Instrumentation. Hewlett-Packard 8452A diode-array and Carl-Zeiss-Jena M40 spectrometers were used to measure the electronic absorption spectra. The IR spectra were recorded on Philips PU9800 FTIR and Nicolet 7199B FTIR spectrometers at resolutions of 4 and 1 cm^{-1}, respectively. EPR spectra were measured using a Varian E4 X-band spectrometer. The temperature-dependent ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AM 400 instrument. The resonance Raman spectra were measured with a Dilor XY spectrometer with excitation by the lines of a SP 2016 Ar$^+$ laser or by a CR-590 dye laser employing Coumarine 6 or Rhodamine 6G dyes pumped by the Ar$^+$ laser. The solutions of both DBCat complexes **1** and **2** were placed in 1-cm quartz cells. Resonance Raman spectra of all other compounds were measured by employing an IR-OTTLE cell[42] equipped with a Pt-minigrid working electrode (6 × 5 mm rectangle; 32 wires/cm) and NaCl windows. The laser beam was directed at the surface of the working electrode, and the back-scattered light was detected. The same infrared OTTLE cell was also employed to measure IR (with KBr windows) and UV–vis spectra (with CaF$_2$ windows) of the spectroelectrochemically generated DBSQ and DBQ complexes. The controlled-potential electrolyses within the OTTLE cell were carried out using a Model PA4 polarographic analyser (Laboratorní Přístroje, Prague) or a PAR Model 173 potentiostat equipped with Instruments) x-y recorders, respectively. All potentials are referenced to that of the Fc/Fc$^+$ couple.[49] The low-temperature IR measurements were performed using an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat. The low-temperature UV–vis spectra were obtained with a Leybold Heraeus ROK 10-300 refrigerator-controlled helium cryostat. The sample solutions in standard 1cm cuvettes were sealed under high vacuum and placed in a homemade Cu sample holder.

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Synthesis and Chemistry of Diborylphosphanes

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Syntheses for (*i*-Pr$_2$N)$_2$BP(SiMe$_3$)$_2$ and (*i*-Pr$_2$N)$_2$BPH$_2$ from (*i*-Pr$_2$N)$_2$BCl and LiP(SiMe$_3$)$_2$ or LiPH$_2$ and for {[Li·DME][(*i*-Pr$_2$N)$_2$BP(H)]}$_2$ from (*i*-Pr$_2$N)$_2$BPH$_2$ and BuLi are described. The species {[Li·DME][(*i*-Pr$_2$N)$_2$BP(H)]}$_2$ is a useful synthon for diborylphosphines, and preparations of [(*i*-Pr$_2$N)$_2$B]$_2$PH, Ph$_2$NB[P(H)B(*i*-Pr$_2$N)$_2$]$_2$, and [(*i*-Pr$_2$N)$_2$B][(R$_2$N)(Cl)B]PH (R$_2$N = *i*-Pr$_2$N, tmp, [Me$_3$Si]$_2$N) are presented. Metal carbonyl coordination chemistry and selected substitution chemistry of these reagents are also described. The molecular structures of {[Li·DME][(*i*-Pr$_2$N)$_2$BP(H)]}$_2$ (**3**), [(*i*-Pr$_2$N)$_2$B][tmpB(Cl)]PH (**7**), [(*i*-Pr$_2$N)$_2$B][tmpB(Cl)]PH·Cr(CO)$_5$ (**13**), and [(*i*-Pr$_2$N)$_2$B]$_2$PH·Cr(CO)$_5$ (**12**) have been determined by single-crystal X-ray diffraction analyses: **3** (C$_{16}$H$_{39}$BLiN$_2$O$_2$P) crystallizes in the monoclinic space group $P2_1/n$ with a = 9.458 (2) Å, b = 22.054 (3) Å, c = 11.574 (2) Å, β = 111.86 (1)°, and Z = 4; **7** (C$_{21}$H$_{47}$B$_2$N$_3$PCl) crystallizes in the monoclinic space group $P2_1/n$ with a = 16.661 (3) Å, b = 9.218 (2) Å, c = 18.068 (4) Å, β = 103.88 (3) Å, and Z = 4; **13** (C$_{26}$H$_{47}$B$_2$N$_3$O$_5$PClCr) crystallizes in the triclinic space group $P\bar{1}$ with a = 10.395 (2) Å, b = 10.923 (2) Å, c = 15.800 (3) Å, α = 103.51 (2)°, β = 83.92 (2)°, γ = 104.45 (2)°, and Z = 2; **12** (C$_{29}$H$_{57}$B$_2$N$_4$O$_5$PCr) crystallizes in the monoclinic space group $P2_1/n$ with a = 10.534 (2) Å, b = 19.991 (4) Å, c = 18.005 (4) Å, β = 95.16 (3)°, and Z = 4.

Introduction

Elimination reactions between appropriate phosphane and borane reagents produce a variety of monomeric phosphinoboranes, R$_2$PBX$_2$, small-ring phosphinoboranes (R$_2$PBX$_2$)$_n$ (n = 2, 3), and polymeric compounds.[1-21] Recent reevaluations of this chemistry have indicated that there are additional synthetic objectives that may be achieved with this chemistry.[22-51] In particular, it has been revealed that novel, multiply bonded species and clusters can be obtained by careful design of precursors. In this regard, our groups have found that phosphinoboranes with diethylpropyl, trimethylsilyl, or hydrogen substituents on phosphorus are particularly useful precursors.[43,46-51] In this report, the utilization of {[Li·DME][(*i*-Pr$_2$N)$_2$BP(H)]}$_2$ to prepare diborylphosphines [(*i*-Pr$_2$N)$_2$B]$_2$PH, Ph$_2$NB[P(H)B(*i*-Pr$_2$N)$_2$]$_2$, and [(*i*-Pr$_2$N)$_2$B][(R$_2$N)(Cl)B]PH is described along with selected chemistry of these reagents.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Nicolet 6000 FT-IR spectrometer from solution cells or KBr pellets. Mass spectra were obtained from a Finnegan mass spectrometer by using a GC inlet system or heated solids probe. NMR spectra were recorded on Bruker WP 250 and JEOL GSX-400 spectrometers. All NMR samples were sealed in 5-mm tubes with a deuterated lock solvent, and the spectra were referenced with Me$_4$Si (^{13}C, ^{1}H), BF$_3$·Et$_2$O (^{11}B), LiBr (^{7}Li), and 85% H$_3$PO$_4$ (^{31}P). Elemental

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analyses were performed by R. Ju of the UNM Analytical Services Laboratory.

Materials. Reagents i-Pr_2NBCl_2,[52] $(i$-$Pr_2N)_2BCl$,[52] $tmpBCl_2$,[53] Ph_2NBCl_2,[54] $(Me_3Si)_2NBCl_2$,[55] $LiP(SiMe_3)_2{\cdot}2THF$,[56] $LiPH_2{\cdot}DME$,[57] and $Cr(CO)_5{\cdot}NMe_3$[58] were prepared as described in the literature,[59] and NH_3 (Matheson), BuLi (Aldrich), and Me_3SiCl (Aldrich) were either used as received or purified by distillation. All solvents were dried and degassed by standard techniques, and solvent transfers were accomplished by vacuum distillation.

Synthesis and Characterization of Compounds. Bis(diisopropylamino)[bis(trimethylsilyl)phosphino]borane (1a). A 3.3-g (10-mmol) sample of $LiP(SiMe_3)_2{\cdot}2THF$ was dissolved in 40 mL of benzene, and this solution was added to a solution of 2.5 g (10 mmol) of $(i$-$Pr_2N)_2BCl$ in 15 mL of benzene. The mixture was refluxed for 3 h, and the resulting slurry was filtered. The solvent was vacuum evaporated from the filtrate, leaving a yellow oil. Distillation at the boiling point of 110 °C (10^{-3} Torr) provided a colorless crystalline solid: mp 64 °C; yield 2.4 g (62%). Mass spectrum (55 eV) [*m/z* (%)]: 373 ($M - CH_3^+$, 10), 211 (100), 73 (100). Infrared spectrum (hexane, cm^{-1}): 1423 (m), 1401 (m), 1384 (w), 1362 (m), 1295 (s), 1244 (s), 1218 (s), 1199 (s), 1185 (m), 1151 (m), 1133 (m), 1108 (m), 1068 (m), 851 (s), 833 (vs), 758 (m), 747 (m), 687 (m), 687 (w), 631 (s), 467 (w). Anal. Calcd for $C_{18}H_{46}BN_2Si_2P$ (388.54): C, 55.70; H, 11.86; N, 7.22. Found: C, 56.07; H, 11.80; N, 7.01.

