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Synthesis, Structural Characterization, and Catalytic Properties of Group 4 Metal Complexes Incorporating a Phosphorus-Bridged Indenyl-Carboranyl Constrained-Geometry Ligand

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Interaction of $^{i}\mathrm{Pr_2NP(C_9H_7)(C_2B_{10}H_{11})}$ with 1 equiv of $\mathrm{M(NR_2)_4}$ in toluene gave constrained-geometry group 4 metal amides $[\eta^5{:}\sigma\text{-}^{i}\mathrm{Pr_2NP(C_9H_6)(C_2B_{10}H_{10})]M(NMe_2)_2}$ (R = Me, M = Ti (**1**), Zr (**2**), Hf (**3**); R = Et, M = Hf (**4**)) in good yields. Compound **2** reacted with 3 equiv of PhNCO to produce the tri-insertion product $[\eta^5{:}\sigma\text{-}^{i}\mathrm{Pr_2NP(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}OC(NMe_2)\text{-}NPh][\eta^2\text{-}OC(NMe_2)N(Ph)C{=}(NPh)O]}$ (**5**). No further insertion reaction occurred with another equivalent of PhNCO. Instead, the trimer $\mathrm{(PhNCO)_3}$ was isolated. Compound **2** reacted with 2 equiv of *n*-BuLi in toluene to afford, after recrystallization from DME/toluene, the dilithium salt $\mathrm{[Li(DME)_3]}[\eta^5{:}\sigma\text{-}^{i}\mathrm{Pr_2NP(C_9H_6)(C_2B_{10}H_{10})Li(DME)]}$ (**6**). An equimolar reaction of **2** with acetylacetone resulted in the formation of $\mathrm{Zr(acac)_4}$. **2** exhibited an ethylene polymerization activity of 3.7×10^3 g PE mol^{-1} atm^{-1} h^{-1} upon activation with MMAO. Furthermore, **2** was also able to efficiently initiate the polymerization of ϵ-caprolactone to give polymers of high molecular weights ($M_n > 40\,000$) and low polydispersities ($M_w/M_n < 1.4$) through the action of the nucleophilic amido-nitrogen atom, which represents the first example of the polymerization of ϵ-caprolactone catalyzed by group 4 metal amides.

Introduction

Ansa-bridged group 4 metallocenes have attracted considerable attention because of their applications as catalyst precursors for olefin polymerizations.[1] It has been well documented that the bridging atoms and the molecular structures are among the important factors that greatly impact the polymerization behavior of the catalysts.[1,2] Phosphorus-bridged systems have drawn our attention since the phosphorus atom has a covalent radius similar to that of silicon,[3] and yet they have very different electronic characteristics. In fact, phosphorus-bridged ligands exhibit a wide range of structural types: (1) metallocenes bridged by four-coordinate phosphorus moieties where the formal pentavalent phosphorus bears one positive charge,[4] and (2) metallocenes bridged with three-coordinate phosphorus linkages where the trivalent phosphorus possesses a lone pair of electrons.[5]

The electronic effects of the RP linkages on the catalytic activity of metallocene catalysts are an interesting subject. As judged by both ν_{co} and the $E°$ values, the RP bridges behave as "electron-withdrawing" units, leading to an electrophilic metal center.[2,4g] For example, complex $\mathrm{[PhP(\eta^5\text{-}C_5Me_4)_2]ZrCl_2}$ showed an activity in ethylene polymerization very similar to that of $\mathrm{[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2}$.[4g] On the other hand, complexes $\mathrm{[PhP(\eta^5\text{-}C_{13}H_8)_2]ZrCl_2}$ (2.54×10^6 g PE mol^{-1} atm^{-1} h^{-1})[5d] and $[\eta^5{:}\,\sigma\text{-}^{t}\mathrm{BuP(}^{t}\mathrm{BuC_5H_3)(N}^{t}\mathrm{Bu)]TiCl_2}$ (1.0×10^5 g PE mol^{-1} atm^{-1} h^{-1})[5b] were reported to be less active by 10−20 times in ethylene polymerization than $\mathrm{[Me_2Si(\eta^5\text{-}C_{13}H_8)_2]ZrCl_2}$ (5.76×10^7 g PE mol^{-1} atm^{-1} h^{-1})[6] and

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[η^5: σ-Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (9.5 × 10^5 g PE mol^{-1} atm^{-1} h^{-1}),[7] respectively, suggesting that the RP moieties function as "electron-donating" groups. It is also noteworthy that [η^5: σ-^{t}BuP(^{t}BuC$_5$H$_3$)(N^{t}Bu)]TiCl$_2$ represents a rare example of a P-bridged constrained-geometry catalyst.[5b]

In view of the impact of the interesting electronic effects of the RP linkages on the catalytic performance of group 4 metal complexes and our earlier work on [η^5: σ-Me$_2$A(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]M(NMe$_2$)$_2$ (M = Ti, Zr, Hf; A = C, Si)[8] and [η^5: σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]M(NMe$_2$)$_2$,[9] we have extended our research on group 4 metal chemistry to include a newly developed ^{i}Pr$_2$NP-bridged constrained-geometry carboranyl ligand system,[10] [^{i}Pr$_2$NP(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]$^{2-}$, in the hope that a series of closely related complexes, [A(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]M(NMe$_2$)$_2$, which differ in the nature of the *ansa* bridges, will allow the features responsible for the various *ansa* effects (linkage effects) to be ascertained. We report herein the synthesis and structural characterization of group 4 metal complexes containing the [^{i}Pr$_2$NP(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]$^{2-}$ ligand as well as their catalytic behavior in ethylene and ϵ-caprolactone polymerizations.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. M(NR$_2$)$_4$[11] (M = Ti, Zr, Hf; R = Me, Et) and ^{i}Pr$_2$(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$)[10] were prepared according to literature methods. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. Molecular weights of polyesters were estimated by gel permeation chromatography (GPC) using a Waters 1515 instrument equipped with microstyragel columns (HR1, HR2, HR3) and a RI detector at 30 °C. Polystyrene standards purchased from American Polymer Standards were used as a calibration standard, and THF was used as the eluant at a flow rate of 1.0 mL/min. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B and ^{31}P NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 and 161.91 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts, to external BF$_3$·OEt$_2$ (0.00 ppm) for boron chemical shifts, and to external 85% H$_3$PO$_4$ (0.00 ppm) for phosphorus chemical shifts. Elemental analyses were performed by MEDAC Ltd., U.K.

