

The common intermediacy of  $\eta^3$ -enolates in these seemingly disparate systems may help in unifying our understanding of their sometimes divergent reactivity patterns.

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- (12) (a) Bennett, M. A.; Robertson, G. B.; Watt, R.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* 1971, 752-753. (b) Robertson, G. B.; Whimp, P. O. *Inorg. Chem.* 1973, 12, 1740-1745. (c) Guggolz, E.; Ziegler, M. L.; Biersack, H.; Herrmann, W. A. *J. Organomet. Chem.* 1980, 194, 317-324.

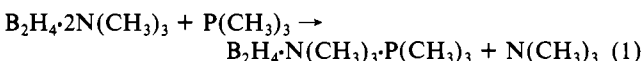
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### Formation and Reaction Chemistry of Trimethylamine-Trimethylphosphine-Diborane(4)

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We reported in an earlier communication<sup>1</sup> to this journal that trimethylamine-trimethylphosphine-diborane(4), B<sub>2</sub>H<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub>, was formed by a ligand displacement reaction of bis(trimethylamine)-diborane(4), B<sub>2</sub>H<sub>4</sub>·2N(CH<sub>3</sub>)<sub>3</sub>, with trimethylphosphine (see eq 1). The product was the first repre-

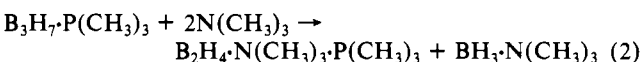


sentative of a previously unknown mixed-ligand adduct of diborane(4). Displacement of the second trimethylamine proceeded very slowly.<sup>1</sup>

The mixed-ligand adduct, B<sub>2</sub>H<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub>, can now be prepared in pure form by the reaction of B<sub>3</sub>H<sub>7</sub>·P(CH<sub>3</sub>)<sub>3</sub> with trimethylamine. Furthermore, this finding has provided a new insight into the reaction mechanism of base cleavage of triborane(7) adducts. In this paper, we describe the characterization and reaction chemistry of the mixed adduct of diborane(4).

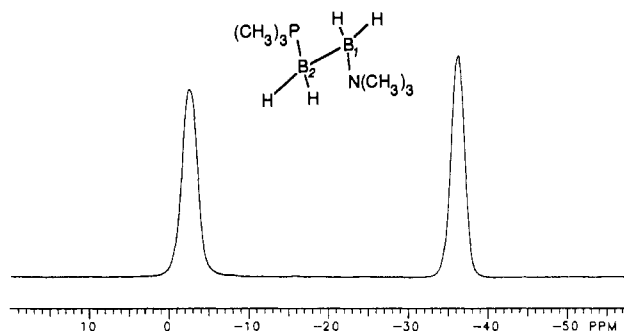
### Results

**A. Cleavage of P(CH<sub>3</sub>)<sub>3</sub> and N(CH<sub>3</sub>)<sub>3</sub> Adducts of B<sub>3</sub>H<sub>7</sub>.** (a) **Reaction of B<sub>3</sub>H<sub>7</sub>·P(CH<sub>3</sub>)<sub>3</sub> with N(CH<sub>3</sub>)<sub>3</sub>.** Formation of B<sub>2</sub>H<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub>. The reaction of B<sub>3</sub>H<sub>7</sub>·P(CH<sub>3</sub>)<sub>3</sub> with 2 molar equiv of N(CH<sub>3</sub>)<sub>3</sub> in dichloromethane at room temperature proceeds according to eq 2. The mixed-ligand adduct of B<sub>2</sub>H<sub>4</sub> can



be separated from BH<sub>3</sub>·N(CH<sub>3</sub>)<sub>3</sub> as a colorless solid by fractional sublimation at room temperature. The compound is stable in the absence of air. It slowly decomposes in solution at room temperature.

