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Main Group Heterocycles from Lithiated Phosphinimines

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Reaction of the phosphinimines $\mathrm{(Me)}\mathit{t}\mathrm{Bu_2PNSiMe_3}$ (**1**), $\mathrm{(Me)}\mathit{t}\mathrm{Bu_2PNC_6H_2Me_3}$ (**3**), and $\mathrm{(PhCH_2)}\mathit{t}\mathrm{Bu_2PNSiMe_3}$ (**6**) with *n*BuLi and subsequently $\mathrm{(C_6F_5)_2BCl}$ affords the four-membered heterocycles $[((\mathrm{C_6F_5})_2\mathrm{BCH_2})\mathit{t}\mathrm{Bu_2PNSiMe_3}]$ (**2**), $[((\mathrm{C_6F_5})_2\mathrm{BCH_2})\mathit{t}\mathrm{Bu_2PNC_6H_2Me_3}]$ (**5**), and $[((\mathrm{C_6F_5})_2\mathrm{BCH(Ph)})\mathit{t}\text{-}\mathrm{Bu_2PNSiMe_3}]$ (**7**), respectively. The related phosphinimine $(\mathit{i}\mathrm{Pr})\mathit{t}\mathrm{Bu_2PNSiMe_3}$ (**8**) reacts with *t*BuLi to give $(\mathrm{LiCMe_2})\mathit{t}\mathrm{Bu_2PNSiMe_3}$ (**9**), which reacts with $\mathrm{(C_6F_5)_2BCl}$ to yield the five-membered heterocycle $[((\mathrm{C_6F_5})_2\mathrm{BCH_2CH(Me)})\mathit{t}\mathrm{Bu_2PNSiMe_3}]$ (**10**). Similarly, the species $[(\mathrm{Me_2AlCMe_2})\mathit{i}\mathrm{Pr_2PNSiMe_3}]$ (**12**) and $[((\mathrm{Me_2N})_2\mathrm{BCMe_2})\mathit{i}\mathrm{Pr_2PNSiMe_3}]$ (**13**) were prepared from lithiation of the phosphinimine $\mathit{i}\mathrm{Pr_3PNSiMe_3}$ (**11**). In exploring the chemistry of these heterocycles, compound **2** reacts with $[\mathrm{Me_3NH}]\mathrm{Cl}$ and MeOH to open the heterocycle, giving $[(\mathrm{C_6F_5})_2\mathrm{B(Cl)CH_2P}\mathit{t}\mathrm{Bu_2NH(SiMe_3)}]$ (**14**) and $((\mathrm{C_6F_5})_2\mathrm{B(OMe)CH_2})\mathit{t}\mathrm{Bu_2PNH_2}$ (**15**), respectively. Subsequent treatment of **15** with $\mathrm{Me_3SiCl}$ affords the species $((\mathrm{C_6F_5})_2\mathrm{B(Cl)CH_2})\mathit{t}\mathrm{Bu_2PNH_2}$ (**16**), while treatment of **16** with *n*BuLi gives $[((\mathrm{C_6F_5})_2\mathrm{BCH_2})\mathit{t}\mathrm{Bu_2PNH})]$ (**17**). Compound **17** coordinates $\mathrm{AlMe_3}$ to give $((\mathrm{C_6F_5})_2\mathrm{BCH_2})\mathit{t}\mathrm{Bu_2PNH}](\mathrm{AlMe_3})$ (**18**), while **15** reacts with $\mathrm{AlMe_3}$ to give the six-membered heterocycle $[((\mathrm{C_6F_5})_2\mathrm{B(OMe)CH_2})\mathit{t}\mathrm{Bu_2PNH})(\mathrm{AlMe_2})]$ (**19**). This chemistry is discussed and the implications are considered. X-ray crystallographic data are reported for **2**, **5**, **7**, **9**, **10**, **14**, and **17**.

Introduction

Studies over the last decade of the chemistry of transition metal phosphinimide and phosphinimine complexes have led to the development of highly effective olefin polymerization catalysts,[1] as well as the unique chemistry of chelated carbenoid complexes.[2−5] The corresponding development of the chemistry of main group phosphinimines and phosphinimides has drawn much less attention. Ten years ago, Dehnicke and co-workers reviewed the older literature concerning main group phosphinimine derivatives.[6] More recently, the work by Meyer and co-workers[7,8] has elegantly demonstrated that phosphinimines can participate in metathesis chemistry and catalyze imine/imine and imine/carbodiimine cross-metathesis. Our own work has probed the structural and chemical behavior of Li,[9] Mg,[10,11] Si, Sn, and Ge[12] phosphinimide derivatives. For these latter compounds, methyl abstraction from Si and Sn was shown to yield a variety of cationic derivatives depending on the bulk of the substituents on P.

More recently, our interests have focused on group 13 species, as only a few phosphinimine or phosphinimide derivatives were known. Some years ago, Dehnicke and co-workers reported several boron−phosphinimides derivatives including $[(\mathrm{Et_3PN})_2\mathrm{B})_2]^{2+}$,[13] $[(\mathrm{Et_3PNBH})_3]^{3+}$,[14] $[(\mathrm{Et_3PNBH})_4\mathrm{NPEt_3}]^{3+}$,[15] and $[(\mathrm{Ph_3PN})_3\mathrm{B}]$.[16] In more recent efforts, we have reported the spontaneous formation of $[(\mathit{t}\mathrm{Bu_3PN})_2\mathrm{B}]\mathrm{Cl}$.[17] The novel linear structure of this borinium cation salt results from the steric demands of the substituents on P. The related chemistry of Al−phosphinimide complexes results in dimeric products, presumably a consequence of the larger metal center.[18,19] The impact of steric demands is also seen in the reactions of catechol and pinachol boranes with phosphinimines,[20,21] as bulk appears to control the formation of the monomeric and dimeric complexes of the form $\mathrm{R_3PNB(O_2C_2Me_4)}$ and $[\mathrm{R_3PNB(O_2C_6H_4)}]_2$, respectively. In this report, we have devised synthetic routes to group 13 four-membered phosphinimine heterocycles and demonstrate that steric effects can lead to ring expansion to a five-membered heterocycle. In addition, the reactivity of selected heterocycles is explored and the expansion to a six-membered heterocycle achieved.

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Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an MBraun or Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing a Grubbs-type solvent purification system manufactured by Innovative Technologies. All organic reagents were purified by conventional methods. Deuterated benzene and toluene were purchased from Cambridge Isotopes Laboratories, vacuum distilled from the appropriate drying agents and freeze−pump−thaw degassed (3×). C_6D_6 was used to record the NMR spectra unless otherwise indicated. For ^1H and $^{13}C\{^1H\}$ NMR spectra, trace amounts of protonated solvents were used as references, and NMR chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra are referenced to 85% H_3PO_4, $^{11}B\{^1H\}$ NMR spectra are referenced to $BF_3{\cdot}OEt_2$, and ^{19}F NMR spectra are referenced to CCl_3F. Combustion analyses were performed at the University of Windsor Chemical Laboratories. In some instances several repeated analyses were required as a result of the moisture and air sensitivity of the compounds. $(C_6F_5)_2BCl$ was prepared by literature methods. $BrB(NMe_2)_2$ and $ClAlMe_2$ were purchased from Strem Chemical Co. (Me)*t*$Bu_2PNSiMe_3$ (**1**),[1] $(PhCH_2)$*t*$Bu_2PNSiMe_3$ (**6**),[22] and *i*$Pr_3PNSiMe_3$ (**11**) were prepared by literature methods.[23]

Synthesis of (*i*Pr)*t*Bu$_2$PNSiMe$_3$, 8. N_3SiMe_3 (0.78 mL; 5.877 mmol) was added to (*i*Pr)*t*Bu_2P (1.000 g; 5.316 mmol) in 15 mL of toluene at 25 °C. The off-white solution was heated with stirring at 100 °C for 5 h. The solvent was removed under vacuum to give a pale yellow oil, **8** (1.300 g; 93%). ^1H NMR: 1.88 (m, 1H, C*H*Me$_2$), 1.13 (dd, $^3J_{HH} = 7$ Hz, $^3J_{PH} = 6$ Hz, 6H, PCH*Me*$_2$), 1.09 (d, $^3J_{PH} = 13$ Hz, 18H, *t*Bu, 0.40 (s, 9H, SiMe$_3$). $^{13}C\{^1H\}$ NMR: 38.2 (d, $^1J_{PC} = 59$, *t*Bu), 29.4 (d, $^1J_{PC} = 56$, P*C*HMe$_2$), 28.5 (s, *t*Bu), 20.09 (s, PCHMe$_2$), 5.2 (s, SiMe$_3$). ^{31}P NMR: 29.2. Anal. Calcd for $C_{14}H_{34}NPSi$: C, 61.04; H, 12.44; N, 5.08. Found: C, 60.57; H, 12.77; N, 4.96.

