THE STUDY OF SUBSTITUENT EFFECTS IN INORGANIC AND ORGANOMETALLIC MOLECULES BY ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY

by

MICHAEL LATTMAN

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11/4/76
date

Chairman of Examining Committee

11/4/76
date

Executive Officer

Michael A. Weiner

Neil McKelvie

Arthur D. Baker
Supervisory Committee

The City University of New York

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GENERAL INTRODUCTION

This work consists of a series of projects involving the use of ultraviolet photoelectron spectroscopy (pes). Because of the significant differences among the systems investigated, this thesis is divided into four parts. Part I consists of a general description of the experimental techniques, apparatus, and conditions. Parts II, III, and IV are detailed discussions of the projects. Representative spectra are reproduced in the appendix.

PART I

EXPERIMENTAL TECHNIQUE

Theory

The technique of ultraviolet photoelectron spectroscopy (pes) is extremely useful in determining the electronic structure of atoms and molecules.[1] The technique involves the irradiation of a sample molecule by ionizing photons of energy $h\nu$. Electrons can then be ejected from the highest occupied molecular orbitals and their kinetic energies analyzed. The kinetic energy of the electron, T, depends on the difference between the energy of the ionizing photon ($h\nu$) and the energy required to remove the electron from its molecular orbital, i.e., the ionization potential (IP). This is Einstein's photoelectric law,

$$T_j = h\nu - IP_j \qquad (1)$$

where j refers to a specific molecular orbital. If the T_j's are measured and subtracted from $h\nu$, a series of ionization bands are recorded, arising from the various high energy molecular orbitals. This is the photoelectron spectrum.

The energy necessary to ionize the neutral molecule to the cation in its ground vibrational state is defined as the adiabatic ionization potential (IP_a). Non-adiabatic ionizations can result in the observation of vibrational fine structure on the ionization bands, which can be related to the frequency, ν, of a vibrational mode of the molecule. According to the Franck-Condon principle, the most populated vibrational level in the cation will be the one that has the closest geometry to the neutral molecule. An ionization of this type is defined as a vertical ionization potential (IP_v). This is the band maximum in a photoelectron ionization band. For

nonbonding or very weakly bonding orbitals it is usually seen that $IP_a = IP_v$. For bonding orbitals, $IP_a < IP_v$.

T. Koopmans has related the vertical ionization potential to the energy of the molecular orbital from which the electron was ejected (ϵ):

$$IP_{v,j} = -\epsilon_j. \tag{2}$$

This relationship is known as Koopmans' Theorem.[2] Although the theorem makes quite substantial assumptions, it has been very successful in interpreting photoelectron spectra. With the use of this theorem, a molecular orbital energy level diagram can be constructed from the values of the observed IP_v's. Thus, providing assignments can be made, valuable information concerning electronic structure can be derived.

There is another technique of photoelectron spectroscopy which utilizes high energy (x-ray) photons; this technique is commonly referred to as ESCA (Electron Spectroscopy for Chemical Analysis). Although the ionization process involved is the same as with pes, the type of information obtained is quite different. ESCA is used to obtain information from the core orbitals localized on the atoms in the molecules, while pes is used to investigate the valence electrons which are usually delocalized in the molecular orbitals. The ultraviolet technique has been used exclusively in the experimental portion of this thesis.

Apparatus and Experimental Conditions

All pes data was recorded on a Perkin-Elmer Model PS-18 Photoelectron Spectrometer. The instrument uses 584Å radiation (21.21 eV) from a DC Helium discharge as a source of irradiating photons ($h\nu$). A gold-plated brass cylindrical analyzer (127° curvature) is used in the instrument. Detectors of electron multiplier (EMI type 9643/2B) and channel multiplier (Mullard B419 BL) type were used. Spectra were calibrated with argon (15.759 eV line) and xenon (12.130 eV line) used as internal standards, unless otherwise noted. Resolution was usually about 20 meV (full width as half height) for the 15.759 eV argon line. This degraded to about 50 meV at times. All ionization potentials (IP's) recorded are vertical IP's and read as the peak maxima, unless otherwise noted. A direct inlet probe was used for samples which required elevated temperatures, while a volatile probe was used for samples with adequate vapor pressures at room temperature. (Table 1).