Bis(diisopropylamino)phosphinoborane (2). A solution containing 15 g (60 mmol) of $(i$-$Pr_2N)_2BCl$ in 25 mL of hexane was combined at 0 °C with 7.8 g (60 mmol) of $LiPH_2{\cdot}DME$ in 25 mL of hexane. The solution was warmed to 23 °C and stirred for 12 h. The resulting cloudy mixture was filtered, and the solvent was removed from the filtrate by vacuum evaporation, leaving a slightly yellow oil: bp 55–62 °C (10^{-3} Torr); yield 14 g (96%). Mass spectrum (30 eV): [*m/z* (%)]: 243 (M^+, 0.1), 211 (100), 110 (20), 68 (10), 43 (70). Infrared spectrum (neat, cm^{-1}): 2967–2813 (s, br), 2319 (m), 1469 (m), 1439 (m), 1411 (w), 1380 (m), 1365 (s), 1298 (s), 1224 (m), 1184 (s), 1143 (s), 1062 (m), 1036 (m), 771 (w). Anal. Calcd for $C_{12}H_{38}BN_2P$ (244.16): C, 59.03; H, 12.39; N, 11.47. Found: C, 59.04; H, 12.50; N, 11.29.

Lithium–Dimethoxyethane [Bis(diisopropylamino)boryl]phosphide (3). A solution containing 6.6 g (27 mmol) of **2** in 50 mL of DME was cooled to −78 °C, and 17 mL (27 mmol) of BuLi solution (1.6 M in hexanes) was added dropwise. The resulting yellow solution was stirred for 2 h at −78 °C and then warmed to 23 °C and stirred for 12 h. The solvent was removed by vacuum evaporation, leaving a yellow residue that was washed with cold hexane (3 × 5 mL). A white solid was collected by filtration: mp 86–88 °C; yield 8.5 g (93%). Infrared spectrum (cyclohexane, cm^{-1}): 2271 (w), 1438 (m), 1416 (m), 1369 (m), 1321 (s), 1297 (w), 1257 (m), 1212 (m), 1190 (m), 1142 (m), 1128 (m), 1107 (m), 1091 (s), 1053 (m), 1036 (m), 870 (m), 729 (m). Anal. Calcd for $C_{16}H_{39}LiBN_2O_2P$ (340.22): C, 56.48; H, 11.55; N, 8.23. Found: C, 56.40; H, 11.74; N, 8.24.

Bis[bis(diisopropylamino)boryl]phosphane (4). A solution of 2.2 g (8.9 mmol) of $(i$-$Pr_2N)_2BCl$ in 25 mL of hexane was cooled to −78 °C and added to 3.0 g (8.9 mmol) of **3** in 25 mL of hexane. The combined solutions were stirred at −78 °C for 1 h and then warmed to 23 °C and stirred for another 12 h. The cloudy, white mixture was filtered, and the filtrate was vacuum evaporated, leaving a colorless oil. A NMR spectrum showed that no further purification was necessary. Yield: 3.8 g (94%). Mass spectrum (30 eV) [*m/z* (%)]: 211 (100), 167 (30), 110 (50). Infrared spectrum (neat, cm^{-1}): 2966 (s), 2930 (s), 2870 (m), 2326 (w), 1467 (m), 1422 (m), 1408 (m), 1377 (m), 1362 (s), 1319 (m), 1299 (s), 1214 (s), 1200 (s), 1185 (m), 1149 (m), 1132 (m), 1113 (m), 1066 (m). Anal. Calcd for $C_{24}H_{57}B_2N_4P$ (454.34): C, 63.45; H, 12.64; N, 12.33. Found: C, 63.11; H, 11.75; N, 12.80.

[Bis(diisopropylamino)boryl][(diisopropylamino)chloroboryl]phosphane (5). A solution of 0.64 g (3.5 mmol) of i-Pr_2NBCl_2 in 25 mL of hexane was combined with 1.2 g (3.5 mmol) of **3** in 25 mL of hexane at −78 °C. The mixture was stirred for 1 h, warmed to 23 °C, and stirred for 12 h. The white, cloudy mixture was filtered, and the solvent removed from the filtrate by vacuum evaporation, leaving a colorless oil that decomposed during attempted distillation. Yield: 1.3 g (96%). Mass spectrum (30 eV) [*m/z* (%)]: 388 (M^+, 2), 211 (100), 167 (50), 127 (40), 110 (60), 100 (50), 85 (50), 58 (90). Infrared spectrum (neat, cm^{-1}): 2303 (w), 1474 (m), 1442 (s), 1429 (m), 1407 (m), 1365 (s), 1308 (vs), 1225 (s), 1201 (s), 1186 (s), 1139 (s), 1115 (s), 1075 (m), 1007 (m), 912 (m), 904 (m). Anal. Calcd for $C_{18}H_{43}B_2N_3PCl$ (389.61): C, 55.49; H, 11.12; N, 10.78. Found: C, 56.29; H, 11.24; N, 10.23.

Bis[(bis(diisopropylamino)boryl)phosphino](diphenylamino)borane (6). A solution containing 0.25 g (1.0 mmol) of Ph_2NBCl_2 in 25 mL of hexane was combined with 0.68 g (2.0 mmol) of **3** in 25 mL of hexane at −78 °C. The solution was stirred for 1 h, warmed to 23 °C, and stirred for an additional 12 h. The resulting mixture was filtered and the solvent vacuum evaporated from the filtrate, leaving a yellow solid. The residue was recrystallized from 5 mL of hexane at −10 °C, leaving colorless crystals: mp 127–129 °C; yield 0.60 g (90%). Mass spectrum (30 eV) [*m/z* (%)]: 434 (20), 211 (100), 110 (20), 100 (20). Infrared spectrum (cyclohexane, cm^{-1}): 2300 (w), 1592 (m), 1491 (s), 1462 (s), 1424 (s), 1405 (s), 1376 (s), 1362 (s), 1324 (s), 1304 (vs), 1248 (s), 1221 (vs), 1199 (vs), 1150 (s), 1135 (s), 1112 (s), 1072 (s), 756 (s), 697 (s). Anal. Calcd for $C_{36}H_{68}B_3N_5P_2$ (665.35): C, 64.99; H, 10.30; N, 10.53. Found: C, 64.38; H, 10.38; N, 10.00.

[Bis(diisopropylamino)boryl][(2,2,6,6-tetramethylpiperidino)chloroboryl]phosphane (7). A solution containing 2.0 g (8.9 mmol) of $tmpBCl_2$ in 25 mL of hexane was combined with 3.0 g (8.9 mmol) of **3** in 25 mL of hexane at 23 °C. The solution was stirred for 12 h and filtered, and the filtrate was concentrated by removal of approximately half of the solvent by vacuum evaporation. Colorless crystals deposited from the solution upon standing overnight at 0 °C: mp 108–110 °C; yield 2.6 g (68%). Mass spectrum (30 eV) [*m/z* (%)]: 313 (10), 211 (100), 195 (20), 167 (40), 110 (50), 100 (30), 85 (40), 69 (60), 58 (80). Infrared spectrum (cyclohexane, cm^{-1}): 2326 (w), 1429 (m), 1407 (m), 1386 (m), 1365 (s), 1320 (s), 1311 (s), 1284 (m), 1225 (m), 1202 (m), 1184 (m), 1171 (m), 1151 (m), 1130 (m), 1076 (m), 995 (m). Anal. Calcd for $C_{21}H_{47}B_2N_3PCl$ (429.67): C, 58.70; H, 11.03; N, 9.78. Found: C, 58.82; H, 11.02; N, 9.83.

[Bis(diisopropylamino)boryl][(2,2,6,6-tetramethylpiperidino)aminoboryl]phosphane (8). A 1.2-g (2.8-mmol) sample of **7** was dissolved in 50 mL of hexane and the solution frozen at −196 °C. Excess dry NH_3 was condensed on the sample, and the mixture was warmed to −78 °C and stirred for 2 h. The reaction mixture was filtered, and the solvent and excess NH_3 were removed by vacuum evaporation, leaving a colorless

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(59) Abbreviations used in the text include Me = methyl, i-Pr = isopropyl, tmp = 2,2,6,6-tetramethylpiperidinyl, Ph = phenyl, THF = tetrahydrofuran, DME = ethylene glycol dimethyl ester, TMS = trimethylsilyl, and Mes = mesityl.

