Synthesis and Chemistry of Bis(borylphosphino)silanes and -germanes

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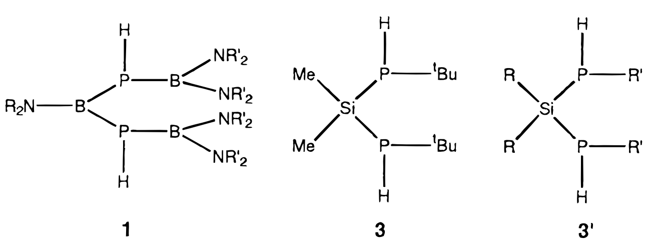
The reactions of Me_2SiCl_2, Ph_2SiCl_2, and Ph_2GeCl_2 with $LiP(H)B(N^iPr_2)_2$ in a 1:2 ratio and the reaction of Ph_2SiCl_2 with $LiP(H)B(N^iPr_2)[N(SiMe_3)_2]$ in a 1:2 ratio give good yields of the respective diphosphinosilanes, $Me_2Si[P(H)B(N^iPr_2)_2]_2$, $Ph_2Si[P(H)B(N^iPr_2)_2]_2$, $Ph_2Ge[P(H)B(N^iPr_2)_2]_2$, and $Ph_2Si[P(H)B(N^iPr_2)[N(SiMe_3)_2]]_2$. These species, when combined with BuLi in a 1:2 ratio, give lithium diphosphinosilanes and -germanes of the general type $(DME{\cdot}Li)_2\{[PB(NR_2)_2]_2ER'_2\}$. All of the species have been characterized by spectroscopic methods. The molecular structures of three of the lithio compounds, $(DME{\cdot}Li)_2\{[PB(N^iPr_2)_2]_2SiPh_2\}$ (**11**), $(DME{\cdot}Li)_2\{[PB(N^iPr_2)N(SiMe_3)_2]_2SiPh_2\}$ (**15**), and $(DME{\cdot}Li)_2\{[PB(N^iPr_2)_2]_2GePh_2\}$ (**13**), have been determined by X-ray diffraction techniques. **11** crystallized in the triclinic space group $P\bar{1}$ with $a = 11.071(2)$ Å, $b = 14.937(3)$ Å, $c = 18.080(4)$ Å, $\alpha = 91.31(3)°$, $\beta = 101.23(3)°$, $\gamma = 109.95(3)°$, and $Z = 2$, and **13** crystallized in the triclinic space group $P\bar{1}$ with $a = 11.083(1)$ Å, $b = 14.978(2)$ Å, $c = 18.134(2)$ Å, $\alpha = 91.17(1)°$, $\beta = 101.43(1)°$, $\gamma = 110.05(1)°$, and $Z = 2$. **15** crystallized in the monoclinic space group $P2_1/n$ with $a = 11.939(2)$ Å, $b = 24.516(3)$ Å, $c = 21.572(3)$ Å, $\beta = 101.52(1)°$, and $Z = 4$. The reactions of the lithio compounds were surveyed with R_2ECl_2 reagents. The metathesis reactions are sluggish, but the 1:1 reaction of $(DME{\cdot}Li)_2\{[PB(N^iPr_2)_2]_2GePh_2\}$ with $^tBu_2SnCl_2$ gave the four-membered-ring compound $Ph_2GePB(N^iPr_2)_2Sn(^tBu)_2PB(N^iPr_2)_2$. The 1:2 reaction of $Me_2(Cl)SiSi(Cl)Me_2$ with $LiP(H)B(N^iPr_2)_2$ yielded the (borylphosphino)silane $[Me_2SiP(H)B(N^iPr_2)_2]_2$.

Introduction

Organyllithium compounds serve as key reagents in modern organic syntheses, and lithum phosphides play a similar critical role in the synthesis of new phosphorus compounds. We are interested in exploring the utility of lithium borylphosphide reagents, $(R_2N)(X)BP(Y)Li$, particularly for the synthesis of new boron−phosphorus ring and cage compounds. In this regard, we have observed that diphosphatriboretanes **1** are obtained in



good yield from 2:1 reactions of $(^iPr_2N)_2BP(H)Li{\cdot}DME$ (**2**) with aminodichloroboranes, R_2NBCl_2.[1−4] The possibility that **1** might undergo double deprotonation forming bis(phosphide) salts is intriguing, and this topic is now being studied.

In related chemistry, Fritz and co-workers[5] have observed the formation of a diphosphinosilane, **3**, from reaction of Me_2SiCl_2 and $^tBuP(H)Li{\cdot}2DME$. Deprotonation of **3** with BuLi was proposed to give a lithium bis(phosphide) although its structure was not determined. Klingebiel and co-workers[6] reported syntheses for additional diphosphinosilanes, **3′** (R = ^{t}Bu, R′ = Ph; R = ^{i}Pr, R′ = H; R = ^{t}Bu, R′ = ^{t}Bu). Combination of **3′** (R = ^{t}Bu, R′ = Ph) with 2 equiv of BuLi followed by addition of $F_2PN(^tBu)(SiMe_3)$ gave the four-membered-ring compound $Me_2SiP(Ph)P[N(^tBu)(SiMe_3)]PPh$. Although the issue is not discussed, the outcome of this reaction suggests the intermediate formation of a bis(phosphide), $Me_2Si(PPhLi)_2$. Driess and co-workers[7] recently directed new attention to lithium phosphide reagents. In particular, they reported reaction of $(^iPr_3C_6H_2)(^tBu)Si(PH_2)_2$ with BuLi followed by additions of R'_3SiCl (R′ = Ph, ^{i}Pr, Me), which gave $R_2Si[P(H)SiR'_3](PH_2)$. Subsequent reaction with 2 equiv of BuLi led to a dimer, $[R_2SiP(H)PSiRLi_2]$. The molecular structures of these species were not determined, but they were proposed to have polycyclic structures illustrated by **4**. This compound combines with LiCl in hot toluene, giving a cluster molecule containing two units of **4** linked through a Li_2Cl_2 "middle deck".

The molecular structures of several simpler lithium phosphides, $LiPR_2$ (R = H, alkyl, aryl, silyl, boryl, aminoboryl) have been examined.[1−3,8−15] All of these compounds are associated in the solid state, forming oligomers or polymers. It might be

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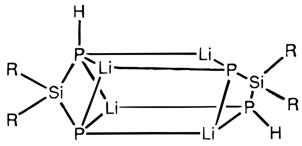

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concluded that reducing the availability of the phosphido ligand lone pair by steric or electronic means might result in the stabilization of monomeric phosphido salts. In this regard, we have studied the formation of lithio bis(phosphides) that carry electron-withdrawing aminoboryl substituent groups, and we report here the syntheses, characterizations, and crystal structure determinations for several examples that are monomeric in the solid state.