Preparation of [η^5:σ-^{i}Pr$_2$NP(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Ti(NMe$_2$)$_2$ (1). A toluene (10 mL) solution of ^{i}Pr$_2$NP(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (389 mg, 1.0 mmol) was added to a toluene (10 mL) solution of Ti(NMe$_2$)$_4$ (225 mg, 1.0 mmol) at room temperature. The reaction mixture was heated to 60 °C and stirred overnight. The resulting dark red solution was filtered and concentrated to about 5 mL. **1** was isolated as dark red crystals after this solution stood at room temperature for 3 days (283 mg, 54%). ^{1}H NMR (pyridine-d_5): δ 8.23 (d, J = 8.4 Hz, 1H, indenyl), 7.24 (t, J = 7.2 Hz, 1H, indenyl), 7.15 (d, J = 3.0 Hz, 1H, indenyl), 6.92 (t, J = 7.2 Hz, 1H, indenyl), 6.46 (d, J = 3.0 Hz, 1H, indenyl), 6.14 (d, J = 8.4 Hz, 1H, indenyl), 4.45 (m, 2H, NC*H*(CH$_3$)$_2$), 3.02 (s, 6H, N(C*H*$_3$)$_2$), 2.54 (s, 6H, N(C*H*$_3$)$_2$), 1.39 (d, J = 6.3 Hz, 6H, NCH(C*H*$_3$)$_2$), 1.09 (br, 3H, NCH(C*H*$_3$)$_2$), 0.76 (br, 3H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (pyridine-d_5): δ 131.9 (d, $^2J_{PC}$ = 43.0 Hz), 130.5 (d, $^1J_{PC}$ = 55.0 Hz), 128.2, 127.6, 126.7, 125.5, 123.1, 122.7, 109.1 (*C*$_9$H$_6$), 99.8, 96.2 (d, $^1J_{PC}$ = 64.0 Hz) (cage *C*), 53.0 (br), 47.0 (br) (N*C*H(CH$_3$)$_2$), 54.0, 46.7 (N(*C*H$_3$)$_2$), 31.4, 27.2, 24.3, 23.9 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −1.1 (2B), −3.1 (1B), −4.8 (2B), −7.6 (2B), −9.7 (3B). ^{31}P NMR (pyridine-d_5): δ 36.0. IR (KBr, cm^{-1}): ν_{BH} 2562 (vs). Anal. Calcd for C$_{21}$H$_{42}$B$_{10}$N$_3$PTi: C, 48.18; H, 8.09; N, 8.02. Found: C, 48.49; H, 8.38; N, 7.79.

Preparation of [η^5:σ-^{i}Pr$_2$NP(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Zr(NMe$_2$)$_2$ (2). A toluene (10 mL) solution of ^{i}Pr$_2$NP(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (389 mg, 1.0 mmol) was added to a toluene (10 mL) solution of Zr(NMe$_2$)$_4$ (267 mg, 1.0 mmol) with stirring at room temperature, followed by the identical procedure reported for **1** to give **2** as pale yellow crystals (385 mg, 68%). ^{1}H NMR (pyridine-d_5): δ 8.22 (d, J = 8.4 Hz, 1H, indenyl), 7.25 (t, J = 8.1 Hz, 2H, indenyl), 7.18 (d, J = 3.6 Hz, 1H, indenyl), 6.91 (t, J = 8.1 Hz, 1H, indenyl), 6.46 (d, J = 3.6 Hz, 1H, indenyl), 6.15 (d, J = 8.4 Hz, 1H, indenyl), 4.46 (m, 2H, NC*H*(CH$_3$)$_2$), 3.02 (s, 6H, N(C*H*$_3$)$_2$), 2.53 (s, 6H, N(C*H*$_3$)$_2$), 1.39 (d, J = 6.3 Hz, 6H, NCH(C*H*$_3$)$_2$), 1.09 (br, 3H, NCH(C*H*$_3$)$_2$), 0.68 (br, 3H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (pyridine-d_5): δ 131.0 (d, $^2J_{PC}$ = 31.4 Hz), 128.3 (d, $^1J_{PC}$ = 56.0 Hz), 127.8, 125.1, 124.7, 123.9, 123.4, 111.8, 105.6 (*C*$_9$H$_6$), 98.4, 86.9 (d, $^1J_{PC}$ = 41.0 Hz) (cage *C*), 56.2 (br), 50.6 (br) (N*C*H(CH$_3$)$_2$), 45.0, 44.7 (N(*C*H$_3$)$_2$), 31.0, 25.1, 22.1, 21.7 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −1.8 (2B), −3.3 (1B), −5.3 (2B), −8.1 (3B), −10.3 (2B). ^{31}P NMR (pyridine-d_5): δ 34.5. IR (KBr, cm^{-1}): ν_{BH} 2571 (vs). Anal. Calcd for C$_{21}$H$_{42}$B$_{10}$N$_3$PZr: C, 44.49; H, 7.47; N, 7.41. Found: C, 44.56; H, 7.98; N, 7.01.

Preparation of [η^5:σ-^{i}Pr$_2$NP(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Hf(NMe$_2$)$_2$ (3). This compound was prepared as pale yellow crystals from the reaction of ^{i}Pr$_2$NP(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (389 mg, 1.0 mmol) with Hf(NMe$_2$)$_4$ (354 mg, 1.0 mmol) in toluene (20 mL) using the same procedure reported for **1**: yield 392 mg (60%). ^{1}H NMR (pyridine-d_5): δ 8.20 (d, J = 8.1 Hz, 1H, indenyl), 7.54 (d, J = 3.0 Hz, 1H, indenyl), 7.30 (t, J = 7.5 Hz, 1H, indenyl), 6.95 (t, J = 7.5 Hz, 1H, indenyl), 6.52 (d, J = 3.0 Hz, 1H, indenyl), 6.29 (d, J = 8.1 Hz, 1H, indenyl), 4.74 (m, 2H, NC*H*(CH$_3$)$_2$), 3.04 (s, 6H, N(C*H*$_3$)$_2$), 2.53 (s, 6H, N(C*H*$_3$)$_2$), 1.38 (d, J = 6.3 Hz, 6H, NCH(C*H*$_3$)$_2$), 1.06 (br, 3H, NCH(C*H*$_3$)$_2$), 0.77 (br, 3H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (pyridine-d_5): δ 130.9 (d, $^2J_{PC}$ = 41.9 Hz), 128.7 (d, $^1J_{PC}$ = 55.9 Hz), 127.4, 125.1, 124.3, 123.4, 123.3, 110.8, 106.4 (*C*$_9$H$_6$), 104.7, 87.7 (d, $^1J_{PC}$ = 56.4 Hz) (cage *C*), 56.3 (br), 50.7 (br) (N*C*H(CH$_3$)$_2$), 44.8, 44.3 (N(*C*H$_3$)$_2$), 31.0, 25.1, 22.1, 20.6 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −1.8 (2B), −3.7 (1B), −5.5 (2B), −8.6 (3B), −12.8 (2B). ^{31}P NMR (pyridine-d_5): δ 34.3. IR (KBr, cm^{-1}): ν_{BH} 2566 (s). Anal. Calcd for C$_{21}$H$_{42}$B$_{10}$HfN$_3$P: C, 38.56; H, 6.47; N, 6.42. Found: C, 38.93; H, 6.46; N, 6.36.

