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Preparation of Phosphine-Amido Hafnium and Zirconium Complexes for Olefin Polymerization

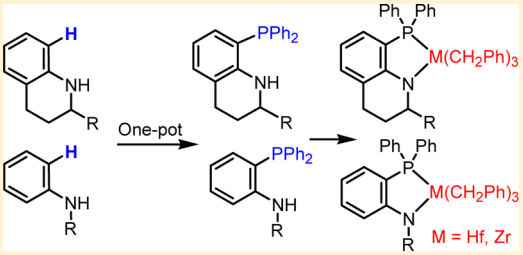
Sung Hae Jun,[†] Ji Hae Park,[†] Chun Sun Lee,[†] Seong Yeon Park,[†] Min Jeong Go,[‡] Junseong Lee,[‡] and Bun Yeoul Lee*,[†]

[†]Department of Molecular Science and Technology, Ajou University, Suwon 443-749, South Korea

[‡]Department of Chemistry, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 500-757, South Korea

Supporting Information

ABSTRACT: Aniline (*N*-R-C_6H_5NH) and 1,2,3,4-tetrahydroquinoline (2-R-C_9H_9NH) derivatives were ortho-lithiated via conversion of the respective −NH groups to −N(COOLi), followed by treatment with *t*BuLi. The resulting ortho-lithiated compounds were transformed to *ortho*-Ph_2P-substituted derivatives on treatment with $Ph_2P(OPh)$. Further reaction of the resulting compounds with $M(CH_2Ph)_4$ (M = Zr, Hf) afforded a series of Hf and Zr complexes: (2-R-8-$Ph_2PC_9H_9N$)$Hf(CH_2Ph)_3$ (**8**, R = H; **9**, R = Me; **10**, R = *i*Pr; **11**, R = *n*Bu), (N-R-2-$Ph_2PC_6H_4N$)$Hf(CH_2Ph)_3$ (**12**, R = Me; **13**, R = Et; **14**, R = *i*Pr), (2-R-8-$Ph_2PC_9H_9N$)$Zr(CH_2Ph)_3$ (**15**, R = H; **16**, R = Me; **17**, R = *i*Pr; **18**, R = *n*Bu), and (N-R-2-$Ph_2PC_6H_4N$)$Zr(CH_2Ph)_3$ (**19**, R = Me; **20**, R = Et)]. X-ray crystallographic studies of **9**, **14**, **16**, and **19** revealed a distorted trigonal-bipyramidal structure with two benzyl moieties in equatorial positions and the remaining benzyl ligand occupying an apical position; in solution, however, three benzyl ligands became scrambled, as evidenced by a single set of benzyl signals in the corresponding ^1H NMR spectra. The complexes showed comparable activities (17−48 × 10^6 g/mol-M·h) to the Ti-based constrained geometry catalyst (CGC) (36 × 10^6 g/mol-Ti·h) in ethylene/1-octene copolymerization, despite their inferior 1-octene incorporation capabilities (3−8 mol % versus 17 mol %). Compound **15** showed a moderate 1-octene incorporation capability (7.7 mol %), whereas the others showed low 1-octene incorporations (2−4 mol %). Compounds **9** and **16** provided high-molecular-weight polymers with M_w > 200 000 even at high reaction temperatures of 100−130 °C.



INTRODUCTION

Currently, approximately 5 million tons of polyethylene (PE) and 1.5 million tons of polypropylene (PP) are produced annually using single-site homogeneous Ziegler catalysts.[1] Methyl aluminoxane (MAO)-activated group 4 metallocenes were introduced as single-site homogeneous Ziegler catalysts by Kaminsky;[2] catalytic species were later expanded to half-metallocenes constructed with a cyclopentadienyl and an amido ligand.[3−5] Single-site polyolefin catalysts were further extended to postmetallocenes comprising noncyclopentadienyl ligand systems.[6−9] Most of the known single-site polyolefin catalysts have the common structure "LMX_2". The spectator ligand L, attached permanently to the metal center, imparts an electronic and a steric influence to the metal center. One of the ligands X (alkyl) is abstracted by an activator to generate a cationic metal center, while the polymer chain grows from the other X moiety. Different types of highly active catalysts possessing the "LMX_3" structure (M: Zr or Hf; L: ether-amido ligand; X: benzyl) were discovered by Dow and Symyx by high-throughput screening methods;[10] since this discovery, the spectator ligand L has been further diversified to include imine-amido, imine-enamido, and aminotroponiminato derivatives for use in catalytic olefin polymerization.[11−16] These species were followed by reports of [*N*,*N*,*C*]-HfX_2 complexes based on the pyridine-amido ligand system, incorporating ortho-metalated aryl moieties;[17−22] such [*N*,*N*,*C*]-HfX_2 complexes have been successfully utilized in chain shuttling polymerization reactions.[23−27] Similar types of pyridine-2-phenolate-6-(σ-aryl) derived complexes were also reported.[28,29] Phosphine and its related ligands have rarely been utilized in the construction of group-4-metal based polymerization catalysts.[30−32] In this work, we report fabrication of LMX_3-type complexes constructed using phosphine-amido ligands and examine their olefin polymerization reactivities.

RESULTS AND DISCUSSION

Ligand Synthesis. We have previously developed a simple protocol for the directed ortho-lithiation of tetrahydroquinoline derivatives, which allows the facile construction of a series of half-metallocenes.[33−35] Several half-metallocenes prepared by this method showed excellent catalytic performances in ethylene/α-olefin copolymerization reaction, with potential applicability in commercial processes.[36,37] The lithium carbamate [−N(COOLi)] group, generated from tetrahydroquinoline derivatives by sequential treatment with *n*-BuLi and CO_2, acts as a directing group in the directed ortho-lithiation process, facilitating the deprotonation of the aryl ortho-proton upon treatment with *t*BuLi (Scheme 1). Advantageously, the

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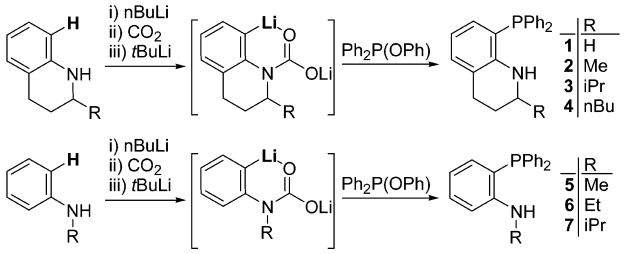
Scheme 1. Ligand Synthesis

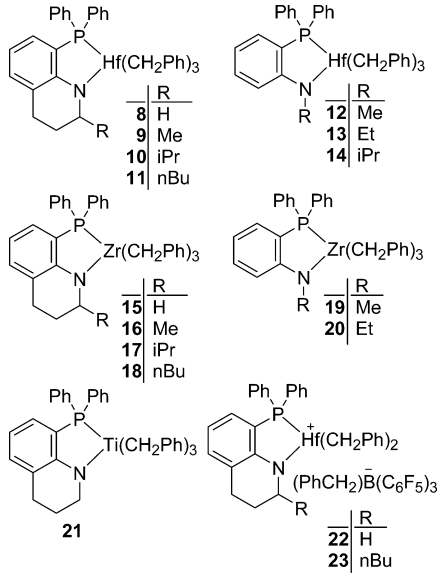


original amino group (−NH−) is easily recovered during the acidic workup procedure. Katritzky attempted ortho-lithiation of the lithium carbamate of tetrahydroquinoline over two decades ago by treatment with *t*BuLi−KO*t*Bu in THF. The resulting product was not the ortho-lithiated analogue; rather, an *α*-lithiated product was obtained.[38] We observed that the treatment of a tetrahydroquinoline-derived lithium carbamate in a nonpolar solvent (diethyl ether) with *t*BuLi containing a residual amount of THF yielded the desired ortho-lithiated product; when this product was reacted with chlorodiphenylphosphine (Ph_2PCl), a negligible amount of the desired product was obtained. We attributed this failure to the high reactivity of Ph_2PCl, which might react not only with the ortho-lithiated carbon nucleophile but also with the carbamate anion. Replacing Ph_2PCl with the less reactive reagent $Ph_2P(OPh)$ afforded the desired products (**1**−**4**) in fair yields (50−77%, Scheme 1). Further, compound purification could be achieved using column chromatography without aerobic oxidation. The synthesis of **2** was recently reported; however, its preparation required a tedious five-step procedure from an expensive starting material (8-bromoquinoline).[39] The ^1H, ^{13}C, and ^{31}P NMR spectra and high-resolution mass data were in good agreement with the expected structure.