Experimental Section

General Information. Standard inert-atmosphere techniques were employed for the manipulations of all reagents and products. Infrared spectra were recorded on a Mattson 2020 Galaxy FT-IR spectrometer from KBr pellet samples. Mass spectra were obtained by the University of Nebraska Midwest Center for Mass Spectrometry on a Kratos MS-50 spectrometer with FAB analysis. NMR spectra were recorded on Bruker WP-250 and JEOL GSX-400 spectrometers, and data are summarized in Table 1. Downfield shifts were assigned $+\delta$ values, and the references used were Me_4Si (^1H, ^{13}C), 85% H_3PO_4 (^{31}P), LiBr in D_2O (^7Li), and $F_3B{\cdot}OEt_2$ (^{11}B). The NMR samples were dissolved in a deuterated lock solvent and contained in sealed 5 mm tubes.

Materials. Me_2SiCl_2 and Ph_2SiCl_2 (Aldrich) and Ph_2GeCl_2 (Strem) were purchased and used as received. $[Me_2(Cl)Si]_2$,[16] $(^iPr_2N)_2BP(H)$-$Li{\cdot}DME$[2] (**5**), and $(^iPr_2N)[(Me_3Si)_2N]BP(H)Li{\cdot}DME$[3] (**6**) were prepared as described in the literature. All solvents were dried and degassed, and solvent transfers were accomplished by vacuum distillation.

Synthesis and Characterization of Compounds. (a) Bis{[bis-(diisopropylamino)boryl]phosphino} dimethylsilane (7). A solution of Me_2SiCl_2 (0.20 g, 1.55 mmol) in hexane (30 mL) was combined with a solid sample of $(^iPr_2N)_2BP(H)Li{\cdot}DME$ (1.05 g, 3.10 mmol) at 0 °C, and the mixture was stirred (23 °C, 5 h). The insoluble material (LiCl) was removed by filtration. The solvent was evaporated from the filtrate under reduced pressure, leaving a colorless oil, **7**. No further purification was necessary: yield 0.85 g (100%). Mass spectrum (EI, 30 eV) [*m/z* (%)]: 211 (100, $(^iPr_2N)_2B^+$). Infrared spectrum (neat oil, cm^{-1}): 2967 (s), 2930 (s), 2874 (m), 2309 (w,ν_{PH}), 1462 (m), 1414 (s), 1364 (s), 1306 (s), 1200 (s), 1117 (s), 1073 (s), 1003 (w), 907 (w), 833 (m), 787 (m), 762 (m), 654 (w), 488 (w), 428 (w). Anal. Calcd for $C_{26}H_{64}B_2N_4P_2Si$ (M_r = 544.23): C, 57.38; H, 11.88; N, 10.30. Found: C, 57.63; H, 12.68; N, 10.06.

(b) 1,2-Bis{[bis(diisopropylamino)boryl]phosphino}-1,1,2,2-tetramethyldisilane (8). A solution of $Me_4Si_2Cl_2$ (0.66 g, 3.5 mmol) in hexane (30 mL) was combined with a solid sample of $(^iPr_2N)_2BP(H)$-$Li{\cdot}DME$ (2.4 g, 7.1 mmol) at 0 °C, and the mixture was stirred (23 °C, 5 h). The insoluble material (LiCl) was removed by filtration, and the filtrate was concentrated (10 mL). Colorless crystals, **8**, deposited at −10 °C: yield 1.60 g (75.6%); mp 106−108 °C. Mass spectrum (EI, 30 eV) [*m/z* (%)] 211 (100, $(^iPr_2N)_2B^+$), 197 (83). Infrared spectrum (KBr, cm^{-1}): 2967 (s), 2924 (s), 2870 (m), 2301 (m, ν_{PH}), 1464 (m), 1421 (m), 1362 (m), 1306 (m), 1221 (m), 1200 (m), 1132 (m), 1111 (m), 1071 (m), 1001 (w), 907 (w), 831 (m), 774 (m), 712 (w), 654 (w), 567 (w), 527 (w), 428 (w). Anal Calcd for $C_{28}H_{70}B_2N_4P_2Si_2$ (M_r = 602.62): C, 55.80; H, 11.71; N, 9.30. Found: C, 55.88; H, 12.00; N, 9.16.

(c) 1,2-Bis(lithiodimethoxyethane)−1,2-Bis{[bis(diisopropylamino)-boryl]phosphino}-1,1,2,2-tetramethyldisilane (9). A solution of **8** (1.30 g, 2.16 mmol) in DME (30 mL) was cooled (−78 °C), and a hexane solution of BuLi (2.6 mL, 1.6 M, 4.2 mmol) was added slowly with an airtight syringe. The mixture was stirred (−78 °C, 2 h; then 23 °C, 16 h). The DME was evaporated and replaced with hexane (20 mL); then the hexane solution was filtered. Colorless crystals, **9**, deposited when the filtrate was cooled (−10 °C): yield 1.0 g (59%). Mass spectrum (EI, 30 eV) [*m/z* (%)]: 211 (100, $(^iPr_2N)_2B^+$), 197 (70). Anal. Calcd for $C_{36}H_{88}B_2N_4Li_2O_2P_2Si_2$ (M_r = 794.71): C, 54.41; H, 11.16; N, 7.05. Found: C, 54.81; H, 11.79; N, 7.05.

(d) Bis{[bis(diisopropylamino)boryl]phosphino}diphenylsilane (10). A solution of Ph_2SiCl_2 (0.74 g, 2.9 mmol) in hexane (30 mL) was combined with a solid sample of $(^iPr_2N)_2BP(H)Li{\cdot}DME$ (2.00 g, 5.88 mmol) at 0 °C, and the mixture was stirred (23 °C, 5 h). The insoluble material (LiCl) was removed by filtration, and the solvent was evaporated under reduced pressure, leaving a yellow oil, **10**. Attempts to purify the oil by vacuum distillation failed. The oil was characterized only by ^{31}P NMR: δ −186.3, $^1J_{P-H}$ = 235 Hz.

