

cyano complexes on oxidation to the iron(III) state. Other investigators have reported and discussed similar effects for iron cyanide complexes.<sup>7-10</sup> The bands for the solvated dicyano complexes differ from those of the nonsolvated, consistent with the fact that the cyanide ligands possess appreciable basic character.<sup>2,3,6</sup> On comparing the frequencies for  $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$ ,  $[\text{Ru}(\text{bipy})_2(\text{CN})_2]$ , and  $[\text{Os}(\text{bipy})_2(\text{CN})_2]$  recovered from  $\text{CHCl}_3$ , two regularities are evident: the splitting increases and both bands move to lower frequencies as the atomic number of the metal increases. The latter suggests increasing  $\pi$ -bond character between metal and cyanide ligands<sup>1,10</sup> going from iron to osmium. The relative basicities of the three complexes are also consistent with such a trend in bond character.<sup>3</sup>

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## Enhancement of P-H Bonding in a Phosphine Monoborane

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Received March 30, 1964

Infrared absorption bands for N-H stretching have quite generally been observed at lower frequencies when nitrogen is bonded to four atoms rather than three.<sup>1</sup> In phosphorus compounds, however, this rule seems to be reversed: four-coordinate phosphorus shows higher P-H stretching frequencies than are found for phosphines.<sup>2</sup> An explanation for this indication of stronger P-H bonding for four-coordinate P might be found in the rehybridization of phosphorus bonding orbitals when a fourth atom is attached.<sup>3</sup> For example, the phosphorus valence angles in the methylated phosphines all are below  $100^\circ$ ,<sup>4</sup> meaning that the lone-pair electrons on P in a phosphine have far more s-character than such electrons on nitrogen; then a four-bonded phosphorus would offer a more nearly perfect tetrahedral  $3sp^3$  hybrid for the P-H bond than the s-deficient hybrid used for bonding H in a phosphine. This principle does not apply well to the corresponding nitrogen compounds, for the almost tetra-

(1) L. J. Bellamy, "Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, New York, N. Y., 1958, pp. 203-262. The most obvious reason for lower N-H frequencies in undisturbed  $\text{HNR}_3$  units would be the positive charge related to four-coordinate N, whereby the N-H bond would be weakened. Less important would be a slightly increased contribution by the four-bonded N to the reduced mass of the N-H oscillator.

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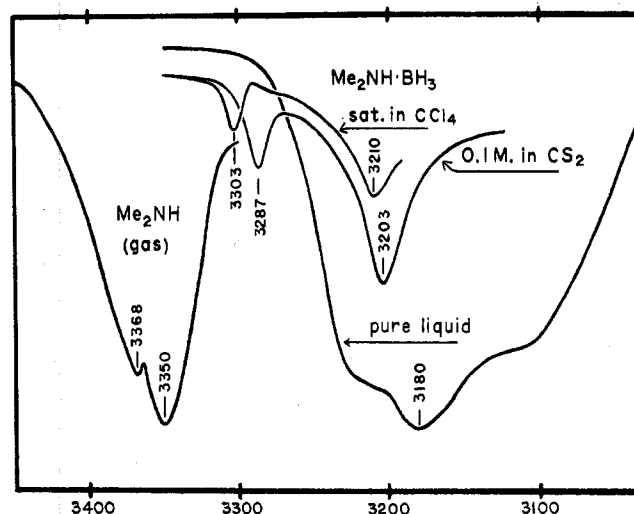


Fig. 1.—Comparison of the N-H stretching bands of  $(\text{CH}_3)_2\text{NH}$  (gas) and  $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$  (liquid vs. solutions). Here and in Fig. 2 and 3 transmission is measured upward while the abscissa shows frequencies in  $\text{cm}^{-1}$ .

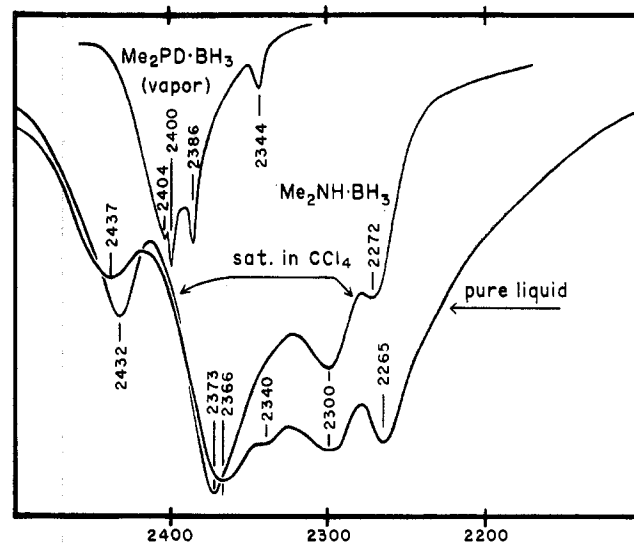


Fig. 2.—Comparison of the B-H stretching bands of  $(\text{CH}_3)_2\text{PD}\cdot\text{BH}_3$  (vapor) and  $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$  (liquid and solution).

hedral nitrogen hybrids in an amine would change little in forming the fourth bond.