Preparation of [η^5:σ-^{i}Pr$_2$NP(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Hf(NEt$_2$)$_2$ (4). This compound was prepared as pale yellow crystals from the reaction of ^{i}Pr$_2$NP(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (389 mg, 1.0 mmol) with Hf(NEt$_2$)$_4$ (467 mg, 1.0 mmol) in toluene (20 mL) using the identical procedure reported for **1**: yield 340 mg (48%). ^{1}H NMR (pyridine-d_5): δ 8.28 (d, J = 7.8 Hz, 1H, indenyl), 7.52 (d, J = 3.3 Hz, 1H, indenyl), 7.42 (m, 2H, indenyl), 7.24 (d, J = 7.8 Hz, 1H, indenyl), 6.99 (d, J = 3.3 Hz, 1H, indenyl), 4.74 (m, 1H, NC*H*(CH$_3$)$_2$), 3.28 (m, 1H, NC*H*(CH$_3$)$_2$), 3.59 (q, J = 6.9 Hz, 4H, N(C*H*$_2$CH$_3$)$_2$), 2.80 (q, J = 6.9 Hz, 4H, N(C*H*$_2$-

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Table 1. Crystal Data and Summary of Data Collection and Refinement for 1–6

	1	2	3	4	5·CH_3CN	6
formula	$C_{21}H_{42}B_{10}N_3P$-Ti	$C_{21}H_{42}B_{10}N_3P$-Zr	$C_{21}H_{42}B_{10}HfN_3P$	$C_{25}H_{50}B_{10}Hf$-N_3P	$C_{44}H_{60}B_{10}N_7O_3$-PZr	$C_{33}H_{70}B_{10}Li_2$-NO_8P
cryst size (mm)	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.20	0.80 × 0.60 × 0.10	0.45 × 0.30 × 0.15	0.80 × 0.50 × 0.30
fw	523.6	566.9	654.1	710.2	965.3	761.9
cryst syst	triclinic	orthorhombic	orthorhombic	monclinic	triclinic	triclinic
space group	$P(-1)$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$	$P(-1)$	$P(-1)$
a, Å	11.144(2)	9.088(2)	9.083(3)	9.272(1)	11.033(1)	10.896(2)
b, Å	15.657(3)	15.854(3)	15.803(3)	17.799(1)	12.101(1)	14.752(2)
c, Å	17.844(4)	20.741(4)	20.704(4)	21.339(1)	20.085(2)	16.354(2)
α, deg	106.77(3)	90	90	90	102.19(1)	77.52(1)
β, deg	91.85(3)	90	90	101.15(1)	91.26(1)	78.82(1)
γ, deg	98.91(3)	90	90	90	102.50(1)	69.93(1)
V, Å^3	2935.3(10)	2988.4(10)	2971.8(10)	3455.1(3)	2552.7(3)	2390.2(4)
Z	4	4	4	4	2	2
D_{calcd}, Mg/m^3	1.185	1.260	1.462	1.365	1.256	1.059
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.8 to 51.5	5.0 to 50.1	4.0 to 50.0	3.0 to 56.0	2.1 to 50.0	3.0 to 56.1
μ, mm^{-1}	0.363	0.438	3.581	3.086	0.292	0.099
F(000)	1104	1176	1304	1432	1004	820
no. of obsd reflns	9060	2919	2965	8304	8961	11361
no. of params refnd	649	325	325	361	595	496
goodness of fit	1.086	1.013	1.022	0.960	0.933	0.741
R1	0.050	0.048	0.046	0.028	0.062	0.067
wR2	0.151	0.138	0.124	0.078	0.158	0.189

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1–4[a]

	1[b]	2	3	4
(M)	(Ti)	(Zr)	(Hf)	(Hf)
av M–C(ring)	2.403(3) [2.411(3)]	2.551(8)	2.515(15)	2.531(3)
M–C(cage)	2.208(3) [2.226(3)]	2.354(8)	2.297(13)	2.330(3)
av M–N	1.894(3) [1.889(3)]	2.020(7)	2.004(12)	2.012(3)
C(ring)–P–C(cage)	97.3 (1) [97.7(1)]	98.7(3)	98.1(6)	98.6(2)
N–M–N	103.9(2) [103.0(1)]	110.0(3)	107.2(6)	107.5(2)
Cent–M–C(cage)	110.0 [109.9]	106.6	107.1	106.6

[a] Cent: the centroid of the five-membered ring of the indenyl group. [b] Distances and angles in brackets are those of a second molecule.

$CH_3)_2$), 1.39 (d, J = 5.4 Hz, 6H, $NCH(CH_3)_2$), 1.07 (m, 9H), 0.83 (m, 9H) ($NCH(CH_3)_2 + N(CH_2CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 132.8 (d, $^2J_{PC}$ = 31.3 Hz), 128.3 (d, $^1J_{PC}$ = 55.9 Hz), 125.9 125.8, 125.7, 123.5 111.8, 111.0, 106.1 (C_9H_6), 103.2, 91.9 (d, $^1J_{PC}$ = 49.2 Hz) (cage C), 50.9 (br), 44.9 (br) ($NCH(CH_3)_2$), 42.6, 39.9 ($N(CH_2CH_3)_2$), 31.0, 25.1, 22.1, 21.5 ($NCH(CH_3)_2$), 13.6, 13.1 ($N(CH_2CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ −1.0 (2B), −3.2 (1B), −4.7 (2B), −7.8 (2B), −10.1 (3B). ^{31}P NMR (pyridine-d_5): δ 35.3. IR (KBr, cm^{-1}): ν_{BH} 2576 (vs). Anal. Calcd for $C_{25}H_{50}B_{10}HfN_3P$: C, 42.28; H, 7.10; N, 5.91. Found: C, 41.99; H, 7.11; N, 5.58.

