TABLE I

REACTIONS OF B_5H_9 WITH NH_3 AND CH_3NH_2

Reactants, mmol					Products, mmol				
B_5H_9	NH_3	CH_3NH_2	Temp, °C	Time, hr	μ-$CH_3NHB_2H_5$	$H_3B_3N_3H_3$	$H_3B_3N_3H_2CH_3$	$H_3B_3N_3H(CH_3)_2$	$H_3B_3N_3(CH_3)_3$
1.20	1.20	1.20	25	23	0.25	...	0.01	0.01	*a*
1.20	1.20	1.20	100	1	0.83	0.45	0.21	0.01	*a*
1.20		1.20	25	23	0.24	...	*a*	*a*	0.06
1.20		1.20	100	1	0.85	...	*a*	*a*	0.33

[a] Very small, but easily detectable, amounts.

of μ-$CH_3NHB_2H_5$ (1.40 mmol) was condensed into a previously evacuated 20-ml reactor cooled in liquid nitrogen, after which the flask was sealed, the liquid nitrogen removed, and the reactor and its contents, allowed to warm to room temperature. After heating in an oven at 110° for 1 hr, the reactor was again cooled in liquid nitrogen and opened into the vacuum line. The volatile materials were transferred into the vacuum line and separated by gas chromatography. The resulting products, with yields, were: B_5H_9 (0.06 mmol), B_2H_6 (0.02 mmol), $H_3B_3N_3(CH_3)_3$ (0.4 mmol), recovered μ-$CH_3NHB_2H_5$ (0.33 mmol), and trace amounts of $H_3B_3N_3H_3$, $H_3B_3N_3H_2CH_3$, and $H_3B_3N_3H(CH_3)_2$.

Results and Discussion

As shown in Table I, $H_3B_3N_3H_3$, $H_3B_3N_3H_2CH_3$, $H_3B_3N_3H(CH_3)_2$, $H_3B_3N_3(CH_3)_3$, and μ-$CH_3NHB_2H_5$ were prepared by allowing B_5H_9 to react with NH_3 and CH_3NH_2 in the gas phase at 100°. With the exception of unsubstituted borazine the same products were formed in the reaction between B_5H_9 and CH_3NH_2; however, the yields of unsymmetrical derivatives were lower than in the reactions which included NH_3, while the yield of the trimethyl derivative was higher. In addition to the volatile products a small amount of nonvolatile, highly viscous liquid formed in every reaction. Others have reported some work on the characterization of this liquid.[3]

Borazine and $H_3B_3N_3(CH_3)_3$ were identified by comparison of the infrared spectra with that of the published spectra.[4] $H_3B_3N_3H_2CH_3$ and $H_3B_3N_3H(CH_3)_2$ were identified by infrared, proton nmr, and mass spectra. The data corresponded very closely to those reported by Beachley.[2] μ-Methylaminodiborane was identified by comparing the infrared and mass spectra with that of an authentic sample made by the method of Burg and Randolph.[5]

The presence of μ-methylaminodiborane also suggested a possible mechanism for the formation of the borazine ring in which B_5H_9 and the amine(s) react to form μ-methylaminodiborane followed by conversion to the borazine ring system. This would be consistent with the work of Schlesinger, Ritter, and Burg,[6] who reported obtaining high yields of borazine by heating μ-aminodiborane. When 1.40 mmol of μ-methylaminodiborane was heated at 110° for 1 hr good yields of $H_3B_3N_3(CH_3)_3$ were obtained along with trace amounts of $H_3B_3N_3H_3$, $H_3B_3N_3H_2CH_3$, and $H_3B_3N_3H(CH_3)_2$. This result strongly supports the above mechanism for the formation of the trimethyl derivatives but the formation of unsymmetrical derivatives probably involves some additional interaction between μ-$CH_3NHB_2H_5$ and one or more of the original reactants. This aspect is currently being investigated.