Table 1: Temperature Ranges Necessary to Obtain Photoelectron Spectra.

Compound	Temperature Range (°C)
$(RC_6H_4)_3P$	60 - 150[a]
$RC_5H_4N \cdot BH_3$	35 - 90
$RC_5H_4N{-}O$	60 - 100
$Cr(CO)_5SR_2$	25 - 35
$Cr(CO)_5PR_3$	35 - 75
RC_5H_4N	volatile probe
PR_3	volatile probe
SR_2	volatile probe

[a] $(Me_2NC_6H_4)_3P$ was run at 240°C.

PART II

ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY OF SOME SUBSTITUTED TRIARYLPHOSPHINES

Introduction

The use of pes to study the electronic structure of phosphorus compounds has grown rapidly over the past few years. Table 2 lists the vertical IP's arising from the highest occupied molecular orbitals of many of the organophosphines studied to date. IP_1 is assigned to the phosphorus "lone pair" (n_{Phos}) orbital, unless otherwise indicated, and the other IP assignments are listed in parentheses adjacent to their corresponding values.

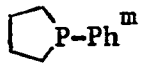
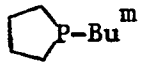
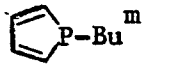
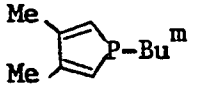
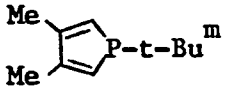
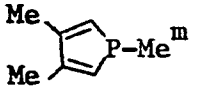
There are several effects to consider in interpreting the pes data on phosphines, i.e., how the substituents on the phosphorus atom affect the IP of the (n_{Phos}) orbital, as well as how the phosphorus atom affects the substituent IP's. One interaction arises from the inductive nature of the substituent. This interaction is transmitted through the σ framework of the molecule and is dependent on the electronegativity of the substituent: the more electronegative the substituent, the more it will withdraw density from the phosphorus atom. Thus, the n_{Phos} orbital energy is lowered, leading to a higher IP. Another, and less obvious, effect to consider is the bond angle the phosphorus atom makes with the coordinated atoms; this directly affects the "hybridization" of the phosphorus orbitals. A decrease in the bond angle results in greater s character for the lone pair on phosphorus. This stabilizes the n_{Phos} orbital and results in a higher IP. For example, the n_{Phos} IP's for $PH_3(94°)$,[3] $P(CH_3)_3(99°)$,[4] and $P(C_6H_5)_3(103°)$,[5] are 10.6, 8.6, and 7.9 eV, respectively (Table 2).

Table 2: Vertical Ionization Potentials (eV) of the Highest Occupied Molecular Orbitals of Various Organophosphines and Other Selected Phosphines.

PHOSPHINE	IP_1 [a]	IP_2	IP_3
PH_3 [b]	10.60	13.4(P-H) [c]	13.9(P-H)
PMe_3 [d]	8.63	11.3(P-C)	
PPh_3 [e]	7.92	9.20(πb_1, πa_2)	
Me_2NPCl_2 [d]	9.50(P:/N:) [c]	10.00(P:/N:)	
$(Me_2N)_2PCl$ [d]	8.25(P:/N:)	8.95(N:)	9.50(P:/N:)
$(Me_2N)_3P$ [d]	7.30(P:/N:)	7.95(N:)	8.60(N:)
Me_2NPF_2 [d]	9.60(N:)	10.50(P:)	
Et_2NPF_2 [d]	9.45(N:)	10.25(P:)	
PF_3 [b]	12.27	19.5(P-F)	
PCl_3 [b]	10.5		
PBr_3 [b]	10.0		
Me_2PH [d]	9.08		
$MePH_2$ [d]	9.72		

