Bis(amido)cyclodiphosph(III)azane Hafnium Complexes and Their Activation by Tris(perfluorophenyl)borane

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Received October 5, 2004

Bis(amido) hafnium complexes $[(RN)(t\text{-BuNP})]_2HfCl_2$ (R = 2,6-*i*-$Pr_2C_6H_3$ (**5**), 2,5-*t*-$Bu_2C_6H_3$ (**6**)) bearing a *N-tert*-butyl cyclodiphosph(III)azane bridge were prepared by direct metalation of corresponding ligand precursors with $Hf(NMe_2)_4$ followed by chlorination by Me_3SiCl. Complexes **5** and **6** and the already known $[(t\text{-BuN})(t\text{-BuNP})]_2HfCl_2$ (**4**) were subsequently converted to their methyl derivatives $[(RN)(t\text{-BuNP})]_2HfMe_2$ by the alkylation by MeMgBr in Et_2O. The solid state structure of $[(t\text{-BuN})(t\text{-BuNP})]_2HfMe_2$ (**7**) reveals a highly distorted trigonal-bypiramidal configuration at the metal center. Activation of the dimethyl complexes with $B(C_6F_5)_3$ led to the generation of corresponding cationic species, which were investigated by ^1H, ^{13}C, ^{31}P, and ^{19}F NMR. In the solid state, the metal center of $\{[(t\text{-BuN})(t\text{-BuNP})]_2HfMe(\mu\text{-Me})B(C_6F_5)_3\}$ has a distorted trigonal-bypiramidal configuration and the $[MeB(C_6F_5)_3]^-$ anion is only weakly coordinated with cationic hafnium. In deuterobenzene solution $\{[(t\text{-BuN})(t\text{-BuNP})]_2HfMe(\mu\text{-Me})B(C_6F_5)_3\}$, like in the solid state, exhibited C_s symmetry as a result of the additional coordination of the high electrophilic hafnium atom with one of the nitrogens of the P_2N_2 ring. This additional metal−ligand interaction in solution is absent in the case of the activated complexes **8** and **9**, having bulky aryl substituents. The compounds **4** and **7** revealed moderate catalytic activity in the ethene polymerization, while hafnium complexes bearing aryl groups remained inactive in the same conditions.

Introduction

The basic discovery in the middle 1970s that group 4 metallocene dichlorides can be activated with methylaluminoxanes (MAO)[1] has provided a solid basis for the development of homogeneous single-center polymerization catalysts. Therefore, during the last 30 years we have witnessed significant advances in the design of organometallic and inorganic complexes and their application in α-olefin polymerization.[2,3] The function of MAO in the activation process is rather well established and includes the alkylation of the catalyst precursor followed by the formation of a cationic metal center by alkyl abstraction.[2a]

Since the advent of MAO, new strong Lewis acid activators displaying similar and even higher efficiency were reported to be valuable cocatalysts for homogeneous Ziegler−Natta olefin polymerization systems.[4] Started by Chen, Marks,[5] and Ewen,[6] activators based on perfluoroarylboranes and salts of arylammonium cations with noncoordinating anions are widely used in investigation of activation of metallocenes,[7] constrained geometry,[8] and nonmetallocene complexes.[9] Due to the high instability of activated species, they are generated and investigated mainly in situ by different NMR techniques.[4,7−9] These cationic complexes facilitate direct insight and offer fundamental information on the catalytically active species, leading to new opportunities for rational development of homogeneous polymerization catalyts.[4] The catalytic species formed during the activation process can exhibit a geometry differing from the one of the parent complex, i.e., configuration of the central atom and/or coordination of the activator. Therefore, knowing the structural features of the catalyst precursor is not enough, and it appears necessary to study the activation reaction of the precatalyst and the

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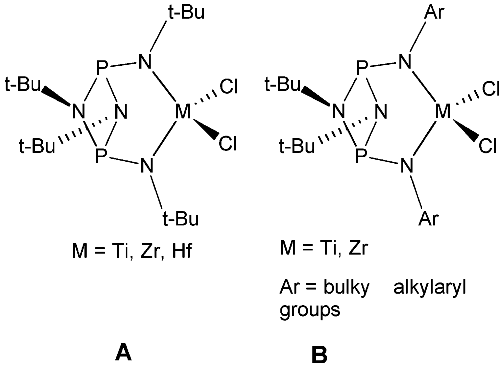
10.1021/om0492303 CCC: $30.25

Chart 1



actual structure of the catalytic species generated under conditions resembling those used during the polymerization process.[4]

Zirconium, hafnium, and titanium *cis*-bis(*tert*-butylamido) complexes bearing a cyclodiphosph(III)azane bridge (structure A, Chart 1) have recently attracted attention as homogeneous catalyst precursors for ethene polymerization.[10−12] Nevertheless, the presence of an electron-rich phosphor-nitrogen cycle in the vicinity of metal center raises the question of the determination of the site of MAO coordination during the activation step. Presumably, an aluminum species can also coordinate to phosphorus(III) atoms and, as a result, initiate the decomposition of the catalyst.[11]

Recently we reported on new *cis*-bis(amino)cyclodiphosph(III)azanes bearing bulky arylamine substituents and their Ti and Zr derivatives (structure B, Chart 1).[13,14] After MAO activation, these catalysts showed an increased stability if compared with *tert*-butylamido-substituted analogues and high activity in ethene polymerization. It was also established that stability of the catalysts, displayed average activities, and properties of the produced polyethylene depend on the size and nature of the amido substituents. A rational explanation can reside in the more or less efficient protection of the central metal atom provided by amido substituents of different bulkiness toward monomer and/or cocatalyst (MAO) coordination.[14] Among group 4 transition metals, the most stable alkyl derivatives are those of hafnium,[4] and their use can thus permit precise structural determination of in situ generated cationic species and too fast decomposition of the generated cationic species can be avoided.

Accordingly, to get insight into the activation step of *cis*-bis(amido)cyclodiphosph(III)azane group 4 metal complexes, and to understand the true nature of the activated catalyst precursor, the synthesis of new *cis*-bis(amido)cyclodiphosph(III)azane Hf methyl complexes was undertaken, and their activation by perfluorophenylborane was investigated by means of NMR and X-ray diffraction techniques.

