Journal of Organometallic Chemistry 772-773 (2014) 172–181

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Preparation of [bis(amido)-phosphine] and [amido-phosphine sulfide or oxide] hafnium and zirconium complexes for olefin polymerization

Chun Sun Lee [a], Ji Hae Park [a], Eun Yeong Hwang [a], Geun Ho Park [a], Min Jeong Go [b], Junseong Lee [b], Bun Yeoul Lee [a, *]

[a] Department of Molecular Science and Technology, Ajou University, Suwon 443-749, South Korea
[b] Department of Chemistry, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 500-757, South Korea

ARTICLE INFO

Article history:
Received 27 June 2014
Received in revised form
2 September 2014
Accepted 5 September 2014
Available online 16 September 2014

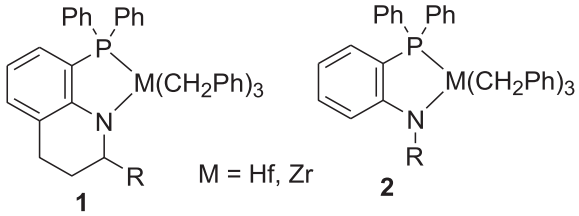
Keywords:
Post-metallocene
Phosphine ligands
Hafnium complexes
Zirconium complexes
Ethylene polymerization

ABSTRACT

New phosphine-based bidentate ligands, 2-Me-8-$Ph_2P(X)C_9H_8NH$ (**3**, X = O; **4**, X = S) and *N*-R-2-$Ph_2P(X)C_6H_4NH$ (**5**, R = Et, X = O; **6**, R = Me, X = S; **7**, R = Et, X = S) were prepared *via ortho*-lithiation of 1,2,3,4-tetrahydroquinaldine (2-Me-C_9H_9NH) and aniline derivatives (*N*-R-C_6H_5NH). Reaction of the *ortho*-lithiated compounds with 0.5 equiv of $PhP(OPh)_2$ afforded the bis(amido)-phosphine ligands (2-Me-C_9H_8NH-8-yl)$_2$PPh (**8**) and (*N*-R-C_6H_4NH-2-yl)$_2$PPh (**9**, R = Me; **10**, R = Et). Using these ligands, [amido-phosphine oxide]$Hf(CH_2Ph)_3$, [amido-phosphine sulfide]$Hf(CH_2Ph)_3$, [bis(amido)-phosphine]MX_2 (M = Hf, Zr; X = CH_2Ph, Cl, Me), and [amido-phosphine-amine]MCl_3 complexes were prepared. The molecular structures of [amido-phosphine sulfide]$Hf(CH_2Ph)_3$ (**13**) (prepared using **6**), [bis(amido)-phosphine]$ZrMe_2$ (**22**) (prepared using **8**), and [amido-phosphine-amine]MCl_3 (**23**, M = Hf; **24**, M = Zr; prepared using **9**) were confirmed by X-ray crystallography. Most of the prepared complexes exhibited negligible or low activity for ethylene/1-octene copolymerization. The [amido-phosphine sulfide]$Hf(CH_2Ph)_3$ complex (**13**) exhibited relatively high copolymerization activity (19×10^6 g/mol-Hf h); however, this activity was unsatisfactory compared to that of the related [amido-phosphine]$Hf(CH_2Ph)_3$ complexes (up to 48×10^6 g/mol-Hf h).

Introduction

The development of single-site polyolefin catalysts is a rapidly expanding field in both academic and industrial settings. Initially, single-site polyolefin catalysts were introduced by Kaminsky through the serendipitous discovery of methyl aluminoxane (MAO) [1]. These catalytic species were expanded from zirconocene complexes to half-metallocenes constructed with a cyclopentadienyl and an amido ligand [2–4], and further to post-metallocenes comprising non-cyclopentadienyl ligands [5–8]. Currently, approximately 5 million ton of polyethylene (PE) are produced annually using single-site homogeneous catalysts [9]. In the early 2000s, Dow and Symyx reported a simple protocol for fabricating post-metallocenes by reacting arrays of ligands with $M(CH_2Ph)_4$ (M = Hf, Zr) [10]. This simple protocol allowed for the construction of various $LM(CH_2Ph)_3$-type complexes with diverse spectator ligands L (L = imine-amido, imine-enamido, or aminotroponiminato) [11–16] and $LM(CH_2Ph)_2$-type complexes with ortho-metalated aryl moieties [17,18]. Recently, we reported $LM(CH_2Ph)_3$-type complexes with phosphine-amido spectator ligands (**1** and **2**), which exhibited good catalytic performance in ethylene/1-octene copolymerization [19]. Phosphine and its related ligands have been actively utilized in the construction of group 4 and group 5 metal complexes for catalysis [20–26]. Most of these complexes were constructed using chelating phenoxy-phosphine ligands. In this work, we report group-4 metal complexes constructed using derivatives of the phosphine-amido ligands and their catalytic performance in the ethylene/1-octene copolymerization.



* Corresponding author. Tel.: +82 31 219 1844.
E-mail address: bunyeoul@ajou.ac.kr (B.Y. Lee).

http://dx.doi.org/10.1016/j.jorganchem.2014.09.009
0022-328X/

Results and discussion

Ligand synthesis

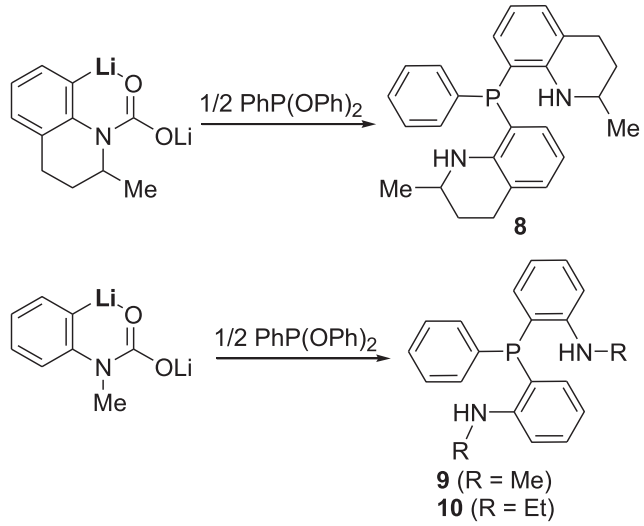
In recent reports, phenoxy-phosphine ligands were converted to chelating phenoxy-phosphine oxide, from which vanadium, chromium, and zirconium complexes were successfully prepared for olefin polymerization [27–29]. Stimulated by these reports, we prepared phosphine oxide as well as phosphine sulfide ligands from the phosphine-amido ligands that were used in the construction of **1** and **2** (Scheme 1). The phosphine-amido ligands were straightforwardly prepared from tetrahydroquinoline or secondary aniline derivatives by a one-pot procedure [19]. The key of this simple protocol was *ortho*-lithiation directed by in situ generated lithium carbamate. This simple *ortho*-lithiation allowed us to construct a series of half-metallocenes [30–32], one of which is now commercially used [33,34]. When the ligands used for constructing **1** and **2** were treated with H_2O_2 in CH_2Cl_2, the desired phosphine oxide compounds **3** and **5** were generated in excellent yields (92% and 96%, respectively). After oxidation, the ^{31}P NMR signal was shifted significantly from −21 to 35 ppm. The ^{1}H, ^{13}C, ^{31}P NMR and IR spectra were in agreement with the expected structures. When the phosphine compounds were treated with sulfur in toluene, the desired phosphine sulfide compounds **4**, **6**, and **7** were also afforded in good yields (54–61%). The ^{31}P NMR signals were observed at 40 ppm and shifted further up-field compared to the chemical shift observed for phosphine oxide compounds **3** and **5**.

When 2 equiv of the *ortho*-lithiated compound of tetrahydroquinaldine-derived lithium carbamate was reacted with $PhP(OPh)_2$, the desired bis(amido)-phosphine compound **8** was obtained (Scheme 2). Addition of $PhPCl_2$ did not afford the desired product. Using the *ortho*-lithiated compounds of the aniline derivatives also furnished the corresponding bis(amido)-phosphine compounds **9** and **10**. The ^{31}P NMR spectra of **9** and **10** were characterized by a signal at −36 ppm whereas three signals were observed at −35.1, −35.3, and −35.6 ppm in the corresponding spectrum of **8**.

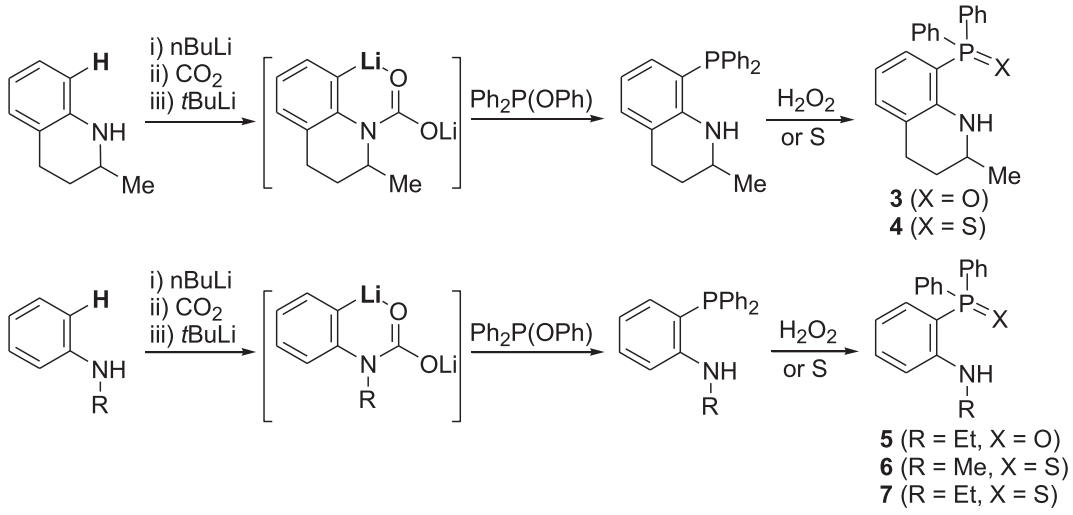
Metalation reaction

Reaction of phosphine oxide ligands **3** and **5** with $Hf(CH_2Ph)_4$ for 1 h at room temperate afforded Hf-complexes **11** and **12** in high yield (88–92%). Yellow powders were isolated after trituration in hexane, whose purity was confirmed from ^{1}H NMR spectral analysis. The ^{1}H NMR spectrum of **11** showed a set of AB spin system signals for the three benzyl-CH_2 at 2.5 and 2.2 ppm with a large geminal coupling constant ($^{2}J_{H-H}$ = 12 Hz). This observation indicated that the three benzyls underwent rapidly scrambling with each other. Under the rapid scrambling conditions, the three benzyls are equivalent; however, the two protons in the methylene are diastereotopic because of the presence of a chiral center in the ligand, and thus exhibit the characteristics of the AB spin system. In the ^{1}H NMR spectrum of **12** prepared from an achiral ligand, a single benzyl-CH_2 signal was observed at 2.3 ppm as a singlet. The ^{31}P signals observed at 44 ppm showed more downfield shift compared to the chemical shift of the ligand (35 ppm).

