which means, for complexes of comparable stability, the acid-dissociation rate constant should increase in the order cationic < neutral < anionic.

3. The dissociation rates of both anionic and cationic complexes can be accelerated by coordinating anions but very weakly complexing anions can cause the reduction in rate of dissociation of cationic complexes by ion-pair formation.

4. For complexes of rigid and sterically crowded ligands such as macrocyclic compounds, the contribution from the metal-catalyzed pathway in metal-exchange reactions could be minimal. The same ligand may also prevent the anion attack on the metal center, depending on the structure of the complex.

5. The formation reaction rates of macrocyclic ligands will be considerably slower as compared to water-exchange rates of lanthanide ions, because the rate-determining step may shift from dissociative loss of water molecule to metal ion incorporation into ligand cavity.

Further experimental testing of these postulates by careful design of thermodynamic and kinetic studies is obviously needed.

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Registry No. LaK22DA$^+$, 107985-45-5; EuK22DA$^+$, 107985-46-6; LuK22DA$^+$, 107985-47-7; PrK22DA$^+$, 107985-48-8; YbK22DA$^+$, 107985-49-9.

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nido-Methylenephosphahexaboranes: $R_2CPB_5H_8$

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Two routes to a new class of heteroborane clusters, the *nido*-methylenephosphahexaboranes $R_2CPB_5H_8$, have been developed. $(Me_3Si)_2CPB_5H_8$ has been prepared from the phosphaalkene $(Me_3Si)_2C{=}PCl$ and the $B_5H_8^-$ anion, while both $R_2CPB_5H_8$ compounds, where R = Me_3Si or Ph, have been prepared by dehydrochlorination of the corresponding phosphino-bridged pentaborane derivatives $(\mu\text{-}R_2CHPCl)B_5H_8$.

Introduction

Investigations of synthetic routes to molecular heteroborane clusters containing heteroatoms other than carbon have led to the discovery of a surprising number of new classes of cluster molecules. One synthetic approach on which we have focused is the direct insertion of heteroatoms ranging from beryllium to gallium into boron hydride clusters. Recently we have expanded our explorations to include nitrogen group elements. The initial results of these investigations are the syntheses of the first examples of phosphahexaboranes, reported below.

Prior to the present work, no examples have been reported of phosphaborane clusters containing fewer than nine boron atoms. The known phosphaboranes include $C_6H_5PB_{11}H_{11}$,[1] a phosphadodecaborane; $RPB_{10}H_{12}$,[2] a phosphaundecarborane; and several phosphacarboranes: 1,2- and 1,7-$CHPB_{10}H_{10}$,[1,3] $CHP(CH_3)B_9H_{10}$, and the $CHPB_9H_{10}^-$ anion.[4] Transition-metal complexes of several of these compounds have been prepared.[2,4a,5,6]

Results and Discussion

Table I. ^{11}B NMR Data for Isomers a and b of $(\mu\text{-}RPCl)B_5H_8$ Derivatives[a]

	chem shift, δ					
	B(4,5)		B(2,3)		B(1)	
R	a	b	a	b	a	b
CH_3	−1.0	+0.2	−24.2[b] (88)	−8.7[b] (88)	−45.4	−46.0
C_6H_5	−0.1	−0.1	−21.7 (93)	−9.9 (93)	−43.7	−45.5
$CH(C_6H_5)_2$, **1**	−0.5	−0.5	−21.8 (88)	−10.0 (88)	−44.8	−45.8
$CH(SiMe_3)_2$, **2**	−0.1	−0.1	−17.4 (88)	−8.8 (96)	−44.5	−46.4

[a] The δ values are chemical shifts measured relative to external $BF_3{\cdot}O(C_2H_5)_2$ = 0 ppm. Values in parentheses are terminal B–H coupling constants in hertz. [b] Apparent triplets due to ^{31}P coupling of similar magnitude to that of terminal ^1H. See ref 7 for details.