However, this P-H vs. N-H contrast has lacked a secure experimental basis, for the reported  $\text{R}_3\text{N-H}$  and  $\text{R}_3\text{P-H}$  spectra were for condensed phases, wherein N-H--X bonding effects could account for lower N-H frequencies; but for P-H compounds any such hydrogen-bonding effects would be far less important. Also, most of the reported four-bonded P compounds<sup>2</sup> had terminal P=O bonds, with uncertain effect upon the P-H bond energy.

A more effective comparison would be afforded by the  $\text{BH}_3$  complexes of  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_2\text{PH}$ , for the acidic protons would not interact strongly with a bound  $\text{BH}_3$  group, and any weak interaction would be minimized by dilution. In fact, the vapor-phase spectrum of  $(\text{CH}_3)_2\text{PH}\cdot\text{BH}_3$  (or its D analogs, which avoid band superposition) does show a stronger P-H bond than is demonstrated for free gaseous  $(\text{CH}_3)_2\text{PH}$ ;

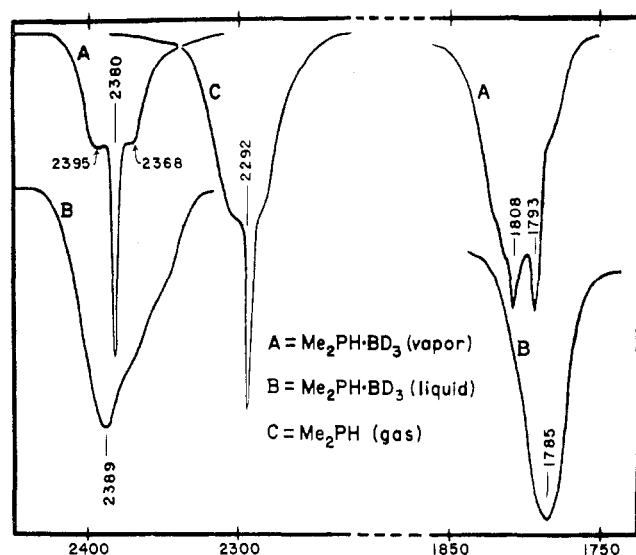


Fig. 3.—Comparison of the P-H stretching bands of  $(\text{CH}_3)_2\text{PH}$  (gas) and  $(\text{CH}_3)_2\text{PH}\cdot\text{BD}_3$  (vapor vs. liquid); also the B-D stretching bands of the latter.

whereas solutions of  $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$  in  $\text{CS}_2$  or  $\text{CCl}_4$  show N-H stretching at lower frequencies than are found for free gaseous  $(\text{CH}_3)_2\text{NH}$ . The amine complex is not sufficiently stable for study as a vapor at elevated temperatures, but comparison of the solutions with pure liquid  $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$  shows that a definite N-H-- $\text{H}_3\text{B}$  interaction is largely removed by dilution. Hence it is safe to conclude that the lowering of the N-H stretching force constant for four-coordinate nitrogen is a real effect, contrasting to the increase for four-coordinate phosphorus.

**Experimental Results.**—The bands most pertinent to this study are shown in Fig. 1, 2, and 3. Figure 1 compares the extremely weak N-H stretching band of  $(\text{CH}_3)_2\text{NH}$  (30% absorption by the gas at 800 mm. pressure in an 11-cm. cell with KBr windows, using the Beckman IR7 instrument with a 0.27-mm. slit)<sup>5</sup> with N-H stretching in  $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$ . The extreme widening of the band for the pure liquid indicates a perturbation of the N-H bond; but dilution to 0.1 *M* in  $\text{CS}_2$  removes this effect, with some increase in the average frequency. In the yet more dilute  $\text{CCl}_4$  solution the slightly higher frequencies still are far short of the peak frequencies for gaseous  $(\text{CH}_3)_2\text{NH}$ . The extra peak for either solution doubtless can be explained (impurities due to slight reaction, or Fermi resonance with either a N-H bending overtone or a B-H bending second overtone?) without affecting the significant conclusions.

