Boroxide Complexes of the Group 4 Metals: A “Noninnocent” Ligand in Olefin Polymerization[†]

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The synthesis of a series of group 4 metal complexes supported by the boroxide anion, $[OB(mes)_2]^-$, is described and their application in α-olefin polymerization discussed. The compounds $M\{OB(mes)_2\}_2Cl_2(THF)_2$ [**1**, M = Ti; **2**, M = Zr; **3**, M = Hf] have been synthesized from $MCl_4(THF)_n$ [M = Ti, $n = 0$; M = Zr/Hf, $n = 2$] and 2 equiv of lithiated dimesitylborinic acid. Accidental hydrolysis during the preparation of the zirconium analogue afforded the dimeric hydroxyl species $[Zr\{OB(mes)_2\}_3(\mu\text{-}OH)]_2$ (**4**), which was characterized crystallographically. The four-coordinate titanium bis(amide) complex, $Ti\{OB(mes)_2\}_2(NEt_2)_2$ (**5**), was prepared by protonolysis of the titanium-tetra(amide) using the parent borinic acid. X-ray structural analyses of **1** and **3** showed distorted, octahedral geometry at the metal with *cis*-boroxide and *trans*-chloride ligands. A series of mixed-ligand cyclopentadienyl/boroxide chlorides of the group 4 metals are also described. $TiCp'\{OB(mes)_2\}Cl_2$ ($Cp' = \eta\text{-}C_5Me_4H$, **6**) and $MCp_2\{OB(mes)_2\}Cl$ [**7**, M = Ti; **8**, M = Zr] are formed upon replacement of a chloride with a boroxide ligand using the appropriate $TiCp'Cl_3$ and MCp_2Cl_2 starting materials. X-ray diffraction studies showed compounds **6** and **7** exist as monomers in the solid state, with distorted tetrahedral geometry around the metal. Selected complexes were tested for ethylene polymerization activity, using MAO as activator. Polymerization behavior was observed similar to that of $ZrCp_2Cl_2$ tested under the same conditions, which, supplemented by complementary reactivity studies and polymer analysis, suggests possible transfer of the boroxide ligand to aluminum during polymerization. To circumvent the problems associated with activation using MAO, a family of group 4 alkyl compounds have been synthesized. The titanium and hafnium compounds $M\{OB(mes)_2\}_n(CH_2Ph)_{4-n}$ [**9**, M = Ti, $n = 2$; **10**, M = Ti, $n = 3$; **11**, M = Hf, $n = 3$; **12**, M = Hf, $n = 4$] were synthesized by protonolysis of the tetra(benzyl) compounds. NMR studies of the reaction between **9** and $B(C_6F_5)_3$ demonstrated that a well-defined cationic titanium compound was generated in solution; however, strong interaction with the anion prevented the system from being active for polymerization.

1. Introduction

Alkoxide $[OR']^-$ and aryloxide $[OAr]^-$ anions remain prominent ligands in organometallic chemistry, and the range of catalytic applications demonstrated by their metal complexes has grown steadily in the last fifty years.[1] The properties of these ligands are routinely altered through derivatization of the *O*-substituent, allowing the facile generation of diverse steric and electronic environments at metal centers. For example, sterically demanding groups have been extensively used to restrict the aggregation of metal alkoxides to molecular species, in contrast to the formation of cluster systems, by disfavoring bridging through the oxygen atom. Substituted phenyl frameworks, affording aryloxide compounds, are often used in this context,[2] where the availability of a large number of substituted phenols as precursors ensures access to a wide number of variants.

In addition to varying the steric requirements of alkoxide-type ligands, it is possible to exercise control over the electronic properties, which may have a profound effect on the reactivity of the complex. For example, it was demonstrated at an early stage in the development of the Schrock catalysts, Mo(NAr)(CHR)-$(OR')_2$, that employing electron-poor fluoroalkoxide ligands markedly increased the reactivity toward certain substrates.[3] An alternative approach to exercising control of the donor properties of alkoxide-type ligands that circumvents the use of (often expensive) fluorinated alcohols is to incorporate an element that has π-acceptor properties adjacent to the oxygen atom. Siloxide $[OSiR'_3]^-$ and boroxide $[OBR'_2]^-$ ligands fit this criterium, where in the latter class, the empty p-orbital on the boron is able to accept electron density from the oxygen lone-pairs generating an “electron-poor” alkoxide. Work with this system was pioneered by Power and co-workers,

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[†] Part of this work, including the crystal structures of compounds **10** (CCDC reference number 250060) and **12** (CCDC reference number 250061), has been previously communicated. See ref 11.

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where it was demonstrated that the boroxides $[OBR'_2]^-$ (R' = mes = 2,4,6-$Me_3C_6H_2$; 2,4,6-$^iPr_3C_6H_2$) are able to coordinate to group 8 and 9 metals in either a bridging or terminal coordination mode.[4,5] Of late, this ligand has been used in main group systems,[6] and the structural report of a dimeric zinc compound has recently been presented in the literature.[7]

Work in our group has attempted to show that the effect of the boron atom is significant both in the solid state and solution, using a series of d^0-early transition metal imido compounds.[8] Crystallographic analysis showed a trend for the lengthening of the metal−oxygen bond in boroxide compounds compared to the sterically similar $[OCH(mes)_2]^-$ alkoxide. In addition, solution-state (^{13}C NMR) measurements of the $\Delta\delta$ value[9] for $Mo(N^tBu)_2\{OB(mes)_2\}_2$ and $Ti(N^tBu)\{OB(mes)_2\}_2(Py)_2$ indicated reduced electron density at the imido nitrogen atom, consistent with the presence of a higher metal−nitrogen bond order predicted for a more electron-deficient metal center. These data support the idea that boroxide ligands behave as electron-deficient alkoxides. More recently we have reported a series of lithium, zinc, and magnesium complexes incorporating the dimesitylboroxide ligand $[OB(mes)_2]^-$, in which exclusive formation of the μ_2-$OB(mes)_2$ coordination mode was observed.[10]

We have been interested in the use of boroxide ligands to support group 4 metals as olefin polymerization precatalysts and have reported a series of group 4 boroxide complexes with benzyl ligands, $M\{OB(mes)_2\}_n(CH_2Ph)_{4-n}$.[11] Investigation of the activation of these compounds indicated that the boroxide ligands successfully supported a cationic metal, although complications with cation···anion interactions were observed. This study has been extended, and we now report our results with the corresponding group 4 metal chlorides and an investigation of their ability to polymerize olefins upon activation using MAO.

2. Experimental Section

2.1. General Considerations. All manipulations were carried out under dry nitrogen using standard Schlenk and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agent and degassed prior to use. The compounds $(mes)_2BOH$[12] and $Cp'TiCl_3$ [$Cp' = C_5HMe_4$][13] were synthesized according to literature procedures. ^nBuLi (2.5 M solution in hexanes, Acros) and $Ti(NEt_2)_4$ (subsequently diluted to form 0.2 M solution in toluene) were purchased from commercial sources and used without further purification. Elemental analyses were performed by S. Boyer at the London Metropolitan University. GPC measurements were performed by Dr. S. Holding at RAPRA Technology Ltd. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300 (^1H) and 75 ($^{13}C\{^1H\}$) MHz, from samples at 298 K in [$^2H_6$]-benzene, unless otherwise stated. Coupling constants, J, are quoted in Hz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances and reported as parts per million relative to tetramethylsilane. Assignment of carbon resonances is based on DEPT ^{13}C NMR experiments.

2.2. Experimental Details. $Ti\{OB(mes)_2\}_2Cl_2(THF)_2$ (1). ^nBuLi (0.63 mL, 1.58 mmol, 1.05 equiv) was added dropwise via a syringe to a stirred solution of $(mes)_2BOH$ (0.40 g, 1.50 mmol) in 25 mL of toluene at 0 °C. The mixture was allowed to warm to room temperature and stirred for 1 h, during which time formation of a yellow solution and white precipitate was observed. This slurry was added dropwise to a solution of $TiCl_4$ (0.75 mL, 0.75 mmol, 0.5 equiv), which had been further diluted with 15 mL of toluene, resulting in immediate formation of a red solution. After 4 days the volatiles were removed under reduced pressure, and the resultant brown sticky solid was dissolved in ~10 mL of THF. After 10 min stirring the THF was removed in vacuo. The yellow solid was crystallized from pentane at 4 °C, affording **1** as pale yellow crystals. Yield: 0.25 g (42%). Anal. Calc for $C_{44}H_{60}B_2Cl_2O_4Ti$ (*793.34*): C, 66.61; H, 7.62. Found: C, 66.71; H, 7.57. ^1H NMR: δ 6.66 (s, 8H, C_6H_2), 3.70 (br s, 8H, THF), 2.37 (s, 24H, 2,6-Me_2), 2.16 (s, 12H, 4-Me), 1.31 (br s, 8H, THF). ^{13}C NMR: δ 141.6 (C), 141.4 (CH), 139.1 (br, C), 128.8 (C), 70.7 (CH_2, THF), 25.5 (CH_2, THF), 23.0 (CH_3), 21.3 (CH_3).