Methylenephosphahexaborane Syntheses. Geometrical isomers of the phosphorus-bridged (μ-phosphino)pentaboranes of general formula $RR'PB_5H_8$ (in which R ≠ R′), have been previously reported.[7] The presence of geometrical isomers led the authors to suggest that the bridging phosphorus atom in these compounds is not bound to an edge of the pentaborane pyramid via a three-center–two-electron bond, as is the silicon atom in $(\mu\text{-}Me_3Si)B_5H_8$[8] but that the original lone pair of electrons on phosphorus is also involved in bonding and the environment at the phosphorus is therfore approximattely tetrahedral. The isomerism of these (μ-phosphino)pentaboranes result from the different environments of the two terminal substituents on phosphorus with respect to the pentaborane cluster. In the (μ-phosphino)pentaboranes, the phosphorus contributes three electrons to the cluster but is not itself a cluster atom. The five boron atom cluster is formally considered, on the basis of its electron count,[9] to have an arachno structure analogous to that of the isoelectronic pentaborane(11), B_5H_{11}, and $(\mu\text{-}Me_2NCH_2)B_5H_8$,[10] in both of which B(2) is not expected to be within distance of B(3).

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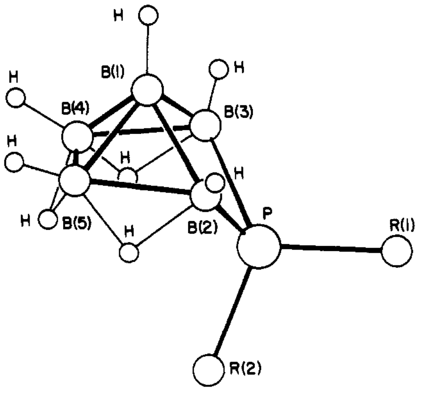

Figure 1. Proposed structure of (μ-phosphino)pentaborane derivatives.

This structural feature has been observed in (μ-diphenylphosphino)decaborane(14), in which the phosphorus-bridged boron–boron distance is 2.69 Å,[11] compared to 1.77 Å in the parent decaborane(14).[12] The proposed structure of the (μ-phosphino)pentaboranes is shown in Figure 1. Our search for rational synthetic routes to group V (group 15[27]) heteroatom–boron clusters has led to the syntheses of new (μ-phosphino)pentaboranes in which R is a halogen and R′ contains hydrogen on the α-carbon atom, such that dehydrohalogenation might lead to insertion of the phosphorus into the borane cluster. In addition we have investigated the direct insertion of phosphorus into the borane cluster using the phosphaalkene $(Me_3Si)_2C{=}PCl$.[13]

In the reaction of Ph_2CHPCl_2 with the $B_5H_8^-$ anion (eq 1) we have observed a predominance of a single isomer of the (μ-phosphino)pentaborane, (μ-$Ph_2CHPCl)B_5H_8$ (**1a**). In some

$$\mathrm{Ph_2CHPCl_2 + B_5H_8^- \rightarrow \underset{\textbf{1a}}{(\mu\text{-}Ph_2CHPCl)B_5H_8} + Cl^-} \qquad (1)$$

syntheses the ^{11}B NMR spectra of the reaction mixture also show the presence of a small amount of another product, **3**, whose resonances are substantially shifted from those of **1a**. Compound **3** is also produced by reaction of **1a** with 1 equiv of 2,6-lutidine. Addition of anhydrous HCl to the reaction mixture containing **3** produced **1b**, the second isomer of (μ-$Ph_2CHPCl)B_5H_8$, whose ^{11}B NMR spectrum is slightly different from that of **1a**. A solution of **1b** converted to its **1a** isomer (plus B_5H_9) after sitting at 25 °C for 2 days. Considerable decomposition in each of the reactions described above was indicated by a steady increase in the relative concentration of B_5H_9 in the reaction mixtures.

The reaction of $(Me_3Si)_2CHPCl_2$ with the $B_5H_8^-$ anion, on the other hand, produces a mixture of nearly equal quantities of the two isomers of $[\mu\text{-}(Me_3Si)_2CHPCl]B_5H_8$, **2a** and **2b**, along with a much larger amount of another compound, **4**, which is an analogue of **3**. Reaction of this mixture with 2,6-lutidine (2,6-lut) results in nearly quantitative conversion to **4**. Subsequent reaction of **4** with anhydrous HCl produces **2b**, which then slowly converts to **2a** on standing at 25 °C. The ^{11}B NMR spectral data for these isomers are tabulated in Table I.