Experimental Section

All manipulations were done under inert argon atmosphere using standard Schlenk techniques or in a glovebox. The hydrocarbon and ethereal solvents were refluxed over sodium and benzophenone, distilled, and stored under argon with sodium flakes. Dichloromethane was refluxed with CaH_2 powder and distilled before use. Deuterated solvents were carefully dried (CD_2Cl_2 with P_4O_{10} and deuterobenzene with sodium) and stored over molecular sieves in a glovebox. Mass spectra were measured on a JEOL SX102 spectrometer, and the ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer and referenced relative to $CHDCl_2$ (5.28 and 53.73 ppm, respectively) or C_6D_5H (7.24 and 128.0 ppm, respectively). ^{31}P NMR spectra were collected with Bruker AMX 400 and Bruker Avance DRX 500 spectrometers and referenced relative to an external standard (85% H_3PO_4 solution). ^{19}F NMR spectra were recorded with a Bruker Avance DRX 500 spectrometer and referenced relative to $CFCl_3$. Elemental analyses were performed by Analytische Laboratorien (Prof. Dr. H. Malissa und G. Reuter) GmbH, Lindlar, Germany. Chlorotrimethylsilane (Fluka), tris(perfluorophenyl)borane (Strem), *n*-BuLi (Aldrich), and MeMgBr (Aldrich) were used as received. $Hf(NMe_2)_4$ (Strem) was dissolved in a fixed amount of dry toluene and used as a stock solution. Methylalumoxane (MAO, 30 wt % solution in toluene) was received from Borealis Polymers Oy. Ligand precursors $[(t\text{-BuNH})(t\text{-BuNP})]_2$[15] (**1**), *cis*-$[(2,6\text{-}i\text{-}Pr_2C_6H_3NH)(t\text{-BuNP})]_2$[13] (**2**), and *cis*-$[(2,5\text{-}t\text{-}Bu_2C_6H_3NH)(t\text{-BuNP})]_2$[13] (**3**) were prepared according to literature procedures.

$[(t\text{-BuN})(t\text{-BuNP})]_2HfCl_2$ (4) was prepared according to a modified literature procedure.[12] A hexane solution of *n*-BuLi (1.6 M, 18 mL, 28 mmol) was added via a syringe to a solution of **1** (4.5 g, 13 mmol) in THF (30 mL) at −50 °C. After 20 min, the reaction mixture was allowed to warm to room temperature and refluxed during 3 h. All volatiles were removed in vacuo, and toluene (30 mL) was added. Solid $HfCl_4$ (4.14 g, 13 mmol) was added with vigorous stirring to the toluene suspension, and the resulting mixture was refluxed during 1 day. All volatiles were removed in vacuo, and the solid residue was extracted by a toluene−hexane mixture, followed by filtration. Evaporation of the solvents from the filtrate under reduced pressure gave a yellow crystalline solid (6.04 g, 78%). Anal. Calcd for $C_{16}H_{36}Cl_2HfN_4P_2$: C, 32.25; H, 6.09. Found: C, 32.12; H, 6.09. ^1H NMR (200 MHz, C_6D_6, 29 °C): δ_H 1.37 (s, 18H, *t*-Bu, P_2N_2 cycle), 1.49 (s, 18H, *t*-Bu). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 21 °C): δ_P 102.03 (s). MS(EI): *m/z* (%) 596 (35, M^+), 580 (90, $M^+ - CH_3$), 525 (25, $M^+ - 2Cl$), 352 (60, ligand).

$[(2,6\text{-}i\text{-}Pr_2C_6H_3N)(t\text{-BuNP})]_2HfCl_2$ (5). $Hf(NMe_2)_4$ (2.39 g, 6.75 mmol) in toluene (25 mL) was added to the toluene (30 mL) solution of *cis*-$[(2,6\text{-}i\text{-}Pr_2C_6H_3NH)(t\text{-BuNP})]_2$ (**2**) (3.75 g, 6.75 mmol) and refluxed overnight. Excess of Me_3SiCl (7.3 mL, 6.23 g, 57.3 mmol) was further added via a syringe to the resulting yellow solution at room temperature and stirred overnight. All volatiles were then removed in vacuo, and the residue was extracted three times with a mixture of hexane (30 mL) and CH_2Cl_2 (10 mL) followed by filtration of extracts. Solvents were then removed under vacuum, and a yellow sticky material residue was obtained (4.12 g, 76%). This complex absorbs solvents so strongly that even under harsh drying conditions they cannot be removed completely. Several attempts were made to get proper elemental analysis data, but in all of them the increased content of carbon was detected. Anal. Calcd for $C_{32}H_{52}Cl_2HfN_4P_2$: C, 47.80; H, 6.52; N, 6.97. Found: C, 48.39; H, 6.63; N, 7.30. ^1H NMR (200 MHz, C_6D_6, 29 °C): δ_H 1.37 (s, 18H, *t*-Bu), 1.42 (d, 24H, C*H*$_3$, *i*-Pr), 3.97 (m, 4H, C*H*, *i*-Pr), 7.19 (m, 4H, H−Ar), 7.28 (2H, H−Ar). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 29 °C): δ_C 24.17 (CH_3, *i*-Pr),

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29.17 (t, *C*H, *i*-Pr), 31.36 (t, J_{PC} = 6.5 Hz, *C*H_3, *t*-Bu), 51.60 (t, J_{PC} = 14.5 Hz, *C, t*-Bu), 123.98 (Ar), 136.37 (Ar), 140.96 (Ar), 144.57 (Ar). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 21 °C): δ_P 115.63 (s). MS (EI): *m/z* (%) 804 (5, M^+), 732 (10, $M^+ - 2Cl$), 556 (20, ligand).

[(2,5-*t*-Bu$_2$C$_6$H$_3$N)(*t*-BuNP)]$_2$HfCl$_2$ (6) was synthesized similarly to **5** from a toluene (20 mL) solution of *cis*-[(2,5-*t*Bu$_2$C$_6$H$_3$NH)(*t*BuNP)]$_2$ (**3**) (3.11 g, 5.07 mmol) and Hf(NMe$_2$)$_4$ (1.8 g, 5.07 mmol) in toluene (19 mL). Excess Me_3SiCl (6.7 mL, 5.68 g, 43.10 mmol) was added with a syringe to the resulting yellow solution at room temperature. After overnight stirring all volatiles were removed in vacuo, and the residue was extracted several times with a mixture of hexane (20 mL) and CH_2Cl_2 (10 mL). After filtration of the extracts, solvents were removed under reduced pressure to yield a pale yellow solid (3.60 g, 82%). Anal. Calcd for $C_{36}H_{60}Cl_2HfN_4P_2$: C, 50.26; H, 7.03; N, 6.51. Found: C, 50.54; H, 7.56; N, 6.92. ^1H NMR (200 MHz, C_6D_6, 29 °C): δ_H 1.45 (s, 36H, *t*-BuAr), 1.57 (s, 18H, *t*-Bu), 7.00 (dd, 2H, ^1J = 6.2 Hz, ^2J = 2.2 Hz, 4-H−Ar), 7.38 (2H, 3-H−Ar), 8.26 (dd, 2H, ^1J = 3.3 Hz, ^2J = 2.2 Hz, 6-H−Ar). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 29 °C): δ_C 31.0 (*C*H_3, 5-*t*-BuAr), 31.33 (t, J_{PC} = 6.6 Hz, *C*H_3, *t*-Bu), 31.53 (*C*H_3, 2-*t*-BuAr), 34.00 (*C*, 5-*t*-BuAr), 34.50 (*C*, 2-*t*-BuAr), 51.7 (t, J_{PC} = 13.73 Hz, *C, t*-Bu), 113.83 (Ar), 114.50 (Ar), 117.17 (Ar), 131.18 (Ar), 138.90 (d, *J* = 9.9 Hz, Ar), 150.10 (t, *J* = 1.2 Hz, Ar). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 21 °C): δ_P 99.80 (s). MS(EI): *m/z* (%) 862 (2, M^+), 804 (10, M^+ − *t*-Bu), 613 (90, ligand).