Preparation of [η^5: σ-^{i}$Pr_2NP(C_9H_6)(C_2B_{10}H_{10})$]Zr[$\eta^2$-OC($NMe_2$)NPh][$\eta^2$-OC($NMe_2$)N(Ph)C=(NPh)O]·$CH_3CN$ (5·CH_3CN). A THF (10 mL) solution of PhNCO (357 mg, 3.0 mmol) was added dropwise to a THF (20 mL) solution of 2 (567 mg, 1.0 mmol) at room temperature with stirring, and the mixture was then stirred for 2 days. Removal of the solvent gave a pale yellow solid. Recrystallization from a mixed solvent of THF/toluene/CH_3CN (10 mL) at room temperature afforded **5**·CH_3CN as pale yellow crystals (598 mg, 62%). ^1H NMR (pyridine-d_5): δ 8.33 (d, J = 7.8 Hz, 1H, indenyl), 7.87 (d, J = 7.8 Hz, 1H, C_6H_5), 6.98 (d, J = 3.3 Hz, 1H, indenyl), 7.44–7.15 (m, 16 H, indenyl+C_6H_5), 6.39 (d, J = 3.3 Hz, 1H, indenyl), 6.02 (d, J = 7.8 Hz, 1H, indenyl), 4.45 (m, 2H, $NCH(CH_3)_2$), 2.69 (s, 6H, $N(CH_3)_2$), 1.94 (s, 6H, $N(CH_3)_2$), 1.40 (d, J = 6.3 Hz, 6H, $NCH(CH_3)_2$), 0.98 (d, J = 6.3 Hz, 3H, $NCH(CH_3)_2$), 0.79 (d, J = 6.3 Hz, 3H, $NCH(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 164.9, 160.9, 152.3 (NCO), 132.9 (d, $^2J_{PC}$ = 42.5 Hz), 128.9, 128.7, 128.5 (d, $^1J_{PC}$ = 56.9 Hz), 127.9, 126.5, 125.5, 125.4, 125.1, 124.9, 124.7, 124.6, 121.9, 121.3, 118.9, 107.0 (C_9H_6 + C_6H_5), 103.0, 91.6 (d, $^1J_{PC}$ = 63.8 Hz) (cage C), 51.2 (br), 45.9 (br) ($NCH(CH_3)_2$), 38.3, 36.6 ($N(CH_3)_2$), 30.9, 25.1, 22.1, 20.6 ($NCH(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ −2.6 (3B), −3.7 (2B), −6.1 (2B), −8.3 (3B). ^{31}P NMR (pyridine-d_5): δ 37.3. IR (KBr, cm^{-1}): ν 3060 (w), 2964 (m), 2600 (m), 2562 (s), 1641(vs), 1577 (vs), 1490 (vs), 1443 (s), 1408 (s), 1262 (m), 1116(m), 1069 (m), 1019 (m), 798 (s), 747 (s). Anal. Calcd for $C_{42}H_{57}B_{10}N_6O_3PZr$ (**5**): C, 54.58; H, 6.22; N, 9.09. Found: C, 54.61; H, 6.50; N, 8.81.

Reaction of 5 with Excess PhNCO. PhNCO (360 mg, 3.0 mmol) was added to a THF (20 mL) solution of **5**·CH_3CN (97 mg, 0.1 mmol) at room temperature. The mixture was stirred overnight. The resulting dark brown solution was concentrated under vacuum to about 10 mL, to which was added 5 mL of toluene. Colorless crystals (180 mg, 50%) were obtained after this solution stood at −30 °C for 2 days. The product was identified as $(PhNCO)_3$ by ^1H and ^{13}C NMR.[12]

Reaction of 2 with *n*-BuLi. Isolation of [Li(DME)$_3$][η^5: σ-^{i}$Pr_2NP(C_9H_6)(C_2B_{10}H_{10})$Li(DME)] (6). A 1.6 M solution of *n*-BuLi in hexane (1.3 mL, 2.0 mmol) was slowly added to a toluene (20 mL) solution of **2** (594 mg, 1.0 mmol) with stirring at −78 °C. The reaction mixture was warmed to room temperature and stirred overnight. After removal of the solvent under vacuum, the oily residue was extracted with a mixed solvent of DME and toluene (3:1, 10 mL × 2). The solutions were combined and concentrated to about 10 mL; **6** was obtained as colorless crystals after this solution stood at room temperature for 2 days (298 mg, 39%). ^1H NMR (pyridine-d_5): δ 8.59 (d, J = 7.8 Hz, 1H, indenyl), 7.94 (d, J = 3.6 Hz, 1H, indenyl), 7.87(d, J = 7.8 Hz, 1H, indenyl), 7.11 (t, J = 7.2 Hz, 1H, indenyl), 7.02 (t, J = 7.2 Hz, 1H, indenyl), 6.83 (d, J = 3.6

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Hz, 1H, indenyl), 4.95 (m, 2H, NCH(CH$_3$)$_2$), 3.48 (s, 16H, DME), 3.25 (s, 24H, DME), 1.60 (br, 6H, NCH(CH_3)$_2$), 1.38 (br, 3H, NCH(CH_3)$_2$), 0.77 (br, 3H, NCH(CH_3)$_2$). ^{13}C NMR (pyridine-d_5): δ 138.7 (d, $^2J_{PC} = 39.8$ Hz), 132.6, 127.9 (d, $^1J_{PC} = 59.2$ Hz), 121.8, 118.7, 117.4, 114.5, 113.5, 102.7 (C_9H$_6$), 90.5, 84.1 (d, $^1J_{PC} = 74.9$ Hz) (cage C), 71.4, 57.9 (DME), 51.6 (br), 44.2 (br) (NCH(CH$_3$)$_2$, 31.1, 25.4, 22.1, 21.8, (NCH(CH$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −3.9 (4B), −6.9 (2B), −9.5 (4B). ^{31}P NMR (pyridine-d_5): δ 40.3. IR (KBr, cm^{-1}): ν_{BH} 2558 (vs). Anal. Calcd for $C_{25}H_{50}B_{10}Li_2NO_4P$ (**6** − 2DME): C, 51.63; H, 8.66; N, 2.41. Found: C, 51.31; H, 9.09; N, 2.20.

