

# Phosphinimido Complexes of Silicon, Tin, and Germanium

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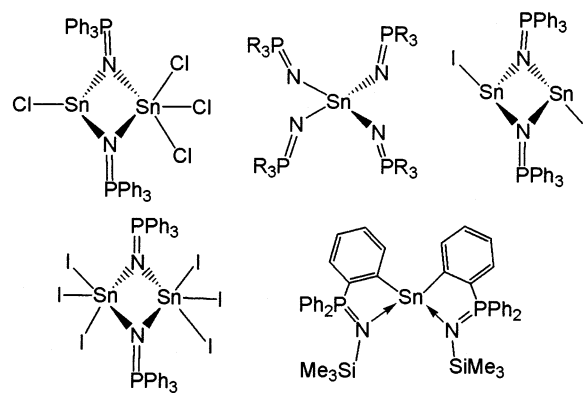
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The preparation of a silyl–phosphinimide of the form  $(R_3PN)SiMe_3$  ( $R = Me$  (**1**),  $i$ -Pr (**2**), Ph (**3**),  $t$ -Bu (**4**)) was achieved by the conventional literature methodology of oxidation of phosphine by  $N_3SiMe_3$ . The analogous species  $(t$ -Bu<sub>3</sub>PN)MMe<sub>3</sub> ( $M = Ge$  (**5**), Sn (**6**)) were derived via a stoichiometric reaction of the salt  $Li[NP$ - $t$ -Bu<sub>3</sub>] with  $Me_3MCl$ . Similarly, the species  $(t$ -Bu<sub>3</sub>PN)<sub>2</sub>MMe<sub>2</sub> ( $M = Si$  (**7**), Ge (**8**), Sn (**9**)),  $(i$ -Pr<sub>3</sub>PN)SnMe<sub>3</sub> (**10**),  $(i$ -Pr<sub>3</sub>PN)<sub>2</sub>SnMe<sub>2</sub> (**11**), and  $(t$ -Bu<sub>3</sub>PN)<sub>2</sub>SnMeCl (**12**) were prepared. Subsequent reactions of **12** afforded  $(t$ -Bu<sub>3</sub>PN)<sub>3</sub>SnMe (**13**) and  $(t$ -Bu<sub>3</sub>PN)<sub>2</sub>Sn( $o$ - $t$ -Bu)Me (**14**). In analogous metathesis reactions  $R_3$ -PNSnPh<sub>3</sub> ( $R = t$ -Bu (**15**),  $i$ -Pr (**16**)),  $(t$ -Bu<sub>3</sub>PN)<sub>2</sub>SnPh<sub>2</sub> (**17**), and  $(t$ -Bu<sub>3</sub>PN)<sub>2</sub>Sn( $t$ -Bu)<sub>2</sub> (**18**) were also prepared. Reaction of  $i$ -Pr<sub>3</sub>PNH and  $ClSnMe_3$  gave  $(i$ -Pr<sub>3</sub>PNH)SnMe<sub>3</sub>Cl (**19**), whereas **6** was obtained from the reaction of  $t$ -Bu<sub>3</sub>PNH with  $Me_3SnCl$ . The reaction of **1** with  $B(C_6F_5)_3$  resulted in the formation of  $Me_3PN(SiMe_3)B(C_6F_5)_3$  (**20**), whereas the phosphinimines **2** and **3** react with  $B(C_6F_5)_3$  in a 2:1 ratio to give  $[R_3PNSiMe_2(N(PR_3)SiMe_3)][MeB(C_6F_5)_3]$  ( $R = i$ -Pr (**21**), Ph (**22**)). In contrast, reaction of **4** and **6** with  $B(C_6F_5)_3$  afforded  $[(\mu$ - $t$ -Bu<sub>3</sub>PN)-MMe<sub>2</sub>]<sub>2</sub>[MeB(C\_6F\_5)<sub>3</sub>]<sub>2</sub> ( $M = Si$  (**23**), Sn (**24**)). The analogous reaction of **7** and **9** with  $B(C_6F_5)_3$  gave products formulated as  $[(t$ -Bu<sub>3</sub>PN)<sub>2</sub>MMe<sub>2</sub>]<sub>2</sub>[MeB(C\_6F\_5)<sub>3</sub>]<sub>2</sub> ( $M = Si$  (**25**), Sn (**26**)) and  $[(i$ -Pr<sub>3</sub>PN)<sub>2</sub>SnMe<sub>2</sub>]<sub>2</sub>[MeB(C\_6F\_5)<sub>3</sub>]<sub>2</sub> (**27**). Complexes **7–9**, **17**, **19**, **20**, and **24** were characterized crystallographically. The implications of this chemistry with regard to the steric demands of phosphinimide ligands are considered.

## Introduction

The synthesis and chemistry of phosphinimido complexes of group 14 has drawn some attention as early as the 1970s, when Wolfsberger synthesized a variety of complexes of the form  $t$ -Bu<sub>3</sub>PNMMe<sub>3</sub> ( $M = Si, Ge, Sn$ ).<sup>1</sup> Subsequently the related species  $Sn(NPPPh_3)_4$  was isolated.<sup>2</sup> Roesky and co-workers showed that partial oxidation of  $SnCl_2$  with  $Ph_3PNSiMe_3$  gave the mixed-valent dimer  $SnCl(\mu$ - $NPPPh_3$ )<sub>2</sub> $SnCl_3$ .<sup>3</sup> More recently, Dehnicke and co-workers showed that oxidative addition of  $Ph_3PNI$  to Sn resulted in the formation of the dimeric stannylene complexes  $[ISn-\mu(NPPPh_3)]_2$  and  $(I_3Sn(\mu$ - $NPPPh_3))_2$ ,<sup>4</sup> while Stalke and co-workers utilized the ortho-lithiated phosphinimine  $Li[o$ -C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>PNSiMe<sub>3</sub>] to form the diarylstannylene complex  $Sn(o$ -C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>PN-SiMe<sub>3</sub>)<sub>2</sub>.<sup>5</sup>

Our interest in group 14 phosphinimide species began with the use of such compounds as synthons for early-metal phosphinimide complexes that provide extremely active olefin polymerization catalysts.<sup>6–9</sup> These systems



were shown to undergo unusual deactivation pathways as a result of the interactions of the metal-bound phosphinimide ligand with a Lewis acid activator.<sup>10–16</sup> This prompted examinations of the chemistry of group

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13-phosphinimide complexes. Most recently, we have described the ability of sterically bulky substituents to stabilize linear borinium cations such as [(*t*-Bu<sub>3</sub>PN)<sub>2</sub>B]-Cl.<sup>17</sup> In continuing the study of the effects of steric demands, we describe herein the synthesis and characterization of group 14 phosphinimides. The chemistry of these derivatives with the Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is also probed.

### Experimental Section

**General Data.** All preparations were done under an atmosphere of dry, O<sub>2</sub>-free N<sub>2</sub>, employing both Schlenk line techniques and a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were purified by employing a Grubb's type solvent purification system manufactured by Innovative Technology.<sup>18</sup> All organic reagents were purified by conventional methods. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on Bruker Avance-300 and -500 instruments operating at 300 and 500 MHz, respectively. All spectra were recorded in C<sub>6</sub>D<sub>6</sub> at 25 °C unless otherwise noted. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to SiMe<sub>4</sub>. <sup>31</sup>P{<sup>1</sup>H}, <sup>11</sup>B{<sup>1</sup>H}, <sup>119</sup>Sn{<sup>1</sup>H}, and <sup>19</sup>F NMR spectra were recorded on a Bruker Avance-300 instrument and are referenced to external 85% H<sub>3</sub>PO<sub>4</sub>, saturated aqueous NaBH<sub>4</sub>, SnMe<sub>4</sub>, and F<sub>3</sub>CCO<sub>2</sub>H, respectively. Chemical shifts are reported in units of δ (ppm). Guelph Chemical Laboratories in Guelph, Ontario, Canada, performed combustion analyses. All tin reagents were purchased from either Aldrich Chemical Co. or Strem. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was received as a gift from NOVA Chemicals Corp. Li[NPR<sub>3</sub>] and R<sub>3</sub>-PNSiMe<sub>3</sub> (R = Me (**1**), *i*-Pr (**2**), Ph (**3**)) were prepared by a previously published method.<sup>1</sup>

**Synthesis of (*t*-Bu<sub>3</sub>PN)SiMe<sub>3</sub> (**4**).** To *t*-Bu<sub>3</sub>P (4.00 g, 0.0197 mmol) was added N<sub>3</sub>SiMe<sub>3</sub> (2.62 mL, 0.0197 mmol), and the reaction mixture was heated at reflux over 10 h. The mixture was pumped dry, to yield a white powder. Yield: 5.46 g (96%). Spectroscopic data confirmed the formulation of **4** was as previously reported.<sup>1</sup> <sup>1</sup>H NMR: 1.16 (d, [<sup>3</sup>J<sub>P-H</sub>] = 13 Hz, 27H, *t*-Bu), 0.40 (s, 9H, SiMe<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR: 32.3. <sup>13</sup>C{<sup>1</sup>H} NMR: 39.9 (d, [<sup>1</sup>J<sub>P-C</sub>] = 55 Hz, P/C), 29.6 (CMe<sub>3</sub>), 4.8 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR: -20.6 (d, [<sup>2</sup>J<sub>Si-P</sub>] = 25 Hz).

