the case of **3A**. The expected septet due to the coupling of the hydrido hydrogens with ^{10}B is also observed except in **3C**. Except for the dioxane peak, integrations are consistent with the proposed formulation. The integration for dioxane peaks in ^1H NMR spectra can show a degree of variability, which is an artifact of the methods employed to purify these compounds. Excess solvent is removed from the precipitates by subjecting the solids to vacuum conditions for varying lengths of time. The dioxane also slowly evolves from the dried solid. For this reason, elemental analyses were generally not satisfactory. However, all other characterization data support the proposed structures.

Carbon adjacent to boron in all three compounds is observed in the ^{13}C NMR spectra as a quartet of very weak intensity, due to coupling with ^{11}B; coupling due to ^{10}B is not noticeable. Signals of other carbons in each compound are consistent with the proposed structures (Table II).

The IR spectra for the dioxane complexes of the (α-cyanoalkyl)trihydroborates are consistent with the proposed structures, showing peaks in the range of 2235–2278 cm^{-1} for B—H, 2200–2215 cm^{-1} for C≡N, and 1125–1140 cm^{-1} for the C—O bond of the dioxane molecule.

The lithium salts of (α-cyanoalkyl)trihydroborates are converted into their corresponding sodium (**4A–4C**) and potassium (**5A–5C**) salts by using aqueous sodium fluoride and potassium fluoride, respectively. Once formed, the dioxane adducts of the sodium and potassium salts are stable to moisture for relatively longer times, unlike their comparable lithium salts, which are moisture-sensitive.

The ^{11}B, ^1H, and ^{13}C NMR and IR spectra of these sodium and potassium (α-cyanoalkyl)trihydroborates are similar to those of the lithium salts. The ^7Li NMR spectra of the lithium salts of (α-cyanoalkyl)trihydroborate–dioxane complexes show a single sharp peak at −1.4 ppm for **3A** and **3B** and −1.3 ppm for **3C**. The ^7Li NMR spectra of the Na and K salts of (α-cyanoalkyl)trihydroborate–dioxane complexes obtained from the previous Li salts, recorded after a much longer accumulation time, did not show any signal due to the presence of the lithium salt as a contaminant.

The behavior of these compounds as reducing agents toward organic functional groups indicates they are intermediate in reducing power between tetrahydroborate and cyanotrihydroborate and also differ depending on the CRR′ substituents. These results will be reported in a subsequent paper as will the ability of the anions to complex to metals.

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Contribution from the Chemistry Department,
University of Virginia, Charlottesville, Virginia 22901

Cocondensation Reaction between Phosphine and Fluorine: Matrix Infrared Spectra of PH_3F_2, PHF_2, and PH_2F

Lester Andrews* and Robert Withnall

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Argon/F_2 and argon/PH_3 samples codeposited at 16 K yielded reaction product infrared absorptions identified as PH_3F_2, PHF_2, and the new molecule PH_2F. In contrast the analogous NH_3 and F_2 system gave only the NH_3--F_2 complex, which required photolysis to produce the NH_2F--HF complex. The phosphine–fluorine reaction apparently proceeds through a pentavalent activated complex. This activated complex either is relaxed by the matrix to give PH_3F_2 or dissociates to the PHF_2 or PH_2F products, which are trapped in the matrix.

Introduction

The increased reactivity of second-row hydrides compared to first-row hydrides can be illustrated with NH_3 and PH_3. Although each forms a symmetrical complex with ozone,[1] photolysis of the PH_3--O_3 complex proceeds with red light and gives an extensive array of products including H_2POH and the higher oxidation state oxide H_3PO and acid $HOPO_2$ whereas the NH_3--O_3 complex requires blue light for dissociation and gives only H_2NOH.[2,3] Although ammonia and fluorine react explosively in the gas phase at room temperature, when separate samples were condensed at 12 K with excess argon, only the NH_3--F_2 complex forms.[4] However, mercury arc photolysis converts this complex quantitatively to NH_2F--HF complexes and provides a means for synthesis of the elusive NH_2F species,[4] which has very recently been observed by microwave spectroscopy.[5] The analogous PH_3 and F_2 matrix reactions have been done in order to synthesize phosphinous fluoride, PH_2F, and to explore the greater reactivity of second-row hydrides. There is no previous experimental evidence for PH_2F, although a number of theoretical calculations have been performed on this subject molecule largely concerned with the barrier to inversion,[6,8] hybridization of phosphorus,[9] and ab initio calculation of force fields.[10]

Experimental Section

The cryogenic apparatus and experimental techniques have been described previously.[4] Fluorine (Matheson) was handled in a passivated stainless-steel vacuum system, and Ar/F_2 = 150/1 samples were passed through a U-tube immersed in liquid nitrogen to remove HF before deposition; however, traces of the usual volatile impurities CF_4, OCF_2, SiF_4, and NF_3 were found in these samples. Phosphine and PF_3 (Matheson), PD_3, and $(CH_3)_3P$ were handled and prepared as described previously.[11,12] Argon-diluted samples of reagent (Ar/R = 200/1) and