Synthesis of [((C$_6$F$_5$)$_2$BCH$_2$)*t*Bu$_2$PNSiMe$_3$], 2. *n*BuLi (2.5 M) (0.09 mL; 0.225 mmol) was added slowly at 25 °C to a toluene solution (5 mL) of **1** (0.048 g; 0.197 mmol). The pale yellow solution was stirred for 1 h. $(C_6F_5)_2BCl$ (0.075 g; 0.197 mmol) was dissolved in 3 mL of toluene, then added dropwise to the above solution and stirred for 3 h. LiCl was removed by filtration through Celite, and toluene was removed under vacuum to give a crystalline solid, which was washed with hexanes (2 × 2 mL) and dried under vacuum to give a yellowish solid (0.105 g, 92%). ^1H NMR: 1.77 (d, $^2J_{PH} = 11$ Hz, 2H, C*H*$_2$), 0.83 (d, $^3J_{PH} = 15$ Hz, 18H, *t*Bu), 0.11 (s, 9H, SiMe$_3$). $^{13}C\{^1H\}$ NMR: 148.0 (d, $^1J_{CF} = 234.9$ Hz, *o*-C$_6$F$_5$), 140.1 (d, $^1J_{CF} = 257$, *p*-C$_6$F$_5$), 137.9 (d, $^1J_{CF} = 250$, *m*-C$_6$F$_5$), 38.0 (d, $^1J_{PC} = 31$, *t*Bu), 27.3 (s, *t*Bu, 10.21 (br, *C*H$_2$), 4.5 (SiMe$_3$). ^{19}F NMR: −131.21 (d, $^3J_{FF} = 11$, 4F, *o*-F), −165.10 (t, $^3J_{FF} = 10$, 2F, *p*-F), −171.58 (m, 4F, *m*-F). ^{31}P NMR: δ 94.1. ^{11}B NMR: −3.2. Anal. Calcd for $C_{24}H_{29}BF_{10}NPSi$: C, 48.75; H, 4.94; N, 2.37. Found: C, 48.79; H, 5.22; N, 2.88.

Synthesis of (Me)*t*Bu$_2$PNC$_6$H$_2$Me$_3$, 3. $N_3C_6H_2Me_3$ (1.26 mL; 7.821 mmol) was dissolved in 5 mL of toluene, then added slowly to a toluene solution (10 mL) of (Me)*t*Bu_2P (1.145 g; 7.153 mmol) at 25 °C. A slow bubbling was observed. The solution was heated with stirring at 80 °C for 2 h. Toluene was removed under vacuum to give a tan solid (1.900 g, 90%). ^1H NMR: 6.98 (s, 2H, Ph), 2.38 (s, 6H, *o*-Me), 2.32 (s, 3H, *p*-Me), 1.15 (d, $^2J_{PH} = 10$, 3H, PMe), 1.03 (d, $^3J_{PH} = 13$, 18H, *t*Bu). $^{13}C\{^1H\}$ NMR: 147.3, 130.3, 129.7 (*C*H, Ph), 125.79, 37.7 (d, $^1J_{PC} = 69$, *t*Bu, 27.7 (s, *t*Bu), 22.5 (s, 2C, *o*-Me), 21.2 (s, *p-Me*), 10.9 (d, $^1J_{PC} = 45$, PMe). ^{31}P NMR: 12.8. Anal. Calcd for $C_{18}H_{32}NP$: C, 73.68; H, 10.99; N, 4.77. Found: C, 73.71; H, 11.53; N, 4.43.

Synthesis of (LiCH$_2$)*t*Bu$_2$PNC$_6$H$_2$Me$_3$, 4. *n*BuLi (2.5 M) (0.17 mL; 0.425 mmol) was added slowly at 25 °C to a toluene solution (5 mL) of **2** (0.114 g; 0.388 mmol). The pale yellow solution turned orange upon addition. It was stirred for 2 h before removing toluene under vacuum to give a yellow solid (0.110 g, 94%). ^1H NMR: 6.94 (s, 2H, Ph), 2.46 (s, 6H, *o*-Me), 2.25 (s, 3H, *p*-Me), 1.19 (d, $^3J_{PH} = 12$, 18H, *t*Bu), −0.68 (d, $^2J_{PH} = 10$, 2H, PC*H*$_2$Li). $^{13}C\{^1H\}$ NMR: 149.1, 132.7, 130.1, 38.6 (d, $^1J_{PC} = 46$, *t*Bu), 28.8 (s, *t*Bu), 22.6 (s, 2C, *o*-Me), 21.11 (s, *p*-Me), −1.4 (d, $^1J_{PC} = 55$, P*C*H$_2$Li). ^{31}P NMR: 55.2. Anal. Calcd for $C_{18}H_{31}NPLi$: C, 72.22; H, 10.44; N, 4.68. Found: C, 72.19; H, 10.97; N, 4.18.

Synthesis of [((C$_6$F$_5$)$_2$BCH$_2$)*t*Bu$_2$PNC$_6$H$_2$Me$_3$], 5. $(C_6F_5)_2BCl$ (0.099 g; 0.260 mmol) was dissolved in 3 mL of toluene, then added dropwise to a toluene solution (5 mL) of **3** at 25 °C. The solution was stirred for 3 h. LiCl was removed by filtration through Celite and toluene under vacuum to give a tan solid. It was further washed with pentane (3 × 3 mL) and dried under vacuum (0.130 g, 79%). ^1H NMR (CD_2Cl_2): 6.79 (s, 2H, Ph), 2.29 (d, $^2J_{PH} = 10$, 2H, C*H*$_2$), 2.21 (s, 9H, *o*-Me and *p*-Me), 1.39 (d, $^3J_{PH} = 14$, 18H, *t*Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 147.7 (d, $^1J_{CF} = 240$, *o*-C$_6$F$_5$), 139.6 (d, $^1J_{CF} = 257$, *p*-C$_6$F$_5$), 137.4 (d, $^1J_{CF} = 250$, *m*-C$_6$F$_5$), 139.7, 136.4, 134.8, 130.8, 40.4 (d, $^1J_{PC} = 26$, *t*Bu), 29.0 (s, *t*Bu), 23.3 (s, 2C, *o-Me*), 20.6 (s, *p-Me*), 9.6 (br, *C*H$_2$). ^{19}F NMR (CD_2Cl_2): −127.82 (s, 2F, *o*-F), −135.51 (s, 2F, *o*-F), −161.16 (t, $J_{FF} = 20$, 2F, *p*-F), −165.49 (m, 2F, *m*-F), −165.85 (m, 2F, *m*-F). ^{31}P NMR (CD_2Cl_2): 94.8. ^{11}B NMR (CD_2Cl_2): −0.4. Anal. Calcd for $C_{30}H_{31}BF_{10}NP$: C, 56.53; H, 4.90; N, 2.20. Found: C, 56.75; H, 5.44; N, 1.78.