**Synthesis of (*t*-Bu<sub>3</sub>PN)MMe<sub>3</sub> (M = Ge (**5**), Sn (**6**)), (*t*-Bu<sub>3</sub>PN)<sub>2</sub>MMe<sub>2</sub> (M = Si (**7**), Ge (**8**), Sn (**9**)), (*i*-Pr<sub>3</sub>PN)SnMe<sub>3</sub> (**10**), (*i*-Pr<sub>3</sub>PN)<sub>2</sub>SnMe<sub>2</sub> (**11**), (*t*-Bu<sub>3</sub>PN)<sub>2</sub>SnMeCl (**12**), (*t*-Bu<sub>3</sub>PN)<sub>3</sub>SnMe (**13**), R<sub>3</sub>PNSnPh<sub>3</sub> (R = *t*-Bu (**15**), *i*-Pr (**16**)), (*t*-Bu<sub>3</sub>PN)<sub>2</sub>SnPh<sub>2</sub> (**17**), and (*t*-Bu<sub>3</sub>PN)<sub>2</sub>Sn(*t*-Bu)<sub>2</sub> (**18**).** These complexes were prepared in a similar manner, and thus only a single representative preparation is described, using the appropriate compound R<sub>3</sub>MCl or R<sub>2</sub>MCl<sub>2</sub>. To a solution of *t*-Bu<sub>3</sub>PNLi (0.074 g, 0.331 mmol) in toluene was added Me<sub>3</sub>GeCl (0.051 g, 0.331 mmol) at 25 °C. This mixture was heated at reflux for 6 h and filtered. The remaining solvent was removed under vacuum to yield a white powder. Recrystallization from toluene/hexane gave 0.069 g of **5** (85% yield). <sup>1</sup>H NMR: 1.21 (d, [<sup>3</sup>J<sub>P-H</sub>] = 13 Hz, 27H, *t*-Bu), 0.5 (s, 9H, GeMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 32.7. <sup>13</sup>C{<sup>1</sup>H} NMR: 40.3 (d, [<sup>1</sup>J<sub>P-C</sub>] = 53 Hz, P/C), 29.8 (CMe), 4.6 (GeMe). Anal. Calcd for C<sub>15</sub>H<sub>36</sub>PNGe: C, 53.93; H, 10.86; N, 4.19. Found: C, 53.77; H, 10.22; N, 4.01. **6**: yield 87%. <sup>1</sup>H NMR: 1.23 (d, [<sup>3</sup>J<sub>P-H</sub>] = 12 Hz, 27H, *t*-Bu), 0.36 (d, [<sup>2</sup>J<sub>Sn-H</sub>] = 55 Hz, 9H, SnMe<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR: 37.2. <sup>13</sup>C{<sup>1</sup>H} NMR: 45.0 (d, [<sup>1</sup>J<sub>P-C</sub>] = 50 Hz, P/C), 34.5 (CMe), 1.6 (SnMe).

<sup>119</sup>Sn NMR: 13.7. Anal. Calcd for C<sub>15</sub>H<sub>36</sub>PNSn: C, 47.39; H, 9.55; N: 3.68. Found: C, 47.21; H, 9.50; N, 3.70. **7**: yield 74%. <sup>1</sup>H NMR: 1.32 (d, [<sup>3</sup>J<sub>P-H</sub>] = 12 Hz, 54H, *t*-Bu), 0.56 (s, 6H, SiMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 25.3. <sup>13</sup>C{<sup>1</sup>H} NMR: 40.8 (d, [<sup>1</sup>J<sub>P-C</sub>] = 54 Hz, P/C), 30.2 (CMe), 8.2 (SiMe). <sup>29</sup>Si NMR: -44.3 (t, [<sup>2</sup>J<sub>Si-P</sub>] = 33 Hz). Anal. Calcd for C<sub>26</sub>H<sub>60</sub>P<sub>2</sub>N<sub>2</sub>Si: C, 63.63; H, 12.32; N, 5.71. Found: C, 64.02; H, 12.16; N, 5.52. **8**: yield 81%. <sup>1</sup>H NMR: 1.34 (d, [<sup>3</sup>J<sub>P-H</sub>] = 7 Hz, *t*-Bu), 0.75 (s, 6H, GeMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 28.4. <sup>13</sup>C{<sup>1</sup>H} NMR: 40.9 (d, [<sup>1</sup>J<sub>P-C</sub>] = 51 Hz, P/C), 29.9 (CMe), 1.5 (GeMe). Anal. Calcd for C<sub>26</sub>H<sub>60</sub>P<sub>2</sub>N<sub>2</sub>Ge: C, 58.33; H, 11.30; N, 5.23. Found: C, 58.94; H, 11.69; N, 5.60. **9**: yield 64%. <sup>1</sup>H NMR: 1.34 (d, [<sup>3</sup>J<sub>P-H</sub>] = 12 Hz, 27H, *t*-Bu), 0.56 (d, [<sup>2</sup>J<sub>Sn-H</sub>] = 62 Hz, 6H, SnMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 35.4. <sup>13</sup>C{<sup>1</sup>H} NMR: 41.0 (d, [<sup>1</sup>J<sub>P-C</sub>] = 50 Hz, P/C), 30.3 (s, CMe), 1.6 (s, SnMe). <sup>119</sup>Sn{<sup>1</sup>H} NMR: -46.2 (s). Anal. Calcd for C<sub>26</sub>H<sub>60</sub>P<sub>2</sub>N<sub>2</sub>Sn: C, 53.71; H, 10.40; N, 4.82. Found: C, 53.26; H, 10.25; N, 4.82. **10**: 62% yield. <sup>1</sup>H NMR: 1.70 (m, 3H, PCH), 1.01 (dd, [<sup>3</sup>J<sub>P-H</sub>] = 14 Hz, [<sup>3</sup>J<sub>H-H</sub>] = 7 Hz, 18H, CMe), 0.34 (d, 9H, [<sup>3</sup>J<sub>Sn-H</sub>] = 55 Hz, SnMe). <sup>13</sup>C{<sup>1</sup>H} NMR: 27.4 (d, [<sup>1</sup>J<sub>P-C</sub>] = 58 Hz, P/C), 17.8 (s, CMe), -2.6 (s, SnMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 32.2 (s). <sup>119</sup>Sn{<sup>1</sup>H} NMR: 21.7 (d, [<sup>2</sup>J<sub>Sn-P</sub>] = 39 Hz). Anal. Calcd for C<sub>12</sub>H<sub>30</sub>NPSn: C, 42.64; H, 8.95; N, 4.14. Found: C, 42.62; H, 8.79; N, 4.17. **11**: 75% yield. <sup>1</sup>H NMR: 1.91 (m, 6H, PCH), 1.10 (dd, [<sup>3</sup>J<sub>P-H</sub>] = 14 Hz, [<sup>3</sup>J<sub>H-H</sub>] = 7 Hz, 36H, CMe), 0.49 (s, 6H, SnMe). <sup>13</sup>C{<sup>1</sup>H} NMR: 27.2 (d, [<sup>1</sup>J<sub>P-C</sub>] = 59 Hz, P/C), 17.9 (s, CMe), 1.7 (s, SnMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 42.6 (s). <sup>119</sup>Sn{<sup>1</sup>H} NMR: 17.3 (s). Anal. Calcd for C<sub>20</sub>H<sub>48</sub>N<sub>2</sub>P<sub>2</sub>Sn: C, 48.31; H, 9.73; N, 5.63. Found: C, 48.81; H, 9.45; N, 5.79. **12**: 71% yield. <sup>1</sup>H NMR: 1.32 (d, [<sup>3</sup>J<sub>P-H</sub>] = 12 Hz, 54H, CMe), 0.91 (s, 3H, SnMe). <sup>13</sup>C{<sup>1</sup>H} NMR: 41.2 (d, [<sup>1</sup>J<sub>P-C</sub>] = 50 Hz, P/C), 30.4 (s, CMe), 4.5 (s, SnMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 42.2 (s); <sup>119</sup>Sn{<sup>1</sup>H} NMR: -93.3 (s). Anal. Calcd for C<sub>25</sub>H<sub>57</sub>ClN<sub>2</sub>P<sub>2</sub>Sn: C, 49.89; H, 9.55; N, 4.65. Found: C, 49.81; H, 9.89; N, 4.31. **13**: 69% yield. <sup>1</sup>H NMR: 1.48 (d, [<sup>3</sup>J<sub>P-H</sub>] = 12 Hz, 81H, CMe), 0.73 (s, 3H, SnMe). <sup>13</sup>C{<sup>1</sup>H} NMR: 41.2 (d, [<sup>1</sup>J<sub>P-C</sub>] = 49 Hz, P/C), 30.7 (s, CMe), 5.7 (s, SnMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 35.9 (s). <sup>119</sup>Sn{<sup>1</sup>H} NMR: -139.7 (s). Anal. Calcd for C<sub>37</sub>H<sub>84</sub>N<sub>3</sub>P<sub>3</sub>Sn: C, 56.78; H, 10.82; N, 5.37. Found: C, 56.95; H, 10.21; N, 4.87. **15**: 75% yield. <sup>1</sup>H NMR: 7.92 (d, [<sup>3</sup>J<sub>H-H</sub>] = 6 Hz, 6H, SnPh), 7.24 (m, 9H, SnPh), 1.21 (d, [<sup>3</sup>J<sub>P-H</sub>] = 12 Hz, 27H, CMe). <sup>13</sup>C{<sup>1</sup>H} NMR: 137.5, 130.1, 129.7, 129.3 (s, SnPh), 41.3 (d, [<sup>1</sup>J<sub>P-C</sub>] = 49 Hz, P/C), 30.3 (s, CMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 43.2 (s). <sup>119</sup>Sn{<sup>1</sup>H} NMR: -120.4 (d, [<sup>2</sup>J<sub>Sn-P</sub>] = 22 Hz). Anal. Calcd for C<sub>30</sub>H<sub>42</sub>NPSn: C, 63.63; H, 7.48; N, 2.47. Found: C, 63.49; H, 7.64; N, 2.29. **16**: 79% yield. <sup>1</sup>H NMR: 7.91 (d, [<sup>3</sup>J<sub>H-H</sub>] = 7 Hz, 6H, SnPh), 7.19 (m, 9H, SnPh), 1.73 (m, 3H, PCH), 0.97 (dd, [<sup>3</sup>J<sub>P-H</sub>] = 14 Hz, [<sup>3</sup>J<sub>H-H</sub>] = 7 Hz, 18H, CMe). <sup>13</sup>C{<sup>1</sup>H} NMR: 137.4, 130.3, 129.8, 129.7 (s, SnPh), 27.5 (d, [<sup>1</sup>J<sub>P-C</sub>] = 58 Hz, P/C), 17.8 (s, CMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 37.2 (s). <sup>119</sup>Sn{<sup>1</sup>H} NMR: -114.6 (d, [<sup>2</sup>J<sub>Sn-P</sub>] = 21 Hz). Anal. Calcd for C<sub>27</sub>H<sub>36</sub>NPSn: C, 61.86; H, 6.92; N, 2.67. Found: C, 60.45; H, 6.73; N, 2.49. **17**: 73% yield. <sup>1</sup>H NMR: 8.10 (d, [<sup>3</sup>J<sub>H-H</sub>] = 6 Hz, 4H, *o*-SnPh), 7.34 (t, [<sup>3</sup>J<sub>H-H</sub>] = 7 Hz, 4H, *m*-SnPh), 7.21 (m, 2H, *p*-SnPh), 1.29 (d, [<sup>3</sup>J<sub>P-H</sub>] = 12 Hz, 54H, CMe). <sup>13</sup>C{<sup>1</sup>H} NMR: 147.3, 137.3, 129.3, 125.6 (s, SnPh), 41.0 (d, [<sup>1</sup>J<sub>P-C</sub>] = 49 Hz, P/C), 30.1 (s, CMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 40.2. <sup>119</sup>Sn{<sup>1</sup>H} NMR: -142.0 (s). Anal. Calcd for C<sub>36</sub>H<sub>64</sub>N<sub>2</sub>P<sub>2</sub>Sn: C, 61.28; H, 9.14; N, 3.97. Found: C, 56.94; H, 8.67; N, 3.51. **18**: 69% yield. <sup>1</sup>H NMR: 1.46 (s, 18H, SnCMe), 1.25 (d, [<sup>3</sup>J<sub>P-H</sub>] = 12 Hz, 54H, PCMe). <sup>13</sup>C{<sup>1</sup>H} NMR: 39.5 (d, [<sup>1</sup>J<sub>P-C</sub>] = 46 Hz, P/C), 38.1 (s, SnC), 31.1 (s, SnCMe), 30.1 (s, PCMe). <sup>31</sup>P{<sup>1</sup>H} NMR: 42.3. <sup>119</sup>Sn{<sup>1</sup>H} NMR: -82.6 (s). Anal. Calcd for C<sub>32</sub>H<sub>72</sub>N<sub>2</sub>P<sub>2</sub>Sn: C, 57.75; H, 10.90; N, 4.21. Found: C, 57.58; H, 10.39; N, 3.82.