$Zr\{OB(mes)_2\}_2Cl_2(THF)_2$ (2). ^nBuLi (3.16 mL, 7.90 mmol, 1.05 equiv) was added dropwise via a syringe to a stirred solution of $(mes)_2BOH$ (2.00 g, 7.51 mmol) in 30 mL of toluene at 0 °C. The mixture was allowed to warm to room temperature and stirred for 1 h, during which time formation of a yellow solution and white precipitate was observed. The mixture was added dropwise to $ZrCl_4(THF)_2$ (0.36 g, 0.94 mmol, 0.50 equiv) at −78 °C in THF. This afforded a colorless solution, which was stirred at room temperature for 14 h. The volatiles were removed under reduced pressure, and the resultant colorless, greasy solid was extracted with hot toluene. Cooling to −35 °C yielded **2** as a white powder. Yield: 2.95 g (94%). Anal. Calc for $C_{44}H_{60}B_2Cl_2O_4Zr$ (*836.70*): C, 63.16; H, 7.23. Found: C, 63.17; H, 7.05. ^1H NMR: δ 6.75 (s, 8H, C_6H_2), 3.83 (br s, 8H, THF), 2.52 (s, 24H, 2,6-Me_2), 2.18 (s, 12H, 4-Me), 1.15 (br s, 8H, THF). ^{13}C NMR: δ 141.1 (C), 140.2 (br, C), 137.6 (C), 128.5 (CH), 73.9 (CH_2, THF), 25.2 (CH_2, THF), 23.1 (CH_3), 21.3 (CH_3).

$Hf\{OB(mes)_2\}_2Cl_2(THF)_2$ (3). Compound **3** was prepared using the general procedure outlined for **2**, using $(mes)_2BOH$ (0.40 g, 1.50 mmol) and $HfCl_4(THF)_2$ (0.35 g, 0.75 mmol). The resultant white solid was extracted with Et_2O. Concentration and storage at room temperature yielded **3** as colorless crystals. Yield: 0.21 g (30%). Anal. Calc for $C_{44}H_{60}B_2Cl_2HfO_4$ (*923.96*): C, 57.20; H, 6.55. Found: C, 56.92; H, 6.73. ^1H NMR: δ 6.75 (s, 8H, C_6H_2), 3.80 (br s, 8H, THF), 2.54 (s, 24H, 2,6-Me_2), 2.26 (s, 12H, 4-Me), 1.11 (br s, 8H, THF). ^{13}C NMR: δ 141.2 (C), 140.9 (br, C), 137.6 (C), 128.9 (CH), 65.0 (CH_2, THF), 25.4 (CH_2, THF), 23.0 (CH_3), 21.3 (CH_3).

$Ti\{OB(mes)_2\}_2(NEt_2)_2$ (5). $(mes)_2BOH$ (0.50 g, 1.88 mmol) in toluene was added dropwise to a stirred solution of $Ti(NEt_2)_4$ (4.70 mL of a 0.20 M solution in toluene, 0.94 mmol) further diluted with an additional 20 mL of toluene. This afforded a yellow solution, which was stirred for 16 h. The volatiles were removed under reduced pressure, and the resultant yellow solid was crystallized from pentane at room temperature, yielding **5** as a yellow powder. Yield: 0.51 g (76%). ^1H NMR: δ 6.77 (s, 8H, C_6H_2), 3.43 (q, J = 7.0, 12H, C_2H_5), 2.47 (s, 24H 2,6-Me_2) 2.17 (s, 12H, 4-Me), 0.78 (t, J = 7.0, 8H C_2H_5). ^{13}C NMR: δ 140.8 (CH), 139.7 (br, C), 137.7 (C), 128.6 (C), 46.1 (CH_2), 23.0 (CH_3), 21.3 (CH_3), 14.4 (CH_3).

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TiCp′{OB(mes)$_2$}Cl$_2$ (6). ^{n}BuLi (0.31 mL, 0.77 mmol, 1.05 equiv) was added via syringe to a solution of (mes)$_2$BOH (0.19 g, 0.73 mmol) in toluene (20 mL) at 0 °C. The resultant mixture was allowed to warm to ambient temperature and stirred for 1 h, during which time the solution turned yellow and a fine white precipitate formed. The slurry was added to a solution of TiCp′Cl$_3$ [Cp′ = C$_5$HMe$_4$] (0.19 g, 0.73 mmol) in toluene (20 mL) that had been cooled to −78 °C, affording a red solution, which was stirred at room temperature for 14 h. The volatiles were removed under reduced pressure, and the resultant sticky red solid was extracted from LiCl with pentane. Concentration and storage at −35 °C yielded **6** as red crystals, contaminated with orange crystals of the unreacted starting material TiCp′Cl$_3$. The red crystals were mechanically separated. Yield: 0.11 g (29%). ^{1}H NMR: δ 6.63 (s, 4H, C_6H_2), 5.15 (s, 1H, C_5Me_4H), 2.11 (s, 6H, 4-*Me*), 2.01 (s, 12H 2,6-*Me*$_2$), 1.90 (br s, 6H C_5Me_4H), 1.77 (br s, 6H C_5Me_4H). ^{13}C NMR data were not recorded due to insufficient solubility.

TiCp$_2${OB(mes)$_2$}Cl (7). Compound **7** was prepared using the general procedure outlined for **6**, using (mes)$_2$BOH (0.40 g, 1.50 mmol) and TiCp$_2$Cl$_2$ (0.37 g, 1.50 mmol). The resultant sticky red solid was extracted with pentane. Concentration and storage at −35 °C yielded **7** as red crystals. Yield: 0.41 g (57%). Anal. Calc for $C_{28}H_{32}BClOTi$ (*478.68*): C, 70.25; H, 6.74. Found: C, 69.95; H, 6.53. ^{1}H NMR: δ 6.79 (s, 4H, C_6H_2), 5.83 (s, 10H, C_5H_5), 2.45 (s, 12H, 2,6-*Me*$_2$), 2.17 (s, 6H 4-*Me*). ^{13}C NMR: δ 141.2 (br, *C*), 140.3 (*C*), 137.6 (*C*), 128.6 (*C*H), 117.6 (C_5H$_5$), 23.6 (*C*H$_3$), 21.2 (*C*H$_3$). MS (EI$^+$, *m/z*): 443 [M]$^+$ − Cl.

ZrCp$_2${OB(mes)$_2$}Cl (8). Compound **8** was prepared using the general procedure outlined for **6**, using (mes)$_2$BOH (0.40 g, 1.50 mmol) and ZrCp$_2$Cl$_2$ (0.44 g, 1.50 mmol). The resultant pale yellow solid was extracted with pentane. Concentration and storage at −35 °C yielded **8** as a white powder. Yield: 0.34 g (44%). Anal. Calc for $C_{28}H_{32}BClOZr$ (*522.04*): C, 62.96; H, 8.30. Found: C, 62.59; H, 8.12. ^{1}H NMR: δ 6.79 (s, 4H, C_6H_2), 5.86 (s, 10H, C_5H_5), 2.44 (s, 12H, 2,6-*Me*$_2$), 2.16 (s, 6H 4-*Me*). ^{13}C NMR: δ 140.9 (*C*), 140.3 (br, *C*), 137.8 (*C*), 128.7 (*C*H), 114.5 (*C*H), 23.4 (*C*H$_3$), 21.2 (*C*H$_3$).

Ti{OB(mes)$_2$}$_2$(CH$_2$Ph)$_2$ (9). (mes)$_2$BOH (0.349 g, 1.31 mmol) dissolved in 20 mL of toluene was added dropwise to a stirred solution of Ti(CH$_2$Ph)$_4$ (0.271 g, 0.66 mmol) in 25 mL of toluene at room temperature to afford a red solution. After 3 h the volatiles were removed under reduced pressure, and the resultant red oil was crystallized from pentane at −35 °C, yielding **9** as red crystals. Yield: 0.274 g (55%). ^{1}H NMR: δ 6.95 (t, 4H, C_6H_5), 6.82 (t, 4H, C_6H_5), 6.80 (s, 8H, C_6H_2), 6.72 (s, 2H, C_6H_5), 2.86 (s, 4H C*H*$_2$), 2.27 (s, 24H, 2,6-*Me*$_2$), 2.15 (s, 12H, 4-*Me*). ^{13}C NMR: δ 142.6 (*C*), 141.0 (*C*H), 138.6 (*C*H), 128.9 (*C*H), 128.8 (C), 128.7 (*C*), 124.3 (*C*H), 93.0 (*C*H$_2$), 22.9 (*C*H$_3$), 21.3 (*C*H$_3$).