Reaction of phosphine sulfide ligand **4**, derived from tetrahydroquinaldine, with $Hf(CH_2Ph)_4$ generated the desired complex but with messy side products. Attempts to eliminate these side products failed. However, phosphine sulfide ligands **6** and **7** cleanly afforded the desired complexes **13** and **14**. A single benzyl-CH_2 signal was observed at 2.4 ppm as a singlet in the ^{1}H NMR spectra of **13** and **14**, indicating a rapid scrambling of the three benzyls. The



Scheme 2. Synthesis of bis(amido)-phosphine ligands.

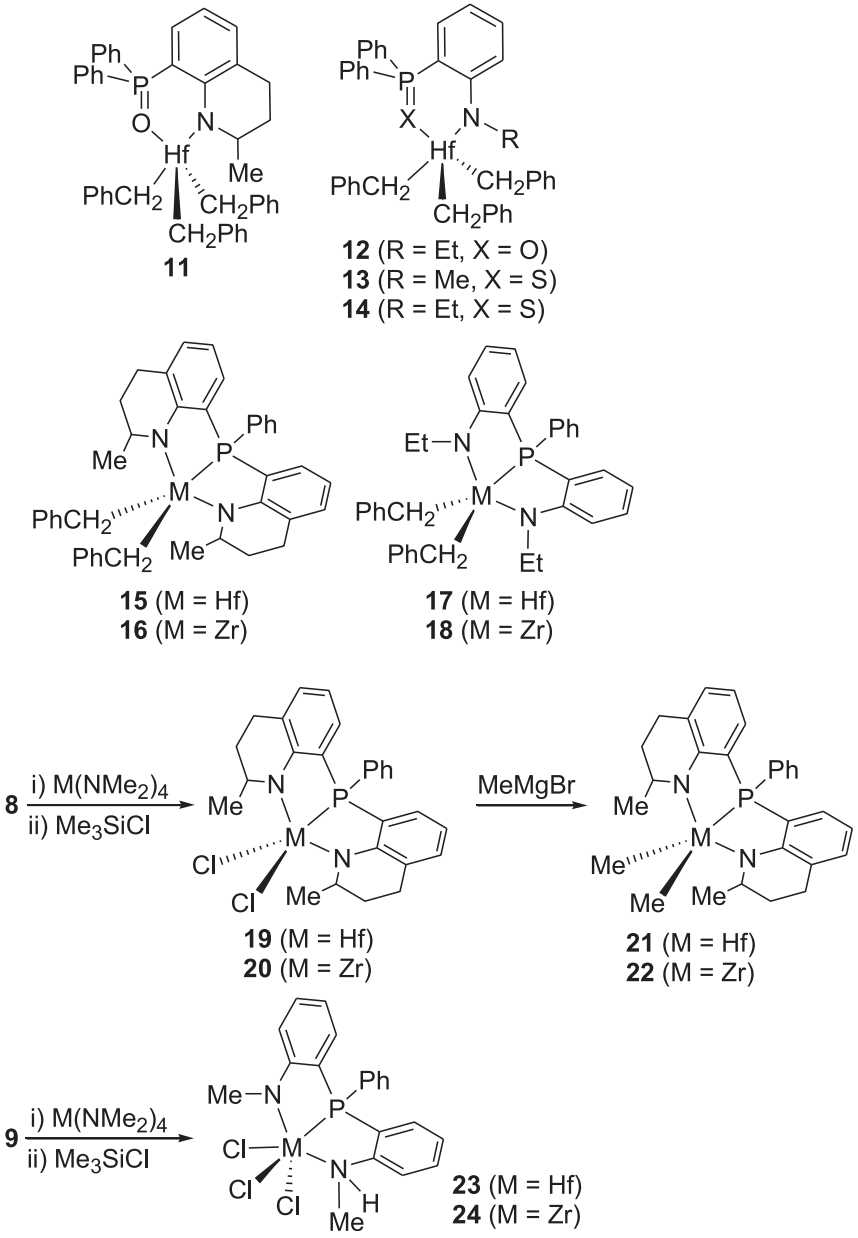


Scheme 1. Synthesis of phosphine oxide and sulfide ligands.

^{31}P signal was observed at 37 and 35 ppm, slightly up-field shifted from the chemical shift of the ligand (40 ppm). The Hf-complexes were rather unstable in C_6D_6, undergoing slowly decomposition during the overnight ^{13}C NMR data acquisition period. Reacting phosphine sulfide ligands **4**, **6**, and **7** with $Zr(CH_2Ph)_4$ generated the desired complexes in a short time (~30 min); however, these complexes were unstable and decomposed in C_6D_6.

Reaction of bis(amido)-phosphine ligands **8** and **10** with either $Hf(CH_2Ph)_4$ or $Zr(CH_2Ph)_4$ resulted in the clean formation of the desired complexes **15**–**18**, even though the reaction rate was slow, requiring several days for complete conversion. Contrary to the observation of three signals in the ^{31}P NMR spectrum of ligand **8**, a single signal was observed in the corresponding spectra of **15** and **16**. A set of clearly assignable signals was also observed in the ^{1}H NMR spectrum of **15** and **16**. Coordination with Hf and Zr led to disappearance of the N–H signal observed in the ligand spectrum, and the NC*H*Me signal was shifted from 3.1 to 4.6 and 4.7 ppm. Benzyl-CH_2 signals were observed as a pair of singlets at 2.0 and 2.4 ppm for **15** and at 2.3 and 2.8 ppm for **16**, indicating that the two benzyls were not equivalent. In **17** and **18**, the phosphorous atom is a dissymmetric center and the two protons on the NCH_2 unit are diastereotopic, thereby creating a set of doublet quartet signals (J = 14 and 6.8 Hz) at 3.4 and 3.9 ppm in the ^{1}H NMR spectrum of **17** and at 3.4 and 4.0 ppm in that of **18**. A pair of benzyl-CH_2 singlet signals was also observed at 2.1 and 2.5 ppm for **17** and at 2.4 and 2.8 ppm for **18**.

Dichloro- and dimethyl-hafnium and zirconium complexes were also prepared using bis(amido)-phosphine ligand **8** (Scheme 3). Reacting the ligand with $Hf(NMe_2)_4$ or $Zr(NMe_2)_4$ resulted in the formation of the desired bis(dimethylamido) complexes, which were converted to dichloro-complexes **19** and **20** upon treatment with Me_3SiCl. As-prepared **19** and **20** contained side product contaminates, whose removal was not successful. Subsequent to treatment with MeMgBr, the corresponding dimethyl complexes **21**



Scheme 3. Synthesis of [bis(amido)-phosphine] Zr and Hf complexes.

and **22** were cleanly isolated. A set of clearly assignable signals were observed in the ^{1}H NMR spectra of **21** and **22**. Two Hf–CH_3 signals were observed at 0.35 and 0.01 ppm and two Zr–CH_3 signals were observed at 0.50 and 0.10 ppm in the ^{1}H NMR spectra of **21** and **22**, respectively. When the same strategy was utilized for aniline-derived ligand **9**, unexpected complexes were obtained. Treatment of the intermediate dimethylamido hafnium or zirconium complex, generated by the action of $Hf(NMe_2)_4$ or $Zr(NMe_2)_4$ on **9**, with Me_3SiCl generated trichloro-complexes **23** and **24**, in which one of the amido ligands was protonated. Residual HCl in Me_3SiCl might be responsible for the formation of such undesired complexes. However, even when the same batch of Me_3SiCl was used, formation of similar protonated complexes were not severe in the case of formation of **19** and **20**, indicating that the tetrahydroquinaldine-derived complexes were more resistant toward impurity HCl. Complexes **23** and **24** were sparingly soluble in C_6D_6, $CDCl_3$, and CD_2Cl_2. Preparation of titanium complexes using the ligands **3**–**10** were unsuccessful.

X-ray crystallographic studies

Single crystals of the tribenzyl hafnium complex of the sulfide ligand (**13**) were grown in a cosolvent comprising toluene and hexane at −35 °C, and the structure of the complex was confirmed by X-ray crystallography (Fig. 1). The metrical parameters of the coordination sphere of the Hf atom indicated a distorted trigonal bipyramidal structure. Two benzyl and amido ligands formed an equatorial plane with Hf, whereas the sulfide and the remaining benzyl ligands occupied the apical positions. The benzyls situated at the equatorial position showed some η^3-bonding character, as inferred from the short Hf–CH_2 (2.245(6) and 2.268(5) Å) and Hf–C(ipso) (2.900(5) and 2.941(7) Å) distances. The corresponding distances were longer for the apical benzyl, which formed η^1-bond (2.289(6) and 3.233(6) Å, respectively). The Hf-C–C(ipso) angles were also acute because of the η^3-bonding character of the equatorial benzyl (99.7(3)° and 101.6(3)°). The Hf–C–C(ipso) angle was 116.4(3)° for the apical benzyl. The sum of the bond angles around the nitrogen atom was 356.8°, which deviated somewhat from the ideal sp^2 hybridization of the N atom (360°) for π-donation, which is frequently observed in amido complexes of early transition metals. The S and Hf atoms were situated above the N–C(2)–C(7)–P plane with large torsional angles of C(7)–C(2)–N–Hf (−72.6(5)°) and C(2)–C(7)–P–S (66.6(4)°).

Single crystals of the dimethyl zirconium complex of the bis(amido)phosphine ligand (**22**) were grown in a cosolvent consisting of toluene and hexane at −35 °C, and the structure of the complex was confirmed by X-ray crystallography (Fig. 2). This complex also adopted a distorted trigonal bipyramidal structure. Two methyl and phosphine ligands formed a perfect equatorial plane with the Zr center, where the sum of the bond angles of C(28)–Zr–P, C(27)–Zr–P, and C(27)–Zr–C(28) were 360°, whereas the N(1)–Zr–N(2) angle was 134.9(2)°, which deviated from the ideal value of 180° expected for the trigonal bipyramidal structure. The sum of the bond angles around the nitrogen atoms (358.7 and 356.3°) deviated slightly from that of ideal sp^2 hybridization of the N atom (360°) for π-donation. The Zr–P (2.7397(16) Å) and Zr–N distances (2.083(4) and 2.083(4) Å) were slightly shorter than those observed for complexes **1** and **2** (2.7558, 2.7498 Å and 2.104, 2.113 Å, respectively).