(e) Bis(lithiodimethoxyethane)−Bis{[bis(diisopropylamino)boryl]-phosphino}diphenylsilane (11). The yellow oil **10** obtained above was dissolved in DME (30 mL), and the solution was cooled (−78 °C). BuLi/hexane solution (3.7 mL, 1.7 M, 5.9 mmol) was added to the cooled solution with an airtight syringe, and the mixture was stirred (−78 °C, 2 h; then 23 °C, 16 h). The resulting mixture was filtered and the solvent evaporated under reduced pressure, leaving a yellow oily solid, which was washed with cold hexane (2 × 10 mL), from which a yellow powder, **11**, was recovered: yield 1.5 g (60%); mp 196−198 °C (dec). Mass spectrum (EI, 30 eV) [*m/z* (%)]: 211 (100, $(^iPr_2N)_2B^+$), 197 (55). Infrared spectrum (KBr, cm^{-1}): 3045 (m), 2967-(vs), 2930 (s), 2872 (s), 1466 (m), 1424 (s), 1364 (m), 1312 (m), 1275 (w), 1200 (s), 1107 (s), 1078 (s), 1034 (m), 1003 (m), 901 (w), 872 (w), 843 (w), 756 (m), 700 (m), 652 (w), 580 (w), 503 (m), 451 (w). Anal. Calcd for $C_{44}H_{86}B_2Li_2N_4O_4P_2Si$ (M_r = 860.87): C, 61.38; H, 10.09; N, 6.51. Found: C, 61.40; H, 10.48, N, 6.63.

(f) Bis{[bis(diisopropylamino)boryl]phosphino}diphenylgermane (12). A solution of Ph_2GeCl_2 (1.23 g, 4.13 mmol) in hexane (30 mL) was combined with a solid sample of $(^iPr_2N)_2BP(H)Li{\cdot}DME$ (2.80 g, 8.23 mmol) at 0 °C, and the mixture was stirred (23 °C, 5 h). Insoluble material (LiCl) was removed by filtration, and the solvent was evaporated under reduced pressure, leaving a pale yellow oil, **12**: yield 2.90 g (100%). No further purification was necessary. Infrared spectrum (KBr, cm^{-1}): 2967 (vs), 2924 (s), 2870 (m), 2301 (m, ν_{PH}), 1464 (m), 1422 (s), 1362 (m), 1306 (s), 1221 (m), 1200 (s), 1132 (m), 1111 (m), 1071 (s), 1001 (w), 970 (w), 831 (m), 774 (s), 712 (w), 654 (w), 567 (w), 527 (w), 428 (w). Anal. Calcd for $C_{36}H_{68}B_2GeN_4P_2$ (M_r = 713.09): C, 60.63; H, 9.61; N, 7.86. Found: C, 61.46; H, 10.79; N, 7.60.

(g) Bis(lithiodimethoxyethane)−Bis{[bis(diisopropylamino)boryl]-phosphino}diphenylgermane (13). A solution of **12** (2.8 g, 4.0 mmol) in DME (30 mL) was cooled to −78 °C, and BuLi (5.0 mL, 1.6 M, 8.0 mmol) in hexane was added slowly with an airtight syringe. The reaction mixture was stirred (−78 °C, 2 h; then 23 °C, 16 h). The resulting mixture was filtered and the filtrate reduced in volume to ∼10 mL. Pale yellow crystals formed, which were washed with cold hexane (2 × 10 mL), leaving a pale yellow solid, **13**: yield 2.2 g (60%); mp 162−164 °C (dec). Infrared spectrum (KBr, cm^{-1}): 3050 (w), 2967 (s), 2928 (s), 2872 (m), 1579 (w), 1468 (m), 1429 (m), 1362 (m), 1310 (m), 1273 (m), 1200 (s), 1111(m), 1078 (s), 1030 (m), 901 (w), 872 (w), 758 (m), 733 (m), 700 (m), 654 (w), 596 (w), 574 (w), 527 (w), 461 (m). Anal. Calcd for $C_{44}H_{86}B_2Li_2GeN_4O_4P_2$ (M_r = 905.19): C, 58.37; H, 9.58; N, 6.19. Found: C, 58.11; H, 9.89; N, 6.38.

(h) Bis(lithiodimethoxyethane)−Bis{[(bis(trimethylsilyl)amino)-(diisopropylamino)boryl]phosphino}diphenylsilane (15). This compound was prepared exactly as described for **11**. The intermediate phosphine, **14**, was not isolated. The crystalline solid, **15**, was pale

