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A Mechanistic Model for the Reactions of Ammonia and the Methylamines with Phosphine–Borane

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When H_3PBH_3 is dissolved in liquid ammonia at −45° and allowed to stand, the final product is the ionic solid, $[NH_4][H_2P(BH_3)_2]$. At temperatures above −45° increasing amounts of the covalent ammonia–borane, H_3NBH_3, are formed along with the ionic product, $[NH_4][H_2P(BH_3)_2]$. Methylamine and dimethylamine behave quite differently. At temperatures of −45° and below only the covalent amine–borane, $[CH_3H_2NBH_3]$ or $[(CH_3)_2HNBH_3]$, is obtained as a product. At temperatures above −45° increasing amounts of the ionic product, $[CH_3NH_3][H_2P(BH_3)_2]$ or $[(CH_3)_2NH_2][H_2P(BH_3)_2]$, are found in the amine–borane. It is significant that temperature effects are completely reversed in these two systems. Finally $(CH_3)_3N$ gives only the covalent base addition compound, $(CH_3)_3NBH_3$, under all conditions studied. A mechanistic model dealing with the anion $H_2PBH_3^-$ is advanced to interpret the above observations.

The reaction of phosphine–borane, H_3PBH_3, with ammonia is known[1] to give the ionic solid, $[NH_4][H_2P(BH_3)_2]$, and PH_3. In contrast the reaction of H_3PBH_3 with trimethylamine under comparable conditions is known to give immediate base displacement with formation of $(CH_3)_3NBH_3$ and PH_3.[2] Thermodynamic differences in product stability cannot alone account for the above set of observations since H_3NBH_3 and $[(CH_3)_3NH][H_2P(BH_3)_2]$ can be made independently by other methods and are known to be stable under the conditions of these experiments. Mechanistic factors must be important in accounting for the differences in the reactions of NH_3 and $(CH_3)_3N$ with H_3PBH_3.

In an earlier report from this laboratory[3] it was suggested that the reactions of bases with H_3PBH_3 can be interpreted in terms of the following competing steps:

$$\begin{tikzcd}
H_3PBH_3 + \text{base} \arrow[r, shift left, "\text{step 1}"] & {[\text{base H}]^+[H_2PBH_3]^-} \arrow[l, shift left] \\
+ & + \\
\text{base} \arrow[d, shift right] & H_3PBH_3 \arrow[d, shift right, "\text{step 2}"'] \\
\text{base BH}_3 + PH_3 \arrow[u, shift right, "\text{step 3}"'] & {[\text{base H}]^+[H_2P(BH_3)_2]^- + PH_3} \arrow[u, shift right]
\end{tikzcd}$$

Note that steps 1 and 2 generate ionic products while step 3 generates a covalent base displacement product. Evidence in support of this representation follows; extensions of the model to explain reaction details with ammonia and the methylamines are also presented.

1. The Ionization of Phosphine–Borane in Liquid Ammonia (Step 1). An NMR study provides evidence for the ionization of H_3PBH_3 in liquid ammonia. In a nonionizing solvent (weak Bronsted bases) such as toluene, tetrahydrofuran, and dimethyl ether, the ^1H and ^{11}B NMR spectra of H_3PBH_3 are essentially the same as those reported[4] for liquid H_3PBH_3 (Table I). In neat H_3PBH_3 protons attached to the phosphorus atom appear as a doublet centered at $\delta = -4.3$ with J_{P-H} equal to 372 Hz. Each member of the doublet is split into a 1:3:3:1 quartet by HBPH coupling. The coupling constant is 8 Hz. Similar J_{P-H} values of 378 ± 8 Hz are also seen for the compound in the four solvents which have low effectiveness as Bronsted–Lowry acids or bases. The protons attached to boron show J_{B-H} values of 103 ± 1 Hz for the neat H_3PBH_3. J_{B-H} values of 102 ± 2 Hz are seen for the four nonionizing solvents. The boron atom shows a δ value of 60.8 ppm for neat H_3PBH_3. In the four nonionizing solvents the value observed is 61.7 ± 0.8 ppm. In contrast to the foregoing observations, the spectral properties of H_3PBH_3 in ammonia, methylamine, or dimethylamine differ markedly from those seen for neat H_3PBH_3. Of great significance is the fact that the doublet for protons attached to phosphorus collapses to a singlet as a result of a rapid proton exchange process (step 1). Further the value of J_{B-H} drops from 102 ± 2 Hz in nonionizing solvents to 90 ± 1 Hz in ammonia.[5] The value of δ for the boron atom drops from 61.7 ± 0.8 ppm in nonionizing solvents to 55.5 ± 0.5 ppm in liquid ammonia. The values of J_{B-H} and δ for boron are those found for the $H_2PBH_3^-$ ion of KH_2PBH_3 in liquid ND_3. The fact that the δ value for boron is essentially the same in the H_3PBH_3 liquid ammonia solution as it is in the KH_2PBH_3 liquid ammonia solution indicates that the proton transfer equilibrium for H_3PBH_3 lies far to the right. The activity of un-ionized H_3PBH_3 in liquid ammonia appears to be low.

The situation would appear to resemble to some degree the behavior of HCl in liquid ammonia. For this system Clutter and Swift[6] assumed essentially complete proton transfer from HCl to ammonia (step 1 below), but reported an equilibrium constant of 0.5×10^{-4} for the break-up of the ion cluster to give free ions in solution (step 2 below):

$$\mathrm{HCl} + \mathrm{NH_3} \xrightarrow[\text{complete}]{1.} \frac{1}{n}\underbrace{\{[\mathrm{NH_4}^+][\mathrm{Cl}^+]\}_n}_{\text{ion cluster}} \overset{2.}{\rightleftharpoons} \mathrm{NH_4}^+ + \mathrm{Cl}^+ \quad K = 0.5 \times 10^{-4}$$

The dominant species in solution would be the ammonium chloride ion cluster with low concentrations of free NH_4^+, Cl^-,

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Table I. Nuclear Magnetic Resonance Data for H_3PBH_3 in Various Solvents