When a solution of the bis(dimethylamido)-Hf complex in toluene was layered with a solution of excess Me_3SiCl solution in pentane, yellow single crystals were deposited. X-ray crystallographic studies revealed an unexpected trichloro Hf complex (**23**) (Fig. 3), which may have been formed from the residual HCl in Me_3SiCl that was generated unintentionally by impurity water. The N(1)–Hf distance was relatively long (Hf–N(1), 2.483(18) Å), whereas the Hf–N(2) distance (2.080(19) Å) was comparable to the N–Hf distances observed for other amido Hf-complexes. The bond angles around the N(1) atom indicated sp^3-hybridization: the sum of the bond angles around the N(1) atom (344°) was close to the sum for the ideal sp^3-hybridized atom ($109.5 \times 3 = 328.5°$). The sum of the bond angles around the N(2) atom was 359.7°, indicating sp^2-hybridization. The distance of Hf–Cl bond opposite the amido

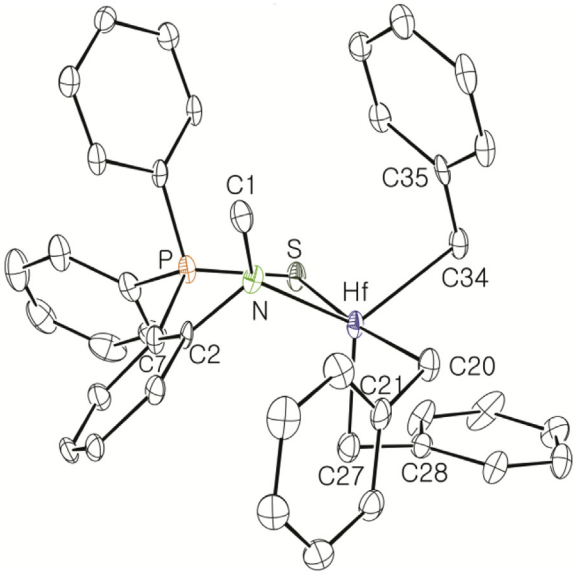


Fig. 1. Thermal ellipsoid plot (30% probability level) of **13**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Hf–S, 2.745(1); Hf–N, 2.047(4); C(20, apical)–Hf, 2.289(6); C(27,eq)–Hf, 2.245(6); C(34, eq)–Hf, 2.268(5); P–S, 1.993(2); C(21, apical)–Hf, 3.233(6); C(28, eq)–Hf, 2.900(5); C(35, eq)–Hf, 2.941(7); C(20, apical)–Hf–S, 171.8(1); N–Hf–C(27, eq), 117.8(2); N–Hf–C(34, eq), 120.4(2); C(27)–Hf–C(34), 120.9(2); Hf–C(27, eq)–C(28), 99.7(3); Hf–C(34, eq)–C(35, eq), 101.6(3); Hf–C(20, axial)–C(21), 116.4(3); C(2)–N–C(1), 116.5(4); C(2)–N–Hf, 109.5(3); C(1)–N–Hf, 130.8(3); C(7)–C(2)–N–Hf, −72.6(5); C(2)–C(7)–P–S, 66.6(4); P–S–Hf–N, −20.0(1).

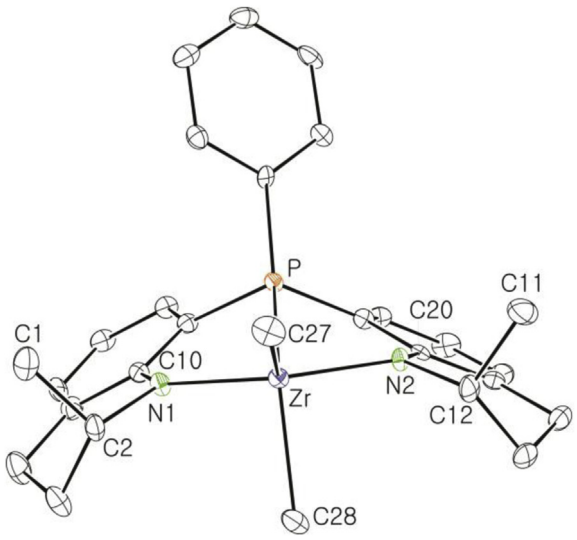


Fig. 2. Thermal ellipsoid plot (30% probability level) of **22**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P–Zr, 2.7397(16); N(1)–Zr, 2.083(4); N(2)–Zr, 2.083(4); C(27)–Zr, 2.233(6); C(28)–Zr, 2.258(6); C(28)–Zr–P, 124.4(2); C(27)–Zr–P, 126.2(2); C(27)–Zr–C(28), 109.4(2); N(2)–Zr–N(1), 134.9(2); C(20)–N(2)–Zr, 127.6(3); C(20)–N(2)–C(12), 117.2(4); C(12)–N(2)–Zr, 111.5(3).

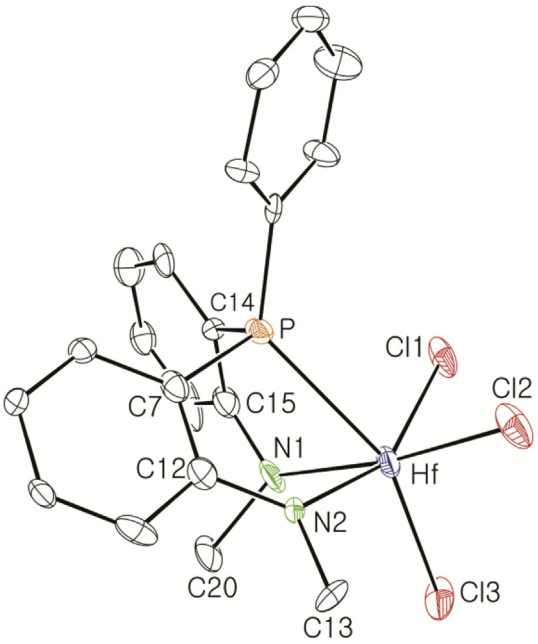


Fig. 3. Thermal ellipsoid plot (30% probability level) of **23**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Hf–P, 2.680(5); Hf–N(1, sp^3), 2.483(18); Hf–N(2, sp^2), 2.080(19); Hf–Cl(1), 2.453(6); Hf–Cl(2), 2.365(6); Hf–Cl(3), 2.387(5); C(15)–N(1)–C(20), 111.3(15); C(15)–N(1)–Hf, 120.7(10); C(20)–N(1)–Hf, 110.0(15); C(12)–N(2)–C(13), 116.3(2); C(12)–N(2)–Hf, 131.6(14); C(13)–N(2)–Hf, 111.8(15); C(14)–C(15)–N(1)–Hf, −26; C(14)–C(15)–N(1)–C(20), 105; C(7)–C(12)–N(2)–Hf, −7; C(7)–C(12)–N(2)–C(13), 168.

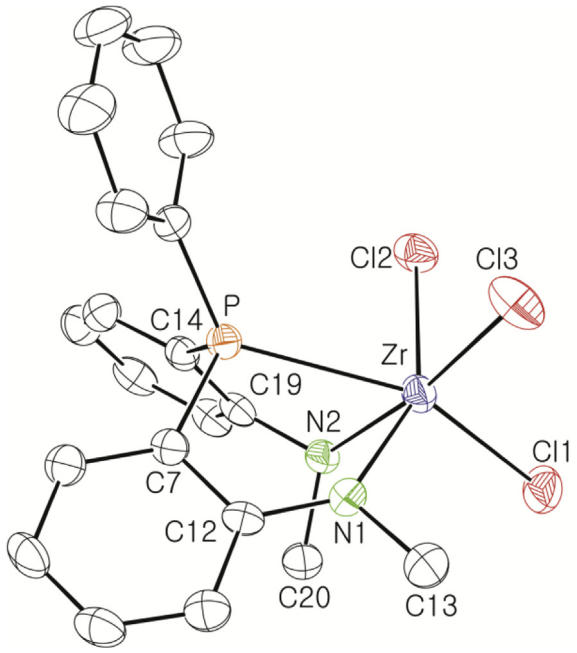


Fig. 4. Thermal ellipsoid plot (30% probability level) of **24**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Zr–P, 2.7068(16); Zr–N(2, sp^3), 2.483(4); Zr–N(1), 2.069(5); Zr–Cl(1), 2.413(2); Zr–Cl(2), 2.464(2); Zr–Cl(3), 2.393(2); C(19)–N(2)–C(20), 108.5(4); C(19)–N(2)–Zr, 120.9(3); C(20)–N(2)–Zr, 112.6(4); C1(2)–N(1)–C(13), 115.2(5); C(12)–N(1)–Zr, 134.8(4); C(13)–N(1)–Zr, 110.0(4); C(19)–C(14)–P–Zr, 19.4(5); C(14)–C(19)N(2)–C(20), 106.8(6); C(12)–C(7)–P–Zr, 6.2(5); C(7)–C(12)–N(1)–Zr, −10.1(9).

ligand was longer (Hf–Cl(1), 2.453(6) Å) than that of the other Hf–Cl distances opposite neutral amine and phosphine ligands (Hf–Cl(2), 2.365(6); Hf–Cl(3), 2.387(5) Å). The methyl carbon (C(20)) attached to the sp^3-amine N(1) atom and the Hf atom deviated from the plane formed by the N(1)–C(15)–C(14)–P atoms with the torsional angles of C(14)–C(15)–N(1)–Hf and C(14)–C(15)–N(1)–C(20) being −26° and 105°, respectively, while the methyl carbon (C(13)) attached to the sp^2-amide N atom and Hf atom was roughly situated on a plane formed by the N(2)–C(12)–C(7)–P atoms with the torsional angles of C(7)–C(12)–N(2)–Hf and C(7)–C(12)–N(2)–C(13) being −7° and 168°, respectively. Single crystals of the trichloro–Zr complex of the same ligand (**24**) were also obtained by layering a solution of the corresponding bis(dimethylamido)–Zr complex in toluene onto a solution of excess Me_3SiCl solution in pentane. X-ray crystallographic studies revealed a similar structural arrangement as that of **23** (Fig. 4).