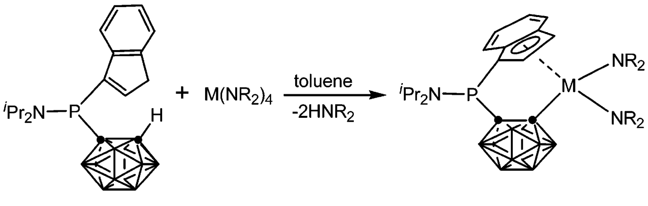
Reaction of 2 with Acetylacetone. A toluene (10 mL) solution of acetylacetone (Hacac) (50 mg, 0.5 mmol) was added slowly to a toluene (10 mL) solution of **2** (297 mg, 0.5 mmol) at −30 °C. The reaction mixture was then stirred at room temperature for 4 h. After removal of toluene, the residue was washed with hexane and extracted with a mixed solvent of toluene and hexane (3:1; 15 mL). Slow evaporation gave colorless crystals (83 mg, 34% based on Hacac), which were identified as Zr(acac)$_4$ by ^{1}H and ^{13}C NMR and unit cell measurement.[13]

Ethylene Polymerization. This experiment was carried out in a 150 mL glass reactor equipped with a magnetic stirrer and gas inlets. The reactor was charged with the catalysts (3.0 μmol) together with MMAO (4.5 mmol) and toluene (50 mL). The mixture was stirred at room temperature for 1 h. Ethylene gas was then introduced to the reactor, and its pressure was maintained continuously at 1 atm by means of bubbling. The polymerization was terminated by addition of acidic ethanol (100 mL). The white precipitate was filtered off and washed with ethanol and acetone. The resulting powder was finally dried in a vacuum oven at 80 °C overnight.

Polymerization of ϵ-Caprolactone. A solution of **2** (20 mg, 3.6×10^{-3} mmol) in toluene, CH$_2$Cl$_2$, or THF (10 mL) was maintained at the chosen temperature. Neat monomer was then added using a syringe, with a monomer/**2** molar ratio of 500:1 or 250:1. The yellow solution was stirred at different temperatures for 2 h. The polymerizations were terminated by methanol addition (10 mL). The resulting polymers were precipitated from methanol (150 mL), filtered, and dried in a vacuum. ^{1}H NMR (CDCl$_3$): δ 4.04 (t, $J = 6.6$ Hz, 436H, OCH_2), 2.99 (s, 3H, N(CH_3)$_2$), 2.93 (s, 3H, N(CH_3)$_2$), 2.29 (t, $J = 7.5$ Hz, 436H, COCH_2), 1.64 (m, 872H, CH_2), 1.36 (m, 436H, CH_2).

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N$_2$ in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[14] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.[15a] For noncentrosymmetric structures, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[15b] There are two independent molecules in the unit cell of **1**. Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 1. Selected bond distances and angles are compiled in Table 2. Further details are included in the Supporting Information.

Scheme 1



	1	**2**	**3**	**4**
M	Ti	Zr	Hf	Hf
R	Me	Me	Me	Et

Results and Discussion

Amide Complexes. Our previous work showed that interaction of group 4 metal dialkylamides M(NR$_2$)$_4$ (R = Me, Et) with protic reagents Me$_2$A(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$), Me$_2$A(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$) (A = C, Si), and ^{i}Pr$_2$NB(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) in toluene resulted in the clean formation of the corresponding constrained-geometry group 4 metal amides.[8,9] The two acidic protons in ^{i}Pr$_2$NP(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$)[10] would allow similar amine elimination reactions to occur. Treatment of ^{i}Pr$_2$NP(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) with 1 equiv of M(NR$_2$)$_4$ (M = Ti, Zr, R = Me; M = Hf, R = Me, Et) in toluene at 60 °C gave the desired compounds [η^5:σ-^{i}Pr$_2$NP(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]M(NR$_2$)$_2$ (R = Me, M = Ti (**1**), Zr (**2**), Hf (**3**); R = Et, M = Hf (**4**)) in 48−68% yield (Scheme 1). Unlike the boron-bridged ligand ^{i}Pr$_2$NB(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$), no deborated products were detected.[9] These reactions were closely followed by ^{31}P NMR, and the results indicated that such amine elimination reactions did not proceed at all at room temperature. Several new ^{31}P NMR peaks appeared if the reaction temperature was higher than 70 °C, suggestive of the complexity of the reactions at higher temperatures.

The ^{31}P chemical shifts for **1**−**4** fell in the range 34.3−36.0 ppm, which can be compared to the 40.1 and 74.1 ppm observed in the parent ligand ^{i}Pr$_2$NP(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$).[10] Their ^{1}H NMR spectra showed six multiplets in the aromatic region and the presence of diastereotopic ^{i}Pr$_2$NP and NR$_2$ groups, typically observed in the constrained-geometry carboranyl group 4 metal amides.[8,9] These results were consistent with the ^{13}C NMR data. The ^{11}B NMR spectra exhibited a 2:1:2:2:3 splitting pattern for **1** and **4** and a 2:1:2:3:2 splitting pattern for **2** and **3**, respectively.