By employing the same ortho-lithiation method,[40] *N*-R-2-(diphenylphosphanyl)anilines (R = Me, Et, *i*Pr) were prepared from *N*-alkylanilines (Scheme 1). In our previous report, ortho-lithiation was not facile for substrates bearing sterically bulky substituents around the nitrogen atom, such as *N*-isopropylaniline.[40] We determined that difficulties arose during the CO_2-addition step, which was resolved by replacing diethyl ether—the reaction solvent used in this step—with THF. Katritzky previously reported the ortho-lithiation of *N*-methylaniline,[41] which was successfully utilized by others in the preparation of *N*-methyl-2-(diphenylphosphanyl)aniline (**5**).[42−44] Synthesis of *N*-ethyl-2-(diphenylphosphanyl)aniline (**6**) was also reported by a different route, but as a mixture of para-isomers in low yield (25%).[45]

Metalation and Activation Reaction. The overnight reaction of **1**−**7** with $Hf(CH_2Ph)_4$ in toluene at room temperature afforded the desired complexes **8**−**14**, respectively, in good yields (71−82%, Chart 1). The rate of metalation depended on the ligand structure. For **8** and **9**, the metalation completed in several hours, but for the others, it needed overnight stirring for the completion. Yellow powders were isolated by trituration in hexane, which were clean according to the ^1H NMR spectral analysis. The NH signals observed at 4.7−5.0 ppm in the ^1H NMR spectra of **1**−**7** disappeared in the corresponding spectra of **8**−**14**. In the ^1H NMR spectra of **8** and **12**−**14** prepared from achiral ligands, a single benzyl-CH_2 signal was observed at 2.4 ppm as a singlet, indicating that the three benzyl ligands were equivalent in solution. As shown in Figure 2, the crystalline complexes adopted a distorted trigonal-

Chart 1. Metal Complexes Prepared Using Phosphine-Amido Ligands



bipyramidal structure, in which two benzyl ligands and a phosphine ligand formed a plane with the metal center, while the remaining benzyl and amido ligand occupied the apical sites. The apical and equatorial benzyl ligands were expected to appear differentiated if the solid structure persisted in the solution; however, only a single benzyl-CH_2 signal was observed, indicating that the three benzyl ligands rapidly scrambled in solution. In the ^1H NMR spectra of **9**−**11** prepared from chiral ligands, the benzyl-CH_2 signals were observed at 2.5 ppm (dd, J = 12 and 2.4 Hz) and 2.3 ppm (d, J = 12 Hz) with an equal integration value. Because of the presence of a chiral center, the two benzyl methylene protons were diastereotopic, exhibiting distinct chemical shifts with a large geminal coupling constant ($^2J_{H-H}$ = 12 Hz). Further coupling, as noted by the accompanying smaller coupling constant, was attributed to coupling with the phosphorus atom ($^3J_{P-H}$ = 2.4 Hz). The ^{31}P signals were observed at 30−33 ppm after Hf metal coordination, corresponding to a distinct upfield chemical shift from that observed for the free ligands (−20 ppm). For **10**, the ^{31}P signal was observed at 19 ppm, a deviation from the chemical shifts of the other complexes (30−33 ppm).

The same procedure and conditions used for the synthesis of Hf complexes afforded the Zr complexes **15**−**20** when $Zr(CH_2Ph)_4$ was used. The reaction rate for the formation of **17** was comparatively slow, requiring 3 days, whereas the other complexes were afforded after stirring overnight. Reaction of *N*-isopropyl-2-(diphenylphosphanyl)aniline did not afford the desired Zr complex; instead, a black intractable solid was formed. The ^1H NMR spectra of the Zr complexes exhibited the same benzyl methylene proton signal pattern in almost the same region as was observed for the Hf complexes, indicating that all three benzyl ligands were equivalent because of rapid scrambling. The ^{31}P signals were observed at 22−24 ppm, downfield-shifted from the chemical shifts observed for the Hf complexes. For **17**, the ^{31}P signal was also observed at 17 ppm, deviating from the chemical shifts of other Zr species in a manner similar to that of the Hf complexes. It is suggested that the steric influence of the isopropyl group provided interference at the metal center, resulting in the slower metalation reaction

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rate and shift in the ^{31}P signals from the typical values observed for the other complexes. Contrary to the failure in metalation of the related amine-based ligand systems, titanium complex **21** was successfully prepared, possibly by the aid of a phosphine unit, according to the same procedure and conditions using $Ti(CH_2Ph)_4$. A single benzyl-CH_2 signal was also observed at 3.5 ppm as a singlet, and a ^{31}P signal was observed at 29 ppm. The Hf and Zr complexes were yellowish solids, whereas the titanium complex was a reddish brown solid.

When 1 equiv of $B(C_6F_5)_3$ was added to a solution of **8** in C_6D_6, an oily compound was deposited, which became soluble by the addition of a small amount of C_6H_5Cl.[46] The ^1H NMR spectrum was quite clean and assignable to the structure of ion-paired complex **22** (Chart 1 and Figure 1). The methylene signal in $[PhCH_2B(C_6F_5)_3]^-$ was observed at 3.5 ppm as a singlet, while that of the other two benzyl moieties attached at the Hf center were observed at 5.7 ppm as a doublet ($^3J_{P-H}$ = 7.2 Hz), significantly downfield-shifted from the chemical shift observed for **8** (2.4 ppm). The significant change in the chemical shift is thought to be due to a change in the hapticity (from η^1 to η^3) of the benzyl ligand. The $-CH_2N-$ signal was fairly upfield-shifted from 3.4 ppm in **8** to 2.3 ppm in **22**. The complex was stable in the solution; therefore, negligible changes were observed in the ^1H NMR spectrum after allowing the NMR sample in the solution to stand at room temperature for 3 h. However, the appearance of an additional unassigned Hf-CH_2Ph doublet signal at 6.2 ppm was observed when the sample was kept overnight in the solution. The assignment was also confirmed by the analysis of the ^1H NMR spectrum of **23**. The methylene signal in $[PhCH_2B(C_6F_5)_3]^-$ was observed at the same chemical shift (3.5 ppm, singlet) as that found in **22**. The $-CH_2Ph$ signal corresponding to the other two benzyl groups on Hf was observed in the region similar to that for **22**; however, the signal was split into two doublet signals at 6.0 and 5.7 ppm because of the presence of a chiral center in the ligand framework. The $-CHN-$ signal was also upfield-shifted from 4.0 ppm in **11** to 3.1 ppm in **23**. Furthermore, **23** was more stable in solution than **22**; the ^1H NMR spectrum remained unchanged even after keeping the sample in the solution for 1 day. In the ^{19}F NMR spectra, only a set of signals was observed at −130.6, −164.1, and −166.9 ppm, assignable to a solvent separated free anion.[15] In related amidoquinoline complexes, two sets of ^{19}F NMR signals were observed: one was a solvent separated free anion and the other minor was a coordinated ion.[15] When ethylene gas was fed into the NMR cell containing **23**, rapid consumption of ethylene was observed with formation of polymer precipitates.

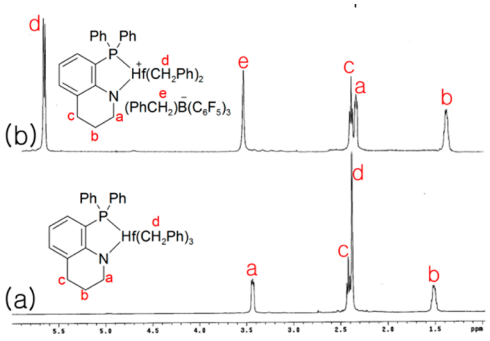

Figure 1. ^1H NMR spectra of **8** and **22**.