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Metal-Metal Stretching Frequencies in Polymetallic Carbonyls

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In recent years, Raman and far-infrared spectroscopies have been shown to be effective tools for studying metal–metal stretching vibrations.[1-3] Having recently prepared several novel linear polymetallic carbonyls,[4-6] we report the results of an investigation of the Raman and far-infrared spectra of these and other similar compounds.

Table I summarizes the metal–metal stretching frequencies which have been observed in the present work along with earlier published data. In most cases, there is little uncertainty about the assignments of these bands to metal–metal stretching vibrations since in metal carbonyls ν_{M-CO} and δ_{MCO} lie above 300 cm^{-1} and δ_{CMC} modes are found below 120 cm^{-1}.[3] One can further distinguish between ν_{M-M} and δ_{CMC} by means of intensity, the metal–metal stretching modes being more intense, especially in the Raman spectrum.

For the bimetallic homonuclear carbonyls ν_{M-M} appears as an intense polarized line in the Raman spectra.[1] This vibration is not allowed in the infrared spectrum. However, when the molecule is heteronuclear, $\nu_{M'-M}$ is both Raman and ir active but is generally weak in the far-infrared region.[3] For $ReMn(CO)_{10}$ our assignment differs from that of Gager, Lewis, and Ware.[1] They assigned a band at 182 cm^{-1}

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TABLE I

METAL–METAL STRETCHING FREQUENCIES (cm^{-1}) AND FORCE CONSTANTS (MDYN/Å)

Compound	ν_1	ν_3	k_1[a]	k_2[a]	k_i[a]
$Mn_2(CO)_{10}$	159		0.41 (1.45)		
$Re_2(CO)_{10}$	120		0.79 (1.38)		
$MnRe(CO)_{10}$	154		0.58 (1.70)		
$ReCo(CO)_9$	130		0.43 (1.10)		
$Re_2Fe(CO)_{14}$	107	*b*			
$Mn_2Fe(CO)_{14}$	143	214, 220	0.58 (1.98)		0.07 (0.36)
$ReFeMn(CO)_{14}$	135	217, 225	0.58 (1.98)[c]	0.53 (1.40)[c]	0.25 (0.59)[c]

[a] Effective mass equal to atomic weight of metal; value in parentheses obtained by including carbonyl groups in the effective mass. [b] Ir spectra not obtained for this compound. [c] See text.

to $\nu_{M'-M}$ while attributing the band at 154 cm^{-1} to an $Mn_2(CO)_{10}$ impurity. However, our data show this band (154 cm^{-1}) to be very intense and also present in the infrared spectrum as a weak band at 159 cm^{-1}. We do not observe a band in the 180-cm^{-1} region. Thus for $ReMn(CO)_{10}$ we prefer to assign the band at 154 cm^{-1} to $\nu_{M'-M}$. An attempt was made to observe $\nu_{M'-M}$ for $MnCo(CO)_9$ also. However, due to rapid decomposition of the sample by the He–Ne laser, the Raman spectra could not be obtained.

For the linear trinuclear systems $Mn_2Fe(CO)_{14}$ and $Re_2Fe(CO)_{14}$ ($D_{\infty h}$ point group) $\nu_1[\Sigma_g^+]$ is allowed in the Raman effect and $\nu_3[\Sigma_u^+]$ is allowed in the infrared. However, for $ReFeMn(CO)_{14}$ ($C_{\infty v}$ point group) $\nu_1[\Sigma^+]$ and $\nu_3[\Sigma^+]$ are allowed in both the Raman and infrared spectra. In all three cases, these vibrations lead to the most intense bands in the low-frequency spectrum. For $Mn_2Fe(CO)_{14}$ and $ReFeMn(CO)_{14}$ ν_3 appears as two bands separated by some 6–8 cm^{-1}. Single-crystal X-ray analyses have previously revealed the presence of two crystallographically distinct molecules per unit cell for both $Mn_2Fe(CO)_{14}$[7] (Mn–Fe = 2.80 and 2.82 Å) and $Re_2Fe(CO)_{14}$[8] (Re–Fe = 2.8758 and 2.8493 Å). Thus it is suggested that the observed doublet for ν_3 may be attributed to two different crystallographic molecules. However, it is not presently understood why a similar splitting of ν_1 is not observed in these compounds.