Synthesis of [(C$_6$F$_5$)$_2$BCH(Ph))*t*Bu$_2$PNSiMe$_3$], 7. *n*BuLi (2.5 M) (0.110 mL; 0.275 mmol) was added slowly at room temperature to a toluene solution (5 mL) of **6** (0.082 g; 0.253 mmol). The pale yellow solution was stirred for 3 h. $(C_6F_5)_2BCl$ (0.096 g; 0.253 mmol) was dissolved in 3 mL of toluene, then added slowly to the above solution. The resulting solution was stirred for another 3 h. LiCl was removed by filtration through Celite, and toluene was removed under vacuum. The orange solid was washed with hexanes (2 × 3 mL) and dried under vacuum (0.137 g, 81%). ^1H NMR: 6.90 (m, 5H, Ph), 4.93 (d, $^2J_{PH} = 21$, 1H, PC*H*), 1.04 (d, $^3J_{PH} = 14$, 9H, *t*Bu), 0.94 (d, $^3J_{PH} =15$, 9H, *t*Bu), 0.21 (s, 9H, SiMe$_3$). $^{13}C\{^1H\}$ NMR: 148.8 (d, $^1J_{CF} = 233$, C$_6$F$_5$), 147.6 (d, $^1J_{CF} = 246$, C$_6$F$_5$), 140.2 (d, $^1J_{CF} = 244$, C$_6$F$_5$), 138.1 (d, $^1J_{CF} = 250$, C$_6$F$_5$), 137.9 (d, $J = 11$, Ph), 131.5 (d, $J = 7$, Ph), 126.7, 41.6 (d, $^1J_{PC} = 29$, *t*Bu), 40.5 (d, $^1J_{PC} = 24$, *t*Bu), 33.2 (br, *C*H), 28.86 (s, *t*Bu), 28.0 (s, *t*Bu), 5.1 (s, SiMe$_3$). ^{19}F NMR: −128.46 (d, $^3J_{FF} = 20$, 2F, *o*-F), −129.56 (br, 2F, *o*-F), −157.80 (t, $^3J_{FF} = 20$,1F, *p*-F), −159.19 (t, $^3J_{FF} = 20$, 1F, *p*-F), −164.44 (m, 2F, *m*-F), −164.97 (m, 2F, *m*-F). ^{31}P NMR: 93.4. ^{11}B NMR: 0.0. Anal. Calcd for $C_{30}H_{33}BF_{10}NPSi$: C, 53.99; H, 4.98; N, 2.10. Found: C, 54.03; H, 5.51; N, 1.85.

Synthesis of [(LiCMe$_2$)*t*Bu$_2$PNSiMe$_3$]$_2$, 9. *t*BuLi (1.7 M) (3.0 mL; 5.1 mmol) was added slowly to a hexanes solution (8 mL) of **8** (1.200 g; 4.360 mmol) at 25 °C. The pale yellow solution was stirred overnight to form a white precipitate. Cooling the mixture at −35 °C precipitated most of the product, which was filtered and washed with cold pentane (2 × 3 mL) and dried under vacuum (0.800 g, 65%). ^1H NMR: 1.74 (d, $^3J_{PH} = 17$, 6H, CMe$_2$), 1.19 (d, $^3J_{PH} =11$ Hz, 18H, *t*Bu), 0.36 (s, 9H, SiMe$_3$). $^{13}C\{^1H\}$ NMR: 39.81 (d, $^1J_{PC} = 46$, *t*Bu), 29.41 (s, *t*Bu), 24.6 (s, CMe$_2$), 17.32 (d, $^1J_{PC} = 64$, P*C*Me$_2$), 6.55 (SiMe$_3$). ^{31}P NMR: 50.2. Anal. Calcd for $C_{14}H_{33}NPSiLi$: C, 59.75; H, 11.82; N, 4.98. Found: C, 60.20; H, 11.95; N, 4.89.

Synthesis of [((C$_6$F$_5$)$_2$BCH$_2$CH(Me))*t*Bu$_2$PNSiMe$_3$], 10. $(C_6F_5)_2BCl$ (0.142 g; 0.373 mmol) was dissolved in 5 mL of toluene, then added dropwise to a toluene solution (5 mL) of **9** (0.105 g; 0.373 mmol) at 25 °C. The solution was stirred for 6 h. LiCl was removed by filtration through Celite, and toluene was removed under vacuum to give a crystalline solid, which was washed with hexanes (2 × 3

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mL) and dried under vacuum to give a white solid (0.156 g, 67%). ^{1}H NMR: 2.79 (m, C*H*), 2.02 (m, C*H*$_2$), 1.06 (dd, $^3J_{HH}$ = 7, $^3J_{PH}$ = 7, 3H, Me), 0.95 (d, $^3J_{PH}$ = 14, 9H, *t*Bu), 0.91 (d, $^3J_{PH}$ = 14, 9H, *t*Bu), 0.09 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR: 139.3 (d, $^1J_{CF}$ = 242, C$_6$F$_5$), 137.9 (d, $^1J_{CF}$ = 237, C$_6$F$_5$), 39.5 (d, $^1J_{PC}$ = 40, *t*Bu), 38.8 (d, $^1J_{PC}$ = 40, *t*Bu), 34.6 (d, $^1J_{PC}$ = 55, P*C*HMe), 29.6 (s, *t*Bu), 28.7 (s, *t*Bu), 19.8 (s, PCH*Me*), 6.9 (s, SiMe$_3$). ^{19}F NMR: −129.40 (br, 4F, *o*-F), −159.31 (t, $^3J_{FF}$ = 21, 1F, *p*-F), −161.23 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-F), −165.43 (br, 4F, *m*-F). ^{31}P NMR: 90.1. ^{11}B NMR: −1.5. Anal. Calcd for $C_{26}H_{33}BF_{10}NPSi$: C, 50.42; H, 5.37; N, 2.26. Found: C, 50.58; H, 5.19; N, 2.39.

Synthesis of [(Me$_2$AlCMe$_2$)*i*Pr$_2$PNSiMe$_3$], 12, and [((Me$_2$N)$_2$BCMe$_2$)*i*Pr$_2$PNSiMe$_3$], 13. These compounds were prepared in a similar fashion, and thus only one preparation is detailed. A solution of *n*BuLi (4.40 mL; 8.81 mmol) in hexanes was added dropwise to a solution of **11** (1.816 g; 7.34 mmol) in toluene (30 mL) at 25 °C. After stirring for 12 h, the clear yellow solution was cooled to −78 °C and (Me$_2$N)$_2$BBr (1.04 mL, 7.34 mmol) was added dropwise over a 15 min period. The slurry was gradually warmed to 25 °C and stirred for an additional 12 h. The mixture was passed through Celite, and the volatile products were removed *in vacuo*. The thick oil **13** was washed with cold pentanes (3 × 1 mL) and dried (1.740 g, 67%). **12**: Yield: 0.341 g, 54%. ^{1}H NMR: 1.78 (m, 2H, CMe$_2$H), 1.42 (d, 6H, $^3J_{P-H}$ = 19, CMe$_2$), 0.95 (dd, 6H, $^3J_{P-H}$ = 15, $^3J_{H-H}$ = 7, CMe$_2$H), 0.92 (dd, 6H, $^3J_{P-H}$ = 15, $^3J_{H-H}$ = 7, CMe$_2$H), 0.15 (s, 9H, SiMe$_3$), −0.36 (s, 6H, AlMe$_2$). ^{13}C{^{1}H} NMR: 26.8 (d, $^1J_{P-C}$ = 42, CMe$_2$H), 23.8 (br, CMe$_2$), 22.2 (s, CMe$_2$), 17.4 (s, CMe$_2$H), 16.7 (s, CMe$_2$H), 3.4 (s, SiMe$_3$), −7.5 (br, AlMe$_2$). ^{31}P{^{1}H} NMR: 60.4. ^{27}Al NMR: 168.0 (br, $\nu_{1/2} \approx 2500$ Hz). Anal. Calcd for $C_{15}H_{37}AlNPSi$: C, 56.74; H, 11.74; N, 4.41. Found: C, 56.58; H, 11.49; N, 4.39. **13**: ^{1}H NMR: 2.82 (s, 12H, NMe), 2.00 (sep, 2H, $^3J_{H-H}$ = 7, CMe$_2$H), 1.19 (dd, 6H, $^3J_{P-H}$ = 14, $^3J_{H-H}$ = 7, CMe$_2$H), 1.15 (d, 6H, $^3J_{P-H}$ = 15, CMe$_2$), 1.01 (dd, 6H, $^3J_{P-H}$ = 14, $^3J_{H-H}$ = 7, CMe$_2$H), 0.19 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR: 40.8 (s, NMe), 29.0 (d, $^1J_{P-C}$ = 56, CMe$_2$H), 27.5 (d, $^1J_{P-C}$ = 59, CMe$_2$), 21.6 (s, CMe$_2$H), 19.0 (d, $^2J_{P-C}$ = 2 Hz, CMe$_2$), 18.4 (s, CMe$_2$H), −0.42 (s, SiMe$_3$). ^{31}P{^{1}H} NMR: 18.0. ^{11}B{^{1}H} NMR: 25.3. Anal. Calcd for $C_{16}H_{41}BN_3PSi$: C, 55.64; H, 11.96; N, 12.17. Found: C, 55.58; H, 11.77; N, 12.09.