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Table 1. NMR Data

compound	$\delta(^{11}B)$	$\delta(^{31}P)$	$\delta(^{1}H)$	$\delta(^{13}C\{^{1}H\})$	$\delta(^{1}Li)$
$[(^iPr_2N)_2BP(H)]_2SiMe_2$ (**7**)	40.4	−186.1 (d) $^1J_{PH}$ = 213 Hz	0.77 (t) (Me_2Si) $^3J_{PH}$ = 3.7 Hz 1.27 (d) (CH_3) $^3J_{HH}$ = 6.9 Hz 3.84 (sept) (CH) $^3J_{HH}$ = 6.9 Hz	8.4 (t) (Me_2Si) $^2J_{PC}$ = 8.5 Hz 25.1 (CH_3) () 49.0 (CH)	
$[(^iPr_2N)_2BP(H)SiMe_2]_2$ (**8**)	40.4	−212.3 (d) $^1J_{PH}$ = 213 Hz	0.67 (d) (Me_2Si) $^3J_{PH}$ = 4.24 Hz 1.26 (d) (CH_3) $^3J_{HH}$ = 6.9 Hz 1.78 (d) (PH) $^1J_{PH}$ = 213 Hz 3.82 (sept) (CH) $^3J_{PH}$ = 6.9 Hz	0.26 (d) (Me_2Si) $^2J_{PC}$ = 8.3 Hz 25.1 (CH_3) () 49.0 (CH)	
$[(^iPr_2N)_2BPSiMe_2]_2Li_2$•2DME (**9**)	47.1	−254.3	0.77 (Me_2Si) 1.44 (d) (CH_3, ^{i}Pr) $^3J_{HH}$ = 6.9 Hz 3.05 (CH_2, DME) 3.26 (CH_3, DME) 4.58 (sept) (CH) $^3J_{HH}$ = 6.9 Hz	6.0 (Me_2Si) 25.9 (CH_3, ^{i}Pr) 49.2 (CH, ^{i}Pr) 59.5 (CH_2, DME) 70.0 (CH_3, DME)	5.1 (t) $^1J_{PLi}$ = 48 Hz
$[(^iPr_2N)_2BP(H)]_2SiPh_2$ (**10**)	40.8	−186.3 (d) $^3J_{PH}$ = 235 Hz			
$\{[(^iPr_2N)_2BP]_2SiPh_2\}Li_2$•$(DME)_2$ (**11**)	44.7	−212.1 (m) $^1J_{PLi}$ = 43 Hz	1.34 (d) (CH_3, ^{i}Pr) $^3J_{HH}$ = 6.9 Hz 2.95 (s) (CH_2, DME) 4.45 (sept) (CH, ^{i}Pr) $^3J_{HH}$ = 6.9 Hz 7.15−7.35 (Ph)	25.2 (CH_3, ^{i}Pr) 49.0 (CH, ^{i}Pr) 59.6 (CH_2, DME) 70.3 (CH_3, DME) 126.3 (Ph) 136.6 (Ph)	4.5 (t) $^3J_{PLi}$ = 41 Hz
$[(^iPr_2N)_2BP(H)]_2GePh_2$ (**12**)	41.0	−181.2 (d) $^3J_{PH}$ = 215 Hz	1.09 (d) (CH_3, ^{i}Pr) $^3J_{HH}$ = 6.9 Hz 3.71 (sept) (CH, ^{i}Pr) 7.05−7.24 (Ph)	24.8 (CH_3) () 49.0 (CH) 128.1 (Ph) 128.7 135.5 142.1	
$\{[(^iPr_2N)_2BP]_2GePh_2\}Li_2$•2DME (**13**)		−195.3 $^1J_{PLi}$ = 43 Hz	1.30 (d) (CH_3, ^{i}Pr) 3.05 (s) (CH_2, DME) 3.16 (s) (CH_3, DME) 4.39 (sept) (CH, ^{i}Pr) 7.01−7.27 (Ph) 8.07−8.10 (Ph)	25.2 (CH_3, ^{i}Pr) 48.4 (CH, ^{i}Pr) 59.5 (CH_3, DME) 70.6 (CH_2, DME) 126.6 (Ph) 136.0 137.5 152.9	$^1J_{LiP}$ = 43 Hz
$\{\{[(^iPr_2N)(Me_3Si)_2N]BP\}_2SiPh_2\}Li_2$•2DME (**15**)		−198	0.45 (Me_3Si) 0.88 (d) (CH_3, ^{i}Pr) $^1J_{HH}$ = 6.8 Hz 1.42 (d) (CH_3, ^{i}Pr) $^3J_{HH}$ = 6.8 Hz 3.04 (CH_2, DME) 3.12 (CH_2, DME) 4.79 (m) (CH, ^{i}Pr) 5.05 (m) (CH, ^{i}Pr) 7.12−7.27 (Ph) 8.01 (Ph)	4.5 (Me_3Si) 24.5 (CH_3, ^{i}Pr) 25.9 (CH_3, ^{i}Pr) 46.1 (CH, ^{i}Pr) 52.8 (CH, ^{i}Pr) 59.6 (DME) 69.8 (DME) 126.5 (Ph) 136.7 (Ph) 149.8 (Ph)	
$(^iPr_2N)_2BPGe(Ph)_2[(^iPr_2N)_2B]PSn(^tBu)_2$ (**18**)		−164.7 $^1J_{PSn}$ = 791 Hz	1.12 (d) (CH_3, ^{i}Pr) $^3J_{HH}$ = 6.7 Hz 1.63 (SnH) $^3J_{SnH}$ = 75.0 Hz 3.71 (sept) (CH, ^{i}Pr) $^3J_{HH}$ = 6.7 Hz 7.18−7.32 (Ph) 8.37 (Ph)	25.0 (CH_3, ^{i}Pr) 32.4 (CH_3, ^{i}Pr) 36.9 (C, ^{t}Bu) $^2J_{PC}$ = 5.8 Hz 49.0 (CH, ^{i}Pr) 127.6 (Ph) 128.7 (Ph) 136.8 (Ph) 144.0 (Ph) $^2J_{PC}$ = 7.2 Hz	

yellow: yield 67%; mp 191−193 °C (dec). Anal. Calcd for $C_{44}H_{94}B_2Li_2N_4O_4P_2Si_5$ (M_r = 981.29): C, 53.85; H, 9.66; N, 5.71. Found: C, 52.69; H, 10.05; N, 5.83.

(i) 2,4-Bis[bis(diisopropylamino)boryl]-1,1-diphenyl-3,3-di-*tert*-butyl-1,3,2,4-diphosphagermastannane (18). Equimolar amounts of **13** (1.0 g, 1.1 mmol) and $^tBu_2SnCl_2$) (0.33 g, 1.1 mmol) were combined in hexane (30 mL) at −78 °C. The pale orange mixture was stirred (−78 °C, 2 h; then 23 °C, 16 h) and filtered, and the solvent was evaporated from the filtrate. The resulting pale orange oil crystallized upon standing for several days at 23 °C, and pure **18** was recovered: yield 1.1 g (100%); mp 153−156 °C. Mass spectrum (HRFAB), *m*/*z*: calcd for $^{12}C_{44}{}^{1}H_{84}{}^{10}B_2{}^{14}N_4{}^{31}P_2{}^{74}Ge^{120}Sn$, 944.46638; found, 944.46606,

Table 2. Crystallographic Data for {[(^{i}Pr$_2$N)$_2$BP]$_2$SiPh$_2$}Li$_2$·2DME (**11**), {[(^{i}Pr$_2$N)$_2$BP]$_2$GePh$_2$}Li$_2$·DME (**13**), and {{[(^{i}Pr$_2$N)(Me$_3$Si)$_2$N]BP}$_2$SiPh$_2$}Li$_2$·2DME (**15**)

	11	**13**	**15**
empirical formula	$C_{44}H_{86}B_2N_4O_4SiP_2Li_2$	$C_{44}H_{86}B_2N_4O_4GeP_2Li_2$	$C_{44}H_{94}B_2N_4O_4P_2Si_5Li_2$
fw	860.7	905.2	981.1
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	11.071(2)	11.083(1)	11.939(2)
b, Å	14.973(3)	14.978(1)	24.516(3)
c, Å	18.080(4)	18.134(1)	21.572(3)
α, deg	91.31(3)	91.17(1)	90
β, deg	101.23(3)	101.43(1)	101.52(1)
γ, deg	109.95(3)	110.05(1)	90
V, Å^3	2743.7(10)	2758.9(4)	6187(2)
Z	2	2	4
D_{calcd}, g cm^{-3}	1.042	1.090	1.053
T, °C	20	20	20
μ, cm^{-1}	0.140	0.651	0.204
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
R_F,[a] R_{wF},[a] %	4.47, 9.36	4.17, 8.10	3.77, 8.56

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$; $R_{wF} = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o{}^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F) + gF^2$.

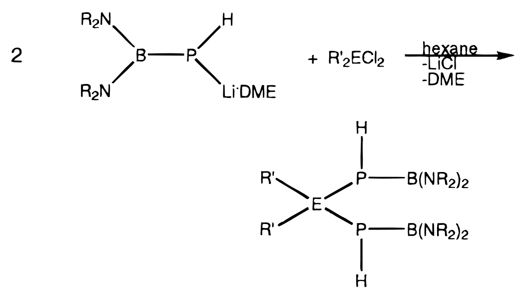
deviation 0.3 ppm. Anal. Calcd for $C_{44}H_{84}B_2GeN_4P_2Sn$ (M_r = 943.99): C, 55.98; H, 8.97; N, 5.94. Found: C, 54.89; H, 9.17; N, 5.58.