PHOSPHINE	IP_1 [a]	IP_2	IP_3
$t\text{-}Bu_3P$ [d]	7.70		
$t\text{-}Bu_2PH$ [d]	8.35		
$t\text{-}BuPH_2$ [d]	9.32		
Me_2PCl [d]	9.19		
$MePCl_2$ [d]	9.83		
$t\text{-}Bu_2PCl$ [d]	8.44		
$t\text{-}BuPCl_2$ [d]	9.32		
Me_2PF [d]	9.37		
$MePF_2$ [d]	10.34		
$t\text{-}Bu_2PF$ [d]	8.50		
$t\text{-}BuPF_2$ [d]	9.63		
$PhPMe_2$ [f]	8.45	$9.2(\pi a_2, \pi b_1)$	
$PhPH_2$ [f]	9.18	$9.66(\pi a_2)$	$10.32(\pi b_1)$
Ph_2PH [f]	8.29	$9.08(\pi a_2)$	$9.84(\pi b_1)$
$(C_2H_3)PBu_2$ [g]	8.25	$9.77(\pi/P\text{-}C)$ [c]	10.5(P-C)
$(C_2H_3CH_2)PBu_2$ [g]	8.20	$9.33(\pi/P\text{-}C)$	10.3(P-C)

PHOSPHINE	IP_1 [a]	IP_2	IP_3
$PhPBu_2$ [g]	8.03	8.97(πb_1/P-C)	9.2(πa_2)
$PhCH_2PBu_2$ [g]	8.09	8.72(πb_1/P-C)	9.16(πa_2)
$MePBu_2$ [g]	8.20	10.48(P-C)	
PBu_3 [h]	8.13		
$P(i\text{-}Pr)_3$ [h]	8.05		
$P(OCH_2)_3CC_2H_5$ [h]	9.8(sh) [i]		
$P(C_2H_3)_3$ [j]	8.48		
PEt_3 [j]	8.31		
$PhPCl_2$ [k]	9.7		
$(MeO)_3P$ [k]	9.0		
$(EtO)_3P$ [k]	8.8		
$(CF_3)_3P$ [l]	11.70	13.53(P-C)	
$(CF_3)_2PH$ [l]	11.50	13.21(P-C)	
$(CF_3)_2PCl$ [l]	11.13	13.61(P-C)	
$(CF_3)PH_2$ [l]	11.18	13.24(P-C)	
$(CF_3)PCl_2$ [l]	10.70	13.88(P-C)	

PHOSPHINE	IP_1[a]	IP_2	IP_3
	9.2(πb_1)	9.8(πa_2)	10.0(P:)
	8.35		
	8.25	10.55(P-C)	
	8.45(πa_2/P:)[c]	10.6(πb_1/P-C)	
	8.15(πa_2/P:)	10.20(πb_1/P-C)	
	8.05(πa_2/P:)	9.95(πb_1/P-C)	
	8.25(πa_2/P:)	10.35(πb_1/P-C)	

[a]Assigned to phosphorus lone pair (P:) unless otherwise noted. [b]Reference 26. [c]Notation: P-X = σ-bonding orbital between P and X (X = H, C, or F); P:/N: = interaction of lone pairs on nitrogen and phosphorus; π/P-C = hyperconjugative interaction between π orbital on substituent and P-C σ bond; π/P: = resonance interaction between π orbital on substituent and phosphorus lone pair. [d]Reference 6. [e]Reference 27. [f]Reference 10. [g]Reference 12. [h]Reference 28. [i]Shoulder. [j]Unpublished results from this laboratory. [k]Reference 29. [l]Reference 30. [m]Reference 31.

These differences appear to reflect the change in bond angle rather than inductive effects.

The above two effects are present with all substituents. However, when considering substituents with π or lone pair orbitals of their own, other interactions must be taken into account as well. One type is the conjugative (resonance) interaction between the n orbitals on the substituent and either the d or n orbitals on the phosphorus. Lappert and coworkers[6] have suggested that the pes of the series $(Me_2N)_nPCl_{3-n}$ (n = 1 - 3) can be interpreted on the basis of resonance interaction between the lone pairs on phosphorus and nitrogen. For example, if the molecule $(Me_2N)_2PCl$ has C_s symmetry, the nitrogen lone pairs transform as a' + a", and the phosphorus lone pair as a'. IP_1 (8.25 eV) and IP_3 (9.50 eV) are assigned to the two a' combinations while IP_2 (8.95 eV) is assigned to the a" nitrogen lone pair (Table 2). Lappert also observed[6] that in the series R_nPX_{3-n} (R = Me or t-Bu; X = H or Cl) the IP of the phosphorus lone pair changes very little with substitution of H by Cl (R kept constant). He suggested that the inductive effect of the chlorine is nearly cancelled by the resonance interaction between the chlorine and phosphorus lone pairs. However, no account was taken of any change in bond angle, and this could serve as an alternative explanation. For example, $PH_3(94°)$[3] and $PCl_3(101°)$[7] have their phosphorus lone pair IP's at 10.6 eV and 10.7 eV, respectively (Table 2). The inductive effect of the chlorine atom could counteract the effect of the bond angle change (<u>vide supra</u>), thus yielding the similar IP's.

