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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.

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

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

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

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

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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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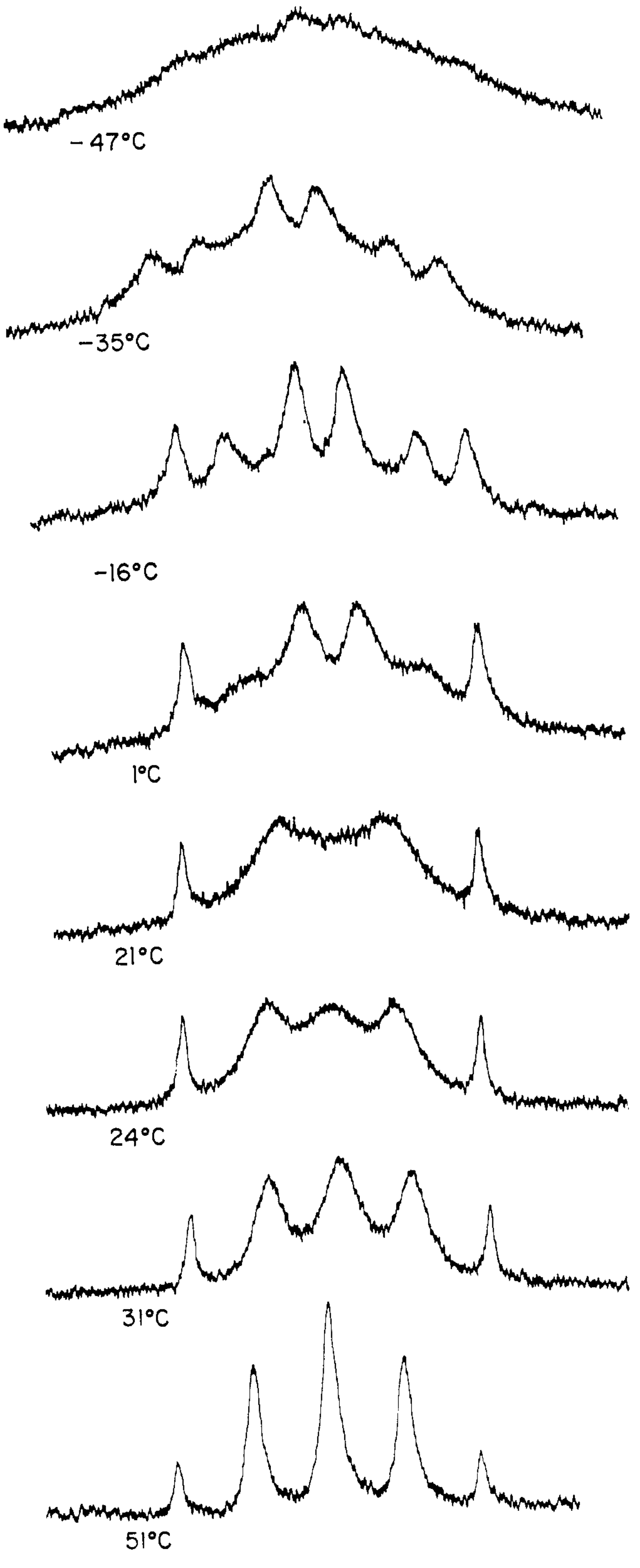

Figure 1. Temperature dependence of the 220-MHz ^1H hydride spectrum of $H_2Fe[C_6H_5P(OCH(CH_3)_2)_2]_4$.

(**1**) and $H_2Fe[C_6H_5P(OC_2H_5)_2]_4$ (**2**). We now report that this phenomenon is exhibited by other dihydrides of iron and ruthenium of the type H_2ML_4, where L represents ligands such as phosphine, phosphite, phosphonite, and phosphinite. Qualitative arguments and X-ray structural data are presented which support the proposed[1] rearrangement mechanism.