Polymerization studies

The newly prepared complexes (**11**–**24**) were screened for ethylene/1-octene copolymerization activity (Table 1). Benzyl complexes **11**–**18** were activated with methylcyclohexane-soluble $[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ (1.2 equiv) using MAO (Al/M = 125) as a scavenger [15,19]. Though the pentacoordinated [N,N,C]HfX_2-type complexes constructed from the pyridine-amido ligand and by incorporating *ortho*-metalated aryl moieties have been extensively studied because of their good polymerization activity [35–40], the [N,P,N]$M(CH_2Ph)_2$-type complexes (M = Hf and Zr, **15**–**18**) developed herein exhibited negligible activity. The related pentacoordinated [bis(amido)-amine] zirconium and hafnium complexes were also prepared for the studies of 1-hexene polymerization [41,42]. The [amido-phosphine oxide]$Hf(CH_2Ph)_3$ complexes (**11**–**12**) showed low polymerization activity (entries 1–2). The [amido-phosphine sulfide]$Hf(CH_2Ph)_3$ complex (**13**) exhibited fairly good polymerization activity (entry 3); however its activity (19×10^6 g/mol-Hf h) was lower than those of the related [amido-phosphine]$Hf(CH_2Ph)_3$ complexes (up to 48×10^6 g/mol-Hf h) and CGC ($[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$) ($36 \times 10^6$ g/mol-Ti h) under similar polymerization conditions. Both [N,P,N]MCl_2 (**19**–**20**) and [N,P,NH]MCl_3 (**23**–**24**) exhibited low or negligible activity when activated with modified-MAO (entries 5 and 6). The dimethyl complexes [N,P,N]MMe_2 (**21**–**22**) also showed negligible activity when activated with $[Ph_3C]^+[B(C_6F_5)_4]^-$. All of the obtained polymers had melting peak at ca. 120 °C in the DSC scans, indicating incorporation of a minimal amount of 1-octene (<2 mol%), which was in fact confirmed by a negligible methyl signal observed in the ^1H NMR spectrum (see SI). The GPC curves of the polymers obtained with **19**/MMAO, **20**/MMOA, and **21**/$[Ph_3C]^+[B(C_6F_5)_4]^-$ indicated bimodal molecular weight distributions; thus M_w/M_n values were very high (entries 5–7). Ethylene homopolymeirzation was carried out with **13** and **19** under the identical conditions, respectively, except in the absence of 1-octene. The activity was slightly lower (11 and 4.9×10^6 g/mol-Ti h, respectively) than in the presence of 1-octene, which phenomenon is common in metallocene catalyst.

Conclusion

New phosphine-based bidentate and tridentate ligands were prepared using *ortho*-lithiated compounds of secondary aniline-derived lithium carbamates. Using these ligands, [amido-phosphine oxide]$Hf(CH_2Ph)_3$, [amido-phosphine sulfide] $Hf(CH_2Ph)_3$, [bis(amido)-phosphine]MX_2 (M = Hf, Zr; X = CH_2Ph, Cl, Me), and [amido-phosphine-amine]MCl_3 complexes were prepared. The molecular structures of [amido-phosphine sulfide] $Hf(CH_2Ph)_3$, [bis(amido)-phosphine]$ZrMe_2$, and [amido-

Table 1
Ethylene/1-octene copolymerization results.[a]

Entry	Catalyst (μmol)	Cocatalyst (mmol)	Yield (g)	Activity ($\times 10^6$ g/mol-M h)	M_w ($\times 10^3$)	M_w/M_n	T_m (°C)
1	**11** (5)	$[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ (6)	0.33	1.3	183	5.67	121
2	**12** (5)	$[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ (6)	0.51	2	178	6.07	120
3	**13** (1)	$[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ (1.2)	0.95	19	158	2.95	118
4	**14** (1)	$[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ (1.2)	0.31	6.2	193	4.29	123
5	**19** (1)	MMAO (3000)	0.39	7.8	279	49.8	121
6	**20** (1)	MMAO (3000)	0.34	6.8	188	53.2	123
7	**21** (5)	$[Ph_3C]^+[B(C_6F_5)_4]^-$ (6)	0.6	2.4	64	13.6	124

[a] Polymerization conditions: methylcyclohexane solution of 1-octene (1.0 M, 30 mL), ethylene (30 bar), 100 °C, 3 min.

phosphine-amine]MCl_3 were confirmed by X-ray crystallography. Most of the newly prepared complexes exhibited negligible or low activity for ethylene/1-octene copolymerization. [Amido-phosphine sulfide]Hf$(CH_2Ph)_3$ showed relatively high activity (19×10^6 g/mol-Hf h); however, this activity was not satisfactory when compared with the activity of related [amido-phosphine] Hf$(CH_2Ph)_3$ complexes (up to 48×10^6 g/mol-Hf·h).

Experimental section

General remarks

All manipulations were performed under inert atmosphere using standard glove box and Schlenk techniques. Diethyl ether, THF, C_6D_6, and $C_6D_5CD_3$ were distilled from benzophenone ketyl. Methylcyclohexane (anhydrous grade), toluene, and 1-octene used for the polymerization reaction were purchased from Aldrich and purified over a Na/K alloy. Ethylene was purified by contact with molecular sieves and copper for more than 12 h under 50 bar pressure. The IR spectrum was recorded from the solid itself using attenuated total reflection (ATR) FTIR. The ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a Varian Mercury plus 400. Elemental analyses were carried out at the Analytical Center, Kyunghee University. Mass spectra were obtained on a JEOL JMS-700.

Synthesis of ligands and complexes

*Compound **3***

H_2O_2 (2.2 mL, 2.9 mmol) was added to a solution of 8-(diphenylphosphino)-1,2,3,4-tetrahydroquinaldine (0.30 g, 0.98 mmol) in methylene chloride (12 mL) at 0 °C and the resulting solution was slowly warmed to room temperature. After water (3 mL) was added, the organic phase was separated out, and was dried over anhydrous $MgSO_4$. Removal of the solvent using a rotary evaporator produced a white solid (0.29 g, 92%). Analytical analysis indicated that the obtained solid was pure and this solid was used for the metalation without further purification. M.p. 110 °C. IR: 3301 (N–H), 1116 (P–O) cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.41 (br s, 1H, NH), 7.84–7.74 (m, 4H, PPh), 7.07–6.95 (m, 6H, PPh), 6.91 (d, J = 6.8 Hz, 1H, 5-quinaldine), 6.82 (dd, J = 6.8, 14 Hz, 1H, 7-quinaldine), 6.39 (dt, J = 7.4, 2.8 Hz, 1H, 6-quinaldine), 3.15–3.04 (m, 1H, 2-quinaldine), 2.56–2.35 (m, 2H, 4-quinaldine), 1.43–1.33 (m, 1H, 3-quinaldine), 1.26–1.08 (m, 1H, 3-quinaldine), 0.93 (d, J = 6.8 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 151.27 (d, J_{PC} = 4.5 Hz), 135.01 (d, J_{PC} = 14 Hz), 133.99 (d, J_{PC} = 13 Hz), 133.10 (d, J_{PC} = 1.5 Hz), 132.52 (d, J_{PC} = 5.3 Hz), 132.42 (d, J_{PC} = 4.6 Hz), 131.45 (d, J_{PC} = 11 Hz), 131.58, 128.58 (d, J_{PC} = 3.7 Hz), 128.46 (d, J_{PC} = 4.6 Hz), 122.12 (d, J_{PC} = 7.6 Hz), 114.39 (d, J_{PC} = 14 Hz), 110.53, 109.48, 47.22, 29.25, 27.62, 22.62 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 35.11 ppm. HRMS(EI): m/z calcd ([M+] $C_{22}H_{22}NOP$) 349.3899. Found: 349.3899.

*Compound **4***

8-(Diphenylphosphino)-1,2,3,4-tetrahydroquinaldine (0.299 g, 0.901 mmol) and sulfur (0.032 g, 0.99 mmol) were mixed in toluene (3 mL). The solution was stirred overnight at room temperature. Removal of volatiles under vacuum gave a residue, which was purified by column chromatography on silica gel eluting with methylene chloride. A white solid was obtained in 61% yield (0.201 g). M.p. 169 °C. IR: 3271 (N–H), 708 (P–S) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.96–7.86 (m, 4H, PPh), 7.18 (br s, 1H, NH), 7.04–6.94 (m, 6H, PPh), 6.90 (d, J = 7.2 Hz, 1H, 5-quinaldine), 6.72 (dd, J = 8.0, 15 Hz, 1H, 7-quinaldine), 6.37 (dt, J = 7.5, 2.8 Hz, 1H, 6-quinaldine), 3.11–3.01 (m, 1H, 2-quinaldine), 2.52–2.34 (m, 2H, 4-quinaldine), 1.40–1.32 (m, 1H, 3-quinaldine), 1.20–1.07 (m, 1H, 3-quinaldine), 0.84 (d, J = 6.4 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 149.17 (d, J_{PC} = 6.0 Hz), 133.86 (d, J_{PC} = 9.1 Hz), 132.98 (d, J_{PC} = 17 Hz), 132.97, 132.72 (d, J_{PC} = 11 Hz), 131.60 (d, J_{PC} = 9.1 Hz), 131.45 (d, J_{PC} = 3.0 Hz), 131.39 (d, J_{PC} = 3.1 Hz), 128.62 (d, J_{PC} = 8.3 Hz), 128.50 (d, J_{PC} = 8.4 Hz), 122.69 (d, J_{PC} = 7.5 Hz), 115.12 (d, J_{PC} = 6.4 Hz), 111.292, 110.42, 47.66, 29.28, 27.57, 22.38 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 40.03 ppm. HRMS(EI): m/z calcd ([M+] $C_{22}H_{22}NSP$) 363.1493. Found: 363.1493.

*Compound **5***

The title compound was synthesized using the same conditions and procedure as those for **3** using 2-(diphenylphosphino)-*N*-ethylaniline (0.49 g, 0.15 mmol). M.p. 129 °C. IR: 3322 (N–H), 1117 (P–O) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.83 (br s, 1H, NH), 7.81–7.71 (m, 4H, PPh), 7.19 (t, J = 7.8 Hz, 1H), 7.10–6.95 (m, 6H, PPh), 6.95 (ddd, J = 1.7, 7.6, 15 Hz, 1H), 6.51 (dd, J = 5.2, 7.4 Hz, 1H), 6.44 (dt, J = 7.3, 2.5 Hz, 1H), 2.80–2.71 (m, 2H, NCH_2), 0.91 (t, J = 6.8 Hz, 1H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 154.36 (d, J_{PC} = 5.3 Hz), 133.81, 133.94 (d, J_{PC} = 11 Hz), 133.72 (d, J_{PC} = 2.3 Hz), 133.47 (d, J_{PC} = 9.1 Hz), 131.64 (d, J_{PC} = 3.1 Hz), 128.55 (d, J_{PC} = 12 Hz), 114.81 (d, J_{PC} = 13 Hz), 112.31, 111.41 (d, J_{PC} = 7.6 Hz), 11.27, 38.10, 14.60 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 35.00 ppm. HRMS(EI): m/z calcd ([M+] $C_{20}H_{20}NOP$) 321.1211. Found: 321.1212.