[(*t*-BuN)(*t*-BuNP)]$_2$HfMe$_2$ (7). A solution of MeMgBr in Et_2O (3M, 2.3 mL, 6.9 mmol) was added via syringe to a solution of [(*t*-BuN)(*t*-BuNP)]$_2$HfCl$_2$ (**4**) (2.0 g, 3.36 mmol) in Et_2O (30 mL) at −50 °C. The reaction mixture was allowed to warm to room temperature, and the stirring was continued overnight. All volatiles were removed in vacuo, and the solid residue was extracted with hexane, followed by filtration in the glovebox through Teflon filters. The resulting clear hexane solution was then evaporated off in vacuo, and a white-yellow crystalline solid (1.76 g; 94.6%) was isolated. Crystals suitable for X-ray analysis were obtained by recrystallization of **7** from Et_2O at −20 °C. The compound revealed high sensitivity to moisture, air, and elevated temperatures, and therefore it turn out to be difficult to obtain reliable elemental analysis data. To confirm the complex composition HR-MS was performed instead (see Supporting Information). Anal. Calcd for $C_{18}H_{42}HfN_4P_2$: C, 38.95; H, 7.63; N, 10.10. Found: C, 38.32; H, 7.27; N, 9.45. ^1H NMR (200 MHz, C_6D_6, 29 °C): δ_H 0.62 (s, 6H, CH_3), 1.38 (s, 18H, *t*-Bu, P_2N_2 cycle), 1.54 (d, *J* = 0.73 Hz, 18H, *t*-Bu). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 29 °C): δ_C 30.44 (t, J_{PC} = 6.1 Hz, *C*H_3, *t*-Bu, P_2N_2 cycle), 34.35 (d, J_{PC} = 9.2 Hz, *C*H_3, *t*-Bu), 54.0 (t, J_{PC} = 12.2 Hz, *C, t*-Bu, P_2N_2 cycle), 57.35 (d, J_{PC} = 16.0 Hz, *C, t*-Bu), 59.34 (t, *J* = 0.8 Hz, *C*H_3). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 21 °C): δ_P 108.3 (s). MS(EI): *m/z* (%) 555 (2, M^+), 541 (8, $M^+ - CH_3$), 349 (90, ligand). HR-MS(EI): *m/z* calcd for $C_{17}H_{39}N_4P_2Hf$ ($M^+ - CH_3$) 539.2090; observed 539.2110, error 4.2 ppm.

[(2,6-*i*-Pr$_2$C$_6$H$_3$N)(*t*-BuNP)]$_2$HfMe$_2$ (8). Solutions of MeMgBr in Et_2O (3 M, 2.0 mL, 6.0 mmol) and [(2,6-*i*-Pr$_2$C$_6$H$_3$N)(*t*-BuNP)]$_2$HfCl$_2$ (**5**) (2.0 g, 2.49 mmol) in Et_2O (20 mL) were combined and treated as described above. Separation of the product was carried out as reported for **7**. The Hf complex was isolated as a yellow oil (1.70 g; 89.5%). Anal. Calcd for $C_{34}H_{58}HfN_4P_2$: C, 53.50; H, 7.66; N, 7.34. Found: C, 53.87; H, 7.78; N, 7.13. ^1H NMR (200 MHz, C_6D_6, 29 °C): δ_H 0.38 (s, 6H, CH_3), 1.38 (s, 18H, *t*-Bu), 1.42 (d, 24H, C*H*$_3$, *i*-Pr), 3.97 (m, 4H, C*H, i*-Pr), 7.20 (m, 4H, H−Ar), 7.27 (2H, H−Ar). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 29 °C): δ_C = 24.17 (*C*H_3, *i*-Pr), 28.43 (*C*H_3), 29.08 (t, *C*H, *i*-Pr), 31.36 (t, J_{PC} = 6.5 Hz, *C*H_3, *t*-Bu), 51.60 (t, J_{PC} = 14.5 Hz, *C, t*-Bu), 123.99 (Ar), 136.37 (Ar), 140.97 (Ar), 144.57 (Ar). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 21 °C): δ_P 115.57 (s). MS (EI): *m/z* (%) 763 (1, M^+), 731 (1, $M^+ - 2CH_3$), 556 (30, ligand).

[(2,5-*t*-Bu$_2$C$_6$H$_3$N)(*t*-BuNP)]$_2$HfMe$_2$ (9). Solutions of MeMgBr in Et_2O (3M, 1.5 mL, 4.5 mmol) and [(2,5-*t*-Bu$_2$C$_6$H$_3$N)(*t*-BuNP)]$_2$HfCl$_2$ (**6**) (1.8 g, 2.1 mmol) in Et_2O (20 mL) were combined and treated as described above, and separation of the product was carried out as reported for **7**. The Hf complex was isolated as a yellow-brown solid (1.40 g; 81.4%). Anal. Calcd for $C_{38}H_{66}HfN_4P_2$: C, 55.70; H, 8.12; N, 6.84. Found: C, 55.61; H, 8.03; N, 6.68. ^1H NMR (200 MHz, C_6D_6, 29 °C): δ_H 0.38 (s, 6H, CH_3), 1.45 (s, 36H, *t*-BuAr), 1.57 (s, 18H, *t*-Bu), 7.00 (dd, 2H, ^1J = 6.2 Hz, ^2J = 2.2 Hz, 4-H−Ar), 7.38 (2H, 3-H−Ar), 8.26 (dd, 2H, ^1J = 3.3 Hz, ^2J = 2.2 Hz, 6-H−Ar). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 29 °C): δ_C 31.0 (*C*H_3, 5-*t*-BuAr), 31.33 (t, J_{PC} = 6.5 Hz, *C*H_3, *t*-Bu), 31.53 (*C*H_3, 2-*t*-BuAr), 34.00 (*C*, 5-*t*-BuAr), 34.50 (*C*, 2-*t*-BuAr), 51.71 (t, J_{PC} = 13.5 Hz, *C, t*-Bu), 62.64 (*C*H_3), 113.83 (Ar), 114.50 (Ar), 117.18 (Ar), 131.19 (Ar), 141.90 (d, *J* = 9.9 Hz, Ar), 150.02 (t, *J* = 1.2 Hz, Ar). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 21 °C): δ_P 98.70 (s). MS(EI): *m/z* (%) 774 (2, M^+ − *t*-Bu), 612 (45, ligand).