By treating the carbonyls approximately as either "diatomic" or "triatomic" molecules, rough metal–metal stretching force constants may be obtained.[9] These results are also summarized in Table I. Force constants are given for two commonly used approximations: (1) the effective mass of the metal is equal to its atomic weight or (2) the effective mass of the metal is equal to the mass of the entire metal carbonyl moiety. Using the first approximation, the metal–metal stretching force constants lie in the order Re–Re > Re–Mn > Re–Co > Mn–Mn. This trend is not surprising since the tendency to form metal–metal bonds increases down the periodic table and at the same time decreases as one moves across the periodic table.[10] Using the second approximation, the order is changed to Mn–Re > Mn–Mn > Re–Re > Re–Co. With these force constants then, the above generalizations no longer hold. The real situation probably lies between these two limits although the first has been previously reported to be the better approximation.[11]

As shown in Table I the metal–metal stretching force constant [k_1] for $Mn_2Fe(CO)_{14}$ is of the same order of magnitude as those for the bimetallic carbonyls. The interaction constant [k_i] is significantly nonzero which is consistent with previous observations.[8] Using this value for k_1, we have computed the Re–Fe stretching force constant k_2 and the interaction constant k_i using ν_1 and ν_3 for $ReFeMn(CO)_{14}$. This method has given rise to a relatively large value for k_i with respect to k_1 and k_2.

To test further the transferability of force constants between molecules, we have attempted to calculate k_i and ν_3 for $Re_2Fe(CO)_{14}$ using the value of k_2 determined for $ReFeMn(CO)_{14}$. However, a value of k_i is obtained which is larger than k_2, thus giving rise to a totally unreasonable value for ν_3. It may therefore be concluded from these observations that a stretching force constant representing a certain metal–metal bond may not be transferred between molecules, even in a closely related series such as this.

After this paper was submitted, a paper appeared[12] in which the authors performed normal-coordinate calculations for $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $MnRe(CO)_{10}$. From their calculations, it is clear that inclusion of carbonyl masses in the "effective masses" of the metals in the diatomic approximation greatly overcorrects for the neglect of coupling with carbonyl motions. However, the coupling with carbonyl motions is shown to be quite substantial when the metals are light as in $Mn_2(CO)_{10}$ but negligible for those involving heavier atoms such as in $Re_2(CO)_{10}$. This effect may be appreciable in $Mn_2Fe(CO)_{14}$ and $ReFeMn(CO)_{14}$ and this could account for the nontransferability of force constants in the trimetallic series.

Experimental Section

$Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were used as received from Pressure Chemical Co. The other carbonyls were prepared by previously

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reported techniques.[4–6,13–15] Raman spectra were obtained with crystalline samples using a Cary Model 81 spectrophotometer equipped with an He–Ne laser source. Infrared spectra were measured on a Beckman IR-11 far-infrared spectrophotometer using Nujol mulls and polyethylene windows.

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Study of Ion–Molecule Reactions in Phosphine by Ion Cyclotron Resonance[1]

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Although numerous mass spectrometric investigations of phosphine have been reported,[3–7] only two groups[3,6] have investigated the ion–molecule chemistry of PH_3, and their work concentrated solely on the formation of the phosphonium cation, PH_4^+. Halmann and Platzner[6] concluded from appearance potential measurements that the PH_4^+ ion was produced by the reaction

$$PH_3^+ + PH_3 \longrightarrow PH_4^+ + PH_2 \text{ (or } PH_4^+ + PH + H) \quad (1)$$

They were unable to detect any contribution to the formation of PH_4^+ from ion–molecule reactions involving PH_2^+ or PH^+.