*Compound **6***

The title compound was synthesized using the same conditions and procedure as those for **4** using 2-(diphenylphosphino)-*N*-methylaniline (0.270 g, 0.928 mmol). The compound was purified by recrystallized in toluene at room temperature. A white solid was obtained in 54% yield (0.162 g). M.p. 154 °C. IR: 3276 (N–H), 709 (P–S) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.91–7.82 (m, 4H, PPh), 7.20–7.08 (m, 1H), 7.18 (br s, 1H, NH), 7.03–6.93 (m, 6H PPh), 6.83 (ddd, J = 1.6, 8.0, 16 Hz, 1H), 6.45–6.38 (m, 2H), 2.21 (d, J = 5.2 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 153.31 (d, J_{PC} = 6.0 Hz), 133.64, 133.55, 133.60 (d, J_{PC} = 2.2 Hz), 133.55, 132.79, 132.76 (d, J_{PC} = 11 Hz), 131.51 (d, J_{PC} = 3.0 Hz), 128.64 (d, J_{PC} = 13 Hz), 115.75 (d, J_{PC} = 13 Hz), 112.98, 112.12, 111.58 (d, J_{PC} = 7.6 Hz), 30.04 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 40.29 ppm. HRMS(EI): m/z calcd ([M+] $C_{19}H_{18}NPS$) 323.0898. Found: 323.0898.

Compound ***7***

The title compound was synthesized using the same conditions and procedure as those for **4** using 2-(diphenylphosphino)-*N*-ethylaniline (0.66 g, 2.2 mmol). The compound was purified by recrystallized in toluene at room temperature. A white solid was obtained in 59% yield (0.43 g). M.p. 123 °C. IR: 3281 (N–H), 708 (P–S) cm^{-1}. ^1H NMR (C_6D_6): δ 7.94–7.82 (m, 4H, PPh), 7.16 (t, $J = 7.8$, 1H), 7.08 (br s, 1H, NH), 7.04–6.92 (m, 6H, PPh), 6.85 (ddd, $J = 15$, 7.9, 1.5 Hz, 1H), 6.49 (dd, $J = 6.0$, 7.6 Hz, 1H), 6.41 (dt, $J = 7.6$, 2.4 Hz, 1H), 2.74–2.64 (m, 2H, NCH_2), 0.85 (t, $J = 7.2$, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.31 (d, $J_{PC} = 6.0$ Hz), 133.69, 133.60, 133.55 (d, $J_{PC} = 2.2$ Hz), 132.76, 132.75 (d, $J_{PC} = 11$ Hz), 131.49 (d, $J_{PC} = 3.0$ Hz), 128.60 (d, $J_{PC} = 13$ Hz), 115.66 (d, $J_{PC} = 13$ Hz), 112.95, 112.08, 112.01, 38.46, 14.38 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 40.13 ppm. HRMS(EI): *m*/*z* calcd ([M+] $C_{20}H_{20}NPS$) 337.1054. Found: 337.1054.

Compound ***8***

*n*BuLi (20.1 mL, 50.3 mmol, 2.5 M solution in hexane) was added dropwise to a solution of 1,2,3,4-tetrahydroquinaldine (0.990 g, 6.73 mmol) in hexane (85 mL) at room temperature. The solution was stirred at room temperature overnight. The resultant white solid precipitated from the solution was subsequently filtered and washed with hexane, yielding the corresponding lithium amide compound in quantitative yield (6.86 g). CO_2 gas was then introduced into the solution of lithium amide (4.16 g, 27.2 mmol) in diethyl ether (65 mL) stirred at −78 °C. The white solid disappeared immediately. The temperature was raised slowly to room temperature while excess CO_2 gas was removed through a bubbler. The solution was stirred overnight, resulting in the precipitation of a white solid. THF (2.15 g, 29.9 mmol) and *t*BuLi (17.6 mL, 29.9 mmol, 1.7 M solution in pentane) were added successively to the slurry at −20 °C, and the solution was stirred for 2 h at this temperature. A solution of $PhP(OPh)_2$ (3.3 g, 11.2 mmol) in diethyl ether (30 mL) was added to the *ortho*-lithiated compound at −20 °C using a syringe. The solution was subsequently stirred for 1 h at −20 °C and warmed slowly to room temperature. After stirring the solution overnight, H_2O (50 mL) was added at 0 °C and the mixture was stirred at room temperature for 30 min. The product was extracted with ethyl acetate (3 × 100 mL). The organic phase was collected and dried over anhydrous $MgSO_4$. The solvent was removed using a rotary evaporator to obtain a residue, which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). A pale yellow viscous oil was obtained in 59% yield (2.63 g). The analytically pure white solid was obtained by recrystallization at −35 °C in hexane. M.p. 120 °C. IR: 3388 (N–H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.65–7.47 (m, 2H, PPh), 7.13 (t, $J = 7.0$ Hz, 1H, 7-quinaldine), 7.08–7.00 (m, 3H, PPh) 6.93 (d, 2H, 5-quinaldine), 6.64–6.56 (m, 2H, 6-quinaldine), 4.84–4.71 (m, 2H, NH), 3.07 (br s, 2H, 2-quinaldine), 2.66–2.45 (m, 4H, 4-quinaldine), 1.53–1.43 (m, 2H, 3-quinaldine), 1.36–1.23 (m, 2H, 3-quinaldine), 0.78 (d, $J = 6.0$, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 148.14 (d, $J_{PC} = 18$ Hz), 135.28 (d, $J_{PC} = 4.6$ Hz), 134.10 (d, $J_{PC} = 19$ Hz), 132.94 (d, $J_{PC} = 4.5$ Hz), 131.00, 128.81 (d, $J_{PC} = 6.9$ Hz), 128.73, 120.85 (d, $J_{PC} = 5.3$ Hz), 117.26 (d, $J_{PC} = 3.1$ Hz), 115.99 (d, $J_{PC} = 3.8$ Hz), 47.82, 30.07, 27.50, 22.64 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −35.08, −35.32, −35.64 ppm. HRMS(EI): *m*/*z* calcd ([M+] $C_{26}H_{29}N_2P$) 400.2068. Found: 400.2069.

Compound ***9***

The title compound was synthesized using the same conditions and procedure as those for **8** using *N*-methylaniline (4.32 g, 38.2 mmol). The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). A pale yellow viscous oil was obtained in 51% yield (2.49 g). Analytically pure white solid was obtained by recrystallization at −35 °C in hexane. M.p. 159 °C. IR: 3381 (N–H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.43–7.35 (m, 2H, PPh), 7.16 (t, $J = 7.6$ Hz, 2H), 7.10 (t, $J = 6.0$ Hz, 2H) 7.02–6.95 (m, 3H, PPh), 6.57 (t, $J = 7.2$ Hz, 2H), 6.44 (dd, $J = 8.0$, 5.6 Hz, 2H), 4.58 (br s, 2H, NH), 2.23 (d, $J = 4.8$ Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.21 (d, $J_{PC} = 18$ Hz), 134.62 (d, $J_{PC} = 4.6$ Hz), 134.51, 133.86 (d, $J_{PC} = 18$ Hz), 131.02, 128.78 (d, $J_{PC} = 3.1$ Hz), 128.73, 117.55 (d, $J_{PC} = 1.5$ Hz), 116.91 (d, $J_{PC} = 3.8$ Hz), 109.73 (d, $J_{PC} = 2.3$ Hz), 30.34 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −36.05 ppm. HRMS(EI): *m*/*z* calcd ([M+] $C_{20}H_{21}N_2P$) 320.1442. Found: 320.1443.

Compound ***10***

The title compound was synthesized using the same conditions and procedure as those for **8** using *N*-ethylaniline (1.23 g, 9.65 mmol). The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 10:1). A pale yellow viscous oil was obtained in 73% yield (0.98 g). Analytically pure white solid was obtained by recrystallization at −35 °C in hexane. M.p. 80 °C. IR: 3351 (N–H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.51–7.44 (m, 2H, PPh), 7.25–7.17 (m, 4H), 7.04 (d, $J = 4.8$ Hz, 3H) 6.23 (t, $J = 7.2$, 2H, PPh), 6.54 (dd, $J = 7.8$, 5.2 Hz, 2H), 4.58 (d, $J = 4.4$, 2H, NH), 2.83–2.68 (m, 4H, NCH_2), 0.78 (d, $J = 7.0$, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 151.63 (d, $J_{PC} = 17$ Hz), 134.98 (d, $J_{PC} = 4.5$ Hz), 134.87 (d, $J_{PC} = 4.5$ Hz), 134.11 (d, $J_{PC} = 19$ Hz), 131.21, 128.99, 128.92, 117.69 (d, $J_{PC} = 3.0$ Hz), 117.14 (d, $J_{PC} = 4.6$ Hz), 110.62 (d, $J_{PC} = 3.0$ Hz), 38.71, 14.75 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −34.69 ppm. HRMS(EI): *m*/*z* calcd ([M+] $C_{22}H_{25}N_2P$) 348.1755. Found: 348.1756.

Complex ***11***

$Hf(CH_2Ph)_4$ (0.156 g, 0.287 mmol) and **3** (0.100 g, 0.287 mmol) were mixed in toluene (2.5 mL) at room temperature, and the solution was stirred for 1 h at this temperature. After the solvent was removed under vacuum, the residue was triturated in hexane (~1 mL). The yellow solid was isolated by decantation (0.202 g, 88%). ^1H NMR (C_6D_6): δ 7.29 (d, $J = 13$ Hz, 1H), 7.26 (dd, $J = 13$, 1.6 Hz, 1H), 7.19–6.84 (m, 24H), 6.52 (dd, $J = 7.8$, 15 Hz, 1H), 6.36 (dt, $J = 7.6$, 3.7 Hz, 1H), 4.04–3.95 (m, 1H, 2-quinaldine), 2.66–2.52 (m, 1H, 4-quinaldine), 2.49 (d, $J = 11$ Hz, 3H, $HfCH_2$), 2.45–2.35 (m, 1H, 4-quinaldine), 2.21 (d, $J = 12$ Hz, 3H, $HfCH_2$), 2.05–1.94 (m, 1H, 3-quinaldine), 1.44–1.33 (m, 1H, 3-quinaldine), 0.572 (d, $J = 6.4$ Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 155.42 (d, $J_{PC} = 3.8$ Hz), 147.47, 135.85, 133.14 (d, $J_{PC} = 11$ Hz), 132.36 (d, $J_{PC} = 11$ Hz), 131.22 (d, $J_{PC} = 14$ Hz), 129.21, 128.91 (d, $J_{PC} = 13$ Hz), 128.38, 127.94, 126.98, 125.31 (d, $J_{PC} = 7.6$ Hz), 121.48, 116.72 (d, $J_{PC} = 15$ Hz), 112.78, 111.67, 81.05, 44.46, 25.90, 23.42, 19.71 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 44.11 ppm. Anal. Calcd ($C_{43}H_{42}NOPHf$): C, 64.70; H, 5.30; N, 1.75. Found: C, 64.80; H, 5.35; N, 1.95%.