Crystallographic Measurements and Structure Solutions. Crystals of **11**, **13**, and **15** were placed in glass capillaries under a dry nitrogen atmosphere. The crystals were centered on a Siemens P3/F automated diffractometer, and determinations of the crystal classes, orientation matrices, and unit cell dimensions were performed in a standard manner.[17] A summary of crystallographic data is given in Table 2. Data were collected in the ω scan mode with Mo Kα (λ = 0.710 73 Å) radiation, a scintillation counter, and a pulse height analyzer. Inspection of small data sets led to assignments of the space groups.[18] Empirical adsorption corrections based on ψ scans were applied.[19] Compound **13** showed a small intensity decay (5%) during data collection.

All calculations were performed on a Siemens SHELXTL PLUS structure determination system.[20] Solutions for the data sets were performed by direct methods, and full-matrix least-squares refinements were employed.[21] Neutral-atom scattering factors and anomalous dispersion terms were used for all non-hydrogen atoms during the refinements. The refinements were well-behaved except that large thermal motions were observed for several of the methyl carbon atoms in the N(SiMe$_3$)$_2$, isopropyl, and DME groups in each compound. Pertinent bond lengths and angles are summarized in Table 3. Additional crystallographic data, heavy-atom coordinates, anisotropic thermal factors, and H atom positional parameters are provided in the Supporting Information.

Results and Discussion

Bis(borylphosphino)silanes **7**, **8**, **10**, and **14** and bis(borylphosphino)germane **12** were prepared in similar fashions by reaction of (R$_2$N)$_2$BP(H)Li·DME with R$_2$ECl$_2$ and [R$_2$(Cl)Si]$_2$ in a 2:1 ratio as summarized in eq 1.



(1)

	7	**8**	**10**	**12**	**14**
R′$_2$E	Me$_2$Si	(Me$_2$Si)$_2$	Ph$_2$Si	Ph$_2$Ge	Ph$_2$Si
R$_2$N	^{i}Pr$_2$N	^{i}Pr$_2$N	^{i}Pr$_2$N	^{i}Pr$_2$N	^{i}Pr$_2$N(Me$_3$Si)$_2$N

The compounds were isolated as colorless to pale yellow oils or as a colorless solid (**8**). Elemental analyses (CHN) for **7**, **8**, and **12** were adequate; however, difficulties were encountered in purifying **10** and **14**, and acceptable analytical data were not obtained. Compound **10** was characterized by ^{31}P NMR only, and **14** was used without characterization. Each compound was found to be relatively fragile toward EI-MS analysis. Consequently, none displayed a parent ion even at low ionization voltage. The (^{i}Pr$_2$N)$_2$B$^+$ ion was generally the ion formed in highest abundance. The infrared spectra of **7**, **8**, **10**, **12**, and **14** each displayed a relatively weak band in the region 2322−2300 cm^{-1} that was assigned to the ν_{PH} stretching mode. NMR spectra for the molecules are consistent with the proposed structures, and the data are summarized in Table 2. In particular, the ^{31}P{^{1}H} spectra contained a singlet at δ −186.1, −212.3, −186.3, and −181.2 for **7**, **8**, **10**, and **12**, respectively. The proton-coupled ^{31}P spectra each displayed a doublet due to one-bond P−H coupling, $^1J_{PH}$ = 213, 213, 235, and 215 Hz, respectively. The ^{11}B{^{1}H} NMR spectra contain a single resonance centered at δ 40.4, 40.4, 40.8, and 41.0, respectively. These data compare favorably with ^{31}P and ^{11}B NMR data for borylphosphanes described previously.[1−3] The ^{1}H and ^{13}C{^{1}H} NMR data are consistent with the presence of B(N^{i}Pr$_2$)$_2$ groups and an R$_2$E group in each molecule. It is noteworthy that the ^{i}Pr group

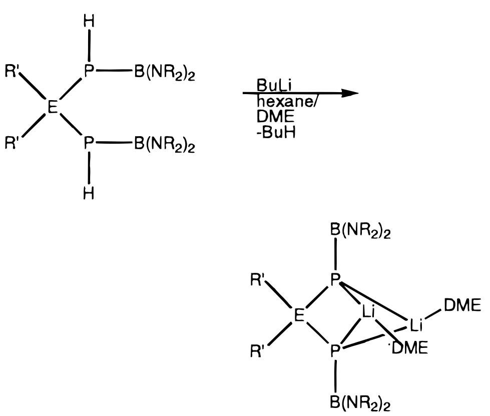
(17) X-ray data collection, cell refinements, and data reduction used *XSCANS*, Version 2.10; Siemens: Madison, WI, 1994.
(18) Space group notation is given in: *International Tables for X-ray Crystallography*; Reidel: Dordrecht, Holland, 1983; Vol. I, pp 73−346.
(19) The empirical absorption corrections used an ellipsoidal model fitted to azimuthal scan data that are then applied to the intensity data: *XPREP*, Version 5.03; Siemens: Madison, WI, 1994.
(20) Structure solutions and refinements employed SHELXL97: Sheldrick, G. M. *Programs for the Refinement of Crystal Structures*; University of Gottingen: Gottingen, Germany, 1997. SHELXTL uses absorption, anomalous dispersion, and scattering data compiled in: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 55−60, 99−101, 149−150. Anomalous dispersion terms were included for all atoms with atomic numbers greater than 2.
(21) A general description of the least-squares algebra is found in: *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; p 187. The least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F)^2 + gF^2]$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds **11**, $\{[(^iPr_2N)_2BP]_2SiPh_2\}Li_2\cdot 2DME$, **13** $\{[(^iPr_2N)_2BP]_2GePh_2\}Li_2\cdot 2DME$, and **15**, $\{\{[(^iPr_2N)(Me_3Si)_2N]BP\}_2SiPh_2\}Li_2\cdot 2DME$

