staff of the University of Colorado cyclotron, and to the U. S. Atomic Energy Commission for its support.

[22] Address correspondence to this author at Department of Chemistry, New Mexico State University, Las Cruces, New Mexico.

A. E. Richardson,[22] **Richard Wolfgang**
Department of Chemistry, University of Colorado
Boulder, Colorado
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The Diammoniate of Pentaborane(9)

Sir:

It is known that diborane(6), tetraborane(10), and pentaborane(11) react with ammonia to give diammoniates containing the $H_2B(NH_3)_2{}^+$ cation, *i.e.*, $[H_2B(NH_3)_2{}^+][BH_4{}^-]$,[1] $[H_2B(NH_3)_2{}^+][B_3H_8{}^-]$,[2] and $[H_2B(NH_3)_2{}^+][B_4H_9{}^-]$,[3] respectively. Structural features of these parent boranes are similar in that each of them contains a BH_2 group bonded by two hydrogen bridge bonds. Pentaborane(9), not having this particular structural feature, has been regarded as a compound that belongs to another category.[4,5] A different kind of reaction might be anticipated.

In 1924 Stock reported[6] the tetraammoniate of pentaborane(9), $B_5H_9 \cdot 4NH_3$, as a stable, white solid. Characterization of the compound, however, was not complete. More recent work by various investigators has revealed that pentaborane(9) reacts with bases in both the Lewis acid and Brønsted acid sense.[7-13] In the present study it has been shown that pentaborane(9) will also react with ammonia under controlled conditions to give the ionic compound $[H_2B(NH_3)_2{}^+][B_4H_7{}^-]$. The $B_4H_7{}^-$ anion has not been isolated previously.

An ethereal solution of pentaborane(9) was stirred at −78° while ammonia gas was introduced slowly above the surface of the solution. The ammonia was absorbed and a white precipitate separated slowly from the initially clear solution. The molar ratios of ammonia and pentaborane(9) used in the reaction vessel varied from run to run and ranged from two up to eight. After a given mixture had been standing at −78° for several days, the volatile components were pumped out while the temperature of the system was held at −78°. The temperature was then raised to −45° and to 25° for *a very few minutes*. The white residue which remained in the reaction vessel was stable below 0°, but decomposed spectacularly on standing at room temperature. For this reason prolonged exposure to the pumps at 25° must be avoided.

The reaction of the solid with *excess* hydrogen chloride in ether at −78° gave a precipitate of $H_2B(NH_3)_2{}^+Cl.^-$[1] The yield of $H_2B(NH_3)_2{}^+Cl^-$ accounted quantitatively for all of the ammonia consumed in the reaction. No hydrogen gas was evolved, and X-ray diffraction did not indicate the presence of ammonium chloride in the precipitate.

When hydrogen chloride was added to the ammoniate of pentaborane(9) in a *one-to-one molar ratio* (no excess HCl used), $H_2B(NH_3)_2{}^+Cl^-$ separated again as a white precipitate. To the supernatant liquid an equivalent amount of $(CH_3)_2NPF_2$ was added at −78°. After standing for about 12 hr at −78° the system was fractionated by a trap-to-trap distillation. A good yield of $(CH_3)_2NPF_2B_4H_8$[14] resulted.

The foregoing observations can be summarized by the following equations.

$$B_5H_9 + 2NH_3 \xrightarrow[\text{ether}]{-78^\circ} [H_2B(NH_3)_2{}^+][B_4H_7{}^-]$$

$$[H_2B(NH_3)_2{}^+][B_4H_7{}^-] + HCl \xrightarrow[\text{ether}]{-78^\circ} H_2B(NH_3)_2{}^+Cl^- + B_4H_8 \cdot O(C_2H_5)_2$$

$$B_4H_8 \cdot O(C_2H_5)_2 + (CH_3)_2NPF_2 \xrightarrow[\text{ether}]{-78^\circ} (CH_3)_2NPF_2B_4H_8 + O(C_2H_5)_2$$

The details of characterization of the diammoniate and the work on related systems will be described in subsequent publications.

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Goji Kodama
Department of Chemistry, The University of Utah
Salt Lake City, Utah 84112
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Structure and Stereochemical Nonrigidity of Six-Coordinate Complexes

Sir:

Earlier[1] we described the stereochemical nonrigidity of two six-coordinate metal hydrides, $H_2Fe[P(OC_2H_5)_3]_4$

Table I. Phosphinometal Dihydrides

$H_2Fe[P(OC_2H_5)_3]_4$	**1**	$H_2Ru[P(OCH_3)_3]_4$	**7**
$H_2Fe[C_6H_5P(OC_2H_5)_2]_4$	**2**	$H_2Ru[P(OC_2H_5)_3]_4$	**8**
$H_2Fe[P(OCH(CH_3)_2)_3]_4$	**3**	$H_2Ru[P(OCH(CH_3)_2)_3]_4$	**9**
$H_2Fe[C_6H_5P(OCH(CH_3)_2)_2]_4$	**4**	$H_2Ru[C_6H_5P(OC_2H_5)_2]_4$	**10**
$H_2Fe[P(OCH_2)_3CC_2H_5]_4$	**5**	$H_2Ru[C_6H_5P(CH_3)_2]_4$	**11**
$H_2Fe[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$	**6**	$H_2Ru[C_6H_5P(C_2H_5)_2]_4$	**12**
		$H_2Ru[(C_6H_5)_2PCH_3]_4$	**13**
		$H_2Ru[(C_6H_5)_2POCH_3]_4$	**14**

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