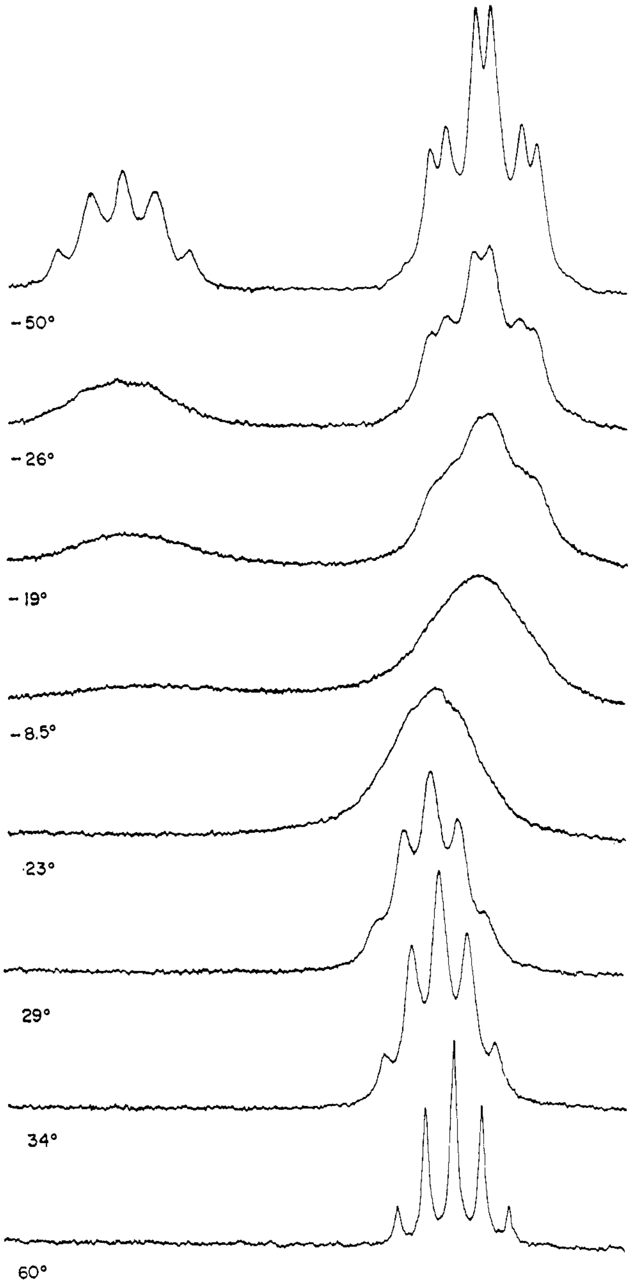

Figure 2. Temperature dependence of the 220-MHz ^1H hydride spectrum of $H_2Fe[C_6H_5P(OC_2H_5)_2]_4$.

Four new iron dihydrides, **3**–**6** (Table I), have been synthesized and their ^1H and ^{31}P nmr spectra examined. Spectral temperature dependencies, like those of **1** and **2**, are consistent with an intramolecular rearrangement which at elevated temperatures is fast enough to produce averagings of the phosphorus and hydride hydrogen environments. Figure 1 depicts the temperature dependence of the hydride resonance of **4**. At $-16°$, the spectrum approximates a triplet of doublets characteristic of a *cis* ground-state geometry.[1] Between $-16°$ and $+50°$, the central part of the spectrum broadens and emerges as part of a quintet.[2] The two outer features of the quintet, remaining sharp throughout, correspond to $|M\ \alpha\alpha\alpha\alpha\rangle \rightarrow |M'\ \alpha\alpha\alpha\alpha\rangle$ transitions (M and M' are quantum numbers of the hydride

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[2] The broadening which occurs below $-16°$ is probably due to hindered rotation in the ligand.

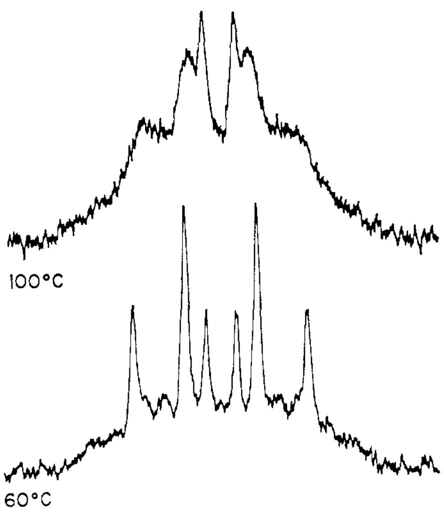

Figure 3. Temperature dependence of the 220-MHz ^1H hydride spectrum of $H_2Ru[C_6H_5P(C_2H_5)_2]_4$. The barrier for the related $H_2Ru[C_6H_5P(CH_3)_2]_4$ complex is higher, ostensibly because of less significant ligand–ligand repulsions.