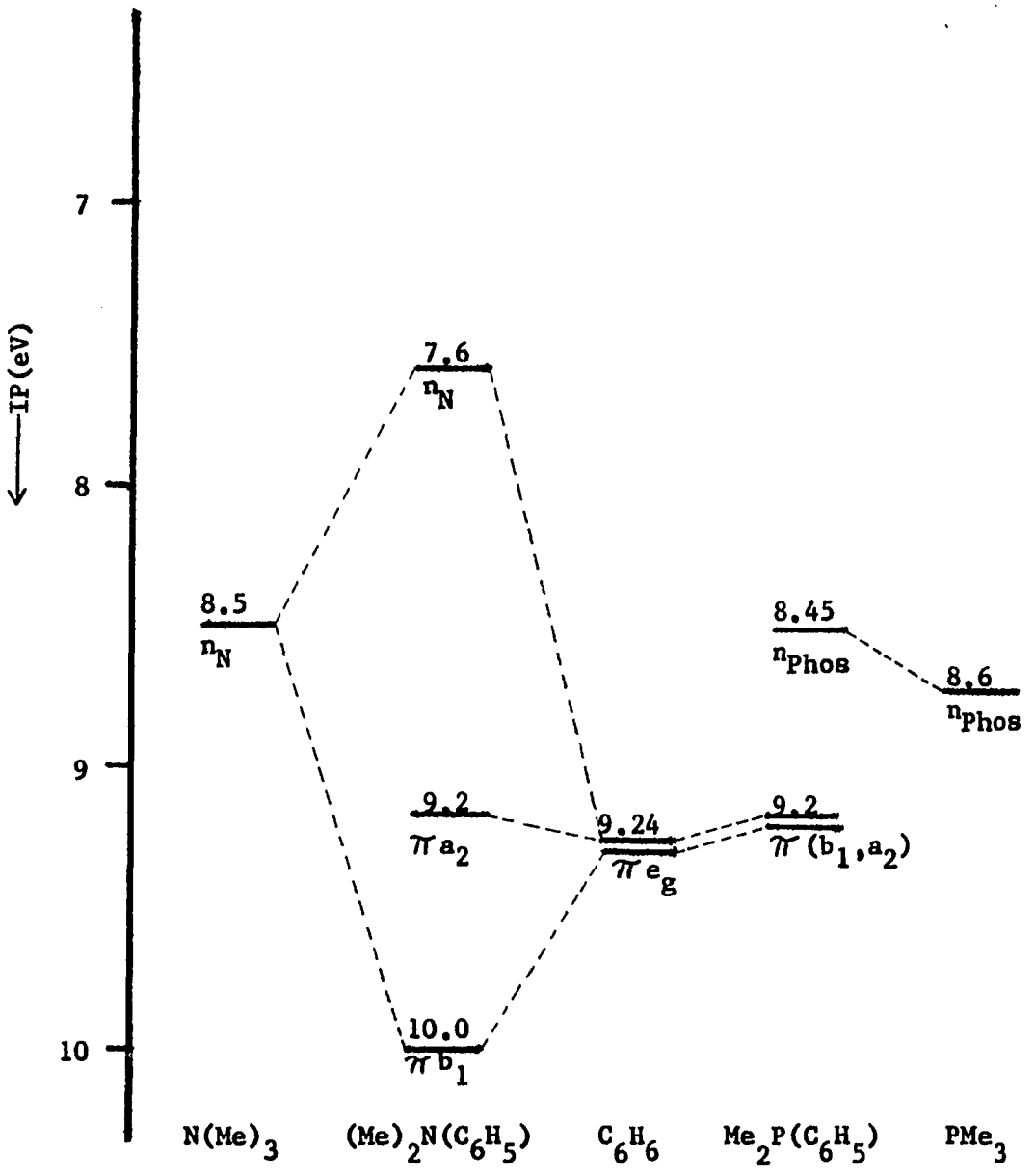
The study of interactions between the phosphorus n or d orbitals and the substituent π orbitals in unsaturated organophosphines has recently been investigated by several groups. Schäfer and Schweig[8] have interpreted the pes of dimethylphenylphosphine in terms of a complete lack of interaction between the aryl group and the trivalent phosphorus. The two highest occupied π molecular orbitals of benzene (e_g) are degenerate and their ionization occurs at 9.24 eV. Monosubstitution separates the e_g orbitals into a_2 and b_1 components (Figure 1). The b_1 orbital is capable of interacting with the substituent, while the a_2 orbital has a nodal plane through the point of substitution. If the b_1 orbital interacts with the substituent to a significant extent, a splitting of the a_2 and b_1 orbitals should be observed in the spectrum.[9] Using the benzene e_g orbitals (9.24 eV) and the trimethylphosphine n orbital (8.63 eV) as bases for the uncoupled orbital energies of the phenyl orbitals and phosphorus n orbital respectively, a correlation diagram can be constructed (Figure 2). The first two IP's of dimethylphenylphosphine occur at 8.45 eV (n) and 9.2 eV (π). The π orbitals show no splitting and their IP is virtually unshifted from benzene itself, while the phosphorus n orbital is only slightly raised in energy (0.15 eV). These results are in direct contrast to the interaction in N,N-dimethylaniline which shows a marked splitting of the a_2 and b_1 phenyl orbitals as well as a significant destabilization of the nitrogen n orbital (Figure 2). These results indicate that there are two virtually uncoupled systems in dimethylphenylphosphine: the phenyl π system and the phosphorus lone pair.