	Solvent							
	No solvent[4]	Toluene	Tetrahydrofuran	$(CH_3)_2O$	CH_3CN	NH_3	$(CH_3)NH_2$	$(CH_3)_2NH$
				Protons on Phosphorus				
J_{PH}[a]	372	374	380	380	386	Exchange	Exchange	Exchange
J_{HBPH}[a]	8	8	8	8	8	Exchange	Exchange	Exchange
$\delta_{(HP)}$[b]	−4.31	−3.0	−4.4	−4.2	−4.5	Exchange	−4.3[d]	−4.6[d]
				Protons on Boron				
J_{BH}[a]	104	103	104	104	100	90	90	90
J_{PBH}[a]	16			16				
$\delta_{(HB)}$[b]	−0.53	−0.82	−0.74	−0.43	−0.57	−0.65	−0.70	−0.74
				Boron-11				
J_{P-B}[a]	27	27	29	27	28	28	27	27
J_{H-B}[a]	103	103	101	102	103	90	91	91
δ[c]	60.8	61.4	62.5	61.3	61.7	55.2	56	56

[a] Coupling constants in Hz. [b] Chemical shift values in ppm relative to tetramethylsilane. [c] Chemical shift values in ppm relative to $B(OCH_3)_3$. [d] Exact position dependent on position of nonexchanging N–H protons and respective concentrations of amine and H_3PBH_3.

and traces of HCl. Comparable processes for the weaker acid H_3PBH_3 would require similar equations:

$$H_3PBH_3 + NH_3 \xrightarrow[\text{complete}]{\text{essentially}} \underset{\text{ion cluster}}{\frac{1}{n}\{[NH_4^+][H_2PBH_3^-]\}_n} \rightleftharpoons NH_4^+ + H_2PBH_3^- \quad K < 0.5 \times 10^{-4}$$

Again the ion cluster would be the dominant species in solution and would be the species observed by the NMR, but because the acid is somewhat weaker than HCl a low, but important, concentration of H_3PBH_3 would exist in solution. Similarly, concentrations of the free ions NH_4^+ and $H_2PBH_3^-$ would be low but significant.

The proton transfer postulated here would give rise to exchange processes which could be studied by isotope exchange methods. For example, H_3PBH_3 dissolved in ND_3 should generate protonated ammonia and deuterated phosphine–borane. Similarly, D_3PBH_3 dissolved in NH_3 should generate protonated phosphine–borane and deuterated ammonia. When 4.05 mmol of H_3PBH_3 was dissolved in 12.1 mmol of ND_3, complete statistical exchange was observed in less than 0.5 hr at −45°. No evidence of B–D exchange was found under these conditions. An identical result was found when 2.13 mmol of D_3PBH_3 was dissolved in 8.24 mmol of NH_3. It was necessary to investigate exchange in the system PH_3–NH_3 in order to properly evaluate the exchange data for H_3PBH_3 mentioned above. When a liquid mixture of PH_3 and NH_3 was examined by ^1H NMR over the temperature range −70 to −30°, the doublet signal for P–H protons was clearly visible. The exchange process is slow compared to the NMR time scale ($\sim 10^{-3}$ sec). On the other hand, when PD_3 was dissolved in NH_3 (or ND_3 in PH_3), at least 85% of the expected exchange had appeared after 6 hr and 100% after 12 hr at −50°. Slow exchange is indicated. As expected coordination of BH_3 to PH_3 brings about a marked increase in the acidity of the P–H protons.

Again an analogy can be drawn between these results and the earlier work of Clutter and Swift.[6] They found that proton exchange is rapid from free ammonium ion to solvent NH_3 in the case of both HCl and HBr solutions in liquid ammonia. On the other hand they found no evidence for proton exchange between ammonium ions in the cluster and solvent ammonia molecules. The process is orders of magnitude slower than that involving the NH_4^+ ions in solution. They also found that the transfer of a proton from H_2O to NH_3 is not detectable by NMR under the conditions used. This latter result is analogous to our result for the PH_3–NH_3 system.

Finally the intermediate solid, $H_3N\cdot H_3PBH_3$, of presumed ionic formulation $-[NH_4][H_2PBH_3]^-$, has been obtained from dimethyl ether solution as a white solid at −63°.

2. The Nature of Authentic $H_2PBH_3^-$ Salts. Since the foregoing discussion has involved the $H_2PBH_3^-$ ion and ion clusters, the synthesis and characterization of salts of this anion under the conditions used above seemed appropriate. The salts $K[H_2PBH_3]$ and $Na[H_2PBH_3]$ were prepared by the reaction of the appropriate alkali metal with H_3PBH_3 in liquid ammonia at −78°.[7] We formulate the process as:

$$\begin{matrix}K\\ \text{or}\\ Na\end{matrix} + [NH_4][H_2PBH_3] \xrightarrow[-78^\circ]{\text{liquid } NH_3} {}^1/_2H_2 + \begin{matrix}K[H_2PBH_3]\\ \text{or}\\ Na[H_2PBH_3]\end{matrix} + NH_3$$

The lithium salt of $H_2PBH_3^-$ was prepared by Mayer[8] from a solution of *n*-butyllithium and H_3PBH_3 in diethyl ether at −20°. We carried out the same reaction independently[9] in toluene at −45° and also obtained LiH_2PBH_3. All salts are very reactive white solids and all turn yellow very easily, particularly in liquid ammonia solution. The potassium and sodium salts are somewhat less reactive than the lithium salt, particularly toward solvolysis. For example, the lithium salt inflames in moist air and explodes on contact with liquid water. The equation for acid hydrolysis is:

$$H_2PBH_3^- + 3H_2O + HCl \rightarrow PH_3 + 3H_2 + Cl^- + B(OH)_3$$

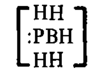
The 60 MHz ^1H NMR data for LiH_2PBH_3 in deuterioacetonitrile were published by Mayer.[8] Because solvent effects can be significant in determining spectral properties, we have obtained 60 MHz ^1H NMR and 32.1 MHz ^{11}B NMR spectra in ND_3 (NH_3 signals overlap lines of interest) for Li, Na, and K salts. The data given below were then used to identify $H_2PBH_3^-$ (or ion clusters containing $H_2PBH_3^-$) in liquid ammonia solutions. In contrast to the spectrum of $[NH_4][H_2PBH_3]$, the proton spectra of $K[H_2PBH_3]$, $Na[H_2PBH_3]$, and $Li[H_2PBH_3]$ in liquid ND_3 show a doublet (δ = −0.97 ppm from TMS, J_{P-H} = 184 ± 5 Hz) assignable to P–H protons. Each member of this doublet is split into a 1:3:3:1 quartet through coupling with the hydrogen atoms of the borane group ($J_{HBPH} \approx 7$ Hz) rather than the 1:1:1:1 quartet from coupling with the boron atom. The data show clearly that proton exchange is significantly slower in a basic liquid ammonia solution (i.e., containing $K[H_2PBH_3]$) than it is in an acidic liquid ammonia solution (i.e., NH_4^+ $[H_2PBH_3]$). The result is consistent with the model. The hydrogen atoms of the borane group appear as a 1:1:1:1 quartet (δ = −0.79 ppm from TMS, J_{B-H} = 89 ± 3 Hz) each member of which is split into a poorly resolved multiplet (presumably a 1:2:1 triplet).