	11		**13**		**15**	
B−P	P(1)−B(1)	1.937(4)	P(1)−B(1)	1.926(5)	P(1)−B(1)	1.941(5)
	P(2)−B(2)	1.931(4)	P(2)−B(2)	1.931(6)	P(2)−B(2)	1.942(5)
P−E	P(1)−Si	2.222(2)	P(1)−Ge	2.296(1)	P(1)−Si(1)	2.230(2)
	P(2)−Si	2.223(1)	P(2)−Ge	2.298(1)	P(2)−Si(1)	2.226(2)
P−Li	P(1)−Li(1)	2.570(6)	P(1)−Li(1)	2.561(8)	P(1)−Li(1)	2.532(8)
	P(1)−Li(2)	2.573(6)	P(1)−Li(2)	2.558(8)	P(1)−Li(2)	2.581(9)
	P(2)−Li(1)	2.522(7)	P(2)−Li(1)	2.596(9)	P(2)−Li(1)	2.650(8)
	P(2)−Li(2)	2.556(6)	P(2)−Li(2)	2.589(8)	P(2)−Li(2)	2.625(8)
B−N	B(1)−N(1)	1.438(5)	B(1)−N(1)	1.417(6)	B(1)−N(1)	1.506(6)
	B(1)−N(2)	1.459(5)	B(1)−N(2)	1.491(6)	B(1)−N(2)	1.420(6)
	B(2)−N(3)	1.429(5)	B(2)−N(3)	1.460(6)	B(2)−N(3)	1.507(6)
	B(2)−N(4)	1.491(5)	B(2)−N(4)	1.431(6)	B(2)−N(4)	1.429(6)
Si−N					Si(2)−N(1)	1.731(4)
					Si(3)−N(1)	1.731(4)
					Si(4)−N(3)	1.733(4)
					Si(5)−N(3)	1.727(4)
P−E−P	P(1)−Si−P(2)	94.01(5)	P(1)−Ge−P(2)	92.65(5)	P(1)−Si(1)−P(2)	95.66(6)
E−O−Li	Si−P(1)−Li(1)	81.5(2)	Ge−P(1)−Li(1)	78.1(2)	Si(1)−P(1)−Li(1)	80.3(2)
	Si−P(1)−Li(2)	77.6(1)	Ge−P(1)−Li(2)	81.7(2)	Si(1)−P(1)−Li(2)	81.3(2)
	Si−P(2)−Li(1)	81.9(2)	Ge−P(2)−Li(1)	77.4(2)	Si(1)−P(2)−Li(1)	77.7(2)
	Si−P(2)−Li(2)	78.0(2)	Ge−P(2)−Li(2)	80.9(2)	Si(1)−P(2)−Li(2)	80.3(2)
Li−P−Li	Li(1)−P(1)−Li(2)	80.5(2)	Li(1)−P(1)−Li(2)	80.6(3)	Li(1)−P(1)−Li(2)	80.1(3)
	Li(1)−P(2)−Li(2)	81.2(2)	Li(1)−P(2)−Li(2)	79.4(3)	Li(1)−P(2)−Li(2)	77.2(3)
P−Li−P	P(1)−Li(1)−P(2)	78.8(2)	P(1)−Li(1)−P(2)	80.2(2)	P(1)−Li(1)−P(2)	79.2(2)
	P(1)−Li(2)−P(2)	78.6(3)	P(1)−Li(2)−P(2)	80.4(2)	P(1)−Li(2)−P(2)	78.8(2)
B−P−E	B(1)−P(1)−Si	120.6(1)	B(1)−P(1)−Ge	123.0(2)	B(1)−P(1)−Si(1)	123.5(2)
	B(2)−P(2)−Si	124.2(1)	B(2)−P(2)−Ge	119.4(2)	B(2)−P(2)−Si(1)	121.5(2)
P−B−N	P(1)−B(1)−N(1)	126.4(3)	P(1)−B(1)−N(1)	128.6(4)	P(1)−B(1)−N(1)	112.9(3)
	P(1)−B(1)−N(2)	114.8(3)	P(1)−B(1)−N(2)	113.5(3)	P(1)−B(1)−N92)	128.2(4)
	P(2)−B(2)−N(3)	127.9(3)	P(2)−B(2)−N(3)	115.0(3)	P(2)−B(2)−N(3)	112.6(3)
	P(2)−B(2)−N(4)	114.5(3)	P(2)−B(2)−N(4)	126.0(3)	P(2)−B(2)−N(4)	129.0(3)
N−B−N	N(1)−B(1)−N(2)	118.6(3)	N(1)−B(1)−N(2)	117.9(4)	N(1)−B(1)−N(2)	118.8(4)
	N(3)−B(2)−N(4)	117.5(3)	N(3)−B(2)−N(4)	118.9(4)	N(3)−B(2)−N(4)	118.4(4)

environments on the aminoboryl fragments are equivalent, consistent with free rotation about the P−B bonds.

The reactions of **8**, **10**, **12**, and **14** with BuLi (1:2) in DME/hexane solution produced the respective bis(phosphides) **9**, **11**, **13**, and **15** as shown in eq 2. Attempts to isolate the phosphide



(2)

	9	**11**	**13**	**15**
R'_2E	$(Me_2Si)_2$	Ph_2Si	Ph_2Ge	Ph_2Si
R_2N	$^iPr_2N$	$^iPr_2N$	$^iPr_2N$	$(^iPr_2N)(Me_3Si)_2N$

derivative of **7** were unsuccessful. Each of the new bis(phosphides) was formed quantitatively as indicated by ^{31}P NMR spectroscopy. The compounds were isolated with reduced yields as pale yellow crystalline solids. The reduced yields result from the high solubility of the compounds. This is normally not a problem since the bis(phosphides) are used in further reactions without intermediate isolation. When the deprotonation reactions were performed with 1 equiv of BuLi, the mono(phosphido) species were not obtained. Instead, mixtures of neutral ligand and bis(phosphido) compound were obtained.

The new compounds gave CHN analytical data consistent with the proposed compositions. Like the respective precursors, the lithio compounds are fragile toward EI-MS analysis, and no parent ions were detected. The ^{31}P NMR spectra for **9**, **11**, **13**, and **15** contain a single resonance with no P−H coupling, and the shifts are generally upfield of the parent ligand, consistent with increased electron density on the phosphorus atoms in the lithio compounds. The ^{31}P resonances for **11** and **13** are split by coordinated Li^+ ions. The spectrum of **13** displays a fully resolved septet due to two equivalent ^{7}Li ions coupling with equivalent phosphorus atoms. The resonance for **11** is less clearly resolved, but the septet structure is evident as shoulders on the broad resonance. This feature is confirmed by one-bond P−Li coupling (triplet, 41−48 Hz) in the ^{7}Li{^{1}H} NMR spectra, δ 5.4, 4.5, and 4.5 for **9**, **11**, and **13**, respectively. The triplets are observed at 20 °C for **11** and **13** but only at −60 °C for **9**. The ^{1}H and ^{13}C{^{1}H} NMR spectra are consistent with the proposed chelating phosphido structures. The ^{i}Pr group environments are equivalent, indicating that the P−B bonds do not experience hindered rotation at room temperature on the NMR time scale.