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Table I. Infrared Absorptions Produced upon Codeposition of Argon/Phosphine and Argon/Fluorine Samples at 16 K

absorption, cm^{-1}		
$PH_3 + F_2$	$PD_3 + F_2$[a]	identification
3962	2896	HF R(0)
3919	2877	HF Q, induced
3881	2846	N_2--HF
3826	2804	$(HF)_2$
3775		?
3627	2669	PH_3--HF
3581		site
2310	1680	3, PH_2F
2304	1673	3, PH_2F
2270	1654	2, PHF_2
1090		3, PH_2F
1022	764	2, PHF_2
974	719	1, PH_3F_2
934	701	3, PH_2F
840	840	2, PHF_2
829	829	2, PHF_2
810	810	2 aggregate
795[b]	798[d]	3, PH_2F
755[c]	749	1, PH_3F_2
	712	2, PHF_2
685		?
477	359	PH_3--HF

[a] Mixed isotopic samples gave new bands at 2306 and 1676 cm^{-1} for the PHDF species. [b] Strong site splitting observed at 798 cm^{-1}. [c] Strong site splitting observed at 758 cm^{-1}. [d] Strong site splitting observed at 803 cm^{-1}.

fluorine were codeposited on a 16 ± 1 K CsI window at rates of 2–3 mmol/h each for 8–12 h, and infrared spectra were recorded on a Perkin-Elmer 983 spectrometer system.

Results

Infrared spectra for PH_3, PD_3, PF_3, and $(CH_3)_3P$ codeposited with fluorine in excess argon will be described in turn.

PH_3. Three codeposition experiments were performed with PH_3 and F_2, and the new product absorptions are listed in Table I. Figure 1 shows bands familiar to the HF system[13] and the PH_3--HF complex (labeled ν_s) reported previously.[11] Considerably more HF is present in Figure 1 than could have come through the liquid-nitrogen trap, so it must be concluded that reaction between PH_3 and F_2 occurred during sample deposition. New bands were observed at 2480 cm^{-1} (broad, weak, labeled 1 in Table I), 2310 and 2304 cm^{-1} (labeled 3), and 2270 cm^{-1} (labeled 2) in the P–H stretching region (Figure 2) and at 1090, 934, and 795 cm^{-1} (labeled 3), 1022, 840, and 829 cm^{-1} (labeled 2) and 974 and 755 cm^{-1} (labeled 1) in the P–H deformation and P–F stretching regions (Figure 3). Finally, very weak (A = absorbance = 0.01), sharp absorptions were observed at 850 and 884 cm^{-1}, which are the strongest bands of PF_3.[12] A second experiment using the 16 ± 1 K window temperature gave essentially the same spectrum. Photolysis with visible and near-ultraviolet radiation produced only a weak O_2F band[14] at 1489 cm^{-1}, which increased on sample annealing to 36 K without changing the rest of the spectrum. A third experiment using a lower 11–12 K window temperature trapped more HF, reduced the yield of band 1 to one-third, and sharpened the bands 2 and 3 with about the same absorbance as when the 16 K window temperature was used.

PD_3. Three investigations were done with F_2 and PD_3 samples containing about 30, 50, and 80% deuterium enrichment. The spectra revealed isolated DF at 2896 cm^{-1}, N_2--DF complex[13] at 2846 cm^{-1}, and PD_3--DF complex[11] at 2669 cm^{-1}, confirming a reaction between PD_3 and F_2. New bands were observed at 2306 cm^{-1} on top of the 2304-cm^{-1} band in the P–H stretching region and at 1676 cm^{-1} in the P–D stretching region (marked by arrows in Figure 2) that appeared along with the PH_3 bands described above using low deuterium enrichment; expanded scale spectra clearly show the 2-cm^{-1} difference between the 2304-cm^{-1} band in Figure 2a and the 2306-cm^{-1} band in Figure 2c. On increasing deuterium enrichment the PH_3 product bands decreased, the 2306- and 1676-cm^{-1} bands remained prominent, and new bands appeared at 1680 and 1673 cm^{-1} (labeled 3) and 1654 cm^{-1} (labeled 2) which are shown in Figure 2c. In the lower region the 934-cm^{-1} band was very weak and a new counterpart appeared at 701 cm^{-1}. The 840- and 829-cm^{-1} bands appeared as with the PH_3 reaction; however, the 795-cm^{-1} band with PH_3 exhibited a counterpart at 798 cm^{-1} with PD_3. Bands labeled 1 at 974 and 755 cm^{-1} with PH_3 revealed strong counterparts at 719 and 749 cm^{-1} with PD_3.