The ^{11}B NMR spectrum shows a 1:3:3:1 quartet (δ = 55.6 ± 0.5 ppm from $B(OCH_3)_3$, J_{B-H} = 90 ± 2 Hz) each member of which is split into a doublet through coupling with the attached phosphorus atom ($J_{P-B} = 29 \pm 2$ Hz). The data provide an unequivocal identification of $H_2PBH_3^-$ (or a cluster containing the ion) in liquid ammonia solution.

3. The Reaction of the $H_2PBH_3^-$ Anion with Phosphine–Borane (Step 2). Acidic Media. The final step suggested for the formation of the $H_2P(BH_3)_2^-$ anion is:

$$H_2PBH_3^- + H_3PBH_3 \rightarrow H_2P(BH_3)_2^- + PH_3$$

This is simply a base exchange process in which the anion



$$\left[\begin{matrix}HH\\:PBH\\HH\end{matrix}\right]$$

acts as a stronger base than PH_3 to displace the latter base from the Lewis acid, BH_3. Mayer[8] and independent studies in this laboratory[9] showed that $H_2PBH_3^-$ will pick up a BH_3 group from diborane to give $H_2P(BH_3)_2^-$. On the other hand we were not able to verify an earlier report that KPH_2 will pick up diborane in diethyl ether.[7] Many attempts using dry diethyl ether gave no reaction, but the reaction did go to give $H_2P(BH_3)_2^-$ in dry dimethyl ether. The formation of $H_2P(BH_3)_2^-$ in dimethyl ether indicates that the $H_2PBH_3^-$ formed by an initial acid–base reaction $PH_2^- + H_3BO(CH_3)_2 \rightarrow H_2PBH_3^- + O(CH_3)_2$, will rapidly displace ether from $H_3BO(CH_3)_2$ to give the $H_2P(BH_3)_2^-$. The discrepancy in results with ref 7 appears to be one of solubility; differences may be related to purity of solid or solvent in the two laboratories. In a somewhat related study Mayer and Laubengayer[10] showed that H_3PBH_3 reacts with $NaBH_4$ to produce $H_2P(BH_3)_2^-$ and H_2.

When a solution of pure H_3PBH_3 in liquid ammonia was allowed to stand at −45°, less than half of the original borane was converted to $[NH_4][H_2P(BH_3)_2]$ after 300 hr. When NH_4I was added to the solution in the ratio of 1 mol of NH_4I to each 2.5 mol of original H_3PBH_3 added, quantitative formation of $[H_2P(BH_3)_2]^-$ occurred in less than 3 min. We attribute the very slow rate in the pure H_3PBH_3 solution to the very low activity of both H_3PBH_3 and $H_2PBH_3^-$ in the solution. As noted earlier, nearly all of the added H_3PBH_3 exists as nonreactive ion clusters, $\{[NH_4^+][H_2PBH_3^-]\}_n$, with relatively low concentrations of the undissociated H_3PBH_3 and the free ion $H_2PBH_3^-$. The relative amount of NH_4I added on a molar basis was fairly large, but because the $H_2PBH_3^-$ concentration in the solution was very small to begin with, addition of NH_4^+ could not increase significantly the concentration of undissociated H_3PBH_3 by a conventional equilibrium shift. Some additional type of process must be invoked to account for the dramatic catalytic effects of the added NH_4I. It is suggested that addition of the excess NH_4I alters the dielectric properties of the solution such that ion clusters break up appreciably in solution[11] to give NH_4^+ and $H_2PBH_3^-$. Some of the $H_2PBH_3^-$ ion is converted directly to H_3PBH_3 by the NH_4^+. Under these conditions the reaction rate would be fast if the rate of the process were given by the relationship:

$$\frac{d[H_2P(BH_3)_2^-]}{dt} = k_1[H_3PBH_3][H_2PBH_3^-]$$

A change in rate by a factor of 10^4 could be rationalized in terms of these concentration changes.

It was noticed that in the original H_3PBH_3 solution (containing no NH_4I) only a trace of H_3NBH_3 could be found in the product. This observation can be rationalized in terms of the low concentration of the undissociated H_3PBH_3 in the solution along with a small rate constant at −45° for the base displacement process[12] generating H_3NBH_3:

$$H_3PBH_3 + NH_3 \rightarrow H_3NBH_3 + PH_3$$

Table II. The Role of Temperature in Determining Product Composition for the Reaction of H_3PBH_3 and NH_3

Temp, of reaction, °C	Time,[a] hr	Product ratio[b] mol % H_3NBH_3/ mol % $[H_2P(BH_3)_2]^-$
0	0.5	0.73
−13	9.0	0.59
−23	100	0.32
−32	200	0.23
−45	312* (67% complete)	Trace H_3NBH_3[c]

[a] Time selected so that the reaction would be complete. [b] Analysis by ^{11}B NMR. Starting ratio of reactants $H_3N-H_3PBH_3$ was 2.6 ± 0.2. [c] In the sample at −45° the starting ratio of NH_3 to H_3PBH_3 was 5.7 to 1, yet only a trace of H_3NBH_3 was formed. The higher $NH_3-H_3PBH_3$ ratio would normally favor H_3NBH_3 formation.

4. The Reaction of the $H_2PBH_3^-$ Anion with Phosphine–Borane in Basic Solutions. The direct reaction between KH_2PBH_3 and H_3PBH_3 was studied by mixing equimolar quantities of the reagents in liquid ammonia solution and allowing the system to stand at −45°. A quantitative yield of $KH_2P(BH_3)_2$ was obtained in less than 10 hr. This value compares with less than 50% conversion in 300 hr for pure ammonia solutions of H_3PBH_3 and with 100% conversion in less than 3 min for solutions containing added NH_4I. It is clear that acid is a very effective catalyst for the process and base is also catalytic, but much less so than the acid.