Single crystals of **11**, **13**, and **15** were obtained, and X-ray diffraction analyses were completed for each. Compounds **11** and **13** are isomorphous; compound **15** adopts a different space

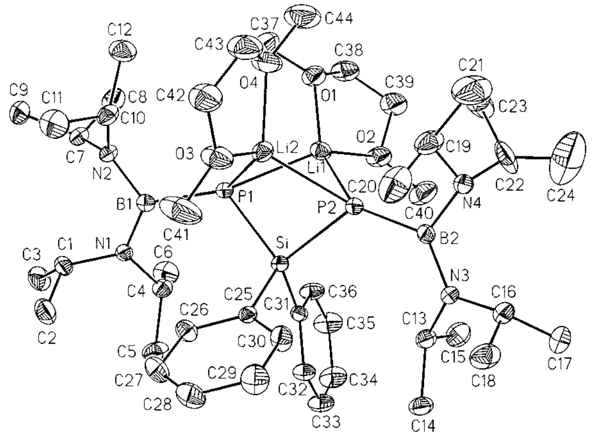


Figure 1. Molecular structure and atom-labeling scheme for {[($^{i}Pr_2N)_2$-$BP]_2SiPh_2$} Li_2·DME, **11**.

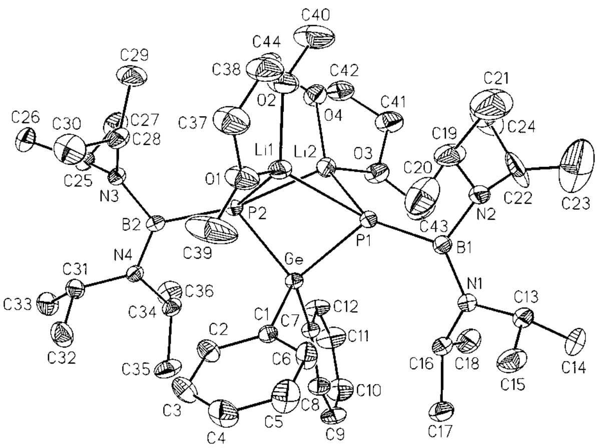


Figure 2. Molecular structure and atom-labeling scheme for {[($^{i}Pr_2N)_2$-$BP]_2GePh_2$} Li_2·DME, **13**.

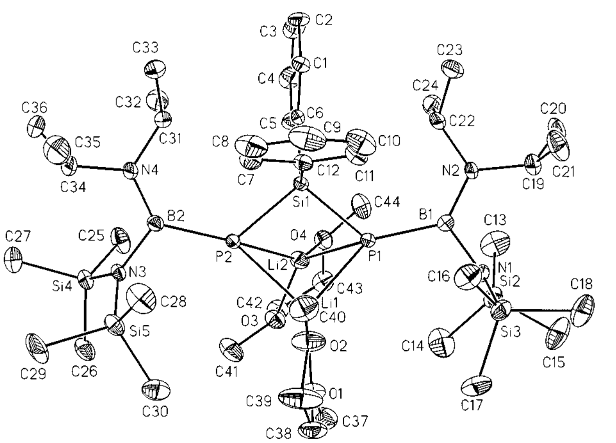


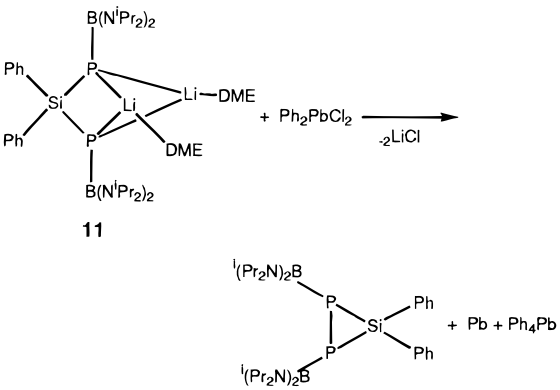
Figure 3. Molecular structure and atom-labeling scheme for {{[(^{i}-$Pr_2N)(Me_3Si)_2N$] BP}$SiPh_2$}Li_2·DME, **15**.

group, but the molecular structure is very similar to the other two structures. Views of the molecules are shown in Figures 1−3, and bond lengths and angles are summarized in Table 3. In each case, the molecular unit is monomeric, and the five heavy atoms, P(1), P(2), Li(1), Li(2), and E (Si or Ge), form a trigonal bipyramidal core. There is a pseudomirror plane that passes through the Li(1), Li(2), and the E atoms, and P(1) and P(2) lie above and below the plane, respectively. The P atoms, in the apical positions, have a tetrahedral geometry with exo $B(NR_2)_2$ groups. The average P−B bond lengths in **11**, 1.934(4) Å, **13**, 1.928(6) Å, and **15**, 1.941(5) Å, are shorter than the average cage core P−B distances in $P_2(BN^{i}Pr_2)_2SiPh_2$, **16**[22] 1.973 Å, and in $P_2(Btmp)_2GePh_2$[23] (tmp = 2,2,6,6-tetramethylpiperidino), **17**, 1.973 Å, but they are typical of P−B single-bond lengths in a variety of (aminoboryl)phosphanes.[1−3] The boron atoms in the exo aminoboryl substituent groups are in a planar environment, and each group has a short and a long B−N bond. This effect has been observed in several (aminoboryl)phosphanes,[1−3] although its origin is not yet fully understood. In cases, e.g. **15**, where different R groups are present on the amino nitrogen atoms, one might expect that variable B−N π-bond overlaps could result in the observed trends in B−N bond lengths. For symmetrical amino groups, e.g. in **11** and **13**, another explanation is required. It is also noted that in **11**, **13**, and **15** the long B−N bond is positioned above the planar, chelating DME molecule and the short B−N bond is positioned above the planar C_6H_5 group.