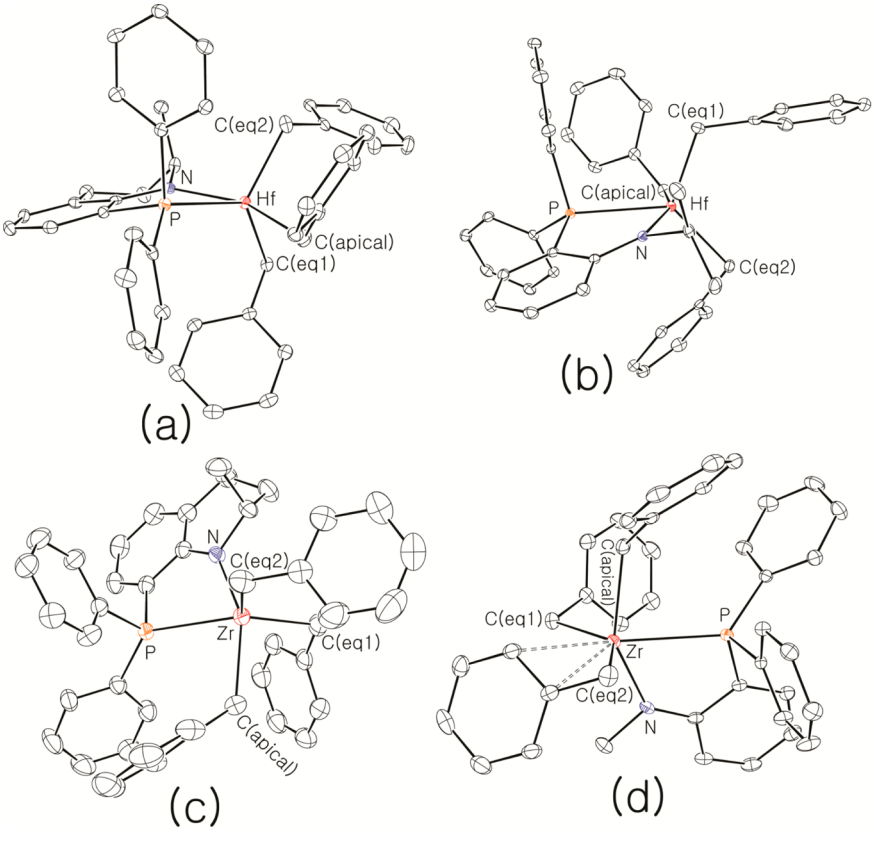

Figure 2. Thermal ellipsoid plots (30% probability level) of **9** (a), **14** (b), **16** (c), and **19** (d). Hydrogen atoms are omitted for clarity.

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Table 1. Selected Bond Distances (Å) and Angles (deg) in 9, 14, 16, and 19

	9 (Hf)	14 (Hf)	16 (Zr)	19 (Zr)
M−P	2.735(1)	2.6808(5)	2.7558(6)	2.7498(7)
M−N	2.086(3)	2.109(2)	2.104(2)	2.113(2)
M−C(eq 1)	2.250(6)	2.232(2)	2.271(3)	2.316(2)
M−C(eq 2)	2.217(7)	2.247(2)	2.246(3)	2.285(3)
M−C(apical)	2.306(6)	2.293(2)	2.322(3)	2.319(2)
M−C(eq 1)−C	101.3(4)	116.88(14)	101.9(2)	101.48(15)
M−C(eq 2)−C	116.0(4)	102.26(13)	111.5(2)	85.48(14)
M−C(apical)−C	125.5(4)	128.53(15)	126.9(2)	125.57(16)
P−M−C(eq 1)	130.20(16)	112.38(6)	129.40(9)	130.34(7)
C(eq 1)−M−C(eq 2)	113.98(15)	118.07(8)	116.87(11)	134.6(1)
C(eq 2)−M−P	115.54(17)	129.46(6)	113.47(10)	95.06(7)
N−M−C(apical)	151.43(18)	152.81(7)	149.36(9)	145.08(9)
C(apical)−M−C(eq 1)	93.5(2)	96.50(8)	93.99(12)	89.37(9)
C(apical)−M−C(eq 2)	98.1(2)	92.44(8)	98.28(13)	98.89(10)
C(apical)−M−P	84.64(15)	84.63(6)	83.51(7)	81.53(7)
N−M−C(eq 1)	96.11(17)	101.44(7)	96.15(11)	95.24(9)
N−M−C(eq 2)	102.33(18)	96.87(7)	102.69(10)	102.14(9)
N−M−P	68.64(10)	69.74(5)	67.76(5)	69.18(6)
M−N−C(sp2)	134.9(3)	135.01(13)	135.54(15)	135.32(16)
M−N−C(sp3)	110.8(3)	104.28(12)	109.71(15)	109.00(17)
C(sp2)−N−C(sp3)	113.9(4)	120.70(16)	114.42(19)	115.2(2)

Table 2. Ethylene/1-Octene Copolymerization Results[a]

entry	catalyst	temp (°C)	yield (g)	activity[b]	[Oct][c] (mol %)	M_w	M_w/M_n	T_m (°C)
1	**8**	100−103−100	0.36	7	3.3	119000	2.72	111
2	**9**	100−123−113	1.10	22	2.1	207000	3.13	118
3	**10**	100−125−112	1.02	20	3.3	81000	2.81	111
4	**11**	100−127−116	1.30	26	3.2	103000	2.59	115
5	**12**	100−135−129	2.42	48	4.3	70000	2.77	116
6	**13**	100−129−125	1.80	36	3.0	94000	2.91	111
7	**14**	100−133−129	2.35	47	3.8	76000	2.70	108
8	**15**	100−130−114	1.33	27	7.7	117000	6.85	108
9	**16**	100−134−113	0.86	17	2.5	250000	5.93	116
10	**17**	100−133−113	1.13	23	3.8	147000	4.33	114
11	**18**	100−141−115	1.47	29	3.6	151000	4.56	115
12	**19**	100−127−114	1.24	25	3.7	115000	3.30	111
13	**20**	100−132−115	1.37	27	3.9	83000	2.58	113
14	**21**	100−100	∼0	∼0				
15[d]	CGC	100−125−113	1.80	36	17.4	127000	2.92	114, 68

[a]Polymerization conditions: methylcyclohexane solution of 1-octene (1.0 M, 30 mL), complex (1.0 μmol), $[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ (1.2 μmol), MAO (Al/M = 125), ethylene (30 bar), 3 min. [b]Activity in units of 10^6 g/mol-M·h. [c]1-Octene mole fraction in the copolymer measured from the ^{1}H NMR spectrum. [d]Complex (1.0 μmol), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (4.0 μmol), and iBu$_3$Al (0.80 mmol) were used.

X-ray Crystallographic Studies. Single crystals of **9**, **14**, **16**, and **19** were grown in toluene/hexane solution in a refrigerator, and their structures were confirmed by X-ray crystallography (Figure 2). The metrical parameters are summarized in Table 1. All complexes adopted a distorted trigonal-bipyramidal structure. Two benzyl and phosphine ligands were situated in equatorial positions, while the amido and remaining benzyl groups occupied the apical positions. The Hf (or Zr) atom was located on a plane formed by the three equatorial ligands, and the sum of the bond angles of P−M−C(eq^1), C(eq^1)−M−C(eq^2), and C(eq^2)−M−P was approximately 360°. The M−C(apical) vector was almost perpendicular to the plane formed by the three equatorial ligands (C(apical)−M−C(eq^1), C(apical)−M−C(eq^2), and C(apical)−M−P angles, 82−99°). The N−M−P angles (68−69°) were acutely deviated from the ideal angle of 90° anticipated for the trigonal-bipyramidal structure. As a result of this deviation, the N−M−C(apical) angles (145−153°) were also distorted from the ideal 180°. The coordinating nitrogen atoms adopted sp^2 hybridization for π-donation, and the sum of bond angles around the nitrogen atom was approximately 360°.

The Hf−P, Hf−N, and Hf−C bond distances were all slightly shorter than the corresponding Zr−P, Zr−N, and Zr−C bond distances. In all structures, the M−C(apical) distance was longer than the M−C(equatorial) distances. The tight binding of the benzyl ligands in the equatorial positions is thought to be due to the partial participation of aromatic π-electrons in bonding with the metal; in all cases, the M−C(eq)−C$_6$ angles were less obtuse than the M−C(apical)−C$_6$ angle. In the structure of **19** prepared from the sterically least encumbered ligand, the metrical parameters around an equatorial benzyl ligand were fairly different from those of either the remaining

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benzyl ligands in the same compound or the benzyl ligands in the other three compounds. The M−C(eq)−C_6 angle was acute (85.5°) compared with those of the others (101−116°). The C(eq^1)−M−C(eq^2) angle (134.6°) also deviated from that observed for the other complexes (113−118°). These parameters suggest that an η^3-binding mode was adopted by the benzyl ligand, which was further supported by the observed distances between Zr and the benzyl carbon atoms; the Zr−C_6(ipso) and Zr−C_6(ortho) distances were shorter (2.605(3) and 2.709(3) Å, respectively) than the corresponding distances observed for the other equatorial benzyl ligand, which adopted an η^1-binding mode (2.981(3) and 3.485(3) Å). However, in the ^{1}H NMR spectrum of **19**, only one benzyl-CH_2 signal was observed as a singlet at 2.55 ppm because of the rapid scrambling.

