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Contribution from the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712

Lewis Base Behavior of Methylated and Fluorinated Phosphines. A Photoelectron Spectroscopic Investigation

A. H. COWLEY,* R. A. KEMP, M. LATTMAN, and M. L. McKEE

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The interaction of the phosphines PF_xH_{3-x} ($x = 0, 2, 3$) and PMe_xH_{3-x} ($x = 1, 2, 3$) with the BH_3 moiety has been investigated by UV photoelectron spectroscopy (UV-PES). Spectral interpretation was facilitated by performing semiempirical (MNDO) calculations on the free and coordinated phosphines. The "lone-pair stabilization energies" are larger for the lower symmetry phosphines with mixed substituents. In turn, this trend is a result of the fact that the lower symmetry phosphines exhibit smaller first ionization energies than expected on the basis of linear interpolation. The destabilization of the HOMO's of the less symmetrical phosphines results from interaction with lower lying MO's of the same symmetry.

Introduction

Some interesting properties are exhibited by the series of relatively simple phosphine ligands PH_3, PFH_2, PF_2H, and PF_3. First, PFH_2 is unknown and appears to have defied all attempts at its synthesis.[1] Second, the base strength of PF_2H toward the borane moiety seems to be abnormally high compared to those of PH_3 and PF_3 in the sense that the order of adduct stability is, e.g., $HF_2P{\cdot}BH_3 \gg F_3P{\cdot}BH_3 \sim H_3P{\cdot}BH_3$.[2,3] In contrast to the foregoing, the base strength of PF_2H toward nickel in Ni(phosphine)$_4$ complexes appears to be normal.[4] The primary motivation of the present work was to measure the UV photoelectron spectra (UV-PES) of the complexes $H_3P{\cdot}BH_3$, $HF_2P{\cdot}BH_3$, and $F_3P{\cdot}BH_3$[5] in order to compare them with those of the free bases. By monitoring the ionization energies (IE's) (and ergo molecular orbital (MO) energies within the framework of Koopmans' theorem[6]) of the bases prior to and after complexation, it was hoped to determine whether PF_2H exhibited any unusual features. The methylated phosphines PMe_xH_{3-x} ($x = 1, 2, 3$) were included as a reference series of bases because (i) complete structural data are available for both the free bases and their BH_3 complexes (vide infra) and (ii) proton affinity data are available[7] for PH_3 and the methylated phosphines. Semiempirical (MNDO) calculations were performed on PF_xH_{3-x} ($x = 0, 1, 2$), PMe_xH_{3-x} ($x = 1, 2, 3$), and their BH_3 complexes to facilitate the UPS interpretations.

Experimental Section

Materials. Phosphine was procured commerically and used without purification. Difluorophosphine was prepared and purified according to the method of Parry, Rudolph, et al.[8] The methylated phosphines $MePH_2$,[9] Me_2PH,[10] and Me_3P[11] and the borane complexes $H_3P{\cdot}BH_3$,[12] $HF_2P{\cdot}BH_3$,[2] $H_2MeP{\cdot}BH_3$,[13] $HMe_2P{\cdot}BH_3$,[14] and $Me_3P{\cdot}BH_3$[11] were all prepared and purified as described in the literature.

Spectroscopic Measurements. All UV-PES were recorded on a Perkin-Elmer Model PS-18 spectrometer using a He I source (21.22 eV). The volatile sample-inlet probe was used for all the compounds, and each spectrum was calibrated with xenon (12.130 eV) and argon (15.759 eV) lines. All IE's are taken to be the band maxima unless noted otherwise. Spectral resolution was maintained between 20 and 50 meV for the argon line. The liquid-nitrogen trap on the spectrometer was kept full while the samples were introduced into the system. Due to the relative instability of $H_3P{\cdot}BH_3$ in the vapor phase, it was necessary to maintain this sample at −10 °C. All other samples were introduced into the volatile probe at ambient temperature.

