Hafnium–phosphinimide complexes

Osamah Alhomaidan, Gregory C. Welch, Guangcai Bai, and Douglas W. Stephan

Abstract: A series of phosphinimide complexes of Hf are prepared and characterized. Reaction of the phosphinimine *t*-Bu_3PNH with $Hf(NEt_2)_4$ gave (*t*-$Bu_3PN)Hf(NEt_2)_3$ (**1**) but this species was not readily converted to the corresponding $HfCl_3$-derivative. The reaction of 2 equiv. of *t*-Bu_3PNH with $Hf(NEt_2)_4$, however, gave (*t*-$Bu_3PN)_2Hf(NEt_2)_2$ (**2**), which was readily converted to (*t*-$Bu_3PN)_2HfCl_2$ (**3**) and (*t*-$Bu_3PN)_2HfMe_2$ (**4**). Employing *t*-Bu_3PNLi and $HfCl_4$ afforded (*t*-$Bu_3PN)_3HfCl$ (**5**) while reaction with $CpHfCl_3$ gave rise to ligand redistribution reactions affording (*t*-$Bu_3PN)_2HfCl_2$ and Cp_2HfCl_2. However, Cp(*t*-$Bu_3PN)_2HfCl$ (**7**) was prepared by treating (*t*-$Bu_3PN)_2HfCl_2$ with CpNa. The related species of Cp_2(*t*-$Bu_3PN)HfCl$ (**8**) was synthesized by the reaction of Cp_2HfCl_2 and *t*-Bu_3PNLi. Ligand redistribution was avoided in the reaction of Cp^*HfCl_3 as Cp*(*t*-$Bu_3PN)HfCl_2$ (**9**) and Cp*(*i*-$Pr_3PN)HfCl_2$ (**10**) were readily obtained and derivatized as Cp*(*t*-$Bu_3PN)Hf(NMe_2)_2$ (**11**) and Cp*(*t*-$Bu_3PN)HfMe_2$ (**12**), respectively. Similarly, $((Me_3Si)_2C_5H_3)$(*t*-$Bu_3PN)HfCl_2$ (**13**) was converted to $((Me_3Si)_2C_5H_3)$(*t*-$Bu_3PN)HfMe_2$ (**14**). Reactions with Lewis acid activators were used to prepare Cp*(*t*-$Bu_3PN)HfMe(THF)MeB(C_6F_5)_3$ (**15**), (Cp*(*t*-$Bu_3PN)HfMe)(B(C_6F_5)_4)$ (**16**), and (*t*-$Bu_3PN)_2Hf(H_2B(C_6F_5)_2)_2$ (**17**). Preliminary testing of **3**, **9**, and **13** in ethylene polymerization is reported. Compounds **3**, **4**, **7**, **9**, and **17** are characterized crystallographically.

Key words: hafnium, phosphinimide, ligand redistribution, cyclopentadienyl ligands, ethylene polymerization.

Résumé : On a préparé et caractérisé une série de complexes de Hf avec le phosphinimide. La réaction de la phosphinimine *t*-Bu_3PNH avec le $Hf(NEt_2)_4$ conduit à la formation du composé (*t*-$Bu_3PN)Hf(NEt_2)_3$ (**1**); toutefois, cette espèce ne se transforme pas facilement en dérivé $HfCl_3$ corrrespondant. Toutefois, la réaction de 2 equiv. de *t*-Bu_3PNH avec du $Hf(NEt_2)_4$ conduit à la formation de (*t*-$BuPN)_2Hf(NEt_2)_2$ (**2**) qu'on peut facilement transformer en (*t*-$Bu_3PN)_2HfCl_2$ (**3**) et en (*t*-$Bu_3PN)_2HfNe_2$ (**4**). L'utilisation de (*t*-BuPNLi) et de $HfCl_4$ conduit à la formation de (*t*-$Bu_3PN)_2HfCl$ (**5**) alors que la réaction avec du $CpHfCl_3$ conduit à une réaction de redistribution de ligand conduisant au (*t*-$Bu_3PN)_2HfCl_2$ et au Cp_2HfCl_2. Toutefois, on a pu préparer le Cp(*t*-$Bu_3PN)_2HfCl$ (**7**) par traitement du (*t*-$Bu_3PN)_2HfCl_2$ avec du CpNa. On a effectué la synthèse de l'espèce apparentée Cp_2(*t*-$Bu_3PN)HfCl$ (**8**) par réaction du Cp_2HfCl_2 avec le *t*-Bu_3PNLi. La réaction de redistribution des ligands a été évitée dans la réaction du Cp^*HfCl_3 et il a été possible d'obtenir facilement de Cp*(*t*-$Bu_3PN)HfCl_2$ (**9**) et Cp*(*t*-$BuPN)HfCl_2$ (**10**) et de les transformer en dérivés Cp*(*t*-$Bu_3PN)Hf(NMe_2)_2$ (**11**) et Cp*(*t*-$BuPN)Hf(NMe_2)_2$ (**12**) respectivement. De la même manière, on a pu transformer le produit $[(Me_3Si)_2C_5H_3]$(*t*-$Bu_3PN)HfCl_2$ (**13**) en $[(Me_3Si)_2C_5H_3]$(*t*-$Bu_3PN)HfCl_2Me_2$ (**14**). On a fait appel à des réactions avec des activateurs d'acide de Lewis pour préparer les produits Cp*(*t*-BuPH)HgMe(THF)$MeB(C_6F_5)_3$ (**15**), (Cp*(*t*-$Bu_3PN)HfMe)(B(C_6F_5)_4)$ (**16**) et (*t*-$Bu_3PN)Hf(H_2B(C_6F_5)_2)_2$ (**17**). On rapporte les résultats préliminaires de l'évaluation des composés **3**, **9** et **13** dans des polymérisations de l'éthylène. Les structures des composés **3**, **4**, **7**, **9** et **17** ont été caractérisées par cristallographie.

Mots-clés : hafnium, phosphonimide, redistribution de ligand, ligands cyclopentadiényles, polymérisation de l'éthylène.

[Traduit par la Rédaction]

Introduction

The drive to discover new homogeneous catalysts for olefin polymerization has stimulated much research over the last 25 years. Several reviews have described such studies.[1–9] While synthetic routes to a large number of potential catalysts have been developed, only very few have been shown to operate effectively under commercial conditions.[10] One system that has indeed been commercialized is based on the early metal derivatives of a cyclopentadienyl-amide ligand,[11] affording the so-called "constrained geometry catalysts".[12–15] Another system that has drawn considerable recent attention is that based on the "FI" catalysts developed by researchers at the Mitsui Chemical Co.[7,16–20] During the last decade, we have studied olefin polymerization catalysts based on Ti-phosphinimide complexes and examined in detail the structure–activity relationship,[21–33] as well as the mechanisms of deactivation.[34–39] These systems yield highly active olefin polymerization catalysts[10,40] and indeed, some of these systems are also operative under commercially relevant conditions.[10,31,40]

While the majority of early metal catalysts have been derived from Ti or Zr complexes,[1–9] we have also probed the reactivity of V[41] and Cr[42] phosphinimide complexes. Derivatives of the third-row element Hf have drawn much less attention, presumably due to the high stability of Hf–C bonds.[43] Nonetheless, recent publications have described nonmetallocene Hf complexes, which are highly active for olefin polymerization. These systems incorporated bis(phenoxy-imine) ligands (Fig. 1*a*),[44–47] first introduced by Mitsui

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researchers for the FI catalysts. In addition, researchers at Dow have described Hf systems based on the pyridyl-amido ligand depicted in Fig. 1*b*.[48–50] In this paper, we describe synthetic routes to a series of Hf–phosphinimide derivatives. The reactivity of these species with Lewis acid activators is considered and a preliminary evaluation of the polymerization activity is presented.