The average P−Si distances in the cage cores of **11**, 2.222(1) Å, and **15**, 2.228(2) Å, are shorter than the average P−Si core distance in **16**, 2.243 Å.[22] Similarly, the average P−Ge distance in **13**, 2.297(2) Å, is shorter than the average P−Ge core distance in **17**, 2.324 Å.[22] The P−Si−P bond angles in **11**, 94.0(1)°, and **15**, 95.7(6)°, are larger than the angle in **16**, 85.7(1)°, and the P−Ge−P bond angle in **13**, 92.6(1)°, is larger than the angle in **17**, 80.7(1)°. These differences are consistent with the smaller size of the Li atoms in the cages of **11**, **13**, and **15** compared to the boron atoms in **16** and **17**. The cage Si atoms and Ge atom are tetrahedral, and the average E−C bond lengths and C−E-C angles are normal: **11**, Si−C 1.905(1) Å, C−Si−C 105.0(2)°; **13**, Ge−C 1.972(2) Å, C−Ge−C 105.1(2)°; **15**, Si−C 1.909(5) Å, C−Si−C 105.9(2)°. It is also noted that, in each molecule, one of the E−Ph groups is oriented perpendicular to the pseudomirror plane and the other is oriented parallel to the pseudomirror plane. The folded P_2Li_2 four-membered ring that composes part of the tricyclic structures of **11**, **13**, and **15** is asymmetric in an unexpected way. It might be anticipated that the phosphido−lithium interactions would be asymmetric, with one short and one long P−Li distance for each of the P(1) and P(2) atoms. Instead, it is observed that one phosphorus shows two shorter P−Li distances while the other phosphorus atom displays two longer P−Li distances: **11**, P(1)−Li(1) 2.571(6) Å, P(1)−Li(2) 2.573(6) Å, P(2)−Li(1) 2.552(7) Å, P(2)−Li(2) 2.556(6) Å; **13**, P(1)−Li(1) 2.561(8) Å, P(1)−Li(2) 2.558(8) Å, P(2)−Li(1) 2.596(9) Å, P(2)−Li(2) 2.589(8) Å; **15**, P(1)−Li(1) 2.532(8) Å, P(1)−Li(2) 2.580(8) Å, P(2)−Li(1) 2.650(8) Å, P(2)−Li(2) 2.625(8) Å. These distances are comparable to the P−Li bond lengths in the dimer [($^{i}Pr_2N)_2$BP(H)Li·DME$]_2$: P−Li 2.535(7) Å, P−Li′ 2.554(7) Å.[2] However, this ring is a planar rhombus. Despite the bond length asymmetry, the internal P−Li−P angles are identical: **11**, P(1)−Li(1)−P(2) 78.8(2)°, P(1)−Li(2)−P(2) 78.6(2)°; **13**, P(1)−Li(1)−P(2) 80.2(2)°, P(1)−Li(2)−P(2) 80.4(2)°; **15**, P(1)−Li(1)−P(2) 79.2(2)°, P(1)−Li(2)−P(2) 78.8(2)°. Each Li atom is tetrahedrally coordinated by the two phosphido phosphorus atoms and the two oxygen atoms of a bidentate DME ligand. It is interesting to note that one DME−Li ring is oriented approximately parallel with the pseudo molecular mirror plane and the second DME−Li ring is oriented approximately perpendicular to the pseudo molecular mirror plane. This is consistent with the bulky groups on the perimeter of the P_2ELi_2 cage attempting to avoid each other.

(22) Dou, D.; Kaufmann, B.; Duesler, E. N.; Chen, T.; Paine, R. T.; Nöth, H. *Inorg. Chem.* **1993**, *32*, 3056.
(23) Chen, T.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Inorg. Chem.* **1997**, *36*, 802.

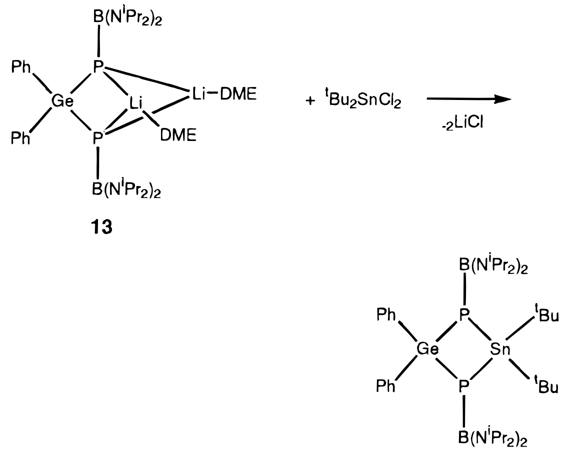
Klingebiel and co-workers[6] previously reported that combination of $^{t}Bu_2Si[P(H)Ph]_2$ with 2 equiv of BuLi followed by treatment with $F_2PN^{t}Bu_2$ gave a four-membered-ring compound, $^{t}Bu_2\overline{SiP(Ph)P(N^{t}Bu_2)P}Ph$. It is presumed that this reaction proceeds through a bis(phosphido) compound, $^{t}Bu_2Si[P(Ph)Li]_2$, although this point was not discussed in any detail. We are interested in the reactivity of such fragments, and some initial attempts have been made to characterize the reactions of **11** and **13**. It is noted that, in general, their reactions are relatively sluggish. This may be due to extensive steric crowding. Combinations of **11** with $^{i}Pr_2NBCl_2$, $(Me_2Si)_2NBCl_2$, R_2SiCl_2 (R = Me, Ph), R_2GeCl_2 (R = Me, Ph), and R_2SnCl_2 (R = Me, Ph, ^{t}Bu) were examined, and at 23 °C no reactions were observed. Under more forcing conditions, degradation reactions took place. Reaction of **11** with Ph_2PbCl_2 rapidly produced redox products as summarized in eq 3. The Pb deposited as a black film on the flask walls, and Ph_4Pb was identified by its ^{1}H and ^{13}C NMR spectra and mass spectrum. The phosphorus-containing product has a single resonance in its ^{31}P NMR spectrum, δ −235, and this may correspond to the indicated three-membered ring or a dimer. Full characterization of this product was not accomplished.



11

(3)

The reaction of **13** with $^{t}Bu_2SnCl_2$, however, produced the anticipated metathesis chemistry with formation of the four-membered-ring compound **18**, having a Ge, Sn, and two P atoms in the ring (eq 4). The pale orange solid provides a parent ion



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18

(4)

in its mass spectrum and adequate CHN analysis. The $^{31}P\{^{1}H\}$ NMR spectrum displays a single resonance, δ −164.7, with P−Sn satellites, $^{1}J_{PSn}$ = 791 Hz. The ^{119}Sn NMR spectrum contains a triplet ($^{1}J_{PSn}$ = 808 Hz), indicating that the two P atoms bonded to Sn are equivalent. There is no evidence for both cis and trans isomers, and it is assumed that the product has the trans geometry. Attempts to obtain suitable crystals for structure analysis have been unsuccessful.

The results of this initial study show that boryl-substituted silyl- and germyldiphosphines can be prepared and that their lithium derivatives are monomeric in the solid state. Their reactivity is surprisingly sluggish; however, their chemistry needs to be explored more closely, under different conditions.

Acknowledgment is made to the National Science Foundation (Grant CHE-9508668) for support of this research. The cooperation of the Center for Mass Spectrometry, University of Nebraska, where FAB-MS data were obtained, is noted.

Supporting Information Available: X-ray crystallographic files, in CIF format, are available free of charge via the Internet at http://pubs.acs.org.

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