Table I. Crystallographic Data for $\{[Li\cdot DME][(i\text{-}Pr_2N)_2BP(H)]\}_2$ (**3**) $[(i\text{-}Pr_2N)_2B][tmpB(Cl)]PH$ (**7**), $[(i\text{-}Pr_2N)_2B]_2P(H)\cdot Cr(CO)_5$ (**12**), and $[(i\text{-}Pr_2N)_2B][tmpB(Cl)]P(H)\cdot Cr(CO)_5$ (**13**)

	3	**7**	**12**	**13**
chem formula	$C_{16}H_{39}BLiN_2O_2P$	$C_{21}H_{47}B_2N_3PCl$	$C_{29}H_{57}B_2N_4O_5PCr$	$C_{26}H_{47}B_2N_3O_5PClCr$
a, Å	9.458 (2)	16.661 (3)	10.534 (2)	10.395 (2)
b, Å	22.054 (3)	9.218 (2)	19.991 (4)	10.923 (2)
c, Å	11.574 (2)	18.068 (4)	18.005 (4)	15.800 (3)
α, deg				103.51 (2)
β, deg	111.86 (1)	103.88 (3)	95.16 (3)	83.92 (2)
γ, deg				104.45 (2)
V, Å^3	2240.6 (6)	2694 (1)	3776 (1)	1685.9 (6)
Z	4	4	4	2
ρ_{calcd}, g cm^{-3}	1.009	1.059	1.137	1.225
fw	340.2	429.7	646.4	621.7
cryst dimen, mm	0.21 × 0.35 × 0.58	0.23 × 0.39 × 0.48	0.16 × 0.35 × 0.35	0.29 × 0.39 × 0.75
cryst system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
T, °C	20	20	20	20
μ, mm^{-1}	0.126	0.210	0.372	0.491
2θ range, deg	2–50	2–50	2–45	2–50
reflcns measd	$\pm h,k,l$	$h,-k,\pm l$	$h,-k,\pm l$	$\pm h,\pm k,\pm l$
tot. no. of reflcns collcd	4309	5254	5449	10,436
no. of unique reflcns	3974	4740	4937	5927
no. of obsd reflcns	2116 ($F \geq 3\sigma(F)$)	2824 ($F \geq 3\sigma(F)$)	3329 ($F \geq 3\sigma(F)$)	4603 ($F \geq 3\sigma(F)$)
transm coeff	0.6966–0.8123	0.7907–0.8492	0.6538–0.6790	0.4280–0.4672
R_F	6.70	7.06	8.89	6.29
R_{wF}	5.70	7.71	5.76	6.36

oil that formed a sticky solid upon standing. Yield: 0.80 g (70%). Mass spectrum (30 eV) [m/z (%)]: 308 ($M - H_2^+$), 243 (10), 211 (100), 167 (90), 111 (30), 100 (30). Infrared spectrum (neat, cm^{-1}): 3501 (w), 3416 (w), 3400 (w), 2980–2870 (s, br), 2327 (w), 1583 (s), 1466 (m), 1423 (s), 1408 (s), 1380 (s), 1362 (vs), 1323 (vs), 1299 (vs), 1254 (s), 1236 (s), 1223 (s), 1202 (s), 1182 (s), 1152 (s), 1133 (s), 1073 (s), 1040 (m), 1013 (m), 997 (w), 973 (w), 766 (w), 525 (w). Anal. Calcd for $C_{21}H_{49}B_2N_4P$ (410.24): C, 61.48; H, 12.04; N, 13.66. Found: C, 62.01; H, 12.23; N, 13.90.

[Bis(diisopropylamino)boryl](trimethylsilyl)phosphane (9). A solution containing 5.5 g (16 mmol) of **3** in 25 mL of hexane was cooled to −78 °C and mixed with 1.8 g (16 mmol) of Me_3SiCl in 25 mL of hexane. The solution was stirred for 1 h, warmed to 23 °C, and stirred for 12 h. The mixture was filtered and the filtrate vacuum evaporated, leaving an oily residue that distilled at 68–72 °C (10^{-3} Torr). Yield: 4.2 g (82%). Mass spectrum (30 eV) [m/z (%)]: 315 (M^+, 5), 211 (100), 167 (50), 110 (90), 100 (50), 73 (90). Infrared spectrum (neat, cm^{-1}): 2965–2870 (s, br), 2307 (w), 1468 (m), 1425 (s), 1408 (s), 1377 (m), 1363 (s), 1324 (s), 1304 (vs), 1245 (s), 1223 (s), 1202 (s), 1185 (s), 1151 (m), 1136 (s), 1113 (s), 1073 (s), 1008 (w), 838 (vs), 764 (m), 749 (m), 688 (m), 629 (m). Anal. Calcd for $C_{15}H_{38}BN_2PSi$ (316.0): C, 57.01; H, 12.02; N, 8.86. Found: C, 57.27; H, 12.23; N, 9.27.

Lithium–Tetrahydrofuran [Bis(diisopropylamino)boryl](trimethylsilyl)phosphide (10). A solution containing 3.3 g (10 mmol) of **9** in 25 mL of THF was combined with 6.5 mL (10 mmol) of BuLi solution (1.6 M in hexanes) in 25 mL of THF at −78 °C. The mixture was stirred for 1 h and then warmed to 23 °C. After 12 h, the solvent was vacuum evaporated, and the yellow residue was recrystallized from hexane at −10 °C: mp 128–130 °C; yield 3.4 g (83%), colorless crystals. Infrared spectrum (hexane, cm^{-1}): 1608 (m), 1398 (m), 1361 (m), 1313 (m), 1275 (m), 1234 (m), 1214 (s), 1151 (m), 1075 (s), 1055 (m), 985 (w), 915 (m), 838 (m). Anal. Calcd for $C_{19}H_{45}LiBN_2OSiP$ (394.39): C, 57.86; H, 11.50; N, 7.10. Found: C, 57.11; H, 11.85; N, 7.32.

[Bis(diisopropylamino)boryl][(bis(trimethylsilyl)amino)chloroboryl]phosphane (11). A solution containing 0.70 g (2.9 mmol) of $(tms)_2NBCl_2$ in 25 mL of hexane was combined at −78 °C with 0.98 g (2.9 mmol) of **3** in 25 mL of hexane. The mixture was stirred at −78 °C for 3 h and then warmed to 23 °C and stirred for an additional 16 h. The cloudy solution was filtered, and solvent was removed by vacuum evaporation, leaving a colorless oil. Yield: 1.2 g (92%). Infrared spectrum (neat, cm^{-1}): 2965–2923 (m), 2328 (w), 2317 (w), 1363 (m), 1314 (m), 1271 (m), 1253 (s), 1217 (vs), 1200 (s), 916 (s), 871 (s), 852 (s). Anal. Calcd for $C_{18}H_{47}B_2N_3Si_2PCl$ (449.82): C, 48.06; H, 10.53; N, 9.34. Found: C, 48.63; H, 10.78; N, 9.47.

[Bis[bis(diisopropylamino)boryl]phosphane]chromium Pentacarbonyl (12). A 0.39-g (0.86-mmol) sample of **4** in 25 mL of hexane was combined with 0.22 g (0.86 mmol) of $Cr(CO)_5\cdot NMe_3$ dissolved in 25 mL of hexane. The mixture was stirred for 15 h at 23 °C, and the solvent was subsequently removed by vacuum evaporation. The yellow solid residue was recrystallized from 5 mL of hexane at −10 °C: mp 138–142 °C dec; yield 0.42 g (76%), yellow crystals. Mass spectrum (30 eV) [m/z (%)]: 322 (10), 294 (50), 211 (100), 197 (50), 169 (50), 127 (40), 110 (60), 100 (40). Infrared spectrum (cyclohexane, cm^{-1}): 2052 (m), 1926 (vs), 1897 (w), 1461 (m), 1417 (m), 1366 (w), 1338 (w), 1215 (w), 1196 (w), 674 (w), 658 (m). Anal. Calcd for $C_{29}H_{57}B_2N_4O_5PCr$ (646.39): C, 53.89; H, 8.89; N, 8.67. Found: C, 54.05; H, 9.01; N, 8.70.

[[Bis(diisopropylamino)boryl][(2,2,6,6-tetramethylpiperidino)chloroboryl]phosphine]chromium Pentacarbonyl (13). A solution containing 0.38 g (0.88 mmol) of **7** in 25 mL of hexane was combined with 0.22 g (0.88 mmol) of $Cr(CO)_5\cdot NMe_3$ in 25 mL of hexane. The mixture was stirred for 30 h at 23 °C, and the solvent was then removed by vacuum evaporation. The yellow residue was recrystallized from 5 mL of hexane at −10 °C: mp 133–136 °C; yield 0.15 g (27%), yellow crystals. Mass spectrum (30 eV) [m/z (%)]: 411 (5), 231 (100), 211 (70), 203 (60), 184 (60). Infrared spectrum (cyclohexane, cm^{-1}): 2056 (m), 1973 (w), 1932 (vs), 1463 (m), 1370 (w), 1331 (m), 1221 (w), 1192 (m), 1126 (m), 1115 (m), 674 (m), 657 (m). Anal. Calcd for $C_{26}H_{47}B_2N_3O_5PCr$ (621.72): C, 50.23; H, 7.62; N, 6.76. Found: C, 50.71; H, 7.91; N, 6.73.

Crystallographic Measurements and Structure Solutions. Crystals of **3**, **7**, **11**, and **12** were placed in glass capillaries under a dry nitrogen atmosphere. The crystals were centered on a Syntex P3/F automated diffractometer, and determinations of crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner. Data were collected in θ–2θ (**3**) or ω scan modes with Mo Kα (λ = 0.710 69 Å) radiation, a scintillation counter, and pulse height analyzer. Selected data collection parameters are summarized in Table I. In each case, inspection of a small data set led to assignment of the indicated space groups.[60] Empirical absorption corrections were applied, based upon ψ scans.[61] No signs of crystal decay were noted.

All calculations were performed on a Siemens SHELXTL PLUS (Microvax II version) structure determination system.[62] Solutions for **3**, **7**, and **12** were by direct methods, and **11** was solved by a Patterson map interpretation. Full matrix refinements were employed.[63] Neutral-atom

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(60) Space group notation as given in: *International Tables for X-Ray Crystallography*; Reidel: Dordrecht, Holland, 1983; Vol. I, pp 73–346.