**Synthesis of (*t*-Bu<sub>3</sub>PN)<sub>2</sub>Sn(O-*t*-Bu)Me (**14**).** To a solution of **12** (60 mg, 0.097 mmol) in THF (3 mL) was added K[O-*t*-Bu] (11 mg, 0.098 mmol). The solution was stirred overnight, the solvent evaporated, and the resulting white powder suspended in toluene and filtered. The solvent was removed from the filtrate, affording 0.049 g of a white powder (78% yield). <sup>1</sup>H NMR: 1.65 (s, 9H, OCM) 1.37 (d, [<sup>3</sup>J<sub>P-H</sub>] = 12 Hz, 54H, CMe), 0.71 (s, 3H, SnMe). <sup>13</sup>C{<sup>1</sup>H} NMR: 70.8 (s, O/C), 41.4 (d, [<sup>1</sup>J<sub>P-C</sub>]

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= 49 Hz, PC), 34.5 (s, O*CMe*), 30.5 (s, PC*Me*), 4.3 (s, Sn*Me*).  $^{31}\text{P}\{^1\text{H}\}$  NMR: 40.7 (s).  $^{119}\text{Sn}$  NMR: -129.1 (s). Anal. Calcd for  $\text{C}_{29}\text{H}_{66}\text{N}_2\text{O}_2\text{P}_2\text{Sn}$ : C, 54.47; H, 10.40; N, 4.38. Found: C, 54.01; H, 10.70; N, 4.37.

**Synthesis of (*i*-Pr<sub>3</sub>PNH)SnMe<sub>3</sub>Cl (19).** To a solution of *i*-Pr<sub>3</sub>PNH (0.020 g, 0.114 mmol) in toluene (2 mL) was added ClSnMe<sub>3</sub> (0.023 g, 0.115 mmol). The solution was stirred for 1 h and the solvent removed, isolating 0.040 g of **19** (95% yield).  $^1\text{H}$  NMR (tol-*d*<sub>6</sub>): 1.82 (m, 1.5H, PC*H*), 1.59 (m, 1.5H, PC*H*), 0.92 (dd, [ $^3J_{\text{P-H}}$ ] = 15 Hz, [ $^3J_{\text{H-H}}$ ] = 7 Hz, 9H, C*Me*), 0.86 (dd, [ $^3J_{\text{P-H}}$ ] = 14 Hz, [ $^3J_{\text{H-H}}$ ] = 7 Hz, 9H, C*Me*) 0.76 (s br, 9H, Sn*Me*).  $^{13}\text{C}\{^1\text{H}\}$  NMR: 25.3 (d, [ $^1J_{\text{P-C}}$ ] = 58.4 Hz, PC), 17.2 (s, C*Me*), 2.5 (s, Sn*Me*).  $^{31}\text{P}\{^1\text{H}\}$  NMR: 57.4 (s). Anal. Calcd for  $\text{C}_{12}\text{H}_{31}\text{ClNPSn}$ : C, 38.49; H, 8.31; N, 3.74. Found: C, 39.04; H, 8.75; N, 3.20.

**Generation of 6.** To a solution of *t*-Bu<sub>3</sub>PNH (0.025 g, 0.114 mmol) in toluene (2 mL) was added ClSnMe<sub>3</sub> (0.023 g, 0.115 mmol). The solution was stirred for 1 h and filtered and the solvent removed under vacuum. The residue (0.040 g, 95%) was identified as **6** by NMR spectroscopy.