Since ion cyclotron single- and double-resonance techniques have proven to be useful methods for the identification of gas-phase ion–molecule reactions,[8–10] these techniques were used to study the reactions which produce PH_4^+. During the course of the investigation, a variety of previously unreported ionic species and ion–molecule reactions occurring in PH_3 were discovered.

Experimental Section

The ion cyclotron resonance (icr) spectra in this study were obtained at room temperature using a Varian ICR-9 ion cyclotron resonance spectrometer, described in previous literature,[9] utilizing the electron energy modulation scheme described by Henis and Frasure.[11] Gaseous phosphine (Matheson Co., Inc.) was used without further purification, while acetone and acetaldehyde (reagent grade) were purified by repetitive freeze–pump–thaw cycles. PD_3 was prepared by exchange between PH_3 and acidified 99.8% D_2O (Stohler Isotope Chemicals Co., Azusa, Calif. 91702) in excess, as reported by Weston and Bigeleisen.[12]

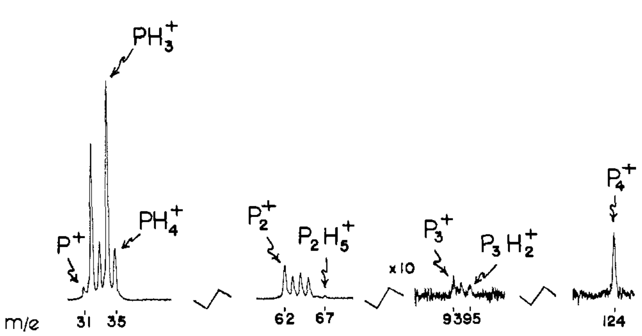

Figure 1.—Icr single-resonance spectrum of positive ions in PH_3 at 2×10^{-5} Torr and 23-eV peak ionizing electron energy.

Results and Discussion

Figure 1 shows an icr single-resonance spectrum of PH_3 at 2×10^{-5} Torr and 23-eV peak ionizing energy. The parent ion, PH_3^+, as well as all three fragment ions PH_2^+, PH^+, and P^+ may be observed. In addition to the m/e 35 PH_4^+ product ion, a large number of other ions, attributable to ion–molecule reactions in PH_3, appear in the higher mass regions. These include $P_2H_n^+$ (n = 0–5), $P_3H_n^+$ (n = 0–2), and P_4^+. With the exception of PH_4^+, none of the higher mass ions has been reported previously as an ion–molecule reaction product in gaseous PH_3. Analogous species have, however, been observed as ion–molecule reaction products in the congener of phosphine, ammonia.[13,14] Derwish, *et al.*, reported formation of the species $N_2H_n^+$ (n = 1–5) in gaseous ammonia.

Using ion cyclotron double-resonance techniques, the ion–molecule reactions listed in Table I were identified. With the exception of reaction 1, none of these reactions has been reported previously. The sign of the icr double-resonance signal, given in Table I for each reaction, depends on the sign of $(\mathrm{d}k/\mathrm{d}E_{\mathrm{ion}})^0$, where k is the reaction rate constant, E_{ion} is the translational energy of the irradiated ion, and the derivative is evaluated in the limit of vanishing field strength of the irradiating oscillator.[15] General observations in this and previous icr studies are that $(\mathrm{d}k/\mathrm{d}E_{\mathrm{ion}})^0$ is (1) negative for exothermic reactions other than charge transfer and (2) positive for exothermic charge-transfer reactions. A reaction which gives a negative double-resonance signal must be occurring at thermal energies and must therefore be exothermic or thermoneutral. A reaction which gives a positive double-resonance signal may be either endothermic or exothermic, but an endothermic reaction must give a

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