In Situ Generation of [(*t*-BuN)(*t*-BuNP)]$_2$Hf(Me)MeB(C$_6$F$_5$)$_3$ (10). In a glovebox, an NMR tube was charged with [(*t*-BuN)(*t*-BuNP)]$_2$HfMe$_2$ (**7**) (40 mg, 72 μmol), $B(C_6F_5)_3$ (36.9 mg, 72 μmol), and 0.6 mL of C_6D_6 at room temperature and shaken vigorously. The product was investigated only by NMR methods because of its high thermal instability and very high air and moisture sensitivity. Crystals suitable for X-ray analysis were grown by layer recrystallization from a toluene−hexane mixture at −20 °C. ^1H NMR (200 MHz, C_6D_6, 29 °C): δ_H 0.87 (s, 3H, CH_3Hf), 1.00 (s, 9H, *t*-Bu, P_2N_2 cycle), 1.07 (s, 9H, *t*-Bu, P_2N_2 cycle), 1.13 (s, 18H, *t*-Bu), 2.93 (br s, 3H, CH_3B). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 29 °C): δ_C 30.86 (m, B*C*H_3), 33.70 (t, J_{PC} = 11.0 Hz, *C*H_3, *t*-Bu, P_2N_2 cycle), 33.80 (d, J_{PC} = 9.2 Hz, *C*H_3, *t*-Bu), 58.7 (d, J_{PC} = 11.8 Hz, *C, t*-Bu), 59.6 (t, J_{PC} = 6.5 Hz, *C, t*-Bu, P_2N_2 cycle), 59.8 (Hf*C*H_3), br signals 126.7 (B−C_{Ar}), 135.0 (Ph_F), 139.9 (Ph_F), 147.0 (Ph_F), 151.8 (Ph_F). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 21 °C): δ_P 91.54 (s). ^{19}F NMR (470 MHz, C_6D_6, 21 °C): δ_F −132.6 (d, J_{FF} = 22.3 Hz, *o-F*, C_6F_5), −159.0 (t, J_{FF} = 20.7 Hz, *m-F*, C_6F_5), −163.9 (t, J_{FF} = 19.0 Hz, *p-F*, C_6F_5).

Preparation of other cationic complexes was done in a manner similar to that described for **10**, and formation of the cationic complexes was followed by NMR methods (see Supporting Information).

Single-Crystal X-ray Diffraction Studies. Crystal data of compounds **7** and **10** were collected with a Nonius KappaCCD area-detector diffractometer at 173(2) K using Mo Kα radiation (graphite monochromator), 0.71073 Å. Data reduction: COLLECT.[16] Absorption correction: SADABS.[17] Solution and refinement: SIR-2002.[18] Graphics: SHELXTL/PC.[19] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined on calculated positions. The displacement factors of the H atoms were 1.2× (1.5×) that of the host atom.

Results and Discussion

Synthesis of Complexes. On the basis of our earlier studies on *cis*-bis(amido)cyclodiphosph(III)azane complexes of group 4 transition metals, the ligand substituents have a significant influence on initial catalytic activity, stability of the catalytic species, and quality of the polymers produced.[13,14] To investigate the activation process more closely, hafnium complexes of *cis*-bis(amino)cyclodiphosph(III)azane ligands were obtained,

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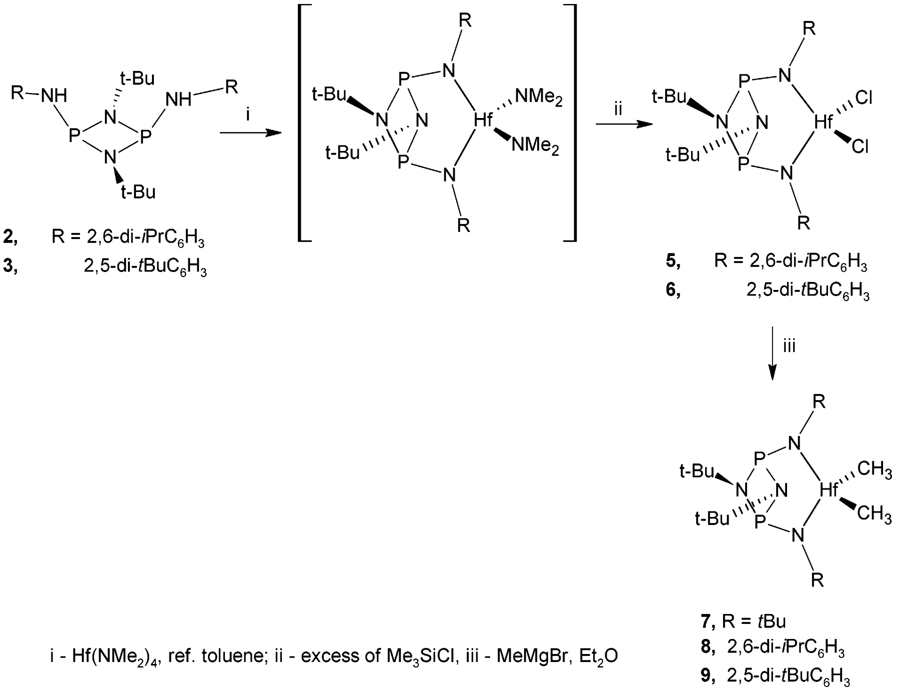
Scheme 1



2, R = 2,6-di-*i*PrC$_6$H$_3$
3, 2,5-di-*t*BuC$_6$H$_3$

5, R = 2,6-di-*i*PrC$_6$H$_3$
6, 2,5-di-*t*BuC$_6$H$_3$

7, R = *t*Bu
8, 2,6-di-*i*PrC$_6$H$_3$
9, 2,5-di-*t*BuC$_6$H$_3$

i - Hf(NMe$_2$)$_4$, ref. toluene; ii - excess of Me$_3$SiCl, iii - MeMgBr, Et$_2$O