Possible mechanisms for the base-catalyzed case, like those for the acid-catalyzed process, cannot be explained in terms of common ion effects involving the $H_2PBH_3^-$ ion, since it is assumed (from earlier evidence) that most of the H_3PBH_3 exists in liquid ammonia as ion clusters, $\{[NH_4^+][H_2PBH_3^-]\}_n$, of very low reactivity. As in the acid-catalyzed case it is necessary to postulate that the first step in the process is a partial breakup of the ion clusters. As in the acid case, such breakup would result from a change in the dielectric properties of the solvent when KH_2PBH_3 is added. Some of the NH_4^+ and $H_2PBH_3^-$ produced would combine to give H_3PBH_3, but the concentration of this species would be significantly lower in the basic solution than in the acidic one. This fact would account for the fact that the rate in basic solution is only 100 times larger than the rate in the noncatalyzed case while the rate in acidic solution is 10,000 times larger.

5. The Role of Temperature Changes in Determining the Composition of the Product Mixture Obtained in the H_3PBH_3–NH_3 System. Data displayed in Table II show clearly that as the temperature of the reacting system is raised above −45°, the overall reaction becomes significantly faster and the relative yield of H_3NBH_3 increases dramatically. The fact that H_3PBH_3 reacts more rapidly with NH_3 as temperature is raised is an expected and easily understood phenomenon. On the other hand, the fact that the yield of H_3NBH_3 increases relative to the yield of $[NH_4][H_2P(BH_3)_2]$ was not anticipated. A more detailed analysis is required.

The obvious conclusion is that the rate constant k_1 for the formation of the H_3NBH_3 increases more rapidly with a temperature increase than does the rate constant k_2 for the formation of $[H_2P(BH_3)_2^-]$. This postulate would demand a higher activation energy for the process giving H_3NBH_3 than for that giving $H_2P(BH_3)_2^-$. Such a difference is easily rationalized. Transfer of a proton from H_3PBH_3 to an NH_3 molecule to give ion pairs or clusters would be a process requiring little energy. (Goes easily at −45° as indicated by NMR which shows no detectable un-ionized H_3PBH_3 in the liquid ammonia solution.) The second step, dissociation of the ion pairs to give NH_4^+ and reactive $H_2PBH_3^-$ (a process which requires charge separation), would be promoted by a high dielectric constant for the solvent and relatively high solvation energy for the ions in the solvent. These quantities, high

Table III. Influence of Original Ammonia Activity upon the Composition of Product in the H_3PBH_3–NH_3 System at −32°C

Reactant ratio mol % H_3N/mol % H_3PBH_3	Product ratio mol % H_3NBH_3/mol % $[NH_4^+][H_2P(BH_3)_2]$
2.0	0.099
2.6	0.136
5.0	0.282

[a] Analysis by ^{11}B NMR; reaction time = 200 hr.

dielectric constant and solvation energy, would be most favorable for ionization in liquid NH_3 at low temperatures.

On the other hand the cleavage of the P–B bond in H_3PBH_3 would require much higher energy and would be much more temperature dependent. It is known for example that the dissociation of free H_3PBH_3 to give H_3P and B_2H_6 increases rapidly with an increase in temperature above −45°. Thus the processes which favor $[NH_4][H_2P(BH_3)_2]$ formation are maximized at low temperatures, while processes which favor H_3NBH_3 formation are larger at higher temperatures. This model correlates well with the very slow formation of *only* $[NH_4][H_2P(BH_3)_2]$ at −45° and the formation of increasing quantities of H_3NBH_3 as the temperature is raised.

6. The Role of Reactant Ratio in Determining Product Composition. The model just proposed suggests that ammonia activity would be important in the process:

$$H_3N + H_3PBH_3 \rightarrow H_3NBH_3 + PH_3$$

and $H_2PBH_3^-$ activity would be important in the competing process:

$$H_2PBH_3^- + H_3PBH_3 \rightarrow H_2P(BH_3)_2^- + H_3P$$

Indeed, at temperatures above −45° where cleavage of the P–B bond in H_3PBH_3 by NH_3 can occur relatively easily, the ratio of H_3NBH_3 to $NH_4[H_2P(BH_3)_2]$ rises as the ratio of H_3N to H_3PBH_3 in the reactant mixture rises. Data for a temperature of −32° are shown in Table III; a plot of reactant ratio values against product ratio values is nearly linear as demanded by the relationship:

$$\frac{\text{rate } [H_3NBH_3] \text{ formation}}{\text{rate } [NH_4][H_2P(BH_3)_2] \text{ formation}} = \frac{k_1[NH_3][H_3PBH_3]}{k_2[H_2PBH_3^-][H_3PBH_3]}$$

or product ratio $\approx k_1/k_2$ (reactant ratio).

The Reaction of Trimethylamine and Phosphine–Borane

Addition of H_3PBH_3 to trimethylamine at −45° results in complete displacement of PH_3 to give $(CH_3)_3NBH_3$ in 5 min. At −78° only 7% of the total PH_3 had been liberated after 300 hr. Because of the low dielectric constant of $(CH_3)_3N$ (2.5 at 25°) and the limited ion solvating power of $(CH_3)_3N$ resulting from its inability to hydrogen bond, the equilibrium producing $H_2PBH_3^-$ should lie far to the side of the undissociated H_3PBH_3. No significant concentration of the $H_2PBH_3^-$ ion should exist in the solution. As a result the solution should contain H_3PBH_3 as a significant component. The foregoing arguments are summarized by the equation below:

$$(CH_3)_3N + H_3PBH_3 \rightleftarrows \frac{1}{n}\underbrace{\{[(CH_3)_3NH][H_2PBH_3]\}_n}_{\text{cluster}} \rightleftarrows (CH_3)_3NH^+ + H_2PBH_3$$

$$\xleftarrow[\text{lies toward left}]{\text{equilibrium}}$$

With a relatively high concentration of H_3PBH_3 and $(CH_3)_3N$ in solution, the reaction to produce $(CH_3)_3NBH_3$ is relatively rapid. No ionic product is formed because of the vanishingly small concentration of $H_2PBH_3^-$.