Computational Procedures. MNDO calculations were performed on all the compounds of concern in this paper. The MNDO method has been described in detail,[15] and the present calculations were carried out with use of the published parameters.[16]

Results and Discussion

Photoelectron Spectroscopic Assignments. The UV-PES of the free bases PH_3,[17] PF_2H,[18] PF_3,[19] $MePH_2$,[20,21] Me_2PH,[21,22] and Me_3P[20,21,23-25] have been published previously. The interpretations of the UV-PES of PH_3, PF_3, and Me_3P are widely accepted and need not be discussed further. Our proposed assignments for PF_2H, $MePH_2$, and Me_2PH are shown in Table I.

A discussion of the UV-PES of the phosphine–boranes is perhaps best based on the simplest compound of this type, $H_3P{\cdot}BH_3$. In its receptor conformation, a BH_3 group features

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Table I. MNDO-Computed Eigenvalues and Experimental UV-PES Data for PF_xH_{3-x} ($x = 0, 2, 3$), PMe_xH_{3-x} ($x = 1, 2, 3$), and Their Borane Complexes

MO	description	MNDO	IE
	(a) PH_3 and Fluorophosphines		
	PH_3		
$5a_1$	P lone pair	−11.43	10.59
2e	P-H σ	−13.56	13.6
	$H_3P{\cdot}BH_3$		
3e	B-H σ	−11.61	11.15
$7a_1$	P-B σ	−12.66	11.8
2e	P-H σ	−15.55	14.8
$6a_1$	B-H σ	−20.34	16.8
	PF_2H		
11a′	P lone pair	−12.27	11.0
10a′	P-H/P-F σ	−14.49	15.1
6a″	F lone pair	−15.54	15.8
5a″	F lone pair	−15.81	
9a′	F lone pair	−16.36	
4a″	F lone pair	−17.73	
8a′	P-F/P-H σ	−17.85	17.6
7a′	P-F/P-H σ	−21.94	18.3
	$F_2HP{\cdot}BH_3$		
14a′	P-B σ	−12.41	12.60
7a″	B-H σ	−13.04	12.25
13a′	B-H σ	−13.70	11.75
	(b) Methylated Phosphines		
	$MePH_2$		
5a′	P lone pair	−10.49	9.70
4a′	P-C σ	−11.96	12.40
2a″	methyl group	−13.37	12.70
3a′	methyl group	−14.68	14.45
	$MePH_2{\cdot}BH_3$		
7a′	B-H σ	−11.45	10.45
3a″	B-H σ	−12.11	11.03
6a′	P-B σ	−12.45	11.64
	Me_2PH		
6a′	P lone pair	−10.43	9.10
4a″	P-C σ	−12.31	12.95
5a′	P-H σ	−12.74	13.65
3a″	Me groups	−14.19	14.15
2a″	Me groups	−14.37	15.00
	$Me_2PH{\cdot}BH_3$		
5a″	B-H σ	−11.29	10.18
8a′	B-H σ	−11.31	10.76
7a′	P-B σ predominantly	−12.05	11.26
	Me_3P		
$8a_1$	P lone pair	−10.30	8.60
6e	P-C σ	−12.21	11.34
$1a_2$	localized on Me groups	−13.96	13.0–16.0
5e	localized on Me groups	−14.20	
4e	localized on Me groups	−14.87	
$7a_1$	localized on Me groups	−15.18	
	$Me_3P{\cdot}BH_3$		
5e	B-H σ	−11.20	10.15
$5a_1$	B-H σ	−11.68	
4e	P-B σ, P-C σ	−13.49	10.88

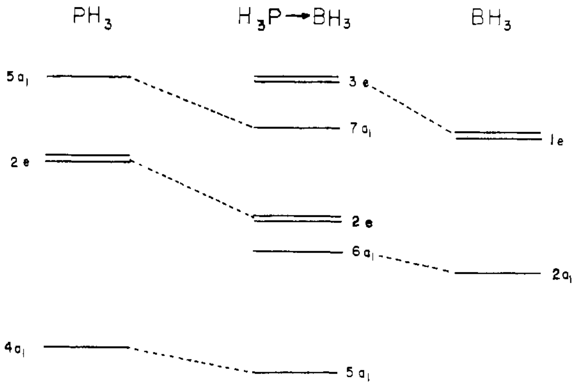


Figure 1. Qualitative scheme for the interaction of PH_3 with a BH_3 unit in C_{3v} symmetry.