Figure 1: The Two Highest Occupied π Molecular Orbitals of Monosubstituted Benzene in C_{2v} Symmetry.[a]

b_1 a_2

[a]The circles represent the numerical value and relative sign of the coefficients on each atom. The dashed lines are nodal planes.

Figure 2: Correlation Diagram of the Highest Occupied Molecular Orbitals of Trimethylamine, N,N-Dimethylaniline, Benzene, Dimethylphenylphosphine, and Trimethylphosphine.[a]



[a] The numbers shown above the levels are vertical ionization potentials; assignments are below the levels.

In contrast to these results, Debies and Rabalais[10] observed, in the pes of phenylphosphine ($C_6H_5PH_2$), a stabilization of the phenyl π orbitals and a splitting of the a_2 and b_1 components, as well as a destabilization of the phosphorus lone pair. It was suggested that this is due to a delocalization of charge from the phenyl π orbitals into the d orbitals on phosphorus. Distefano and coworkers[11] observed a small splitting of the phenyl π orbitals in triphenylphosphine, but Rabalais[10] observed no such splitting.

Recently, another type of interaction has been detected in the pes of several unsaturated organophosphines; this is the hyperconjugative interaction between the P-C σ bond and the phenyl and alkenyl π orbitals. Schmidt and Schweig[12] have reported the pes of vinyldibutyl-, allyldibutyl-, phenyldibutyl-, and benzyldibutylphosphine and found that not only is this interaction present, but that it is the predominant effect to consider in the interpretation of the pes of these molecules. Figure 3 indicates the P-C bonds involved in vinyldibutyl- and allyldibutylphosphine. The correlation diagram using the ethylene π orbital (10.51 eV) and the methyldibutylphosphine n orbital (10.48 eV) as bases for the uncoupled orbital energies is shown in Figure 4. The π level in each phosphine now takes on P-C character and is raised in energy relative to ethylene, while the energy of the phosphorus n orbital remains relatively constant. Again, these results are in contrast to the resonance interaction in N,N-dimethylaniline where the n level is raised in energy while the π b_1 orbital is lowered. It should be noted that the hyperconjugative effect of the allyl substituent

Figure 3: P-C/π Hyperconjugation Interaction for Vinyldibutylphosphine and Allyldibutylphosphine.[a]