**NMR Spectra of B<sub>2</sub>H<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub>.** The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of B<sub>2</sub>H<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub> in Figure 1 shows a broad signal at -2.7 ppm due to the amine-attached boron atom (B<sub>N</sub>) and another at -36.4 ppm due to the phosphine-attached boron atom (B<sub>P</sub>). The <sup>1</sup>H-spin-coupled <sup>11</sup>B signals are broader but do not have any fine structure. These shift values are compared with the values of B<sub>2</sub>H<sub>4</sub>·2N(CH<sub>3</sub>)<sub>3</sub> and B<sub>2</sub>H<sub>4</sub>·2P(CH<sub>3</sub>)<sub>3</sub> in Table Ia. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the compound is a broad, partially collapsed 1:1:1:1 quartet centered at 3.6 ppm with a J<sub>BP</sub> value of ca. 50 Hz. The apparent absence of a doublet feature (B-P coupling) on the B<sub>P</sub> resonance signal (Figure 1) is attributable



**Figure 1.** <sup>11</sup>B{<sup>1</sup>H} NMR (96.2 MHz) spectrum of B<sub>2</sub>H<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub> at +20 °C in CH<sub>2</sub>Cl<sub>2</sub>.

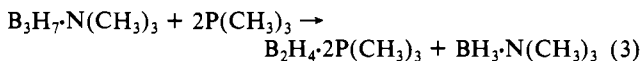
**Table I.** <sup>11</sup>B NMR Shift Data (ppm)

a. B <sub>2</sub> H <sub>4</sub> ·L·L'			
	B-N	B-P	
B <sub>2</sub> H <sub>4</sub> ·2P(CH <sub>3</sub> ) <sub>3</sub> <sup>a</sup>			-37.5
B <sub>2</sub> H <sub>4</sub> ·N(CH <sub>3</sub> ) <sub>3</sub> ·P(CH <sub>3</sub> ) <sub>3</sub>	-2.7		-36.4
B <sub>2</sub> H <sub>4</sub> ·2N(CH <sub>3</sub> ) <sub>3</sub> <sup>b</sup>	-3.5		
b. B <sub>3</sub> H <sub>6</sub> ·L·L'+			
	B-N	B-P	BH <sub>2</sub>
B <sub>3</sub> H <sub>6</sub> ·2P(CH <sub>3</sub> ) <sub>3</sub> <sup>c</sup>		-39.0	-10.5
B <sub>3</sub> H <sub>6</sub> ·N(CH <sub>3</sub> ) <sub>3</sub> ·P(CH <sub>3</sub> ) <sub>3</sub> <sup>d</sup>	-12.4	-41.3	-10.2
B <sub>3</sub> H <sub>6</sub> ·2N(CH <sub>3</sub> ) <sub>3</sub> <sup>b</sup>	-15.8		-9.7

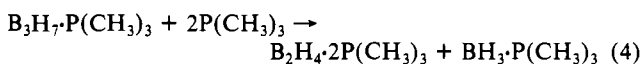
<sup>a</sup>References 14 and 15. <sup>b</sup>Reference 1. <sup>c</sup>Reference 3.

to this small J<sub>BP</sub> value and to the broadness of the signal. The <sup>1</sup>H{<sup>11</sup>B} NMR spectrum shows a singlet at 2.52 ppm (intensity 9, amine CH<sub>3</sub> protons), a quintetlike signal at 1.75 ppm (intensity 2, protons on B<sub>N</sub>), a sharp doublet at 1.14 ppm (<sup>2</sup>J = 9.0 Hz, intensity 9, phosphine CH<sub>3</sub> protons), and a doublet of triplets at 0.03 ppm (<sup>2</sup>J<sub>HBP</sub> = 21 Hz, <sup>3</sup>J<sub>HBBH</sub> = 5.0 Hz, intensity 2, protons on B<sub>P</sub>). The quintetlike signal of the protons attached to B<sub>N</sub> is thought to be due to spin-spin couplings to both the B<sub>P</sub> protons and the phosphorus. On the basis of this assumption, a value of 9.7 Hz is estimated for <sup>3</sup>J<sub>HBBP</sub>.