as their alkylated derivatives are more stable than the corresponding zirconium complexes. For this purpose, ligand precursors with different amino substituents were prepared: [(*t*-BuNH)(*t*-BuNP)]$_2$ (**1**) was synthesized according to an earlier published literature procedure,[15] while [(2,6-*i*-Pr$_2$C$_6$H$_3$NH)(*t*-BuNP)]$_2$ (**2**) and [(2,5-*t*-Bu$_2$C$_6$H$_3$NH)(*t*-BuNP)]$_2$ (**3**), having bulky aryl substituents, were obtained via a synthetic method lately developed in our laboratory.[13] The dichloro hafnium complex of **1** was prepared by deprotonation of the ligand precursor with butyllithium and subsequent treatment of the lithium salt with HfCl$_4$ as reported earlier.[12] On the other hand, direct metalation of the sterically hindered ligands **2** and **3** with Hf(NMe$_2$)$_4$ turned out to be the most efficient method leading to complex synthesis (Scheme 1). The intermediate bis(amido)Hf(NMe$_2$)$_2$ species were not isolated, but ^{1}H NMR and ^{31}P NMR showed that metalation occurred selectively, and only the desired hafnium amido derivatives were identified in ^{1}H NMR. Conversion of the tetra(amido) hafnium complexes to the corresponding dichloride derivatives was carried out by using a large excess of Me$_3$SiCl. As expected, the bonding between the metal center and the ligand was protected efficiently enough, and only substitution of the NMe$_2$ groups occurred.[20] The dichloro hafnium complexes [(2,6-*i*-Pr$_2$C$_6$H$_3$N)(*t*-BuNP)]$_2$HfCl$_2$ (**5**) and [(2,5-*t*-Bu$_2$C$_6$H$_3$N)(*t*-BuNP)]$_2$HfCl$_2$ (**6**) were isolated in good yields (Scheme 1). The ^{1}H NMR spectra of **5** and **6** revealed an apparent C_{2v} symmetry in solution, as all the alkyl and aromatic protons were equivalent. Moreover, NMR data of these hafnium complexes were in accordance with those observed for their Ti and Zr analogues.[13,14]

Table 1. Crystallographic Data for Complexes 7 and 10

	7	**10**
formula	C$_{18}$H$_{42}$N$_4$P$_2$Hf	C$_{36}$H$_{42}$N$_4$P$_2$F$_{15}$BHf
fw	554.99	1066.98
space group	$P2_12_12_1$	$P2_1/c$
a, Å	9.916(1)	12.168(1)
b, Å	15.327(1)	19.986(1)
c, Å	16.582(2)	17.984(1)
β, deg	90	103.561(2)
V, Å^3	2520.2(4)	4251.6(5)
d_{calc}, g cm^{-3}	1.463	1.667
Z	4	4
μ, cm^{-1}	4.275	2.627
Flack param	0.001(7)	
λ, Å	0.71073	0.71073
T, K	173(2)	173(2)
R^a	0.0304	0.0497
$R_w{}^b$	0.0511	0.1211

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ for observed reflections [$I > 2\sigma(I)$]. [b] $R_w = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$ for all data.

Reaction of the dichloro hafnium derivatives **4**−**6** with MeMgBr provided the dimethyl hafnium complexes **7**−**9** with high yield (Scheme 1). During the isolation process, **7**−**9** proved to be highly soluble in aliphatic solvents and exhibited high thermal stability, but were highly air and moisture sensitive. The entire purification process was consequently undertaken in a glovebox so as to avoid the formation of hydrolysis and oxidation products, otherwise easily formed. ^{1}H and ^{13}C NMR measurements of the dimethyl complexes **7**−**9** gave spectra similar to the dichloro analogues, pointing out that **7**−**9** are also C_{2v} symmetric in solution. Moreover, the methyl substituents were found to be chemically equivalent. Recrystallization of complex **7** from a saturated diethyl ether solution at −20 °C yielded yellow crystals suitable for X-ray diffraction analysis. The crystallographic and structural data are collected in Tables 1 and 2.

In the solid state, complex **7** adopts structural features similar to those reported for Zr and Ti bis(amido)-

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(20) For the synthesis of bis(amido) group IV metal complexes see: (a) Armistead, L. T.; White, P. S.; Gagne, M. R. *Organometallics* **1998**, *17*, 216. (b) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organomnetallics* **1997**, *16*, 4415. (c) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumpf, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649.

Table 2. Selected Structural Parameters for Complexes 7 and 10

	7	10
	Distances, Å	
P1−N1	1.698(3)	1.688(5)
P1−N3	1.787(3)	1.802(5)
P1−N4	1.748(4)	1.776(5)
P1−P2	2.709(3)	2.734(2)
Hf1−C21	2.207(5)	2.228(6)
Hf1−C22	2.254(5)	
Hf1−C61		2.473(5)
Hf1−N1	2.078(3)	2.096(5)
Hf1−N2	2.097(3)	2.081(4)
Hf1−N3	2.428(3)	2.315(4)
C61−B1		1.673(8)
C31−B1		1.659(8)
	Angles, deg	
N3−P1−N4	79.19(16)	78.8(2)
N1−P1− N3	93.05(15)	94.0(2)
N1−Hf1−N2	122.59(12)	128.79(17)
C21−Hf1−C22	104.2(2)	
C21−Hf1−C61		100.4(2)
C21−Hf1−N1	111.47(16)	112.0(2)
C61−Hf1−N1		99.62(17)
C21−Hf1−N3	106.52(16)	105.97(19)
C61−Hf1−N3		153.61(18)
Hf1−N3−P1	86.66(12)	86.14(18)
Hf1−C61−B1		172.6(4)
C31−B1−C61		112.8(5)
C31−B1−C51		102.3(4)

cyclodiphosph(III)azanes[10−14] and resembles the structure of the [(*t*-BuN)(*t*-BuNP)]$_2$HfCl$_2$ parent complex.[12] The central Hf atom has a distorted trigonal bipyramidal configuration defined by two amido−hafnium bonds, two hafnium−methyl bonds, and an additional coordination of metal with one of the imino nitrogen atoms from the cyclodiphosph(III)azane ring (Figure 1). The amido nitrogens as well as the methyl substituents are positioned close to the corners of an ideal tetrahedron, and the N−Hf−N angle is 122.59(12)° and Me−Hf−Me is 104.2(2)°. The length of the Hf−N3 bond and P−N$_{\mathrm{amido}}$ bonds are elongated compared to the parent dichloro complex (2.428(3) vs 2.394(9) Å and 1.698(3) vs 1.648(9) Å, respectively).[21] This illustrates the decreased Lewis acid character of the hafnium in compound **7**. It can be explained that in dichloro complexes the electron density is moved from the metal toward the very electronegative chlorine atoms, while in the alkyl derivatives this effect is much weaker because of the smaller electronegativity of the carbon.[22] In **7**, the Hf−CH$_3$ bonds have an average length of 2.231(5) Å, which is usual for Hf−alkyl bond lengths; in [NON]Hf(CH$_2$CMe$_3$)$_2$, bearing 2,4,6-trimethylphenyl groups, it is reported to be 2.225(7) Å.[23]

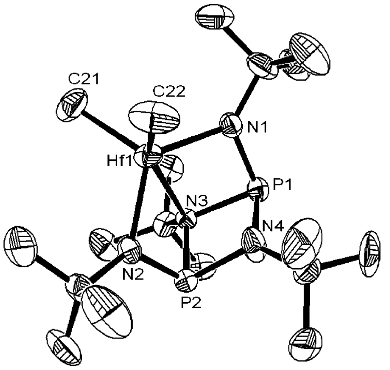

Figure 1. ORTEP plot of **7** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