Synthesis of [((C$_6$F$_5$)$_2$B(Cl)CH$_2$)*t*Bu$_2$PNH(SiMe$_3$)], 14. Compound **2** (0.350 g; 0.591 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$, then added to a CH$_2$Cl$_2$ solution of [Me$_3$NH]Cl (0.073 g; 0.763 mmol) at 25 °C. After stirring the solution for 24 h, the solvent was removed under vacuum to give a white solid. The solid was washed with toluene (3 × 5mL), then dried under vacuum (0.270 g; 0.43 mmol; 73%). ^{1}H NMR: 5.04 (d, $^2J_{PH}$ = 12, N*H*), 2.09 (d, $^2J_{PH}$ = 11, 2H, C*H*$_2$), 0.66 (d, $^3J_{PH}$ = 14, 18H, *t*Bu), 0.09 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR: 148.5 (d, $^1J_{CF}$ = 240, *o*-C$_6$F$_5$), 140.1 (d, $^1J_{CF}$ = 248, *p*-C$_6$F$_5$), 138.0 (d, $^1J_{CF}$ = 266, *m*-C$_6$F$_5$), 36.1 (d, $^1J_{PC}$ = 48, *t*Bu), 26.6 (s, *t*Bu), 14.6 (br, *C*H$_2$), 2.7 (s, SiMe$_3$). ^{19}F NMR: −132.46 (d, $^3J_{FF}$ = 18, 4F, *o*-F), −159.47 (t, $^3J_{FF}$ = 20, 2F, *p*-F), −164.86 (m, 4F, *m*-F). ^{31}P NMR: 77.6. ^{11}B NMR: −4.3. Anal. Calcd for $C_{24}H_{30}BF_{10}NPSi$: C, 45.91; H, 4.82; N, 2.23. Found: C, 45.72; H, 5.22; N, 2.55.

Synthesis of ((C$_6$F$_5$)$_2$B(OMe)CH$_2$)*t*Bu$_2$PNH$_2$, 15. Compound **2** (1.00 g; 1.69 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$. Then 35 mL of dry methanol was added, and the resulting cloudy solution was stirred at room temperature for 24 h. The solvent and excess methanol were removed under vacuum to give a white solid (0.850 g; 1.54 mmol; 91%). ^{1}H NMR (C$_6$D$_6$): 3.22 (s, 3H, OMe), 3.05 (s, 2H, N*H*$_2$), 1.50 (m, 2H, PC*H*$_2$), 0.55 (d, $^3J_{PH}$ = 14 Hz, 9H, *t*Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 149.2 (d, $^1J_{CF}$ = 234 Hz, *o*-C$_6$F$_5$), 139.8 (d, $^1J_{CF}$ = 247 Hz, *p*-C$_6$F$_5$), 137.87 (d, $^1J_{CF}$ = 245 Hz, *m*-C$_6$F$_5$), 52.9 (s, OMe), 34.84 (d, $^1J_{PC}$ = 49 Hz, *t*Bu), 25.81 (s, *t*Bu), 8.21 (br, P*C*H$_2$). ^{19}F NMR (C$_6$D$_6$): −134.5 (d, $^3J_{FF}$ = 17 Hz, 4F, *o*-F), −160.5 (t, $^3J_{FF}$ = 20 Hz, 2F, *p*-F), −165.2 (m, 4F, *m*-F). ^{31}P NMR (C$_6$D$_6$): 74.6. ^{11}B NMR (C$_6$D$_6$): −1.3. Anal. Calcd for $C_{22}H_{25}BF_{10}NOP$: C, 47.94; H, 4.57; N, 2.54. Found: C, 48.27; H, 4.75; N, 2.55.

Synthesis of ((C$_6$F$_5$)$_2$B(Cl)CH$_2$)*t*Bu$_2$PNH$_2$, 16. Compound **15** (0.330 g; 1.81 mmol) was dissolved in 7 mL of Me$_3$SiCl. The clear solution was stirred at room temperature for 24 h. The excess solvent was removed under vacuum to give a white solid, which was washed by pentane and dried under vacuum (0.31 g; 0.56 mmol; 93%). ^{1}H NMR (C$_6$D$_6$): 2.62 (bs, 2H, N*H*$_2$), 1.99 (d, $^2J_{PH}$ = 11 Hz, 2H, C*H*$_2$), 0.53 (d, $^3J_{PH}$ = 15 Hz, 9H, *t*Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 148.6 (d, $^1J_{CF}$ = 244 Hz, *o*-C$_6$F$_5$), 140.0 (d, $^1J_{CF}$ = 250 Hz, *p*-C$_6$F$_5$), 138.0 (d, $^1J_{CF}$ = 244 Hz, *m*-C$_6$F$_5$), 124.3 (br, ipso-C), 35.08 (d, $^1J_{PC}$ = 48 Hz, *t*Bu), 25.8 (s, *t*Bu), 11.2 (br, *C*H$_2$). ^{19}F NMR (C$_6$D$_6$): −132.8 (d, $^3J_{FF}$ = 20 Hz, 4F, *o*-F), −159.7 (t, $^3J_{FF}$ = 20 Hz, 2F, *p*-F), −165.1 (m, 4F, *m*-F). ^{31}P NMR (C$_6$D$_6$): 72.6. ^{11}B NMR (C$_6$D$_6$): −4.8. Anal. Calcd for $C_{21}H_{22}BF_{10}NPCl$: C, 45.39; H, 3.99; N, 2.52. Found: C, 45.27; H, 3.75; N, 2.55.

Synthesis of [((C$_6$F$_5$)$_2$BCH$_2$)*t*Bu$_2$PNH)], 17. Compound **16** (0.080 g; 0.14 mmol) was dissolved in 5 mL of toluene. *n*BuLi (2.5 M) (0.06 mL; 0.15 mmol) was added dropwise at room temperature. The clear solution turned cloudy due to LiCl formation. After stirring for 6 h, the LiCl was removed by filtration through Celite and toluene by vacuum to give a white solid (0.069 g; 0.13 mmol; 93%). ^{1}H NMR (C$_6$D$_6$): 1.99 (bs, 2H, N*H*), 1.58 (d, $^2J_{PH}$ = 10 Hz, 2H, C*H*$_2$), 0.57 (d, $^3J_{PH}$ = 14 Hz, 9H, *t*Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 147.9 (d, $^1J_{CF}$ = 242 Hz, *o*-C$_6$F$_5$), 140.0 (d, $^1J_{CF}$ = 248 Hz, *p*-C$_6$F$_5$), 137.85 (d, $^1J_{CF}$ = 249 Hz, *m*-C$_6$F$_5$), 35.6 (d, $^1J_{PC}$ = 35 Hz, *t*Bu), 25.5 (s, *t*Bu), 7.55 (br, *C*H$_2$). ^{19}F NMR (C$_6$D$_6$): −136.2 (br, 4F, *o*-F), −160.1 (t, $^3J_{FF}$ = 20 Hz, 2F, *p*-F), −164.47 (m, 4F, *m*-F). ^{31}P NMR (C$_6$D$_6$): 89.7. ^{11}B NMR (C$_6$D$_6$): −4.7. Anal. Calcd for $C_{21}H_{21}BF_{10}NP$: C, 48.58; H, 4.08; N, 2.70. Found: C, 48.82; H, 4.40; N, 2.71.

Synthesis of [((C$_6$F$_5$)$_2$BCH$_2$)*t*Bu$_2$PNH](AlMe$_3$), 18. Compound **17** (65 mg; 0.13 mmol) was dissolved in 5 mL of toluene, then cooled to −35 °C. AlMe$_3$ (14.3 μL; 0.15mmol) was added dropwise at the same temperature. After stirring the solution for 1 h, toluene was removed by vacuum to give a white solid, which was washed with pentane and dried under vacuum (0.067 g; 0.11 mmol; 90%). ^{1}H NMR (C$_6$D$_6$): 1.77 (br s, N*H*), 1.38 (d, $^2J_{PH}$ = 16 Hz, 2H, C*H*$_2$), 0.70 (s, 6H, AlMe$_2$), 0.64 (d, $^3J_{PH}$ = 15 Hz, 9H, *t*Bu), 0.14 (s, 3H, AlMe). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 150.5 (d, $^1J_{CF}$ = 233 Hz, *o*-C$_6$F$_5$), 140.8 (d, $^1J_{CF}$ = 287 Hz, *p*-C$_6$F$_5$), 137.5 (d, $^1J_{CF}$ = 279 Hz, *m*-C$_6$F$_5$), 36.3 (d, $^1J_{PC}$ = 51 Hz, *t*Bu), 26.7 (s, *t*Bu), 17.3. ^{19}F NMR (C$_6$D$_6$): −123.32 (d, $^3J_{FF}$ = 16 Hz, 4F, *o*-F), −156.48 (t, $^3J_{FF}$ = 18 Hz, 2F, *p*-F), −162.61 (m, 4F, *m*-F). ^{31}P NMR (C$_6$D$_6$): 74.2. ^{11}B NMR (C$_6$D$_6$): 83.9 (br). Anal. Calcd for $C_{24}H_{30}BF_{10}NPAl$: C, 48.75; H, 5.11; N, 2.37. Found: C, 48.57; H, 4.75; N, 2.22.