(61) The empirical absorption corrections use an ellipsoidal model fitted to azimuthal scan data that are then applied to the intensity data: *SHELXTL Manual, Revision 4*; Nicolet XRD Corp.: Madison, WI, 1983.

(62) Sheldrick, G. M. *Nicolet SHELXTL Operations Manual*; Nicolet XRD Corp.: Cupertino, CA, 1981. 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.

(63) 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 minimizes $\sum w(|F_o| - |F_c|^2$, where $w = 1/[\sigma(F)^2 + gF^2]$. $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_{wF} = [\sum(|F_o| - |F_c|)^2/\sum wF_o^2]$, and GOF = $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO = number of observations and NV = number of variables.

Table II. Atomic Coordinates ($\times 10^4$) and Their Esd's for $\{[\mathrm{Li{\cdot}DME}][(i\text{-}\mathrm{Pr_2N})_2\mathrm{BP(H)}]\}_2$ (**3**)

	x	*y*	*z*
P	1291 (1)	430 (1)	6578 (1)
B	1530 (5)	1173 (2)	7463 (4)
N(1)	313 (3)	1464 (2)	7697 (3)
C(1)	−1192 (5)	1182 (2)	7480 (5)
C(2)	−1044 (6)	636 (2)	8321 (5)
C(3)	−2138 (5)	1063 (3)	6143 (5)
C(4)	421 (5)	2095 (2)	8131 (4)
C(5)	−637 (6)	2517 (2)	7145 (5)
C(6)	177 (5)	2176 (2)	9354 (4)
N(2)	3038 (3)	1488 (1)	7962 (3)
C(7)	3690 (5)	1694 (2)	7071 (4)
C(8)	2481 (5)	2008 (2)	5978 (4)
C(9)	5020 (5)	2130 (2)	7649 (5)
C(10)	4174 (4)	1238 (2)	9136 (4)
C(11)	5157 (5)	720 (2)	8976 (5)
C(12)	3427 (5)	1037 (2)	10025 (4)
Li	304 (8)	524 (3)	4227 (6)
O(1)	−860 (3)	1199 (1)	3058 (3)
O(2)	1842 (3)	711 (1)	3473 (3)
C(13)	−397 (6)	1120 (2)	2036 (4)
C(14)	1290 (6)	1144 (2)	2509 (5)
C(15)	−2491 (6)	1231 (2)	2683 (5)
C(16)	3449 (5)	675 (3)	3977 (5)

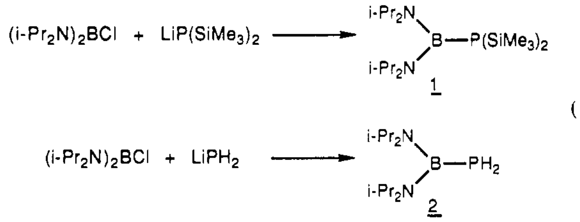
Table III. Atomic Coordinates ($\times 10^4$) and Their Esd's for $[(i\text{-}\mathrm{Pr_2N})_2\mathrm{B}][\mathrm{tmpB(Cl)}]\mathrm{PH}$ (**7**)

	x	*y*	*z*
P	2507 (1)	5971 (1)	1114 (1)
Cl	3487 (1)	3253 (1)	972 (1)
B(1)	3394 (3)	4720 (6)	1621 (3)
N(1)	3905 (2)	4768 (4)	2357 (2)
C(1)	4737 (3)	3995 (6)	2571 (3)
C(2)	5292 (3)	4688 (7)	3281 (3)
C(3)	4940 (3)	4742 (7)	3974 (3)
C(4)	4013 (4)	4860 (6)	3757 (3)
C(5)	3651 (3)	5597 (5)	2983 (2)
C(6)	4621 (4)	2376 (7)	2713 (3)
C(7)	5204 (3)	4191 (8)	1954 (3)
C(8)	3926 (3)	7189 (5)	2999 (3)
C(9)	2713 (3)	5550 (7)	2893 (3)
B(2)	2717 (3)	6384 (5)	102 (3)
N(2)	2240 (2)	5648 (4)	−552 (2)
C(10)	2568 (4)	5440 (6)	−1228 (3)
C(11)	2017 (5)	6088 (8)	−1965 (3)
C(12)	2746 (4)	3849 (7)	−1343 (3)
C(13)	1413 (3)	4991 (6)	−615 (3)
C(14)	793 (3)	6096 (7)	−493 (3)
C(15)	1400 (3)	3632 (6)	−141 (3)
N(3)	3283 (2)	7508 (4)	36 (2)
C(16)	4065 (3)	7683 (5)	619 (3)
C(17)	4813 (3)	7216 (7)	335 (4)
C(18)	4206 (4)	9124 (6)	1025 (3)
C(19)	3009 (3)	8632 (5)	−554 (3)
C(20)	2572 (4)	9896 (6)	−288 (4)
C(21)	3640 (4)	9120 (8)	−978 (3)

scattering factors and anomalous dispersion terms were used for all non-hydrogen atoms during the refinements. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The refinements of **3**, **7**, and **11** were well behaved; however, disorder in the isopropyl group containing C(9)–C(11) in **12** was observed. Two equally occupied sites, C(10) and C(10′), were utilized in the refinements. Additional crystallographic parameters and details of the structure solutions (Table S-1), hydrogen atom positional parameters (Table S-2), anisotropic thermal parameters (Table S-3), full listings of bond distances and angles (Table S-4), and listings of structure factor amplitudes (Table S-5) are provided in the supplementary material. The non-hydrogen atom positional parameters are listed in Tables II–V.

Results and Discussion

Fritz and Hölderich[21] have previously reported on the formation of $(\mathrm{Me_2N})_2\mathrm{BP(SiMe_3)_2}$ from a metathesis reaction between $(\mathrm{Me_2N})_2\mathrm{BCl}$ and $(\mathrm{Me_3Si})_2\mathrm{PLi{\cdot}2THF}$. Although there are few reports of related monomeric (silylphosphino)boranes,[43,46] in fact it was found that combinations of $(i\text{-}\mathrm{Pr_2N})_2\mathrm{BCl}$ and $(\mathrm{Me_3Si})_2\mathrm{PLi{\cdot}2THF}$ or $\mathrm{H_2PLi{\cdot}DME}$ produce good yields of $(i\text{-}\mathrm{Pr_2N})_2\mathrm{BP(SiMe_3)_2}$ (**1**) and $(i\text{-}\mathrm{Pr_2N})_2\mathrm{BPH_2}$ (**2**), as shown in eq 1. Analytical and spectroscopic data summarized in Table VI for **1** and **2** are consistent with the proposed structures. Compound **2** would be expected to show two P–H stretching bands in the region 2400–2200 cm^{-1}; however, as found with $(\mathrm{R_2N})\mathrm{B(Cl)PH_2}$,[51] only one absorption is resolved, and it appears at 2319 cm^{-1}. The region 1500–1300 cm^{-1} typically contains B–N stretching modes. Several frequencies are observed in this range for both **1** and **2**, but unambiguous assignments based on the characteristic $^{11}\mathrm{B}/^{10}\mathrm{B}$ isotope splitting could not be made. The ^{31}P NMR shift for **1**, δ −232, is comparable to the shifts for $(\mathrm{Me_2N})_2\mathrm{BP(SiMe_3)_2}$, δ −245, and the monomeric (diisopropylamino)chlorophosphinoborane $(i\text{-}\mathrm{Pr_2N})\mathrm{B(Cl)P(SiMe_3)_2}$, δ −213.3.[50] Simiarly, $\delta(^{31}\mathrm{P})$ for **2** is comparable with the shift for $(i\text{-}\mathrm{Pr_2N})\mathrm{B(Cl)PH_2}$, δ −197.9 and −198.3 (rotamers).[51] Restoration of proton coupling for **2** reveals a triplet with $^1J_{\mathrm{PH}}$ = 208.1 Hz, which compares favorably with $^1J_{\mathrm{PH}}$ = 209.2 Hz in $(i\text{-}\mathrm{Pr_2N})\mathrm{B(Cl)PH_2}$.



$$(i\text{-}\mathrm{Pr_2N})_2\mathrm{BCl} + \mathrm{LiP(SiMe_3)_2} \longrightarrow (i\text{-}\mathrm{Pr_2N})_2\mathrm{B{-}P(SiMe_3)_2}\ \ \mathbf{1}$$
$$(i\text{-}\mathrm{Pr_2N})_2\mathrm{BCl} + \mathrm{LiPH_2} \longrightarrow (i\text{-}\mathrm{Pr_2N})_2\mathrm{B{-}PH_2}\ \ \mathbf{2} \qquad (1)$$

Several attempts to effect trimethylsilyl group elimination reactions with **1** show that this reagent is sluggish in its chemistry, and this unfortunately reduces its utility as a reagent. Combination