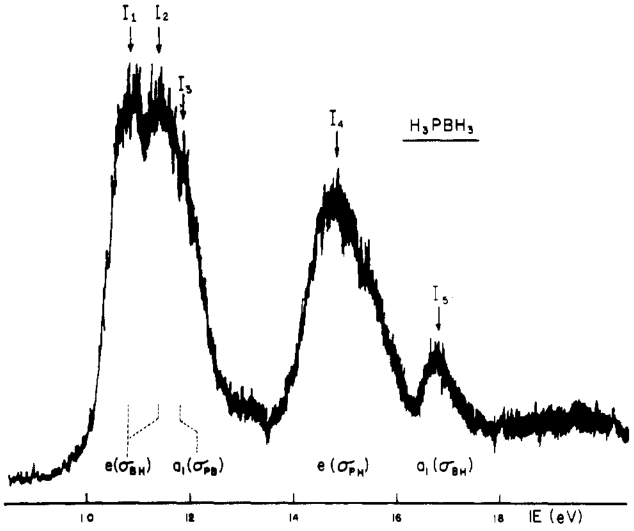
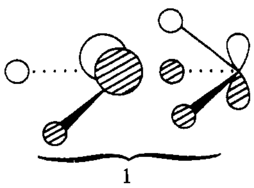


Figure 2. He I UV-PES of $H_3P{\cdot}BH_3$.

a doubly degenerate MO comprising the overlap of $2p_x$ and $2p_y$ AO's with the appropriate combinations of H 1s AO's (**1**) and a singly degenerate MO that involves overlap of the B 2s AO with three H 1s AO's (**2**). When PH_3 interacts with the BH_3 moiety, the "lone pair" MO ($5a_1$) undergoes considerable stabilization as it becomes the P→B dative bond ($7a_1$), and charge is delocalized from the donor toward the acceptor. Other lower lying valence MO's of PH_3 (2e and $4a_1$) are also stabilized upon coordination. On the other hand, the e and a_1 MO's of the BH_3 moiety, **1** and **2**, are destabilized upon coordination due to the influx of charge from the donor. As a consequence of the foregoing, the doubly degenerate BH_3 MO, **1**, becomes the HOMO (3e) in $H_3P{\cdot}BH_3$. The changes in the various MO's are summarized in Figure 1.



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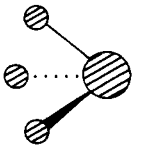

2

The UV-PES of $H_3P{\cdot}BH_3$ (Figure 2) is in excellent accord with both the qualitative considerations presented in Figure 1 and the MNDO calculations (Table I). Note that the ^2E ionic state arising from ionization from the 3e HOMO of $H_3P{\cdot}BH_3$ exhibits Jahn–Teller instability, resulting in splitting of the first UV-PES band into two components (I_1 and I_2). Peak I_3 is caused by ionization from the $7a_1$ MO, which is P→B σ bonding in character. Both the present and previous MO calculations[26,27] on $H_3P{\cdot}BH_3$ indicate that the 3e and $7a_1$ MO's are rather close in energy. Undoubtedly, this is the reason for the overlapping of peaks I_2 and I_3, not only in $H_3P{\cdot}BH_3$ but also in the other phosphine–borane complexes. The broad band I_4, with a maximum at 14.8 eV, is a result of ionization from the 2e P-H σ-bonding MO. Peak I_5 corresponds to electron ejection from the $6a_1$ borane MO, **2**. This ionization is not detectable in the UV-PES of the other phosphine–boranes because other intense peaks usually appear