Synthesis of [(((C$_6$F$_5$)$_2$B(OMe)CH$_2$)*t*Bu$_2$PNH)(AlMe$_2$)], 19. Compound **15** (0.250 g; 0.450 mmol) was dissolved in 5 mL of toluene, then cooled to −35 °C. AlMe$_3$ (48 μL; 0.50 mmol) was added dropwise. Gas evolution was observed. After stirring the solution for 2 h, toluene was removed by vacuum to give a white solid, which was washed with pentane and dried under vacuum (0.230 g; 0.38 mmol; 84%). ^{1}H NMR (C$_6$D$_6$): 3.05 (s, 3H, OMe), 1.58 (d, $^2J_{PH}$ = 17 Hz, 2H, C*H*$_2$), 0.55 (d, $^3J_{PH}$ = 14 Hz, 9H, *t*Bu), −0.35 (s, 6H, AlMe). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 148.9 (d, $^1J_{CF}$ = 237 Hz, *o*-C$_6$F$_5$), 140.5 (d, $^1J_{CF}$ = 251 Hz, *p*-C$_6$F$_5$), 138.0 (d, $^1J_{CF}$ = 268 Hz, *m*-C$_6$F$_5$), 55.48(s, OMe), 35.87 (d, $^1J_{PC}$ = 49 Hz, *t*Bu), 26.5 (s, *t*Bu), 8.90 (br, *C*H$_2$), −8.0 (s, AlMe). ^{19}F NMR (C$_6$D$_6$): −133.40 (d, $^3J_{FF}$ = 18 Hz, 4F, *o*-F), −157.74 (t, $^3J_{FF}$ = 18 Hz, 2F, *p*-F), −163.87 (m, 4F, *m*-F). ^{31}P NMR (C$_6$D$_6$): 69.1. ^{11}B NMR (C$_6$D$_6$): 0.41. Anal. Calcd for $C_{24}H_{30}BF_{10}NOPAl$: C, 47.47; H, 4.98; N, 2.31. Found: C, 47.27; H, 4.75; N, 2.21.

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

Table 1. Crystallographic Data

	2	**5**	**7**	**9**	**10**	**14**	**17**
formula	$C_{24}H_{29}BF_{10}NPSi$	$C_{36}H_{37}BF_{10}NP$	$C_{30}H_{33}BF_{10}NPSi$	$C_{14}H_{31}LiNPSi$	$C_{26}H_{33}BF_{10}NPSi$	$C_{24}H_{30}BClF_{10}NPSi$	$C_{21}H_{21}BF_{10}NP$
fw	591.35	715.45	667.44	276.40	619.40	627.81	519.17
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	Cc	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	9.6071(6)	12.351(2)	9.709(1)	15.672(2)	17.277(4)	11.825(7)	9.455(2)
b (Å)	14.981(1)	23.052(4)	17.605(2)	13.783(2)	8.500(2)	15.730(9)	24.569(5)
c (Å)	19.199(1)	12.236(2)	10.186(1)	18.216(3)	19.357(4)	16.85(1)	20.408(4)
β (deg)		94.344(2)	113.078(1)	111.900(2)	95.428(3)	110.55(1)	99.463(2)
V (Å^3)	2763.3(3)	3473.7(9)	1601.7(3)	3650.9(9)	2830(1)	2934(3)	4677(2)
Z	4	4	2	8	4	4	8
D(calc) (g cm^{-1})	1.421	1.368	1.384	1.017	1.454	1.421	1.475
abs coeff, μ (cm^{-1})	0.225	0.160	0.203	0.202	0.223	0.305	0.206
no. of data collected	13 711	16 594	15 528	34 494	26 232	14 212	43 972
data $F_o^2 > 3\sigma(F_o^2)$	3956	6101	5636	6429	4968	4257	8224
no. of variables	343	407	393	325	361	352	613
R	0.0321	0.0512	0.0445	0.0596	0.0484	0.0527	0.0794
R_w	0.0809	0.1344	0.1131	0.1555	0.1195	0.1147	0.1857
GOF	1.039	1.018	1.011	1.021	1.017	0.733	1.062

were performed on a Siemens SMART System CCD diffractometer. The data 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. The data sets were collected (4.5° $< 2\theta <$ 45−50.0°). A measure of decay was obtained by re-collecting 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 XPREP 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.

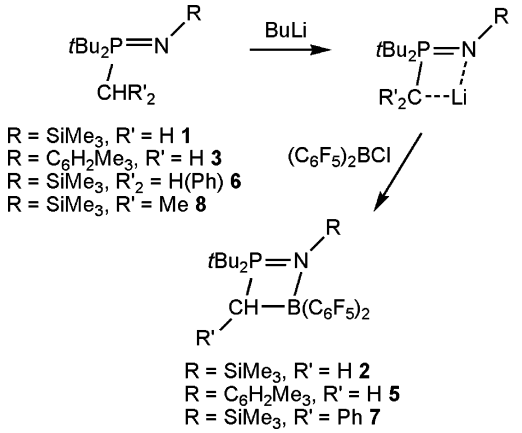
Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[24] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight w 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. 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. For compound **7**, the refinement revealed the presence of a racemic twin. 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 Supporting Information.

Results and Discussion

Reaction of the phosphinimine (Me)tBu$_2$PNSiMe$_3$ (**1**) with nBuLi has been previously shown to generate the species known to generate [(LiCH$_2$)tBu$_2$PNSiMe$_3$].[25] *In situ* generation of this species and subsequent reaction with $(C_6F_5)_2BCl$ results in the isolation of a new product (**2**) in 92% isolated yield (Scheme 1). Compound **2** exhibits ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra consistent with reaction constituents; however they provide no definitive structural information. The ^{31}P NMR spectrum showed a single resonance at 94.1 ppm as well as a ^{11}B NMR resonance at −3.23 ppm. The latter signal suggests the presence of a four-coordinate B atom. An X-ray crystallographic study of **2** (Figure 1) confirmed the formulation of **1** as [((C$_6$F$_5$)$_2$BCH$_2$)tBu$_2$-PNSiMe$_3$]. The core of this molecule is a B−N−P−C four-membered heterocyclic ring. The B−C and B−N distances are 1.661(4) and 1.638(3) Å, respectively, while the P−C and P−N distances are 1.651(2) and 1.775(3) Å, respectively. The B−N distance is longer than the corresponding B−N distance of 1.585(8) and 1.614(4) Å, found in phosphinimine adducts (R$_3$-PNH)B(C$_6$F$_5$)$_3$ (R = iPr, tBu)[19] and the borinium cation [(tBu$_3$-PN)$_2$B]$^+$ (1.41(1) Å).[17] This observation reflects the strain of the four-membered ring. These four atoms are approximately coplanar, with the largest deviation from coplanarity being 0.002 Å. The angles within the core are all approximately 90°: specifically the N−P−C angle is 88.9(1)°, the B−N−P angle is 91.40(13)°, the N−B−C angle is 93.4(2)°, and the B−C−P angle is 86.4(2)°. This geometry dictates a transanular P−B distance of 2.354(3) Å. The exocyclic silyl substituent gives rise to a Si−N distance of 1.768(2) Å and B−N−Si and P−N−Si angles of 134.9(2)° and 132.2(1)°, respectively.