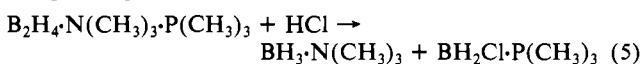
**(b) Reactions of B<sub>3</sub>H<sub>7</sub>·N(CH<sub>3</sub>)<sub>3</sub> and B<sub>3</sub>H<sub>7</sub>·P(CH<sub>3</sub>)<sub>3</sub> with P(CH<sub>3</sub>)<sub>3</sub>.** The trimethylamine adduct of B<sub>3</sub>H<sub>7</sub> slowly reacts with P(CH<sub>3</sub>)<sub>3</sub> at room temperature in dichloromethane. The major products are BH<sub>3</sub>·N(CH<sub>3</sub>)<sub>3</sub> and B<sub>2</sub>H<sub>4</sub>·2P(CH<sub>3</sub>)<sub>3</sub>, and BH<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub> and B<sub>2</sub>H<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub> are detected in minute quantities. Thus, the appropriate equation for the reaction is



The reaction of B<sub>3</sub>H<sub>7</sub>·P(CH<sub>3</sub>)<sub>3</sub> with P(CH<sub>3</sub>)<sub>3</sub> proceeds similarly:<sup>2</sup>



**B. Reactions of B<sub>2</sub>H<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub>.** (a) **With Hydrogen Chloride.** The mixed-base adduct, B<sub>2</sub>H<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub>, reacts with anhydrous HCl at -80 °C in a CH<sub>2</sub>Cl<sub>2</sub> solution according to eq 5. Apparently, an alternative mode of cleavage is unfa-

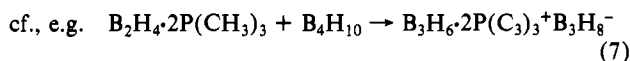
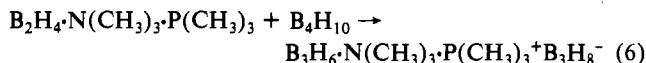


vorable; BH<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub> and BH<sub>2</sub>Cl·N(CH<sub>3</sub>)<sub>3</sub> are produced in trace quantities.

**(b) With Tetraborane(10).** Treatment of B<sub>2</sub>H<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub> with B<sub>4</sub>H<sub>10</sub> results in the formation of a new tetraboron complex cation, (trimethylamine)(trimethylphosphine)hexahydrotriboron(1+) [B<sub>3</sub>H<sub>6</sub>·N(CH<sub>3</sub>)<sub>3</sub>·P(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup> (see eq 6). This reaction is analogous to that of B<sub>2</sub>H<sub>4</sub>·2P(CH<sub>3</sub>)<sub>3</sub> (eq 7) or B<sub>2</sub>H<sub>4</sub>·2N(CH<sub>3</sub>)<sub>3</sub> with B<sub>4</sub>H<sub>10</sub>.<sup>1,3</sup>

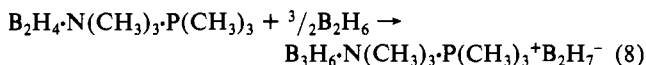
(1) DePoy, R. E.; Kodama, G. *Inorg. Chem.* 1985, 24, 2871.

(2) Kodama, G.; Kameda, M. *Inorg. Chem.* 1979, 18, 3302.

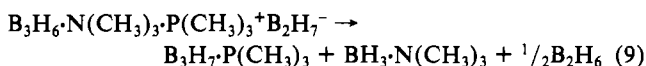


**NMR Spectra of  $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$ .** Figure 2 shows a  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of the salt,  $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$ . The signal at  $-30$  ppm is readily assignable to the  $\text{B}_3\text{H}_8^-$  anion.<sup>4</sup> Shown also in Figure 2 is the proposed structure of the  $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3^+$  cation, which is similar to those of the  $\text{B}_3\text{H}_6\cdot 2\text{N}(\text{CH}_3)_3^+$  and  $\text{B}_3\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3^+$  cations.<sup>3,5</sup> A comparison of the NMR data of these three cations permits an unambiguous assignment of the spectrum (see Table Ib). Thus, the signals at  $-10.2$ ,  $-12.4$ , and  $-41.3$  ppm ( $J_{\text{BP}} = 116$  Hz) are assigned to the B(3), B(1), and B(2) atoms, respectively, of the new triborane cation. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$  shows a well-defined 1:1:1:1 quartet centered at  $-3.3$  ppm with a  $^{11}\text{B}-^{31}\text{P}$  spin-coupling constant of 119 Hz. The variable-temperature  $^1\text{H}\{^{11}\text{B}\}$  NMR spectra of  $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$  reveals that the cation is fluxional with respect to migration of the borane hydrogen atoms around the three-boron framework of the cation. At  $-10$  °C the borane proton signal appears as a singlet at 1.40 ppm. At  $-80$  °C, however, this signal disappears and a singlet signal appears at 2.17 ppm. Other signals of borane protons, which are expected to appear at higher field, could not be identified unequivocally, probably due to the overlap with the phosphine methyl proton signal at 1.39 ppm ( $J_{\text{HP}} = 12$  Hz) and the  $\text{B}_3\text{H}_8^-$  proton signal at 0.02 ppm. Shoulders were discernible on both sides of the 0.02 ppm signal. The signal of the amine methyl protons appears at 2.66 ppm.