Ti{OB(mes)$_2$}$_3$(CH$_2$Ph) (10). (mes)$_2$BOH (0.50 g, 1.88 mmol) dissolved in 20 mL of toluene was added dropwise to a stirred solution of Ti(CH$_2$Ph)$_4$ (0.260 g, 0.63 mmol) in 25 mL of toluene at room temperature to afford a pale red solution, which was stirred for 15 h. The volatiles were removed under reduced pressure, and the resultant orange oil was crystallized from pentane at −35 °C, yielding orange crystals. Yield: 0.414 g (59%). Anal. Calc for $C_{61}H_{73}B_3O_3Ti$ (*934.53*): C, 78.40; H, 7.87. Found: C, 78.90; H, 8.05. ^{1}H NMR: δ 6.87 (d, 2H, C_6H_5), 6.78 (t, 1H, C_6H_5), 6.65 (s, 12H, C_6H_2), 6.52 (d, 2H, C_6H_5), 3.18 (s, 2H C*H*$_2$), 2.25 (s, 36H, 2,6-*Me*$_2$), 2.12 (s, 24H, 4-*Me*). ^{13}C NMR: δ 142.7 (*C*), 141.0 (*C*H), 138.7 (*C*H), 129.0 (*C*H), 128.9 (*C*), 128.8 (C), 124.4 (*C*H), 93.2 (*C*H$_2$), 23.0 (*C*H$_3$), 21.4 (*C*H$_3$).

Hf{OB(mes)$_2$}$_3$(CH$_2$Ph) (11). (mes)$_2$BOH (0.30 g, 1.13 mmol) dissolved in 20 mL of toluene was added dropwise to a stirred solution of Hf(CH$_2$Ph)$_4$ (0.31 g, 0.57 mmol) in 25 mL of toluene at room temperature to afford a pale yellow solution. After 3 h the volatiles were removed under reduced pressure, and the resultant yellow solid was crystallized from pentane at 4 °C, affording colorless crystals. ^{1}H NMR showed a mixture of **11** and the tetrasubstituted complex Hf{OB(mes)$_2$}$_4$, which could not be separated using conventional methods. Single crystals suitable for analysis by X-ray diffraction were separated manually under a microscope and mounted under an inert oil.

Hf{OB(mes)$_2$}$_4$ (12). (mes)$_2$BOH (0.29 g, 1.10 mmol) dissolved in 20 mL of toluene was added dropwise to a stirred solution of Hf(CH$_2$Ph)$_4$ (0.20 g, 0.37 mmol) in 25 mL of toluene at room temperature, to afford a pale yellow solution. After 15 h the volatiles were removed under reduced pressure, and the resultant yellow solid was crystallized from pentane at −35 °C, affording white crystals. Yield: 0.106 g (23%). Despite repeated crystallizations, analytically pure **12** was unobtainable due, we believe, to trace quantities of **11** as an inseparable impurity. ^{1}H NMR: δ 6.62 (s, 16H, C_6H_2), 2.21 (s, 48H, 2,6-*Me*$_2$), 2.13 (s, 24H, 4-*Me*). ^{13}C NMR: δ 140.6 (*C*), 139.4 (br *C*), 138.2 (C), 127.3 (*C*H), 22.6 (*C*H$_3$), 21.3 (*C*H$_3$).

Ti{OB(mes)$_2$}$_2$(CH$_2$Ph)[η^6C$_6$H$_5$CH$_2$B(C$_6$F$_5$)$_3$] (13). To an NMR tube charged with Ti{OB(mes)$_2$}$_2$(CH$_2$Ph)$_2$ (0.006 g, 0.011 mmol) and B(C$_6$F$_5$)$_3$ (0.008 g, 0.011 mmol) was added approximately 0.6 mL of [^{2}H$_6$]-benzene, which was immediately examined by ^{1}H NMR spectroscopy. ^{1}H NMR: δ 7.02 (t, 2H, C_6H_5), 6.98 (d, 2H, C_6H_5), 6.73 (d, 1H, C_6H_5), 6.65 (s, 8H, C_6H_2), 6.46 (d, 2H, C_6H_5), 6.19 (t, 1H, C_6H_5), 5.71 (t, 2H, C_6H_5), 3.55 (br s, 2H C*H*$_2$), 3.39 (s, 2H C*H*$_2$), 2.15 (s, 24H 2,6-*Me*$_2$), 2.08 (s, 12H, 4-*Me*). ^{13}C NMR: δ 149.6 (*C*), 145.7 (*C*), 140.1 (*C*), 140.6 (d, BC_6F_5), 138.5 (d, BC_6F_5), 136.5 (d, BC_6F_5), 136.2 (*o*-*C*H of BCH$_2$*Ph*), 129.2 (*C*H, of C$_6$H$_2$Me$_3$), 129.1 (*p*-*C*H, of BCH$_2$*Ph*), 128.9 (*m*-*C*H, of TiCH$_2$*Ph*), 128.3 (*o*-*C*H, of TiCH$_2$*Ph*), 127.9 (*p*-*C*H, of TiCH$_2$*Ph*), 124.0 (*m*−*C*H, of BCH$_2$*Ph*), 98.3 (*C*H$_2$, of Ti*C*H$_2$Ph), 22.8 (*C*H$_3$, of C$_6$H$_2$Me$_3$), 21.2 (*C*H$_3$, of C$_6$H$_2$-Me$_3$).

2.3. Typical Ethene Polymerization Procedure. A 13.3 mL portion of a 1.5 M solution of MAO in toluene (20 mmol, 1000 equiv) was added to a 1 L medium-pressure glass reactor fitted with an overhead mechanical stirrer. A 0.02 mmol portion of accurately weighed catalyst precursor was dissolved in 200 mL of toluene and added to the reactor vessel. The apparatus was pressurized with 9 bar of ethylene and the reaction stirred for 1 h. Upon completion of the experiment, the apparatus was depressurized and the system *carefully* quenched with acidified methanol to destroy the unreacted MAO. The polymer was collected by filtration and washed with MeOH and H$_2$O to remove the aluminum salts. The product was dried in a vacuum oven overnight and weighed. The activities have been calculated using the standard Gibson scale[14] (Table 9).

2.4. Acquisition of GPC Data. Samples were prepared by adding 15 mL of solvent (1,2,4-trichlorobenzene + antioxidant) to a 7.5 mg sample of polymer and heating at 190 °C for 40 min. The solutions were filtered at 160 °C through a metal sinter into vials that were placed in a heated sample compartment and allowed to sit for 30 min to allow thermal equilibrium. Chromatography was carried out in duplicate on all samples using a Polymer Laboratories GPC220 with PLgel guard plus 2 × mixed bed-B, 30 cm, 10 μm columns, at a rate of 1.0 mL/min. Results were detected using refractive index measurements and Viscotek differential pressure, and all data capture and subsequent handling were carried out using Viscotek Trisec 3.0 software.

2.5. Crystallography. Details of the crystal data, intensity collection, and refinement for complexes **1**, **3**, and **4** are listed in Table 1, for complexes **6** and **7** in Table 4, and for compounds **10**, **11**, and **12** in Table 6. Crystals were covered in oil, and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97.[15] Additional features are described below.

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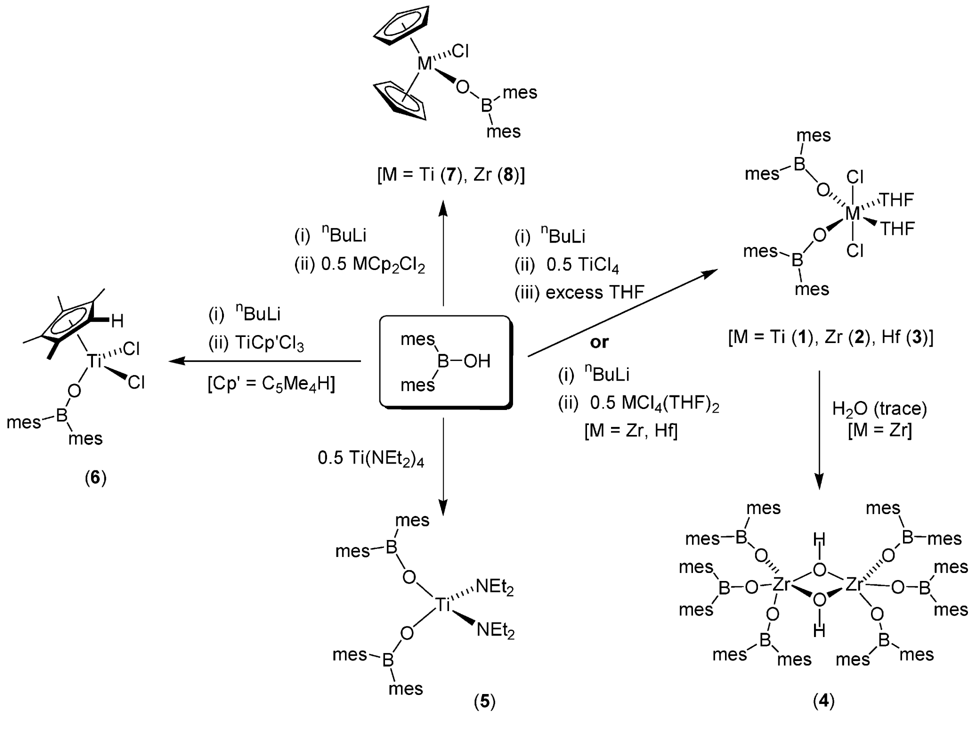
Table 1. Crystal Structure and Refinement Data for Ti{OB(mes)$_2$}$_2$Cl$_2$(THF)$_2$ (1), Hf{OB(mes)$_2$}$_2$Cl$_2$(THF)$_2$ (3), and [Zr{OB(mes)$_2$}$_3$(μ-OH)]$_2$ (4)