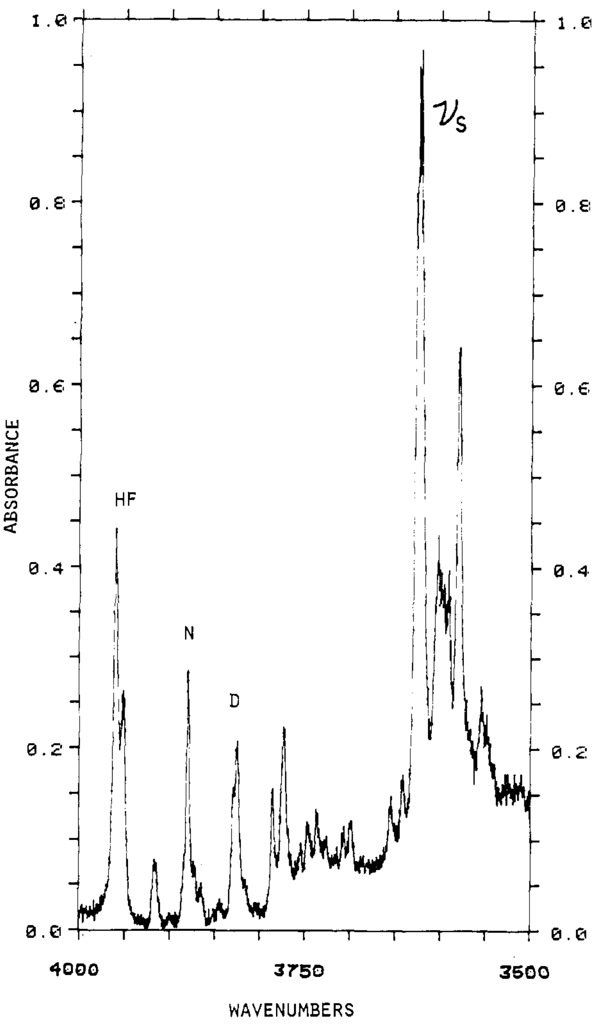

Figure 1. Infrared spectrum in the 4000–3500-cm^{-1} region following codeposition of Ar/PH_3 = 200/1 and Ar/F_2 = 150/1 samples at 16 ± 1 K for 8 h.

PF_3. One experiment was done with PF_3 and F_2. The codeposited sample revealed PF_3,[12] the usual fluorine impurity absorptions,[13] and no PF_5. However, photolysis with the water-filtered high-pressure mercury arc produced very strong PF_5 absorptions[15] at 1023 and 929 cm^{-1}, strong PF_5 bands at 573 and 528 cm^{-1}, and weak PF_5 bands at 504 and 284 cm^{-1}.

$(CH_3)_3P$. A single experiment was done with trimethylphosphine and fluorine. The codeposited sample contained isolated HF and strong $(CH_3)_3P$--HF complex bands at 3240, 3200, and 724 cm^{-1} [11] and new reaction product bands at 1307, 949, 917, 775, and 670 cm^{-1}, which are clearly due to trimethyldifluorophosphorane.[16] A fully-absorbing new band was observed at 1067 cm^{-1} and additional new strong product bands were observed at 1370, 1237, 1045, 518, and 348 cm^{-1}. Photolysis failed to change