Table IV. Atomic Coordinates ($\times 10^4$) and Their Esd's for $[(i\text{-}\mathrm{Pr_2N})_2\mathrm{B}]_2\mathrm{P(H){\cdot}Cr(CO)_5}$ (**12**)

	x	*y*	*z*
Cr	3040 (1)	2754 (1)	2205 (1)
C(1)	4117 (8)	3069 (4)	1530 (4)
O(1)	4798 (6)	3270 (3)	1115 (3)
C(2)	4472 (7)	2623 (4)	2902 (4)
O(2)	5381 (5)	2569 (3)	3297 (3)
C(3)	2870 (7)	3632 (4)	2552 (4)
O(3)	2795 (6)	4185 (3)	2722 (3)
C(4)	3148 (8)	1888 (4)	1797 (4)
O(4)	3227 (7)	1378 (3)	1507 (3)
C(5)	1650 (8)	2900 (4)	1484 (4)
O(5)	847 (6)	3006 (4)	1039 (3)
P	1422 (2)	2382 (1)	3066 (1)
B(1)	1267 (7)	1408 (3)	3393 (4)
N(1)	2229 (5)	1058 (3)	3825 (3)
C(6)	3585 (6)	1244 (3)	3801 (4)
C(7)	4248 (6)	812 (4)	3245 (4)
C(8)	4390 (7)	1268 (4)	4547 (4)
C(9)	1870 (7)	476 (3)	4275 (4)
C(10)	2617 (8)	−178 (3)	4194 (4)
C(11)	1795 (8)	645 (4)	5097 (4)
N(2)	104 (5)	1090 (2)	3099 (3)
C(12)	−1144 (6)	1408 (3)	3163 (4)
C(13)	−2042 (6)	1435 (3)	2455 (4)
C(14)	−1818 (6)	1122 (3)	3814 (4)
C(15)	214 (6)	455 (3)	2678 (4)
C(16)	142 (7)	554 (3)	1831 (4)
C(17)	−661 (7)	−114 (3)	2882 (4)
B(2)	769 (7)	3090 (4)	3746 (4)
N(3)	−494 (5)	3344 (2)	3512 (3)
C(18)	−717 (7)	3623 (3)	2751 (4)
C(19)	−1910 (7)	3359 (3)	2290 (4)
C(20)	−677 (7)	4389 (4)	2731 (4)
C(21)	−1616 (6)	3211 (4)	3932 (4)
C(22)	−1292 (7)	2804 (4)	4622 (4)
C(23)	−2364 (7)	3840 (4)	4108 (5)
N(4)	1535 (5)	3341 (3)	4352 (3)
C(24)	1212 (7)	3996 (3)	4697 (4)
C(25)	1187 (7)	4017 (4)	5538 (4)
C(26)	1984 (8)	4584 (3)	4438 (4)
C(27)	2676 (6)	2972 (3)	4665 (4)
C(28)	3916 (7)	3375 (4)	4756 (4)
C(29)	2472 (8)	2593 (3)	5370 (4)

Table V. Atomic Coordinates (×10^4) and Their Esd's for $[(i\text{-}Pr_2N)_2B][tmpB(Cl)]P(H)\cdot Cr(CO)_5$ (**13**)

	x	y	z
Cr	94 (1)	1335 (1)	3565 (1)
C(1)	1579 (5)	1484 (4)	4166 (3)
O(1)	2493 (3)	1590 (3)	4552 (2)
C(2)	−862 (4)	1702 (4)	4646 (3)
O(2)	−1436 (4)	1932 (4)	5293 (2)
C(3)	1059 (4)	936 (4)	2492 (3)
O(3)	1692 (3)	672 (4)	1868 (2)
C(4)	−403 (4)	−469 (5)	3535 (3)
O(4)	−637 (4)	−1545 (3)	3491 (3)
C(5)	648 (4)	3116 (5)	3552 (3)
O(5)	1034 (4)	4185 (3)	3560 (3)
P	−1982 (1)	1190 (1)	2902 (1)
B(1)	−2830 (4)	−462 (4)	2159 (2)
N(1)	−3229 (3)	3335 (3)	2994 (2)
C(6)	−2832 (5)	3959 (4)	3896 (2)
C(7)	−3820 (5)	3522 (5)	4619 (3)
C(8)	−2417 (7)	5409 (5)	4057 (3)
C(9)	−4499 (5)	3310 (7)	2727 (4)
C(10)	−4996 (12)	4393 (11)	2865 (7)
C(10′)	−5573 (11)	3690 (11)	3177 (7)
C(11)	−4799 (5)	2435 (7)	1844 (3)
N(2)	−1498 (3)	3106 (3)	1746 (2)
C(12)	−1531 (4)	4383 (4)	1579 (2)
C(13)	−1834 (5)	4365 (5)	651 (3)
C(14)	−307 (5)	5447 (4)	1879 (3)
C(15)	−666 (4)	2296 (4)	1172 (2)
C(16)	−1271 (5)	1583 (5)	298 (2)
C(17)	790 (4)	2983 (5)	1035 (3)
B(2)	−2267 (4)	2699 (4)	2454 (2)
Cl	−1627 (1)	−990 (1)	1333 (1)
N(3)	−4129 (3)	−1199 (3)	2205 (2)
C(18)	−4894 (4)	−1269 (4)	3074 (3)
C(19)	−5893 (5)	−2578 (5)	2996 (3)
C(20)	−6915 (6)	−2856 (7)	2323 (4)
C(21)	−6353 (5)	−2194 (6)	1578 (3)
C(22)	−4820 (5)	−2017 (5)	1385 (3)
C(23)	−3961 (4)	−1253 (4)	3761 (3)
C(24)	−5612 (4)	−177 (5)	3378 (3)
C(25)	−4474 (6)	−1291 (5)	645 (3)
C(26)	−4479 (6)	−3320 (5)	1097 (3)

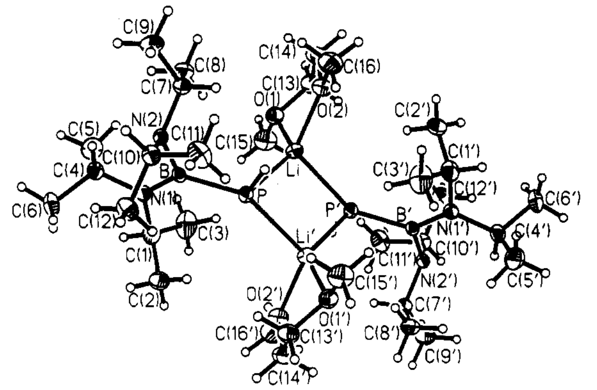
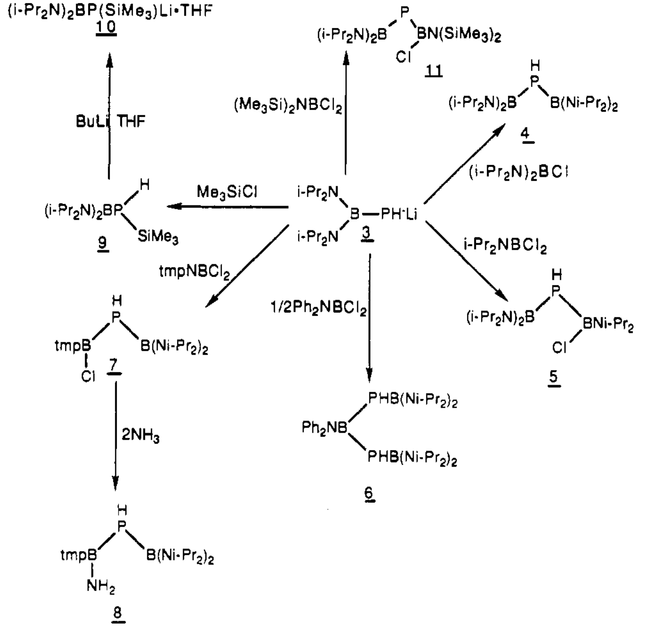


Figure 1. Molecular structure and atomic labeling scheme for $\{[Li\cdot DME][(i\text{-}Pr_2N)_2BP(H)]\}_2$ (**3**).

Scheme I



of **2** with BuLi, on the other hand, leads to formation of $\{[Li\cdot DME][(i\text{-}Pr_2N)_2BP(H)]\}_2$, which proves to be a very useful synthon for the preparation of new families of diborylphosphanes. Indeed, this approach parallels chemistry found useful for preparation of diborylamines.[64] Only a few other examples of diborylphosphanes are known. For example, Nöth and Schrägle[13] reported formation of $PhP[B(NMe_2)_2]_2$ from Li_2PPh and $(Me_2N)_2BCl$ in a 1:2 ratio. Coates and Livingstone[16] observed that $PhPH_2$ and Ph_2BCl eliminated HCl with formation of $PhP(BPh_2)_2$, and Fritz and Hölderich[21] noted that Ph_2BBr and the complex $(Me_3Si)_3P\cdot B(Br)Ph_2$ gave $Me_3SiP(BPh_2)_2$. More recently, Power and co-workers[27] have described the related synthesis of $PhP(BMes_2)_2$ and determination of its crystal structure.