Experimental section

General considerations

All preparations were performed under an atmosphere of dry O_2-free N_2 employing either Schlenk-line techniques or a Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing Grubbs-type column systems manufactured by Innovative Technologies or were distilled from the appropriate drying agents under N_2. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300 and 500 spectrometers. Deuterated benzene, toluene, and methylene chloride were purchased from Cambridge Isotopes Laboratories, vacuum distilled from the appropriate drying agents, and freeze-pump-thaw degassed (three times). Trace amounts of protonated solvents were used as references, and ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, and ^{19}F NMR spectra were referenced to external 85% H_3PO_4, $BF_3{\cdot}Et_2O$, and $CFCl_3$, respectively. Combustion analyses were performed at the University of Windsor Chemical Laboratories employing a PerkinElmer CHN Analyzer. High temperature gel permeation chromatography (GPC) data were provided by the technical staff at NOVA Chemicals Corporation. *t*-Bu_3PNLi[51] and $(Me_3SiC_5H_4)HfCl_3$[52] were prepared as previously reported.

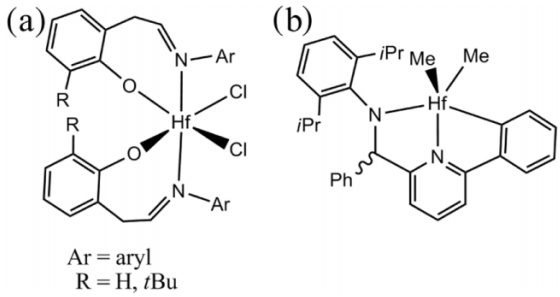
Synthesis of (*t*-Bu_3PN)$Hf(NEt_2)_3$ (1)

t-Bu_3PNH (0.46 g, 2.119 mmol) was dissolved in 5 mL of toluene and then added dropwise to a toluene solution (10 mL) containing $Hf(NEt_2)_4$ (1.0 g, 2.119 mmol) at room temperature. The light yellow solution was heated overnight at 70 °C. Toluene was removed under vacuum to give a crystalline white solid (1.27 g, 2.077 mmol, 96%). ^1H NMR (C_6D_6): 3.60 (q, ^3J = 7.3 Hz, 12H, NCH_2CH_3), 1.29 (t, ^3J = 7.3 Hz, 18H, NCH_2CH_3), 1.28 (d, $^3J_{PH}$ = 13.0 Hz, 27H, P-*t*-Bu). $^{13}C\{^1H\}$ NMR (C_6D_6): 44.3 (NCH_2CH_3), 40.4 (d, $^1J_{PC}$ = 48 Hz, P-*t*-*Bu*), 30.0 (P-*t*-Bu), 16.9 (NCH_2CH_3). ^{31}P NMR (C_6D_6): 38.5. Anal. calcd. for $C_{24}H_{57}N_4PHf$: C 47.16, H 9.40, N 9.17; found: C 46.88, H 9.24, N 9.59.

Synthesis of (*t*-$Bu_3PN)_2Hf(NEt_2)_2$ (2)

t-Bu_3PNH (0.93 g, 4.279 mmol) was dissolved in 5 mL of toluene and then added dropwise to toluene solution (10 mL) containing $Hf(NEt_2)_4$ (1.0 g, 2.119 mmol) at room temperature. The solution was refluxed for 12 h. Toluene was removed under vacuum to give an orange oil. It was dissolved in pentane (5 mL) and stirred for 10 min. Removing pentane under vacuum gave a colorless crystalline solid (1.55 g, 2.052 mmol, 96%). ^1H NMR (C_6D_6): 3.79 (q, ^3J = 7.3 Hz, 8H, NCH_2CH_3), 1.38 (d, $^3J_{PH}$ = 12.5 Hz, 54H, *t*-Bu), 1.36 (t, ^3J = 7.3 Hz, 12 H, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): 44.8 (NCH_2CH_3), 40.7 (d, $^1J_{PC}$ = 45 Hz, P-*t*-*Bu*), 30.4 (P-*t*-Bu), 16.9 (NCH_2CH_3). ^{31}P NMR (C_6D_6): 35.8.

Fig. 1. Recent examples of Hf olefin-polymerization catalysts.



Anal. calcd. for $C_{32}H_{74}N_4P_2Hf$: C 50.88, H 9.87, N 7.42; found: C 50.73, H 10.13, N 6.99.

Synthesis of (*t*-$Bu_3PN)_2HfCl_2$ (3)

Compound **2** (1.00 g, 1.323 mmol) was dissolved in 10 mL of toluene. Me_3SiCl (1.40 mL, 10.590 mmol) was added dropwise to the clear solution at room temperature. A white solid started forming in a few minutes. It was stirred for 8 h and the volatiles removed under vacuum. The white solid was washed with hexanes (5 mL) and then dried under vacuum (0.85 g, 1.257 mmol, 95%). ^1H NMR (C_6D_6): 1.28 (d, $^3J_{PH}$ = 10.0 Hz, 54H, P-*t*-Bu). $^{13}C\{^1H\}$ NMR (C_6D_6): 41.0 (d, $^1J_{PC}$ = 48 Hz, P-*t*-*Bu*), 30.0 (P-*t*-Bu). ^{31}P NMR (C_6D_6): 41.3. Anal. calcd. for $C_{24}H_{54}N_2P_2HfCl_2$: C 42.26, H 7.98, N 4.11; found: C 42.68, H 8.11, N 4.28.

Synthesis of (*t*-$Bu_3PN)_2HfMe_2$ (4)

Compound **3** (0.10 g, 0.147 mmol) was dissolved in 10 mL of diethyl ether. MeMgBr (3 mol/L, 0.19 mL; 0.588 mmol) was added dropwise at room temperature. The solution was stirred overnight and then pumped to dryness. The product was extracted with hot hexanes (10 mL) and then filtered through celite. Removing hexanes under vacuum gave a white solid (0.09 g, 0.145 mmol, 93%). ^1H NMR (C_6D_6): 1.33 (d, $^3J_{PH}$ = 10.5 Hz, 54H, P-*t*-Bu), 0.42 (s, 6H, $HfMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 41.6 ($HfMe_2$), 40.7 (d, $^1J_{PC}$ = 45 Hz, P-*t*-Bu), 30.1 (P-*t*-Bu). ^{31}P NMR (C_6D_6): 37.2. Anal. calcd. for $C_{26}H_{60}N_2P_2Hf$: C 48.70, H 9.43, N 4.37; found: C 48.54, H 9.79, N 4.28.

Synthesis of (*t*-$Bu_3PN)_3HfCl$ (5)

$HfCl_4$ (0.50 g, 1.561 mmol) was suspended in 5 mL of THF. *t*-Bu_3PNLi (1.05 g, 4.685 mmol) in 5 mL of THF was added quickly at room temperature. The suspension became clear within 30 min. It was stirred for another 8 h and the volatiles removed under vacuum. The product was dissolved in 15 mL of toluene and then filtered through celite. The solution was concentrated to ca. 3 mL and then stored in a freezer at −35 °C for 48 h. A white solid precipitated, which was isolated and dried under vacuum (0.83 g, 0.961 mmol, 62%). ^1H NMR (C_6D_6): 1.44 (d, $^3J_{PH}$ = 12.0 Hz, 81H, P-*t*-Bu). $^{13}C\{^1H\}$ NMR (C_6D_6): 41.1 (d, $^1J_{PC}$ = 45 Hz, P-*t*-Bu), 30.7 (P-*t*-Bu). ^{31}P NMR (C_6D_6): 36.0. Anal. calcd. for $C_{36}H_{81}N_3P_3HfCl$: C 50.11, H 9.46, N 4.87; found: C 50.13, H 9.71, N 4.95.