	1	3	4
formula	$C_{44}H_{60}B_2Cl_2O_4Ti$	$C_{44}H_{60}B_2Cl_2HfO_4$	$C_{108}H_{134}B_6O_8Zr_2 \cdot 4(C_5H_{12})$
fw	793.34	923.93	2096.04
temperature (K)	173(2)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst size (mm)	0.10 × 0.05 × 0.05	0.10 × 0.05 × 0.05	0.20 × 0.20 × 0.10
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)	$P\bar{1}$ (No.2)
a (Å)	10.3334(2)	10.3030(1)	14.0750(3)
b (Å)	24.8889(5)	25.2472(3)	15.3388(3)
c (Å)	16.5983(4)	16.7087(2)	16.1859(4)
α (deg)	90	90	99.632(1)
β (deg)	92.251(1)	91.582(1)	115.774(1)
γ (deg)	90	90	94.824(1)
V (Å^3)	4265.57(16)	4344.64(8)	3053.63(12)
Z	4	4	1
D_{calc} (Mg/m^3)	1.24	1.41	1.14
abs coeff (mm^{-1})	0.37	2.56	0.22
θ range for data collection (deg)	3.78 to 22.99	3.75 to 25.04	3.76 to 23.06
no. of reflns collected	20 952	43 845	23 561
no. of indep reflns	5855 [$R_{\text{int}} = 0.081$]	7612 [$R_{\text{int}} = 0.074$]	8396 [$R_{\text{int}} = 0.095$]
reflns with $I > 2\sigma(I)$	4349	6217	6816
no. of data/restraints/params	5855/0/490	7612/0/485	8396/0/665
goodness-of-fit on F^2	1.038	1.060	1.072
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.052$, w$R_2 = 0.108$	$R_1 = 0.036$, w$R_2 = 0.063$	$R_1 = 0.083$, w$R_2 = 0.217$
R indices (all data)	$R_1 = 0.083$, w$R_2 = 0.120$	$R_1 = 0.053$, w$R_2 = 0.068$	$R_1 = 0.102$, w$R_2 = 0.231$
largest diff peak and hole (e Å^{-3})	0.39 and −0.31	0.61 and −0.63	2.06 and −1.17 (near Zr)

Scheme 1



Hf{OB(mes)$_2$}$_4$ (12). The molecule lies on a crystallographic 2-fold rotation axis.

3. Results and Discussion

3.1. Group 4 Chloride, Amide, and Hydroxyl Compounds. For the heavier congeners of group 4, synthesis of the solvated bis(boroxide)dichlorides, M{OB(mes)$_2$}$_2$Cl$_2$(THF)$_2$ (**2**, M = Zr; **3**, M = Hf), was achieved in a straightforward metathesis reaction between MCl$_4$(THF)$_2$ and the in situ generated lithium reagents [Li{OB(mes)$_2$}(solvent)$_x$]$_n$.[10] In the case of titanium however, the optimum metal reagent was found to be the base-free tetrachloride, with subsequent addition of THF to stabilize the product. Crystallization from pentane afforded Ti{OB(mes)$_2$}$_2$Cl$_2$(THF)$_2$ (**1**) as yellow crystals (Scheme 1). NMR data and combustion analysis for **1**−**3** were consistent with formation of the monomeric, six-coordinate complexes in which 2 equiv of THF were retained per metal atom.

X-ray diffraction studies were performed on compounds **1** and **3**; the molecular structure of **1** is illustrated in Figure 1; crystal data for both compounds are summarized in Table 1, and selected bond lengths

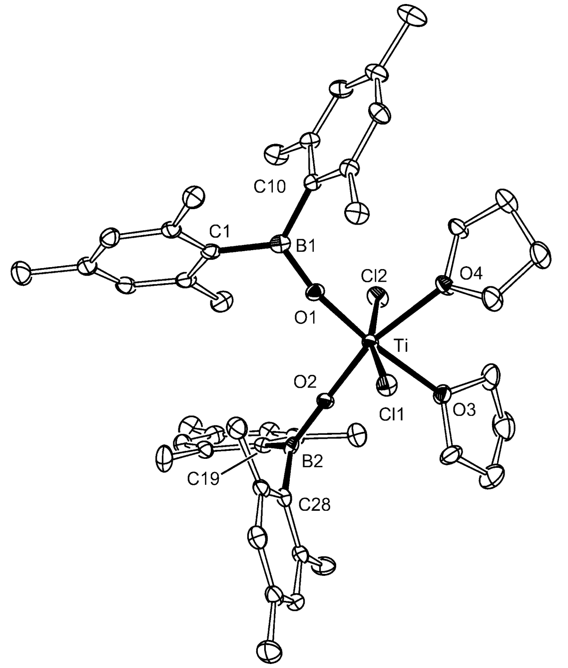


Figure 1. Molecular structure of $\mathrm{Ti\{OB(mes)_2\}_2Cl_2(THF)_2}$ (**1**) with thermal ellipsoids drawn at 30%.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\mathbf{Ti\{OB(mes)_2\}_2Cl_2(THF)_2}$ (1) and $\mathbf{Hf\{OB(mes)_2\}_2Cl_2(THF)_2}$ (3)

	1	3
M−O(1)	1.801(2)	1.943(3)
M−O(2)	1.804(2)	1.940(3)
M−Cl(1)	2.352(1)	2.4577(10)
M−Cl(2)	2.336(1)	2.4396(11)
B(1)−O(1)	1.361(5)	1.353(6)
B(2)−O(2)	1.357(5)	1.352(6)
B(1)−O(1)−M	164.3(3)	164.8(3)
B(2)−O(2)−M	173.3(2)	175.1(3)
O(1)−M−O(2)	100.10(11)	99.89(12)
O(3)−M−O(4)	78.84(10)	79.52(12)
Cl(1)−M−Cl(2)	166.26(4)	165.13(4)

and angles in Table 2. The compounds are isomorphous with no notable structural differences other than the expected increase in the relevant bond lengths commensurate with the larger radius of hafnium. Both **1** and **3** are monomeric, distorted octahedral compounds in the solid state, in which the chloride ligands are in a *trans*-relationship to one another, with mutually *cis*-boroxide and THF groups. This geometry is common to a range of aryloxide[16] and siloxide[17] compounds with general formula $\mathrm{M\{OR\}_2Cl_2(THF)_2}$. In each boroxide compound, one of the ligands is considerably more bent [**1**, 164.3(3)°; **3**, 164.8(3)°] than the other [**1**, 173.3(2)°; **3**, 175.1(3)°]. This cannot, however, be correlated to the extent of π-donation, as the $\mathrm{M{-}O_{boroxide}}$ distances are essentially equal within each compound, and is therefore likely due to crystal packing forces. Comparing **1** with the related aryloxide compound $\mathrm{Ti\{OAr\}_2Cl_2(THF)_2}$ ($\mathrm{Ar = 2,6\text{-}Me_2C_6H_3}$),[16] the $\mathrm{Ti{-}O_{boroxide}}$ bond lengths are identical (within esd's) to the corresponding Ti−OAr distances, although a slight but significant shortening of the metal chloride distances is noted in **1**.

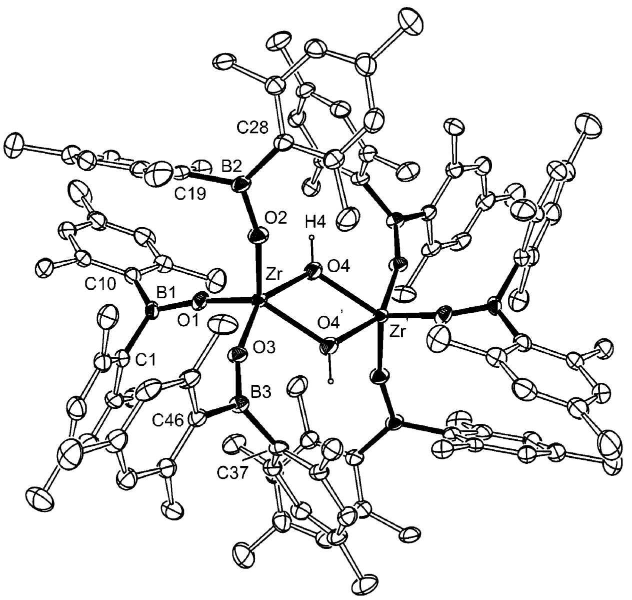


Figure 2. Molecular structure of $\mathrm{[Zr\{OB(mes)_2\}_3(\mu\text{-}OH)]_2}$ (**4**) with thermal ellipsoids drawn at 30% (′ $-x$, $-y$, $-z$).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\mathbf{[Zr\{OB(mes)_2\}_3(\mu\text{-}OH)]_2}$ (4)