Polymerization Studies. The newly prepared complexes (**8**−**21**) were screened for activity toward ethylene/1-octene copolymerization under identical conditions: 1-octene in methylcyclohexane (1.0 M, 30 mL); metal complex (1.0 μmol); $[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ (1.2 μmol); MAO (0.125 mmol); ethylene (30 bar); initial temperature 100 °C; 3 min (Table 2). Methylcyclohexane-soluble $[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ was used as an activator, and MAO was fed as a scavenger.[6] The temperature rapidly increased by the exotherm to reach a maximum value and then dropped slowly either by the cooling with ambient air or by catalyst deactivation (Table 2, column 3). The polymerizations were run for a short time because of difficulties in stirring the reaction mixture due to the formation of a viscous solution in such a short time. Though Hf complex **8** showed a negligible activity (7 × 10^6 g/mol-M·h, entry 1), the other Hf and Zr complexes showed fairly high activities ((17−48) × 10^6 g/mol-M·h, entries 2−13); in contrast, Ti complex **21** was not active at all. The constrained geometry catalyst (CGC) $[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$ showed a similar activity (36 × 10^6 g/mol-Ti·h) under the same temperature and pressure, but was activated with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (B/Ti = 4) and iBu$_3$Al (A1/Ti = 800). Hf complexes **12**−**14** derived from *N*-alkylaniline showed higher activities ((36−47) × 10^6 g/mol-Hf·h, entries 5−7) than those (**9**−**11**) derived from tetrahydroquinoline derivatives ((20−26) × 10^6 g/mol- Hf·h, entries 2−4). Activities of Zr complexes were relatively insensitive to the ligand structure, falling in the range of (20−30) × 10^6 g/mol-Zr·h (entries 8−13). When **12** (1.0 μmol) was activated with just MAO (Al/Hf = 125), a negligible amount of polymer was obtained, but some amount of polymer (0.60 g) was generated when the MAO amount was increased to A1/Hf = 1000. When 2 equiv of $[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ was used instead of 1.2 equiv, the yield was marginally increased from 2.42 to 2.63 g.

The 1-octene contents observed for the polymers prepared with Hf complexes were in the range of 2.1−4.3 mol %. Complexes **12**−**14** derived from *N*-alkylaniline showed slightly higher 1-octene incorporation than those (**9**−**11**) derived from tetrahydroquinoline derivatives. The tetrahydroquinoline-derived Zr complex **15** showed the highest 1-octene incorporation (7.7 mol %) among the prepared Hf and Zr complexes; however, the other Zr complexes showed low 1-octene incorporation (2.5−3.9 mol %), similar to that shown by the Hf complexes. These 1-octene contents were significantly lower than that of the polymer prepared using the CGC under similar conditions (17 mol %, Table 2, entry 15). Because of low 1-octene content, a single and fairly sharp melting signal was observed at ca. 110 °C in the DSC scan, which was similar to that of commercial linear low-density polyethylene (LLDPE). The imine-(en)amido and quinoline-amido LMX_3-type complexes of Hf and Zr also showed moderate 1-octene incorporation in a similar range.[11,13,14,16]

The molecular weights of the obtained polymers were found to be sensitive to the ligand structure; the tetrahydroquinoline-derived Hf complex **8** generated a polymer with M_w = 119 000 (Table 2, entry 1). Attaching a methyl substituent at the 2-position of the tetrahydroquinoline framework resulted in a nearly 2-fold increase in M_w to 207 000 (entry 2), whereas attaching a bulkier isopropyl or *n*-butyl group yielded a decrease in M_w back to ∼100 000 (entries 3−4). A similar trend was observed for Zr complexes: the tetrahydroquinaldine-derived Zr complex **16** generated the highest-molecular-weight polymer (M_w = 250 000), whereas *N*-alkylaniline-derived complexes generated lower-molecular-weight polymers (M_w = 70 000−115 000) than those derived from tetrahydroquinoline derivatives in both the Hf and the Zr complexes. The molecular weight distribution of the polymers prepared using Hf complexes was narrow (M_w/M_n = 2.6−3.1) but was rather broad for the Zr complexes (M_w/M_n = 2.6−6.8).

CONCLUSION

Diphenylphosphanyl groups were easily attached to either the 8-position of 2-alkyl-1,2,3,4-tetrahydroquinolines or the ortho-position of *N*-alkylanilines in a one-pot procedure. Using the resulting compounds, a series of phosphine-amido Hf and Zr complexes were prepared, and the structures of four of these complexes were elucidated by X-ray crystallography. The complexes adopted a distorted trigonal-bipyramidal structure with two benzyl ligands in the equatorial positions and the remaining benzyl moiety occupying the apical position; only a single benzyl signal was observed in the ^{1}H NMR spectra of these complexes, indicating rapid scrambling of the three benzyl ligands in solution. In the complex coordinated by the sterically least encumbering ligand, a benzyl in the equatorial position adopted the η^3-binding mode. The complexes exhibited comparable activities ((17−48) × 10^6 g/mol-M·h) in ethylene/1-octene copolymerizations to those observed with CGC (36 × 10^6 g/mol-Ti·h), even though the 1-octene incorporation capabilities were inferior to those observed for CGC (2−8 mol % versus 17 mol %). Tetrahydroquinaldine-derived Hf and Zr complexes generated high-molecular-weight polymers (M_w > 200 000) even at high reaction temperatures of 100−130 °C.

EXPERIMENTAL SECTION

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox 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 purchased from Conley Gas (99.0%) and was purified by contact with molecular sieves and copper for several days under 50 bar pressure. The ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (376 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. $Hf(CH_2Ph)_4$, $Zr(CH_2Ph)_4$, $Ti(CH_2Ph)_4$, and $[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ were prepared according to the reported procedure and conditions.[47−49]

Compound 1. *n*-BuLi (9.5 mL, 23.7 mmol, 2.5 M solution in hexane) was added dropwise to a solution of 1,2,3,4-tetrahydroquino-

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line (3.00 g, 22.5 mmol) in hexane (42 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 (3.13 g). Then, CO_2 gas was added to a solution of lithium amide (0.59 g, 4.23 mmol) in diethyl ether (10 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 (0.34 g, 4.7 mmol) and *t*BuLi (2.7 mL, 4.7 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 $Ph_2P(OPh)$ (1.00 g, 3.59 mmol) in diethyl ether (10 mL) was added to the ortho-lithiated compound via syringe at −20 °C. The solution was subsequently stirred for 1 h at −20 °C and warmed slowly to room temperature. After stirring the solution overnight, H_2O (10 mL) was added at 0 °C and the mixture was stirred at room temperature for 30 min. The product was extracted with diethyl ether (3 × 20 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 using column chromatography on silica gel by eluting with hexane and diethyl ether (v/v, 50:1). The product was obtained as a pale yellow viscous oil (0.59 g, 52%). ^{1}H NMR (C_6D_6): δ 7.53−7.43 (m, 4H, PPh), 7.10−7.01 (m, 6H, PPh), 6.96−6.90 (m, 1H, 7-quinoline), 6.89 (d, J = 7.2 Hz, 1H, 5-quinoline), 6.56 (t, J = 7.2 Hz, 1H, 6-quinoline), 4.95 (br s, 1H, NH), 2.80−2.70 (m, 2H, 2-quinoline), 2.48 (t, J = 6.8 Hz, 2H, 4-quinoline), 1.53−1.42 (m, 2H, 3-quinoline) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 148.44 (d, J = 19 Hz), 136.81 (d, J = 8.4 Hz), 134.12 (d, J = 18 Hz), 133.01, 132.49 (d, J = 9.9 Hz), 131.15, 128.84 (d, J = 6.1 Hz), 121.08 (d, J = 3.0 Hz), 117.75 (d, J = 6.9 Hz), 117.06, 42.31, 28.14, 22.23 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −21.23 ppm. HRMS(EI): m/z calcd ([M$^+$] $C_{21}H_{20}NP$) 317.1332. Found: 317.1333.