The analogous aryl-substituted phosphinimine (Me)tBu$_2$-PNC$_6$H$_2$Me$_3$ (**3**) was prepared via oxidation of the phosphine (Me)tBu$_2$P with N$_3$C$_6$H$_2$Me$_3$ in 90% isolated yield. This species exhibited the expected downfield shift in the ^{31}P NMR resonance, giving a resonance at 12.8 ppm. Treatment of **3** with nBuLi results in a orange solution arising from deprotonation of the methyl group on P, affording the reagent (LiCH$_2$)tBu$_2$-PNC$_6$H$_2$Me$_3$ (**4**). This salt was isolated as a yellow solid in 94%

Scheme 1



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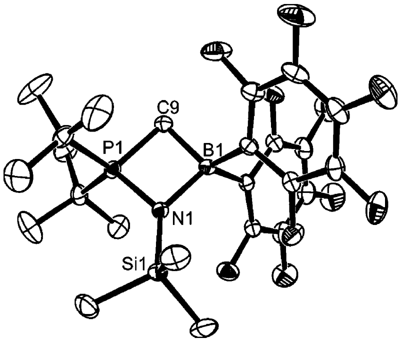


Figure 1. ORTEP drawing of **2**; 30% ellipsoids are shown, H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)−N(1) 1.768(2), P(1)−N(1) 1.6505(19), P(1)−C(9) 1.775(3), P(1)−B(1) 2.354(3), N(1)−B(1) 1.638(3), B(1)−C(9) 1.661(4), N(1)−P(1)−C(9) 88.87(11), B(1)−N(1)−P(1) 91.40(13), B(1)−N(1)−Si(1) 134.91(16), P(1)−N(1)−Si(1) 132.19(12), N(1)−B(1)−C(9) 93.35(18), B(1)−C(9)−P(1) 86.37(15).

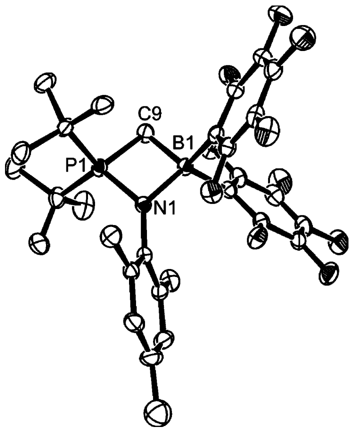


Figure 2. ORTEP drawing of **5**; 30% ellipsoids are shown, H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−N(1) 1.664(3), P(1)−C(9) 1.773(4), P(1)−B(1) 2.384-(4), N(1)−B(1) 1.634(5), C(9)−B(1) 1.659(5), N(1)−P(1)−C(9) 86.58(16), B(1)−N(1)−P(1) 92.6(2), B(1)−C(9)−P(1) 87.9(2), N(1)−B(1)−C(9) 91.4(3).

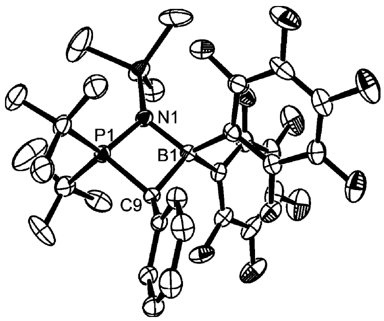


Figure 3. ORTEP drawing of **7**; 30% ellipsoids are shown, H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−N(1) 1.652(3), P(1)−C(9) 1.811(3), P(1)−B(1) 2.369-(3), Si(1)−N(1) 1.770(3), N(1)−B(1) 1.622(4), B(1)−C(9) 1.678-(4), N(1)−P(1)−C(9) 88.00(13), B(1)−N(1)−P(1) 92.74(17), N(1)−B(1)−C(9) 93.7(2), B(1)−C(9)−P(1) 85.47(17).

yield. The species **4** exhibits a ^{31}P NMR resonance at 55.2 ppm and a ^{1}H NMR doublet at −0.68 ppm arising from the methylene fragment. The corresponding ^{13}C{^{1}H} NMR resonance was observed at −1.41 ppm with P−C coupling of 55 Hz. Reaction of **4** with $(C_6F_5)_2BCl$ results in the formation of a new species (**5**) that was subsequently isolated in 79% yield as a tan solid (Scheme 1). The ^{1}H NMR data revealed resonances arising from the precursor **4**, although the signal corresponding to the methylene protons was shifted to 2.29 ppm, consistent with alkylation of B. The ^{13}C{^{1}H} and ^{19}F NMR spectra were consistent with the presence of phosphinimine and boron precursors. Similar to **2**, the ^{31}P NMR spectrum of **5** gave a resonance at 94.8 ppm, while the corresponding ^{11}B NMR signal was seen at −0.4 ppm. The nature of **5** was unambiguously confirmed as $[((C_6F_5)_2BCH_2)t\mathrm{Bu}_2PNC_6H_2Me_3]$ via X-ray crystallography (Figure 2). Similar to **2**, the core of compound **5** is a B−P−N−C four-membered ring. The core metric parameters in **5** are similar to those seen in **2**, as the P−N, P−C, B−C, and B−N distances were found to be 1.664(3), 1.772(4), 1.659-(5), and 1.635(5) Å, respectively, while the N−P−C, B−N−P, B−C−P, and N−B−C angles are 86.6(2)°, 92.6(2)°, 87.9(2)°, and 91.4(3)°, respectively. It is noteworthy that replacement of $SiMe_3$ in **2** with the aryl substituent on N in **5** has a minimal impact on the P−N or B−N distances. Despite these metric similarities to **2**, the largest deviation from B−P−N−C coplanarity in **5** is 0.0704 Å, significantly larger than that seen in **2**. In a similar fashion, the P−B trans-ring distance of 2.384(4) Å in **5** is longer than that seen in **2**. These distortions are thought to occur in response to steric conflicts between the aryl substituent on N and the adjacent substituents on P and B. Similarly, these conflicts result in the orientation of the plane of the N-aryl ring at an angle of 71.5° with respect to the mean B−P−N−C plane.

The benzyl-substituted *N*-silylphosphinimine $(PhCH_2)t\mathrm{Bu}_2$-$PNSiMe_3$ (**6**) was prepared in a fashion similar to **1**. Lithiation with *n*BuLi at 25 °C and subsequent treatment with $(C_6F_5)_2$-BCl resulted in the formation and isolation of the new species **7** in 81% yield (Scheme 1). The ^{1}H NMR data for **7** were consistent with the borylation of the benzylic carbon of **6**, as the resulting methine carbon gave rise to a doublet at 4.93 ppm with a coupling of 21 Hz. The corresponding ^{13}C{^{1}H} NMR resonance was observed at 33.17 ppm. The ^{19}F NMR spectrum was indicative of the presence of the $(C_6F_5)_2B$ fragment, while the ^{31}P signal at 93.4 ppm and the ^{11}B resonance at 0.0 ppm were also consistent with the formulation of **7** as $[((C_6F_5)_2BCH$-$(Ph))t$-$\mathrm{Bu}_2PNSiMe_3]$ (Scheme 1). An X-ray crystallographic study of **7** confirmed that this molecule contained a four-membered B−N−P−C ring (Figure 3). While the P−N distance in **7** (1.652(3) Å) is similar to that seen in **2** and **5**, the P−C distance in the four-membered ring of **7** is significantly longer at 1.811(3) Å. In a similar fashion, the B−C in **7** of 1.678(4) Å is slightly longer than those in **2** and **5**, while the B−N distance of 1.622(4) Å is slightly shorter. These perturbations to the metric parameters about the B−N−P−C core reflect steric congestion resulting from the phenyl substituent on C. The N−P−C, B−N−P, B−C−P, and N−B−C angles within the four-membered ring of **7** were found to be 88.0(1)°, 92.7(2)°, 85.5(2)°, and 93.7(2)°, respectively. Interestingly, the largest deviations of these angles from those in **2** and **5** are the decrease in the angle at C and the corresponding increase at B. These changes presumably accommodate the steric demands of the substituent on C while maintaining the B−N donor−acceptor coordination. Despite these variations the B−N−P−C core is essential planar, with the largest deviation from coplanarity being 0.0143 Å. This geometry prompts a transannular P−B distance of 2.369(3) Å in **7**, which is only slightly longer than that seen in **2**.