**(c) With Diborane(6).** As is the case in the reactions of diborane(6) with  $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$  and  $\text{B}_2\text{H}_4\cdot 2\text{N}(\text{CH}_3)_3$ ,<sup>1,3</sup> the treatment of  $\text{B}_2\text{H}_4\cdot\text{N}(\text{CH}_3)_3$  with  $\text{B}_2\text{H}_6$  at  $-65$  °C produces a  $\text{B}_2\text{H}_7^-$  salt of the  $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3^+$  cation:



The product undergoes a slow decomposition at  $-45$  °C according to eq 9. The decomposition is fast above 0 °C and is quantitative.

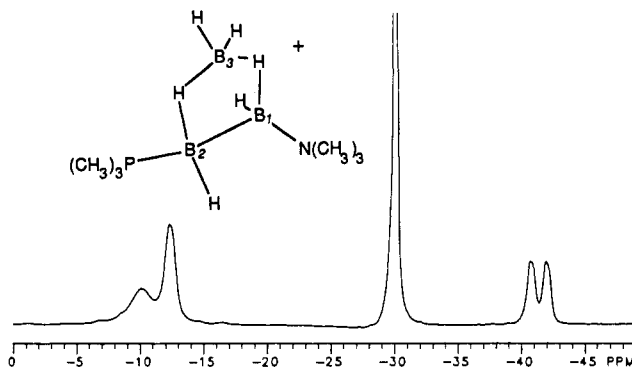


An alternative mode of decomposition that would produce  $\text{B}_3\text{H}_7\cdot\text{N}(\text{CH}_3)_3$  and  $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$  does not occur.

### Discussion

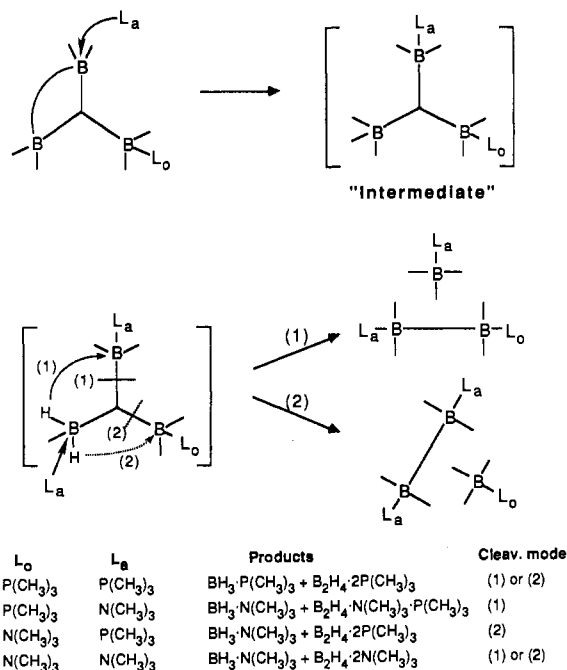
When the B-B bond of  $\text{B}_2\text{H}_4\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$  is cleaved as a result of the reaction with an electrophilic reagent (eq 5 or eq 8 and 9),  $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$  is produced, and the stronger base,  $\text{P}(\text{CH}_3)_3$ , is attached to the stronger acids,  $\text{BH}_2\text{Cl}$  or  $\text{B}_3\text{H}_7$ . Other than this unique feature of the mixed-ligand adduct, the reactions of  $\text{B}_2\text{H}_4\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$  with electrophilic reagents parallel those of  $\text{B}_2\text{H}_4\cdot 2\text{N}(\text{CH}_3)_3$ <sup>1</sup> and  $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ .<sup>3</sup> Reaction chemistry of the new mixed-ligand triborane complex cation,  $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3^+$ , will be described in a separate paper.<sup>6</sup>