The formation of **3** and **4** is clearly the result of dehydrochlorination of the (μ-phosphino)pentaboranes **1** and **2** (eq 2).

$$\begin{array}{ll} (\mu\text{-}\mathrm{R_2CHPCl)B_5H_8} + 2,6\text{-lut} \rightarrow & \mathrm{R_2CPB_5H_8} + 2,6\text{-lut}\cdot\mathrm{HCl} \\ \mathbf{1},\ \mathrm{R = Ph} & \mathbf{3},\ \mathrm{R = Ph} \\ \mathbf{2},\ \mathrm{R = Me_3Si} & \mathbf{4},\ \mathrm{R = Me_3Si} \end{array} \qquad (2)$$

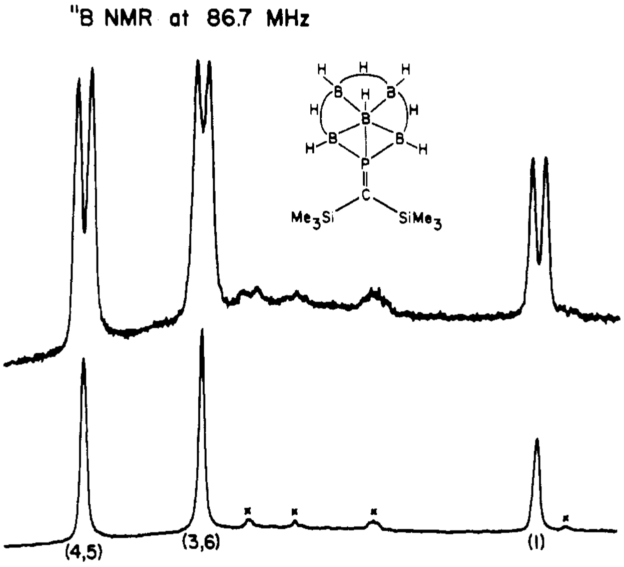

Figure 2. ^{11}B NMR spectra of $(Me_3Si)_2CPB_5H_8$ (**4**) in diethyl ether. Proposed resonance assignments are shown below the lower trace, which is the broad-band ^1H-decoupled spectrum (× = impurities.)

Table II. ^{11}B NMR Spectral Data for **3** and **4** in Diethyl Ether Solutions[a]

	chem shift, δ		
compd	B(4,5)	B(3,6)	B(1)
$H_2CPB_5H_8$	+26.6 (164)	+8.3 (141)	−36.9 (152)
$(C_6H_5)_2CPB_5H_8$ (**3**)	+26.6 (161)	+8.9 (146)	−35.3 (161)
$(Me_3Si)_2CPB_5H_8$ (**4**)	+23.3 (156)	+6.9 (142)	−39.9 (141)

[a] The δ values are chemical shifts measured relative to external $BF_3{\cdot}O(C_2H_5)_2 = 0$ ppm. Values in parentheses are doublet coupling constants in hertz.

That the $B_5H_8^-$ anion can effect this dehydrochlorination (eq 3),

$$\begin{array}{ll} (\mu\text{-}\mathrm{R_2CHPCl)B_5H_8 + B_5H_8^-} \rightarrow & \mathrm{R_2CPB_5H_8 + B_5H_9 + Cl^-} \\ \mathbf{1},\ \mathrm{R = Ph} & \mathbf{3},\ \mathrm{R = Ph} \\ \mathbf{2},\ \mathrm{R = Me_3Si} & \mathbf{4},\ \mathrm{R = Me_3Si} \end{array} \qquad (3)$$

particularly when R = Me_3Si, would account for the observation of some **3** and **4** in the reactions of the $B_5H_8^-$ anion with R_2CHPCl_2 (R = Ph, Me_3Si). However, the reaction of R_2CHPCl_2 with 2 equiv of $B_5H_8^-$ is not suitable for the syntheses of **3** and **4** due to side reactions involving the initial larger excess of the $B_5H_8^-$ anion.