The nature of the N-H bond perturbation is suggested by Fig. 2, which shows a broad range of per-

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turbed B-H stretching frequencies for pure liquid  $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$ , partly superposed upon the spectrum of a comparable effective path length (0.5 mm.) of the saturated  $\text{CCl}_4$  solution. For this solution the sharper peaks and the lower intensities at lower frequencies (as compared with the pure liquid) would suggest less perturbation of B-H stretching vibrations. Thus it is reasonable to assume that pure liquid  $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$  maintains an intermolecular N-H-- $\text{H}_3\text{B}$  interaction comparable to a hydrogen bond. This effect probably is the main reason that  $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$  is far less volatile than  $(\text{CH}_3)_2\text{PH}\cdot\text{BH}_3$ .

Figure 2 shows also the very sharp-peaked B-H stretching absorption by the vapor of  $(\text{CH}_3)_2\text{PD}\cdot\text{BH}_3$ , possibly modified in some small degree by failure to eliminate a very intense P-H stretching band. Here as in all other work in this region, the elimination of any effect of the  $\text{CO}_2$  in the instrument (peaks at 2348 and  $2367\text{ cm}^{-1}$ ) was verified.

Figure 3 compares the P-H stretching bands of  $(\text{CH}_3)_2\text{PH}$  and  $(\text{CH}_3)_2\text{PH}\cdot\text{BD}_3$  (from 99%  $\text{B}_2\text{D}_6$  made by Dr. John R. Spielman), clearly showing the increase of frequency for four-bonded phosphorus. The liquid-film bands show the normal loss of details, but scarcely any evidence of liquid-phase bonding. The B-D modes deviate widely from the normal isotopic shift of frequency because the motion of B is severely affected by the heavy D atoms; then since P is far less affected by one D, there is full separation of P-D and B-D bands in  $(\text{CH}_3)_2\text{PD}\cdot\text{BD}_3$ .

This and other interesting effects of mass upon frequency and intensity can be seen in Table I, which compares the H and D stretching peaks for the four isotopic species of dimethylphosphine monoborane with the free phosphines. All samples were vaporized, often in a 115-mm. cell at the normal  $40^\circ$  instrument temperature; but when it was useful to develop higher pressures of the complex, an 81-mm. cell could be held at controlled temperatures up to  $80^\circ$  in a transite box with a hot-air blower, all within the closed cell chamber.

TABLE I  
COMPARISON OF H AND D PEAKS

	Stretching of			
	P-H	P-D	B-H	B-D
$(\text{CH}_3)_2\text{PH}$ or $(\text{CH}_3)_2\text{PD}$	—?—R (3.3) 2292Q (8.0) —?—P (3.0)	1673R (1.3) 1666Q (5.0) 1661P (1.4)		
$(\text{CH}_3)_2\text{PH}\cdot\text{BH}_3^a$	2392Q (26)	...	2409 (15) 2403 (18) 2380? 2346 (7)	
$(\text{CH}_3)_2\text{PH}\cdot\text{BD}_3$	2395R (1.8) 2380Q (6.6) 2368P (1.8)	...	...	1813 sh (4.5) 1808 (5.9) 1793 (6.0) 1620?
$(\text{CH}_3)_2\text{PD}\cdot\text{BH}_3^a$	...	1743 (0.5) 1737 (0.7) 1730Q (1.0) 1720 (0.6)	2404? 2400 (13?) 2386 (11?) 2344 (2.5)	...
$(\text{CH}_3)_2\text{PD}\cdot\text{BD}_3$	...	—?—R (0.9) 1730Q (2.9) 1720P (1.6)	...	1807 (6.3) 1793 (7.0) 1627 (1.1)

<sup>a</sup> Superposition of P-H and B-H bands makes these frequencies and intensities uncertain.

The relative intensities (in parentheses) were computed as  $k = (100/PL) \log I_0/I$  for pressure  $P$  (reduced to 25°) and path  $L$  (both in cm.), from the literal record of per cent transmission  $I$ .

Attempts to compare the P-H and P-D bending modes for all six species failed because the pertinent bands proved too weak and complex; and CH<sub>3</sub> rocking and wagging interfered.

**Acknowledgments.**—The generous support of this research by the Office of Naval Research is gratefully acknowledged, and reproduction of this note is permitted for any purpose of the United States Government. The Beckman IR7 spectrophotometer was made available through a generous grant (G-14665) from the National Science Foundation.