Ritter and co-workers<sup>7</sup> and Parry and Paine<sup>8</sup> proposed a mechanism for the triborane cleavage reactions. The most important facet of this mechanism is the formation of an intermediate,  $\text{B}_3\text{H}_7\cdot\text{L}_o\cdot\text{L}_a$  where  $\text{L}_o$  and  $\text{L}_a$  represent the Lewis base in the reacting  $\text{B}_3\text{H}_7$  adduct and the attacking Lewis base, respectively. As illustrated in Scheme I, this mechanism adequately



**Figure 2.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (96.2 MHz) spectrum of  $\text{B}_3\text{H}_6\cdot\text{N}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3 + \text{B}_3\text{H}_8^-$  at  $-20$  °C in  $\text{CD}_2\text{Cl}_2$ .

### Scheme I



explains the observed formation of the  $\text{B}_2\text{H}_4$  adducts containing  $\text{P}(\text{CH}_3)_3$  or  $\text{N}(\text{CH}_3)_3$ . It is noted that, whenever amine is involved in the reaction,  $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$  is produced, indicating that elimination of  $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$  from the intermediate is favored over  $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$  elimination.

In the early days, the reaction of a triborane(7) adduct of a strong base [e.g.,  $\text{B}_3\text{H}_7\cdot\text{N}(\text{CH}_3)_3$ ] with a strong base [e.g.,  $\text{N}(\text{CH}_3)_3$ ] was thought to give a complex mixture of borane compounds containing polymeric species.<sup>9</sup> The newly observed formation of the  $\text{B}_2\text{H}_4$  adducts of strongly basic  $\text{P}(\text{CH}_3)_3$  and  $\text{N}(\text{CH}_3)_3$  corrects this earlier misconception.

### Experimental Section

**General Procedures.** Conventional vacuum-line techniques were used throughout. Transfer of air-sensitive solids was performed in a plastic glovebag filled with dry nitrogen gas. The sources of  $\text{B}_2\text{H}_6$ ,  $\text{B}_4\text{H}_{10}$ ,  $\text{P}(\text{CH}_3)_3$ ,  $\text{N}(\text{CH}_3)_3$ , and dichloromethane were described previously.<sup>10</sup> Some samples of  $\text{B}_4\text{H}_{10}$  were prepared from  $(\text{CH}_3)_4\text{N}^+\text{B}_3\text{H}_8^-$  by the treatment with  $\text{BF}_3$ .<sup>11</sup> The NMR spectra were obtained on a Varian XL-300 spectrometer, the observed frequencies being 96.2, 121.4, and 299.9 MHz for  $^{11}\text{B}$ ,  $^{31}\text{P}$ , and  $^1\text{H}$ , respectively. Chemical shifts are expressed in ppm. Standards for the shifts are  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  and 85%

(3) Kameda, M.; Kodama, G. *J. Am. Chem. Soc.* **1980**, *102*, 3647.

(4) Eaton, G. R.; Lipscomb, W. N. *NMR Studies of Boron Hydrides and Related Compounds*; Benjamin: New York, 1969.

(5) Shimoi, M.; Kameda, M.; Kodama, G. *Abstracts, Annual Meeting of the Chemical Society of Japan*, April 1985; Paper No. 1L35.

(6) DePoy, R. E.; Kodama, G. *Inorg. Chem.*, in press.

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(9) Edwards, L. J.; Hough, W. V.; Ford, M. D. *Proc. Int. Congr. Pure Appl. Chem.* **1957**, *16*, 475.

(10) See, for example: Kameda, M.; Kodama, G. *Inorg. Chem.* **1984**, *23*, 3710.

(11) Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1952.

H<sub>3</sub>PO<sub>4</sub> for boron and phosphorus, respectively. Proton shifts are given with respect to the resonance signal of proton impurity in CD<sub>2</sub>Cl<sub>2</sub>, which was taken as 5.28 ppm. Shifts to lower fields are assigned positive values. Generally, reactions were run in 9–10 mm o.d. Pyrex tubes or in 10 mm o.d. resealable NMR sample tubes (products of J. Young, Ltd.) and were monitored on the NMR instrument by observing <sup>11</sup>B spectra.