The foregoing interpretation finds support in the observation that addition of trimethylamine to H_3PBH_3 in dimethyl ether at −63° gives good yields of $(CH_3)_3NBH_5$. It is significant that the ^{11}B NMR shows clearly that H_3PBH_3 is the only species in the ether solution (Table I). On the other hand, the addition of $(CH_3)_3N$ to an ammonia solution of H_3PBH_3 gives no reaction at −63°. This fact can be correlated with the known very low concentration of H_3PBH_3 and high concentration of ion clusters $\{[NH_4^+][H_2PBH_3^-]\}_n$.

Qualitative solubility observations are also consistent with the above model. Because of extensive formation of $[NH_4]^+$ and $[H_2PBH_3]^-$ in liquid ammonia, the solubility of H_3PBH_3 in liquid ammonia is high. On the other hand, the solubility equilibrium for H_3PBH_3 in $(CH_3)_3N$ cannot be shifted extensively by a proton transfer process and H_3PBH_3 has very limited solubility in $(CH_3)_3N$.

The Reaction of Dimethylamine and Phosphine–Borane

Dimethylamine, in contrast to trimethylamine, reacts with H_3PBH_3 very slowly at −45°. Reaction times were 300 to 400 hr as compared to less than 5 min for the trimethylamine system. The rate data are reminiscent of the NH_3–H_3PBH_3 case (even slower), but the products formed are similar to the trimethylamine system. At −45° only traces of ionic dimethylamine product $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ were formed. Produced in essentially pure form was $(CH_3)_2HNBH_3$. The above facts provide a more difficult challenge for any model.

Slow base displacement would be correlated with a relatively low concentration of un-ionized H_3PBH_3 in the dimethylamine solution. This postulate is confirmed by the NMR data, and by exchange studies (ref 8), which show rapid proton exchange between $(CH_3)_2NH$ and H_3PBH_3 (phosphorus–proton coupling collapsed). (See Table I.) The data in Table I also show that the phosphine–borane in dimethylamine (like that in ammonia) is converted almost completely to an ion cluster containing the anion $H_2PBH_3^-$. While these facts explain the slow rate of −45°, they are extremely difficult to harmonize with the formation of essentially pure $(CH_3)_2NHBH_3$. One factor in $(CH_3)_2NHBH_3$ formation might well be the greater base strength of $(CH_3)_2NH$ as compared to NH_3. Presumably such greater base strength could result in a faster reaction rate for the process:

$$(CH_3)_2NH + H_3PBH_3 \rightarrow (CH_3)_2NHBH_3 + PH_3$$

than for the comparable reaction with NH_3. Another factor of major importance would involve reduced rate of formation of ionic product because of reduced chemical activity of the $H_2PBH_3^-$ anion in dimethylamine solution. One can suggest that the free $H_2PBH_3^-$ concentration in $(CH_3)_2NH$ solution would be very low because of the significantly lower dielectric constant[13] of dimethylamine as compared to NH_3 and because of the much lower solvating power of $(CH_3)_2NH$ which results from its reduced hydrogen-bonding capability. In this solvent of low dielectric constant, ion clusters break up preferentially to give H_3PBH_3 rather than the free ions $(CH_3)_2NH_2^+$ and $H_2PBH_3^-$. Thus while the NMR data suggest proton transfer from H_3PBH_3 to the amine, the rate data suggest that the proton transfer product exists as nonreactive ion clusters. Because H_3PBH_3 and $(CH_3)_2NH$ activity are relatively high compared to $H_2PBH_3^-$, the yield of $(CH_3)_2NHBH_3$ is relatively high. Because $H_2PBH_3^-$ activity is very low the yield of $H_2P(BH_3)_2^-$ is very low.

To understand the fact that the relative yield of ionic product goes up in $(CH_3)_2NH$ as the temperature is raised, while it goes down in liquid NH_3, requires additional refinement of the model. (See Table IVA.) An analysis of energy terms is pertinent. In liquid ammonia the $\Delta H°$ value for the de-

Table IV. Role of Temperature in Determining Relative Yields of Covalent and Ionic Products in Reaction of H_3PBH_3 with Dimethylamine and Methylamine

A. Dimethylamine[a]

Temp, °C	Time,[b] hr	Mol product ratio[e] $[(CH_3)_2NHBH_3]/[H_2P(BH_3)_2]$
0	0.5	4.35[c]
−13	9	4.20
−23	102	3.20
−32	200	4.80
−45	400+	Almost ∞[f]

B. Methylamine[d]

Temp, °C	Time,[b] hr	Product ratio[e] $[CH_3NH_2BH_3]/[H_2P(BH_3)_2^-]$
0	0.5	0.97[c]
−13	9	0.78
−23	102	0.47
−32	200	0.32
−45	300+	Essentially ∞[g]

[a] Reactant ratio of dimethylamine–H_3PBH_3 = 2.4 ± 0.3 except for −45 where the ratio was 5.0. [b] Time given is such that reaction of H_3PBH_3 in the system is complete. [c] All analyses by ^{11}B NMR spectroscopy. [d] Reactant ratio of methylamine–H_3PBH_3 was about 2.6 except for −45 where the value was about 5. [e] Because of the way in which this ratio is written (based on table for ammonia reaction), a maximum in yield of *ionic product* corresponds to a minimum value of the ratio. [f] No ionic product. [g] No observable ionic product.

clustering process is slightly negative. Clutter and Swift estimated a $\Delta H°$ of −1 kcal/mol for the declustering of NH_4Cl groups:

$$\frac{1}{n}\{[NH_4][Cl]\}_n \rightarrow [NH_4]^+ + Cl^- \qquad \Delta H° = -1 \text{ kcal}$$

This tendency for declustering is opposed by an entropy term ($\Delta S°$) of −24 cal/(mol deg). In liquid dimethylamine solvation energies would be much lower than in liquid NH_3 because of the lower dielectric constant and lower hydrogen bonding capability in the solvent. One would anticipate a positive $\Delta H°$ for the process in liquid dimethylamine. Thus an increase in temperature over a short range (assume small changes in $\Delta H°$ with T) would *increase* the equilibrium concentration of ionic species in liquid *dimethylamine*, but *reduce* it in liquid *ammonia*.