Complex ***12***

The title complex was synthesized using the same conditions and procedure as those for **11** using **5** (0.100 g, 0.311 mmol). The yellow solid was isolated by trituration (0.220 g, 92%). ^1H NMR (C_6D_6): δ 7.21–7.12 (m, 10H), 7.09–6.98 (m, 9H), 6.91–6.84 (m, 7H), 6.63–6.56 (m, 2H), 6.35 (dt, $J = 7.4$, 3.5 Hz, 1H), 3.24 (quartet, $J = 6.8$ Hz, 2H, NCH_2), 2.33 (s, 6H, $HfCH_2$), 0.43 (t, $J = 6.6$ Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.16 (d, $J_{PC} = 3.8$ Hz), 147.22, 135.59, 133.33 (d, $J_{PC} = 14$ Hz), 133.09 (d, $J_{PC} = 2.3$ Hz), 132.70 (d, $J_{PC} = 11$ Hz), 128.91 (d, $J_{PC} = 13$ Hz), 128.62, 128.44, 127.53, 121.50, 117.06 (d, $J_{PC} = 6.9$ Hz), 116.92 (d, $J_{PC} = 14$ Hz), 114.69, 113.58, 80.62, 39.15, 13.48 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 44.45 ppm. Anal. Calcd ($C_{41}H_{38}NOPHf$): C, 63.77; H, 5.22; N, 1.81. Found: C, 63.55; H, 5.13; N, 1.98%.

Complex ***13***

The title complex was synthesized using the same conditions and procedure as those for **11** using **6** (0.050 g, 0.16 mmol). The

compound was purified by recrystallizing in toluene at −35 °C (0.061 g, 51%). The compound was slowly decomposed in C_6D_6 during the overnight acquisition of the ^{13}C NMR data. ^1H NMR (C_6D_6): δ 7.37 (dd, J = 8.0, 14 Hz, 4H), 7.20–7.04 (m, 13H), 7.01–6.95 (m, 2H), 6.92–6.82 (m, 7H), 6.65 (dd, J = 5.2, 8.0 Hz, 1H), 6.47 (dd, J = 7.8, 14 Hz, 1H), 6.39 (dt, J = 7.2, 3.6 Hz, 1H), 2.48 (s, 3H, CH_3), 2.35 (s, 6H, $HfCH_2$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 37.31 ppm. Anal. Calcd ($C_{40}H_{38}NPSHf$): C, 62.05; H, 4.95; N, 1.81. Found: C, 61.94; H, 4.85; N, 1.95%.

Complex ***14***

The title complex was synthesized using the same conditions and procedure as those for **11** using **7** (0.087 g, 0.25 mmol). The compound was purified by recrystallizing in toluene at −35 °C (0.100 g, 51%). The compound was slowly decomposed in C_6D_6 during the overnight acquisition of the ^{13}C NMR data. ^1H NMR (C_6D_6): δ 7.31 (dd, J = 7.6, 13.6 Hz, 4H), 7.17 (t, J = 7.6 Hz, 6H), 7.07 (d, J = 7.2 Hz, 6H), 6.90 (d, J = 7.6 Hz, 2H), 6.84 (t, J = 7.4 Hz, 4H), 6.79 (dt, J = 7.4, 7.4 Hz, 4H), 6.58–6.46 (m, 2H), 6.33 (dt, J = 7.6, 1.2 Hz, 1H), 3.26–3.17 (quartet, J = 6.4 Hz, 2H, NCH_2), 2.40 (s, 6H, $HfCH_2$), 0.23 (t, J = 6.6 Hz, 3H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 35.29 ppm. Anal. Calcd ($C_{41}H_{40}NPSHf$): C, 62.47; H, 5.11; N, 1.78. Found: C, 62.25; H, 5.02; N, 1.89%.

Complex ***15***

$Hf(CH_2Ph)_4$ (0.132 g, 0.24 mmol) and **8** (0.098 g, 0.24 mmol) were mixed in toluene (2 mL) at −30 °C. The temperature was raised slowly to room temperature, and the solution was stirred overnight. After the solvent was removed under vacuum, the residue was triturated in hexane (~0.5 mL). The yellow solid was isolated by decantation (0.128 g, 70%). ^1H NMR (C_6D_6): δ 7.37 (t, J = 7.0 Hz, 2H), 7.25 (t, J = 7.6 Hz, 2H), 7.10 (d, J = 6.8 Hz, 2H), 7.01 (d, J = 7.6 Hz, 2H), 6.91 (t, J = 6.8 Hz, 2H), 6.93–6.83 (m, 4H), 6.66–6.60 (m, 4H), 6.55 (t, J = 7.6 Hz, 2H), 6.26 (t, J = 7.4 Hz, 1H), 4.67–4.58 (m, 2H, 2-quinaldine), 2.83–2.72 (m, 2H, 4-quinaldine), 2.47–2.37 (m, 2H, 4-quinaldine), 2.41 (s, 2H, $HfCH_2$), 1.93 (s, 2H, $HfCH_2$), 1.87–1.75 (m, 2H, 3-quinaldine) 1.75–1.53 (m, 2H, 3-quinaldine) 1.10 (d, J = 6.4 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.11 (d, J_{PC} = 31 Hz), 149.32, 135.67, 135.49, 135.18, 133.66 (d, J_{PC} = 2.3 Hz), 132.80, 131.75 (d, J_{PC} = 12 Hz), 129.15, 127.29, 126.85, 123.65, 122.35 (d, J_{PC} = 9.9 Hz), 121.45, 118.74 (d, J_{PC} = 6.1 Hz), 118.01, 117.59, 117.80 (d, J_{PC} = 42 Hz), 78.18, 72.74 (d, J_{PC} = 11 Hz), 45.35 (d, J_{PC} = 5.3 Hz), 26.01, 22.34, 19.15 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 5.42 ppm. Anal. Calcd ($C_{40}H_{41}N_2PHf$): C, 63.28; H, 5.44; N, 3.69. Found: C, 63.54; H, 5.61; N, 3.91%.

Complex ***16***

The title complex was synthesized using the same conditions and procedure as those for **15** using **8** (0.050 g, 0.13 mmol) and $Zr(CH_2Ph)_4$ instead of $Hf(CH_2Ph)_4$. It was obtained as a yellow solid in 85% yield (0.071 g). ^1H NMR (C_6D_6): δ 7.41 (t, J = 6.8 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.15 (d, J = 4.8 Hz, 2H), 6.97 (d, J = 7.2 Hz, 3H), 6.91–6.86 (m, 3H), 6.83–6.76 (m, 2H), 6.64 (dt, J = 7.4, 1.4 Hz, 2H), 6.55 (d, J = 6.8 Hz, 2H), 6.47 (t, J = 7.6 Hz, 2H), 6.06 (t, J = 7.2 Hz, 1H), 4.76–4.66 (m, 2H, 2-quinaldine), 2.82–2.68 (m, 2H, 4-quinaldine), 2.76 (s, 2H, $HfCH_2$), 2.48–2.38 (m, 2H, 4-quinaldine), 2.27 (s, 2H, $HfCH_2$), 1.93–1.82 (m, 2H, 3-quinaldine), 1.60–1.50 (m, 2H, 3-quinaldine), 1.05 (d, J = 6.4 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 157.04 (d, J_{PC} = 32 Hz), 150.63, 133.82, 133.55 (d, J_{PC} = 2.2 Hz), 132.74 (d, J_{PC} = 2.2 Hz), 132.17 (d, J_{PC} = 12 Hz), 130.55, 128.53, 128.17, 126.73, 126.01, 124.12, 121.47 (d, J_{PC} = 9.9 Hz), 120.91, 119.48, 119.10 (d, J_{PC} = 2.3 Hz), 119.06, 68.91, 63.29 (d, J_{PC} = 9.1 Hz), 45.60 (d, J_{PC} = 4.6 Hz), 26.34, 22.59, 19.28 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −0.133 ppm. Anal. Calcd ($C_{40}H_{41}N_2PZr$): C, 71.50; H, 6.15; N, 4.17. Found: C, 71.42; H, 5.97; N, 4.46%.

Complex ***17***

The title complex was synthesized using the same conditions and procedure as those for **15** using **10** (0.100 g, 0.287 mmol). It was obtained as a yellow solid in 77% yield (0.155 g). ^1H NMR (C_6D_6): δ 7.37 (t, J = 7.6 Hz, 2H), 7.21 (dt, J = 8.2, 0.8 Hz, 2H), 6.89 (t, J = 7.4 Hz, 2H), 6.85–6.78 (m, 3H), 6.70–6.53 (m, 9H), 6.47–6.36 (m, 4H), 6.09 (dt, J = 7.4, 1.4 Hz, 1H), 3.94–3.82 (m, 2H, NCH_2), 3.50–3.48 (m, 2H, NCH_2), 2.51 (s, 2H, $HfCH_2$), 2.12 (s, 2H, $HfCH_2$), 1.12 (t, J = 6.6 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.19 (d, J_{PC} = 29 Hz), 146.02, 135.34 (d, J_{PC} = 2.3 Hz), 134.40 (d, J_{PC} = 32 Hz), 133.20 (d, J_{PC} = 12 Hz), 132.69, 132.13 (d, J_{PC} = 12 Hz), 129.83, 128.56 (d, J_{PC} = 2.3 Hz), 127.99, 127.86, 127.01 (d, J_{PC} = 3.8 Hz), 124.56, 120.92, 118.70, 118.29, 118.22, 112.28 (d, J_{PC} = 9.1), 73.35 (d, J_{PC} = 8.3) 73.24, 36.90 (d, J_{PC} = 5.3 Hz), 13.34 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 6.69 ppm. Anal. Calcd (C36H37N2PHf): C, 61.14; H, 5.27; N, 3.96. Found: C, 60.94; H, 5.02; N, 4.21%.

Complex ***18***

The title complex was synthesized using the same conditions and procedure as those for **15** using **10** (0.100 g, 0.287 mmol) and $Zr(CH_2Ph)_4$ instead of $Hf(CH_2Ph)_4$. It was obtained as a yellow solid in 71% yield (0.126 g). ^1H NMR (C_6D_6): δ 7.43 (dt, J = 7.7, 1.6 Hz, 2H), 7.18 (dt, J = 5.4, 1.2 Hz, 2H), 6.91 (t, J = 7.6 Hz, 2H), 6.85–6.78 (m, 3H), 6.70–6.57 (m, 7H), 6.47–6.35 (m, 6H), 5.95 (tt, J = 7.0, 1.6 Hz, 1H), 4.07–3.94 (m, 2H, NCH_2), 3.52–3.39 (m, 2H, NCH_2), 2.84 (s, 2H, $HfCH_2$), 2.38 (s, 2H, $HfCH_2$), 1.09 (t, J = 6.6 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 159.91 (d, J_{PC} = 30 Hz), 147.31, 135.14, 132.90, 132.79 (d, J_{PC} = 26 Hz), 132.68, 132.19 (d, J_{PC} = 12 Hz), 130.75, 127.98, 126.42, 125.89, 124.13, 120.28, 119.84, 119.46, 118.56 (d, J_{PC} = 5.3 Hz), 111.83 (d, J_{PC} = 9.8 Hz), 64.61 (d, J_{PC} = 6.8), 64.49, 37.27 (d, J_{PC} = 4.5 Hz), 13.35 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −0.08 ppm. Anal. Calcd (C36H37N2PZr): C, 69.75; H, 6.02; N, 4.52. Found: C, 69.44; H, 5.79; N, 4.72%.