Generation of Cationic Species. The bis(amido)-dimethyl hafnium complexes **7**−**9** were reacted with B(C$_6$F$_5$)$_3$ in order to better understand the formation of cationic bis(amido) hafnium complexes and to ascertain the structure of the activated species. As the high instability of the produced cationic complexes did not permit the separation and isolation of the products, spectroscopic characterization was made in situ. Mixing **7** and B(C$_6$F$_5$)$_3$ in CD$_2$Cl$_2$ in an NMR tube led to the instant reaction, and a clear transparent orange solution was obtained.[24] In ^{1}H NMR, the singlet arising from the Hf−C*H*$_3$ groups of **7** ($\delta_H = 0.62$ ppm) was then split into a sharp singlet corresponding to the cationic Hf−C*H*$_3$ ($\delta_H = 0.04$ ppm) and a broad singlet ascribed to B−C*H*$_3$ ($\delta_H = 0.43$ ppm).[25] The conversion of B(C$_6$F$_5$)$_3$ to a noncoordinating [MeB(C$_6$F$_5$)$_3$]$^-$ anion is supported by ^{19}F NMR ($\Delta\delta(m,p\text{-F}) = 2.56$).[26] However, the reaction proved to be rather unselective, as the ^{31}P NMR spectrum displayed three signals corresponding to as many different species (see Supporting Information). A first peak at $\delta_P = 109.8$ ppm represents the parent complex **7**, the second signal at $\delta_P = 91.1$ ppm is characteristic of the cationic complex, and a third signal was shifted upfield at $\delta_P = 34.8$ ppm (vide infra).

When the reaction was carried out in deuterated benzene, the immediate precipitation of a yellow solid was observed, and the remaining bright yellow solution slowly darkened with time. This implies a decreased solubility but a higher stability of the hafnium cation in hydrocarbon solvents compared to CD$_2$Cl$_2$. According to ^{31}P NMR the reaction proceeded with high selectivety, as only one phosphorus peak ($\delta_P = 91.54$ ppm) appeared in the spectrum. The ^{1}H NMR spectrum also exhibited two peaks instead of the initial Hf−C*H*$_3$ singlet: a broad singlet shifted to $\delta_H = 2.93$ ppm (B−C*H*$_3$) and a sharp one at $\delta_H = 0.87$ ppm (cationic Hf−C*H*$_3$) (Figure 2). The enormous downfield shift of the Me−B group signal indicates the strong coordination of the MeB(C$_6$F$_5$)$_3$ anion via the Hf−Me−B bridge. The ^{19}F NMR data also proved the presence of the coordinated [MeB(C$_6$F$_5$)$_3$]$^-$ anion ($\Delta\delta(m,p\text{-F}) = 4.13$) and corroborated the synthesis of {[(*t*-BuN)(*t*-BuNP)]$_2$HfMe(μ-Me)B(C$_6$F$_5$)$_3$} (**10**) (Scheme 2).

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[21] Similar trends were described for pentacoordinated [NON]ZrX$_2$ (X = Cl or Me) complexes, bearing *tert*-butyl groups. The Zr−O bond was elongated from 2.336(3) Å in [NON]ZrCl$_2$ to 2.418(3) Å in alkyl Zr complex. See ref 20c.

[22] Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper Collins College Publishers: New York, 1993.

[23] Liang, L.-C.; Schrock, R. R.; Davis, W. M. *Organometallics* **2000**, *19*, 2526.

[24] The color of this solution changed to brown during approximately 30 min, which indicated high instability of such complexes in halogenated solvents.

[25] Two different methyl groups were also detected in the ^{13}C NMR spectrum (multiplet at $\delta_C = 21.3$ ppm and singlet at $\delta_C = 58.15$ ppm vs signal at $\delta_C = 59.34$ ppm for parent complex). A triplet at $\delta_C = 29.98$ ppm ($J_{PC} = 6.1$ Hz) and a doublet at $\delta_C = 33.60$ ppm ($J_{PC} = 6.5$ Hz) can be assigned for the *t*-BuN$_{\mathrm{imino}}$ groups. However, due to fact that the reaction was unselective and a decomposition of **7**/B(C$_6$F$_5$)$_3$ occurred during the measurement, several indefinite signals appeared.

[26] The value of $\Delta\delta(m,p\text{-F})$ (^{19}F NMR) is a good probe of coordination of [MeB(C$_6$F$_5$)$_3$]$^-$ to cationic d^0 metals (values of 3−6 ppm indicate coordination; <3 ppm indicates noncoordination). See: Horton, A. D.; de With, J. *Chem. Commun.* **1996**, 1375.

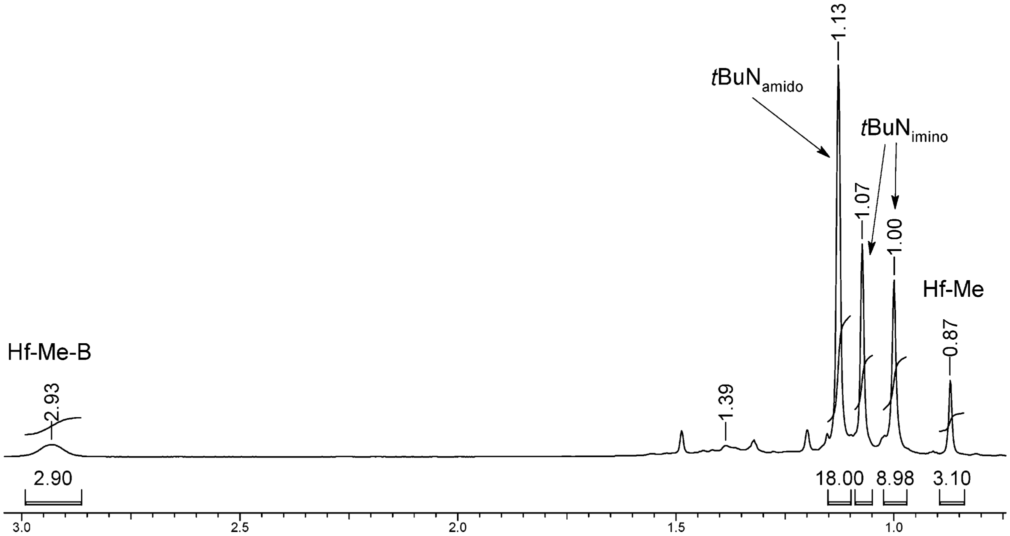
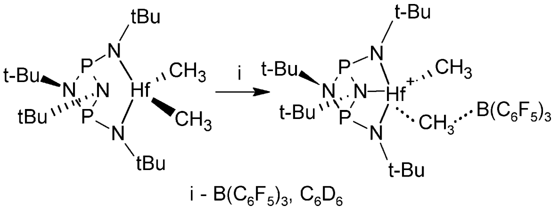


Figure 2. ^{1}H NMR (200 MHz, C_6D_6, 29 °C) spectrum of the hafnium cationic species formed in deuterobenzene by the reaction of $[(t\text{-BuN})(t\text{-BuNP})]_2HfMe_2$ with $B(C_6F_5)_3$.