Zr−O(1)	1.956(4)	Zr−O(2)	1.934(4)
Zr−O(3)	1.974(4)	Zr−O(4)	2.147(5)
Zr−O(4′)	2.147(4)	B(1)−O(1)	1.375(8)
B(1)−O(2)	1.396(8)	B(3)−O(3)	1.340(8)
O(1)−Zr−O(2)	109.77(18)	O(1)−Zr−O(3)	100.68(17)
O(1)−Zr−O(4)	96.53(17)	O(1)−Zr−O(4′)	127.79(18)
O(2)−Zr−O(3)	102.48(18)	O(2)−Zr−O(4)	94.06(18)
O(2)−Zr−O(4′)	120.20(18)	O(3)−Zr−O(4)	150.35(17)
O(3)−Zr−O(4′)	83.24(17)	O(4)−Zr−O(4′)	67.1(2)
B(1)−O(1)−Zr	160.2(4)	B(2)−O(2)−Zr	157.1(4)
B(3)−O(3)−Zr	155.1(4)		

On one occasion during the preparation of compound **2**, a small amount of colorless crystalline material was isolated. Analysis by X-ray diffraction revealed the dimeric compound $\mathrm{[Zr\{OB(mes)_2\}_3(\mu\text{-}OH)]_2}$ (**4**), indicating that hydrolysis had occurred (determination of the mechanism of formation and full characterization of **4** have not been pursued). The molecular structure of **4** (Figure 2; crystal data, Table 1; selected bond lengths and angles, Table 3) demonstrates that, despite the relatively bulky mesityl substituents, the presence of the boron atom displaces the steric bulk away from the metal center, reducing the cone angle of the ligand and allowing three boroxide ligands to coexist around the five-coordinate zirconium center. The resultant geometry is, by definition,[18] closer to a square-based pyramid than trigonal bipyramidal ($\tau = 0.38$), with the base defined by O(1), O(3), O(4), and O(4′), although this is complicated by the bimetallic nature of **4**. The "apical" boroxide is marginally closer to zirconium [Zr−O(2) = 1.934(4) Å] than the corresponding "basal" ligands [Zr−O(1) = 1.956(4); Zr−O(3) = 1.974(4) Å], with symmetrically bridging μ-hydroxide ligands with Zr−O distances of 2.147(5) Å. This central $\mathrm{[Zr(\mu\text{-}OH)]_2}$ motif

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Table 4. Crystal Structure and Refinement Data for $TiCp'\{OB(mes)_2\}Cl_2$ (6) [$Cp' = C_5H(Me)_4$] and $TiCp_2\{OB(mes)_2\}Cl_2$ (7)

	6	**7**
formula	$C_{27}H_{35}BCl_2OTi$	$C_{28}H_{32}BClOTi$
fw	505.16	478.70
temperature (K)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073
cryst size (mm)	0.03 × 0.03 × 0.02	0.20 × 0.10 × 0.10
cryst syst	orthorhombic	monoclinic
space group	*Pbca* (No.61)	$P2_1/n$ (No.14)
A (Å)	14.9688(7)	8.2133(3)
B (Å)	19.8758(11)	24.4108(9)
C (Å)	17.3339(10)	12.7151(6)
β (deg)	90	92.471(2)
V (Å^3)	5157.1(5)	2546.9(2)
Z	8	4
D_{calc} (Mg/m^3)	1.30	1.25
abs coeff (mm^{-1})	0.56	0.46
θ range for data collection (deg)	3.74 to 23.02	3.83 to 23.00
no. of reflns collected	16 975	11 735
no. of indep reflns	3556 [$R_{int} = 0.093$]	3487 [$R_{int} = 0.066$]
reflns with $I > 2\sigma(I)$	2501	2536
no. of data/restraints/params	3556/0/297	3487/0/295
goodness-of-fit on F^2	1.055	1.033
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.052$, $wR_2 = 0.100$	$R_1 = 0.054$, $wR_2 = 0.112$
R indices (all data)	$R_1 = 0.088$, $wR_2 = 0.113$	$R_1 = 0.086$, $wR_2 = 0.127$
largest diff peak and hole (e Å^{-3})	0.24 and −0.28	0.25 and −0.37

has previously been observed in a range of bimetallic zirconium species with coordination numbers 6−8.[19]

The presence of coordinating THF molecules in the compounds **1** to **3** is predicted to be detrimental to their proposed application as procatalysts for olefin polymerization, where the base will compete with the incoming monomer for coordination to the metal center. In an attempt to access the base-free complex therefore, the protonolysis reaction between 2 equiv of $(mes)_2BOH$ and $Ti(NEt_2)_4$ was investigated, where conversion of the amide to the dichloride has previously been shown to occur upon reaction with $Me_2NH{\cdot}HCl$[20] or $SiMe_3Cl$,[21] in noncoordinating solvent. The reaction proceeded cleanly to afford $Ti\{OB(mes)_2\}_2(NEt_2)_2$ (**5**) as a yellow powder in good yield. The compound was pure by NMR spectroscopy (see Supporting Information); the elemental analysis was, however, inaccurate, which we attribute to the formation of involatile titanium nitride upon combustion. Disappointingly conversion to the base-free compound "$Ti\{OB(mes)_2\}_2Cl_2$" did not proceed cleanly using $SiMe_3Cl$, and after repeated attempts no pure product was isolated.

Previous studies have shown that the combination of a cyclopentadienyl anion with an aryloxide ligand gave high catalytic activity for alkene polymerization in titanium compounds upon activation with MAO or $Al^{i}Bu_3/[Ph_3C][B(C_6F_5)_4]$.[22] We therefore targeted related systems that incorporate boroxides in place of the aryloxide, with the premise that the electron-deficient nature of the boroxide versus the alkoxide may increase the activity of the system. Tetramethylcyclopentadienyl titanium trichloride, $TiCp'Cl_3$, ($Cp' = \eta$-C_5Me_4H),[13] reacted with 1 equiv of lithiated borinic acid to afford the corresponding mixed ligand compound $TiCp'\{OB(mes)_2\}Cl_2$ (**6**, Scheme 1). The low yield is attributed to incomplete reaction, from which the product cocrystallizes with the unreacted starting material. Increasing the reaction time and/or temperature did not significantly improve the yield of the reaction. Single crystals of **6** were mechanically separated from the mixture, and the X-ray diffraction study was performed. The molecular structure is illustrated in Figure 3; crystal data are summarized in Table 4, and selected bond lengths and angles in Table 5.

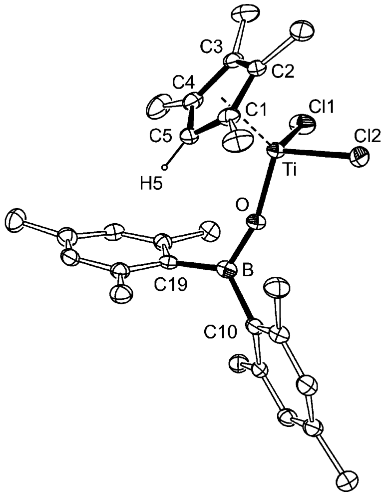

Figure 3. Molecular structure of $TiCp'\{OB(mes)_2\}Cl_2$ (**6**) with thermal ellipsoids drawn at 30%.

Compound **6** crystallizes as the monomeric mixed cyclopentadienyl/boroxide complex $TiCp'\{OB(mes)_2\}Cl_2$, with a pseudo-tetrahedral arrangement of ligands around the titanium center [interligand angles in the range

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for TiCp′{OB(mes)$_2$}Cl$_2$ (6) [Cp′ = C$_5$HMe$_4$] and TiCp$_2${OB(mes)$_2$}Cl (7)[a]

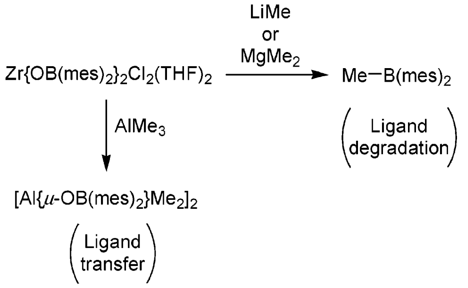
	6	7
Ti–O	1.812(2)	1.888(2)
Ti–M(1)	2.038(4)	2.082(4)
Ti–M(2)		2.076(4)
Ti–Cl(1)	2.2583(13)	2.380(1)
Ti–Cl(2)	2.2635(13)	
B–O	1.374(5)	1.346(5)
O–Ti–M(1)	118.6(1)	105.5(1)
O–Ti–M(2)		108.6(1)
O–Ti–Cl(1)	103.96(9)	99.58(8)
O–Ti–Cl(2)	103.05(9)	
M(1)–Ti–Cl(1)	113.7(1)	104.7(1)
M(1)–Ti–Cl(2)[1]	113.6(1)	105.0(1)
M(2)–Ti–M(1)		129.5(1)
Cl(1)–Ti–Cl(2)	101.98(5)	
O–B–C(1)[2]	115.8(4)	120.2(3)
O–B–C(10)	117.7(4)	118.2(3)
B–O–Ti	163.8(3)	170.1(3)

[a] M(1) = centroid of ring of the C$_5$ ring; [1] **7** M(2)–Ti–Cl(1); [2] **6** O–B–C(19).