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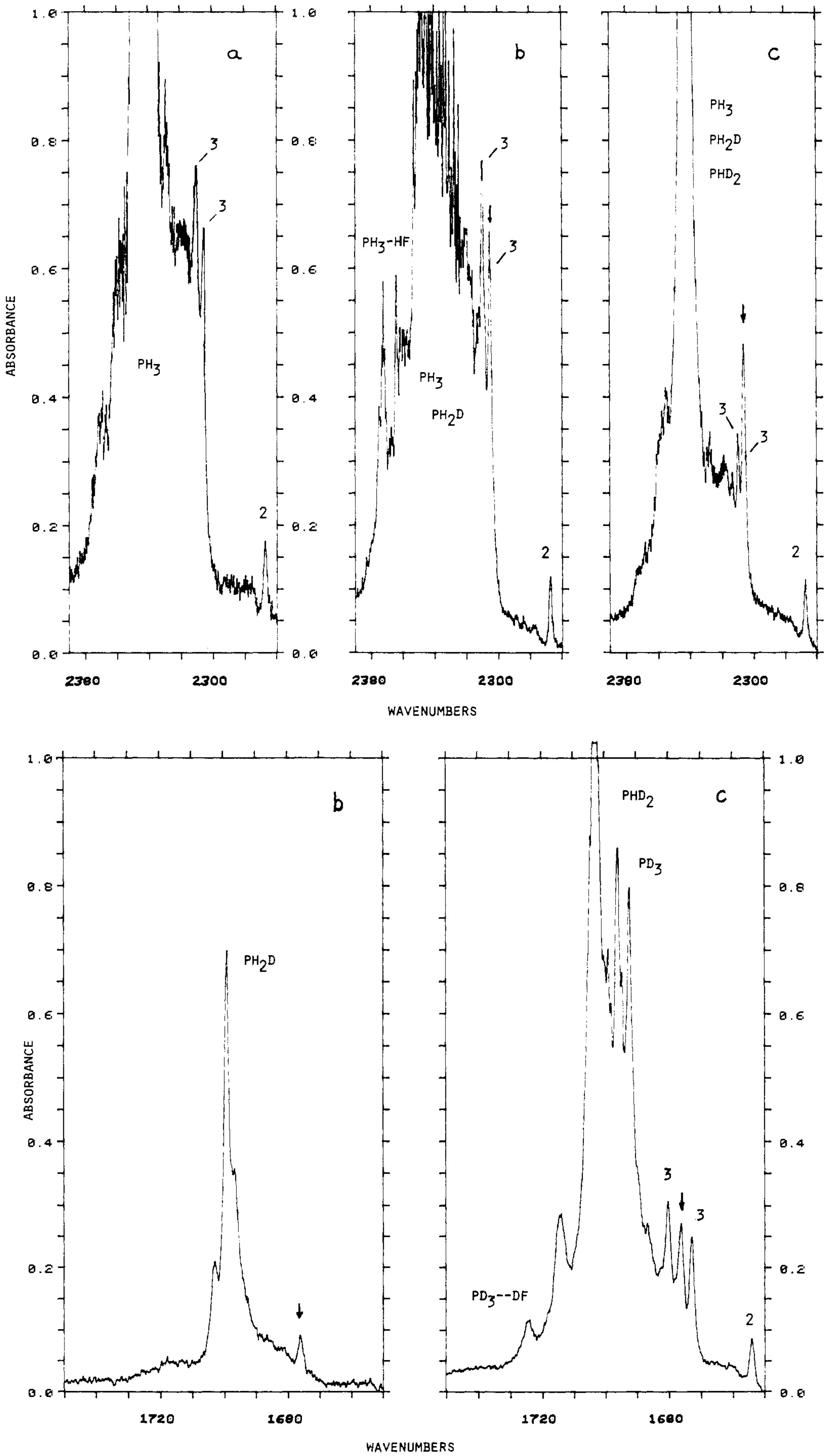

Figure 2. Infrared spectra in the P–H and P–D stretching regions for argon/phosphine = 200/1 samples codeposited with argon/fluorine = 150/1: (a) PH_3, (b) 30% deuteriated phosphine, and (c) 80% deuteriated phosphine.