Synthesis of (*t*-$Bu_3PN)_3HfMe$ (6)

Compound **5** (0.20 g, 0.231 mmol) was dissolved in 5 mL of diethyl ether. MeMgBr (3 mol/L, 0.23 mL, 0.693 mmol)

was added dropwise at room temperature. The solution was stirred for 4 h and the volatiles removed under vacuum. The product was extracted with hexanes (2 × 5 mL) and then filtered through celite. Removing hexanes under vacuum gave a white solid (0.17 g, 0.201 mmol, 87%). ^{1}H NMR (C_6D_6): 1.44 (d, $^3J_{PH}$ = 12.0 Hz, 81H, P-*t*-Bu), 0.36 (s, 3H, HfMe). ^{13}C{^{1}H} NMR (C_6D_6): 41.0 (d, $^1J_{PC}$ = 45 Hz, P-*t-Bu*), 30.7 (P-*t*-Bu), 29.1 (HfMe). ^{31}P NMR (C_6D_6): 34.1. Anal. calcd. for $C_{37}H_{84}N_3P_3HfCl$: C 52.75, H 10.05, N 4.99; found: C 52.63, H 9.99, N 4.95.

Synthesis of Cp(*t*-Bu$_3$PN)$_2$HfCl (7)

Compound **3** (0.13 g, 0.191 mmol) was dissolved in 5 mL of THF. Solid CpNa (16.78 mg, 0.191 mmol) was added to the above at −35 °C. The solution was stirred at room temperature for 8 h and the volatiles removed under vacuum. The product was dissolved in 7 mL of toluene and then filtered through celite. Toluene was removed under vacuum to give a white solid (0.13 g, 0.183 mmol, 95%). ^{1}H NMR (C_6D_6): 6.57 (s, 5H, Cp), 1.31 (d, $^3J_{PH}$ = 12.5 Hz, 54H, P-*t*-Bu). ^{13}C{^{1}H} NMR (C_6D_6): 110.7 (Cp), 41.1 (d, $^1J_{PC}$ = 48 Hz, P-*t*-Bu), 30.4 (P-*t*-Bu). ^{31}P NMR (C_6D_6): 37.4. Anal. calcd. for $C_{29}H_{59}N_2P_2HfCl$: C 48.94, H 8.36, N 3.94; found: C 48.86, H 8.61, N 3.71.

Synthesis of Cp$_2$(*t*-Bu$_3$PN)HfCl (8)

Cp_2HfCl_2 (0.85 g, 2.24 mmol) was dissolved in 10 mL of THF. Solid *t*-Bu$_3$PNLi (0.50 g, 2.24 mmol) was added in portions at room temperature. The cloudy solution was stirred for 24 h and then pumped to dryness. The product was dissolved in 10 mL of toluene and then filtered through celite. The solution was concentrated to ~5 mL and then stored in a freezer at −35 °C for 48 h. A pale yellow solid precipitated, which was isolated and dried under vacuum (0.97 g, 1.73 mmol, 77%). ^{1}H NMR (C_6D_6): 6.15 (s, 10H, Cp), 1.18 (d, $^3J_{PH}$ = 12.5 Hz, 27H, P-*t*-Bu). ^{13}C{^{1}H} NMR (C_6D_6): 111.9 (s, Cp), 41.3 (d, $^1J_{PC}$ = 45 Hz, P-*t*-Bu), 30.3 (s, P-*t*-Bu). ^{31}P{^{1}H} NMR (C_6D_6): 40.8. Anal. calcd. for $C_{22}H_{37}NPHfCl$: C 47.15, H 6.65, N 2.50; found: C 46.90, H 6.30, N 2.23.

Synthesis of Cp*(*t*-Bu$_3$PN)HfCl$_2$ (9)

Cp*$HfCl_3$ (1.09 g, 2.595 mmol) was suspended in 10 mL of toluene. Solid *t*-Bu$_3$PNLi (0.58 g, 2.597 mmol) was added in portions at room temperature. The cloudy solution was stirred for 24 h and then filtered through celite. The solution was concentrated to ~5 mL and then stored in a freezer at −35 °C for 48 h. A white solid precipitated, which was isolated, washed with pentane, and then dried under vacuum (1.30 g, 2.163 mmol, 83%). ^{1}H NMR (C_6D_6): 2.19 (s, 15H, Cp*), 1.21 (d, $^3J_{PH}$ = 12.5 Hz, 27H, P-*t*-Bu). ^{13}C{^{1}H} NMR (C_6D_6): 121.0 (*Cp**), 41.3 (d, $^1J_{PC}$ = 45 Hz, P-*t-Bu*), 30.0 (P-*t*-Bu), 12.3 (Cp*). ^{31}P NMR (C_6D_6): 46.3. Anal. calcd. for $C_{22}H_{42}NPHfCl_2$: C 43.97, H 7.04, N 2.33; found: C 44.08, H 7.07, N 2.34.

Synthesis of Cp*(*i*-Pr$_3$PN)HfCl$_2$ (10)

Cp*$HfCl_3$ (0.11, 0.262 mmol) was suspended in 3 mL of toluene. Solid *i*-Pr$_3$PNLi (0.05 g, 0.276 mmol) was added in portions at room temperature. The cloudy solution was stirred overnight and then filtered through celite. Toluene was removed under vacuum to give a white solid (94 mg, 0.168 mmol, 64%). ^{1}H NMR (C_6D_6): 2.19 (s, 15H, Cp*), 1.64 (m, 3H, PC*H*), 0.95 (dd, $^3J_{PH}$ = 14.0 Hz, ^3J = 7.0 Hz, 18H, *i*-Pr). ^{13}C{^{1}H} NMR (C_6D_6): 120.9 (Cp*), 26.9 (d, $^1J_{PC}$ = 58 Hz, P*C*H), 17.3 (P-*i*-Pr), 12.3 (Cp*). ^{31}P NMR (C_6D_6): 35.3. Anal. calcd. for $C_{19}H_{36}NPHfCl_2$: C 40.83, H 6.49, N 2.51; found: C 41.22, H 6.64, N 2.48.

Synthesis of Cp*(*t*-Bu$_3$PN)Hf(NMe$_2$)$_2$ (11)

Compound **9** (100 mg, 0.166 mmol) was dissolved in 3 mL of THF. Me_2NLi (50 mg, 0.980 mmol) was dissolved in 3 mL of THF and then added dropwise to the above solution at room temperature. The solution was stirred for 36 h and the volatiles removed under vacuum. The product was extracted with hexanes (10 mL) and then filtered through celite. Hexanes were removed under vacuum to give a crystalline solid (91 mg, 0.147 mmol, 88%). ^{1}H NMR (C_6D_6): 3.10 (s, 12H, NMe_2), 2.19 (s, 15H, Cp*), 1.28 (d, $^3J_{PH}$ = 12.0 Hz, 27H, P-*t*-Bu). ^{13}C{^{1}H} NMR (C_6D_6): 116.9 (*Cp**), 46.4 (NMe_2), 40.3 (d, $^1J_{PC}$ = 45 Hz, P-*t-Bu*), 30.1 (P-*t*-Bu), 12.1 (Cp*). ^{31}P NMR (C_6D_6): 38.1. Anal. calcd. for $C_{26}H_{54}N_3PHf$: C 50.51, H 8.80, N 6.80; found: C 50.28, H 8.54, N 6.64.

Synthesis of Cp*(*t*-Bu$_3$PN)HfMe$_2$ (12)

Compound **9** (0.71 g, 1.181 mmol) was suspended in 8 mL of diethylether. MeMgBr (3 mol/L, 1.97 mL, 5.905 mmol) was added dropwise at room temperature. The cloudy solution was stirred for 12 h and the volatiles removed under vacuum. The product was extracted with hot hexanes (2 × 8 mL) and then filtered through celite. Removing hexanes under vacuum gave a white solid (0.62 g, 1.107 mmol, 95%). ^{1}H NMR (C_6D_6): 2.11 (s, 15H, Cp*), 1.24 (d, $^3J_{PH}$ = 11.0 Hz, 27H, P-*t*-Bu), −0.03 (s, 6H, $HfMe_2$). ^{13}C{^{1}H} NMR (C_6D_6): 116.5 (*Cp**), 41.7 ($HfMe_2$), 41.0 (d, $^1J_{PC}$ = 45 Hz, P-*t-Bu*), 30.1 (P-*t*-Bu), 11.9 (Cp*). ^{31}P NMR (C_6D_6): 40.3. Anal. calcd. for $C_{24}H_{48}HfNP$: C 51.46, H 8.64, N 2.50; found: C 51.07, H 8.59, N 2.43.