Compound **4** has also been synthesized directly by the reaction of the $B_5H_8^-$ anion with the phosphaalkene $(Me_3Si)_2C{=}PCl$ (eq 4).

$$\mathrm{(Me_3Si)_2C{=}PCl + B_5H_8^- \rightarrow \underset{\textbf{4}}{(Me_3Si)_2CPB_5H_8} + Cl^-} \qquad (4)$$

A number of substitution reactions at the phosphorus atom of *P*-chlorophosphaalkenes have been reported. For example, Appel and co-workers have synthesized derivatives of $Ph(Me_3Si)C{=}PCl$ in which the chlorine atom is replaced by an alkyl, NR_2, PR_2, OR, or SR group.[14] Recently, Cowley and co-workers have studied the reactions of $(Me_3Si)_2C{=}PCl$ with transition-metal nucleophiles to produce terminal[15] and bridging[16] phosphavinylidene metal complexes.

Methylenephosphahexaborane Characterization. The ^{11}B NMR spectrum of **4** is shown in Figure 2 and the ^{11}B NMR spectral data for **3** and **4** are tabulated in Table II. By analogy with the reactions of simple chlorophosphines with the $B_5H_8^-$ anion, one might expect from reaction 4 a product whose phosphorus atom occupies a bridging position on the pentaborane pyramid as in other (μ-phosphino)pentaboranes. The fact that the ^{11}B NMR spectra differ from those of the (μ-phosphino)pentaboranes, however, leads us to conclude that **3** and **4** are *nido*-phosphahexaboranes rather than (μ-phosphino)pentaboranes. The fact

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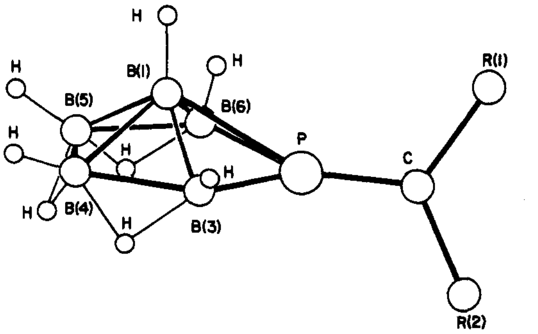
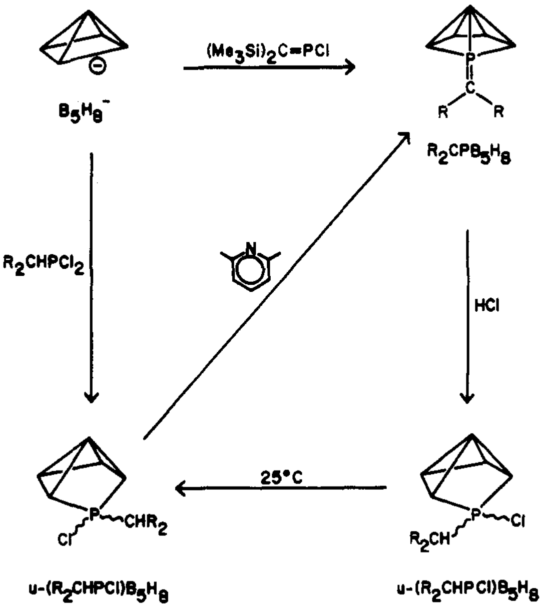


Figure 3. Proposed structure of $R_2CPB_5H_8$ derivatives **3** and **4**. Terminal hydrogens are numbered the same as the boron to which they are attached.

Scheme I



that the low-field ^{11}B NMR resonances of **3** and **4**, which correspond to the basal boron atoms, appear considerably further downfield than those of any known bridge-substituted pentaborane(9) derivatives supports this conclusion. The basal boron chemical shifts for **3** and **4** are intermediate between those observed for the metallahexaboranes containing beryllium,[17] copper,[18] or zinc[19] atoms and those containing transition-metal atoms such as manganese,[20] iron,[21] or cobalt.[22] A proposed structure for *nido*-methylenephosphahexaboranes **3** and **4** is illustrated in Figure 3 and Scheme I.