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## A Lithium Europium Hydride Inverse Perovskite Phase, LiEuH<sub>3</sub>

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Received April 6, 1964

An earlier note from this laboratory<sup>1</sup> described the preparation, and the characterization by X-ray powder diffraction, of the inverse perovskite phases of probable composition LiSrH<sub>3</sub> and LiBaH<sub>3</sub>. With calcium only CaH<sub>2</sub> was found under similar conditions.

These studies have been extended to include europium and ytterbium, since the deuterides of these metals have been found<sup>2</sup> to have the orthorhombic structure of CaH<sub>2</sub>, SrH<sub>2</sub>, and BaH<sub>2</sub>,<sup>3</sup> in contrast with the fluorite structures of the dihydride phases of the other rare earths.

### Experimental

The europium metal, 99.9%, was obtained from the Cerium Metals and Alloys Division of Ronson Metals, Inc., Newark, N. J. The ytterbium metal (99.9%) was obtained from United Mineral and Chemicals Corporation.

The mixed hydrides were prepared, and their powder diffraction patterns taken, essentially by the procedures and under the conditions of the previous research.<sup>1</sup> Molybdenum boats were used as sample containers.

The principal europium preparation (I), with lowest europium content, was reddish orange and finely crystalline. Europium preparation II was reddish black before grinding, and reddish brown afterward. The ytterbium preparations were gray-black before and after grinding. All preparations except europium I, before grinding, had the gross shapes of the original metal lumps.

Preparation III, made from europium from a different source, had the appearance of preparation II. It was presumed impure because it could not be degassed under vacuum at 350° and because it took up so little hydrogen. It was briefly air exposed,

but tested since its appearance was the same as that of sample II. It gave the same lattice constant with the same precision as sample I.

Table I gives information on the preparation and composition of the samples. The hydrogen contents were corrected for diffusion losses through the stainless steel outer bomb, because of the small size of the preparations—of the order of 0.1 g. of Li and 1–2 g. of rare earth metal.

TABLE I  
PREPARATION AND COMPOSITION OF SAMPLES

Sample	Mole % Eu or Yb orig. alloy	% of theor. H <sub>2</sub> uptake	Hydride phase(s)	Other phase(s)
Eu I	32.9	94.7	LiEuH <sub>3</sub>	Unidentified
Eu II	55.6	93.4	EuH <sub>2</sub> , some LiEuH <sub>3</sub>	None
Eu III	42.4	65.5	LiEuH <sub>3</sub> , some EuH <sub>2</sub>	Trace Eu <sub>2</sub> O <sub>3</sub>
Yb I	35.2	82.0	YbH <sub>2</sub>	Trace Yb <sub>2</sub> O <sub>3</sub> Unidentified
Yb II	44.4	94.7	YbH <sub>2</sub>	Trace Yb <sub>2</sub> O <sub>3</sub> Unidentified

### Results and Discussion

For the hydrided lithium–europium samples I and III, 20 sharp, well-defined lines were found, which could be indexed on the basis of a primitive cubic unit cell. By analogy with the earlier research, these were interpreted in terms of a cubic inverse perovskite lattice of LiEuH<sub>3</sub>. In the lithium–ytterbium samples, only ytterbium dihydride was found.

For LiEuH<sub>3</sub> sample I, five extraneous lines were found, all very weak, which could not be assigned to EuH<sub>2</sub> or to any other impurities which might reasonably be expected, including the recently reported LiEuO<sub>2</sub>.<sup>4</sup> Several similar lines were also found in the LiH–YbH<sub>2</sub> system. These suggest the extraneous lines reported in the earlier paper<sup>1</sup> for Sr and Ca samples, which were attributed to residual unhydrided metallic phase. No information could be found in the literature on alloys of lithium with the rare earths.

The values of the lattice constant were determined, after correction for film shrinkage, by extrapolation, using the Nelson–Riley function.<sup>5</sup>

The lattice constant and density values for the perovskite phase from europium samples I and III were: LiEuH<sub>3</sub>,  $a_0 = 3.796 \pm 0.001$  Å.,  $\rho = 3.378$  g. cm.<sup>-3</sup>. The lattice constant value from sample II,  $3.794 \pm 0.002$  Å., was less accurate because of the smaller amount of perovskite phase present.

The amount of europium dihydride phase present in sample II was sufficient to enable an accurate determination of the lattice constants of orthorhombic EuH<sub>2</sub>. These are shown in comparison with the europium di-deuteride values of Warf and Korst.<sup>2</sup> The parameters were determined by the method of least squares, as adapted by Cohen<sup>6</sup> for use in X-ray powder diffrac-

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