In the present study, equimolar mixtures of **3** with $(i\text{-}Pr_2N)_2BCl$, $(i\text{-}Pr_2N)BCl_2$, $tmpBCl_2$, and $(Me_3Si)_2NBCl_2$ produce the new diborylphosphanes $[(i\text{-}Pr_2N)_2B]_2PH$ (**4**), $[(i\text{-}Pr_2N)_2B][(i\text{-}Pr_2N)B(Cl)]PH$ (**5**), $[(i\text{-}Pr_2N)_2B][tmpB(Cl)]PH$ (**7**), and $[(i\text{-}Pr_2N)_2B][(Me_3Si)_2NB(Cl)]PH$ (**11**), respectively. Reaction of **3** with Ph_2NBCl_2 in a 1:1 ratio did not give identified products; however, a 2:1 reaction ratio produced the diborylphosphinoborane $Ph_2NB[P(H)B(N\text{-}i\text{-}Pr_2)_2]_2$ (**6**). These reactions are summarized in Scheme I. Analytical[65] and spectroscopic characterization data for the compounds are consistent with the proposed formulations.

The lithium borylphosphide **3** depicted in Scheme I as a monomeric species displays single resonances at 22 °C in $^{11}B\{^1H\}$, δ 46.8, and $^{31}P\{^1H\}$, δ −213, NMR spectra. Consistent with this structure, restoration of proton coupling in the ^{31}P NMR spectrum results in a doublet with $^1J_{PH}$ = 170.9 Hz. The ^7Li NMR spectrum of **3** at 22 °C also displays a sharp singlet, δ 1.44. However, variable-temperature ^7Li NMR analysis shows that the singlet broadens at 10 °C, and a triplet pattern appears at ∼−18 °C. A nicely resolved triplet appears at −30 °C with J_{LiP} = 46.9 Hz. This behavior is consistent with a dimeric formulation for **3**, and similar NMR data have been recorded for other lithium phosphides.[66]

The $^{31}P\{^1H\}$ NMR spectra for **4**–**7** and **11** each display a single resonance split into a widely spaced doublet (range $^1J_{PH}$ = 200–255 Hz) with restoration of proton coupling. It is interesting that these ^{31}P chemical shifts appear at significantly higher fields than the shifts for the monoborylalkylphosphanes, $Ar_2BP(R)H$ ($\delta(^{31}P)$ −1.6 to −66), reported by Power.[30] The P–H coupling constants are slightly smaller or fall at the low end of the coupling constant range found in $Ar_2BP(R)H$ compounds (J_{PH} = 254–301 Hz). The $^{11}B\{^1H\}$ spectrum of the symmetrical compound **4** displays a single resonance centered at δ 40.7. This value is consistent with data for other aminophosphinoboranes.[51,67] The remaining compounds contain two different boryl groups, and two boron resonances are detected. Due to the similarity in shifts compared to **4**, the $(i\text{-}Pr_2N)_2B$ groups in **5**, **7**, and **11** are assigned to resonances at δ 40.7, 38.5, and 38.5, respectively. The shift for this group in

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[64] Nöth, H.; Prigge, H.; Rotsch, A. R. *Chem. Ber.* **1986**, *119*, 1361.

[65] In some cases, carbon elemental composition determinations are low by more than 1%. This appears to coincide with incomplete combustion and formation of boron carbide-like residues.

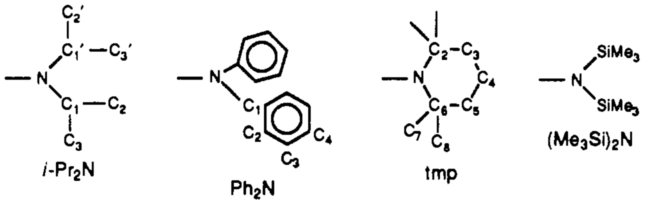
[66] Heig, E.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1989**, *362*, 1.

[67] Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer Verlag: West Berlin, 1978.

Table VI. NMR Data for Phosphinoboranes and Diborylphosphanes

compd[a,b]	$\delta(^{11}B\{^1H\})$	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[(i\text{-}Pr_2N)_2B]P(SiMe_3)_2$ (**1**)	38.7	−232	3.9 (1) 1.3 (2, 3) 0.4 ($SiMe_3$)	49.5, 45.8 (1, 1′) 25.8, 23.2 (2, 3, 2′, 3′) 4.0 ($SiMe_3$)
$[(i\text{-}Pr_2N)_2B]PH_2$ (**2**)	40.9	−206	3.7 (1) 1.2 (2, 3) 2.3 (PH_2)	47.0 (1) 23.7 (2, 3)
$[(i\text{-}Pr_2N)_2B]P(H)Li{\cdot}DME$ (**3**)	46.8	−213	4.0 (1) 1.4 (2, 3) 3.2 (DME) 3.1 (DME)	47.5 (1) 24.6 (2, 3) 70.8 (DME) 59.7 (DME)
$[(i\text{-}Pr_2N)_2B]_2PH$ (**4**)	40.7	−163.5	3.8 (1) 1.3 (2, 3)	48.9 (1) 25.1 (2, 3)
$[(i\text{-}Pr_2N)_2B][(i\text{-}Pr_2N)B(Cl)]PH$ (**5**)	40.7 38.8	−170.0	3.98, 3.83, 3.25 (1) 1.35, 1.32, 0.95, (2, 3) 2.32 (PH)	52.9, 49.1, 46.9 (1) 25.1, 23.6, 21.0 (2, 3)
$Ph_2NB[P(H)B(i\text{-}Pr_2N)_2]_2$ (**6**)	57.0 41.3	−155.4	7.4–7.0 (Ph) 3.9 (1) 1.4 (2, 3) 2.2 (PH)	128.9, 128.4, 124.9 (Ph) 49.3 (1) 25.3 (2, 3)
$[(i\text{-}Pr_2N)_2B][tmpB(Cl)]PH$ (**7**)	46.1 38.5	−143.2	3.7 (1) 1.4 (2, 3) 1.56, 1.50 (tmp) 2.7 (PH)	49.3 (1) 25.3 (2, 3) 56.9, 36.6, 32.7, 15.3 (tmp)
$[(i\text{-}Pr_2N)_2B][tmpB(NH_2)]PH$ (**8**)	41.3	−159.5	3.7 (1) 1.2 (2, 3) 1.41, 1.36 (tmp) 3.5 (NH) 1.9 (PH)	48.7 (1) 25.1 (2, 3) 52.1, 39.6, 32.6, 17.1 (tmp)
$[(i\text{-}Pr_2N)_2B]P(SiMe_3)(H)$ (**9**)	39.8	−201.9	3.7 (1) 1.2 (2, 3) 0.3 ($SiMe_3$)	48.8 (1) 25.1 (2, 3) 3.6 ($SiMe_3$)
$\{[(i\text{-}Pr_2N)_2B]P(SiMe_3)\}Li{\cdot}THF$ (**10**)	45.3	−257.3	4.45 (1) 1.40 (2, 3) 0.52 ($SiMe_3$) 3.81, 1.4 (THF)	49.5 (1) 25.3 (2, 3) 7.0 ($SiMe_3$) 69.0, 25.4 (THF)
$[(i\text{-}Pr_2N)_2B][(Me_3Si)_2NB(Cl)]PH$ (**11**)	53.3 38.5	−136.3	3.8 (1) 2.8 (PH) 1.28 (2, 3) 0.4 ($SiMe_3$)	49.3 (1) 25.1 (2, 3) 4.4 ($SiMe_3$)
$[(i\text{-}Pr_2N)_2B]_2P(H){\cdot}Cr(CO)_5$ (**12**)	38.1	−157.9	3.9 (1) 1.26, 1.21 (2, 3) 2.3 (PH)	50.4 (1) 25.6, 25.3 (2, 3) 223.5, 219.1 (CO)
$[(i\text{-}Pr_2N)_2B][tmpB(Cl)]P(H){\cdot}Cr(CO)_5$ (**13**)	44.5 36.2	−109.5	3.9 (1) 1.23, 1.20 (2, 3) 1.47, 1.43 (tmp)	50.0 (1) 26.0, 24.0 (2, 3) 58.0, 35.6, 33.4 31.5, 14.2 (tmp)

[a] Abbreviations and numbering schemes are as follows:



[b] Coupling constants (Hz): (**1**) $^2J_{CP} = 12.0$ ($SiMe_3$), $^3J_{HH} = 7.0$ (Me), $^3J_{HP} = 4.9$ ($SiMe_3$); (**2**) $^4J_{CP} = 2.8$ (C_3), $^3J_{HH} = 7.3$ (C_3), $^1J_{PH} = 208.1$; (**3**) $^3J_{HH} = 6.7$ (C_3), $^1J_{PH} = 170.9$; (**4**) $^4J_{CP} = 2.0$ (C_1), $^3J_{CP} = 2.1$ (C_1), $^3J_{HH} = 6.9$, $^1J_{PH} = 255.2$; (**5**) $^4J_{CP} = 3.2$ (C_3), $^3J_{CP} = 2.1$, $^3J_{HH} = 6.7$ (C_3, i-Pr_2N), $^3J_{HH} = 7.0$ (C_3, i-Pr_2′N), $^1J_{PH} = 220.2$; (**6**) $^4J_{CP} = 2.5$ (C_3), $^3J_{CP} = 2.1$ (C_1), $^3J_{HH} = 6.9$ (C_3), $^1J_{PH} = 240.1$; (**7**) $^4J_{CP} = 2.8$ (C_3, i-Pr_2N), $^3J_{CP} = 2.5$ (C_1), $^4J_{CP} = 4.8$ ($C_{7,8}$, TMP), $^3J_{HH} = 7.0$ (C_3), $^1J_{PH} = 224.4$; (**8**) $^4J_{CP} = 2.5$ (C_3), $^3J_{CP} = 1.6$ (C_1), $^4J_{CP} = 4.6$ ($C_{7,8}$, TMP), $^3J_{HH} = 6.9$ (C_3), $^1J_{PH} = 226.1$; (**9**) $^4J_{CP} = 2.5$ (C_3), $^3J_{CP} = 2.3$ (C_1), $^2J_{CP} = 9.0$ ($SiMe_3$); (**10**) $^2J_{CP} = 4.9$ ($SiMe_3$), $^3J_{HH} = 7.0$ (C_3); (**11**) $^3J_{HH} = 7.0$ (C_3), $^3J_{HH} = 7.0$ (C_1), $^1J_{PH} = 231.8$, $J_{CP} = 3.0$ (C_1), $^4J_{CP} = 2.3$ (C_3), $^4J_{CP} = 2.8$ ($SiMe_3$); (**12**) $^3J_{CP} = 3.5$ (C_1), $^3J_{HH} = 7.0$ (C_3), $^1J_{PH} = 294.2$; (**13**) $^3J_{CP} = 3.4$ (C_1), $^3J_{HH} = 6.8$ (C_3), $^1J_{PH} = 299.1$.

6 is assigned to the resonance at δ 41.3, since it is approximately two times more intense than a second resonance at δ 57.0. The resonance at δ 57.0 in **6** is therefore assigned to the Ph_2NB unit, and resonances at δ 38.8 in **5**, δ 46.1 in **7**, and δ 53.3 in **11** are assigned to (i-Pr_2N)B(Cl), tmpB(Cl), and $(Me_3Si)_2NB(Cl)$ groups, respectively.

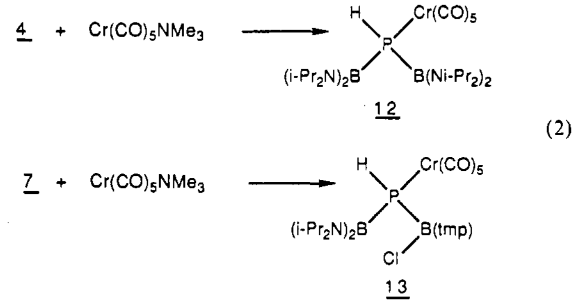
Reactions of **3** with other main group halides, R_nECl, should provide examples of $(i\text{-}Pr_2N)_2BP(H)(ER_n)$ species. Indeed, it is found here that reaction of **3** with Me_3SiCl in a 1:1 ratio produces $(i\text{-}Pr_2N)_2BP(H)(SiMe_3)$ (**9**) (Scheme I). This reagent may be deprotonated, and the corresponding lithium salt, **10**, is isolated as colorless crystals. This reaction provides access to the fragment $[(i\text{-}Pr_2N)_2BP(SiMe_3)^-]$ that was sought from elimination reactions of **1**, and further chemistry of this fragment is under study. Finally, the reaction of **7** with NH_3 in a 1:2 ratio was examined, and the aminolysis product **8**, $[(i\text{-}Pr_2N)_2B][tmpB(NH_2)]PH$, was isolated in good yield. The ^{11}B NMR spectrum of **8** shows a single, broad ($W_{1/2}$ = ~800 Hz) resonance, δ 41.3; the two expected boron environments are not resolved.

The coordination chemistry of **4** and **7** with $Cr(CO)_5{\cdot}NMe_3$ was examined. In each case, displacement of NMe_3 was observed, and the complexes $[(i\text{-}Pr_2N)_2B]_2PH{\cdot}Cr(CO)_5$ (**12**) and [(i-

Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) for {[Li·DME][(*i*-$Pr_2N)_2BP(H)$]}$_2$ (**3**), [(*i*-$Pr_2N)_2B$][tmpB(Cl)]PH (**7**), [(*i*-$Pr_2N)_2B]_2PH·Cr(CO)_5$ (**12**), and [(*i*-$Pr_2N)_2B$][tmpB(Cl)]PH·$Cr(CO)_5$ (**13**)

	molecule			
bond	3	7	12	13
		Bond Lengths		
B–P	1.901 (5)	1.925 (5) (P–B(1))	2.044 (7) (P–B(1))	1.961 (4) (P–B(1))
		1.979 (5) (P–B(2))	2.032 (8) (P–B(2))	2.034 (5) (P–B(2))
B–N	1.429 (6) (B–N(1))	1.397 (5) (B(1)–N(1))	1.407 (8) (B(1)–N(1))	1.393 (5) (B(1)–N(3))
	1.496 (5) (B–N(2))	1.427 (5) (B(2)–N(2))	1.438 (9) (B(1)–N(2))	1.397 (4) (B(2)–N(2))
P–Li	2.535 (7) (P–Li)	1.425 (6) (B(2)–N(3))	1.451 (9) (B(2)–N(3))	1.449 (5) (B(2)–N(1))
	2.554 (7) (P–Li′)		1.391 (8) (B(2)–N(4))	
B–Cl		1.821 (5)		1.806 (4)
Cr–P			2.517 (2)	2.451 (1)
Cr–CO_{ax}			1.846 (9) (Cr–C(1))	1.851 (5) (Cr–C(1))
Cr–CO_{eq}			1.891 (7) (Cr–C(2))	1.893 (4) (Cr–C(2))
			1.877 (8) (Cr–C(3))	1.893 (4) (Cr–C(3))
			1.888 (9) (Cr–C(4))	1.899 (5) (Cr–C(4))
		Bond Angles		
P–B–Cl		108.2 (2)		109.2 (2)
P–B–N	123.2 (3) (P–B–N(1))	131.1 (4) (P–B(1)–N(1))	124.1 (5) (P–B(1)–N(1))	129.7 (3) (P–B(1)–N(3))
	120.9 (3) (P–B–N(2))	119.1 (4) (P–B(2)–N(2))	113.7 (4) (P–B(1)–N(2))	121.2 (3) (P–B(2)–N(2))
		118.9 (3) (P–B(2)–N(3))	114.8 (4) (P–B(2)–N(3))	112.6 (2) (P–B(2)–N(1))
			121.4 (5) (P–B(2)–N(4))	
N–B–N	116.0 (3)	121.7 (4) (N(2)–B(2)–N(3))	122.1 (6) (N(1)–B(1)–N(2))	
			123.6 (6) (N(3)–B(2)–N(4))	126.0 (4) (N(1)–B(2)–N(2))
Cl–B–N		120.7 (4)		121.2 (3)
				174.6 (1)
Li–P–Li′	75.2 (3)			
B–P–Li	115.5 (2)			
B–P–Li′	147.3 (3)			
P–Li–P′	104.8 (3)			

$Pr_2N)_2B$][tmpB(Cl)]PH·$Cr(CO)_5$ (**13**) were isolated as outlined in eq 2. The complexes are yellow crystalline solids that have



(2)

been fully characterized by analytical and spectroscopic data. The ^{11}B NMR spectrum for **12** displays a single boron environment, and the spectrum for **13** shows two resonances, each shifted slightly upfield from the resonances in the free ligand **7**. In the ^{31}P spectrum for **12**, there is only a small, downfield coordination shift, $\Delta = 5.6$ ppm. The P–H coupling constants in the complexes **12**, 294.2 Hz, and **13**, 299.1 Hz, are significantly increased over the values for the free ligand, suggesting that there is increased s character in the P–H bonds upon coordination. This trend is typically found in coordination complexes of primary and secondary phosphines.[68] Infrared spectra for $M(CO)_5L$ complexes are expected to display three carbonyl stretching frequencies in the region 2070–1900 cm^{-1}; however, in many cases, only two bands are resolved. In spectra for **12** and **13**, recorded from cyclohexane solutions, only two bands are detected: **12**, 2052 nd 1926 cm^{-1}; **13**, 2056 and 1932 cm^{-1}.

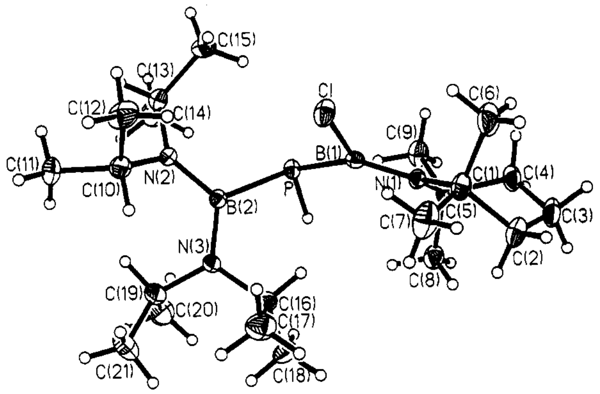


Figure 2. Molecular structure and atomic labeling scheme for [(*i*-$Pr_2N)_2B$][tmpB(Cl)]PH (**7**) (25% probability).