Synthesis of (Me$_3$Si)$_2$Cp(*t*-Bu$_3$PN)HfCl$_2$ (13)

$(Me_3Si)_2CpHfCl_3$ (0.10 g, 0.202 mmol) was dissolved in 5 mL of toluene. Solid *t*-Bu$_3$PNLi (0.45 g, 0.202 mmol) was added to the above at room temperature. The clear solution was stirred at room temperature for a week upon which it became cloudy and the volatiles removed under vacuum. The product was extracted with hot hexanes (5 mL) and then filtered through celite. Hexanes were removed to give a colorless oil, which solidified on standing for a few hours as a white material (0.08 g, 0.118 mmol, 59%). ^{1}H NMR (C_6D_6): 7.01 (t, ^4J = 2.1 Hz, 1H, H2 of Cp″), 6.81 (d, ^4J = 2.1 Hz, 2H, H3 and H4 of Cp″), 1.17 (d, $^3J_{PH}$ = 13.0 Hz, 27H, P-*t*-Bu), 0.46 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR (C_6D_6): C1, C2, and C3 of Cp″ not seen, 120.9 (C4 and C5 of Cp″), 41.4 (d, $^1J_{PC}$ = 45 Hz, P-*t-Bu*), 30.0 (P-*t*-Bu), 0.73 ($SiMe_3$). ^{31}P NMR (C_6D_6): 45.0. Anal. calcd. for $C_{23}H_{48}NPSi_2HfCl_2$: C 40.91, H 7.17, N 2.07; found: C 40.59, H 7.06, N 1.94.

Synthesis of (Me$_3$Si)$_2$Cp(*t*-Bu$_3$PN)HfMe$_2$ (14)

Compound **13** (0.15 g, 0.222 mmol) was dissolved in 3 mL of diethylether. MeMgBr (3 mol/L, 0.37 mL,

Table 1. Crystallographic data.

Crystal	**3**	**4**	**7**	**9**	**17** $0.5(C_6H_5Me)$
Formula	$C_{24}H_{54}Cl_2HfN_2P_2$	$C_{26}H_{60}HfN_2P_2$	$C_{36}H_{81}ClHfN_3P_3$	$C_{22}H_{42}Cl_2HfNP$	$C_{51.5}H_{62}B_2F_{20}HfN_2P_2$
Formula weight	682.02	641.19	862.89	600.93	1351.08
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	13.185(4)	13.2389(11)	21.720(6)	11.855(7)	15.423(10)
b (Å)	15.486(5)	16.5993(13)	12.784(4)	16.683(10)	15.819(5)
c (Å)	16.407(5)	15.5844(13)	17.046(5)	13.521(8)	24.116(10)
α (deg)	89.845(4)				
β (deg)	89.878(4)	106.5240(10)	108.883(3)	97.072(6)	102.001(19)
γ (deg)	73.037(4)				
V (Å^3)	3204.4(17)	3283.3(5)	4479(2)	2654(3)	5755(5)
Z	4	4	4	4	4
D(calcd.) (g cm^{-1})	1.414	1.297	1.280	1.504	1.545
Absorption coeff.,μ (cm^{-1})	3.536	3.289	2.521	4.200	2.013
Data collected	36389	31134	42099	22502	54604
Data $F_o^2 > 3\sigma(F_o^2)$	14392	5785	7884	4623	10154
Variables	559	280	397	244	712
R	0.0335	0.0240	0.0280	0.0630	0.0326
Rw	0.0792	0.0597	0.0825	0.1744	0.0816
GOF	1.043	1.037	0.762	1.297	1.029

Note: Data collected at 20 °C with Mo Kα radiation (λ = 0.71069 Å). $R = \Sigma(F_o - F_c)/\Sigma F_o$. $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]\}^{1/2}$

1.110 mmol) was added dropwise at room temperature. The solution was stirred for 8 h and the volatiles removed under vacuum. The product was extracted with hexanes (5 mL) and then filtered through celite. Hexanes were removed to give a crystalline white solid (0.12 g, 0.189 mmol, 86%). ^{1}H NMR (C_6D_6): 6.75 (t, ^4J = 1.6 Hz, 1H, H2 of Cp″), 6.54 (d, ^4J = 1.6 Hz, 2H, H3 and H4 of Cp″), 1.22 (d, $^3J_{PH}$ = 12.5 Hz, 27H, P-*t*-Bu), 0.38 (s, 18H, $SiMe_3$), 16 (s, 6H, $HfMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 125.2 (C1 and C3 of Cp″), 123.4 (C2 of Cp″), 41.1 (d, $^1J_{PC}$ = 47 Hz, P-*t-Bu*), 39.9 ($HfMe_2$), 30.1 (P-*t*-Bu), 1.0 ($SiMe_3$). ^{31}P NMR (C_6D_6): 39.8 Anal. calcd. for $C_{25}H_{54}NPSi_2Hf$: C 42.58, H 7.72, N 1.99; found: C 42.50, H 7.60, N 1.93.

Synthesis of Cp*(*t*-Bu$_3$PN)HfMe(THF)MeB(C$_6$F$_5$)$_3$ (15)

Compound **12** (50 mg, 0.089 mmol) was dissolved in 2 mL of CH_2Cl_2 containing 72 µL of THF (10 equiv.). $B(C_6F_5)_3$ (45 mg, 0.088 mmol) was dissolved in 2 mL of CH_2Cl_2 and then added dropwise to the above solution at room temperature. The colorless solution was stirred for 30 min and then pumped to dryness to give a white solid, washed with pentane (3 mL), and then dried under vacuum (91 mg, 0.079 mmol, 89%). ^{1}H NMR (CD_2Cl_2): 4.13 (br, 4H, OCH_2CH_2), 2.11 (s, 15H, Cp*), 2.03 (br, 4H, OCH_2CH_2), 1.39 (d, $^3J_{PH}$ = 13.5 Hz, 27H, P-*t*-Bu), 0.47 (br s, 3H, $MeB(C_6F_5)_3$), 0.27 (s, 3H, HfMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 149.0 (dm, $^1J_{CF}$ = 225 Hz, *o*-C_6F_5), 138.1 (dm, $^1J_{CF}$ = 240 Hz, *p*-C_6F_5), 137.1 (dm, $^1J_{CF}$ = 240 Hz, *m*-C_6F_5), 121.9 (*Cp**), 121.9 (*Cp**), 75.9 (OCH_2CH_2), 41.1 (d, $^1J_{PC}$ = 46 Hz, P-*t-Bu*), 29.8 (P-*t*-Bu), 29.1 (HfMe), 26.0 (OCH_2CH_2), 11.7 (Cp*), 11.0 (br, $CH_3B(C_6F_5)_3$). ^{19}F NMR (CD_2Cl_2, 282 MHz): −133.59 (d, $^3J_{FF}$ = 22 Hz, 6F, *o*-F), −165.71 (t, $^3J_{FF}$ = 20 Hz, 3F, *p*-F), −168.25 (m, 6F, *m*-F). ^{31}P NMR (CD_2Cl_2): 51.3. ^{11}B NMR (CD_2Cl_2, 96 MHz): −14.9. The extreme air sensitivity of this species precluded satisfactory elemental analysis.