The solid-state structures of **1**−**4** were all confirmed by single-crystal X-ray analyses. Figures 1 and 2 show the representative structures of compounds **2** and **4**, respectively. The central metal atom is η^5-bound to the five-membered ring of the indenyl group and σ-bound to the cage carbon atom and two amido groups in a distorted-tetrahedral geometry. The sum of the angles around N and P atoms is ~358° and 314°, respectively, indicating that the P atom adopts a trigonal pyramidal geometry. The planar geometry of the nitrogen atoms suggests the presence of N(pπ)−M(dπ) or N(pπ)−P(dπ) bonds.[16,17] Table 2 lists the key structural data of compounds **1**−**4**. The Ti−C(ring), Ti−C(cage), and Ti−N distances are obviously shorter than the corresponding

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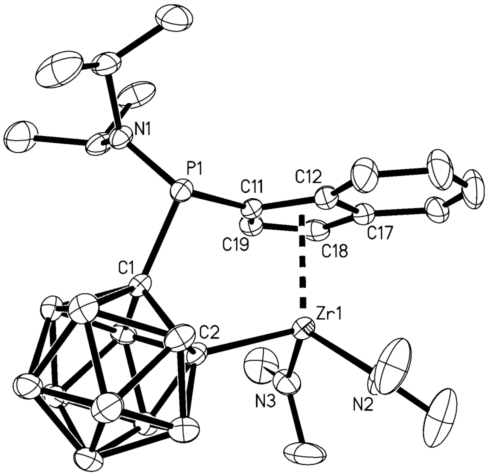


Figure 1. Molecular structure of $[\eta^5:\sigma\text{-}{}^i\mathrm{Pr_2NP(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2}$ (**2**).

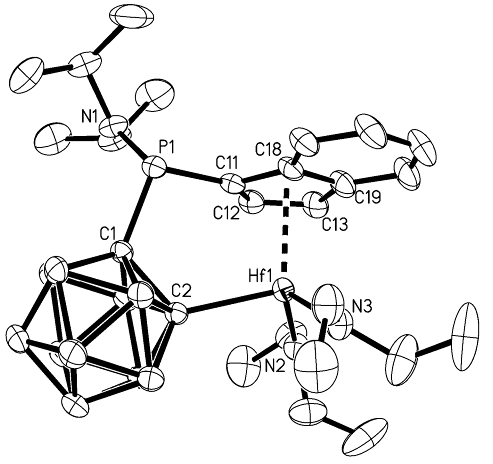


Figure 2. Molecular structure of $[\eta^5:\sigma\text{-}{}^i\mathrm{Pr_2NP(C_9H_6)(C_2B_{10}H_{10})]Hf(NEt_2)_2}$ (**4**).

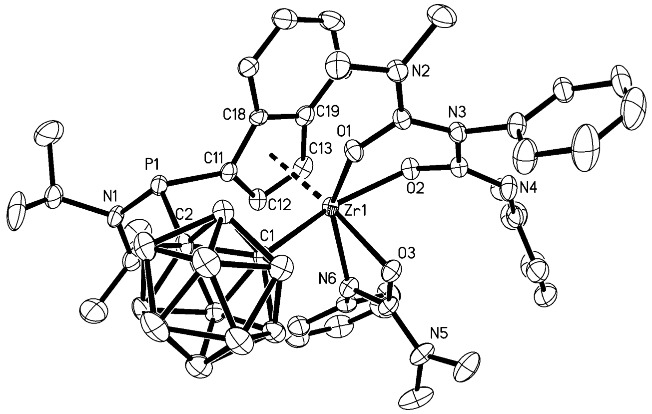


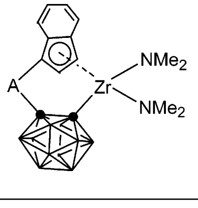
Figure 3. Molecular structure of $[\eta^5:\sigma\text{-}{}^i\mathrm{Pr_2NP(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}OC(NMe_2)NPh]\text{-}[\eta^2\text{-}OC(NMe_2)N(Ph)C{=}(NPh)O]}$ (**5**) (the solvated $\mathrm{CH_3CN}$ molecule is not shown). Selected bond distances (Å) and angles (deg): Zr1−C1 = 2.401(5), Zr1−C11 = 2.666(5), Zr1−C12 = 2.456(5), Zr1−C13 = 2.480(5), Zr1−C18 = 2.675(5), Zr1−C19 = 2.653(5), av Zr1−C(ring) = 2.586(5), Zr1−O1 = 2.124(3), Zr1−O2 = 2.104(3), Zr1−O3 = 2.161(3), Zr1−N6 = 2.186(4), Cent−Zr1−C1 = 92.6, C2−P−C11 = 98.2(2).

values observed in the zirconium and hafnium analogues because of the size effects. The effects of the linkages on the rigidity and structural parameters of $[\eta^5:\sigma\text{-}\mathrm{A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2}$ type compounds are observed as shown in Table 3: (1) both the Zr−C(cage) and Zr−C(ring) distances decrease in the order ${}^i\mathrm{Pr_2NP} > \mathrm{Me_2Si} > {}^i\mathrm{Pr_2NB} > \mathrm{Me_2C}$, (2) the Cent−Zr−C(cage) angles increase in the order $\mathrm{Me_2C} < {}^i\mathrm{Pr_2NB} < {}^i\mathrm{Pr_2NP} < \mathrm{Me_2Si}$, and (3) the C(ring)−A−C(cage) angles follow the order ${}^i\mathrm{Pr_2NB} > \mathrm{Me_2C} > \mathrm{Me_2Si} > {}^i\mathrm{Pr_2NP}$. Thus, **2** can be viewed as a more rigid compound than the Si-linked analogue, as suggested by the Cent−Zr−C(cage) angles. The Zr−C(ring) distance of 2.551(8) Å in **2** is comparable to the corresponding value of 2.527(3) Å found in compound $[\mathrm{PhP}(\eta^5\text{-}\mathrm{C_5Me_4})_2]\mathrm{ZrCl_2}$,[4g] while the Cent−Zr−C(cage) angle of 106.6° in **2** is significantly smaller than that of 125.9° in $[\mathrm{PhP}(\eta^5\text{-}\mathrm{C_5Me_4})_2]\mathrm{ZrCl_2}$.

Reactivity. Our earlier work showed that unsaturated molecules can insert into the Zr−N bonds of $[\eta^5:\sigma\text{-}\mathrm{Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2}$ (A = C, Si) to give multi-insertion products.[18] Compound **2** reacted with PhNCO to afford the tri-insertion product $[\eta^5:\sigma\text{-}{}^i\mathrm{Pr_2NP(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}OC(NMe_2)NPh][\eta^2\text{-}OC(NMe_2)N(Ph)C{=}(NPh)O]}$ (**5**). In the presence of excess PhNCO, no further insertion product was isolated; rather, trimerization of PhNCO proceeded to give $\mathrm{(PhNCO)_3}$. In other words, **2** can catalyze the trimerization of PhNCO, a property that is similar to that of $[\eta^5:\sigma\text{-}\mathrm{Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2}$.[18] Figure 3 shows the molecular structure of **5**, indicating that the central Zr atom is fully protected by the surrounding ligands and no coordination sites are available for further insertion. The fourth equivalent of PhNCO can react only with the coordinated ligand, leading to the formation of trimer.