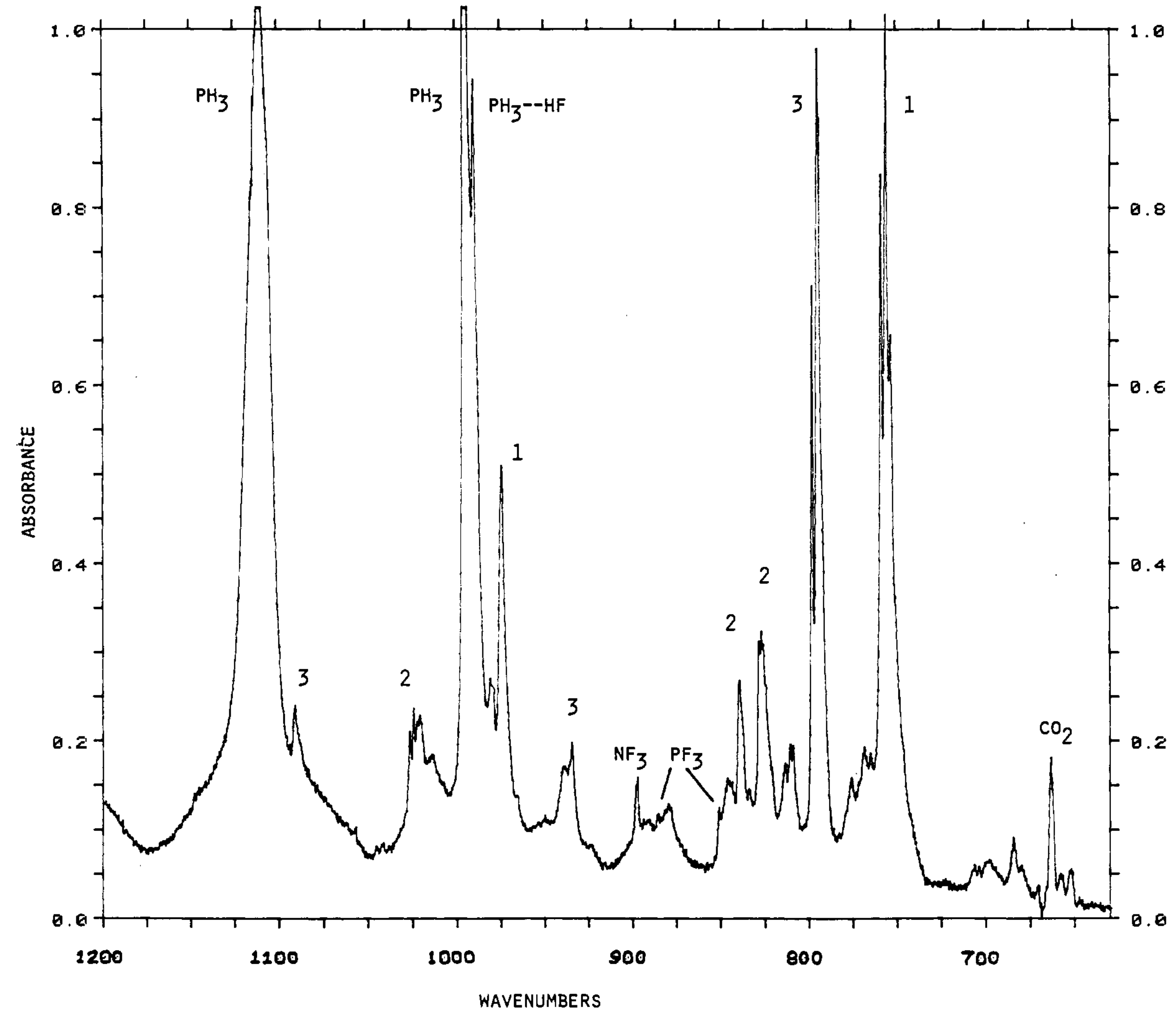

Figure 3. Infrared spectrum in the 1200–700-cm^{-1} region following codeposition of $Ar/PH_3 = 200/1$ and $Ar/F_2 = 150/1$ samples at 16 ± 1 K for 12 h.

these bands or to produce any new absorptions. Results from the trimethylphosphine–fluorine experiment are similar to those reported by Machara and Ault[17] except for the strong 1091-cm^{-1} band, which was not observed here.

Discussion

The new reaction products will be identified and the reaction mechanism will be considered.

Identification. A major product, **1**, in PH_3 and F_2 codeposition reactions is difluorophosphorane, PH_3F_2, based on agreement with the gas-phase spectrum.[18] The strongest matrix band at 755 cm^{-1} is in excellent agreement with the Q branch of the strongest gas-phase band at 759 cm^{-1}, which is due to the antisymmetric diaxial $P-F_2$ stretching mode; this assignment is consistent with the small observed deuterium shift. The next strongest matrix band at 974 cm^{-1} corresponds to a broad gas-phase band at 970 cm^{-1}; the proximity to ν_2 of PH_3 at 994 cm^{-1} and the similar H/D fundamental ratio identify a PH_3 group deformation mode. The weak 2480-cm^{-1} band is the matrix counterpart of the weak 2500-cm^{-1} absorption in the gas phase, which is due to the antisymmetric P–H stretching mode.

The second product, **2**, gives rise to sharp bands at 2270, 1022, 840, and 829 cm^{-1}, which are in exact agreement with the matrix spectrum[19] of HPF_2; the latter two bands are probably due to symmetric and antisymmetric $P-F_2$ stretching modes, respectively, although both fundamentals have 839-cm^{-1} band centers in the gas phase.[20] In the PD_3 studies, absorptions at 1654, 840, 829, 764, and 712 cm^{-1} for DPF_2 were also observed, again in agreement with previous work.[19]

Another major product, **3**, gave a very strong 795-cm^{-1} band with a 798-cm^{-1} satellite, medium-intensity 1090- and 934-cm^{-1} bands, and sharp, strong bands at 2310 and 2304 cm^{-1} on the side of the P–H stretching band of PH_3. Partial deuteriation gave new bands at 2306 and 1676 cm^{-1} (marked by arrows), and complete deuterium substitution gave still different new bands at 1680 and 1673 cm^{-1} on the side of the PD_3 absorption. The strongest band appeared slightly shifted at 798 cm^{-1} on deuteriation and a probable counterpart for the 934-cm^{-1} band was observed at 701 cm^{-1}.

The very strong 795-cm^{-1} band is due to a P–F stretching mode based on its position near other P–F stretching modes discussed above and the small deuterium shift. The 2310- and 2304-cm^{-1} bands are probably due to antisymmetric and symmetric $P-H_2$ stretching modes, and the 1680- and 1673-cm^{-1} bands correspond to the same $P-D_2$ stretching modes in such a group based on comparisons to phosphine itself.[11] The appearance of new intermediate bands at 2306 and 1676 cm^{-1} in each region for the two stretching modes in the corresponding PHD group confirms that product 3 contains two equivalent hydrogen atoms. The H/D fundamental ratios for $PHF_2/PDF_2 = 2270/1654 = 1.372$ and the new species, $2310/1680 = 1.375$ and $2304/1673 = 1.377$, are comparable. The 934-cm^{-1} band is probably due to a symmetric PH_2 deformation mode; the PH_2/PD_2 ratio $934/701 = 1.332$ is reasonable for this motion. Following the 1114-cm^{-1} PH_2 bending