The competing processes to be considered involve proton transfer from the original phosphine–borane to the base:

$$H_3PBH_3 + \text{base} \rightarrow \frac{1}{n}\{[H^+ \text{base}][H_2PBH_3^-]\}_n$$

In both cases it is reasonable to assume that this process is exothermic and $\Delta H°$ is negative. Reasoning from measured proton affinities (dimethylamine is 222 kcal/mol and ammonia is 207 kcal/mol),[14] the $\Delta H°$ value should be more negative for dimethylamine than for ammonia. From this information one can estimate that an increase in temperature should also promote cluster breakup to give H_3PBH_3 and free base in both cases. The change per unit of temperature should be greater for dimethylamine than for NH_3. This process, giving H_3PBH_3, should promote the base displacement reaction.

The foregoing facts and assumptions thus lead to the conclusion that an increase in temperature should increase the yield of base displacement product for ammonia (as observed), but increase the yield of ionic product in dimethylamine. Finally this yield of ionic product should fall as the decomposition of the cluster to free acid and base overwhelms the ion-dissociation process at much higher temperatures. Data shown in Table IVa for the temperature dependence of the system $(CH_3)_2NH$–H_3PBH_3 reveal that the relative yield of $H_2P(BH_3)_2^-$ goes through a maximum near −23°.

The phenomenon of declustering may be compared in some ways to the dissociation of a weak organic acid in water where it is known that the dissociation constant of the acid goes through a maximum as the temperature is raised.[15]

As was observed with ammonia an increase in dimethylamine activity at temperatures well above −45° promoted the formation of $(CH_3)_2NHBH_3$. Although data at a given temperature were not obtained as with ammonia, a roughly linear relationship between the reactant ratio, $(CH_3)_2NH$–H_3PBH_3, and the product ratio, $(CH_3)_2NHBH_3$–$[(CH_3)_2NH_2][H_2P(BH_3)_2]$, was found on samples which were allowed to warm to room temperature through a fixed time–temperature profile. More detailed data are shown elsewhere.[9]

Addition of as much as 50% NH_3 to $(CH_3)_2NH$ did not give measurable quantities of the ionic product, $[\text{cation}^+][H_2P(BH_3)_2^-]$, at temperatures of −45°. More details are available elsewhere.[9] The foregoing fact suggests that the ion cluster, $\{[\text{cation}^+][H_2P(BH_3)_2^-]\}_n$, gives relatively more H_3PBH_3 than $H_2PBH_3^-$ in solution and this H_3PBH_3 species is attacked by the $(CH_3)_2NH$ rather than $H_2PBH_3^-$ because of the higher activity of the strongly basic $(CH_3)_2NH$ in the solution.

The Reaction of Methylamine and Phosphine–Borane

Methylamine behaves very much like dimethylamine except that (1) the yields of the ionic product, $H_2P(BH_3)_2^-$, are significantly higher under comparable conditions and (2) the yield of $H_2P(BH_3)_2^-$ shows a maximum between −32 and −45°. (See Table IVB.) Both of these phenomena can be easily rationalized in terms of the higher dielectric constant of CH_3NH_2 (11.4 at −10°, 9.4 at 25°) and the greater solvating ability of the methylamine. Any maximum would be expected at a lower temperature than that observed for $(CH_3)_2NH$. Thus $(CH_3)NH_2$ behaves as expected based on extrapolations from the data for NH_3 and $(CH_3)_2NH$. Even the solubility of H_3PBH_3 is greater in $(CH_3)NH_2$ than in $(CH_3)_2NH$ and lower than in NH_3.

General Discussion

All of the foregoing reactions can be reduced to two competitive processes in which two bases competitively displace PH_3 from H_3PBH_3. The equations are:

$$H_3PBH_3 + NH_xR_{(3-x)} \rightarrow R_{(3-x)}H_xNBH_3 + PH_3 \qquad \text{(a)}$$

$$H_3PBH_3 + H_2PBH_3^- \rightarrow H_2P(BH_3)_2^- + PH_3 \qquad \text{(b)}$$

$$R = CH_3;\ x = 1, 2, 3$$

Both reactions are slow at −45° if the concentration of substrate, H_3PBH_3, is low. Reactions are far more rapid at −45° if the concentration of H_3PBH_3 is high [i.e., $(CH_3)_3N$ + H_3PBH_3]. All of the existing information on these systems can be understood if the equilibria existing in solutions of H_3PBH_3 in ammonia and amines is formulated as

$$\begin{tikzcd}
H_3PBH_3 + \text{base} \arrow[rr, rightleftharpoons] \arrow[dr, rightleftharpoons] & & \underset{\text{ion cluster}}{\{[\text{base } H^+][H_2PBH_3^-]\}_n} \\
& {[\text{base } H^+] + [H_2PBH_3^-]} \arrow[ur, rightleftharpoons] &
\end{tikzcd}$$

In solutions of ammonia, methylamine, and dimethylamine the ion cluster of low reactivity is the dominant species. In trimethylamine of very low dielectric constant, H_3PBH_3 is dominant.

In good ionizing and solvating media where activity of the anion $H_2PBH_3^-$ is largest, the basic $H_2PBH_3^-$ will displace H_3P from H_3PBH_3 to give $H_2P(BH_3)_2^-$ and PH_3. It should, however, be noted that in all cases the actual concentration of ionized $H_2PBH_3^-$ is relatively low. It is highest in ammonia and falls rapidly in the series $NH_3 > CH_3NH_2 > (CH_3)_2NH \gg (CH_3)_3N$. Thermal dissociation of ion clusters to give ions promotes formation of ionic product, while thermal dissociation of ion clusters to give H_3PBH_3 (or its dissociation products) promotes the formation of the amine–borane or covalent product. In these terms the temperature dependence of the different systems can be understood.

Experimental Section

1. General Procedures and Instrumentation. Standard high vacuum techniques were used throughout. Air and moisture sensitive compounds were handled in a plastic glove bag in a dry nitrogen atmosphere, while volatile materials were purified and stored under vacuum at −196°. Infrared spectra of volatiles were recorded with a Beckman IR-20 spectrophotometer using a 10 cm path length gas cell with KBr optics. Proton magnetic resonance spectra were obtained using a Varian Associates A-56/60 spectrometer and ^{11}B NMR spectra were obtained with a Varian Associates HA-100 spectrometer operating at 32.1 MHz. Chemical shift values were determined for all spectra by tube interchange using $Si(CH_3)_4$ for proton spectra and $B(OCH_3)_3$ as a standard for the ^{11}B data. All low temperature NMR samples were maintained below the reaction temperature during transfer of the sample to the probe of the spectrometer.