The bonding about the phosphorus atom in **3** and **4** could be considered similar to that in the phosphorus ylides $R_3P{=}CR'_2$. This would result in a short P–C distance, approaching that of a P=C double bond. The ^{31}P NMR spectrum of **4** consists of a single, broad resonance at δ +209. While the resonance appears significantly downfield from that of phosphorus ylides (δ 0 to +25) it is far upfield from that of the phosphaalkene $(Me_3Si)_2C{=}PCl$ (δ +343),[13] indicating a significant perturbation from either of these structures. Complexing of the phosphorus lone pair of the $R_2C{=}P$ moiety, as in a $(\mu\text{-}R_2C{=}P)B_5H_8$ structure, would result in a large downfield shift of the phosphorus resonance. Such is the case with the recently characterized phosphavinylidene complexes $(\eta^5\text{-}C_5H_5)(CO)_2Mo{=}P{=}C(SiMe_3)$ (δ +497)[15] and $[(\mu\text{-}(Me_3Si)_2C{=}P)Fe(CO)_3]_2$.[16]

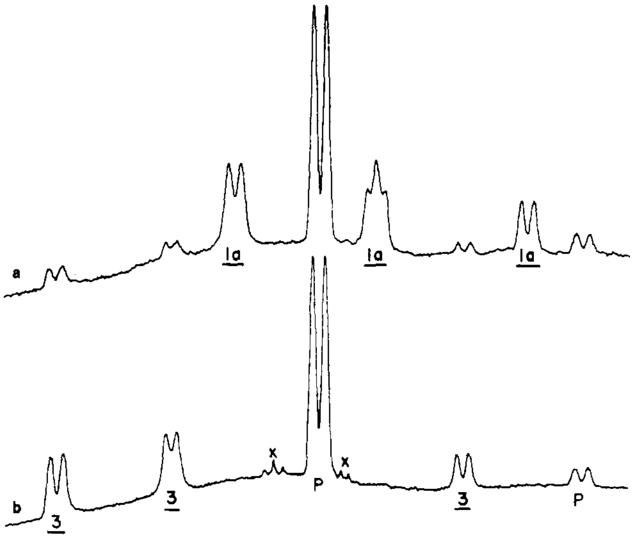


Figure 4. ^{11}B NMR spectra in diethyl ether: (a) Reaction of Ph_2CHPCl_2 with LiB_5H_8; (b) Reaction of the mixture from part a with 2,6-lutidine. Assignments below the traces refer to compound numbers in the text, P = B_5H_9, and X = impurities.

Efforts to obtain single crystals of **3** or **4** suitable for structure determination by X-ray diffraction are under way, as is further exploration of the chemistry of this new class of heteroborane clusters.

Experimental Section

Air-sensitive compounds were handled in dry nitrogen-flushed glovebags or standard high-vacuum lines. The ^{11}B and ^{1}H NMR spectra were obtained at 86.7 and 270.13 MHz, respectively, on a Bruker WP270SY spectrometer. The ^{31}P NMR spectrum was obtained at 80.76 MHz on a JEOL FX 200 spectrometer. Mass spectra were obtained by using a KRATOS MS80 spectrometer.

Preparation of $(Me_3Si)_2CHPCl_2$. Typically, a solution of 40.0 mmol of $(Me_3Si)_2CHLi$[23] in 50 mL of diethyl ether was added dropwise to a solution of 40.0 mmol of PCl_3 in 20 mL of diethyl ether at 0 °C. After addition was complete, the reaction was stirred for 1 h, then warmed to room temperature, and stirred overnight. The LiCl was removed by filtration, and the filtrate was evaporated to a yellow oil by vacuum. Fractional distillation of this oil yielded 4.39 g of $(Me_3Si)_2CHPCl_2$ (16.8 mmol, 42%), bp 46 °C (10^{-4} Torr).

Reaction of Ph_2CHPCl_2 with LiB_5H_8 or KB_5H_8. Under a flow of dry N_2, 0.488 g of Ph_2CHPCl_2[24] (1.81 mmol) was added by syringe to a flask containing 1.80 mmol of LiB_5H_8[25] in 3 mL of diethyl ether at −196 °C. The flask was evacuated and its contents warmed to −70 °C. The flask was then warmed, with continuous stirring, from −70 to −10 °C over a period of 2.5 h. At this point, the solution was slightly yellow and contained a white solid. The solution was warmed to 25 °C briefly, and a sample was transferred by syringe under N_2 to a thin-walled 5-mm-o.d. NMR tube. The ^{11}B NMR spectrum, shown in Figure 4a, consists of the resonances arising from $Ph_2CPB_5H_8$ (**3**), $(\mu\text{-}Ph_2CHPCl)B_5H_8$ (**1a**), and B_5H_9 in a ratio of 1:5:10 (see Tables I and II for chemical shift information).