**Synthesis of Me<sub>3</sub>PN(SiMe<sub>3</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (20).** To a solution of **1** (0.020 g, 0.122 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.063 g, 0.123 mmol). The solution was stirred for 1 h and concentrated, and C<sub>6</sub>H<sub>6</sub> (1–2 mL) was added. After 3 days large colorless crystals were isolated in quantitative yield.  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.73 (d, [ $^3J_{\text{P-H}}$ ] = 7.3 Hz, 9H, P*Me*), 0.15 (s, 9H, Si*Me*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 150.6, 150.2, 147.4, 142.1, 138.9, 135.9 (br, B(C<sub>6</sub>F<sub>5</sub>)), 19.5 (d, [ $^1J_{\text{P-C}}$ ] = 67 Hz, P*Me*), 5.5 (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 44.2 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -11.2 (br s).  $^{19}\text{F}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -130.3 (s, 1F, *o*-F), -130.5 (s, 1F, *o*-F), -131.5 (s, 1F, *o*-F), -132.5 (s, 1F, *o*-F), -133.4 (s, 2F, *o*-F), -158.9 (t, [ $^3J_{\text{F-F}}$ ] = 20 Hz, 1F, *p*-F), -159.2 (t, [ $^3J_{\text{F-F}}$ ] = 20 Hz, 1F, *p*-F), -161.1 (t, [ $^3J_{\text{F-F}}$ ] = 20 Hz, 1F, *p*-F), -164.2 (t, [ $^3J_{\text{F-F}}$ ] = 15 Hz, 1F, *m*-F), -165.2 (s, 1F, *m*-F), -165.4 (s, 1F, *m*-F), -166.2 (s, 1F, *m*-F), -166.6 (s, 1F, *m*-F), -167.0 (s, 1F, *m*-F). Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{BF}_{15}\text{NPSi}$ : C, 42.69; H, 2.69; N, 2.07. Found: C, 42.64; H, 2.64; N, 2.30.

**Synthesis of [R<sub>3</sub>PNSiMe<sub>2</sub>(N(PR<sub>3</sub>)SiMe<sub>3</sub>)] [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (R = *i*-Pr (21), Ph (22)).** To a solution of **2** (0.040 g, 0.162 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (1 mL) was added B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.041 g, 0.080 mmol). Evaporation of the solvent yielded the product **21** as an oil in quantitative yield.  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 3.47 (m, 3H, PC*H*), 2.14 (m, 3H, PC*H*), 1.49 (dd, [ $^3J_{\text{P-H}}$ ] = 16 Hz, [ $^3J_{\text{H-H}}$ ] = 7 Hz, 18H, C*Me*), 1.24 (dd, [ $^3J_{\text{P-H}}$ ] = 15 Hz, [ $^3J_{\text{H-H}}$ ] = 7 Hz, 18H, C*Me*), 0.56 (s, 6H, Si*Me*), 0.53 (s, 9H, Si*Me*), 0.48 (s, 3H, B*Me*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, partial): 150.6, 147.3, 139.2, 136.3 (br, B(C<sub>6</sub>F<sub>5</sub>)), 28.6 (d, [ $^1J_{\text{P-C}}$ ] = 50 Hz, PC*H*), 27.4 (d, [ $^1J_{\text{P-C}}$ ] = 62 Hz, PC*H*), 18.3 (s, C*Me*), 17.5 (s, C*Me*), 10.2 (s, Si*Me*), 7.4 (s, Si*Me*).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 71.5 (s), 35.3 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -20.2 (br).  $^{19}\text{F}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -133.5 (d, [ $^3J_{\text{F-F}}$ ] = 20 Hz, 6F, *o*-F), -165.8 (m, 3F, *p*-F), -168.4 (m, 6F, *m*-F).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.3 (s, NSi*Me*), -18.6 (d, [ $^2J_{\text{Si-P}}$ ] = 25 Hz, NSi*Me*). Anal. Calcd for  $\text{C}_{42}\text{H}_{60}\text{BF}_{15}\text{N}_2\text{P}_2\text{Si}_2$ : C, 50.10; H, 6.01; N, 2.78. Found: C, 50.91; H, 6.65; N, 2.74. **22**: 66% yield.  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.75 (m, 6H, P*Ph*), 7.52 (m, 12H, P*Ph*), 7.37 (td, [ $^3J_{\text{H-H}}$ ] = 11 Hz, [ $^3J_{\text{H-H}}$ ] = 3 Hz, 6H, P*Ph*), 7.25 (m, 6H, P*Ph*), 0.48 (s, br, 3H, B*Me*), 0.18 (s, 6H, Si*Me*), -0.02 (s, 9H, Si*Me*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, partial): 150.4, 147.1, 139.7, 133.6 (br, B(C<sub>6</sub>F<sub>5</sub>)), 134.7, 134.5, 132.6, 132.3, 129.9, 128.8, 127.2, 125.8 (s, P*Ph*), 7.8 (s, Si*Me*), 5.3 (s, Si*Me*).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 37.5 (s), 7.2 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -18.9 (s).  $^{19}\text{F}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -133.5 (d, [ $^3J_{\text{F-F}}$ ] = 21 Hz, 6F, *o*-F), -165.8 (m, 3F, *p*-F), -168.3 (m, 6F, *m*-F).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 14.9 (s, NSi*Me*), -8.9 (d, [ $^2J_{\text{Si-P}}$ ] = 32 Hz, NSi*Me*). Anal. Calcd for  $\text{C}_{57}\text{H}_{39}\text{BF}_{15}\text{N}_2\text{P}_2\text{Si}_2$ : C, 58.72; H, 3.37; N, 2.40. Found: C, 59.09; H, 3.97; N, 2.47.

**Synthesis of [(*μ*-*t*-Bu<sub>3</sub>PN)MMe<sub>2</sub>]<sub>2</sub>[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub> (M = Si (23), Sn (24)).** A single representative preparation is described. To a solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.090 g, 0.175 mmol) in a 50:50 benzene/hexane solution (3 mL) was added **4** (0.051 g, 0.176 mmol). The reaction mixture was stirred for 0.5 h, and

the solvent was decanted from the product. The remaining solvent was removed under vacuum to yield a light yellow oil. **23**: yield 41%.  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.36 (d, 27H, [ $^3J_{\text{H-H}}$ ] = 13 Hz, *t*-Bu), 0.52 (s, 6H, Si*Me*), 0.45 (s, 3H, B*Me*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 154.7, 151.6, 143.0, 139.7 (s, br, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 45.1 (d, [ $^1J_{\text{C-P}}$ ] = 51 Hz, PC), 33.9 (s, C*Me*), 18.5 (s, B*Me*), 7.1 (s, Si*Me*), 18.1, 7.1.  $^{31}\text{P}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 48.9 (s).  $^{11}\text{B}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -21.5 (br).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.6 (s).  $^{19}\text{F}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -55.5 (d, [ $^3J_{\text{F-F}}$ ] = 23 Hz, 6F, *o*-F), -87.7 (t, [ $^3J_{\text{F-F}}$ ] = 18 Hz, 3F, *p*-F), -90.2 (t, [ $^3J_{\text{F-F}}$ ] = 19 Hz, 6F, *m*-F). **24**:  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.33 (d, 27H, [ $^3J_{\text{P-H}}$ ] = 14 Hz, *t*-Bu), 1.22 (s, 6H, Sn*Me*), 0.28 (s, 3H, B*Me*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 154.6, 151.4, 143.3, 140.1 (s, br, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 46.7 (d, [ $^1J_{\text{C-P}}$ ] = 45 Hz, PC), 35.0 (s, C*Me*), 18.5 (s, B*Me*), 15.7 (s, Sn*Me*).  $^{31}\text{P}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 77.2 (s).  $^{11}\text{B}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -17.1 (br).  $^{119}\text{Sn}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 134.8 (s).  $^{19}\text{F}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -133.3 (d, [ $^3J_{\text{F-F}}$ ] = 21 Hz, 6F, *o*-F), -165.4 (t, [ $^3J_{\text{F-F}}$ ] = 20 Hz, 3F, *p*-F), -168.0 (t, [ $^3J_{\text{F-F}}$ ] = 20 Hz, 6F, *m*-F). Anal. Calcd for  $\text{C}_{66}\text{H}_{72}\text{P}_2\text{N}_2\text{Sn}_2\text{B}_2\text{F}_{30}$ : C, 43.82; H, 3.79; N, 1.60. Found: C, 44.00; H, 4.12; N, 1.51.