Complex ***19***

$Hf(NMe_2)_4$ (0.266 g, 0.75 mmol) and **8** (0.300 g, 0.75 mmol) were mixed in toluene (5 mL) at room temperature, and the solution was stirred overnight at this temperature. After the solvent was removed under vacuum, the residue was triturated in hexane (~1 mL). After the resulting bis(dimethylamido)hafnium complex (0.444 g, 0.668 mmol) was dissolved in toluene (15 mL), Me_3SiCl (0.725 g, 6.68 mmol) was added. The solution was stirred at room temperature overnight. After the solvent was removed under vacuum, the residue was triturated in hexane (~1 mL). The yellow solid was isolated by decantation (0.408 g). In the ^1H NMR spectrum, some impurity was detected (see SI), of which removal was unsuccessful. ^1H NMR (C_6D_6): δ 7.34–7.23 (m, 4H), 6.95–682 (m, 5H), 6.67 (dt, J = 7.5, 1.5 Hz, 2H), 5.07–4.98 (m, 2H, 2-quinaldine), 2.66–2.53 (m, 2H, 4-quinaldine), 2.30–2.20 (m, 2H, 4-quinaldine), 1.95–1.83 (m, 2H, 3-quinaldine), 1.60–1.51 (m, 2H, 3-quinaldine), 1.22 (d, J = 6.4 Hz, 6H, CH_3) ppm.

Complex ***20***

The title complex was synthesized using the same conditions and procedure as those for **19** using **8** (0.150 g, 0.375 mmol) and $Zr(NMe_2)_4$ instead of $Hf(NMe_2)_4$. Orange solid was isolated (0.190 g). In the ^1H NMR spectrum, some impurity was detected (see SI), of which removal was unsuccessful. ^1H NMR (C_6D_6): δ 7.32 (t, 2H), 7.25 (ddd, J = 12, 8.0, 1.6 Hz, 2H), 6.92–6.85 (m, 5H), 6.68 (dt, J = 7.4, 1.2 Hz, 2H), 5.61–5.41 (m, 2H, 2-quinaldine), 2.65–2.50 (m, 2H, 4-quinaldine), 2.30–2.20 (m, 2H, 4-quinaldine), 2.02–1.91 (m, 2H, 3-quinaldine), 1.59–1.50 (m, 2H, 3-quinaldine), 1.35–1.25 (d, J = 6.8, 6H, CH_3) ppm.

*Complex **21***

MeMgBr (0.32 mL, 0.972 mmol, 3.0 M solution in diethyl ether) was added dropwise to a solution of **19** (0.300 g, 0.463 mmol) in diethyl ether at −35 °C and the resulting solution was slowly warmed to room temperature. After filtering the solution through Celite, the solvent was removed under vacuum. The residue was triturated in hexane (~1 mL). The yellow solid was isolated by decantation (0.270 g, 96%). ^{1}H NMR (C_6D_6): δ 7.44 (t, J = 7.4 Hz, 2H), 7.28–7.21 (m, 2H), 7.05 (d, J = 6.8 Hz, 2H), 6.95–6.89 (m, 2H), 6.88–6.81 (m, 1H), 6.65 (t, J = 7.4 Hz, 2H), 4.92–4.81 (m, 2H, 2-quinaldine), 2.91–2.78 (m, 2H, 4-quinaldine), 2.49–2.38 (m, 2H, 4-quinaldine), 1.91–1.79 (m, 2H, 3-quinaldine), 1.75–1.63 (m, 2H, 3-quinaldine), 1.34 (d, J = 6.8 Hz, 6H, CH_3), 0.35 (s, 3H, HfMe), 0.01 (s, 3H, HfMe) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 158.74 (d, J_{PC} = 32 Hz), 135.58 (d, J_{PC} = 28 Hz), 134.14, 133.61, 131.51 (d, J_{PC} = 13 Hz), 129.03, 128.93 (d, J_{PC} = 9.1 Hz), 122.24 (d, J_{PC} = 9.9 Hz), 118.55 (d, J_{PC} = 6.1 Hz), 116.64 (d, J_{PC} = 41 Hz), 59.71 (d, J_{PC} = 5.3 Hz), 49.30 (d, J_{PC} = 14 Hz), 45.79 (d, J_{PC} = 6.9 Hz), 25.99, 22.77, 21.09 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −0.77 ppm. Anal. Calcd ($C_{28}H_{33}N_2PHf$): C, 55.40; H, 5.48; N, 4.61. Found: C, 55.13; H, 5.19; N, 4.88%.

*Complex **22***

The title complex was synthesized using the same conditions and procedure as those for **21** using **20** (0.197 g, 0.352 mmol). It was obtained as an orange solid in 79% yield (0.145 g). ^{1}H NMR (C_6D_6): δ 7.46 (t, J = 7.4 Hz, 2H), 7.27–7.19 (m, 2H), 7.03 (d, J = 7.2 Hz, 2H), 6.93–6.81 (m, 3H), 6.66 (t, J = 7.8 Hz, 2H), 5.19–5.09 (m, 2H, 2-quinaldine), 2.92–2.77 (m, 2H, 4-quinaldine), 2.52–2.42 (m, 2H, 4-quinaldine), 1.92–1.82 (m, 2H, 3-quinaldine), 1.72–1.65 (m, 2H, 3-quinaldine), 1.37 (d, J = 6.8 Hz, 6H, CH_3), 0.50 (s, 3H, ZrMe), 0.10 (s, 3H, ZrMe) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 157.73 (d, J_{PC} = 32 Hz), 134.38 (d, J_{PC} = 27 Hz), 133.92 (d, J_{PC} = 1.5 Hz), 133.41 (d, J_{PC} = 2.3 Hz), 131.42 (d, J_{PC} = 13 Hz), 129.05, 128.91 (d, J_{PC} = 9.1 Hz), 121.17 (d, J_{PC} = 11 Hz), 118.54 (d, J_{PC} = 6.0 Hz), 116.78 (d, J_{PC} = 39 Hz), 46.87 (d, J_{PC} = 6.1 Hz), 46.15, 38.55 (d, J_{PC} = 11 Hz), 25.94, 22.85 (d, J_{PC} = 2.3 Hz), 21.52 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −9.24 ppm. Anal. Calcd ($C_{28}H_{33}N_2PZr$): C, 64.70; H, 6.40; N, 5.39. Found: C, 64.89; H, 6.67; N, 5.69%.

*Complex **23***

The title complex was synthesized using the same conditions and procedure as those for **19** using **9**. The final trichlorohafnium complex was sparingly soluble in C_6D_6, $CDCl_3$, and CD_2Cl_2 preventing NMR studies. Single crystals of **23** were obtained through layer diffusion of benzene solutions of the intermediate bis(dimethylamido)hafnium complex and Me_3SiCl. The NMR data for the intermediate bis(dimethylamido)hafnium complex: ^{1}H NMR (C_6D_6): δ 7.51 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.30–7.23 (m, 2H), 6.94–6.86 (m, 3H, PPh), 6.67 (t, J = 6.8 Hz, 2H, PPh), 6.62 (dd, J = 4.8, 6.4 Hz, 2H), 3.24 (s, 6H, CH_3), 2.98 (s, 6H, NMe_2), 2.91 (s, 6H, NMe_2) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 166.17 (d, J_{PC} = 30 Hz), 135.41 (d, J_{PC} = 1.5 Hz), 134.48 (d, J_{PC} = 33 Hz), 133.95, 132.19 (d, J_{PC} = 13 Hz), 128.50 (d, J_{PC} = 2.3), 128.67 (d, J_{PC} = 9.1 Hz), 117.56 (d, J_{PC} = 6.1 Hz), 116.82 (d, J_{PC} = 37 Hz), 112.40 (d, J_{PC} = 9.9 Hz), 41.75 (d, J_{PC} = 1.5 Hz), 41.01, 36.49 (d, J_{PC} = 5.3 Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −6.67 ppm.

*Complex **24***

The title complex was synthesized using the same conditions and procedure as those for **19** using **9** and Zr(NMe_2) instead of Hf(NMe_2)$_4$. The final trichlorozirconium complex was sparingly soluble in C_6D_6, $CDCl_3$, and CD_2Cl_2 preventing NMR studies. Single crystals of **24** were obtained through layer diffusion of benzene solutions of the intermediate bis(dimethylamido)zirconium complex and Me_3SiCl. The NMR data for the intermediate bis(dimethylamido)zirconium complex: ^{1}H NMR (C_6D_6): δ 7.55 (dt, J = 7.7, 1.5 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.30–7.23 (m, 2H), 6.92–6.86 (m, 3H, PPh), 6.69 (t, J = 7.2 Hz, 2H), 6.61 (dd, J = 6.0, 8.4 Hz, 2H), 3.24 (s, 6H, CH_3), 2.94 (s, 6H, NMe_2), 2.84 (s, 6H, NMe_2) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 164.89 (d, J_{PC} = 31 Hz), 135.30, 134.01 (d, J_{PC} = 30 Hz), 133.76, 132.06 (d, J_{PC} = 13 Hz), 128.89, 128.66 (d, J_{PC} = 9.1 Hz), 117.51 (d, J_{PC} = 5.3 Hz), 116.98 (d, J_{PC} = 36 Hz), 111.36 (d, J_{PC} = 9.9 Hz), 42.20, 41.44, 36.51 (d, J_{PC} = 5.3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −15.24 ppm. Anal. Calcd ($C_{20}H_{20}Cl_3N_2PHZr$): C, 46.47; H, 3.90; N, 5.42. Found: C, 46.13; H, 3.61; N, 5.77%.