Compound 2. The title compound was synthesized using the same conditions and procedure as those for **1** using 1,2,3,4-tetrahydroquinaldine (0.62 g, 4.23 mmol). The final product was purified by column chromatography on silica gel eluting with hexane and diethyl ether (v/v, 50:1). The pale yellow viscous oil was obtained in 50% yield (0.60 g). ^{1}H NMR (C_6D_6): δ 7.56−7.40 (m, 4H, PPh), 7.12−7.00 (m, 6H, PPh), 6.99 (t, J = 7.2 Hz, 1H, 7-quinaldine), 6.93 (d, J = 7.2 Hz, 1H, 5-quinaldine), 6.59 (t, J = 7.6 Hz, 1H, 6-quinaldine), 4.96 (br s, 1H, NH), 3.10−2.96 (m, 1H, 2-quinaldine), 2.66−2.42 (m, 2H, 4-quinaldine), 1.53−1.18 (m, 2H, 3-quinaldine), 0.75 (d, J = 6.4 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 148.41 (d, J = 18 Hz), 136.97 (d, J = 8.4 Hz), 136.61 (d, J = 8.4 Hz), 134.14 (d, J = 6.8 Hz), 133.96 (d, J = 6.8 Hz), 133.26 (d, J = 3.8 Hz), 131.03, 128.90, 128.87, 128.83, 128.80, 120.89 (d, J = 3.1 Hz), 117.51 (d, J = 6.8 Hz), 117.17, 47.78, 30.01, 27.53, 22.58 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −20.94 ppm. HRMS(EI): m/z calcd ([M$^+$] $C_{22}H_{22}NP$) 331.1490. Found: 331.1490.

Compound 3. THF (10 mL) was added dropwise to a flask containing the lithium amide (0.77 g, 4.23 mmol) at −78 °C. After CO_2 gas was added at −78 °C, the clear solution was stirred for 1 h at −78 °C. The temperature was slowly raised to 0 °C while excess CO_2 gas was removed through a bubbler. The solvent was removed by vacuum, and then diethyl ether (10 mL) was added. After cooling to −20 °C, THF (0.34 g, 4.7 mmol) and *t*BuLi (2.7 mL, 4.7 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 $Ph_2P(OPh)$ (1.00 g, 3.59 mmol) in diethyl ether solution (10 mL) was added to the ortho-lithiated compound via syringe at −20 °C. The solution was subsequently stirred for 1 h at −20 °C and warmed slowly to room temperature. The workup procedure was the same with that of **1**. The final product was purified by column chromatography on silica gel eluting with hexane and diethyl ether (v/v, 50:1). A pale yellow solid was obtained in 77% yield (1.00 g). mp 68−69 °C. ^{1}H NMR (C_6D_6): δ 7.56−7.43 (m, 4H, PPh), 7.14−7.01 (m, 6H, PPh), 7.00−6.91 (m, 2H, 5- and 7-quinoline), 6.59 (t, J = 7.6 Hz, 1H, 6-quinoline), 4.96 (br s, 1H, NH), 2.84−2.74 (m, 1H, 2-quinoline), 2.68−2.48 (m, 2H, 4-quinoline), 1.59−1.48 (m, 1H, CH), 1.48−1.29 (m, 2H, 3-quinoline), 0.69 (d, J = 7.2 Hz, 3H, CH_3), 0.67 (d, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 148.20 (d, J = 17 Hz), 136.70 (d, J = 8.3 Hz), 136.46 (d, J = 8.3 Hz), 134.28 (d, J = 9.1 Hz), 134.09 (d, J = 9.1 Hz), 132.84 (d, J = 3.8 Hz), 130.73, 128.91, 128.87, 128.85, 128.78, 121.27 (d, J = 3.0 Hz), 117.93 (d, J = 6.8 Hz), 116.99 (d, J = 3.1 Hz), 57.86, 32.98, 27.61, 24.86, 18.62, 18.53 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −19.87 ppm. HRMS(EI): m/z calcd ([M$^+$] $C_{24}H_{26}NP$) 360.1880. Found: 360.1881.

Compound 4. The title compound was synthesized using the same conditions and procedure as those for **3** using 2-*n*-butyl-1,2,3,4-tetrahydroquinaline (0.80 g, 4.23 mmol). The final product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). The pale yellow viscous oil was obtained in 77% yield (1.04 g). ^{1}H NMR (C_6D_6): δ 7.60−7.40 (m, 4H, PPh), 7.14−7.00 (m, 6H, PPh), 7.01−6.92 (m, 2H, 5- and 7-quinoline), 6.60 (t, J = 7.2 Hz, 1H, 6-quinoline), 5.01 (br s, 1H, NH), 3.10−2.83 (m, 1H, 2-quinoline), 2.76−2.40 (m, 2H, 4-quinoline), 1.68−1.54 (m, 1H, 3-quinoline), 1.46−1.29 (m, 1H, 3-quinoline), 1.25−0.94 (m, 6H, CH_2), 0.77 (t, J = 6.8 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 148.07 (d, J = 18 Hz), 136.79 (d, J = 8.3 Hz), 136.51 (d, J = 8.3 Hz), 134.21 (d, J = 5.3 Hz), 134.02 (d, J = 5.3 Hz), 132.99 (d, J = 3.8 Hz), 130.93, 128.90, 128.85, 128.80, 128.79, 121.11 (d, J = 3.0 Hz), 117.74 (d, J = 6.9 Hz), 117.06 (d, J = 2.3 Hz), 52.16 (d, J = 1.5 Hz), 36.68, 28.30, 28.24, 27.35, 23.27, 14.61 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −20.09 ppm. HRMS(EI): m/z calcd ([M$^+$] $C_{25}H_{28}NP$) 374.2037. Found: 374.2038.

Compound 5. The title compound was synthesized using the same conditions and procedure as those for **1** with *N*-methylaniline (0.45 g, 4.23 mmol). The final product was purified by column chromatography on silica gel eluting with hexane and diethyl ether (v/v, 50:1) (0.73 g, 70%). mp 117 °C. ^{1}H NMR (C_6D_6): δ 7.50−7.35 (m, 4H, PPh), 7.21 (t, J = 7.2 Hz, 1H), 7.07 (t, J = 6.8 Hz, 1H) 7.10−6.88 (m, 6H, PPh), 6.63 (t, J = 7.6 Hz, 1H), 6.48 (dd, J = 8.4, 5.6 Hz, 1H), 4.83 (br s, 1H, NH), 2.26 (d, J = 5.2 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 152.67 (d, J = 19 Hz), 136.49 (d, J = 7.6 Hz), 134.96, 134.10 (d, J = 18 Hz), 131.21, 128.91 (d, J = 3.1 Hz), 128.86, 119.05 (d, J = 7.6 Hz), 117.59, 109.91 (d, J = 3.1 Hz), 30.57 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −21.10 ppm. HRMS(EI): m/z calcd ([M$^+$] $C_{19}H_{18}NP$) 291.1176. Found: 291.1177.

Compound 6. The title compound was synthesized using the same conditions and procedure as those for **1** using *N*-ethylaniline (0.51 g, 4.23 mmol). The final product was purified by column chromatography on silica gel eluting with hexane and diethyl ether (v/v, 50:1) (0.77 g, 70%). mp 71−72 °C. ^{1}H NMR (C_6D_6): δ 7.57−7.37 (m, 4H, PPh), 7.21 (dt, J = 7.2, 1.6 Hz, 1H), 7.11 (dt, J = 6.8, 1.6 Hz, 1H), 7.09−6.97 (m, 6H, PPh), 6.28 (t, J = 7.2 Hz, 1H), 6.55 (dd, J = 8.0, 5.2 Hz, 1H), 4.83 (br s, 1H, NH), 2.90−2.65 (m, 2H, NCH_2), 0.78 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 151.83 (d, J = 17 Hz), 136.50 (d, J = 7.6 Hz), 135.31, 134.04 (d, J = 18 Hz), 131.23, 128.89 (d, J = 4.6 Hz), 128.85, 118.96 (d, J = 7.6 Hz), 117.56, 110.59, 38.77, 14.75 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −20.56 ppm. HRMS(EI): m/z calcd ([M$^+$] $C_{20}H_{20}NP$) 306.1412. Found: 306.1412.