Synthesis of (Cp*(*t*-Bu$_3$PN)HfMe)(B(C$_6$F$_5$)$_4$) (16)

Compound **12** (50 mg, 0.09 mmol) and $(Ph_3C)(B(C_6F_5)_4)$ (82 mg, 0.09 mmol) were dissolved in 2 mL of CH_2Cl_2 in two separate vials. The borate solution was added dropwise to the other at −35 °C. The clear yellow solution was stirred for 15 min and the volatiles removed under vacuum to give an orange foam. It was washed with benzene (3 × 3 mL) and then dried under vacuum for 12 h. ^{1}H NMR (CD_2Cl_2): 2.07 (s, 15H, Cp*), 1.40 (d, $^3J_{PH}$ = 13.0 Hz, 27H, *t*-Bu), 0.03 (s, HfMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 148.7 (d, $^1J_{CF}$ = 240 Hz, *o*-C_6F_5), 138.8 (dm, $^1J_{CF}$ = 240 Hz, *p*-C_6F_5), 136.9 (d, $^1J_{CF}$ = 247 Hz, *m*-C_6F_5), 120.1 (s, *Cp**), 41.8 (s, HfMe), 41.5 (d, $^1J_{PC}$ = 45 Hz, *t*-Bu), 30.0 (s, *t*-Bu), 11.7 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): −133.5 (s, 8F, *o*-F), −164.1 (t, $^3J_{FF}$ = 20 Hz, 4F, *p*-F), −168.0 (m, 8F, *m*-F). ^{31}P NMR (CD_2Cl_2): 48.2. ^{11}B NMR (CD_2Cl_2, 96 MHz): −16.9. The extreme air sensitivity of this species precluded satisfactory elemental analysis.

Synthesis of (*t*-Bu$_3$PN)$_2$Hf(H$_2$B(C$_6$F$_5$)$_2$)$_2$ (17)

Compound **4** (15 mg, 0.023 mmol) and $HB(C_6F_5)_2$ (33 mg, 0.093 mmol) were combined in a small vial containing 1 mL of benzene. The vial was capped and sonicated for 10 min at room temperature. The cloudy solution was heated at 50 °C for 30 min until it became clear. The product precipitated as colorless crystals on cooling to room temperature. The solvent was removed under vacuum to give a white solid. The solid was washed thoroughly with hexanes (5 × 2 mL) to remove $MeB(C_6F_5)_2$ and side products and then dried under vacuum (25 mg, 0.019 mmol, 83%). ^{1}H NMR (C_6D_6): 4.67 (br q, µ-H, J_{HB} = 65 Hz, 4H), 0.92 (d, $^3J_{PH}$ = 10 Hz, 54H, *t*-Bu). $^{13}C\{^1H\}$ NMR (C_6D_6): 148.3 (d, $^1J_{CF}$ = 241 Hz, *o*-C_6F_5), 139.5 (dm, $^1J_{CF}$ = 250 Hz, *p*-C_6F_5), 138.1 (d, $^1J_{CF}$ = 245 Hz, *m*-C_6F_5), 40.2 (d, $^1J_{PC}$ = 45 Hz, *t*-Bu), 29.2 (s, *t*-Bu). ^{19}F NMR (C_6D_6): −130.7 (s, 8F, *o*-F), −157.8 (t, $^3J_{FF}$ = 28 Hz, 4F, *p*-

F), −163.9 (m, 8F, *m*-F). ^{31}P NMR (C_6D_6): 47.2. ^{11}B NMR (C_6D_6): −15.0 (t, J_{BH} = 65 Hz). Anal. calcd. for $C_{48}H_{58}B_2F_{20}N_2P_2Hf$: C 44.18, H 4.48, N 2.15; found: C 44.09, H 4.33, N 2.03.

X-ray data collection and reduction

Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data ($4.5^\circ < 2\theta < 45^\circ - 50.0^\circ$) were collected in a hemisphere of data in 1329 frames with 10 s exposure times. The observed extinctions were consistent with the space groups in each case. A measure of decay was obtained by recollecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and SHELXTL processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package.

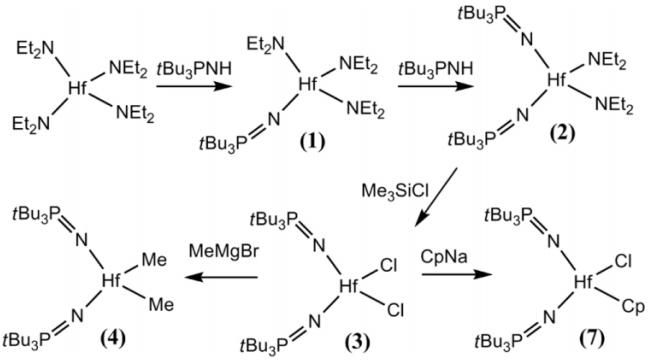
Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations.[53] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $\omega(F_o - F_c)^2$ where the weight, ω, is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the Supplementary data.

Polymerization protocol

For comparable results, routine standards were run regularly to ensure reproducibility. The polymerizations were performed in a 1 L Buchi reactor system. Following assembly, the reactor vessel and solvent storage unit were refilled with nitrogen via four refill and evacuation cycles over at least 90 min. Approximately 600 mL of toluene was transferred to the solvent storage container from the purification column. The solvent was purged with dry nitrogen for 20 min and then transferred to the reactor vessel by differential pressure. The solvent was stirred at 1500 ± 5 rpm and the temperature was kept constant at 30 ± 2 °C. The system was then exposed to ethylene via five vent and refill cycles. The precatalyst, cocatalyst, and scrubber stock solutions were freshly prepared and loaded into syringes in a glovebox, then transferred to the reactor immediately before injection to limit the possibility of catalyst decomposition. A prepared solution of TiBAl (3.0 mL) was injected into the reaction vessel through the catalyst injection inlet and allowed to stir for 5 min. The prepared precatalyst solution (1.0 mL) was injected, followed immediately with the injection of the $B(C_6F_5)_3$ solution (1.5 mL) into the reactor vessel. The mixture was stirred at 1500 ± 5 rpm at 30 °C under 2 atm (1 atm = 101.325 kPa) of dynamic ethylene flow for 10 min. The temperature and ethylene flow rate were recorded manually at regular intervals. After 5−10 min, the polymerization was stopped by closing the ethylene inlet valve and venting the reactor, the stirring was stopped, and the reactor was disassembled. The contents of the reactor were emptied into a 4 L beaker containing approximately 100 mL of 10% HCl (*v*/*v*) in MeOH. The precipitated polymer was collected by filtration, washed with toluene and acetone, and dried overnight. The resulting polymer was weighed and polymerization activity calculated.

Scheme 1. Synthetic routes to **1**−**4**.



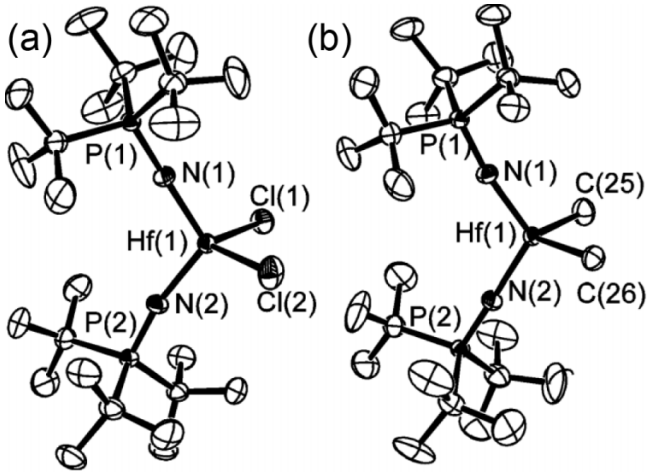
Results and discussion

The dehalosilylation reaction of silyl-phosphinimides and a titanium halide proved to be a simple and successful method for the preparation of titanium-phosphinimide complexes. However, this method does not work well for zirconium.[54] Previously, several phosphinimide complexes of Zr and Hf have been prepared at high temperature using an equimolar amount of KF to remove a N-silyl substituent as the by-product Me_3SiF.[54,55] However, the most convenient route to Zr compounds involves either salt metathesis (LiCl) or alkane or amine elimination. Thus, using these latter methods we targeted Hf−phosphinimide complexes.