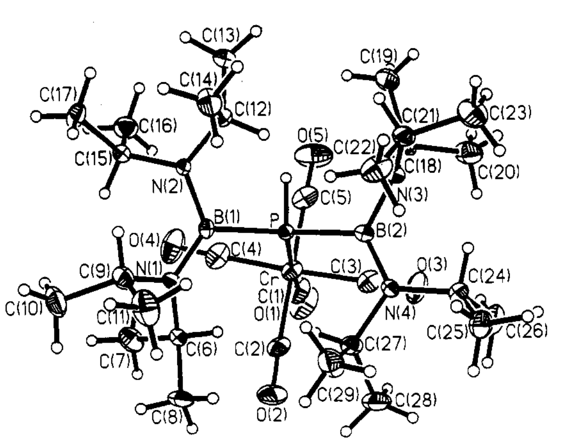


Figure 3. Molecular structure and atomic labeling scheme for [(*i*-$Pr_2N)_2B]_2P(H)·Cr(CO)_5$ (**12**) (25% probability).

Since molecular structure data for borylphosphanes are limited,[32] the structures of **3**, **7**, **11**, and **13** were determined. Views of the molecules are shown in Figures 1–4, and selected bond distances and bond angles are summarized in Table VII.

Power and co-workers[26,30,32] have previously reported structures of several lithium borylphosphides: {[$Li(Et_2O)_2$][Mes_2BP)(c-C_6H_{11})]} (**14a**), {[$Li(Et_2O)_2$][Mes_2BPMes]} (**14b**), {[$Li(Et_2O)_2$][Mes_2BP(1-Ad)]} (**14c**), {[$Li(Et_2O)_2$][TripBP(*t*-Bu)]} (**14d**), and {[Li(thf)$_3$][$Mes_2BP(SiMe_3)$]} (**14e**). These compounds display closely related structures that consist of discrete monomeric molecular units with a short P–B bond (1.823–1.836 Å) connecting planar phosphorus and boron atoms, and the Li cation is bonded

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[68] Verkade, J. G.; Mosbo, J. A. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1987; Chapter 13.

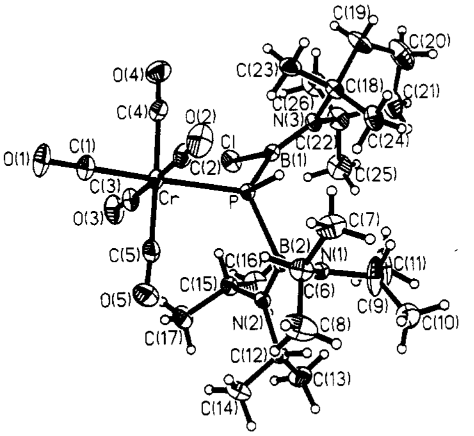

Figure 4. Molecular structure and atomic labeling scheme for $[(i\text{-}Pr_2N)_2B][tmpB(Cl)]P(H)\cdot Cr(CO)_5$ (**13**) (25% probability).

to the phosphorus atom (P–Li = 2.451–2.460 Å). In contrast, **3** displays a dimeric structure with a crystallographically imposed center of symmetry. The central Li_2P_2 ring is rhomboidal, and as might be expected, the Li–P distances, 2.535 (7) and 2.554 (7) Å, are significantly longer than those found in the monomeric borylphosphides **14a–e**. The rhomboidal character of the ring is indicated by the ring internal angles: Li–P–Li′ = 75.2 (3)° and P–Li–P′ = 104.8 (3)°. The sum of the bond angles about phosphorus (338.0°) indicates that this atom is pyramidal. The sum is comparable with the sum in $Ph_2NB[P(SiMe_3)_2]_2$[51] but greater than the values found for most phosphanes. The boron atom geometry in **3** is planar, and the P–B distance of 1.901 (5) Å is significantly longer than the distances in the monomeric borylphosphides **14a–e**. However, the distance is similar to the range found in several diphosphadiboretanes (1.91–1.97 Å)[32,43,46] and in the diphosphaborane $MesB(PPh_2)_2$ (1.879 (2), 1.901 (2) Å). The distance in **3** suggests that there is significantly less B–P multiple-bond character in this compound relative to examples of **14**, and this is due to the anticipated strong π-bonding in the B–N bonds of **3**.

The BNC_2 groups in the $BN(i\text{-}Pr)_2$ units of **3** are planar, and the planes are twisted with respect to each other by 89.2°. The orientation of the B–N(1)–C(1)–C(4) plane with respect to the phosphorus atom suggests good π B–N interaction, while the B–N(2)–C(7)–C(10) plane orientation suggests no B–N π bonding. These observations are consistent with a short B–N(1) distance, 1.429 (6) Å, and a long B–N(2) distance, 1.496 (5) Å. The PBN(1)N(2) plane is nearly perpendicular, 81.1°, to the LiPLi′P′ plane.

The structures of diborylphosphane **7** and the two coordination complexes **12** and **13** contain discrete molecular units, each with a pyramidal phosphorus atom and planar boron and nitrogen atoms. The ligand **7** shows two different P–B bond distances, 1.925 (5) and 1.979 (5) Å, with the shorter distance associated with the B(Cl)tmp group. This is consistent with stronger P–B bonding with the more electron-deficient boron fragment, B(Cl)tmp. Enhanced P–B π overlap in this fragment is suggested by the orientation of ClB(1)N(1) plane relative to the phosphorus atom in comparison to the B(2)N(2)N(3) plane: dihedral angle 79.6°, angle between planes PB(1)Cl and B(1)N(1)C(1)C(5) 21.8°. The B(1)–N(1) bond distance, 1.397 (5) Å, in the B(Cl)tmp unit is also shorter than the B–N bonds in the $B\text{–}N(i\text{-}Pr_2)$ group, average 1.426 Å.

As expected, the coordination complex **13** displays significantly lengthened B–P bonds: P–B(1) = 1.961 (4) and 2.034 (5) Å. The B–N bond distance in the B(Cl)tmp unit is not affected by coordination; however, the $B\text{–}N(i\text{-}Pr_2)_2$ bond distances are affected: one distance is shorter and one is longer than in **7**. The shorter distance associated with B(2)–N(2) is consistent with its favorable orientation for π overlap: the B(2)N(2)C(12)C(15) plane is twisted by only 7.7° with respect to the B(2)N(1)N(2) plane, while the B(2)N(1)C(6)C(9) plane is twisted by 71.3°.

The $Cr(CO)_5P$ unit is pseudooctahedral, and the Cr–P bond distance, 2.451 (1) Å, is similar to that reported for $(CO)_5Cr\cdot PPh_3$, 2.422 (1) Å,[69] and for $[tmpBPH]_2\cdot Cr(CO)_5$, 2.458 (2) Å. The $Cr\text{–}CO_{ax}$ bond distance, 1.846 (9) Å, is comparable to the average $Cr\text{–}CO_{eq}$ distance, 1.887 Å. These features suggest that **7** is not a particularly strong π-accepting ligand.

The structure of **12** is similar to that of **13**, except that the P–B bond distances are more nearly alike, average 2.038 Å, and similar to the longer of the two distances in **13**. The Cr–P distance (2.517 (2) Å) is longer than in **13**, and there is one short and one long B–N bond distance associated with each $B\text{–}N(i\text{-}Pr_2)_2$ group.

The results presented here indicate that the phosphinoborane **2**, its salt **3**, and presumably related aminoboryl analogues should continue to reveal a rich body of coordination and reagent chemistry. Indeed this is proving to be the case, and further elaboration of that chemistry as well as the chemistry of diborylphosphanes will be reported separately.

Acknowledgment is made to the National Science Foundation (Grant CHE-8503550) (R.T.P.) and the Fonds der Chemischen Industrie (H.N.). A NATO grant allowed the cooperation of our research groups. Support from the Department of Energy URIP (Grant DE-FG05-86ER75294) assisted in the purchase of the JEOL GSX-400 NMR spectrometer, and funds from the NSF (Grant CHE-8807358) supported purchase of the Bruker WP-250 spectrometer.

Registry No. **1**, 139914-02-6; **2**, 139914-03-7; **3** (coordination compound entry), 139914-11-7; **3** (salt entry), 139914-13-9; **4**, 139942-86-2; **5**, 139942-87-3; **6**, 139914-04-8; **7**, 139914-05-9; **8**, 139914-06-0; **9**, 139914-07-1; **10**, 139914-14-0; **11**, 139914-08-2; **12**, 139914-09-3; **13**, 139914-10-6; $Cr(CO)_5\cdot NMe_3$, 15228-26-9; $LiP(SiMe_3)_2$, 59624-91-8; $LiPH_2$, 24167-79-1; $(i\text{-}Pr_2N)_2BCl$, 28049-80-1; $i\text{-}Pr_2NBCl_2$, 44873-49-6; Ph_2NBCl_2, 1139-65-7; $tmpBCl_2$, 79855-29-1; Me_3SiCl, 75-77-4; $(tms)_2NBCl_2$, 6591-26-0.

Supplementary Material Available: Tables S-1–S-4, giving full descriptions of the X-ray analyses, anisotropic thermal parameters, hydrogen atom positional parameters, and complete bond distances and bond angles (37 pages); Table S-5, giving calculated and observed structure factors (72 pages). Ordering information is given on any current masthead page.

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(69) Plastos, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265.