Compound 7. The title compound was synthesized using the same conditions and procedure as those for **3** with *N*-isopropylaniline (0.57 g, 4.23 mmol). The final product was purified by column chromatography on silica gel eluting with hexane and diethyl ether (v/v, 50:1) (0.55 g, 48%). mp 53−54 °C. ^{1}H NMR (C_6D_6): δ 7.51−7.38 (m, 4H, PPh), 7.20 (dt, J = 7.6, 1.6 Hz, 1H), 7.14 (dt, J = 6.6, 1.2 Hz, 1H), 7.11−6.99 (m, 6H, PPh), 6.67−6.56 (m, 2H), 4.75 (br s, 1H, NH), 3.46−3.32 (m, 1H, NCH), 0.87 (d, J = 6.8 Hz, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 150.92 (d, J = 17 Hz), 136.44 (d, J = 8.4 Hz), 135.64 (d, J = 6.1 Hz), 134.00 (d, J = 19 Hz), 131.20, 128.87 (d, J = 4.5 Hz), 128.83, 119.10 (d, J = 7.6 Hz), 117.30 (d, J = 3.8 Hz), 111.33 (d, J = 3.0 Hz), 44.59, 22.96 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −19.59 ppm. HRMS(EI): m/z calcd ([M$^+$] $C_{21}H_{22}NP$) 320.1568. Found: 320.1568.

Complex 8. $Hf(CH_2Ph)_4$ (0.42 g, 0.77 mmol) and **1** (0.25 g, 0.77 mmol) were mixed in toluene (5 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 (~1 mL). The yellow solid was isolated by decantation, and the residual solvent was removed by evacuation (0.47 g, 80%). ^{1}H NMR (C_6D_6): δ 7.03−6.77 (m, 26H), 6.73 (dt, J = 7.6, 1.2 Hz, 1H), 6.50 (dt, J = 7.2, 1.2 Hz, 1H), 3.49−3.38 (m, 2H, 2-quinoline), 2.43 (t, J = 6.4 Hz, 2H, 4-quinoline), 2.37 (s, 6H, $HfCH_2$), 1.58−1.46 (m, 2H, 3-quinoline) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 159.66 (d, J = 27 Hz), 144.56, 133.91 (d, J = 6.9 Hz), 133.82, 131.39, 130.57, 129.69 (d, J = 30 Hz), 129.11 (d, J = 9.1 Hz), 128.83, 128.20, 123.34 (d, J = 7.6 Hz), 122.39, 120.30 (d, J = 39 Hz), 119.39 (d, J = 5.3 Hz), 83.25 ($HfCH_2$), 44.23, 27.88, 21.56 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 31.03 ppm. Anal. Calcd ($C_{42}H_{40}NPHf$): C, 65.66; H, 5.25; N, 1.82. Found: C, 65.95; H, 5.56; N, 2.14%.

Complex 9. The title complex was synthesized using the same conditions and procedure as those for **8** using **2** (0.24 g, 0.73 mmol). It was obtained as a yellow solid in 82% yield (0.47 g). ^{1}H NMR (C_6D_6): δ 7.14−6.72 (m, 26H), 6.63 (dt, J = 7.2, 1.2 Hz, 1H), 6.51 (dt, J = 7.2, 1.6 Hz, 1H), 4.18−4.06 (m, 1H, 2-quinaldine), 2.76−2.58 (m, 1H, 4-quinaldine), 2.50 (dd, J = 11.6, 2.4 Hz, 3H, $HfCH_2$), 2.41−2.29 (m, 1H, 4-quinaldine), 2.20 (d, J = 11.6 Hz, 3H, $HfCH_2$), 1.89−1.76 (m, 1H, 3-quinaldine), 1.53−1.44 (m, 1H, 3-quinaldine), 0.91 (d, J = 6.0 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 157.85 (d, J = 25 Hz), 144.71, 134.55 (d, J = 13 Hz), 133.59, 133.27 (d, J = 12 Hz), 131.06, 130.64, 129.55, 129.25 (d, J = 8.3 Hz), 128.96, 128.89, 128.49, 122.44, 122.38, 122.05, 121.60 (d, J = 9.1 Hz), 119.38 (d, J = 6.0 Hz), 82.79 (d, J = 3.8 Hz, $HfCH_2$), 44.83, 25.27, 22.31, 19.59 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 33.86 ppm. Anal. Calcd ($C_{43}H_{42}NPHf$): C, 66.02; H, 5.41; N, 1.79. Found: C, 66.35; H, 5.70; N, 2.12%.

Complex 10. The title complex was synthesized using the same conditions and procedure as those for **8** using **3** (0.12 g, 0.33 mmol). It was obtained as a yellow solid in 74% yield (0.20 g). ^{1}H NMR (C_6D_6): δ 7.15−6.75 (m, 26H), 6.62 (t, J = 7.6 Hz, 1H), 6.52 (t, J = 7.6 Hz, 1H), 3.79 (d, J = 9.2 Hz, 1H, 2-quinoline), 2.64−2.44 (m, 4H, $HfCH_2$ and 4-quinoline), 2.42−2.22 (m, 4H, $HfCH_2$ and 4-quinoline), 1.91−1.77 (m, 2H, 3-quinoline), 1.60−1.45 (m, 1H, $CHCH_3$), 0.73 (d, J = 6.4 Hz, 3H, CH_3), 0.40 (d, J = 6.4 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 156.73 (d, J = 24 Hz), 144.65, 134.44 (d, J = 12 Hz), 133.63 (d, J = 12 Hz), 131.44, 131.00 (d, J = 27 Hz), 130.66, 130.59, 130.46, 130.21, 129.15 (d, J = 8.4 Hz), 128.89, 128.71, 123.48 (d, J = 7.6 Hz), 122.62, 122.06, 121.70, 119.75 (d, J = 5.3 Hz), 84.07 ($HfCH_2$), 55.20, 30.23, 23.21, 22.77, 20.78, 19.76 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 19.11 ppm. Anal. Calcd ($C_{45}H_{46}NPHf$): C, 66.70; H, 5.72; N, 1.73. Found: C, 66.47; H, 5.46; N, 1.98%.

Complex 11. The title complex was synthesized using the same conditions and procedure as those for **8** using **4** (0.20 g, 0.54 mmol). It was obtained as a yellow solid in 71% yield (0.31 g). ^{1}H NMR (C_6D_6): δ 7.15−6.73 (m, 26H), 6.62 (t, J = 7.2, 1H), 6.51 (dt, J = 7.2 Hz, 1H), 4.01 (br s, 1H, 2-quinoline), 2.74−2.57 (m, 1H, 4-quinoline), 2.53 (dd, J = 11.6, 2.4 Hz, 3H, $HfCH_2$), 2.44−2.30 (m, 1H, 4-quinoline), 2.23 (d, J = 11.6 Hz, 3H, $HfCH_2$), 1.94−1.71 (m, 2H, 3-quinoline), 1.60−1.00 (m, 6H, CH_2), 0.81 (t, J = 7.2 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.18 (d, J = 25 Hz), 144.79, 134.50 (d, J = 12 Hz), 133.57, 133.35 (d, J = 12 Hz), 131.13, 130.60 (d, J = 9.0 Hz), 129.83, 129.50, 129.21 (d, J = 8.4 Hz), 128.94, 128.86, 128.52, 122.42, 122.28, 122.11 (d, J = 8.4 Hz), 121.87, 119.42 (d, J = 6.0 Hz), 83.33 ($HfCH_2$), 49.68, 33.35, 28.81, 23.64, 22.29, 22.02, 14.64 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 31.98 ppm. Anal. Calcd ($C_{46}H_{48}NPHf$): C, 67.02; H, 5.87; N, 1.70. Found: C, 67.33; H, 5.56; N, 2.03%.

Complex 12. The title complex was synthesized using the same conditions and procedure as those for **8** using **5** (0.19 g, 0.65 mmol). It was obtained as a yellow solid in 73% yield (0.35 g). ^{1}H NMR (C_6D_6): δ 7.20 (t, J = 6.8 Hz, 1H), 7.20−6.60 (m, 26H), 6.53 (t, J = 7.2 Hz, 1H), 6.34 (dd, J = 8.0, 5.2 Hz, 1H), 2.80 (s, 3H, CH_3), 2.40 (s, 6H, $HfCH_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 163.45 (d, J = 27 Hz), 144.09, 133.77 (d, J = 13 Hz), 133.60, 130.58, 129.65, 129.13 (d, J = 9.8 Hz), 128.79, 128.24, 122.49, 120.87, 120.48, 119.37 (d, J = 5.3 Hz), 111.84 (d, J = 9.1 Hz), 83.30 ($HfCH_2$), 32.63 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 30.16 ppm. Anal. Calcd ($C_{40}H_{38}NPHf$): C, 64.73; H, 5.16; N, 1.89. Found: C, 64.55; H, 4.84; N, 1.62%.