**Generation of [(R<sub>3</sub>PN)<sub>2</sub>MMe][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (R = *t*-Bu, M = Si (25), Sn (26); R = *i*-Pr, M = Sn (27)).** These complexes were prepared in a similar manner, and thus, only a single representative preparation is described. To a solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.039 g, 0.076 mmol) in a 50/50 benzene/hexane solution was added **7** (0.037 g, 0.075 mmol) in a similar solution mixture. The reaction mixture was stirred for 0.5 h, followed by decanting of the solvent. The remaining solvent was removed under vacuum to yield a light yellow oil. These species proved to be quite sensitive, and consequently elemental analyses of these products were not obtained. **25**:  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.37 (d, 54H, [ $^3J_{\text{H-H}}$ ] = 13 Hz, *t*-Bu), 0.61 (s, 3H, Si*Me*), 0.47 (s, 3H, B*Me*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 154.7, 151.5, 142.7, 140.1 (s, br, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 45.1 (d, [ $^1J_{\text{P-C}}$ ] = 53 Hz, PC), 34.2 (s, C*Me*), 19.2 (s, B*Me*), 8.6 (s, Si*Me*).  $^{31}\text{P}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 41.4.  $^{11}\text{B}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -21.2.  $^{29}\text{Si}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -8.21.  $^{19}\text{F}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -55.4 (d, [ $^3J_{\text{F-F}}$ ] = 23 Hz, 6F, *o*-F), -87.7 (t, [ $^3J_{\text{F-F}}$ ] = 21 Hz, 3F, *p*-F), -90.2 (t, [ $^3J_{\text{F-F}}$ ] = 17 Hz, 6F, *m*-F). **26**:  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.38 (d, 54H, [ $^3J_{\text{P-H}}$ ] = 13 Hz, *t*-Bu), 0.49 (s, 3H, B*Me*), 0.12 (s, 3H, Sn*Me*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 154.5, 151.3, 142.8, 139.3 (s, br, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 45.6 (d, [ $^1J_{\text{P-C}}$ ] = 45 Hz, PC), 34.3 (s, C*Me*), 32.0 (s, Sn*Me*), 19.7 (s, B*Me*).  $^{31}\text{P}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 52.8,  $^{11}\text{B}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -21.5.  $^{119}\text{Sn}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -17.3.  $^{19}\text{F}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -55.3 (d, [ $^3J_{\text{F-F}}$ ] = 23 Hz, 6F, *o*-F), -87.6 (t, [ $^3J_{\text{F-F}}$ ] = 19 Hz, 3F, *p*-F), -90.2 (t, [ $^3J_{\text{F-F}}$ ] = 21 Hz, 6F, *m*-F). **27**: 95% yield.  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.15 (m, 6H, PC*H*), 1.18 (dd, [ $^3J_{\text{P-H}}$ ] = 16 Hz, [ $^3J_{\text{H-H}}$ ] = 8 Hz, 36H, C*Me*), 0.49 (s, br, 3H, B*Me*), 0.14 (s, 3H, Sn*Me*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 149.9, 147.8, 138.6, 135.6 (s, br, B(C<sub>6</sub>F<sub>5</sub>)), 27.3 (d, [ $^1J_{\text{P-C}}$ ] = 58 Hz, PC), 23.2 (s, C*Me*), 17.3 (s, B*Me*), 1.4 (s, Sn*Me*).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): 50.9 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -18.5 (s).  $^{19}\text{F}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): -56.4 (d, [ $^3J_{\text{F-F}}$ ] = 22 Hz, 6F, *o*-F), -87.4 (t, [ $^3J_{\text{F-F}}$ ] = 20 Hz, 3F, *p*-F), -90.3 (m, 6F, *m*-F).

**X-ray Data Collection and Reduction.** Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O<sub>2</sub>-free environment for each crystal. Diffraction experiments 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° < 2θ < 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 operating on a Pentium computer.

**Structure Solution and Refinement.** Non-hydrogen atomic scattering factors were taken from the literature

Table 1. Crystallographic Data

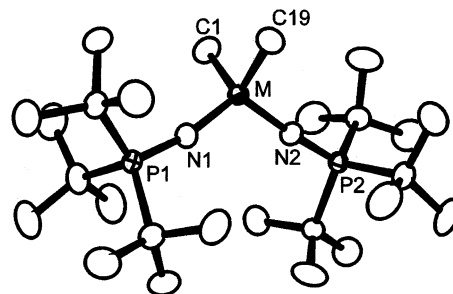
	4	5	6	14	16	17	21
formula	C <sub>26</sub> H <sub>60</sub> N <sub>2</sub> - P <sub>2</sub> Si	C <sub>26</sub> H <sub>60</sub> Ge- N <sub>2</sub> P <sub>2</sub>	C <sub>26</sub> H <sub>60</sub> N <sub>2</sub> - P <sub>2</sub> Sn	C <sub>72</sub> H <sub>101</sub> N <sub>4</sub> - P <sub>4</sub> Sn <sub>2</sub>	C <sub>12</sub> H <sub>31</sub> Cl- NPSn	C <sub>24</sub> H <sub>18</sub> BF <sub>15</sub> - NPSi	C <sub>33</sub> H <sub>36</sub> BF <sub>15</sub> - NPSn
fw	490.79	535.29	581.39	1383.83	374.49	675.26	1784.20
<i>a</i> (Å)	12.95260(10)	12.8400(2)	13.1664(3)	13.636(8)	9.111(4)	9.047(6)	12.1269(6)
<i>b</i> (Å)	16.10210(10)	15.9141(2)	16.4090(5)	17.974(10)	12.083(6)	9.469(6)	13.1303(6)
<i>c</i> (Å)	15.3534(2)	15.0513(2)	15.4534(4)	18.508(10)	16.784(8)	16.927(10)	13.1661(6)
$\alpha$ (deg)				69.191(11)		87.066(12)	64.8660(10)
$\beta$ (deg)	106.35(9)	106.6140(10)	106.5750(10)	70.378(11)		88.849(13)	74.4760(10)
$\gamma$ (deg)				83.628(13)		69.860(10)	70.3690(10)
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	triclinic	triclinic
<i>V</i> (Å <sup>3</sup> )	3072.61(5)	2947.14(7)	3199.94(15)	3994(4)	1847.8(15)	1359.7(14)	1768.33(14)
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 1	<i>P</i> 1
<i>d</i> (calcd) g cm <sup>-3</sup>	1.061	1.206	1.207	1.151	1.346	1.649	1.67
<i>Z</i>	4	4	4	2	4	2	2
abs coeff, $\mu$ , cm <sup>-1</sup>	0.196	1.164	0.913	0.743	1.597	0.266	0.873
no. of data collected	15 359	14 806	16 389	17 416	7850	5524	9368
no. of data, <i>F</i> <sub>o</sub> <sup>2</sup> > 3 $\sigma$ ( <i>F</i> <sub>o</sub> <sup>2</sup> )	5341	5124	5608	11 423	2619	3690	6110
no. of variables	280	280	280	681	145	388	459
<i>R</i>	0.0474	0.0514	0.0407	0.0477	0.023	0.0849	0.0299
<i>R</i> <sub>w</sub>	0.1493	0.1274	0.1036	0.0946	0.0774	0.2182	0.0867
GOF	1.240	0.967	1.096	0.777	0.989	1.090	1.027

tabulations.<sup>19</sup> 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  $w(|F_o| - |F_c|)^2$ , where the weight *w* is defined as  $4F_o^2/2\sigma(F_o^2)$  and *F*<sub>o</sub> and *F*<sub>c</sub> 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. In cases where disorder was implied by the difference maps or the thermal parameters, attempts to model the disorder were undertaken. Such a model was deemed acceptable if the thermal parameters were typical and the geometry was chemically reasonable. 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.

Crystallographic data are given in Table 1.

## Results and Discussion

The preparation of silyl-phosphinimides of the form (R<sub>3</sub>PN)SiMe<sub>3</sub> was achieved by the conventional literature methodology of oxidation of phosphine by N<sub>3</sub>SiMe<sub>3</sub>. In this fashion the compounds (R<sub>3</sub>PN)SiMe<sub>3</sub> (R = Me (**1**), *i*-Pr (**2**), Ph (**3**), *t*-Bu (**4**)) were prepared and characterized. The analogous species (*t*-Bu<sub>3</sub>PN)MMe<sub>3</sub> (M = Ge (**5**), Sn (**6**)) were derived via an alternative synthetic strategy. Stoichiometric reaction of the salt Li[NP-*t*-Bu<sub>3</sub>] with Me<sub>3</sub>MCl resulted in halide metathesis, affording **5** and **6** in high yields. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **5** and **6** showed resonances at 32.7 and 37.2 ppm, respectively, significantly downfield from Li[NP-*t*-Bu<sub>3</sub>]. <sup>31</sup>P–<sup>119</sup>Sn coupling was not observed for these Sn–phosphinimide derivatives and stands in contrast