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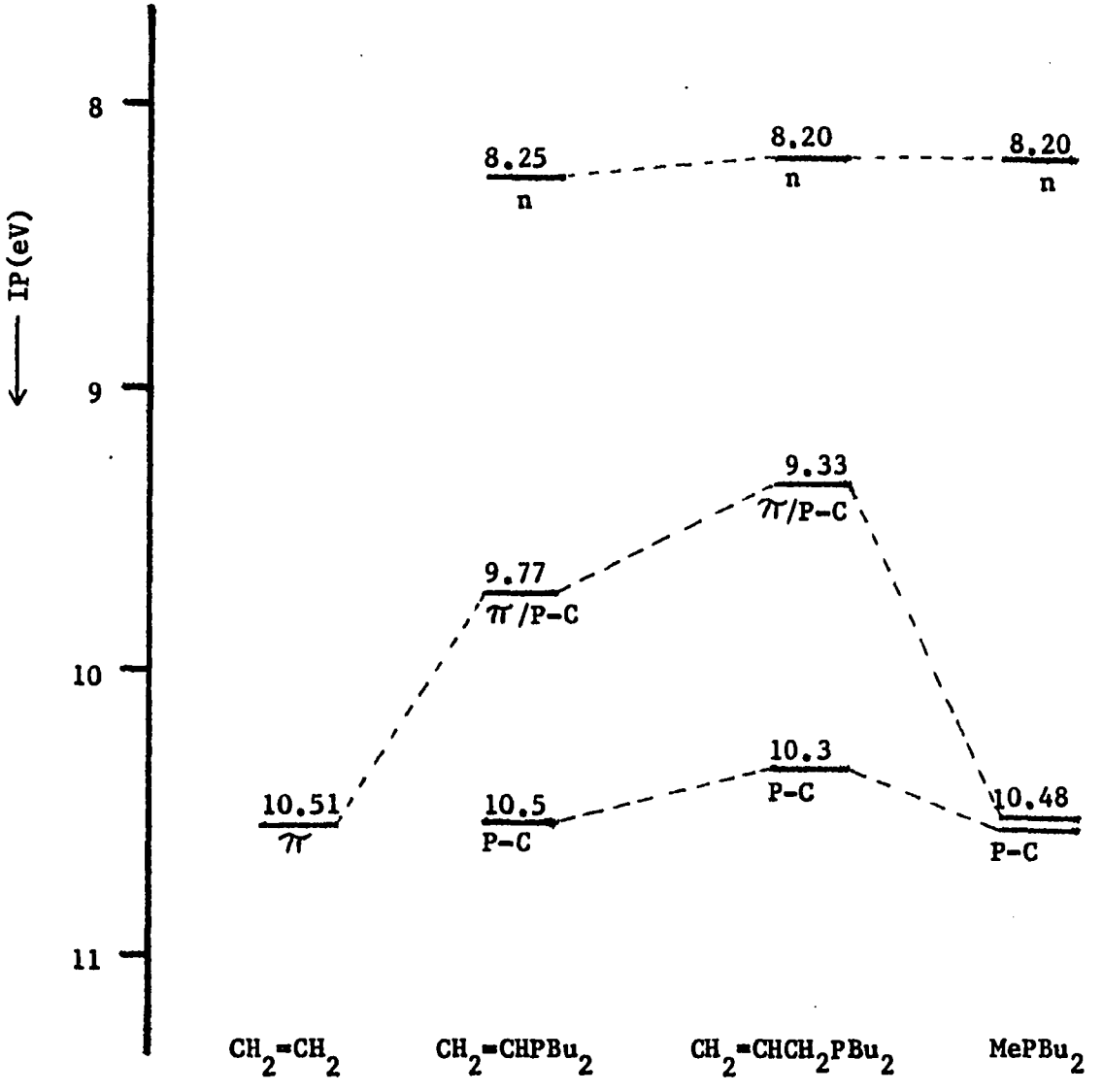
[a] The ~~~ bond indicates the P-C σ bond involved in the hyperconjugation.

Figure 4: Correlation Diagram of the Highest Occupied Molecular Orbitals of Ethylene, Di-n-butylvinylphosphine, Allyldi-n-butylphosphine, and Di-n-butylmethylphosphine.[a]



[a]The numbers shown above the levels are vertical ionization potentials; assignments are below the levels.

appears to be greater than the vinyl substituent. Similar conclusions were drawn from the pes of phenyldibutyl- and benzyldibutylphosphine.