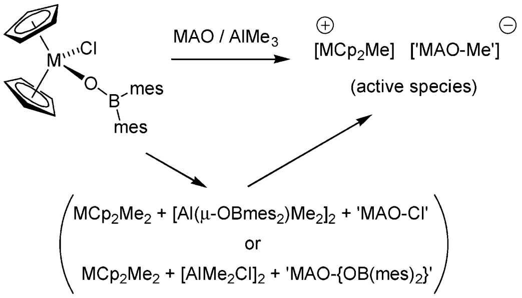
101.98(5)–118.6(1)°]. The structural parameters are within the limits of those found in an extensive series of substituted cyclopentadienyl/alkoxide or aryloxide titanium dichlorides,[22,23] where there is an observed decrease in Ti–Cl distance on replacing one of the cyclopentadienyl anions in TiCp$_2$Cl$_2$[24] [Ti–Cl = 2.367(2) and 2.361(2) Å] with the oxygen-based ligand. For compound **6**, the Ti–Cl distances [2.258(13) and 2.264(13) Å] are toward the low end of this range, suggestive of an electron-deficient titanium center.

3.2. Alkylation Studies. Alkylation of the dichloride compounds **1**–**3** was attempted using a number of standard reagents in an attempt to access dialkyl precatalysts of general formula M{OB(mes)$_2$}$_2$R$_2$. The Grignard reagents RMgX [R = Me, Mes, CH$_2$CMe$_2$Ph, X = Br, Cl] were initially investigated, where it was anticipated that the bulkier mesityl and neophyl substituents would help to stabilize the compound through steric protection of the metal center. Unfortunately, under a number of reaction conditions investigated, only mixtures of compounds were produced that could not be separated using conventional techniques. The reagents LiMe[25] and MgMe$_2$ were also tested as a method of replacing the chloride ligands with methyl groups. In these instances the methylborane compound, Me-B(mes)$_2$, was identified as a ligand decomposition product by spectroscopic and combustion analysis, suggesting an inherent instability associated with the boroxide ligand (Scheme 2). Finally, the reaction was attempted between Zr{OB(mes)$_2$}$_2$Cl$_2$(THF)$_2$ (**2**) and AlMe$_3$, which has previously been shown to be a successful methylating reagent.[20,21] In this case a white powder was isolated from the reaction, which was shown by ^{1}H NMR and mass spectral analysis to be the previously reported aluminum compound [Al{μ-OB(mes)$_2$}Me$_2$]$_2$.[6] These data clearly indicate the noninnocent behavior of the boroxide ligand at a group 4 metal center, displaying two possible pathways for unwanted side reactions, namely, degradation to form the borane, Me-B(mes)$_2$, and ligand transfer from zirconium to aluminum to form the dimethylaluminum compound, [Al{μ-OB(mes)$_2$}Me$_2$]$_2$.

Scheme 2



Scheme 3



3.3. Bis(cyclopentadienyl)metal Boroxide Compounds. We were intrigued by the possibility of exploiting boroxide transfer from Zr to Al in polymerization reactions. The accepted active species in Ziegler–Natta type polymerization is the alkyl cation [L$_x$MR]$^+$, supported by an ancillary ligand set, L$_x$. The activator methylalumoxane (MAO) is successful in the generation of such species starting from the group 4 dichloride precatalysts, where the reagent is responsible for both methylating the metal center and abstracting a methide anion to afford the desired cation. As one of the components of MAO is known to be unreacted AlMe$_3$, the possible formation of similar cationic species can be postulated for the reaction of the metallocene complexes MCp$_2${OB(mes)$_2$}Cl (Scheme 3). While this admittedly does not offer any advantages over existing systems, necessitating the synthesis of the boroxide starting material, it does lend valuable information on the likely success of the role of boroxides as ancillary ligands. In addition, these observations open up the question of the stability of alkoxide compounds with respect to MAO, given the high oxophilicity of aluminum.

As proof of concept, our studies were therefore extended to target the metallocene complexes MCp$_2${OB(mes)$_2$}Cl, where any observable olefin polymerization activity is implicit of formation of the [MCp$_2$R]$^+$ cation,

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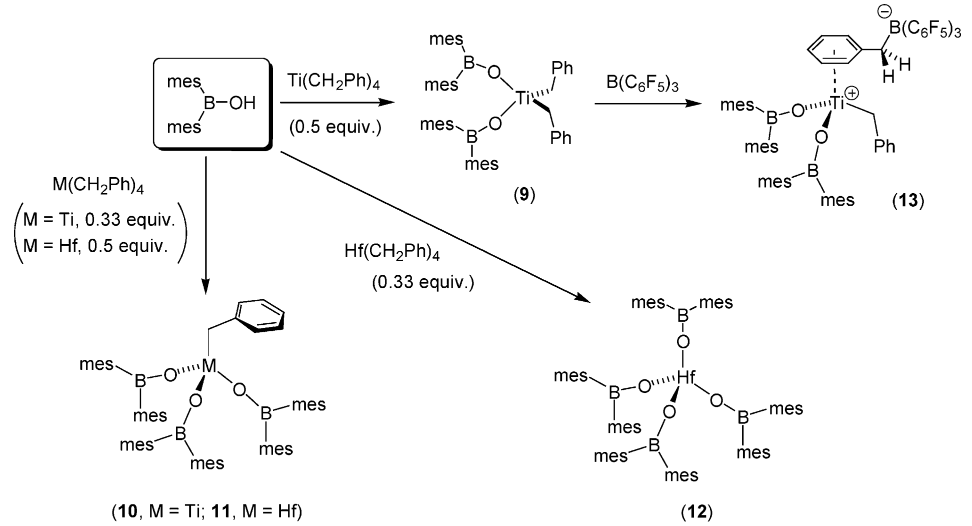
Table 6. Crystal Structure and Refinement Data for Ti{OB(mes)$_2$}$_3$(CH$_2$Ph) (10), Hf{OB(mes)$_2$}$_3$(CH$_2$Ph) (11), and Hf{OB(mes)$_2$}$_4$ (12)

	10	**11**	**12**
formula	$C_{61}H_{73}B_3O_3Ti\cdot(C_5H_{12})$	$C_{61}H_{73}B_3HfO_3\cdot0.5(C_5H_{12})$	$C_{72}H_{88}B_4HfO_4$
fw	1006.67	1101.19	1239.15
temperature (K)	173(2)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst size (mm)	0.40 × 0.40 × 0.40	0.10 × 0.10 × 0.10	0.015 × 0.015 × 0.01
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)	$C2/c$ (No.15)
a (Å)	14.0992(7)	12.2043(4)	23.147(2)
b (Å)	14.5950(7)	15.7658(4)	14.8478(7)
c (Å)	17.1898(9)	16.3282(6)	21.429(2)
α (deg)	93.847(2)	105.180(2)	90
β (deg)	95.609(2)	94.640(2)	119.350(3)
γ (deg)	118.391(2)	104.603(2)	90
V (Å^3)	3070.8(3)	2897.62(16)	6419.4(9)
Z	2	2	4
D_{calc} (Mg/m^3)	1.09	1.26	1.28
abs coeff (mm^{-1})	0.18	1.84	1.67
θ range for data collection (deg)	3.74 to 25.05	3.67 to 25.03	3.81 to 22.96
no. of reflns collected	21 573	37 582	17 771
no. of indep reflns	10 802 [$R_{\mathrm{int}} = 0.053$]	10 193 [$R_{\mathrm{int}} = 0.055$]	4414 [$R_{\mathrm{int}} = 0.193$]
no. of reflns with $I > 2\sigma(I)$	7204	8752	3036
no. of data/restraints/params	10 802/0/676	10 193/0/632	4414/0/374
goodness-of-fit on F^2	1.014	0.915	1.052
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.062$, w$R_2 = 0.142$	$R_1 = 0.044$, w$R_2 = 0.118$	$R_1 = 0.070$, w$R_2 = 0.122$
R indices (all data)	$R_1 = 0.104$, w$R_2 = 0.163$	$R_1 = 0.056$, w$R_2 = 0.128$	$R_1 = 0.121$, w$R_2 = 0.141$
largest diff peak and hole (e Å^{-3})	0.38 and −0.43	0.98 and −0.68	0.61 and −0.60

Scheme 4



which necessitates transfer of the boroxide ligand to aluminum. The metallocene dichlorides MCp$_2$Cl$_2$ (M = Ti, Zr) reacted cleanly with 1 equiv of lithiated borinic acid to afford the desired complexes TiCp$_2${OB(mes)$_2$}Cl (**7**) and ZrCp$_2${OB(mes)$_2$}Cl (**8**) in moderate yield after purification (Scheme 1). The NMR and analytical data were consistent with the postulated formulas, and a single-crystal X-ray analysis of **7** confirmed the structure. The molecular structure is illustrated in Figure 4; crystal data are summarized in Table 4, and selected bond lengths and angles in Table 5.