**Figure 1.** ORTEP drawing of **7–9**. Thermal ellipsoids at the 30% probability level are shown. Hydrogen atoms are omitted for clarity. These complexes are isomorphous. Distances (Å) and angles (deg) are as follows. (a) M = Si (**7**): Si(1)–N(1) = 1.6566(17), Si(1)–N(2) = 1.6564(16), Si(1)–C(1) = 1.858(2), Si(1)–C(19) = 1.863(2), P(1)–N(1) = 1.5149(17), P(2)–N(2) = 1.5122(16); N(1)–Si(1)–N(2) = 112.98(9), N(1)–Si(1)–C(1) = 108.83(11), N(2)–Si(1)–C(1) = 110.35(11), N(1)–Si(1)–C(19) = 111.27(11), N(2)–Si(1)–C(19) = 107.90(11), C(1)–Si(1)–C(19) = 105.24(12), P(1)–N(1)–Si(1) = 167.45(13), P(2)–N(2)–Si(1) = 172.83(13). (b) M = Ge (**8**): Ge(1)–N(2) = 1.726(3), Ge(1)–N(1) = 1.732(3), Ge(1)–C(1) = 1.893(4), Ge(1)–C(19) = 1.900(3), P(1)–N(1) = 1.485(3), P(2)–N(2) = 1.476(3); N(2)–Ge(1)–N(1) = 110.12(15), N(2)–Ge(1)–C(19) = 106.62(18), N(1)–Ge(1)–C(19) = 112.70(18), N(2)–Ge(1)–C(1) = 111.21(18), N(1)–Ge(1)–C(1) = 108.9(2), C(19)–Ge(1)–C(1) = 107.3(2), P(1)–N(1)–Ge(1) = 162.3(2), P(2)–N(2)–Ge(1) = 170.8(3). (c) M = Sn (**9**): Sn(1)–N(2) = 1.933(4), Sn(1)–N(1) = 1.946(4), Sn(1)–C(19) = 2.125(4), Sn(1)–C(1) = 2.130(5), P(1)–N(1) = 1.513(4), P(2)–N(2) = 1.509(4); N(2)–Sn(1)–N(1) = 108.0(2), N(2)–Sn(1)–C(1) = 105.6(2), N(1)–Sn(1)–C(19) = 113.0(2), N(2)–Sn(1)–C(1) = 111.6(3), N(1)–Sn(1)–C(1) = 109.3(2), C(19)–Sn(1)–C(1) = 109.4(2), P(1)–N(1)–Sn(1) = 158.1(3), P(2)–N(2)–Sn(1) = 167.1(4).

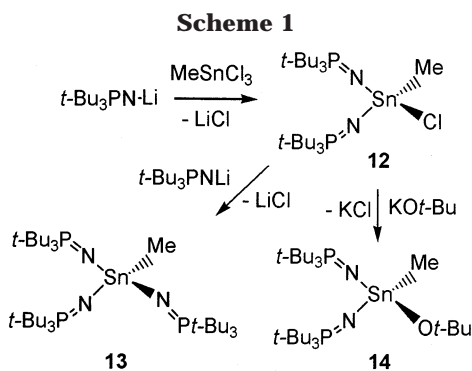
to the diarylstannylene complex Sn(*o*-C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>PN-SiMe<sub>3</sub>)<sub>2</sub>,<sup>5</sup> where Sn–P coupling of ca. 60 Hz was seen. This may be attributed to the markedly polarized nature of the approximately linear P–N bond.

In a similar manner, the species (*t*-Bu<sub>3</sub>PN)<sub>2</sub>MMe<sub>2</sub> (M = Si (**7**), Ge (**8**), Sn (**9**)) were prepared by employing a 2:1 reaction of Li[NP-*t*-Bu<sub>3</sub>] and Me<sub>2</sub>MCl<sub>2</sub>. Subsequent workup and isolation gave **7–9** in yields ranging from 64 to 81%. Crystallographic studies of **7–9** (Figure 1)

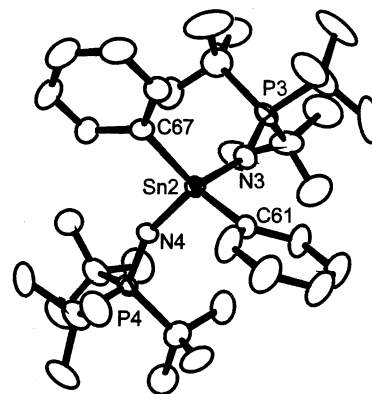
(19) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 324.

revealed that these species were isomorphous with each other as well as with (*t*-Bu<sub>3</sub>PN)<sub>2</sub>TiMe<sub>2</sub>.<sup>8</sup> The structural features of these molecules are as expected, with a pseudotetrahedral geometry about the metal centers. The M–N distances were found to vary considerably between compounds, with average values of 1.6565(16), 1.729(3), and 1.939(5) Å for **7–9**, respectively. The Si–N distance in **7** is considerably shorter than that in **8** or **9**; however, it is comparable to that found in (Ph<sub>3</sub>PN)–SiMe<sub>3</sub> (1.686 Å). The increasing M–N distance in **7–9** is consistent with the increasing ionic radius of M. The corresponding M–C bond distances in **7–9** were found to average 1.860(2), 1.897(4), and 2.127(5) Å, respectively. P–N distances in **7–9** range from 1.475(3) to 1.5147(18) Å and are similar to those seen in [(Ph<sub>3</sub>PN)–SiMe<sub>3</sub>] (1.542 Å) and [(Me<sub>3</sub>PN)GeCl<sub>3</sub>] (1.572 Å),<sup>3</sup> while the P–N–M bond angles in **7–9** vary from 158.1(3) to 172.83(13)°.

A series of related derivatives, including (*i*-Pr<sub>3</sub>PN)–SnMe<sub>3</sub> (**10**), (*i*-Pr<sub>3</sub>PN)<sub>2</sub>SnMe<sub>2</sub> (**11**), and (*t*-Bu<sub>3</sub>PN)<sub>2</sub>SnMeCl (**12**), were prepared in a similar fashion using other phosphinimides as well as other tin precursors. Subsequent reaction of **12** with Li[NP-*t*-Bu<sub>3</sub>] was used to prepare (*t*-Bu<sub>3</sub>PN)<sub>3</sub>SnMe (**13**). In a similar manner reaction of **12** with Li[O-*t*-Bu] gave the species (*t*-Bu<sub>3</sub>PN)<sub>2</sub>Sn(O-*t*-Bu)Me (**14**) (Scheme 1). In analogous me-



tathesis reactions R<sub>3</sub>PNSnPh<sub>3</sub> (R = *t*-Bu (**15**), *i*-Pr (**16**)), (*t*-Bu<sub>3</sub>PN)<sub>2</sub>SnPh<sub>2</sub> (**17**), and (*t*-Bu<sub>3</sub>PN)<sub>2</sub>Sn(*t*-Bu)<sub>2</sub> (**18**) were also prepared. Spectroscopic data, including <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>29</sup>Si, and <sup>119</sup>Sn NMR spectra, confirmed the above formulations. It is interesting to note that for compounds where more than one phosphinimide ligand is incorporated, Sn–H coupling to tin-bound methyl groups was not observed. Similar observations have been made for sterically crowded tin derivatives.<sup>20–24</sup> In a related solid-state NMR study, the presence of isotopically abundant NMR-active nuclei was shown to broaden lines, precluding the resolution of Sn–methyl coupling constants.<sup>25</sup> X-ray crystallography confirmed the formulation of **17** (Figure 2). The Sn–N bond



**Figure 2.** ORTEP drawing of **17**. Thermal ellipsoids at the 30% probability level are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg) are as follows: Sn(1)–N(2) = 1.966(6), Sn(1)–N(1) = 1.977(6), Sn(1)–C(25) = 2.155(7), Sn(1)–C(31) = 2.155(7), Sn(2)–N(3) = 1.962(5), Sn(2)–N(4) = 1.972(6), Sn(2)–C(61) = 2.127(7), Sn(2)–C(67) = 2.150(7), P(1)–N(1) = 1.532(6), P(2)–N(2) = 1.560(6), P(3)–N(3) = 1.535(6), P(4)–N(4) = 1.530(6); N(2)–Sn(1)–N(1) = 108.7(2), N(2)–Sn(1)–C(25) = 105.5(3), N(1)–Sn(1)–C(25) = 114.6(3), N(2)–Sn(1)–C(31) = 115.4(2), N(1)–Sn(1)–C(31) = 104.1(3), C(25)–Sn(1)–C(31) = 108.8(3), N(3)–Sn(2)–N(4) = 109.8(2), N(3)–Sn(2)–C(61) = 103.3(3), N(4)–Sn(2)–C(61) = 115.0(3), N(3)–Sn(2)–C(67) = 116.6(3), N(4)–Sn(2)–C(67) = 103.5(3), C(61)–Sn(2)–C(67) = 109.0(3), P(1)–N(1)–Sn(1) = 150.4(4), P(2)–N(2)–Sn(1) = 148.9(3), P(3)–N(3)–Sn(2) = 153.0(4), P(4)–N(4)–Sn(2) = 153.2(4).

distance is slightly elongated with an average value of 1.969(6) Å in comparison to **7**, but the Sn–C bond length is comparable with a value of 2.147(8) Å. The P–N–Sn bond angle average of 151.4(8)° is more bent than that observed in **9**.