The parent phosphinimine, *t*-Bu_3PNH, was reacted stoichiometrically with $Hf(NEt_2)_4$ to afford (*t*-Bu_3PN)$Hf(NEt_2)_3$ (**1**) in 96% yield (Scheme 1). Subsequent treatment of **1** with excess Me_3SiCl in an effort to affect amide cleavage and prepare (*t*-Bu_3PN)$HfCl_3$ proved to be problematic. Based on spectroscopic data it appeared Me_3SiCl effects nonselective Hf−N bond cleavage.

Similarly, reaction of *t*-Bu_3PNH with $Hf(NEt_2)_4$ in a 2:1 ratio afforded the species (*t*-$Bu_3PN)_2Hf(NEt_2)_2$ (**2**) in 96% yield. In contrast to the above species, **2** reacts cleanly at room temperature with excess Me_3SiCl to give (*t*-$Bu_3PN)_2HfCl_2$ (**3**). This compound showed a singlet at 41.3 ppm and a doublet at 1.28 ppm in the ^{31}P NMR and ^{1}H

Fig. 2. ORTEP drawings of (a) **3** and (b) **4**; 20% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): **3**: Hf(1)—N(2) 1.922(3), Hf(1)—N(1) 1.927(3), Hf(1)—Cl(1) 2.3855(13), Hf(1)—Cl(2) 2.3856(14), P(1)—N(1) 1.569(3), P(2)—N(2) 1.570(4); N(2)–Hf(1)–N(1) 111.22(15), N(2)–Hf(1)–Cl(1) 109.81(12), N(1)–Hf(1)–Cl(1) 108.87(12), N(2)–Hf(1)–Cl(2) 109.70(12), N(1)–Hf(1)–Cl(2) 109.89(12). Cl(1)–Hf(1)–Cl(2) 107.27(6), P(1)–N(1)–Hf(1) 175.0(3), P(2)–N(2)–Hf(1) 168.3(2); **4**: Hf(1)—N(2) 1.946(3), Hf(1)—N(1) 1.948(3), Hf(1)—C(26) 2.237(4), Hf(1)—C(25) 2.251(5), N(1)—P(1) 1.554(3), N(2)—P(2) 1.555(3); N(2)–Hf(1)–N(1) 114.92(13), N(2)–Hf(1)–C(26) 108.74(15), N(1)–Hf(1)–C(26) 110.11(15), N(2)–Hf(1)–C(25) 109.69(17), N(1)–Hf(1)–C(25) 109.06(18), C(26)–Hf(1)–C(25) 103.73(17), P(1)–N(1)–Hf(1) 170.8(2), P(2)–N(2)–Hf(1) 175.7(2).



NMR spectra, respectively. The pseudotetrahedral arrangement around Hf was confirmed by X-ray crystallography (Fig. 2*a*). The Hf–N distances were found to be 1.922(3) Å and 1.927(3) Å and the Hf–Cl distances were 2.3855(13) Å and 2.3856(14) Å. The P–N–Hf angles (175.0(3)° and 168.3(2) °) are approximately linear and typical of early metal phosphinimide complexes.[54,56] This geometry suggests the presence of some degree of multiple bonding character in the Hf–N bond.

Compound **3** was subsequently alkylated with MeMgBr to give (t-$Bu_3PN)_2HfMe_2$ (**4**) as a white solid in 93% yield. An upfield shift in ^{31}P NMR at 37.2 ppm is consistent with the presence of electron donating methyl substituents. The structure of **4**, determined by X-ray crystallography (Fig. 2*b*), was similar to **3**, although the Hf–N bonds were longer at 1.946(3) and 1.948(3) Å. In addition, the P–N bonds (1.554(3) and 1.555(3) Å) were shorter, a consequence of the more electron-rich Hf.

It has been previously shown that efforts to prepare Zr analogs of **3** and **4** employing (t-Bu_3PNLi) and $ZrCl_4$ were unsuccessful as the tris ligand complexes, (t-$Bu_3PN)_3ZrCl$, were preferentially formed.[36] In a similar fashion, reactions of the lithium phosphinimide with $HfCl_4$ in a 1:1 ratio did not give (t-$Bu_3PN)HfCl_3$. Instead, a product mixture was evidenced by ^{31}P NMR spectroscopy. However, by employing a 3:1 ratio of reagents the phosphinimide compound (t-$Bu_3PN)_3HfCl$ (**5**) was prepared and isolated in 62% yield. The structure of this white product (**5**) was also confirmed crystallographically (Fig. 3). The Hf–N bonds in

Scheme 2. Synthetic routes to **5** and **6**.

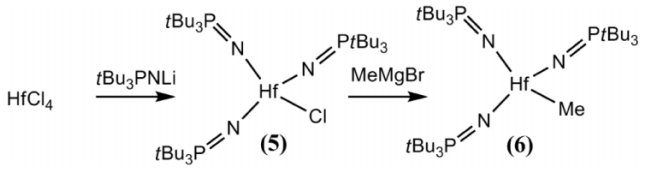
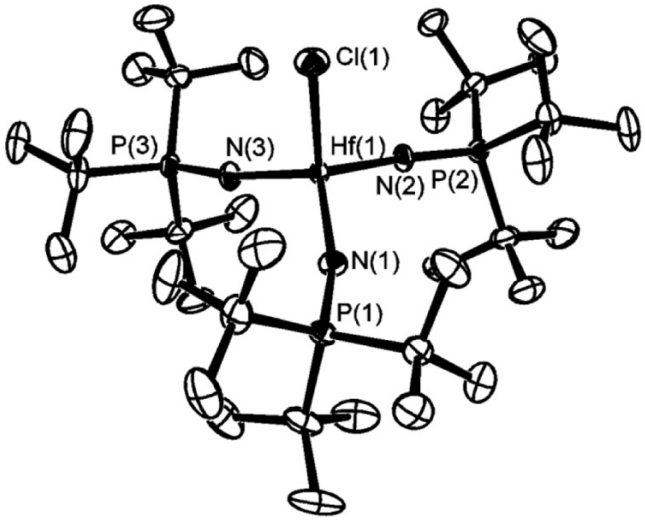


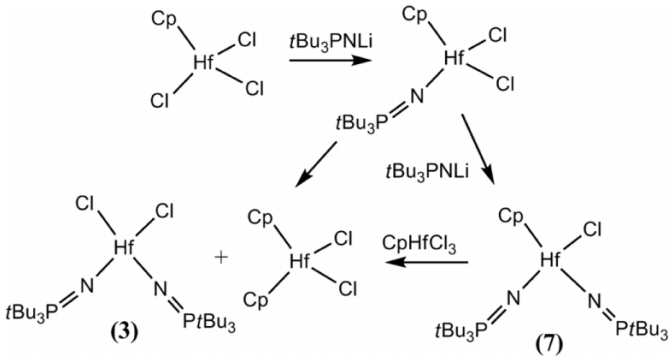
Fig. 3. ORTEP drawing of **5**; 20% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Hf(1)—N(3) 1.969(3), Hf(1)—N(2) 1.971(3), Hf(1)—N(1) 1.983(3), Hf(1)—Cl(1) 2.4272(13), P(1)—N(1) 1.551(4), P(2)—N(2) 1.557(3), P(3)—N(3) 1.561(3); N(3)–Hf(1)–N(2) 111.16(16), N(3)–Hf(1)–N(1) 112.93(16), N(2)–Hf(1)–N(1) 110.95(15), Hf(1)–Cl(1) 107.64(11), N(2)–Hf(1)–Cl(1) 106.50(11), N(1)–Hf(1)–Cl(1) 107.31(11), P(1)–N(1)–Hf(1) 164.8(2), P(2)–N(2)–Hf(1) 165.0(2), P(3)–N(3)–Hf(1) 168.1(2).