**Reaction of B<sub>3</sub>H<sub>7</sub>P(CH<sub>3</sub>)<sub>3</sub> with N(CH<sub>3</sub>)<sub>3</sub>.** A 1.0-mmol sample of N(CH<sub>3</sub>)<sub>3</sub> was condensed into a reaction tube containing 0.50 mmol of B<sub>3</sub>H<sub>7</sub>P(CH<sub>3</sub>)<sub>3</sub> (prepared from B<sub>4</sub>H<sub>10</sub> and P(CH<sub>3</sub>)<sub>3</sub><sup>12</sup>) and approximately 1 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reactants were mixed well at -80 °C and then allowed to warm slowly. When the temperature reached about 20 °C, the reactants had been completely converted to a mixture of B<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub> and BH<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub> (-8.3 ppm).<sup>13</sup> The solvent and the BH<sub>3</sub> adduct were pumped out at -45 and 0 °C, respectively, and the remaining solid residue was sublimed under high vacuum at room temperature onto a 0 °C cold finger.

Samples of B<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub> for reaction studies were prepared by allowing the initial mixture of reactants to stand at room temperature for 15 min and then by removing the solvent and the BH<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub> as described above. The solid residues thus obtained were sufficiently pure for general use.

**Reaction of B<sub>3</sub>H<sub>7</sub>N(CH<sub>3</sub>)<sub>3</sub> with P(CH<sub>3</sub>)<sub>3</sub>.** A 1.05-mmol sample of P(CH<sub>3</sub>)<sub>3</sub> was condensed onto a frozen CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.49 mmol of B<sub>3</sub>H<sub>7</sub>N(CH<sub>3</sub>)<sub>3</sub>, and the solution was mixed thoroughly at -80 °C. Trimethylamine-borane(3) and B<sub>2</sub>H<sub>4</sub>·2P(CH<sub>3</sub>)<sub>3</sub> (-37.5 ppm)<sup>14,15</sup> slowly formed in the reaction mixture at room temperature. The reaction was nearly complete after 3 h at this temperature.

**Reaction of B<sub>3</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub> with HCl.** Anhydrous HCl (0.25 mmol) was condensed into a reaction tube containing 0.18 mmol of B<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub> and approximately 1 mL of CH<sub>2</sub>Cl<sub>2</sub> frozen at -196 °C. As the mixture was allowed to melt, the reaction occurred immediately. The <sup>11</sup>B NMR spectrum of the reaction mixture indicated the formation of BH<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub> and BH<sub>2</sub>Cl·P(CH<sub>3</sub>)<sub>3</sub> (-18.8 ppm)<sup>14</sup> with traces of BH<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub> (-37.1 ppm)<sup>4</sup> and BH<sub>2</sub>Cl·N(CH<sub>3</sub>)<sub>3</sub> (-7.8 ppm).<sup>13</sup>

**Reaction of B<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub> with B<sub>4</sub>H<sub>10</sub>.** A 0.55-mmol sample of B<sub>4</sub>H<sub>10</sub> was condensed into a 10-mm NMR tube containing 0.50 mmol of B<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub> and approximately 1 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reactants were mixed well at -80 °C and then allowed to slowly warm. At -60 °C the formation of B<sub>3</sub>H<sub>6</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>B<sub>3</sub>H<sub>8</sub><sup>-</sup> was observed. Then, the tube was warmed to room temperatures to ensure that the reaction had gone to completion. The solution was then cooled to -10 °C, and the solvent and unchanged B<sub>4</sub>H<sub>10</sub> were removed by pumping. The resulting white solid residue, B<sub>3</sub>H<sub>6</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>B<sub>3</sub>H<sub>8</sub><sup>-</sup>, was redissolved in CD<sub>2</sub>Cl<sub>2</sub> for the NMR study.

**Reaction of B<sub>3</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub> with B<sub>2</sub>H<sub>6</sub>.** A 0.81-mmol sample of B<sub>2</sub>H<sub>6</sub> was condensed into a reaction tube containing 0.52 mmol of B<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub> and approximately 1 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reactants were mixed well at -80 °C, and then the tube was allowed to warm slowly. At -65 °C the formation of B<sub>3</sub>H<sub>6</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>B<sub>2</sub>H<sub>7</sub><sup>-</sup> was observed. At -45 °C the reaction was faster, and the formation of BH<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub> and B<sub>3</sub>H<sub>7</sub>P(CH<sub>3</sub>)<sub>3</sub> (-15.6 and -45.0 ppm)<sup>16</sup> was observed. When the temperature reached 25 °C, only the signals of BH<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub>, B<sub>3</sub>H<sub>7</sub>P(CH<sub>3</sub>)<sub>3</sub>, and B<sub>2</sub>H<sub>6</sub> were present.

