), 7.34 (d, $J=7.2$ Hz, 2H), 7.10–6.98 (m, 6H), 6.96–6.84 (m, 6H), 6.79 (d, $J=8.4$ Hz, 1H), 6.64–6.60 (m, 2H), 6.56–6.54 (m, 2H), 6.49 (ABd, $J=7.8$ Hz, 1H), 6.45 (ABd, $J=7.8$ Hz, 1H), 5.12 (dd, $J=10.0$, 5.6 Hz, 1H), 3.56–3.45 (m, 2H), 3.16 (d, $J=8.8$ Hz, 1H), 2.76 (d, $J=10.0$ Hz, 1H), 2.39 (d, $J=10.0$ Hz, 1H), 2.30 (d, $J=8.8$ Hz, 1H), 1.77 (s, 9H), 1.29 (s, 9H); ¹³C NMR (100 MHz, C_6D_6) δ : 160.2, 159.1, 145.3, 142.6, 139.9, 139.5, 136.5, 135.9, 135.1, 133.2, 132.1, 131.1, 130.3, 129.7, 129.6, 128.9, 128.3, 127.5, 127.0, 126.3, 125.7, 123.8, 122.5, 122.4, 120.2, 119.4, 112.1, 80.5, 71.6, 49.6, 35.5, 34.4, 31.7, 30.8. Anal. calcd for $\text{C}_{48}\text{H}_{51}\text{NOSTi}$ (**3a**): C 78.13, H 6.97, N 1.90; found C 78.07, H 6.84, N 1.77.

4.2 Preparation of [ONP]TiBn₂ (**3b**)

To a solution of TiBn_4 (412 mg, 1.0 mmol) in toluene (10 mL) was added dropwise **2b** (494 mg, 1.0 mmol) in toluene (5 mL) at room temperature, and the mixture was stirred for 12 h at room temperature. Concentration of the solution gave a crude product, which was recrystallized from toluene at -30 °C, affording **3b** as a yellow solid

(719 mg, 88%). Crystals suitable for X-ray analyses were grown from a saturated toluene/hexane solution. ^1H NMR (400 MHz, C_6D_6) δ : 7.79–7.72 (m, 4H), 7.54–7.47 (m, 5H), 7.38 (t, $J=7.4$ Hz, 1H), 7.22–7.01 (m, 9H), 6.94 (t, $J=7.8$ Hz, 1H), 6.86 (t, $J=10.0$ Hz, 1H), 6.82–6.80 (m, 2H), 6.75 (d, $J=2.4$ Hz, 1H), 6.55–6.49 (m, 6H), 6.46–6.40 (m, 1H), 4.81 (dd, $J=11.2, 3.6$ Hz, 1H), 3.56 (dd, $J=8.0, 4.8$ Hz, 1H), 3.44 (t, $J=12.8$ Hz, 1H), 3.24 (dd, $J=12.8, 3.6$ Hz, 1H), 2.64 (dd, $J=10.8, 6.8$ Hz, 1H), 2.55 (t, $J=7.2$ Hz, 1H), 2.47 (dd, $J=10.8, 5.6$ Hz, 1H), 1.77 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) δ : 162.8, 162.5, 158.90, 158.88, 147.38, 147.36, 142.0, 140.2, 137.764, 137.757, 136.8, 136.6, 134.71, 137.70, 134.68, 134.5, 133.14, 133.12, 133.07, 132.7, 132.6, 132.35, 132.34, 131.8, 131.08, 131.05, 131.0, 130.9, 130.5, 129.8, 129.73, 129.71, 129.15, 129.06, 128.7, 128.6, 128.3, 128.2, 128.13, 128.08, 128.07, 127.93, 127.92, 127.88, 127.76, 127.694, 127.685, 127.4, 126.3, 126.1, 126.0, 123.7, 122.5, 122.2, 122.0, 120.8, 120.7, 113.5, 113.4, 79.0, 78.9, 78.4, 74.52, 74.50, 50.2, 35.6, 34.4, 31.8, 30.8; ^{31}P NMR (121 MHz, CDCl_3) δ : 3.52. Anal. calcd for $\text{C}_{54}\text{H}_{56}\text{NOPTi}$ (**3b**): C 79.69, H 6.94, N 1.72; found C 79.74, H 7.10, N 1.70.