Compound **2** reacted with 2 equiv of *n*-BuLi in toluene to give, after recrystallization from DME/toluene, the dilithium salt of $[\mathrm{Li(DME)_3}][\eta^5\text{:}\ \sigma\text{-}{}^i\mathrm{Pr_2NP(C_9H_6)(C_2B_{10}H_{10})Li(DME)}]$ (**6**) in 39% isolated yield. This is not very unusual in view of the formation of $\mathrm{CpZr(^nBu)_3}$ and CpLi from the reaction of $\mathrm{Cp_2ZrCl_2}$ with 3.3 equiv of *n*-BuLi in benzene.[19] This result suggests that the alkyllithium

Table 3. Key Structural Data for $[\eta^5\text{:}\ \sigma\text{-}\mathrm{A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2}$



A	av Zr−C(ring)	Zr−C(cage)	av Zr−N	C(ring)−A−C(cage)	Cent−Zr−C(cage)	ref
${}^i\mathrm{Pr_2NB}$	2.522(2)	2.345(2)	2.026(2)	114.0(2)	103.0	9
$\mathrm{Me_2C}$	2.521(8)	2.326(7)	2.016(8)	109.4(6)	101.6	8
$\mathrm{Me_2Si}$	2.541(5)	2.348(5)	2.019(4)	104.8(2)	109.9	8
${}^i\mathrm{Pr_2NP}$	2.551(8)	2.354(8)	2.020(7)	98.7(3)	106.6	this work

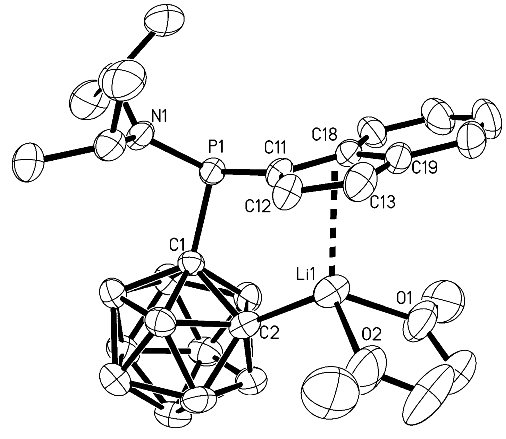


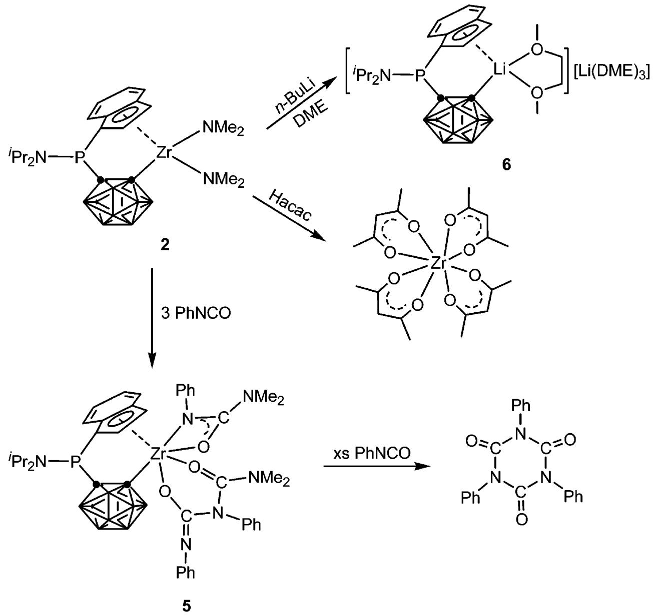
Figure 4. Molecular structure of the anion [η^5:σ-^{i}Pr$_2$NP(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)Li(DME)]$^-$ in **6**. Selected bond distances (Å) and angles (deg): Li1−C2 = 2.116(8), Li1−C11 = 2.456(7), Li1−C12 = 2.309(7), Li1−C13 = 2.590(8), Li1−C18 = 2.736(8), Li1−C19 = 2.816(8), av Li1−C(ring) = 2.581(8), Li1−O1 = 2.002 (8), Li1−O2 = 2.055 (8), O1−Li1−O2 = 80.1(3), Cent−Li−C2 = 116.6.

might not be a good alkylating reagent for the syntheses of group 4 metal alkyl compounds incorporating constrained-geometry carboranyl ligands. The molecular structure of **6** was confirmed by a single-crystal X-ray analysis. It consists of well-separated, alternating layers of discrete tetrahedral anions [η^5:σ-^{i}Pr$_2$NP(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)Li(DME)]$^-$ and octahedral cations [Li(DME)$_3$]$^+$. In the anion, the Li$^+$ ion is η^5-bound to the indenyl group and σ-bound to the cage carbon atom and coordinated to two oxygen atoms from one DME molecule in a distorted-tetrahedral geometry as shown in Figure 4. The average Li−C(ring) distance of 2.581(8) Å and the Li−C(cage) distance of 2.116(8) Å compare to the corresponding values of 2.332(8) and 2.149(7) Å observed in [Li(THF)$_4$][{[(μ-η^5):σ-Me$_2$Si(C$_5$Me$_4$)(C$_2$B$_{10}$H$_{10}$)]Li(THF)}$_2$Li].[20]

An equimolar reaction of **2** with acetylacetone resulted in the isolation of the known compound Zr(acac)$_4$ in 34% yield. The ^{31}P NMR was used to monitor this reaction and showed that even at −30 °C two new peaks at about 74.0 and 41.0 ppm attributable to the neutral ligand ^{i}Pr$_2$NP(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$)[10] were observed. The high acidity of acetylacetone may lead to the low selectivity of the equimolar reaction, resulting in the completed protonation of **2**.[21] The above reactions are outlined in Scheme 2.