2. Materials. Diborane (Callery Chemical Co.), PH_3,[16] and PD_3[17] were purified by low-temperature fractionation in the vacuum line. *N*-Butyllithium (Alfa Inorganics) was used as obtained. Methyl-, dimethyl-, and trimethylamine were liberated from their respective hydrochloride salts (Eastman). Commercial NH_3 (Matheson) was used. ND_3 was prepared from Mg_3N_2 and D_2O; it was purified by low-temperature vacuum fractionation after being dried over metallic sodium. Deuteriodimethylamine was synthesized from $(CH_3)_2NH_2Cl$ and D_2O.[18] All amines were purified by low-temperature vacuum fractionation after being dried over CaH_2. Phosphine–borane was prepared as described in the literature.[1b]

3. The Preparation of Li^+, Na^+, and KH_2PBH_3. (a) Preparation of LiH_2PBH_3. An 8.21-mmol sample of H_3PBH_3 was prepared in a reaction tube and 5 ml of dry toluene was condensed on the solid. The mixture was warmed to −45°, and while being vigorously stirred by a magnetic jump stirrer, excess LiBu solution was slowly added (5 ml of 2.25 *M* butyllithium in hexane containing an additional 5 ml of toluene) through a micro addition funnel. Reaction was evidenced by immediate formation of a white precipitate. After reaction was complete, the solvents were fractionated through −95 and −196° traps resulting in a 7 mmol recovery of butane in the −196° trap and a mixture of toluene, hexane, and butane in the −95° trap. The solid material remaining in the reaction tube was then purified by vacuum filtration. The product was washed with toluene and vacuum dried at room temperature for several hours.

(b) Preparation of NaH_2PBH_3 and KH_2PBH_3. To 3.24 mmol of H_3PBH_3, which was prepared in a reaction tube, was added a 3-ml sample of NH_3 and slightly more than a 3.2-mmol sample of metallic sodium contained in a section of glass tubing. A −78° cold bath was then placed around the reaction tube, allowing the NH_3 to melt and dissolve the sodium. The dissolving sodium formed a blue layer which diffused down the reaction tube and was decolorized upon contact with the H_3PBH_3. After reaction, 1.57 mmol of H_2 was separated and the slight excess of sodium was destroyed by addition of NH_4I until the blue color of sodium was gone (2 or 3 crystals of NH_4I). Removal of the ammonia resulted in a white solid, NaH_2PBH_3. The potassium salt, KH_2PBH_3, was prepared in an identical manner using potassium metal.

4. Hydrolysis of Li^+ and KH_2PBH_3. A 0.028-g (0.40 mmol) sample of NaH_2PBH_3 was placed in a reaction tube; 2 ml of 4 *N* HCl was condensed onto the salt, then the tube was warmed to room temperature. Hydrolysis was allowed to proceed for 2 hr after which 1.13 mmol of H_2 was separated from 0.38 mmol of PH_3 (salt H_2–PH_3 ratio = 2.97; theory = 3.0). The PH_3 was condensed in a −196° trap after it passed through a −160° trap. The solids remained in the reaction tube. Similar data were obtained for the Li^+ and K^+ salts.

5. Reaction of H_3PBH_3 and KH_2PBH_3. In a reaction tube 1.29 mmol of H_3PBH_3 and 1.29 mmol of KH_2PBH_3 were allowed to react at −45° in 5 ml of NH_3. Since no reaction was noted, the reactants were concentrated by removal of NH_3 until about 0.75 ml of the original sample of ammonia remained. Relatively rapid reaction was then observed. A 1.27-mmol sample of PH_3 was liberated in 10 hr. Removal of the volatiles left a white solid, identified as $KH_2P(BH_3)_2$ from its proton NMR spectrum in cold water. (Diluted KOH solution was added to retard hydrolysis).

6. Reaction of H_3PBH_3 and NH_3 Followed by ^{11}B NMR Spectroscopy. In these reactions H_3PBH_3 was prepared in a 5-mm NMR tube. A desired quantity of NH_3 was condensed onto the H_3PBH_3, the tube was sealed under vacuum, and the contents were allowed to react as required (Table II). After reaction, ^{11}B NMR spectra of the products were obtained. For reactions conducted above −45°, two products were observed: H_3NBH_3 and $H_2P(BH_3)_2^-$. Boron-11 NMR values used for identification of H_3NBH_3[19] were δ from $B(OCH_3)_3$ = 41.4 ppm with J_{BH} = 91 Hz; values for $H_2P(BH_3)_2^-$ were[1a] δ from $B(OCH_3)_3$ = 59.8 ppm with J_{BH} = 91 Hz, and J_{PB} = 60 Hz. At −45° ^{11}B resonance for unreacted H_3PBH_3 (actually $H_2PBH_3^-$) was also observed in addition to the above two product signals. It was identified by the following NMR values: δ from $B(OCH_3)_3$ = 55.2 ppm with J_{BH} = 90 Hz and J_{PB} = 28 Hz. From the area ratios of the respective resonances, yields of covalent and ionic product were calculated (Table II).

7. Reaction of H_3PBH_3 and NH_3 Followed by Chemical Analysis. In these reactions H_3PBH_3 was prepared in a small reaction tube with a high-pressure Teflon stopcock. Onto the H_3PBH_3 was condensed the desired quantity of NH_3 (Table II). This was allowed to melt and dissolve the H_3PBH_3 at −45°. The reaction was conducted by simply removing the −45° cold bath from the tube and allowing the system to warm to ambient temperature. Reactions were evidenced by formation of bubbles which ceased after about 5 min. Fractionation of the volatiles remaining in the tube through a −126° trap to a −196° trap allowed PH_3 (identified by ir spectroscopy) to be measured in the −196° trap. From the PH_3 recovered, compared to the PH_3 contained in the H_3PBH_3, a product distribution could be calculated.

8. Reaction of $(CH_3)_2O$–H_3PBH_3 Solution with NH_3. In a reaction tube was prepared and dissolved 2.8 mmol of H_3PBH_3, in 2 ml of $(CH_3)_2O$ at −63°. To this solution slowly was added 2.8 mmol of NH_3 by expansion of the NH_3 over the solution which was stirred by a magnetic jump stirrer. As the NH_3 reacted, the solution became cloudy. After about 1 hr the unreacted NH_3 was condensed into the tube and the solution was warmed to −35° with stirring. After cooling the solution to −63°, a white solid settled out. Fractionation of all volatiles from this solid (maintained at −63°) revealed that NH_3 had been consumed and no PH_3 had been released; formation of $[NH_4H_2PBH_3]$ was indicated. When this solid was warmed, rapid decomposition resulted.