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Table II. Infrared Absorptions (cm^{-1}) for PH_2F in Solid Argon

PH_2F	PHDF	PD_2F	assignment	PH_2F calc[a]
2310	2306	1680	$\nu_5(a'')$, P–H(D) stretching	2317
2304	1676	1673	$\nu_1(a')$, P–H(D) stretching	2320
1090			$\nu_2(a')$, H–P–H bending	1111
934		701	$\nu_3(a')$, P–H_2 deformation	975
795		798	$\nu_4(a')$, P–F stretching	815

[a] Scaled ab initio frequencies.[10]

mode of PH_3, the 1090-cm^{-1} band is assigned to the symmetric H–P–H bending mode of PH_2F.

The assignment of one P–F and two P–H stretching fundamentals for species **3** identifies the new molecule PH_2F, which is produced on codeposition and reaction of PH_3 and F_2. Phosphinous fluoride, PH_2F, is a pyramidal molecule with C_s symmetry and with four symmetric (a′) and two antisymmetric (a″) vibrational fundamentals. With phosphine[11] used as a model, the upper P–H stretching band for PH_2F is probably due to the antisymmetric P–H stretching mode $\nu_5(a'')$ and the lower P–H stretching band is likely the symmetric P–H stretching mode $\nu_1(a')$. These assignments and those described above are summarized in Table II. The remaining antisymmetric deformation fundamental $\nu_6(a'')$ may be too weak to observe or masked by other absorptions.

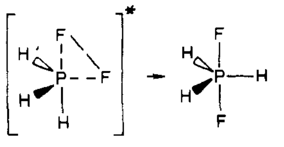
Since the gas-phase PH_2F species has not been observed, the matrix fundamentals can be used to predict gas-phase values. The stretching modes of PH_3 are blue-shifted 17 cm^{-1} by the matrix;[11] this predicts 2290 ± 10 cm^{-1} for the P–H stretching fundamentals of gaseous PH_2F. The strongest PH_3F_2 band, the antisymmetric P–F_2 stretching fundamental, is red-shifted 4 cm^{-1} by the matrix: this predicts 800 ± 5 cm^{-1} for the P–F stretching mode of PH_2F in the gas phase. Other fundamentals should exhibit small (less than 4 cm^{-1}) matrix shifts.

A final comparison must be made between the matrix observations for PH_2F and scaled frequencies calculated from an ab initio force field by using the 6-31G** basis set,[10] which appeared after the present matrix infared paper was submitted. The right-hand column in Table II compares the calculated frequencies with the matrix data. The agreement is excellent considering the accuracy of the scale factors chosen.[10] Furthermore this agreement provides strong support for the matrix identification and vibrational assignments for the new molecule PH_2F. Notice also that the calculation predicts a small blue shift for the ν_4(P–F) stretching fundamental of PD_2F, as observed. Finally, the ab initio intensities are in general agreement with the observed band absorbances although ν_2 and ν_3 are relatively weaker than predicted and the weakest band, ν_6, was not observed here.

Mechanism. The most interesting aspects of these studies are the contrasting matrix reactions of NH_3 and PH_3 with F_2 and the observation of PH_2F for the first time. The cocondensation reaction of NH_3 and F_2 gave only the NH_3- -F_2 complex, which on photolysis produced the NH_2F- -HF complex.[4] However, the PH_3 and F_2 reaction gave the three products identified below.

$$\begin{aligned} PH_3 + F_2 \rightarrow [PH_3F_2]^* &\rightarrow PH_3F_2\ (\mathbf{1}) \\ &\rightarrow PHF_2 + H_2\ (\mathbf{2}) \\ &\rightarrow PH_2F + HF\ (\mathbf{3}) \end{aligned}$$

A key element in the difference is clearly the pentavalency of phosphorus. The initially formed activated complex contains considerable excess energy (two P–F bonds – one F–F bond = approximately 120 kcal/mol)[21] and probably has the unstable structure with one axial and one equatorial fluorine, since such an initial structure would require minimum rearrangement for the original PH_3 submolecule.



(1)

It is proposed that this energized species rearranges and relaxes in the cold matrix to give the more stable[22] diaxial difluorophosphorane isomer (**1**), eliminates H_2 to give PHF_2 (**2**), or eliminates HF to produce PH_2F (**3**). On the basis of P–H and P–F stretching fundamental band absorbances (Figures 2 and 3), the markedly stronger PH_2F bands at 2310 and 2304 cm^{-1}, relative to PHF_2 at 2270 cm^{-1}, and the stronger PH_2F band at 795 cm^{-1}, relative to PHF_2 bands at 840 and 829 cm^{-1}, indicate that HF elimination is the dominant decomposition pathway. Finally, there is no evidence for a relaxed axial–equatorial PH_3F_2 species trapped in these matrices. This structure, expected to be less stable[22] than diaxial PH_3F_2, would exhibit a single axial P–F stretching fundamental between 640 and 755 cm^{-1}, which represent symmetric and antisymmetric diaxial values,[15,18] and no significant absorption was observed in this region (see Figure 3).