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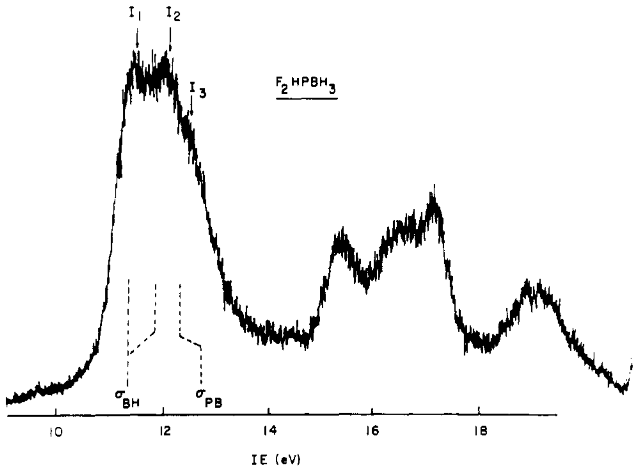

Figure 3. He I UV-PES of $F_2HP{\cdot}BH_3$.

Table II. Lone-Pair Stabilization Energies, Δa_1, for $R_3P{\cdot}BH_3$ and $R_3PCr(CO)_5$ Complexes

R_3E	$\Delta a_1(BH_3)$, eV	$\Delta a_1(Cr(CO)_5)$, eV
PH_3	1.22	0.84^b
$MePH_2$	2.04	
Me_2PH	2.16	
Me_3P	2.20	1.40^c
PF_2H	1.6	
PF_3	$\sim 0.5^a$	0.2

[a] Data from ref 5. [b] Data from ref 28a. [c] Data from ref 28d.

in this spectral region. All the MO calculations on $H_3P{\cdot}BH_3$ indicate that the $5a_1$ P 3s MO is >21.22 eV; consequently, ionization from this MO is not detectable in the He I UV-PES experiment.

The UV-PES of the other phosphine–boranes are necessarily more complex than that of $H_3P{\cdot}BH_3$. As noted by Lloyd and Lynaugh[5b] in their UV-PES study of $F_3P{\cdot}BH_3$, interpretational difficulties arise because of the closeness in energy of the B–H and P→B σ-bonding ionizations, σ_{BH} and σ_{PB}. With the exception of $F_2HP{\cdot}BH_3$, the MNDO calculations on the various phosphine–boranes (Table I) indicate that σ_{BH} is the HOMO and thus of higher energy than the σ_{PB} MO. The remarkable similarities in the UV-PES of $F_2HP{\cdot}BH_3$ and $H_3P{\cdot}BH_3$ (cf. Figures 2 and 3) suggest that the same interpretation should be used for the low-IE bands of both molecules; i.e., the MNDO-computed order for the σ_{BH} and σ_{PB} ionizations should be reversed as indicated in Table I. However, on the basis of the present evidence we cannot exclude the possibility that the MNDO-computed sequence is, in fact, correct. This ambiguity should be borne in mind in the next section, which deals with phosphine basicities.

Comments on the Trends of Basicity of Phosphines toward the Borane Unit. Coordination of phosphines to the BH_3 moiety is expected to resemble their ligative behavior toward transition metals. In both cases, stabilization of the phosphine HOMO occurs upon coordination. The "lone-pair stabilization energies", Δa_1, can be taken as crude indicators of σ-donor ability. Comparison of the data for BH_3 and $Cr(CO)_5$ complexes[28] (Table II) reveals that (i) the Δa_1 values are larger for the BH_3 complexes, indicating that σ donation is more important for the BH_3 than for the $Cr(CO)_5$ complexes, and (ii) the trends in the Δa_1 values are the same for the BH_3 and $Cr(CO)_5$ complexes.

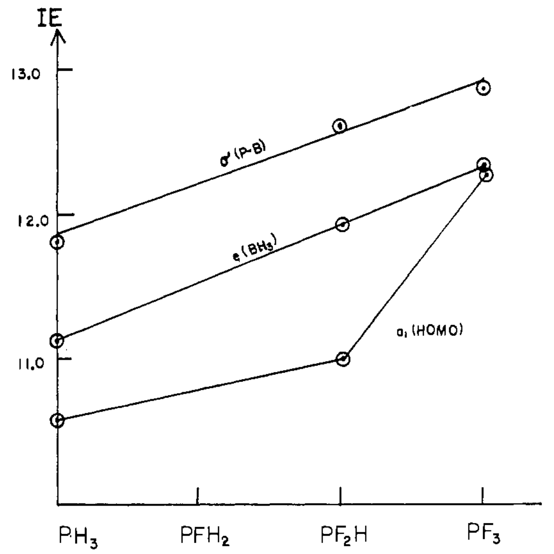

Figure 4. Ionization energies (eV) of the HOMO's of PH_3, PF_2H, and PF_3, the P→B dative bonds of the BH_3 adducts, and the BH_3 e MO's.