4.3 Preparation of [ONS]ZrBn₂ (4a)

To a solution of ZrBn_4 (1.092 g, 2.4 mmol) in toluene (10 mL) was added dropwise **2a** (1.063 g, 2.4 mmol) in toluene (5 mL) at room temperature, and the mixture was stirred for 12 h at room temperature. Concentration of the solution gave a crude product, which was recrystallized from toluene at -30 °C, affording **4a** as a yellow solid (1.591 g, 85%). Crystals suitable for X-ray analyses were grown from a saturated Et_2O /hexane solution. ^1H NMR (300 MHz, C_6D_6) δ : 7.49 (d, $J=2.1$ Hz, 1H), 7.38 (t, $J=7.8$ Hz, 2H), 7.14–7.25 (m, 3H), 7.02–7.10 (m, 7H), 6.84–6.90 (m, 7H), 6.62–6.73 (m, 4H), 6.43 (dd, $J=15.6, 7.8$ Hz, 2H), 5.11 (dd, $J=10.2, 4.8$ Hz, 1H, CHCH_2), 3.65 (dd, $J=12.0, 12.0$ Hz, 1H, CH_2CH), 3.50 (dd, $J=12.0, 4.8$ Hz, 1H, CH_2CH), 2.55 (d, $J=9.0$ Hz, 1H, CH_2Ph), 2.03 (d, $J=11.4$ Hz, 1H, CH_2Ph), 1.80 (d, $J=9.0$ Hz, 1H, CH_2Ph), 1.72 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.56 (d, $J=11.4$ Hz, 1H, CH_2Ph), 1.29 (s, 9H, $\text{C}(\text{CH}_3)_3$). Anal. calcd for $\text{C}_{48}\text{H}_{51}\text{NOSZr}$ (**4a**): C 73.80, H 6.58, N 1.79; found C 73.68, H 6.39, N 1.52.

4.4 Preparation of [ONP]ZrBn₂ (4b)

To a solution of ZrBn_4 (137 mg, 0.3 mmol) in toluene (15 mL) was added dropwise **2b** (148 mg, 0.3 mmol) in toluene (5 mL) at room temperature, and the mixture was stirred for 24 h at room temperature. Concentration of the solution gave a crude product, which was recrystallized from toluene at -30 °C, affording **4b** as a yellow solid (208 mg, 81%). Crystals suitable for X-ray analyses were grown from a saturated toluene/hexane solution. ^1H NMR (400 MHz, C_6D_6) δ : 7.53 (t, $J=8.4$ Hz, 3H), 7.48–7.40 (m, 6H), 7.10–7.04 (m, 10H), 6.80–6.73 (m, 8H), 6.65 (t, $J=7.2$ Hz, 2H), 6.54–6.47 (m, 2H), 4.78 (d, $J=8.4$ Hz, 1H), 3.52 (t, $J=12.0$ Hz, 1H), 3.20 (d, $J=9.6$ Hz, 1H), 2.81 (d, $J=8.4$ Hz, 1H), 2.34 (d, $J=6.4$ Hz, 1H), 1.85 (dd, $J=18.0, 12.0$ Hz, 2H), 1.69 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) δ : 162.7, 162.5, 156.85, 156.82, 156.82, 144.61, 144.60, 141.4, 140.3, 139.4, 136.1, 135.9, 135.6, 133.43, 133.41, 133.0, 132.9, 132.7, 132.5, 132.3, 132.0, 131.5, 130.99, 130.98, 130.13, 130.11, 129.8, 129.64, 129.59, 129.1, 129.0, 128.8, 128.7, 128.3, 128.1,

127.87, 127.86, 126.4, 126.0, 124.5, 124.4, 122.1, 122.0, 119.5, 119.22, 119.16, 119.1, 115.5, 115.4, 72.7, 65.6, 63.6, 48.9, 35.4, 34.3, 31.8, 30.5; ^{31}P NMR (121 MHz, CDCl_3) δ : 4.67. Anal. calcd for $\text{C}_{54}\text{H}_{56}\text{NOPZr}$ (**4b**): C 75.66, H 6.58, N 1.63; found C 75.45, H 6.72, N 1.80.

4.5 Preparation of [ONSe]ZrBn₂ (4c)

To a solution of ZrBn_4 (139 mg, 0.3 mmol) in toluene (15 mL) was added dropwise **2c** (138 mg, 0.3 mmol) in toluene (5 mL) at room temperature, and the mixture was stirred for 12 h at room temperature. Concentration of the solution gave a crude product, which was recrystallized from toluene at -30 °C, affording **4c** as a yellow solid (194 mg, 78%). Crystals suitable for X-ray analyses were grown from a saturated toluene/hexane solution. ^1H NMR (400 MHz, C_6D_6) δ : 7.44 (d, $J=2.4$ Hz, 1H), 7.36 (t, $J=7.6$ Hz, 2H), 7.26–7.24 (m, 2H), 7.18–7.20 (m, 1H), 7.08–6.83 (m, 14H), 6.54 (m, 4H), 6.40–6.34 (m, 2H), 5.00 (dd, $J=11.2, 4.4$ Hz, 1H), 3.63 (t, $J=12.4$ Hz, 1H), 3.41 (dd, $J=12.4, 4.4$ Hz, 1H), 2.61 (d, $J=8.8$ Hz, 1H), 1.99 (d, $J=11.2$ Hz, 1H), 1.88 (d, $J=8.8$ Hz, 1H), 1.67 (s, 9H), 1.30 (d, $J=11.2$ Hz, 1H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) δ : 161.6, 157.0, 143.3, 142.0, 140.2, 138.5, 137.2, 136.1, 132.8, 131.9, 131.5, 131.2, 129.8, 129.6, 129.3, 128.5, 128.2, 127.9, 126.4, 126.2, 125.0, 124.7, 122.4, 122.0, 118.1, 116.9, 114.4, 71.4, 64.8, 63.9, 48.6, 35.3, 34.4, 31.7, 30.6. Anal. calcd for $\text{C}_{48}\text{H}_{51}\text{NOSeZr}$ (**4c**): C 69.62, H 6.21, N 1.69; found C 69.53, H 5.93, N 1.71.