9. Ionization of H_3PBH_3 in Ammonia Followed by Isotopic Labeling. In a reaction tube a 2.02-mmol sample of H_3PBH_3 was prepared and dissolved in 7.5 mmol of ND_3 at −45°. After 0.5 hr, and with the tube maintained at −45°, the volatiles were removed and fractionated through −126 and −196° cold traps. In the −196° trap was found 0.38 mmol of PD_3 and PH_3 (3:1 ratio) while a 6.7-mmol sample of ND_3 and NH_3 was recovered in the −126° trap. Compounds were identified by ir spectroscopy. The H_3PBH_3 remaining was allowed to dissociate by warming it to room temperature causing some white clouds of H_3BNH_3 to form. The trace NH_3 impurity had no effect upon the isotopic distribution of the liberated PH_3. The volatiles formed from the dissociation amounted to 1.74 mmol of PD_3 and PH_3 in a 3:1 mol ratio. Only normal B_2H_6 (nondeuterated) was recovered. An identical reaction with D_3PBH_3 and NH_3 at −45° gave similar results as did a 2-hr reaction between D_3PBH_3 and NH_3 at −78°.

10. Reaction of H_3PBH_3 with NH_3 Containing NH_4I. In a 5-mm NMR tube was prepared 2.37 mmol of H_3PBH_3 to which 10.28 mmol of NH_3 and several crystals of NH_4I were added. The tube was sealed under vacuum and warmed to −45° at which temperature the proton NMR spectrum was recorded. The only detected compound was $H_2P(BH_3)_2^-$ indicating a very rapid reaction between the NH_3 and H_3PBH_3 in the presence of NH_4^+.

In another reaction, 2.56 mmol of H_3PBH_3, 1.5 ml of NH_3, and approximately 0.2 g of NH_4I were allowed to react at −45° in a small tube attached to a 2-atm manometer. The pressure of the system slowly rose and came to equilibrium in several minutes. Fractionation of the volatiles through −160 and −196° cold traps resulted in a 1.30-mmol recovery of PH_3 in the −196° trap. After removal of the volatiles a white solid remained which was identified as $H_2P(BH_3)_2^-$ by its NMR spectrum in dilute KOH solution.

11. Reactions of H_3PBH_3 with the Methylamines. The descriptions of the reactions of H_3PBH_3 are similar to the investigations involving NH_3.

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Registry No. Ammonia, 7664-41-7; methylamine, 74-89-5; dimethylamine, 124-40-3; H_3PBH_3, 15120-00-0; $K[H_2PBH_3]$, 56942-31-5; $Na[H_2PBH_3]$, 56942-32-6; $Li[H_2PBH_3]$, 34390-49-3.

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Phosphorus-Substituted Hydrazines. III. Group 6B Metal Carbonyl Derivatives of Selected Phosphinohydrazines[1]

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Reactions of the group 6B metal carbonyls with the phosphinohydrazines *N*-diphenylphosphino-*N*′,*N*′-dimethylhydrazine (DMPH), diphenylphosphinotrimethylhydrazine (TMPH), and *N,N*-bis(diphenylphosphino)-*N*′,*N*′-dimethylhydrazine (DPH) have yielded several new derivatives: $M(CO)_5(L)$, M = Cr, Mo, and W and L = DMPH, TMPH, and DPH; *cis*- and *trans*-$M(CO)_4(DMPH)_2$, M = Cr, Mo, and W; *trans*-$M(CO)_4(TMPH)_2$, M = Cr, Mo, and W; *cis*-$M(CO)_4(DPH)$, M = Cr, Mo, and W; $M(CO)_4(TMPH)$, M = Cr, Mo, and W; *cis*-$M(CO)_3(DMPH)_3$, M = Mo and W; $M(CO)_3(TMPH)_2$, M = Mo and W. The nature of the phosphinohydrazine to metal bonding could be ascertained effectively from an analysis of the ν(CO) and ν(NH) stretching frequencies in the infrared and the proton and phosphorus NMR data. Although phosphorus to metal bonding was always evident, chelation involving the terminal amine group occurred in the $M(CO)_4(TMPH)$ and $M(CO)_3(TMPH)_2$ derivatives.

Introduction

Mono- and polydentate, trivalent group 5A ligands, particularly amines and phosphines, are quite numerous and because of their many structural variations exhibit a diversity of electronic and steric properties. Most commonly, chelating agents have been designed with Lewis base centers located strategically along a carbon chain or in ortho ring positions. Being a rather unique chelating system involving two bonded nitrogen atoms, phosphinohydrazines offer a variety of potential bonding activities.[1-5] Examples in the P–N(P)–N unit include unidentate bonding through one of the four donor sites, chelation to a metal through the two phosphorus atoms or one phosphorus and a nitrogen, and bridging between two different metal centers. Although previous studies indicate that phosphorus centers are more basic toward low valent metal atoms than are amine groups,[2] evidence of nitrogen chelation has been cited.[4] As part of a program to ascertain the nature and extent of phosphinohydrazine interactions with transition metal systems, we shall describe results of group 6B metal carbonyl reactions with selected ligands.

Experimental Section

Microanalyses and molecular weights were performed by M-H-W Laboratory, Garden City, Mich. Infrared spectra were recorded in methylene chloride or methylcyclohexane solutions and KBr pellets on a Model 621 Perkin-Elmer spectrometer. Proton NMR spectra were taken on Varian Associates Model T-60 and HA-100 instruments in chloroform-*d* with tetramethylsilane as an internal standard. Phosphorus NMR spectra were obtained on the HA-100 instrument operating at 40.5 MHz with 85% H_3PO_4 as an external standard. Melting points were taken in open capillaries and are uncorrected. Dry nitrogen was used routinely for deaeration of solvents, maintenance of an inert atmosphere over reaction mixtures, and admission to evacuated vessels. Analytical data and physical properties of the new phosphinohydrazine metal carbonyl derivatives are contained in Table I.

Reagents. Chemicals were obtained from the following sources: chlorodiphenylphosphine and metal hexacarbonyls (Pressure Chemical