Complex 13. The title complex was synthesized using the same conditions and procedure as those for **8** using **6** (0.27 g, 0.87 mmol). It was obtained as a yellow solid in 74% yield (0.49 g). ^{1}H NMR (C_6D_6): δ 7.20−6.77 (m, 26H), 6.72 (dt, J = 8.0, 1.6 Hz, 1H), 6.48 (t, J = 7.2 Hz, 1H), 6.32 (dd, J = 8.4, 5.2 Hz, 1H), 3.37 (quintet, J = 6.4 Hz, 2H, NCH_2), 2.36 (s, 6H, $HfCH_2$), 0.89 (t, J = 6.4 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.26 (d, J = 25 Hz), 144.43, 133.80 (d, J = 13 Hz), 133.67, 133.26, 130.70, 129.15 (d, J = 9.1 Hz), 128.77, 128.41, 122.36, 122.32, 121.91, 119.11 (d, J = 5.3 Hz), 112.36 (d, J = 8.3 Hz), 82.67 ($HfCH_2$), 37.02, 13.10 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 32.95 ppm. Anal. Calcd ($C_{41}H_{40}NPHf$): C, 65.12; H, 5.33; N, 1.85. Found: C, 64.79; H, 5.05; N, 1.62%.

Complex 14. The title complex was synthesized using the same conditions and procedure as those for **8** using **7** (0.23 g, 0.73 mmol). It was obtained as a yellow solid in 80% yield (0.45 g). ^{1}H NMR (C_6D_6): δ 7.30−6.80 (m, 28H), 6.57 (t, J = 7.6 Hz, 1H), 4.18−4.05 (m, 1H, NCH), 2.34 (s, 6H, $HfCH_2$), 1.28 (d, J = 6.4 Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.76 (d, J = 24 Hz), 145.28, 134.09 (d, J = 13 Hz), 133.86, 132.97, 130.69, 129.15 (d, J = 9.1 Hz), 128.90, 128.36, 123.34, 122.95, 122.40, 119.93 (d, J = 5.3 Hz), 116.21 (d, J = 6.8 Hz), 81.90 ($HfCH_2$), 44.40, 20.96 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 29.74 ppm. Anal. Calcd ($C_{42}H_{42}NPHf$): C, 65.49; H, 5.50; N, 1.82. Found: C, 65.20; H, 5.28; N, 1.51%.

Complex 15. The title complex was synthesized using the same conditions and procedure as those for **8** using **1** (0.15 g, 0.48 mmol) and $Zr(CH_2Ph)_4$ (0.22 g, 0.48 mmol) instead of $Hf(CH_2Ph)_4$. It was obtained as a yellow solid in 61% yield (0.20 g). ^{1}H NMR (C_6D_6): δ 7.20−6.75 (m, 26H), 6.80 (t, J = 7.6 Hz, 1H), 6.55 (dt, J = 7.2 Hz, 1.6 Hz, 1H), 3.33−3.20 (m, 2H, 2-quinoline), 2.53 (d, J = 1.6 Hz, 6H, $HfCH_2$), 2.43 (t, J = 6.4 Hz, 2H, 4-quinoline), 1.54−1.43 (m, 2H, 3-quinoline) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.66 (d, J = 28 Hz), 144.40, 133.91 (d, J = 12 Hz), 133.72, 131.31, 130.50, 129.85 (d, J = 28 Hz), 129.33, 129.07 (d, J = 9.1 Hz), 128.01, 122.38, 122.22 (d, J = 9.1 Hz), 120.53 (d, J = 38 Hz), 119.47 (d, J = 5.3 Hz), 72.71 ($ZrCH_2$), 45.46, 27.96, 21.71 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 23.44 ppm. Anal. Calcd ($C_{42}H_{40}NPZr$): C, 74.08; H, 5.92; N, 2.06. Found: C, 74.43; H, 6.15; N, 1.78%.

Complex 16. The title complex was synthesized using the same conditions and procedure as those for **15** using **2** (0.17 g, 0.50 mmol). It was obtained as a yellow solid in 82% yield (0.28 g). ^{1}H NMR (C_6D_6): δ 7.14−6.77 (m, 26H), 6.67 (t, J = 7.2 Hz, 1H), 6.55 (dt, J = 7.2, 1.6 Hz, 1H), 3.91−3.82 (m, 1H, 2-quinaldine), 2.72−2.50 (m, 4H, $HfCH_2$ and 4-quinaldine), 2.46−2.26 (m, 4H, $HfCH_2$ and 4-quinaldine), 1.79−1.66 (m, 1H, 3-quinaldine), 1.46−1.34 (m, 1H, 3-quinaldine), 0.91 (d, J = 6.0 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 156.96 (d, J = 27 Hz), 144.44, 134.56 (d, J = 13 Hz), 133.34 (d, J = 12 Hz), 131.00, 130.56, 129.68, 129.31, 129.13 (d, J = 8.4 Hz), 128.90 (d, J = 9.8 Hz), 127.34, 122.83, 122.42, 122.33, 120.42 (d, J = 9.1 Hz), 119.39 (d, J = 5.3 Hz), 72.42 ($ZrCH_2$), 45.56, 25.18, 22.27, 19.88 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 25.65 ppm. Anal. Calcd ($C_{43}H_{42}NPZr$): C, 74.31; H, 6.09; N, 2.02. Found: C, 74.53; H, 6.40; N, 2.35%.

Complex 17. The title complex was synthesized using the same conditions and procedure as those for **15** using **3** (0.15 g, 0.42 mmol). The reaction time was 3 days. It was obtained as a yellow solid in 63% yield (0.19 g). ^{1}H NMR (C_6D_6): δ 7.15−6.87 (m, 24H), 6.75−6.66 (m, 2H), 6.62 (t, J = 7.2 Hz, 1H), 6.53 (dt, J = 7.2, 1.6 Hz, 1H), 3.78−3.62 (m, 1H, 2-quinoline), 2.81 (dd, J = 10.4, 3.2 Hz, 3H, $HfCH_2$), 2.64−2.41 (m, 4H, $HfCH_2$ and 4-quinoline), 2.41−2.26 (m, 1H, 4-quinoline), 1.92−1.72 (m, 2H, 3-quinoline), 1.68−1.48 (m, 1H, $CHCH_3$), 0.76 (d, J = 6.4 Hz, 3H, CH_3), 0.43 (d, J = 6.4 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 156.85 (d, J = 27 Hz), 144.42, 134.26 (d, J = 12 Hz), 133.86 (d, J = 13 Hz), 133.37, 131.41, 131.06, 130.69, 130.40, 130.10, 129.21, 128.75 (d, J = 9.0 Hz), 128.61, 122.69, 122.48, 122.32, 122.05 (d, J = 9.0 Hz), 119.56 (d, J = 5.3 Hz), 74.85 ($ZrCH_2$), 55.97, 55.92, 30.67, 22.76, 20.53, 19.92 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.60 ppm. Anal. Calcd ($C_{45}H_{46}NPZr$): C, 74.75; H, 6.41; N, 1.94. Found: C, 74.97; H, 6.19; N, 2.25%.

Complex 18. The title complex was synthesized using the same conditions and procedure as those for **15** using **4** (0.14 g, 0.38 mmol).

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It was obtained as a yellow solid in 76% yield (0.22 g). ^{1}H NMR (C_6D_6): δ 7.15−6.75 (m, 26H), 6.66 (t, J = 7.2 Hz, 1H), 6.55 (dt, J = 7.2, 1.6 Hz, 1H), 3.86−3.72 (m, 1H, 2-quinoline), 2.68 (dd, J = 10.4, 2.4 Hz, 3H, $HfCH_2$), 2.64−2.49 (m, 1H, 4-quinoline), 2.41 (dd, J = 10.4, 2.4 Hz, 3H, $HfCH_2$), 2.38−2.22 (m, 1H, 4-quinoline), 1.84−1.67 (m, 2H, CH_2, 3-quinoline), 1.58−1.01 (m, 6H, CH_2), 0.80 (t, J = 6.8, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 157.44 (d, J = 27 Hz), 144.52, 134.49 (d, J = 13 Hz), 133.42 (d, J = 12 Hz), 133.40, 131.07, 130.53 (d, J = 16 Hz), 129.98, 129.66, 129.29, 129.12 (d, J = 8.4 Hz), 128.87 (d, J = 9.9 Hz), 128.34, 122.68, 122.35, 122.25, 120.92 (d, J = 9.1 Hz), 119.40 (d, J = 5.3 Hz), 73.08 ($ZrCH_2$), 50.53, 33.36, 28.69, 23.61, 22.28, 21.88, 14.64 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 24.45 ppm. Anal. Calcd ($C_{46}H_{48}NPZr$): C, 74.96; H, 6.56; N, 1.90. Found: C, 75.26; H, 6.64; N, 2.11%.