5 (1.969(3), 1.971(3), and 1.983(3) Å) were longer than those seen in **3**, presumably a result of reduced Lewis acidity and greater steric congestion at Hf. The methylated analog (t-$Bu_3PN)_3HfMe$ (**6**) was obtained from the treatment of **5** with MeMgBr. This species exhibited a sharp ^{31}P NMR signal at 34.1 ppm and two ^1H NMR signals, a doublet at 1.44 ppm for *tert*-butyl groups and a singlet at 0.36 ppm for methyl protons, consistent with the formulation.

Complexes of the form Cp(t-$Bu_3PN)MCl_2$ (M = Ti, Zr) have been shown to be active olefin polymerization catalysts.[30,56,57] Thus, the Hf analog was targeted. Reaction of 1equiv. of t-Bu_3PNLi with $CpHfCl_3$ was performed. The product showed a single ^{31}P NMR resonance at 41.3 ppm and two ^1H NMR signals, a singlet at 5.82 ppm for the cyclopentadienyl group and a doublet at 1.28 ppm for *tert*-butyl protons. The ^{31}P and ^1H NMR spectra for the phosphinimide ligand correspond to those observed for **3** while the ^1H NMR resonance attributed to the cyclopentadienyl group corresponds to that seen for Cp_2HfCl_2. Indeed, **3** was isolated as a crystalline product from this reaction mixture and its identity confirmed crystallographically. It is noteworthy that the reaction of $IndHfCl_3$ with t-Bu_3PNLi proceeding in a similar fashion yielded **3** and Ind_2HfCl_2. Attempts to probe the mechanism of this ligand redistribution reaction were

Scheme 3. Proposed ligand redistribution process to **3**.



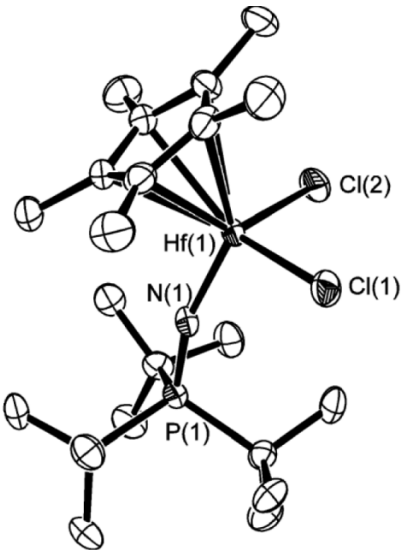
performed by a variable temperature ^{31}P NMR spectroscopy. Although solubility was problematic, on mixing at 15 °C, a broad resonance at 56.6 ppm was observed, which slowly transformed to a sharp signal at 41.3 ppm corresponding to **3**. One possible mechanism could involve metathesis generating Cp(*t*-Bu_3PN)$HfCl_2$,which then undergoes ligand redistribution to give (*t*-$Bu_3PN)_2HfCl_2$ and Cp_2HfCl_2. Alternatively, the improved solubility of Cp(*t*-Bu_3PN)$HfCl_2$ could result in a second metathesis to give Cp(*t*-$Bu_3PN)_2HfCl$, which could then react with $CpHfCl_3$ to give the two redistribution products (Scheme 3). This would suggest that the initial species giving rise to the resonance at 56.6 ppm could be Cp(*t*-Bu_3PN)$HfCl_2$, although the mechanistic details of this disproportionation were not confirmed.

The proposed intermediate in the latter mechanism, Cp(*t*-$Bu_3PN)_2HfCl$ (**7**), was prepared independently in 95% yield by treating (*t*-$Bu_3PN)_2HfCl_2$ with an equimolar amount of CpNa. Compound **7** gave rise to ^{31}P resonance at 37.4 ppm and a ^1H NMR signal at 6.57 ppm arising from the cyclopentadienyl protons. This species is stable on its own at elevated temperature. However, upon addition of a stoichiometric amount of $CpHfCl_3$, **7** reacts to give **3** and Cp_2HfCl_2, thus supporting the role of **7** in the ligand redistribution process described above. In a related and analogous synthesis, the species Cp_2(*t*-Bu_3PN)HfCl (**8**) was readily synthesized in 77% isolated yield by reacting Cp_2HfCl_2 with *t*-Bu_3PNLi.

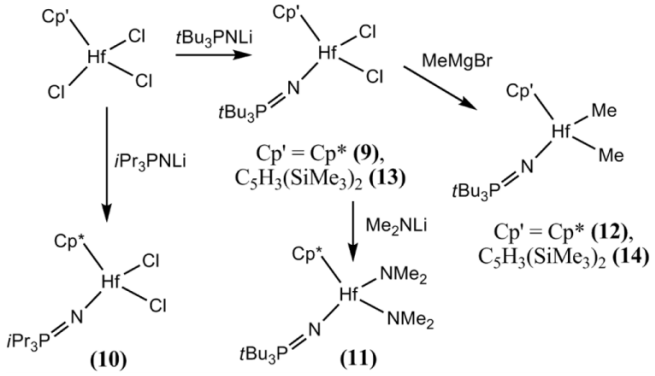
While the species Cp(*t*-Bu_3PN)$HfCl_2$ was not accessible, use of substituted cyclopentadienyl groups afforded the target species that were stable with respect to ligand redistribution. For example, Cp*$HfCl_3$ reacts with *t*-Bu_3PNLi smoothly to give Cp*(*t*-Bu_3PN)$HfCl_2$ (**9**) as evidenced by NMR data. The pseudotetrahedral arrangement about Hf was unambiguously confirmed by X-ray crystallography (Fig. 4). The Hf−N distance was found to be 1.925(7) Å while the Hf−Cl distances were 2.398(3) Å and 2.402(3) Å, which are quite similar to those in **3**. Additionally, the approximately linear P−N−Hf vector (163.2(4)°) in **9** is significantly larger than that observed in $(Hf_3Cl_6(NPMe_3)_5)^+(Hf_2Cl_7(NPMe_3)_2)^-$ (133.1(8)°, 125.9(6)°, and 132.6(8)°),[55] where the phosphinimide ligand bridges two Hf atoms.

In addition, reaction of Cp*$HfCl_3$ with *i*-Pr_3PNLi afforded Cp*(*i*-Pr_3PN)$HfCl_2$ (**10**). The ^1H NMR signal attributable to the Cp* group was observed at 2.19 ppm, downfield from that seen for Cp*$_2HfCl_2$ (1.88 ppm). The halide atoms in **9** could be readily replaced with amides or methyl groups via reaction with $LiNMe_2$ or MeMgBr, affording Cp*(*t*-$Bu_3PN)Hf(NMe_2)_2$ (**11**) and Cp*(*t*-Bu_3PN)$HfMe_2$ (**12**) in yields of 88% and 95%, respectively (Scheme 4).

Fig. 4. ORTEP drawing of **9**; 20% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Hf(1)—N(1) 1.925(7), Hf(1)—Cl(2) 2.398(3), Hf(1)—Cl(1) 2.402(3), N(1)—P(1) 1.574(8); N(1)−Hf(1)−Cl(2) 104.3(2), N(1)−Hf(1)−Cl(1) 103.3(2), Cl(2)−Hf(1)−Cl(1) 103.46(12), P(1)−N(1)−Hf(1) 163.2(4).