Compound **7** exists as a monomeric, pseudo-tetrahedral complex TiCp$_2${OB(mes)$_2$}Cl with angles in the range 99.58(8)−129.5(1)°. The Ti−Cl bond length [2.380(1) Å] and the Ti−M (M = centroid of the Cp ring) bond distances [2.082(4) and 2.076(4) Å] are in good agreement with those found in other titanocene chloride complexes.[26] The Ti−O bond length [1.888(2) Å] is longer than in the related bis(cyclopentadienyl)titanium alkoxide complex TiCp$_2${O(C$_2$H$_5$)}Cl [1.855(2) Å],[27] suggestive of a lower Ti−O bond order, although the B−O−Ti angle [170.1(3)°] is suggestive of at least partial multiple character in the B−O-M bond.

3.4. Protonolysis Studies of M(CH$_2$Ph)$_4$. The lack of success during attempted alkylation of the dichloride species prompted us to investigate a protonolysis pathway as a route to the dialkyl species,[10,11,28] employing dimesitylborinic acid as the ligand source (Scheme 4). A complication associated with this protocol was the tendency for the isolated products to contain a greater number of boroxide ligands than merited by the stoichiometry of the reaction. This problem was alleviated

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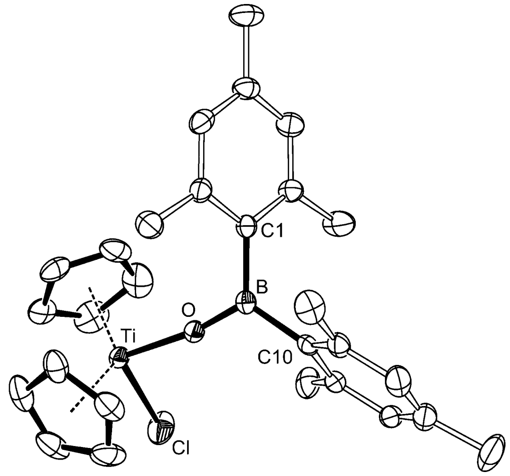

Figure 4. Molecular structure of TiCp$_2${OB(mes)$_2$}Cl (**7**) with thermal ellipsoids drawn at 30%.

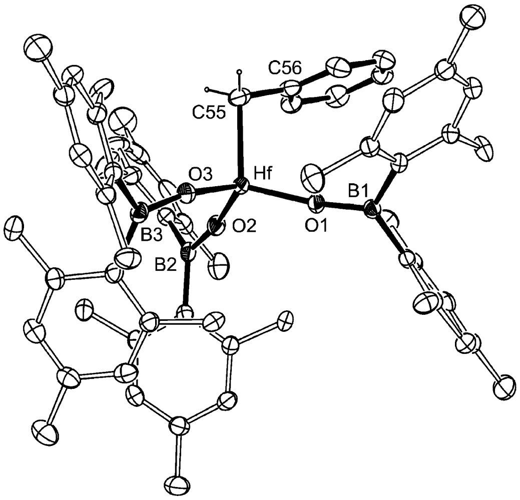

Figure 5. Molecular structure of Hf{OB(mes)$_2$}$_3$(CH$_2$Ph) (**11**) with thermal ellipsoids drawn at 20%.

in the case of titanium through careful control of the reaction time. For example, it was established that reacting a 2:1 and 3:1 ratio of (mes)$_2$BOH and Ti(CH$_2$Ph)$_4$ for 3 and 15 h, respectively, proved optimal for the synthesis of Ti{OB(mes)$_2$}$_2$(CH$_2$Ph)$_2$ (**9**) and Ti{OB(mes)$_2$}$_3$(CH$_2$Ph) (**10**). The same reaction times and conditions for the analogous hafnium reactions, however, resulted in formation of mixtures of the tris- and tetrakis-boroxides Hf{OB(mes)$_2$}$_3$(CH$_2$Ph) (**11**) and Hf{OB(mes)$_2$}$_4$ (**12**), respectively.

X-ray diffraction studies were performed on the tris-boroxide mono-benzyl compounds **10** and **11**; the molecular structure of **11** is illustrated in Figure 5; crystal data for both compounds are summarized in Table 6, and selected bond lengths and angles in Table 7. Both tris(boroxide) mono(benzyl) compounds crystallize as the monomer, with the three terminal boroxide ligands and the benzyl group forming a distorted tetrahedral array about the central metal atom. Surprisingly there are no analogous tris(aryloxide) mono-benzyl complexes (containing terminal oxygen ligands) with which to directly compare the structural parameters of **10** and **11**. The ability to accommodate these boroxide ligands about the metal centers is therefore likely to rely on the presence of the boron atom, which effectively displaces the bulk of the ligand further from the immediate vicinity of the metal (vide supra). The average M–O distances [**10**, 1.794 Å; **11**, 1.919 Å] are marginally shorter than in the dichloride compounds **1** and **3**, likely reflecting the reduction in coordination number. Despite the formal low electron count for the metal in each compound, there are no indications of any η^2-type interaction with the benzyl group, with nonbonding distances to the *ipso*-carbon [**10**, Ti···C56 = 2.942 Å; **11**, Hf···C56 = 2.994 Å] and reasonable angles at the methylene carbon atom [**10**, Ti–C55–C56 = 109.98(18)°; **11**, Hf–C55–C56 = 106.0(4)°].

Table 7. Selected Bond Lengths (Å) and Angles (deg) for Ti{OB(mes)$_2$}$_3$(CH$_2$Ph) (10) and Hf{OB(mes)$_2$}$_3$(CH$_2$Ph) (11)

	10	**11**
M–O(1)	1.7965(18)	1.922(4)
M–O(2)	1.7923(18)	1.916(4)
M–O(3)	1.7918(19)	1.918(4)
M–C(55)	2.081(3)	2.214(7)
B(1)–O(1)	1.371(4)	1.365(7)
B(2)–O(2)	1.383(4)	1.374(8)
B(3)–O(3)	1.367(4)	1.362(8)
O(1)–M–O(2)	115.49(9)	114.72(17)
O(1)–M–O(3)	110.58(9)	112.44(18)
O(2)–M–O(3)	114.29(9)	109.13(19)
O(1)–M–C(55)	107.31(11)	107.5(2)
O(2)–M–C(55)	104.02(11)	107.4(3)
O(3)–M–C(55)	104.00(10)	105.1(2)
M–O(1)–B(1)	162.57(19)	172.7(4)
M–O(2)–B(2)	163.6(2)	166.6(4)
M–O(3)–B(3)	160.60(18)	161.2(4)
M–C(55)–C(56)	109.98(18)	106.0(4)

The bulky phenoxide ligands 2,6-^{i}Pr$_2$C$_6$H$_3$,[29] 2-^{t}BuC$_6$H$_4$, and 2,3,5,6-Me$_4$C$_6$H[30] have been shown to form the homoleptic titanium(IV) compounds Ti(OAr)$_4$. The corresponding siloxides M(OSiR$_3$)$_4$, where R = O^{t}Bu[31,32] or Ph,[33] are known for all members of the group. The only reported homoleptic boroxide compounds are of general formula [M{OBAr$_2$}{μ-OBAr$_2$}]$_2$ [M = Fe, Mn; Ar = mes, 2,4,6-^{i}Pr$_3$C$_6$H$_2$],[5] in which the boroxides are present in both a terminal and bridging coordination mode. In contrast, the molecular structure of the homoleptic hafnium compound Hf{OB(mes)$_2$}$_4$ (**12**, Figure 6, Tables 6 and 8) is monomeric, with a distorted tetrahedral metal [intraligand angles in the range 107.9(3)–111.7(4)°]. The slight deviation from ideal tetrahedral geometry suggests a relatively unstrained system, further indication of the small cone angle of the ligand. The Hf–O bond lengths [1.902(7) and 1.916(7) Å] tend toward the low end of the range observed in the tetrasiloxides [1.935(4)–1.949(4) Å][31] and the tris(alkoxide) species, Hf{OAr}$_3$Cl [Ar = 2,6-^{t}BuC$_6$H$_3$: 1.917(3)–1.938(3) Å],[34] although in the absence of solution-state data, these effects may be attributable to purely

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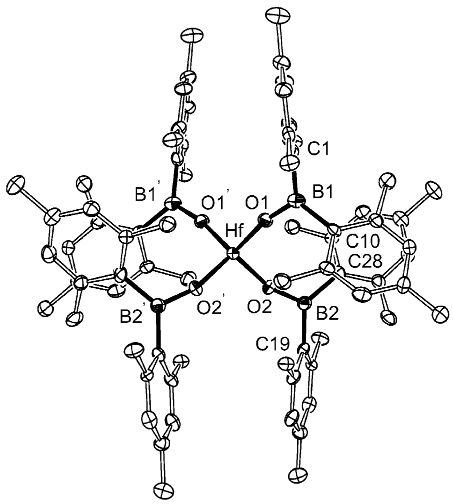

Figure 6. Molecular structure of Hf{OB(mes)$_2$}$_4$ (**12**) with thermal ellipsoids drawn at 30% (′ $-x$, $-y$, $-z+1/2$).