An alternative strategy involving the reactions of *i*-Pr<sub>3</sub>PNH and ClSnMe<sub>3</sub> was explored. This led to the formation of the new product **19**, as evidenced by a downfield shift in the <sup>31</sup>P{<sup>1</sup>H} NMR from 47.6 ppm for *i*-Pr<sub>3</sub>PNH to 57.4 ppm. The <sup>1</sup>H NMR spectrum of **19** displayed two sets of signals for the isopropyl groups in a 1:1 ratio, and the Sn–Me resonances were broadened, suggestive of an exchange process. However, even upon cooling to 193 K, exchange was not slow on the <sup>119</sup>Sn{<sup>1</sup>H} NMR time scale and thus no signal was observed. An X-ray crystallographic study revealed **19** to be the adduct (*i*-Pr<sub>3</sub>PNH)SnMe<sub>3</sub>Cl (Figure 3). The geometry about tin was best described as trigonal bipyramidal, with the methyl groups occupying the equatorial plane and the phosphinimine and the chloride ligand occupying the axial sites. The C–Sn–C angles average 119.8(4)°, while the N–Sn–Cl angle is almost linear at 174.17(9)°. Such geometries are commonly observed for R<sub>3</sub>SnX adducts with Lewis bases.<sup>26</sup> The P–N bond is slightly elongated to 1.598(3) Å, consistent with coordination of N to Sn, while the P–N–Sn angle is bent with a value of 147.7(2)°. It is of interest to note that the related reaction of *t*-Bu<sub>3</sub>PNH with Me<sub>3</sub>–SnCl does not result in the Lewis base adduct. Instead, **6** is formed via HCl elimination. This may reflect the steric congestion that one would expect in the *t*-Bu<sub>3</sub>PNH analogue of **19**.

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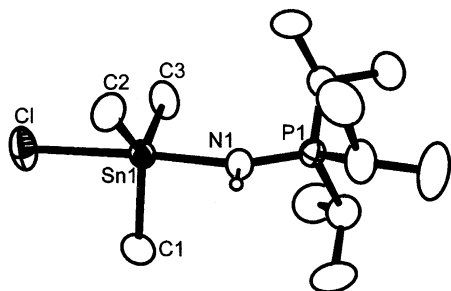
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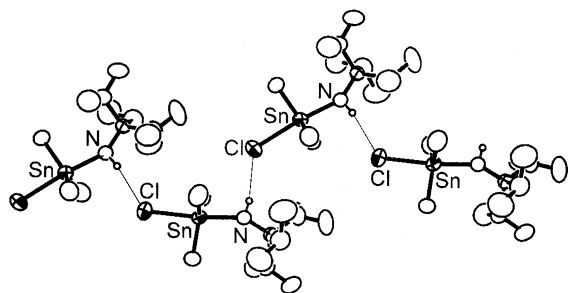
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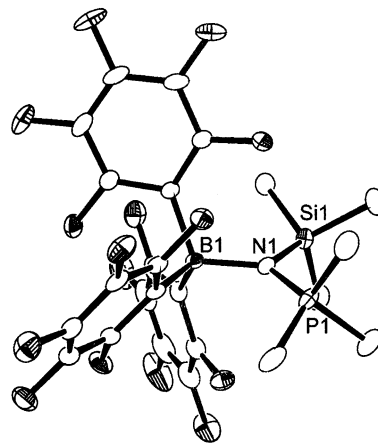
**Figure 3.** ORTEP drawing of **19**. Thermal ellipsoids at the 30% probability level are shown. Hydrogen atoms have been omitted for clarity. Selected bond distances and angles are as follows: Sn(1)–C(1) = 2.111(5), Sn(1)–C(3) = 2.125(4), Sn(1)–C(2) = 2.138(5), Sn(1)–N(1) = 2.246(3), Sn(1)–Cl = 2.7650(17), P(1)–N(1) = 1.598(3); C(1)–Sn(1)–C(3) = 117.6(2), C(1)–Sn(1)–C(2) = 120.8(2), C(3)–Sn(1)–C(2) = 120.9(2), C(1)–Sn(1)–N(1) = 90.68(17), C(3)–Sn(1)–N(1) = 98.85(16), C(2)–Sn(1)–N(1) = 88.61(17), C(1)–Sn(1)–Cl = 87.05(15), C(3)–Sn(1)–Cl = 86.96(14), C(2)–Sn(1)–Cl = 87.95(16), N(1)–Sn(1)–Cl = 174.17(9), P(1)–N(1)–Sn(1) = 147.7(2).



**Figure 4.** ORTEP drawing of **19**, showing the extended chain of NH...Cl hydrogen bonding in the solid state. Thermal ellipsoids at the 30% probability level are shown. The remaining hydrogen atoms are omitted for clarity.

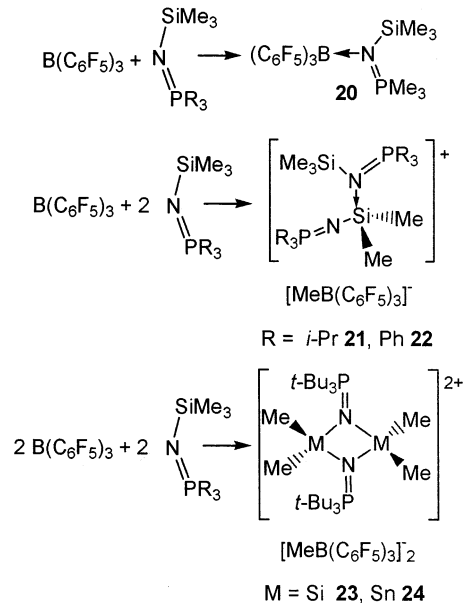
The molecules of **19** form an extended polymeric chain in the solid state via NH...Cl hydrogen bonding (Figure 4). The H...Cl distance was found to be 2.630 Å, which is considerably longer than the NH...Cl distances of 1.66(2) and 1.70(3) Å found in [R<sub>3</sub>PNH<sub>2</sub>]Cl (R = Me, Et).<sup>27</sup> This presumably reflects both the steric congestion and the lesser acidity of the NH proton in **19**.

**Reactions with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.** The reaction of **1** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> resulted in the quantitative formation of the new species **20**, as indicated by a downfield <sup>31</sup>P{<sup>1</sup>H} NMR chemical shift from –2.5 to 44.2 ppm. This compound exhibits a <sup>11</sup>B{<sup>1</sup>H} resonance at –11.2 ppm, which is in accord with the formation of a four-coordinate boron environment. The corresponding <sup>19</sup>F{<sup>1</sup>H} NMR spectrum consists of 15 resonances attributable to the 15 fluorine atoms in the borane. This confirms restricted rotation of the perfluorinated phenyl rings on the boron. This observation presumably arises from the tight donor–acceptor interaction between the N of the phosphinimine and the Lewis acidic boron center. An X-ray crystallographic study further confirmed the suspected connectivity of **20**, in which the phosphinimine and borane form the simple 1:1 Lewis acid–base adduct Me<sub>3</sub>PN(SiMe<sub>3</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (Figure 5,



**Figure 5.** ORTEP drawing of **20**. Thermal ellipsoids at the 30% probability level are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg) are as follows: B(1)–N(1) = 1.623(6), P(1)–N(1) = 1.637(4), N(1)–Si(1) = 1.802(4); B(1)–N(1)–P(1) = 127.1(3), B(1)–N(1)–Si(1) = 117.0(3), P(1)–N(1)–Si(1) = 115.8(2).

### Scheme 2



Scheme 2). The B–N bond distance in **20** was found to be 1.623(6) Å, which is similar to that observed in other B–N adducts. The P–N and N–Si bond lengths in **20** were determined to be 1.637(4) and 1.802(4) Å, while the Si–N–P angle in **20** was found to be 115.8(2)°. Studies of **1** by gas-phase diffraction showed P–N and N–Si bond lengths of 1.542(5) and 1.705(5) Å with an Si–N–P angle of 144.6(11)°.<sup>28</sup> Dehnicke and co-workers<sup>29</sup> described single-crystal data for a cocrystal of **1** and a copper cluster, in which the P–N and N–Si distances in the free phosphinimine were 1.63 and 1.76 Å, respectively, with an Si–N–P angle of 133.9°. The elongation of the P–N and N–Si bond lengths is consistent with electron donation to boron, while the smaller Si–N–P angle in **20** reflects substantial steric crowding about the N. These distances are similar to

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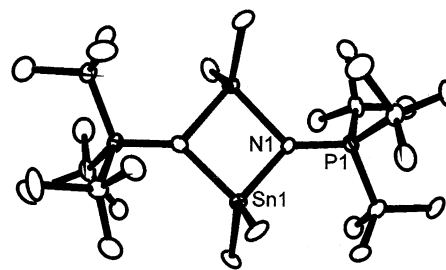
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those reported for the cationic species  $[R_3PN(SiMe_3)_2]X$  ( $R = Me, Et, Ph, X = I, I_3$ ), where the P–N and the Si–N bond lengths range from 1.637(6) to 1.660(3) Å and from 1.783(6) to 1.835(6) Å, respectively.<sup>27</sup>