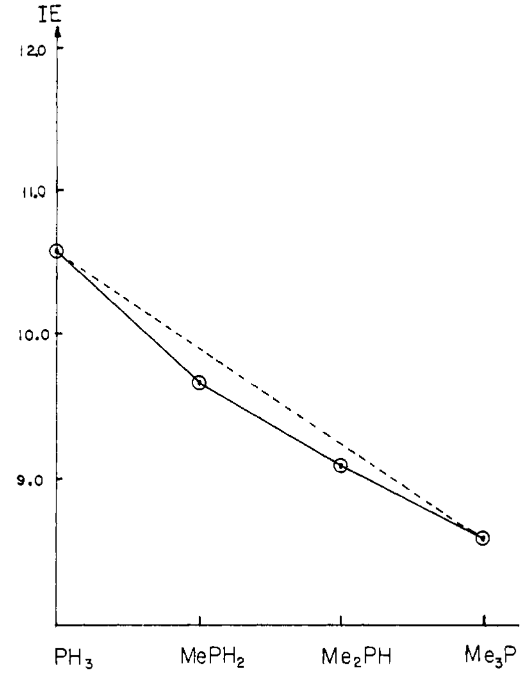

Figure 5. Ionization energies (eV) of the HOMO's of Me_xPH_{3-x}, x = 0–3.

Regarding the basicity trend, $PF_2H >> PF_3 \sim PH_3$, toward BH_3, it is interesting to compare the IE's that are associated with electron ejection from (i) the HOMO's of the uncoordinated phosphines, PH_3, PF_2H, and PF_3, (ii) the BH_3 orbitals, and (iii) the P→B dative bonds. The most obvious feature of these data (Figure 4) is the nonlinear relationship of the IE's of the HOMO's of the uncoordinated bases. Difluorophosphine exhibits a significantly smaller first IE than would be anticipated on the basis of interpolating the corresponding IE's for PH_3 and PF_3. In turn, this results in an increased lone-pair stabilization energy, Δa_1, as the HOMO of PF_2H becomes the P→B dative bond. As noted above, Δa_1 can be taken as a crude measure of the σ-donor ability of the phosphine ligand.

It could, of course, be argued that the nonlinear behavior of the lone-pair IE's of the PF_xH_{3-x} series is caused by the high value for PF_3. To investigate this question, we measured the UV-PES of the series PMe_xH_{3-x} and the corresponding BH_3

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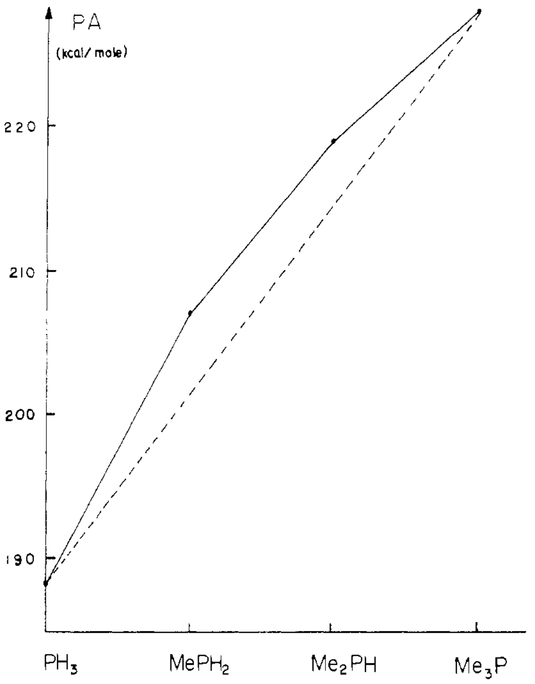