2,6-Lutidine (0.45 g, 4.34 mmol) was added to the reaction flask by condensation at −196 °C. As the contents of the flask were warmed to −78 °C, a white solid precipitated. The mixture was stirred as it was warmed from −78 to −15 °C over a period of 2.5 h and then at 25 °C for 1 h. An NMR sample was removed under N_2 as before. The ^{11}B NMR spectrum, shown in Figure 4b, consists of the resonances arising from **3** and B_5H_9 in a 1:3 ratio.

The reaction of 0.887 g (3.30 mmol) of Ph_2CHPCl_2 with 3.25 mmol of KB_5H_8[26] in 4 mL of dimethyl ether in place of LiB_5H_8 in diethyl ether

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occurred similarly. After the dimethyl ether was removed by vacuum distillation at −35 °C and 3 mL of diethyl ether was added by condensation at −196 °C, the mixture was warmed to 25 °C and an NMR sample was removed under N_2 by syringe. The ^{11}B NMR spectrum showed only **1a** and B_5H_9. 2,6-Lutidine (0.429 g, 4.00 mmol) was added to the flask by condensation at −196 °C. The contents of the flask were warmed to −78 °C and stirred for 1.5 h and then warmed from −78 to 0 °C over a period of 1.5 h. The ^{11}B NMR spectrum of an NMR sample, removed as before, showed only **3** and B_5H_9.

Reaction of $Ph_2CPB_5H_8$ (3) with HCl. Anhydrous HCl (5.0 mmol) was added to the flask containing a solution of **3** and B_5H_9 (described above) by condensation at −196 °C. The contents of the flask were stirred at −78 °C for 1 h and then warmed to 0 °C over a period of 3 h. The flask was then cooled to −78 °C and opened on the vacuum line to distill out any unreacted HCl. An NMR sample was removed at 25 °C under N_2 by syringe. The ^{11}B NMR spectrum showed much B_5H_9 plus a doublet at −0.5 ppm, a triplet at −10.0 ppm, and a doublet at −45.8 ppm (ratio 2:2:1). In the $^{11}B\{^1H\}$ NMR spectrum this set of resonances was collapsed to a singlet, a doublet (J = 88 Hz), and a singlet, respectively. These resonances are assigned to $(\mu\text{-}Ph_2CHPCl)B_5H_8$, isomer **1b**. Another $^{11}B\{^1H\}$ NMR spectrum of this sample, obtained after 2 days at 25 °C, consisted of the resonances of isomer **1a** (doublet at −23.0 ppm) plus an increased amount of B_5H_9.

Reaction of $(Me_3Si)_2CHPCl_2$ with KB_5H_8. Under N_2 flow, 0.390 g of $(Me_3Si)_2CHPCl_2$ (1.49 mmol) was added by syringe to a frozen solution of 1.5 mmol of KB_5H_8 in 3 mL of dimethyl ether at −196 °C. The reaction mixture was warmed to −78 °C and stirred for 5.5 h. The volatile components were then removed by vacuum distillation at −78 °C, and 3 mL of diethyl ether were added by condensation at −196 °C. After the reaction mixture was warmed to 25 °C, a portion of the ether extract was removed under N_2 for NMR analysis. The ^{11}B NMR spectrum consisted of the resonances arising from both isomers of $[\mu\text{-}(Me_3Si)_2CHPCl]B_5H_8$ (**2a** and **2b**, see Table I), $(Me_3Si)_2CPB_5H_8$ (**4**, see Table II), and B_5H_9 in a ratio of 1:1:5:10. The NMR sample was returned to the reaction flask, and 0.170 g of 2,6-lutidine (1.58 mmol) was added to the flask by condensation at −196 °C. It was stirred continuously as it was warmed to −78 °C for 3 h and then from −78 to +10 °C over a period of 2.5 h. The volatile components were removed by vacuum distillation at −10 °C, and 3 mL of benzene-d_6 were added by condensation at −196 °C. The flask was then warmed to 25 °C with stirring and a portion of the resulting solution was removed under N_2 by syringe. The ^{11}B NMR spectrum of this solution exhibited only the resonances of **4** and **2a** in a ratio of ca. 15:1. The ^1H NMR spectrum showed, in addition to the resonances of protons attached to boron atoms, two Me_3Si resonances in a 2:1 ratio. The NMR sample was returned to the reaction flask. The benzene-d_6 was removed by vacuum distillation at 25 °C. A total of 3 mL of diethyl ether was added by condensation at −196 °C, followed by 0.125 g (1.17 mmol) of 2,6-lutidine. This mixture was stirred at −78 °C for 3.5 h and then at 0 °C for 1 h. Volatile components were removed by vacuum distillation at 25 °C. A 3-mL aliquot of diethyl ether was added by condensation at −196 °C, and the mixture was warmed to 25 °C and stirred briefly. The ^{11}B NMR spectrum of this solution, shown in Figure 2, consists of three resonances arising from $(Me_3Si)_2C{=}PB_5H_8$ (**4**), plus a very small amount of **2a**. The ^{31}P NMR spectrum of this sample was made up of two resonances: a sharp singlet at 223.5 ppm arising from $(Me_3Si)_2CHPCl_2$ (lit. 222.7 ppm) and a broad resonance at 209.0 ppm, assigned to **4**. The high-resolution mass spectrum of **4** confirmed its molecular formula: calcd for $^{12}C_7{}^1H_{26}{}^{11}B_5{}^{28}Si_2{}^{31}P$, 252.1976; found, 252.1980.