In contrast, the phosphinimines **2** and **3** react with  $B(C_6F_5)_3$  in a 2:1 ratio, as determined by careful titration and concurrent monitoring by  $^{19}F\{^1H\}$  NMR spectroscopy. This stoichiometry was observed regardless of the reagent ratio. The resulting products, **21** and **22**, respectively, exhibited  $^{31}P\{^1H\}$  NMR spectra comprised of two signals separated by more than 30 ppm in a 1:1 intensity ratio.  $^1H$  NMR spectra show two sets of signals of equal intensities for the phosphorus substituents and two resonances attributable to the Si-bound methyl groups with integral ratios of 2:3. An additional resonance attributable to a methyl group was observed at 0.48 ppm for each compound. The  $^{11}B\{^1H\}$  NMR resonances at –20.2 and –18.9 ppm for **21** and **22**, respectively, and the  $^{19}F\{^1H\}$  NMR data were consistent with the formation of the borate anion  $[MeB(C_6F_5)_3]^-$ .  $^{29}Si\{^1H\}$  NMR spectra revealed two resonances for each compound. Although efforts to obtain X-ray-quality crystals of these species have been unsuccessful, the NMR data as well as elemental analyses are consistent with the formulation of **21** and **22** as the silylium salts  $[R_3PNSiMe_2(\mu-N(PR_3)SiMe_3)][MeB(C_6F_5)_3]$  ( $R = i-Pr$  (**21**),  $Ph$  (**22**)). These salts are formed by abstraction of a Si-bound methyl group, affording a silylium cation which is stabilized by coordination of a second phosphinimine molecule (Scheme 2). Although a variety of routes to silylium cations have been described,<sup>30–35</sup> to our knowledge this represents the first involving methyl abstraction.

In a similar, albeit unique, vein, reaction of **4** with  $B(C_6F_5)_3$  proceeds sluggishly in a 1:1 stoichiometry, to form the new species **23** in about 50% yield. A single new resonance was observed in the  $^{31}P\{^1H\}$  NMR spectrum.  $^1H$ ,  $^{13}C\{^1H\}$ ,  $^{19}F\{^1H\}$ ,  $^{29}Si\{^1H\}$ , and  $^{11}B\{^1H\}$  NMR data were consistent with the formation of the  $[MeB(C_6F_5)_3]$  anion and a symmetric cation, resulting in the formulation of **23** as  $[(\mu-t-Bu_3PN)SiMe_2][MeB(C_6F_5)_3]_2$  (Scheme 2).

Efforts to obtain X-ray-quality crystals of **23** were unsuccessful; thus, the analogous Sn species was also prepared from the reaction of **6** and  $B(C_6F_5)_3$ . The product **24** was isolated in 41% yield. The NMR data for **24** were similar to those observed for **23** with single  $^{31}P\{^1H\}$ ,  $^{11}B\{^1H\}$ , and  $^{119}Sn\{^1H\}$  resonances at 77.2, –17.1, and 134.8 ppm, respectively. While the observation of a broad  $^1H$  NMR resonance attributed to the borane-bound methyl group at 0.28 ppm and the  $^{19}F\{^1H\}$  and  $^{11}B\{^1H\}$  NMR spectra were consistent with the formation of the  $[MeB(C_6F_5)_3]^-$  anion, the formulation of **24** as  $[\mu-(t-Bu_3PN)SnMe_2][MeB(C_6F_5)_3]_2$  was unambiguously confirmed by a single-crystal study (Figure 6).



**Figure 6.** ORTEP drawing of **24**. Thermal ellipsoids at the 30% probability level are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg) are as follows: Sn(1)–N(1) = 2.098(2), P(1)–N(1) = 1.654(2), C(15)–B(1) = 1.638(5); N(1)–Sn(1)–N(2) = 84.43(8), P(1)–N(1)–Sn(1) = 132.63(12), Sn(1)–N(1)–Sn(1') = 95.57(8).

The X-ray data revealed that the coordination sphere of each tin atom in the dication of **24** has a distorted pseudo-tetrahedral geometry (Figure 2), with Sn–N and Sn–C bond distances averaging 2.116(5) and 2.134(3) Å, respectively. This compares to the Sn–N distance previously reported for the neutral mixed-valent Sn(IV)/Sn(II) dimer  $[\mu-(Ph_3PN)SnCl_2]_2$  (2.04(10) Å).<sup>36</sup> The longer Sn–N distances in **24** reflect the steric demands of the phosphinimine ligands. The C–Sn–C and N–Sn–C angles are 117.75(14) and 112.48(5)°, while the four-membered  $Sn_2N_2$  core gives rise to N–Sn–N and Sn–N–Sn angles averaging 84.43(8) and 95.57(8)°, respectively. This results in a Sn···Sn separation of 3.133(3) Å. The geometry about nitrogen is planar with an average P–N–Sn angle of 132.90(12)°. This value was slightly greater than the 128.3(5)° found for  $[(Ph_3PN)SnCl_2]_2$ , again reflecting the steric demands of the substituents.<sup>36</sup> The overall geometry of the dication is reminiscent of that observed for the neutral aluminum phosphinimide dimer  $[Me_2Al(\mu-NP-t-Bu_3)]_2$ . The geometries of the two methyl-borate anions  $[MeB(C_6F_5)_3]^-$  are unexceptional, with an average B–methyl B–C bond length of 1.638(5) Å. The shortest distance from B to Sn is 6.647 Å, while the closest approach between the ions is an F–methyl hydrogen contact at 2.356 Å. In an early report, Schmidbaur et al.<sup>38</sup> have proposed that similar chloride salts of related dications are obtained via methyl/halide redistribution reactions, although the formulations were not confirmed crystallographically.

Reaction of the disubstituted complexes **7** and **9** with  $B(C_6F_5)_3$  produced new cationic species in quantitative yield, as evidenced by multinuclear NMR spectroscopy. The structure of these cations was not unambiguously determined from the spectroscopic data. The NMR data confirm the formation of the borate anion  $[MeB(C_6F_5)_3]^-$ , as the  $^1H$  NMR spectra show resonances attributable to borane- and metal-bound methyl groups while the  $^{11}B\{^1H\}$  NMR resonances are consistent with the formation of the borate anion. The observation of single  $^{31}P$  NMR resonances that are downfield from the starting materials is consistent with the formation of cationic products. The chemical shifts do not suggest bridging phosphinimide groups. As the possibility of a

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fast terminal–bridging exchange process cannot be ruled out, a dimeric formulation is possible. On the other hand, these species could be solvent-stabilized monomeric cations of the formulas  $[(t\text{-Bu}_3\text{PN})_2\text{MMe}(\text{solvent})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  ( $\text{M} = \text{Si}$  (**25**),  $\text{Sn}$  (**26**)) and  $[(i\text{-Pr}_3\text{PN})_2\text{SnMe}(\text{solvent})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**27**). This latter suggestion is perhaps supported by the highly sensitive nature of these species, which also precluded elemental analyses. In any case, the precise nature of **25**–**27** could not be confirmed crystallographically, as repeated efforts failed to yield X-ray-quality crystals.

Extension of this chemistry to obtain tricoordinate tin species was considered. Tricoordinate tin complexes are rare, although a few neutral tricoordinate tin complexes have been isolated.<sup>39,40</sup> Similarly, Lambert and Kuhlmann have shown that  $\text{B}(\text{C}_6\text{F}_5)_3$  abstracts hydride from  $\text{Bu}_3\text{SnH}$  and  $\text{Me}_3\text{SnH}$  in solution, forming tricoordinate tin cations.<sup>41</sup> Reaction of **13** with  $\text{B}(\text{C}_6\text{F}_5)_3$  was attempted. Although resonances attributed to the borate anion  $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  were observed in  $^1\text{H}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy revealed the formation of several products, none of which could be isolated or characterized.

The formation of compounds **20**–**24** clearly reflects steric influence over the reaction pathways between a

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Lewis acid and a Lewis base. In the absence of steric congestion, as in **1**, the phosphinimine reacts with  $\text{B}(\text{C}_6\text{F}_5)_3$  to give the anticipated and simple donor–acceptor adduct. Increasing steric congestion by use of **2** and **3** affords instead methyl abstraction from Si. In these cases, steric demands strike a balance, being congested enough about the N atoms of the phosphinimines to preclude a simple donor–acceptor interaction with the borane and yet sufficiently accessible to coordinate to the electrophilic and less crowded silylium cations, resulting in the species **21** and **22**. A further increase in the congestion about N, as in **4**, precludes the interception of the cation by excess phosphinimine, resulting in dimerization to afford the disilylium and distannylium dications **23** and **24**, respectively. These observations clearly harbor implications for the design and synthesis of cationic species, including early-metal phosphinimide-based olefin polymerization catalysts. Suitably modified ligands are currently being targeted. In addition, fundamental studies of the unique reactivity derived from sterically demanding phosphinimines or phosphinimide systems continue to be the subject of our investigations.

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**Supporting Information Available:** Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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