4.6 Preparation of [ONS]HfBn₃ (5a)

To a solution of HfBn_4 (164 mg, 0.3 mmol) in toluene (5 mL) was added dropwise **2a** (127 mg, 0.3 mmol) in toluene (5 mL) at room temperature, and the mixture was stirred for 12 h at room temperature. Concentration of the solution gave a crude product, which was recrystallized from toluene at -30 °C, affording **5a** as an orange red solid (204 mg, 77%). Crystals suitable for X-ray analyses were grown from a saturated toluene/hexane solution at -30 °C. ^1H NMR (400 MHz, C_6D_6) δ : 7.68 (d, $J=2.4$ Hz, 1H), 7.58 (s, 1H), 7.18–7.11 (m, 2H), 7.10–7.02 (m, 11H), 6.97 (t, $J=8.0$ Hz, 1H), 6.90–6.84 (m, 2H), 6.83–6.77 (m, 4H), 6.70–6.56 (m, 5H), 2.52 (s, 6H), 1.61 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ : 169.7, 159.3, 155.5, 146.8, 141.3, 138.9, 135.1, 133.0, 132.0, 131.7, 130.0, 129.2, 129.1, 128.2, 128.1, 127.9, 127.1, 124.1, 121.5, 121.1, 79.4, 35.5, 34.2, 31.4, 30.2. Anal. calcd for $\text{C}_{48}\text{H}_{51}\text{NOSHf}$ (**5a**): C 66.38, H 5.92, N 1.61; found C 66.14, H 6.16, N 1.71.

4.7 Preparation of [ONS]HfBn₂ (6a)

To a solution of HfBn_4 (163 mg, 0.3 mmol) in toluene (10 mL) was added dropwise **2a** (124 mg, 0.3 mmol) in toluene (5 mL) at room temperature, and the mixture was stirred for 24 h at 80 °C. Concentration of the solution gave a crude product, which was recrystallized from toluene at -30 °C, affording **6a** as a pale yellow solid (215 mg, 85%). Crystals suitable for X-ray analyses were grown from a saturated hexane solution. ^1H NMR (400 MHz, C_6D_6) δ : 7.49 (s, 1H), 7.35 (t, $J=7.2$ Hz, 2H), 7.24–6.82 (m, 17H), 6.72–6.40 (m, 4H), 6.50–6.44 (m, 1H), 6.40 (t, $J=7.2$ Hz, 1H), 5.21 (dd, $J=10.4, 4.8$ Hz, 1H), 3.55 (t, $J=11.6$ Hz, 1H), 3.43 (dd, $J=12.4, 4.4$ Hz, 1H), 2.37 (d, $J=10.4$ Hz, 1H), 1.86 (d, $J=12.0$ Hz, 1H), 1.71 (s, 9H),

1.64 (d, $J=10.4$ Hz, 1H), 1.37 (d, $J=12.0$ Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ : 160.5, 156.6, 143.5, 141.9, 140.0, 138.9, 136.7, 136.5, 133.9, 132.6, 131.7, 131.6, 129.7, 129.5, 128.7, 128.6, 128.4, 128.3, 128.2, 127.2, 126.2, 124.9, 124.4, 122.6, 122.2, 118.1, 116.7, 114.5, 69.8, 69.3, 68.9, 48.1, 35.3, 34.3, 31.8, 30.6. Anal. calcd for $\text{C}_{48}\text{H}_{51}\text{NOSHf}$ (**5a**): C 66.38, H 5.92, N 1.61; found C 66.54, H 5.99, N 1.67.

4.8 Alternative method

A C_6D_6 (0.5 mL) solution of complex **5a** (18 mg, 0.02 mmol) in J-Young NMR tube was heated at 80 °C. The solution was monitored by ^1H NMR spectrum. Complex **5a** was completely converted to **6a** in 24 h.

4.9 Procedures for ethylene polymerization and copolymerization of ethylene with 1-hexene

Under 1 atm ethylene, toluene (25 mL) was added to the desired amount of MMAO (1.88 mol/L in heptane). After scavenging for 5 min, a desired amount of 1-hexene was added in the case of copolymerization of ethylene with 1-hexene (Table 2). At the desired temperature, catalyst (4.0 μmol , 1.0 mol/L in toluene) was added and the polymerization was carried out for 15 min. The reaction was quenched with concentrated HCl in ethanol (HCl/EtOH, 1/20, V/V) and the resulting mixture was further stirred for 2 h. The precipitated polymer was collected, washed with ethanol, and dried *in vacuo* at 70 °C overnight. The 1-hexene content of the copolymer was measured by ^1H NMR spectra.^[24]

4.10 X-ray structure determination

All single crystals were immersed in Paraton-N oil and sealed under nitrogen in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo $K\alpha$ radiation. An empirical absorption correction was applied using the SADABS program.^[26] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares on F^2 using the SHELXTL program package.^[27] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 4. Further details are included in the Supporting Information.

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