An alternate explanation is that PHF_2 is produced as the result of a secondary F_2 reaction with PH_2F rather than as outlined above involving the pentavalent activated complex. The detection of only a trace of PF_3 in these experiments suggests that secondary F_2 reactions make little contribution to the matrix reactions observed here.

It is also of interest that there is little evidence for a PH_2F- -HF complex. The weak 3775-cm^{-1} band could be ν_s(HF) for such a species, but even if this is the case, most of the PH_2F produced here escapes complexation by HF. This again verifies that the highly exothermic reaction occurs during condensation in the fluid matrix phase where energetic molecules can undergo more diffusion before trapping. In contrast the ammonia–fluorine reaction required photolysis of the coaxial NH_3- -F_2 complex[4,23] *in the cold matrix cage*, and the NH_2F and HF products were trapped together as NH_2F- -HF complexes in the matrix.[4]

Another interesting comparison is the PH_3 and Cl_2 matrix reaction. Machara and Ault have observed evidence for strong complex formation, but no reaction even with photolysis.[24] The analogous PH_3 and ClF reaction gave a similar result. Apparently, two electronegative fluorine atoms are required to form the pentavalent activated complex for the molecular halogen reaction with PH_3 under these matrix reaction conditions.

Substituted Phosphines. The effect of substituents on the phosphine–fluorine reaction is noteworthy. Trimethylphosphine reacts with fluorine on deposition to give trimethyldifluorophosphorane, HF, and an unidentified product. The latter bands include a probable C–F stretching mode (1067 cm^{-1}) and an F–C–X deformation mode (518 cm^{-1}), which suggest fluorine substitution for hydrogen in the precursor coupled with HF elimination. The very strong 1067-cm^{-1} (or weaker 1045-cm^{-1}) band is not likely due to CH_3F, which absorbs strongly at 1040 cm^{-1}.[25] Although the addition reaction to give $(CH_3)_3PF_2$ appears to dominate, the other reaction products are most likely to be $P(CH_2F)(CH_3)_2$ and HF. Much of the HF produced in the matrix reaction is trapped as $(CH_3)_3P$- -HF complexes. Phosphorus trifluoride is, however, not reactive with molecular fluorine during sample condensation, but ultraviolet photolysis to give fluorine atoms yielded PF_5. The inductive effect of fluorine again diminishes the reactivity of PF_3 as compared to PH_3.

Conclusion

The codeposition reaction between PH_3 and F_2 in excess argon gave three reaction products (**1**) diaxial PH_3F_2, (**2**) PHF_2, and (**3**) PH_2F, which are identified from matrix infrared spectra. Deuterium substitution verifies two equivalent hydrogen atoms and supports the vibrational assignments and this first experimental identification of phosphinous fluoride, PH_2F. Excellent agreement with scaled ab initio frequencies[10] also substantiates this spectroscopic characterization of the PH_2F molecule. The PH_3 and

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F_2 cocondensation reaction apparently proceeds through a pentavalent activated complex, which rearranges and relaxes to diaxial PH_3F_2 or decomposes to give the PHF_2 and PH_2F products on the condensing sample surface. Apparently HF elimination is the more favorable decomposition pathway as PH_2F absorptions are stronger than PHF_2 bands. In contrast, the NH_3 and F_2 cocondensation reaction produced only a coaxial NH_3--F_2 complex, which required photolysis to give the NH_2F--HF product.[4] The greater reactivity of the second-row hydride and expanded valence capability are manifested in these fluorine matrix reactions.

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Contribution from the Institüt für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Strasse 1,
D-5300 Bonn 1, West Germany, and Laboratoire de Synthêse, Structure et Rêactivitê de Molécules phosphorées, UA 454,
and Laboratoire des Organométalliques, UA 477, Universitê Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex, France

Reactivity of Phosphonitriles with Low-Coordinated Phosphorus Double-Bonded Compounds

Jürgen Böske,† Edgar Niecke,*,† Martin Nieger,† Edgar Ocando,‡ Jean-Pierre Majoral,*,‡
and Guy Bertrand*,§