Table 8. Selected Bond Lengths (Å) and Angles (deg) for Hf{OB(mes)$_2$}$_4$ (12)

Hf−O(1)	1.902(7)	Hf−O(2)	1.916(7)
O(1)−B(1)	1.380(14)	O(2)−B(2)	1.396(14)
O(1)−Hf−O(1′)	111.7(4)	O(1)−Hf−O(2)	107.9(3)
O(1′)−Hf−O(2)	110.6(3)	O(2)−Hf−O(2′)	108.0(4)
Hf−O(1)−B(1)	167.7(7)	Hf−O(2)−B(2)	160.0(7)

steric factors rather than the electronic influence of the boron atom.

3.5. Cation Generation with "Well-Defined" Activators. Within this study, the bis(boroxide) species Ti{OB(mes)$_2$}$_2$(CH$_2$Ph)$_2$ (**9**) constitutes the most promising precursor for the generation of well-defined [ML$_2$R]$^+$ cations, and so the reaction between **9** and the borane activator B(C$_6$F$_5$)$_3$ was investigated using NMR spectroscopy. Formation of a single new species (**13**) was observed, which was characterized spectroscopically in solution. The ^{1}H NMR spectrum of **13** showed two signals for the C*H*$_2$Ph protons [δ 3.55 and 3.39], each of which are shifted downfield from the corresponding singlet in the neutral dialkyl precursor, **9** [δ 2.86]. The higher frequency resonance appears as an unresolved multiplet which collapses to a broadened singlet in the ^{1}H{^{11}B} experiment, showing that this resonance corresponds to a boron-bound benzyl group of the anion [B(C$_6$F$_5$)$_3$(CH$_2$Ph)]$^-$. The aromatic resonances associated with this component appear at higher field than expected for the free ion, indicative of an η^6-interaction between the titanium cation and the boroxide anion.[35] Such interactions have previously been observed for group 4 systems employing aryloxide ligands,[36] further demonstrating the similarity between the aryloxide and boroxide systems. NMR reactions between **9** and [Ph$_3$C][B(C$_6$F$_5$)$_4$] and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] were also investigated. An immediate reaction was observed in each case; however, no clean products could be identified from the complicated NMR spectra of the reaction mixtures.

3.6. Polymerization Studies with MAO. Compounds **1**−**3**, **7**, and **8** were tested for activity as olefin polymerization precatalysts, using MAO as the activator (Table 9); activities are compared to ZrCp$_2$Cl$_2$ tested under the same conditions [entry 1]. The dichloride complexes M{OB(mes)$_2$}$_2$Cl$_2$(THF)$_2$ display low activity on the Gibson scale[14] (entries 2−4), with the zirconium (**2**) and hafnium complexes (**3**) displaying considerably higher activities than the titanium compound, **1**. Analysis of the polyethylene samples by GPC and GPC-viscosity indicated a very high molecular weight product for **1** with a fairly narrow molecular weight distribution [$M_w/M_n = 2.9$], while polymer from both **2** and **3** was insoluble (presumably due to high levels of cross-linking or ultrahigh molecular weight material).

The bis(cyclopentadienyl) complexes MCp$_2${OB(mes)$_2$}-Cl [**7** and **8**] both displayed moderate activity as polymerization catalysts [entries 5 and 6], comparable with the ZrCp$_2$Cl$_2$ test run [entry 1]. Given the previous observation that the boroxide ligand will transfer from zirconium to aluminum (Section 3.2), this is perhaps not too surprising, as the likelihood exists for formation of the same active species during the polymerization experiment, namely, the [MCp$_2$R]$^+$ cation (Scheme 3). Comparison of the polymer analysis data from ZrCp$_2$Cl$_2$ [entry 1] and ZrCp$_2${OB(mes)$_2$}Cl [entry 6] shows notable differences in the polymer, where the broader molecular weight distribution for ZrCp$_2$Cl$_2$ is attributable to a lower molecular weight fraction present in the polymer sample. The higher molecular weight fraction does, however, appear to be of molecular weight similar to that produced using compound **8**, and intrinsic viscosity plots show very similar characteristics, indicative of a similar structure and composition of the two polymer samples. While these data are not conclusive as to the boroxide transfer reaction from Zr to Al, evidence is strong that a similar active species is being formed in solution, in agreement with our synthetic studies.

Attempted polymerization with the in situ generated benzyl cation Ti{OB(mes)$_2$}$_2$(CH$_2$Ph)[η^6-C$_6$H$_5$CH$_2$B(C$_6$F$_5$)$_3$] (**13**) gave no observable polymerization activity. This may be attributable to the retention of a strongly held ion-pair in solution preventing the approach of the ethylene monomer to the cationic titanium center, although the presence of small amounts of moisture in the system can never be totally ruled out. Controlled experiments into the reactivity of **13**, and related compounds, form part of a continuing study in this area of research and will be reported in due course.

4. Conclusions

We have demonstrated that the boroxide anion, [OB(mes)$_2$]$^-$, may be introduced to a group 4 metal center either using the metathesis reaction between the in situ generated lithium salt and the transition metal chloride or via protonolysis using the tetrabenzyl reagents M(CH$_2$Ph)$_4$. Analysis of the dichlorides indicated that two molecules of THF were retained in the bis(boroxide) dichloride complexes and X-ray diffraction data showed a *cis*-arrangement of boroxides with *trans*-chlorides. Accidental hydrolysis during a preparation of the zirconium complex afforded the five-coordinate hydroxyl-bridged species [Zr{OB(mes)$_2$}$_3$(μ-OH)]$_2$, demonstrating the relatively small cone angle of the ligand. Attempted alkylation of the dichlorides identified two

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Table 9. Ethene Polymerization and Polymer Analysis Results (molar ratio of M:MAO = 1:1000; 25 °C; 9 bar ethylene; 100 mL toluene; 1 h)[a]

entry	catalyst	yield PE (g)	activity (gPE $mmol^{-1}$ h^{-1} bar^{-1})	M_w	M_n	M_w/M_n
1	$ZrCp_2Cl_2$	6.60	27.7	348 500	861 00	4.0
2	$Ti\{OB(mes)_2Cl_2(THF)_2$ (**1**)	0.28	2.8	1 945 000	672 500	2.9
3[b]	$Zr\{OB(mes)_2Cl_2(THF)_2$ (**2**)	1.64	8.1			
4[b]	$Hf\{OB(mes)_2Cl_2(THF)_2$ (**3**)	1.69	8.0			
5	$TiCp_2\{OB(mes)_2\}Cl$ (**7**)	6.91	31.8	1 140 000	270 500	4.2
6[c]	$ZrCp_2\{OB(mes)_2\}Cl$ (**8**)	6.17	27.5	454 800	180 300	2.5
7[d]	$Ti\{OB(mes)_2\}_2(CH_2Ph)[\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3]$ (**13**)		0			

[a] Values given in the table are the average from two runs performed on the same material. [b] Sample insoluble. [c] Average value over 2 samples. [d] Generated in situ prior to injection into the polymerization reactor.

possible complications associated with the boroxide ligand on group 4 metals. With LiMe and $MgMe_2$, methylation of the boron atom and formation of $MeB(mes)_2$ were confirmed by NMR and elemental analysis, while with $AlMe_3$, transfer of the intact boroxide from Zr to Al was evident from the formation of the previously reported aluminum complex $[Al\{\mu\text{-}OB(mes)_2\}Me_2]_2$. Mixed cyclopentadienyl-boroxide compounds were also accessed using standard synthetic procedures. A series of benzyl complexes $M\{OB(mes)_2\}_n(CH_2Ph)_{4-n}$ (M = Ti, Hf; $n = 2-4$) were isolated from reactions of the borinic acid $(mes)_2BOH$ with $M(CH_2Ph)_4$, where a tendency for "oversubstitution" of the alkyl group for the boroxide was noted. Conversion to the cationic titanium monobenzyl compound using $B(C_6F_5)_3$ as an alkyl abstraction agent was probed by NMR, demonstrating formation of the desired species in solution. However, strong interactions between the cation and anion prevented polymer growth under the conditions investigated.

Polymerization experiments performed using the dichloride precatalysts with MAO activator under 9 bar of ethylene pressure gave low activities. However, moderate activities (of the same order of magnitude as that for $ZrCp_2Cl_2$, which was tested under the same reaction conditions) were observed for the compounds $MCp_2\{OB(mes)_2\}Cl$, where loss of the boroxide must occur to generate the accepted active cationic species $[MCp_2R]^+$, in agreement with previously observed ligand transfer from a group 4 metal to aluminum. In summary, while we have been successful in the synthesis of a range of group 4 boroxide complexes, the suitability of this group as an ancillary ligand in olefin polymerization is questionable due to reactivity with other components employed during these polymerization reactions.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of **5**, **6** (^1H only), **9**, **12**, and representative mixtures of **11/12** (^1H only). Crystallographic data in CIF format for compounds **1**, **3**, **4**, **6**, **7**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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