Scheme 2



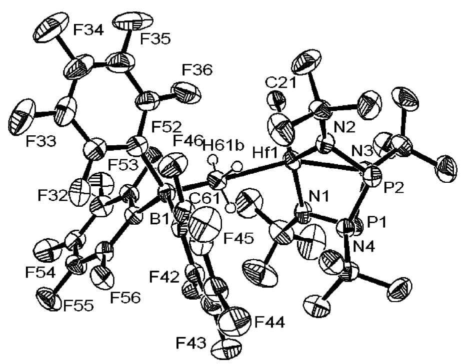


Figure 3. ORTEP plot of **10** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms, except hydrogens at the CH_3−B group, were omitted for clarity.

As activated nonmetallocene complexes are generally characterized by their poor stability (which usually is synonymous with high reactivity), their solid state structures have scarcely been reported in the literature.[4,9] However, crystals of **10** suitable for X-ray analysis were successfully grown from a toluene−hexane layer at −20 °C. The ORTEP diagram is presented in Figure 3, and crystallographic data as well as selected structural parameters are collected in Tables 1 and 2, respectively.

In **10** hafnium is pentacoordinated, which is a common feature for bis(amido)cyclodiphosph(III)azane complexes in the solid state, and the distorted trigonal-bipyramidal configuration is achieved as a result of an additional Hf1−N3 bonding from the diphosph(III)azane ring. The coordination of $B(C_6F_5)_3$ to one of the hafnium methyl groups significantly elongated the Hf−Me distance (2.473(5) Å), while the bond length between the hafnium and the other methyl group remained without apparent changes (2.228(6) vs 2.254(5) Å in the parent complex **7**). The methyl−boron bond is short (1.673(8) Å)[27] and the configuration of the boron atom is close to tetrahedral, with CBC angles varying from 102.4(4)° to 116.1(5)°. This emphasizes the increased contribution of sp^3 hybridization, which is common for anionic tetracoordinated boron. The charge-separated character of this complex is unambiguously established by the much longer $Zr-CH_3$ (bridging) distance than the $Zr-CH_3$ (terminal) distance and the relatively normal $B-CH_3$ distances. The $B\cdots CH_3\cdots Hf$ bonding (B−C−Hf angle is 172.6(4)°) can here be considered as ionic and **10** in the solid state as a tight ion pair ($[LHfMe]^+$-$[MeB(C_6F_5)_3]^-$), where the hafnium cation is weakly associated with a boronate anion through a highly unsymmetrical $Hf-CH_3-B$ bridge.[28]

As a result of the abstraction of one of its methyl groups, hafnium acquires a high Lewis acid character, which is materialized in the shortening of the Hf−N$_{imino}$ bond (2.315(4) vs 2.428(3) Å in $[(t\text{-BuN})(t\text{-BuNP})]_2HfMe_2$ vs 2.394(9) Å in $[(t\text{-BuN})(t\text{-BuNP})]_2HfCl_2$) and in an increased degree of puckering of the phosph(III)azane cycle. This distortion of the diphosph(III)azane cycle prompts the electron-rich imino nitrogen atoms to get closer to the cationic hafnium center, as it can be seen from the distance between the metal center and the noncoordinated imino nitrogen (N4), which is much shorter than in **7** (2.765(5) Å in **10** vs 3.000(5) Å in **7**) and resembles the Hf−N4 distance in $[(t\text{-BuN})(t\text{-BuNP})]_2HfCl_2$ (2.793 Å).[12]

^{1}H NMR spectra in C_6D_6 show that **10** adopts C_s symmetry in solution: the coordination of $B(C_6F_5)_3$ reduces the complex symmetry as the methyl groups are rendered nonequivalent. In addition, two different signals in the ^{1}H NMR corresponding to the *t*-BuN$_{imino}$ groups denote their chemical nonequivalence (Figure 2), which is noteworthy, as the parent complex **7** is strictly C_{2v}-symmetric in solution. We assume that this phenomenon arises from the increased Lewis acidity of the

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[27] This value indicates that $[MeB(C_6F_5)_3]^-$ is weakly coordinated to the hafnium cation. See ref 5a.

[28] Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

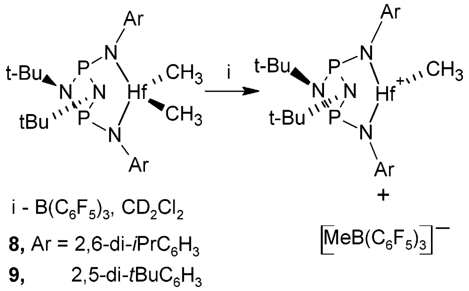
metal center, which favors in solution the formation of an additional coordination from the diphosph(III)azane cycle in a manner similar to that displayed in the solid state structure of **10**.

Stability of in situ formed cationic hafnium species was reported to be improved in deuterated benzene by coordination with the electron-donating solvent molecules.[29] In a similar manner, **10** bearing relatively small *tert*-butyl groups can be stabilized in noncoordinating deuterated dichloromethane by intermolecular donor−acceptor interactions of the highly electrophilic cationic hafnium with phosphorus(III) free electron pairs of a second hafnium cationic complex. This is illustrated by the ^{31}P NMR spectrum of the $B(C_6F_5)_3$-activated $[(t\text{-BuN})(t\text{-BuNP})]_2HfMe_2$ in CD_2Cl_2, with the appearance of the largely upfield peak at 34.8 ppm.[30]

Likewise, dimethyl complexes **8** and **9** were treated with $B(C_6F_5)_3$ in deuterobenzene, and in both cases, a phase separation occurred from the very unstable (quickly darkening) solution, verifying that a reaction did occur. According to ^{1}H, ^{31}P, and ^{19}F NMR, the deuterobenzene phases contained mainly the unreacted parent complexes and $B(C_6F_5)_3$, and only minor amounts of the noncoordinated $[MeB(C_6F_5)_3]^-$ anion (10%, $\Delta\delta(m,p\text{-F}) = 2.39$ for **8** and 5%, $\Delta\delta(m,p\text{-F}) = 2.5$ for **9**) were detected in ^{19}F NMR, clearly indicating that the activation was not quantitative.