Typical procedure for ethylene/1-octene copolymerization (entry 3 in Table 1)

In a glove box, a dried 75 mL bomb reactor was charged with a solution of 1-octene (4.0 g, 1.0 M) in methylcyclohexane (27 mL) and MMAO-4 (Akzo, 7.0 wt% Al in toluene, 29 mg, Al/M = 75). The reactor was assembled and brought out from the glove box. The reactor was then heated to 100 °C using an oil bath. $[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ (1.00 g) and **13** (5.0 mg) were respectively dissolved, in 22.3 and 1.00 g of toluene to make stock solutions. The stock solution of $[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ (34 mg, 1.2 μmol) was taken and then diluted with toluene to be 1.0 mL. MMAO-4 solution (19 mg, Al/M = 50) was taken and diluted with toluene to be 1.0 mL. The stock solution of the complex (1.0 μmol) was taken and also diluted with toluene to be 1.0 mL. The three solutions were mixed and injected into the reactor using a syringe. Ethylene gas (30 bar) was immediately fed into the reaction vessel. After conducting the polymerization for 3 min, ethylene gas was vented and methanol (10 mL) was added immediately. The isolated polymer lump was dried under vacuum at 150 °C for several hours.

X-ray crystallography

Reflection data for **13**, **22**, **23**, and **24** were collected at 100 K on a Bruker APEX II CCD area diffractometer using graphite-monochromated Mo K-α radiation (λ = 0.7107 Å). Specimens of suitable quality and size were selected, mounted, and centered in the X-ray beam by using a video camera. The hemisphere of the reflection data was collected as φ and ω scan frames at 0.5°/frame and an exposure time of 10 s/frame. The cell parameters were determined and refined by the SMART program. Data reduction was performed using the SAINT software. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Crystallographic data for **13** (CCDC #, 1001475): $C_{40}H_{38}HfNPS$, M = 774.25, monoclinic, a = 15.9509(10), b = 11.2180(7), c = 19.9492(12) Å, β = 111.554(2)°, V = 3320.0(4) Å^3, T = 100(2) K, space group $P2_1/c$, Z = 4, 5765 unique (R(int) = 0.0545) which were used in all calculations. The final wR_2 was 0.0919 ($I > 2\sigma(I)$). Crystallographic data for **22** (CCDC #, 1001472): $C_{28}H_{33}N_2PZr$, M = 519.75, monoclinic, a = 12.6555(11), b = 12.4693(10), c = 16.2297(12) Å, β = 98.383(6)°, V = 2533.8(4) Å^3, T = 100(2) K, space group $P2_1/n$, Z = 4, 20,457 reflections measured, 4452 unique (R(int) = 0.1496) which were used in all calculations. Crystallographic data for **23** (CCDC #, 1001473): $C_{20}H_{20}Cl_3HfN_2P$, M = 604.19, triclinic, a = 9.8889(6), b = 10.3368(5), c = 14.8825(8) Å, α = 93.148(4)°, β = 93.843(4)°, γ = 116.625(3)°, V = 1350.74(13) Å^3, T = 100(2) K, space group $P\text{-}1$, Z = 2, 17,513 reflections measured, 4684 unique (R(int) = 0.1405)

which were used in all calculations. Crystallographic data for **24** (CCDC #, 1001474): $C_{27}H_{28}Cl_3N_2PZr$, $M = 608.05$, triclinic, $a = 9.8702(6)$, $b = 10.4979(7)$, $c = 15.1155(9)$ Å, $\alpha = 94.352(4)^\circ$, $\beta = 92.311(4)^\circ$, $\gamma = 116.190(4)^\circ$, $V = 1396.59(15)$ Å^3, $T = 100(2)$ K, space group *P-1*, $Z = 2$, 21,447 reflections measured, 4904 unique (R(int) = 0.0617) which were used in all calculations.

Acknowledgments

This work was supported by Mid-carrier Researcher Program (No. 2012-003303) and by Basic Science Research Program (No. 2009-0093826) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education.

Appendix A. Supplementary material

CCDC 1001472–1001475 and 649338 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.09.009.

References

[1] W. Kaminsky, Macromolecules 45 (2012) 3289–3297.
[2] J. Cano, K. Kunz, J. Organomet. Chem. 692 (2007) 4411–4423.
[3] K. Nomura, Dalton Trans. (2009) 8811–8823.
[4] D.W. Stephan, J.C. Stewart, F. Guérin, S. Courtenay, J. Kickham, E. Hollink, C. Beddie, A. Hoskin, T. Graham, P. Wei, R.E.V.H. Spence, W. Xu, L. Koch, X. Gao, D.G. Harrison, Organometallics 22 (2003) 1937–1947.
[5] M. Lamberti, M. Mazzeo, D. Pappalardo, C. Pellecchia, Coord. Chem. Rev. 253 (2009) 2082–2097.
[6] H. Makio, H. Terao, A. Iwashita, T. Fujita, Chem. Rev. 111 (2011) 2363–2449.
[7] K. Press, V. Venditto, I. Goldberg, M. Kol, Dalton Trans. 42 (2013) 9096–9103.
[8] W. Zhang, W.-H. Sun, C. Redshaw, Dalton Trans. 42 (2013) 8988–8997.
[9] A.H. Tullo, Chem. Eng. News 88 (2010 Oct 18) 10–16.
[10] T.R. Boussie, G.M. Diamond, C. Goh, K.A. Hall, A.M. LaPointe, M. Leclerc, C. Lund, V. Murphy, J.A.W. Shoemaker, U. Tracht, H. Turner, J. Zhang, T. Uno, R.K. Rosen, J.C. Stevens, J. Am. Chem. Soc. 125 (2003) 4306–4317.
[11] P.P. Fontaine, R. Figueroa, S.D. McCann, D. Mort, J. Klosin, Organometallics 32 (2013) 2963–2972.
[12] P. De Waele, B.A. Jazdzewski, J. Klosin, R.E. Murray, C.N. Theriault, P.C. Vosejpka, J.L. Petersen, Organometallics 26 (2007) 3896–3899.
[13] R. Figueroa, R.D. Froese, Y. He, J. Klosin, C.N. Theriault, K.A. Abboud, Organometallics 30 (2011) 1695–1709.
[14] R.D.J. Froese, B.A. Jazdzewski, J. Klosin, R.L. Kuhlman, C.N. Theriault, D.M. Welsh, K.A. Abboud, Organometallics 30 (2011) 251–262.
[15] P.P. Fontaine, J. Klosin, N.T. McDougal, Organometallics 31 (2012) 6244–6251.
[16] E. Szuromi, J. Klosin, K.A. Abboud, Organometallics 30 (2011) 4589–4597.
[17] L.C. So, C.C. Liu, M.C.W. Chan, J.C.Y. Lo, K.H. Sze, N. Zhu, Chem. Eur. J. 18 (2012) 565–573.
[18] J.C.Y. Lo, M.C.W. Chan, P.K. Lo, K.C. Lau, T. Ochiai, H. Makio, Organometallics 32 (2013) 449–459.
[19] S.H. Jun, J.H. Park, C.S. Lee, S.Y. Park, M.J. Go, J. Lee, B.Y. Lee, Organometallics 32 (2013) 7357–7365.
[20] L.P. He, J.Y. Liu, Y.G. Li, S.R. Liu, Y.S. Li, Macromolecules 42 (2009) 8566–8570.
[21] R.J. Long, V.C. Gibson, A.J.P. White, Organometallics 27 (2007) 235–245.
[22] E. Despagnet-Ayoub, L.M. Henling, J.A. Labinger, J.E. Bercaw, Organometallics 32 (2013) 2934–2938.
[23] Y.-C. Hu, C.-C. Tsai, W.-C. Shih, G.P.A. Yap, T.-G. Ong, Organometallics 29 (2010) 516–518.
[24] X.Y. Tang, Y.X. Wang, B.X. Li, J.Y. Liu, Y.S. Li, J. Polym. Sci. Part A Polym. Chem. 51 (2013) 1585–1594.
[25] S.W. Zhang, L.P. Lu, B.X. Li, Y.S. Li, J. Polym. Sci. Part A Polym. Chem. 50 (2012) 4721–4731.
[26] S.W. Zhang, G.B. Zhang, L.P. Lu, Y.S. Li, J. Polym. Sci. Part A Polym. Chem. 51 (2013) 844–854.
[27] S.W. Zhang, L.P. Lu, Y.Y. Long, Y.S. Li, J. Polym. Sci. Part A Polym. Chem. 51 (2013) 5298–5306.
[28] P. Tao, H.L. Mu, J.Y. Liu, Y.S. Li, Organometallics 32 (2013) 4805–4812.
[29] X.Y. Tang, Y.X. Wang, S.R. Liu, J.Y. Liu, Y.S. Li, Dalton Trans. 42 (2013) 499–506.
[30] C.J. Wu, S.H. Lee, H. Yun, B.Y. Lee, Organometallics 26 (2007) 6685–6687.
[31] J.H. Park, S.H. Do, A. Cyriac, H. Yun, B.Y. Lee, Dalton Trans. 39 (2010) 9994–10002.
[32] S. Kim, J. Park, B. Song, S.-W. Yoon, M. Go, J. Lee, B. Lee, Catalysts 104 (2013) 104–124.
[33] C.H. Lee, E.J. Lee, S.W. Jung, J.A. Lee, B.R. Lee, B.Y. Lee, L. Chem (Eds.), LG Chem., 2011.
[34] J.-F. Tremblay, Chem. Eng. News 90 (2012 Feb 27) 7.
[35] T.R. Boussie, G.M. Diamond, C. Goh, K.A. Hall, A.M. LaPointe, M.K. Leclerc, V. Murphy, J.A.W. Shoemaker, H. Turner, R.K. Rosen, J.C. Stevens, F. Alfano, V. Busico, R. Cipullo, G. Talarico, Angew. Chem. Int. Ed. 45 (2006) 3278–3283.
[36] V. Busico, R. Cipullo, R. Pellecchia, L. Rongo, G. Talarico, A. Macchioni, C. Zuccaccia, R.D.J. Froese, P.D. Hustad, Macromolecules 42 (2009) 4369–4373.
[37] R.D.J. Froese, P.D. Hustad, R.L. Kuhlman, T.T. Wenzel, J. Am. Chem. Soc. 129 (2007) 7831–7840.
[38] C. Zuccaccia, V. Busico, R. Cipullo, G. Talarico, R.D.J. Froese, P.C. Vosejpka, P.D. Hustad, A. Macchioni, Organometallics 28 (2009) 5445–5458.
[39] K.A. Frazier, R.D. Froese, Y. He, J. Klosin, C.N. Theriault, P.C. Vosejpka, Z. Zhou, K.A. Abboud, Organometallics 30 (2011) 3318–3329.
[40] J.C.Y. Lo, M.C.W. Chan, P.-K. Lo, K.-C. Lau, T. Ochiai, H. Makio, Organometallics 32 (2013) 449–459.
[41] Z.J. Tonzetich, C.C. Lu, R.R. Schrock, A.S. Hock, P.J. Bonitatebus Jr., Organometallics 23 (2004) 4362–4372.
[42] R.R. Schrock, J. Adamchuk, K. Ruhland, L.P.H. Lopez, Organometallics 24 (2005) 857–866.