Reaction of $(Me_3Si)_2CPB_5H_8$ (7) with HCl. The solution of **4** and $(Me_3Si)_2CHPCl_2$, described above, was evacuated to dryness at 25 °C and the residue then dissolved in 3 mL of diethyl ether. At −196 °C, 3.0 mmol of anhydrous HCl were added by condensation. The resulting mixture was warmed to −78 °C and stirred for 2.5 h. Volatile components were then removed by vacuum distillations as the sample was warmed to 25 °C. A total of 3 mL of diethyl either was added by condensation at −196 °C, the sample was warmed to 25 °C, and a portion of the resulting solution was removed by syringe under N_2. The ^{11}B NMR spectrum of this sample indicated a mixture of **4** and **2b** (see Table I) in a ratio of 1:2. Then, 3.0 mmol was added to the reaction flask by condensation at −196 °C. It was stirred at −78 °C for 9 h and then opened to vacuum at −78 °C to remove any unreacted HCl. The reaction mixture was warmed to 25 °C, and an NMR sample was removed by syringe Under N_2. The ^{11}B NMR spectrum consisted of the three resonances arising from **2b** plus a triplet at −23.4 ppm and some small resonances due to decomposition products. The rest of the reaction mixture was stirred at 25 °C for 2 days. At this point the ^{11}B NMR spectrum of the solution showed three resonances arising from **2a** along with increased amounts of unidentified decomposition products.

Reaction of $(Me_3Si)_2C{=}PCl$ with KB_5H_8. Typically, $(Me_3Si)_2C{=}PCl$ (0.540 g, 2.4 mmol) was added by syringe under N_2 flow to a solution of 2.5 mmol of KB_5H_8 in 3 mL of diethyl ether at −196 °C. The mixture was warmed to −78 °C and stirred for 1.5 h. At this point, the reaction mixture consisted of a yellow solution and a white solid. The volatile components were removed by vacuum distillation as the sample was warmed to 25 °C. The remaining yellow-orange material was extracted with 5 mL of pentane. The ^{11}B NMR spectrum of this pentane solution consisted of the three resonances arising from $(Me_3Si)_2CPB_5H_8$ (**4**, see Table II), B_5H_9, and several unidentified impurities. The pentane solution was transferred via a steel cannula to a Pyrex tube (12 mm o.d.) connected to the vacuum line; the pentane was removed by vacuum distillation. With the tube in a horizontal position, the end containing the sample was heated to 100 °C and then to 160 °C over a period of 1.5 h under continuous evacuation. A colorless, crystalline solid condensed in a section of the tube cooled to −78 °C. As this material was warmed to ambient temperature, it melted to a colorless liquid. The ^{11}B NMR spectrum of a benzene-d_6 solution of the liquid was that of **4**, still containing several small impurities, but cleaner than before sublimation. The reaction of $(Me_3Si)_2C{=}PCl$ with LiB_5H_8 in diethyl ether gave similar results.

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(26) Johnson, H. D., II; Geanangel, R. A.; Shore, S. G. *Inorg. Chem.* **1970**, *9*, 908–912.

(27) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)