Ethylene Polymerization. Compounds **1**−**4** underwent preliminary testing for catalytic activity in ethylene polymerization using modified methylalumoxane (MMAO) as cocatalyst (Al/M = 1500) in toluene at 25 °C (1 atm of ethylene). Among them, **1**, **3**, and **4** showed very low catalytic activity, whereas **2** exhibited an activity of 3.7 × 10^3 g PE mol^{-1} atm^{-1} h^{-1}. The molar mass and the polydispersity of the resulting polyethylene were 2.16 × 10^5 g/mol and 1.87, respectively. Thus, **2** was proved to be much less active than its Me$_2$C-, Me$_2$Si-, and ^{i}Pr$_2$NB-bridged analogues.[8,9] In view of their structural parameters (Table 3), we may conclude that the electronic properties of the bridging atoms lead to the significant differences in catalytic activities in ethylene polymerization. The electron-deficient boron atom may increase the Lewis acidity of the central metal atom, resulting in the higher catalytic activity of the resultant metal compounds. In contrast, the electron-rich phosphorus atom could decrease the Lewis acidity of the central metal atom, leading to the lower catalytic activity. Our work supports the argument that the RP moiety serves as an "electron-donating" group in metallocene catalysts.

Scheme 2



Polymerization of ϵ-Caprolactone. Polylactones are an important class of biodegradable polymers. Rare earth metal complexes were found to efficiently catalyze the polymerization of lactones because of the highly electropositive nature of the lanthanides.[22] Both lanthanide-amide complexes[22d−g] and organozirconium cations[23] can initiate the ring-opening polymerization of ϵ-caprolactone. Up to now, group 4 metal amides have not been reported to initiate the polymerization of lactones. In view of the role of the carboranyl moiety in MMA polymerization,[24] we wondered if group 4 metal amides containing constrained-geometry carboranyl ligands could initiate the polymerization of lactones. To our surprise, **2** was able to initiate the polymerization of ϵ-caprolactone, and the results are summarized in Table 4. Solvent, reaction temperature, and monomer-to-catalyst ratio all affected the polymerization results. THF was found to be the best solvent. As the reaction

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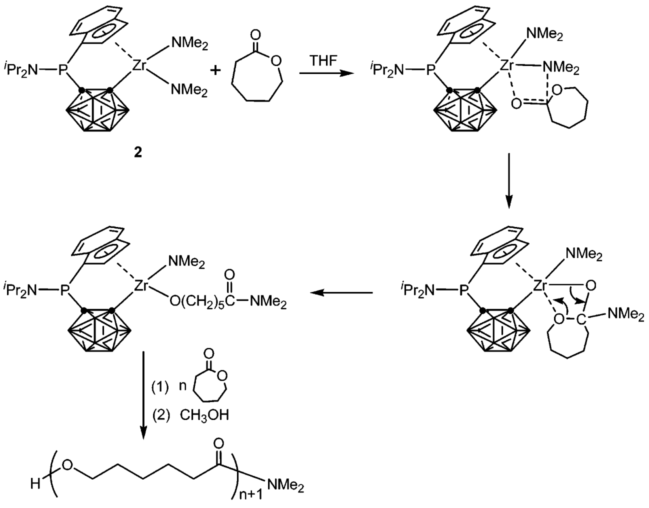
Table 4. Polymerization of ϵ-Caprolactone by 2[a]

entry	solvent	[monomer]/**2**	temp (°C)	conversion (%)	M_n ($\times 10^{-4}$)[b]g/mol	M_w ($\times 10^{-4}$)[b]g/mol	M_w/M_n
1	THF	250	25	58	2.34	3.00	1.29
2	THF	500	25	55	4.23	5.34	1.26
3	CH_2Cl_2	500	25	4.7	10.52	14.17	1.35
4	toluene	500	25	33	3.27	4.56	1.39
5	THF	500	45	92	5.32	6.88	1.29
6	THF	500	60	95	5.67	7.54	1.33

[a] Conditions: **2**: 20 mg, 3.6×10^{-3} mmol, 2 h. [b] Determined by GPC relative to polystyrene standards.

Scheme 3



temperature increased, polymerization became very rapid with 95% conversion; the molar masses and polydisperisities of the polymers were slightly increased. The resulting polyesters were generally of high molar masses ($M_n > 40\,000$) and showed narrow polydispersities ($M_w/M_n < 1.4$). The ^1H NMR experiments showed that the two NMe_2 peaks at 3.02 and 2.53 ppm in **2** disappeared immediately upon addition of 2 equiv of ϵ-caprolactone, and the new resonances at 2.93 and 2.99 ppm attributable to the $-CONMe_2$ group were generated. These two peaks were also observed in the ^1H NMR spectra of the resulting polyesters. These observations are consistent with the reported polymerization of ϵ-caprolactone using $Y\{N(SiMe_3)_2\}_3$ as catalyst.[22g] On the basis of these facts, it is most likely that the attack by one of the nucleophilic amido-nitrogen atoms at the lactone carbonyl-carbon atoms is the initial step of the polymerization followed by acyl bond cleavage as shown in Scheme 3. Evidently the increase in the electron-donating ability of the RP-bridged ligand resulted in a more nucleophilic amido group.

Conclusion

Several new group 4 metal amides with a $^iPr_2NP$-bridged constrained-geometry carboranyl ligand were synthesized and fully characterized. Reactivity studies showed that (1) the zirconium amide was able to catalyze the trimerization of PhNCO, and PhNCO inserted exclusively into the Zr−N bonds, and (2) both the Zr−C(cage) σ-bond and Zr−indenyl π-bond were broken in the reactions of **2** with n-BuLi or Hacac to generate $[Li(DME)_3][\eta^5{:}\sigma{-}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})Li(DME)]$ and $Zr(acac)_4$, respectively.

The zirconium amide **2** catalyzed ethylene polymerization with an activity of 3.7×10^3 g PE mol^{-1} atm^{-1} h^{-1} in the presence of MMAO, which is the lowest one among its carbon-, silcon-, and boron-linked analogues, although their geometries are similar. The results suggest that the electronic properties of the bridging atoms have great effects on the catalytic performance of the group 4 metal compounds. The electron-rich phosphorus can decrease the electron-deficiency of the metal center, leading to a lower catalytic activity in ethylene polymerization. This work supports the argument that the RP moiety acts as an "electron-donating" group in metallocenes.[5b,d]

The zirconium amide **2** was able to initiate the ring-opening polymerization of ϵ-caprolactone to give polyesters with high molecular weights and low polydispersities. This represents the first example of the polymerization of lactones catalyzed by group 4 metal amides. This result also shows that carboranyl ligands can enhance the electrophilicity of the group 4 metal center. It is another example to illustrate the role of carborane in catalysis.

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Supporting Information Available: Crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1**−**6** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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