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**Registry No.** B<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub>, 97551-46-7; B<sub>3</sub>H<sub>7</sub>P(CH<sub>3</sub>)<sub>3</sub>, 97012-38-9; B<sub>3</sub>H<sub>7</sub>N(CH<sub>3</sub>)<sub>3</sub>, 57808-48-7; BH<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub>, 75-22-9; B<sub>2</sub>H<sub>4</sub>·2P(CH<sub>3</sub>)<sub>3</sub>, 67113-98-8; BH<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub>, 1898-77-7; BH<sub>2</sub>Cl·P(CH<sub>3</sub>)<sub>3</sub>, 64160-46-9; HCl, 7647-01-0; B<sub>4</sub>H<sub>10</sub>, 18283-93-7; B<sub>3</sub>H<sub>6</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>B<sub>3</sub>H<sub>8</sub><sup>-</sup>, 112925-44-7; B<sub>2</sub>H<sub>6</sub>, 19287-45-7; B<sub>3</sub>H<sub>6</sub>N(CH<sub>3</sub>)<sub>3</sub>P(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>B<sub>2</sub>H<sub>7</sub><sup>-</sup>, 112968-02-2.

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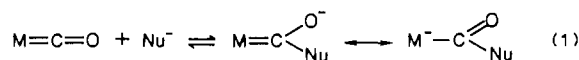
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### Ketone-like Derivatization Reactions of Metal Carbonyls. Attempts To Measure the Equilibrium Constant for Ketalization of a Carbonyl Ligand in [Re(CO)<sub>6</sub>]<sup>+</sup> by Ethylene Glycol

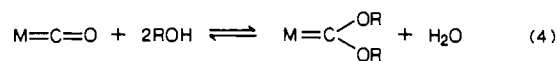
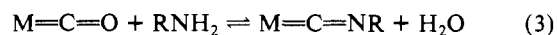
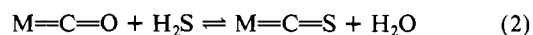
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Simple nucleophilic addition reactions of metal carbonyls (eq 1) are well-known. Grubbs et al. have suggested that these



reactions could be used as a new way to activate carbon monoxide toward hydrogenation.<sup>2</sup> We envisioned an alternative approach based on ketone-like metal carbonyl derivatization reactions, exemplified by eq 2-4. Such reactions would convert a metal



carbonyl complex into other common ligand systems such as thiocarbonyls, isocyanides, and carbenes, all of which are reported to be more susceptible to hydrogenation.<sup>3</sup> Evaluation of our idea, however, was hampered by the lack of detailed studies regarding the equilibria represented by eq 2-4. Literature reports provide circumstantial evidence that equilibria 2 and 3 may be unfavorable.<sup>4</sup> We report here our observations regarding equilibrium 4, for which no previous data appear to exist.

### Results

Metal carbonyls normally react with alcohols only in the presence of a base, leading then to the production of metal alkoxides<sup>5</sup> or metalloesters.<sup>6</sup> Not surprisingly, therefore, attempts to ketalize simple metal carbonyls such as W(CO)<sub>6</sub> and Fe(CO)<sub>5</sub> with alcohols under typical neutral or acidic conditions were unsuccessful.

In order to test whether this was a kinetic or a thermodynamic problem, the reaction was then approached from the reverse direction. One of the few dialkoxycarbene complexes known at the time this work was begun was Fe(CO)<sub>4</sub>(COCMe<sub>2</sub>CMe<sub>2</sub>O),<sup>7</sup> formally derived from iron pentacarbonyl and pinacol. This carbene complex could not be hydrolyzed in wet tetrahydrofuran under neutral, basic (Et<sub>3</sub>N), or acidic (*p*-toluenesulfonic acid) conditions.

We then shifted our attention to cationic complexes, for which both the forward and reverse reaction kinetics were expected to

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