Complex 19. The title complex was synthesized using the same conditions and procedure as those for **15** using **5** (0.12 g, 0.42 mmol). It was obtained as a yellow solid in 76% yield (0.21 g). ^{1}H NMR (C_6D_6): δ 7.20 (t, J = 7.2 Hz, 1H), 7.14−6.78 (m, 26H), 6.59 (t, J = 7.2 Hz, 1H), 6.32 (dd, J = 8.0, 5.2 Hz, 1H), 2.67 (s, 3H, CH_3), 2.55 (d, J = 2.0 Hz, 6H, $HfCH_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 162.32 (d, J = 28 Hz), 143.98, 133.81 (d, J = 12 Hz), 133.54 (d, J = 6.9 Hz), 130.52, 129.78, 129.49, 129.33, 129.10 (d, J = 9.0 Hz), 122.46, 121.11, 120.74, 119.50 (d, J = 5.3 Hz), 110.84 (d, J = 9.1 Hz), 72.50 ($ZrCH_2$), 33.94 (d, J = 6.1 Hz) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 22.46 ppm. Anal. Calcd ($C_{40}H_{38}NPZr$): C, 73.36; H, 5.85; N, 2.14. Found: C, 73.05; H, 5.66; N, 2.42%.

Complex 20. The title complex was synthesized using the same conditions and procedure as those for **15** using **6** (0.10 g, 0.32 mmol). It was obtained as a yellow solid in 69% yield (0.15 g). ^{1}H NMR (C_6D_6): δ 7.15−6.82 (m, 26H), 6.77 (dt, J = 7.8, 1.2 Hz, 1H), 6.52 (t, J = 7.2 Hz, 1H), 6.26 (dd, J = 8.0, 5.2 Hz, 1H), 3.11 (quintet, J = 6.4 Hz, 2H, NCH_2), 2.51 (d, J = 2.0 Hz, 6H, $HfCH_2$), 0.91 (t, J = 6.4 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 160.24 (d, J = 27 Hz), 144.24, 133.85 (d, J = 12 Hz), 133.51, 133.06, 130.61, 129.25, 129.08 (d, J = 9.0 Hz), 128.66, 128.16, 122.72, 122.30, 119.18 (d, J = 5.4 Hz), 111.18 (d, J = 9.0 Hz), 72.26 ($ZrCH_2$), 37.79, 13.48 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 24.65 ppm. Anal. Calcd($C_{41}H_{40}NPZr$): C, 73.61; H, 6.03; N, 2.09. Found: C, 73.93; H, 6.23; N, 1.75%.

Complex 21. The title complex was synthesized using the same conditions and procedure as those for **8** using **1** (0.10 g, 0.29 mmol) and $Ti(CH_2Ph)_4$ (0.12 g, 0.29 mmol) instead of $Hf(CH_2Ph)_4$. It was obtained as a dark brown solid in 77% yield (0.14 g). ^{1}H NMR (C_6D_6): δ 7.05−6.74 (m, 26H), 6.66 (t, J = 7.6 Hz, 1H), 6.55 (dt, J = 7.2, 1.6 Hz, 1H), 3.97−3.80 (m, 2H, 2-quinoline), 3.54 (d, J = 2.4 Hz, 6H, $HfCH_2$), 2.40 (t, J = 6.4 Hz, 2H, 4-quinoline), 1.60−1.43 (m, 2H, 3-quinoline) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 159.27 (d, J = 29 Hz), 148.04, 133.79 (d, J = 13 Hz), 133.73, 131.37, 130.49, 129.98 (d, J = 28 Hz), 128.99 (d, J = 9.1 Hz), 128.60, 127.75, 122.67 (d, J = 38 Hz), 122.31, 121.20 (d, J = 9.1 Hz), 120.63 (d, J = 5.3 Hz), 93.61 ($TiCH_2$), 49.34, 27.82, 21.66 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 28.90 ppm. Anal. Calcd ($C_{42}H_{40}NPTi$): C, 79.12; H, 6.32; N, 2.20. Found: C, 78.95; H, 6.66; N, 2.50%.

Complex 22. $B(C_6F_5)_3$ (14 mg, 0.03 mmol) was added to a solution of **8** (21 mg, 0.030 mmol) in C_6D_6 (0.4 mL). An oily compound was deposited, which was soluble by the addition of C_6H_5Cl (0.2 mL). The compound was not isolated due to its instability. ^{1}H NMR: δ 7.40−6.54 (m, 28H), 5.75 (d, J_{P-H} = 7.2 Hz, 4H, $HfCH_2$), 3.52 (s, 2H, $PhCH_2B(C_6F_5)_3$), 2.31 (t, J = 6.4 Hz, 2H, 4-quinoline), 2.28−2.20 (m, 2H, 2-quinoline), 1.32−1.16 (m, 2H, 3-quinoline) ppm. ^{19}F NMR: δ −130.6 (d, J = 22 Hz, 2F, o-C_6F_5), −164.1 (t, J = 21 Hz, 1F, p-C6F5), −166.9 (t, J = 18 Hz, 2F, m-C_6F_5) ppm. $^{31}P\{^1H\}$ NMR: δ 26.87 ppm.

Complex 23. The solution for NMR studies was prepared using the same conditions and procedure as those for **22** using **11** (30 mg, 0.04 mmol). ^{1}H NMR: δ 7.40−6.40 (m, 28H), 6.07−5.92 (br, 2H, $HfCH_2$), 5.83−5.66 (br, 2H, $HfCH_2$), 3.54 (s, 2H, $PhCH_2B(C_6F_5)_3$), 3.10−3.00 (br, 1H, 2-quinoline), 2.60−2.31 (m, 1H, 4-quinoline), 2.31−2.16 (m, 1H, 4-quinoline), 2.13−1.94 (m, 2H, 3-quinoline), 1.59−1.44 (m, 1H, CH_2), 1.20−0.79 (m, 5H, CH_2), 0.74 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{19}F NMR: δ −130.4 (d, J = 21 Hz, 2F, o-C_6F_5), −164.2 (t, J = 21 Hz, 1F, p-C_6F_5), −166.9 (t, J = 19 Hz, 2F, m-C_6F_5) ppm. $^{31}P\{^1H\}$ NMR: δ 28.79 ppm.

Ethylene/1-Octene Copolymerization. In a glovebox, 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 glovebox. The reactor was then heated to 100 °C using a mantle. $[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ (1.00 g) and 10 mg of the complex were dissolved, respectively, in 22.3 and 1.99 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 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 via syringe. Ethylene gas (30 bar) was fed immediately into the reaction vessel. The mantle was removed immediately, after injecting ethylene gas, to allow the generated heat to dissipate. After conducting polymerization for 3 min, the ethylene gas was vented and methanol (10 mL) was added immediately. The isolated polymer lump or powder was dried under vacuum at 150 °C for several hours. The 1-octene contents were calculated by the analysis of the copolymer ^{1}H NMR spectra; the methyl (CH_3) signals (0.93−1.02 ppm) were well isolated from the methine (CH) and methylene (CH_2) signals (1.30−1.50 ppm), allowing for the 1-octene content to be calculated from the integration values of the two regions. The copolymer (10 mg) was dissolved in $C_6D_5CD_3$, and the ^{1}H NMR spectra were recorded at 80 °C. For the polymerization with CGC (Table 2, entry 15), the activated catalyst, which was prepared by mixing CGC (1.0 μmol), $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ (4.0 μmol), and $(i$Bu$)_3$Al (0.80 mmol, Al/M = 800) in toluene (3 mL), was fed to the reactor just containing a solution of 1-octene (4.0 g, 1.0 M) in methylcyclohexane (27 mL) without MAO at 100 °C.[33,34]

X-ray Crystallography. Reflection data for **9**, **14**, **16**, and **19** 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. Further details are listed in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The CIF files; crystal data and structure refinement for **9**, **14**, **16**, and **19**; and ^{1}H NMR spectra for metal complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: bunyeoul@ajou.ac.kr. Tel: 82-31-219-1844.

Notes

The authors declare no competing financial interests.

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