The related phosphinimine $(i\mathrm{Pr})t\mathrm{Bu}_2PNSiMe_3$ (**8**) was prepared in the conventional fashion as described above. Reaction

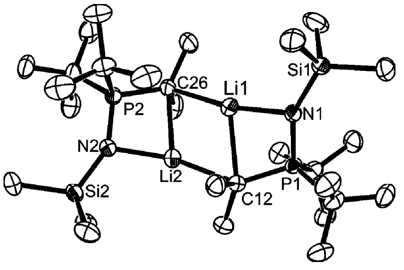
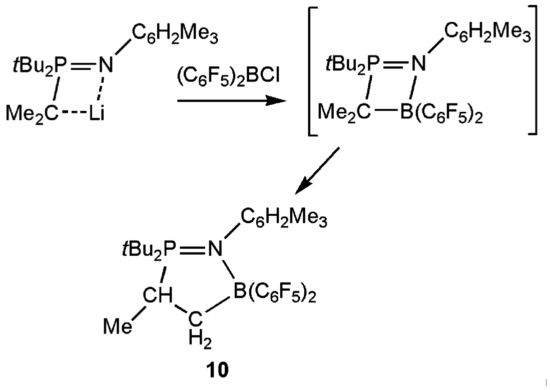


Figure 4. ORTEP drawing of **9**; 30% ellipsoids are shown, H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−N(1) 1.592(3), P(2)−N(2) 1.591(3), P(1)−C(9) 1.767(4), P(2)−C(23) 1.779(4), Si(1)−N(1) 1.682(3), Si(2)−N(2) 1.687(3), N(1)−Li(1) 1.980(7), N(2)−Li(2) 1.980(7), Li(1)−C(23) 2.234(7), Li(1)−C(9) 2.306(7), Li(2)−C(9) 2.202(7), Li(2)−C(23) 2.238(8), N(1)−P(1)−C(9) 105.95(16), P(1)−N(1)−Li(1) 92.6(2), N(1)−Li(1)−C(9) 77.1(2), P(1)−C(9)−Li(1) 78.0(2), N(2)−P(2)−C(23) 105.27(16), P(2)−N(2)−Li(2) 93.3(2), N(2)−Li(2)−C(23) 78.7(3), P(2)−C(23)−Li(2) 80.1(2).

Scheme 2



of **8** with *t*BuLi in hexanes proceeded to give a white precipitate (**9**) with the empirical formula (LiCMe$_2$)*t*Bu$_2$PNSiMe$_3$ in 65% yield. ^{1}H NMR data confirmed deprotonation of the isopropyl group, as evidenced by the doublet at 1.74 ppm attributable to the *gem*-dimethyl groups. The corresponding methyl resonance was observed at 24.6 ppm in the ^{13}C{^{1}H} NMR spectrum. The formation of the Li salt **9** also gave rise to a downfield ^{31}P NMR signal at 50.2 ppm. The absence of coordinating solvent suggests that **9** may be an oligomer. X-ray quality crystals were grown from hexanes, and a crystallographic study revealed that indeed **9** is formulated as the dimer [(LiCMe$_2$)*t*Bu$_2$PNSiMe$_3$]$_2$ in the solid state (Figure 4). This structure consists of two four-membered P−N−Li−C rings, in which the Li and C atoms bridge to the adjacent C and Li atom, respectively, thus forming a "ladder" of three consecutive four-membered rings. Within the P−N−Li−C cores, the P−N, N−Li, and P−C distances average 1.592(3), 1.980(7), 2.322(7), and 1.773(4) Å, respectively. The corresponding angles at P, N, Li, and C about these cores average 105.6(2)°, 93.0(2)°, 77.8(2)°, and 79.0(2)°, respectively. The transannular P−Li distances were found to be 2.604(6) Å. The bridging Li−C distances between the P−N−Li−C cores average 2.218(7) Å. The dimeric ladder-type structure of **9** is similar to that reported for [(LiCMe$_2$)*i*Pr$_2$PNSiMe$_3$]$_2$ by Dehnicke and co-workers.[25] Both of these species stand in contrast to the tetrameric structure observed for [(LiCH$_2$)Me$_2$PNSiMe$_3$]$_4$, which results from the presence of lesser steric demands.

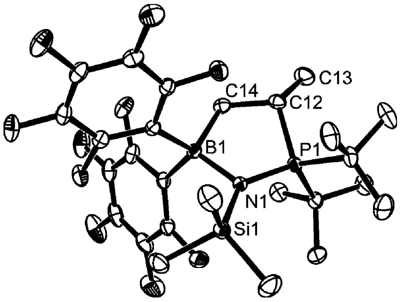
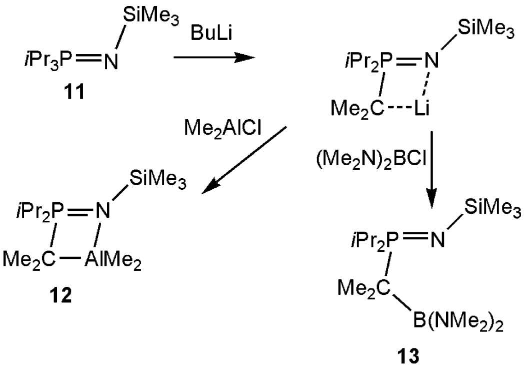


Figure 5. ORTEP drawing of **10**; 30% ellipsoids are shown, H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−N(1) 1.648(2), P(1)−C(12) 1.824(3), Si(1)−N(1) 1.786(2), C(12)−C(13) 1.528(4), B(1)−C(14) 1.634(4), B(1)−N(1) 1.636(4), N(1)−P(1)−C(12) 99.91(12), C(14)−B(1)−N(1) 105.1(2), B(1)−N(1)−P(1) 110.61(17), B(1)−N(1)−Si(1) 116.11(16), P(1)−N(1)−Si(1) 132.80(13).

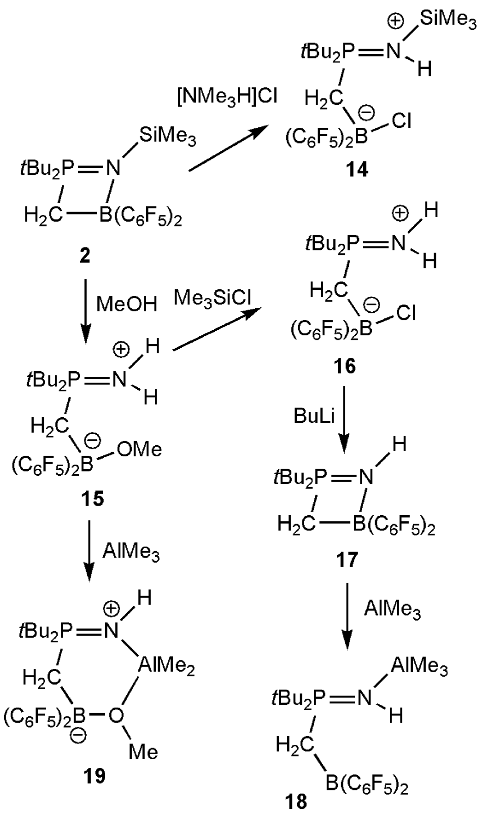
Scheme 3



Subsequent reaction of **9** with (C$_6$F$_5$)$_2$BCl afforded a new species (**10**) in 67% isolated yield. While the observations of a ^{31}P NMR resonance at 90.1 ppm and a ^{11}B NMR signal at −1.5 ppm are reminiscent of the four-membered-ring species **2**, **5**, and **7**, the presence of resonances at 2.79, 2.02, and 1.06 ppm is consistent with the presence of methine, methylene, and methyl groups resulting from isomerization of the isopropyl fragment. The corresponding ^{13}C NMR resonances were observed at 34.60 and 19.83 ppm. These data support the formulation of **10** as the five-membered heterocycle [((C$_6$F$_5$)$_2$BCH$_2$CH(Me))*t*Bu$_2$PNSiMe$_3$] (Scheme 2). This formulation was confirmed by a crystallographic study of **10** (Figure 5) with P−N, P−C C−C, C−B, and B−N distances of 1.648(2), 1.824(3), 1.528(4), 1.634(4), and 1.636(4) Å, respectively. The increase in the ring size to 5 in **10** results in an increase in the angles at P, B, and N to 99.9(1)°, 105.1(2)°, and 110.6(2)°, respectively.

In a preparation analogous to that used to prepare **10**, the phosphinimine *i*Pr$_3$PNSiMe$_3$ (**11**) was reacted with *n*BuLi, and subsequently Me$_2$AlCl or (Me$_2$N)$_2$BBr was added to afford the species [(Me$_2$AlCMe$_2$)*i*Pr$_2$PNSiMe$_3$] (**12**) and [((Me$_2$N)$_2$BCMe$_2$)*i*Pr$_2$PNSiMe$_3$] (**13**) in 54% and 67% yield, respectively (Scheme 3). The former product, an oil, exhibits ^{1}H NMR data consistent with alumination of an isopropyl carbon, as evidenced by the observation of the resonance at 1.42 ppm attributable to the *gem*-dimethyl groups. The corresponding ^{13}C NMR signals for the borylated C and *gem*-dimethyl groups were observed at 23.8 and 22.2 ppm, respectively. The species **12** also gives rise to a ^{31}P{^{1}H} NMR resonance at 60.4 ppm and a broad ^{27}Al NMR signal at 168.0 ppm. These data support the view that **12** is also a four-membered heterocyclic compound. The species **13** is also a thick oil that shows NMR data consistent with borylation of an isopropyl carbon. However, compound **13** exhibits a ^{31}P{^{1}H} NMR signal at 18.0 ppm, which is markedly

Scheme 4



upfield from those observed for the heterocyclic species above. In addition, the ^{11}B resonance for **13** observed at 25.3 ppm is consistent with a three-coordinate B center. These data infer an open chain formulation for **13**. The formation of **10** from the reaction of **9** reflects the steric strain inherent in the four-membered ring. Attempts to monitor the reaction of **9** with $(C_6F_5)_2BCl$ at low temperature shed no light on possible intermediates. Nonetheless, it is reasonable to suggest formation of a transient four-membered ring, which as a result of steric crowding and ring strain undergoes a ring expansion via proton migration to afford **10** (Scheme 2). This view is consistent with the preparation of **12** and **13**, where the lesser steric demands permit substitution without ring expansion.