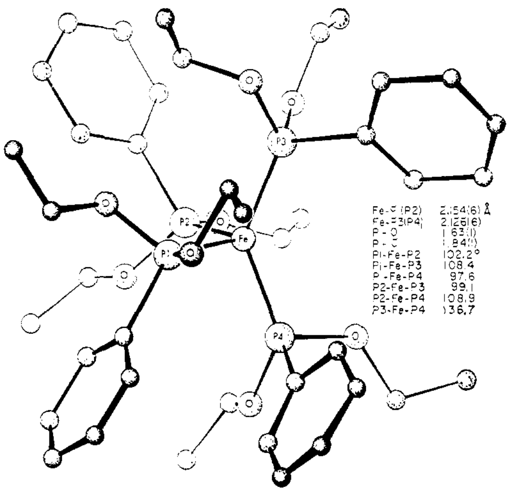

Figure 4. Structure of $H_2Fe[C_6H_5P(OC_2H_5)_2]_4$. The hydride hydrogen atoms are presumed to be vicinal as indicated by their *trans* influence on the Fe–P(1) and Fe–P(2) bond distances. The shortest nonhydrogen contacts between atoms on different phosphorus atoms involve oxygen contacts with methylene or benzene carbon atoms.

spin system) which are unaffected by permutations of the phosphorus spins. The iron dihydrides have similar rearrangement barriers, although complex **5**, in which the ligand has the smallest cone angle,[3] appears to have the highest barrier. Complex **2**, which is the only member of the series existing in both *cis* and *trans* forms, possesses a spectral temperature dependence (Figure 2) differing markedly from those of **1**, **3**, and **4–6**. The salient features of the spectra are a low-temperature quintet and a triplet of doublets diagnostic of the *trans* and *cis* forms, respectively, and the collapse to the high-temperature quintet *without* retention of any sharp features.

The ruthenium complexes synthesized and examined are set forth in Table I. Complex **13** has been prepared previously and its low-temperature hydride spectrum explained by a *cis* structure.[4] All new complexes except **10** display low-temperature spectra similar to that of **13** and are assigned *cis* structures. Complex **10**, like its iron analog, exists as both *cis* and *trans* isomers in solution.

Figure 3 shows the 60 and 100° hydride spectra of **12**. Broadening of the low-temperature spectrum is not observed for any of the ruthenium hydrides below 60°. In fact, the fast exchange limit, which should be a 1:4:6:4:1 quintet, has not been detected for any Ru complexes owing to their thermal instability and the high temperatures (>150°) which are required. The rearrangement barriers are all qualitatively higher than those for the iron set. It should be noted that the sharp features attributable to the $|M\ \alpha\alpha\alpha\alpha\rangle \rightarrow |M'\ \alpha\alpha\alpha\alpha\rangle$ transitions remain distinct, and because of differences in signs and magnitudes of coupling constants are now the inner lines of the low-temperature spectrum and the outer lines of the high-temperature quintet.

The crystal structure of $H_2Fe[C_6H_5P(OC_2H_5)_2]_4$ was solved from 3900 pieces of single-crystal data collected on an automatic diffractometer using Mo Kα radiation. Crystals are triclinic, space group P$\bar{1}$, with cell dimensions of a = 11.786 (8), b = 17.491 (12), c = 11.970 (8) Å, α = 90.20 (3), β = 114.97 (9), and γ = 85.03 (3)°. The molecule (Figure 4) has no imposed or idealized molecular symmetry. The iron–phosphorus geometry is nearly midway between that expected for octahedral and tetrahedral phosphorus disposition, with the rms angular deviation favoring the tetrahedral geometry.

We had tentatively proposed that the mechanism of the polytopal rearrangement in these metal dihydrides comprises vibrational population of a pseudotetrahedral ML_4 state with hydride tunneling of face and edge positions. Our new data are consistent with this proposal. The X-ray determination shows that the complex is, in fact, distorted in the manner proposed earlier.[1] Furthermore, if the LL nonbonding repulsions provide some driving force for the rearrangement, those complexes based on the smaller metal atom and bulkier ligands should have lower barriers. This is the experimental observation. In contrast, if a trigonal twist mechanism were primarily responsible for the rearrangement, steric arguments would suggest that the complexes with the larger metal and the more compact ligands have the lower barriers.[5]

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Intramolecular Exchange and "Thermal" Decoupling in $B_3H_8^-$ Compounds

Sir:

During an investigation of the apparent discrepancy between the crystal structure of the $B_3H_8^-$ anion (I)[1]

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