To ascertain their exact nature, the resulting red oily precipitates were separated from the solvent phase and dissolved in CD_2Cl_2.[31] In fact, from ^{1}H NMR, **8**/$B(C_6F_5)_3$ and **9**/$B(C_6F_5)_3$ possess two different Hf−Me groups: a sharp singlet at $\delta_H = 0.26$ ppm corresponds to the methyl not coordinated to boron, while a broader one at $\delta_H = 0.43$ ppm can be assigned to the Hf−Me−B group. Concerning the ligand framework, ^{1}H and ^{13}C NMR spectra displayed a molecular symmetry similar to the parent Hf dimethyl complexes. The ^{31}P NMR spectrum displayed only a slight upfield shifting after the addition of the boron activator: $\delta_P = 114.74$ vs 115.56 ppm for **8** and $\delta_P = 98.25$ vs 98.67 ppm for **9**. In ^{19}F NMR, peaks corresponding to the noncoordinated $[MeB(C_6F_5)_3]^-$ ($\Delta\delta(m,p\text{-F}) = 2.56$ for **8**; $\Delta\delta(m,p\text{-F}) = 2.58$ for **9**) were recorded (see Supporting Information). These data clearly underline that the additional cyclodiphosph(III)azane imino nitrogen coordination to hafnium observed for **10** is not occurring in the case of $B(C_6F_5)_3$ activation of **8** and **9** (Scheme 3) and that the Lewis acidity of the hafnium center is lower than in **10**, presumably due to additional donation of electron density from the aryl substituents through the amido nitrogen atoms.

Scheme 3



i - $B(C_6F_5)_3$, CD_2Cl_2

8, Ar = 2,6-di-*i*PrC_6H_3

9, 2,5-di-*t*BuC_6H_3

On the basis of the experimental data, it seems that in deuterated benzene the cationic species resulting from the addition of the boron activator to the hafnium complex precipitate as a denser oily phase, while only the unreacted parent complex and $B(C_6F_5)_3$ with a small amount of product can be detected in the solvent phase. It can be inferred from ^{1}H NMR measurement that the red oily phase contains the desired activated complex with a large amount of coordinated deuterated benzene.[29] In CD_2Cl_2, the formed cationic compounds remain soluble in the solvent and can thus be investigated by means of NMR methods. In this same solvent, the rate of activation, as well as decomposition, was accelerated, and the presence of the parent hafnium complex could not be detected.

Polymerization Activity. Complex $[(t\text{-BuN})(t\text{-BuNP})]_2HfCl_2$ and its methyl derivative showed a moderate ethene polymerization activity after activation by MAO or $B(C_6F_5)_3$, respectively, while no activity was observed in the case of complexes **5** and **6** bearing bulky aromatic substituents and their methyl analogues **8** and **9** under the same conditions.[32] This difference in polymerization behavior can be explained by the poor ability of Hf complexes bearing bulky aryl groups to be activated in aromatic hydrocarbon solvents (vide supra). Furthermore, the different geometry and coordination number adopted in solution by the complexes bearing *tert*-butyl and bulky aryl substituents after boron activation can also have a detrimental effect on the rates of monomer coordination, insertion, and β-H elimination.

Conclusions

Two new bis(amido)cyclodiphosph(III)azane dichloro hafnium complexes bearing bulky aryl groups were synthesized and were converted to their dimethyl derivatives, as well as $[(t\text{-BuN})(t\text{-BuNP})]_2HfCl_2$, with MeMgBr. Both dichloro and dimethyl complexes were found to be C_{2v} symmetric in solution, on account of the absence of chemically nonequivalent groups. After $B(C_6F_5)_3$ activation, the hafnium derivatives showed different properties (geometry, coordination number, activation and decomposition rates) depending on the

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[29] For arene coordination to the positively charged IVb group metal atom see: (a) Ref 4. (b) Gillis, D. J.; Tudoret, M.-J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543. (c) Gillis, D. J.; Quyoum, R.; Tudoret, M.-J.; Wang, Q.; Jeremic, D.; Roszak, A. W.; Baird, M. C. *Organometallics* **1996**, *15*, 3600. (d) Lancaster, S. J.; Robinson, O. B.; Bochmann, M. *Organometallics* **1995**, *14*, 2456.

[30] The coordination of the complex species, where the transition metal reveals electron pair acceptor properties, with cyclodiphosph(III)azane ligands via P(III) atoms leads in ^{31}P NMR to the upfield shift of the signals corresponding to those coordinated phoshorus atoms. See: (a) Hitchcock, P. B.; Lappert, M. F.; Layh, M. *Eur. J. Inorg. Chem.* **1998**, 751. (b) Scherer, O. J.; Quintus, P.; Kaub, J.; Sheldrick, W. S. *Chem. Ber.* **1987**, *120*, 1463. (c) Jenkins, L. S.; Willey, G. R. *Dalton Trans.* **1979**, 777. (d) Reddy, V. S.; Krishnamurthy, S. S.; Nethaji, M. *Dalton Trans.* **1995**, 1933. (e) Scherer, O. J.; Krieger, K. D. *Z. Naturforsch., Ser. B* **1982**, *37B*, 1041.

[31] In the first part of the experiments the reagents were mixed in CD_2Cl_2, as was described for $[(t\text{-BuN})(t\text{-BuNP})]_2HfMe_2$ and $B(C_6F_5)_3$. In the second part the red liquid product obtained in deuterobenzene was separated from the solvent phase and dissolved in dichlorodeuteromethane. In both cases identical NMR spectra were observed. There was little difference in peak shifts due to solvent change (from C_6D_6 to CD_2Cl_2).

[32] Polymerization conditions: steel autoclave, volume of the polymerization toluene 200 mL, MAO/Hf ratio 1000 or Hf/$B(C_6F_5)_3$ ratio 1 (with addition of TIBA as a scavenger TIBA/Hf 500), polymerization temperature 50 °C for MAO activation and 30 °C for borane activation, ethene pressure 3.8 bar.

reaction solvent and the nature of their amido substituents. It appeared that in deuterated benzene the activated complexes were more stable than in deuterated dichloromethane, but the activation was faster in the latter solvent. $B(C_6F_5)_3$-activated [(*t*-BuN)-(*t*-BuNP)]$_2$HfMe$_2$ readily produced pentacoordinated highly Lewis acidic hafnium species in both solvents, and in deuterobenzene a strong hafnium cation−boronate anion coordination occurred. Conversely, the activation of the aryl-substituted hafnium complexes was not quantitative, and the additional hafnium−ligand coordination was not observed in solution. Presumably, the electron-rich aryl substituents donate electron density to the hafnium center via the amide nitrogens and therefore reduce its Lewis acidity. These results are in good agreement with the ethene polymerization results previously reported for zirconium dichloride analogues: the *tert*-butyl-substituted complex gave higher polymerization activity than the aryl-substituted ones after their activation with MAO.

Acknowledgment. Support of this work by Academy of Finland (project 204408) and Finnish National Technology Agency (TEKES) (project 209739) is gratefully acknowledged. Great thanks to Pascal Castro for helpful discussion and manuscript correction.

Supporting Information Available: Listings of spectral data of compounds **5**, **6**, and **7**; activation of complexes with spectral characteristics observed. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0492303