Attempts to explore the reactivity of these heterocycles were undertaken. For example, reactions with a variety of donors such as pyridines or phosphines failed to effect cleavage of the dative B−N bonds. Attempts to react the *N*-silyl heterocycles **2**, **7**, and **10** with early transition metal chlorides failed to effect metal−phosphinimide complex formation, resulting in no discernible reaction. Compound **2** was shown however to react with sources of HCl. For example, reaction of **2** with $[Me_3NH]Cl$ resulted in the formation of a new species, **14**, in 73% isolated yield (Scheme 4). Compound **14** exhibits ^{31}P and ^{11}B NMR signals at 77.6 and −4.33 ppm, respectively. While the ^{1}H NMR spectrum shows resonances attributable to the fragments in **2**, a new doublet is observed at 5.04 ppm. This resonance is thought to result from protonation of the phosphinimine N atom. These data support the formulation of **14** as $[(C_6F_5)_2B(Cl)CH_2P\mathit{t}Bu_2NH(SiMe_3)]$. A crystallographic study subsequently confirmed the addition of HCl across the B−N bond of **2**, affording the phosphinamonium cation and the chloro-borate anion (Figure 6). The B−Cl distance was found to be 1.935(6) Å. Evidence of Cl···HN hydrogen bonding is evident from the close approach distance of N and Cl of 3.173 Å.

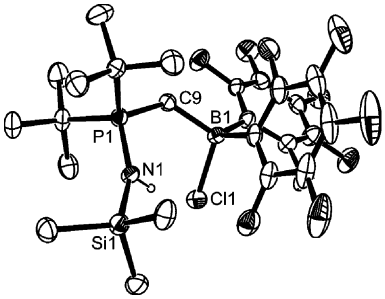


Figure 6. ORTEP drawing of **14**; 30% ellipsoids are shown, H-atoms except for the NH are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)−N(1) 1.767(4), Cl(1)−B(1) 1.935(6), P(1)−N(1) 1.650(4), N(1)−Si(1)−C(12) 113.9(2), N(1)−P(1)−C(9) 109.0(2), P(1)−N(1)−Si(1) 149.1(2), B(1)−C(9)−P(1) 122.6(3), C(9)−B(1)−Cl(1) 108.3(4).

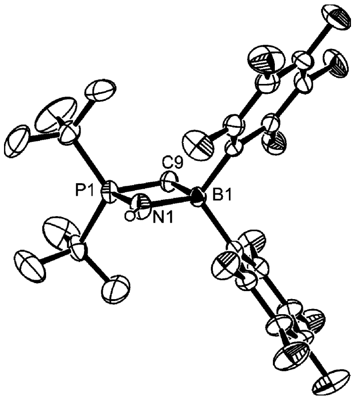


Figure 7. ORTEP drawing of one of the two molecules of **17** in the asymmetric unit; 30% ellipsoids are shown, H atoms except for the NH are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−N(1) 1.665(5), P(2)−N(2) 1.641(5), P(1)−C(9) 1.687(6), P(2)−C(30) 1.732(6), B(1)−C(9) 1.620(8), B(2)−C(30) 1.641(9), B(1)−N(1) 1.596(8), B(2)−N(2) 1.587(8), P(1)−B(1) 2.360(6), P(2)−B(2) 2.351(7), N(1)−P(1)−C(9) 85.8(3), C(30)−P(2)−N(2) 86.6(3), N(1)−B(1)−C(9) 90.4(4), C(30)−B(2)−N(2) 91.5(4), B(1)−N(1)−P(1) 92.7(4), B(2)−N(2)−P(2) 93.5(4), B(1)−C(9)−P(1) 91.0(4), B(2)−C(30)−P(2) 88.3(4).

In an analogous fashion, compound **2** also reacts cleanly with methanol to give a new product, **15**, in 91% isolated yield (Scheme 4). ^{1}H NMR data show resonances at 3.22 and 3.05 ppm attributable to methoxy and NH_2 fragments. In addition, compound **15** exhibits a ^{31}P signal at 74.6 ppm and a ^{11}B NMR resonance at −1.3 ppm. These data together with the $^{13}C\{^{1}H\}$ and ^{19}F NMR data support the formulation of **15** as the phosphinammonium methoxy borate species $((C_6F_5)_2B(OMe)CH_2)\mathit{t}Bu_2PNH_2$. Subsequent treatment of **15** with Me_3SiCl effects metathesis of the methoxy group for chloride, affording the species $((C_6F_5)_2B(Cl)CH_2)\mathit{t}Bu_2PNH_2$ (**16**) in 93% yield (Scheme 4). This formulation was consistent with the NMR data and in particular the similar ^{31}P and ^{11}B chemical shifts at 72.6 and −4.8 ppm, respectively. Further treatment of **16** with *n*BuLi effected the removal of HCl from **16**, affording the species **17** in 93% isolated yield (Scheme 4). On the basis of NMR parameters similar to those described above and the presence of a broad ^{1}H NMR signal at 1.99 ppm ascribed to the NH proton, this species was formulated as $[((C_6F_5)_2BCH_2)\mathit{t}Bu_2PNH)]$. This formulation of **17** was confirmed crystallographically (Figure 7). As with **2**, **5**, and **7**, compound **17** is a four-membered ring with similar metric parameters. The P−N, N−B, B−C, and C−P distances were found to average 1.653(5), 1.591(8), 1.630(8), and 1.709(6) Å, respectively. The diminished steric effects in **17** result in N−P−C and N−B−C angles that average 86.2(3)° and 90.9(4)°, respectively. These are smaller than those found in the more hindered **2**, **5**, and **7** species. The corresponding B−N−P and B−C−P angles, which average 93.1(4) and 89.7(4) Å in **17**, are slightly larger than those in the analogues described above. The formation of **16** and **17** reflects the basicity of the phosphinimine N in these heterocycles. It is noteworthy that the formation of phosphinammonium salts is often observed by products of phosphinimine syntheses, as such species are effective proton scavengers.[6]

Aluminum derivatives of these heterocycles were also explored. Reaction of **17** with $AlMe_3$ affords a white solid, **18**, in 90% yield (Scheme 4). The species **18** gives rise to a ^{31}P NMR signal at 74.2 ppm and a ^{11}B NMR resonance at XXX ppm. Of the basis of these data and the corresponding ^{1}H, $^{13}C\{^{1}H\}$, and ^{19}F NMR data this species is formulated as the simple Lewis acid adduct $[((C_6F_5)_2BCH_2)tBu_2PNH](AlMe_3)$, in which Al coordinates to N. In a similar reaction of **15** with $AlMe_3$ a white solid, **19**, is also isolated in 84% yield (Scheme 4). This product exhibits ^{1}H NMR resonances at 3.05, −0.03, and −0.35 ppm attributable to OMe, NH, and H $AlMe_2$ fragments. In addition, the ^{31}P and ^{11}B NMR resonances at 69.1 and 0.41 ppm are consistent with the formulation of **19** as the six-membered heterocycle $[((C_6F_5)_2B(OMe)CH_2)tBu_2PNH)(AlMe_2)]$. Repeated attempts to obtain crystals of **19** suitable for X-ray crystallography were unsuccessful, and this formulation could not be unambiguously confirmed.

In summary, metalated phosphinimines prove to be convenient synthons for the synthesis of four- and five-membered main group heterocycles. These compounds are generally robust, although the B−N dative bonds can be cleaved by protonation with acid or alcohol. In the latter case, reaction of the phosphinammonium salt affords the unusual six-membered heterocycle in which all six atoms are different. Further reactivity of main group phosphinimine and phosphinimide derivatives continues to be the subject of study in our laboratories.

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Supporting Information Available: Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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