Figure 6. Proton affinities for Me_xPH_{3-x}, x = 0–3 (data from ref 7).

complexes. The relevant IE data are presented in Table I. It is immediately obvious that (i) the lone-pair IE's of $MePH_2$ and Me_2PH are somewhat smaller than anticipated (Figure 5) and (ii) the Δa_1 values are larger than anticipated on the basis of interpolation of the values for PH_3 and Me_3P. Proton affinity (PA) data are available[7] for the series PMe_xH_{3-x} (Figure 6), and it is interesting to note that the PA's of $MePH_2$ and Me_2PH are somewhat larger than would be estimated by linear interpolation of the PA's of Me_3P and PH_3. Furthermore, a similar trend is apparent in the ^{31}P–^{11}B NMR coupling constants for the BH_3 complexes of PMe_xH_{3-x}.[29] It seems, therefore, that Lewis basicity abnormalities are associated with the phosphines with mixed substituents. In most instances these slight differences in donor ability will pass unnoticed; however, when the borane complexes are of marginal stability, as in the PF_xH_{3-x} series, a difference of 2–4 kcal/mol in proton affinity will have a profound influence on the properties of the borane complex.

We turn now to the theoretical reasons for the elevated basicities of the phosphines with mixed substituents. The first point to note is that ab initio MO calculations[30] reproduce the trends in the first IE's of PH_3, PFH_2, PF_2H, and PF_3. This trend can be understood by considering the s/p ratios for the lone-pair MO's of PF_xH_{3-x}. It is particularly significant that PF_2H and PFH_2 feature somewhat lower s/p ratios than expected on a linear interpolation basis. In turn this reduction of percent s character in the phosphorus lone-pair MO accounts for the reduced first IE's of PFH_2 and PF_2H.

These basicity trends can perhaps be best understood by considering the symmetries of the MO's of the uncoordinated phosphines. When the symmetry of the base descends from C_{3v} to C_s, all MO's must transform as either a′ or a″. As a consequence, many more interactions become possible in the less symmetrical phosphines. Of particular concern is the interaction between the HOMO's of PF_2H and PFH_2 (a′ symmetry) and lower lying MO's of a′ symmetry, which results in destabilization of the HOMO. The extensive orbital mixing is clearly apparent in the composition of, e.g., the $5a_1$ (P $3p_z$ lone pair) and 2e (σ_{PH}) MO's of PH_3 compared with the corresponding MO's of PH_2F and PHF_2. In PH_3 the 2e MO features no P $3p_z$ contribution, while the a′ MO of PH_2F or PHF_2 (formerly a component of the e MO) has a significant eigenvector for P $3p_z$.

Structurally, the foregoing effects are manifested as discontinuities in the sums of bond angles at phosphorus. Thus the sums of bond angles at phosphorus in PH_3,[31] PF_2H,[32] and PF_3[32] are 280.2, 294.3, and 290.6°, respectively. A similar effect is apparent in the methylated phosphines: PH_3 (280.2°),[31] $MePH_2$ (288.4°),[33] Me_2PH (318.8°),[34] and Me_3P (295.8°).[34] The relationship between the sum of bond angles and basicity may be thought of in terms of a reorganization energy necessary for widening the X–P–X angles of the phosphine as it undergoes coordination. The species with mixed substituents, having wider bond angles, require less reorganization energy and so exhibit slightly elevated basicities. As expected, the foregoing electronic/structural considerations have other stereochemical implications. for example, the pyramidal inversion barriers of PF_2H and PFH_2 are computed to be somewhat lower than expected from a linear interpolation standpoint.[30]

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Registry No. PH_3, 7803-51-2; $H_3P{\cdot}BH_3$, 19121-56-3; PF_2H, 14984-74-8; $F_2HP{\cdot}BH_3$, 16089-15-9; $MePH_2$, 593-54-4; $MePH_2{\cdot}BH_3$, 14975-23-6; Me_2PH, 676-59-5; $Me_2PH{\cdot}BH_3$, 4268-35-3; Me_3P, 594-09-2; $Me_3P{\cdot}BH_3$, 1898-77-7; $F_3PCr(CO)_5$, 18461-42-2.

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