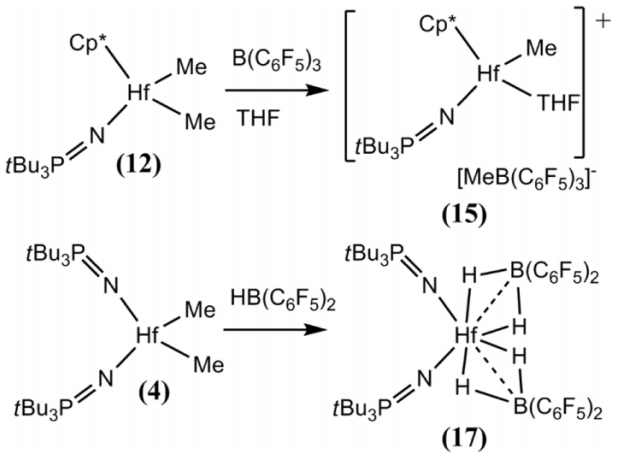
Scheme 4. Synthetic routes to **9**−**14**.



In a procedure similar to that employed for the synthesis of **8**, other cyclopentadienyl derivatives could be employed. For example, $((Me_3Si)_2C_5H_3)HfCl_3$ reacted stoichiometrically with *t*-Bu_3PNLi to form $((Me_3Si)_2C_5H_3)$(*t*-Bu_3PN)$HfCl_2$ (**13**). This reaction proceeded slowly, presumably as a result of the sterically demanding substituents on the Cp-ring. Nonetheless, this afforded **13** in 59% isolated yield. Compound **13** exhibits a sharp ^{31}P NMR signal at 45.0 ppm and four ^1H NMR resonances at 7.01, 6.81, 1.17, and 0.46 ppm attributable to the Cp, *tert*-butyl, and trimethylsilyl groups, respectively. This species was readily alkylated with MeMgBr to give $((Me_3Si)_2C_5H_3)$(*t*-Bu_3PN)$HfMe_2$ (**14**) as a crystalline white solid in a high yield of 86% (Scheme 4).

The reactions of Lewis acid activators are commonly used to generate cationic species, which serve as single-site catalysts in olefin polymerization.[58] Reaction of **12** with $B(C_6F_5)_3$ in CH_2Cl_2 under various conditions, showed no clear indica-

Scheme 5. Reactions of Hf−dialkyls with boranes.

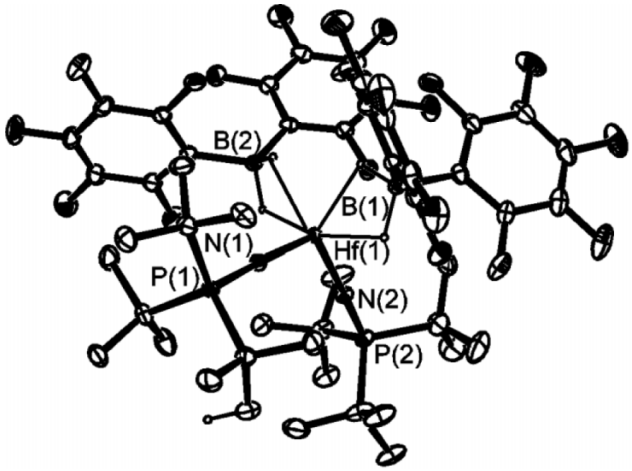


tion of the formation of a cationic species by NMR spectroscopy. However, reaction in the presence of THF afforded [Cp*(*t*-Bu_3PN)HfMe(THF)][$MeB(C_6F_5)_3$] (**15**) in 89% yield (Scheme 5). The ^{1}H NMR spectrum showed a broad singlet at 0.47 ppm attributable to the Me-B and a sharp singlet at 0.27 ppm attributable to the Hf−Me. The sharp ^{11}B NMR signal at −14.9 ppm confirmed a tetracoordinate boron environment.[59] In a similar fashion, methyl-abstraction by [Ph_3C][$B(C_6F_5)_4$] from **12** affords the cationic species [Cp*(*t*-Bu_3PN)HfMe][$B(C_6F_5)_4$] (**16**). In this species, the Hf−Me gave rise to a broad singlet at 0.03 ppm in the ^{1}H NMR spectrum, while a sharp ^{11}B NMR signal was observed at −16.9 ppm. This reactivity towards Lewis acids resembles that of the analogous Zr species, Cp(*t*-Bu_3PN)$ZrMe_2$.[60]

The corresponding reactions of **4** with $B(C_6F_5)_3$ or [Ph_3C][$B(C_6F_5)_4$] gave complex mixtures of unidentified products. However, **4** was found to react cleanly with $(C_6F_5)_2BH$ at room temperature. The resulting product was isolated as a white solid (**17**) in 89% yield. The ^{1}H NMR spectrum exhibited a resonance centered at 4.67 ppm consisting of four broad peaks separated by 65 Hz. The ^{11}B NMR showed a triplet at −15.00 ppm. This complex (**17**) was further confirmed by X-ray crystallography and confirmed to be (*t*-Bu_3PN)$_2$Hf($H_2B(C_6F_5)_2$)$_2$ (Scheme 5, Fig. 5). The Hf−N distances in **17** were found to be 1.909(3) Å and 1.921(3) Å, while the P−N−Hf angles were nearly linear at 177.4(2)° and 173.3(2)°. The Hf−B distances of 2.588(5) Å and 2.655(4) Å were consistent with the close proximity of one *ortho*-F of a C_6F_5 group (Hf···F 2.678(3) Å). This interaction was not seen in the related zirconocene complex, $Cp_2Zr(H_2B(C_6F_5)_2)_2$.[61]

Preliminary testing of the ability of compounds **3**, **9**, and **13** to effect ethylene polymerization was probed. The polymerizations were performed for 5 min at 30 °C, under 2 atm of ethylene, and using Al(*i*-Bu)$_3$ as a scavenger. Employing 500 equiv. of methylaluminoxane (MAO) as the alkylatingand activating reagent, negligible amounts of polyethylene were obtained. Similarly, using **12** and **14** while employing 2 equiv. of $B(C_6F_5)_3$ as the activator, no polymer formation occurred. However, activation of **12** and **14** with [Ph_3C][$B(C_6F_5)_4$] gave rise to activities of 5900 and 5800 g/mol/h/atm, respectively. This compares to 6400 and 8000 g/mol/h/atm, obtained for Cp_2HfMe_2 and Cp(*t*-Bu_3PN)$TiMe_2$, respectively, under the same condition. The insolubility of the resulting polyethylene, which precluded GPC data infers high molecular weight. Similar observations have been made for other phosphinimide-based olefin polymerization catalysts.[54]

Fig. 5. ORTEP drawing of **17**; 20% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Hf(1)—N(1) 1.909(3), Hf(1)—N(2) 1.921(3), Hf(1)—B(1) 2.588(5), Hf(1)—B(2) 2.655(4), Hf(1)—F(16) 2.678(3), P(1)—N(1) 1.594(3), P(2)—N(2) 1.587(3); N(1)−Hf(1)−N(2) 112.85(14), N(1)−Hf(1)−B(1) 104.05(14), N(2)−Hf(1)−B(1) 111.07(15), N(1)−Hf(1)−B(2) 101.36(14), N(2)−Hf(1)−B(2) 113.45(14), B(1)−Hf(1)−B(2) 113.32(15), P(1)−N(1)−Hf(1) 177.4(2), P(2)−N(2)−Hf(1) 173.3(2).



Conclusions

Phosphinimide complexes of hafnium can be synthesized either by salt metathesis or amine elimination. Cyclopentadienyl redistribution precludes the synthesis of Cp(*t*-Bu_3PN)$HfCl_2$, although use of bulkier substituted cyclopentadienyl ligands readily affords the analogous derivatives. Activation of several Hf−phosphinimide-dihalide species proved to be inactive in olefin polymerization upon activation by MAO. In contrast, activation of dimethyl analogs by [Ph_3C][$B(C_6F_5)_4$] generate catalysts of moderate activity.

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3979. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 732437−732441 contain the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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