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Several trapping reactions of photochemically generated phosphonitriles ($>P\equiv N$) by iminophosphanes ($-P{=}N-$) are reported. Depending on the nature of the substituents of both reaction partners, quite different products are obtained. Irradiation of bis(diisopropylamino)azidophosphine (**1a**) in the presence of (2,2,6,6-tetramethylpiperidino)((trimethylsilyl)imino)phosphane (**2a**) led to the iminophosphorane–iminophosphane **3**. In contrast, photolysis of **1a**, in the presence of [bis(trimethylsilyl)amino]-[(trimethylsilyl)imino]phosphane (**2c**) afforded the 1,3,2λ^3,4λ^5-diazadiphosphetidine **6**, which can be converted to the corresponding imino- and thiodiazadiphosphetidines **7** and **8** by using tosyl azide and sulfur, respectively. Similarly, irradiation of **1a** with the (trimethylsilyl)[bis(trimethylsilyl)amino]phosphaalkene **2d** led to the 2,4-bis(diisopropylamino)-4-[(trimethylsilyl)imino]-1,2λ^3,4λ^5-azadiphosphetidine **9**. Compound **9** reacted with sulfur, affording the corresponding thioazadiphosphetidine **10**. Addition of carbon tetrachloride to the 1,3,2λ^3,4λ^3-diazadiphosphetidine **15** gave [((diisopropylamino)chloro((trimethylsilyl)imino)-phosphoranyl)imino](diisopropylamino)phosphane (**16**), characterized at low temperature. **16** dimerized at room temperature to the diazadiphosphetidine **17**, while addition of carbon tetrachloride, at −40 °C, led to the corresponding adduct **18**. Addition of carbon tetrachloride to the 2,4-bis(diisopropylamino)-1,3,2λ^3,4λ^3-diazadiphosphetidine **19** afforded the iminophosphorane–iminophosphane **20**, which rearranged into 2-[bis(trimethylsilyl)amino]-1,3-bis(trimethylsilyl)-4-chloro-4-[(trimethylsilyl)imino]-1,3,2λ^3,4λ^5-diazadiphosphetidine (**21**). The crystal and molecular structure of $C_{24}H_{55}N_5P_2Si$ (**3**) has been determined by X-ray crystallography. The crystals of **3** are triclinic and belong to the space group $P1$ with a = 10.361 (3) Å, b = 12.308 (7) Å, c = 12.759 (6) Å, α = 89.65 (4)°, β = 82.89 (3)°, γ = 80.03 (4)°, and Z = 2. The constitution of **3** disproves the mechanism of a (2 + 2) cycloaddition in this case. A new type of rearrangement could be observed in this example: the valence isomerization of two phosphorus atoms in β positions via the 1,3-shift of an amino group.

Introduction

It has already been shown that phosphonitriles are formed in the photolysis of phosphine azides (I).[1] In the absence of trapping agents, depending on the nature of the phosphorus substituents, these phosphorus nitrogen species dimerize, trimerize, or polymerize, giving cyclodi-, cyclotri-, or cyclopolyphosphazenes,[2] or even undergo 1 → 3 migration leading to tricoordinated, pentavalent phosphorus derivatives.[3] Up to now, the study of the reactivity of phosphonitriles was rather limited: [1, 2] additions with methanol, dimethylamine, or alkylchlorosilanes; [2 + 2] cycloadditions with phenyl isocyanate or dimethyl sulfoxide; [2 + 3] cycloadditions with trimethylsilyl azide.[1,2] The reactivity of phosphonitriles ($>P\equiv N$, II) with dicoordinated phosphorus compounds ($-P{=}X$, III) was of interest since both of the reagents are potentially extremely versatile. All the reactions of phosphonitriles, previously described, involved phosphorus–nitrogen multiple-bonded character ($>P^+{=}N^-$). However, since these species can also be formulated as phosphinonitrenes ($>P-N$), nitrene-type reactivity could be expected. On the other hand, iminophosphanes ($-P{=}N-$) and phosphaalkenes ($-P{=}C<$) are known to react either via the phosphorus lone pair or through the (p–p)π double bond.[4] Thus, four possible reactions could be expected: (i) a [2 + 2] cycloaddition of the π systems of both species giving mono unsaturated four-membered rings; (ii) a [2 + 1] cycloaddition involving the phosphorus–nitrogen multiple bond of II and the phosphorus lone pair of III leading to 3,1λ^5,2λ^5-azadiphosphirines; (iii) a [1 + 2] cycloaddition of the nitrene on the (p–p)* double bond of III, affording saturated three-membered rings; (iv) a [1 + 1] addition of the nitrene on the phosphorus lone pair of III giving a tricoordinated, pentavalent phosphorus derivative.

Indeed, examples of each of reactions i–iv are observed in this work.

Experimental Section

All experiments were performed under an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^1H NMR spectra were recorded on a Bruker WM250 or a Bruker WP80 spectrometer. ^1H chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR spectra were obtained on a Bruker AC80 spectrometer at 32.43 MHz and a Varian FT80A spectrometer at 32.203 MHz. Downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. ^{13}C NMR spectra were recorded on a Bruker AC80 spectrometer at 20.15 MHz or a Varian FT80A spectrometer at 20.00 MHz. ^{29}Si NMR spectra were obtained on a Bruker AM300

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† Universitat Bonn.
‡ UA 454, Universitê Paul Sabatier.
§ UA 477, Universitê Paul Sabatier.

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