Results and Discussion

Pes has been used to study the effect of substituents on the highest occupied MO's of benzene (Figure 1).[13-19] The types of substituents studied can be divided into three different classes. The first type acts primarily through a resonance interaction and includes substituents such as $-OCH_3$[15] and $-CH_3$.[16,19] These substituents destabilize the b_1 orbital (lower IP) relative to the a_2 orbital, the latter remaining virtually unshifted from the unsubstituted benzene (9.24 eV). A second class of substituents, such as the halogens,[16,18] shows the same resonance effect, but an electron withdrawing inductive effect is also present which stabilizes both orbitals. Thus, the order of orbital energies remains the same as with the first class, but both IP's are higher. A third class of substituents, $-C(CH_3)_3$,[20] $-Si(CH_3)_3$,[20] and $-CF_3$,[20] results in ionizations from the a_2 and b_1 orbitals which are so close in energy that they are either poorly resolved or not at all. This last case results in bond envelopes which are raised or lowered in IP from that of benzene, depending on the electron-withdrawing or -donating nature of the substituent.

The pes of the substituted triarylphosphines (Table 3) show one or more peaks in the region assigned to ionization of the phenyl π electrons in the corresponding monosubstituted benzenes

Table 3: Vertical Ionization Potentials[a] of $(RC_6H_4)_3P$.

Compd	R	IP_1[b]	IP_2[c]	IP_3[c]	IP_4
1	4-CF_3	8.65	9.8[d]	9.9	
2	4-Cl	8.18	9.16	9.63	11.40[e]
3	4-F	8.12	9.6[f]		
4	4-H	7.92	9.20		
5	4-$(CH_3)_3Si$	7.67	8.84	9.02	
6	4-CH_3	7.6	8.9[f]		
7	4-$(CH_3)_2CH$	7.53			
8	4-$(CH_3)_3C$	7.52	8.8[f]		
9	4-CH_3O	7.48	8.30	9.00	
10	4-$(CH_3)_2N$	6.9-7.0[d]	7.30[g]	8.67	9.56[h]
11	2-CF_3	8.30	9.5[d]	9.68	
12	2-CH_3	7.64	8.62	9.4[d]	
13	2-CH_3O	7.37	8.22	8.71	
14	3-F	8.32	9.2	9.6-9.7[d]	
15	3-CH_3	7.68	8.58	9.53	
16	3-CH_3O	7.72	8.35	9.03	

[a] In eV. [b] Phosphorus lone pair. [c] Phenyl π electrons. [d] Shoulder. [e] Chlorine lone pair. This band is accompanied by a shoulder at 11.7 eV, also assigned to a chlorine lone pair. [f] IP_2 and IP_3 are unresolved. The value listed is the maximum of the resulting peak. [g] Ionization apparently from $(CH_3)_2N$ lone pair. [h] Assigned to an ionization from a phenyl π orbital.

(Table 4). In most cases the number of IP's observed in this region corresponds to the number of IP's observed for the monosubstituted benzene. In addition to these, a low IP band is observed in each of the spectra, which is readily assigned, as by the previous authors,[8,10] to ionization from the lone pair of electrons on phosphorus.

Although the complexity of the molecules studied appears to inhibit the use of vibrational fine structure in assigning the bands in the phenyl region, it seems likely that the band assignments for the triarylphosphines generally correspond to the assignments made for the monosubstituted benzenes. The following reasons are apparent:

(1) In almost all cases, and independent of the nature of the substituent, the IP's assigned to the phenyl electrons in $aryl_3P$ correspond closely to the IP's found for the monosubstituted benzene. Particularly, in the case of $aryl_3P$ substituted with methoxy and dimethylamino groups, the separation of ionizations from the a_2 and b_1 orbitals is so large that it is unlikely that the assignments could be reversed upon substitution into the phosphino system, with one energy level raised and the other lowered from the value in the monosubstituted benzene.

(2) There is no great change in the phenyl IP values among the ortho, meta, or para isomers with a given substituent. The effect of substitution into the phosphino system on the relative a_2 and b_1 IP's would be expected to vary with the position of substitution.

(3) In the $aryl_3P$ containing CF_3, $(CH_3)_3C$, and $(CH_3)_3Si$

Table 4: Vertical Ionization Potentials[a] of RC_6H_5.

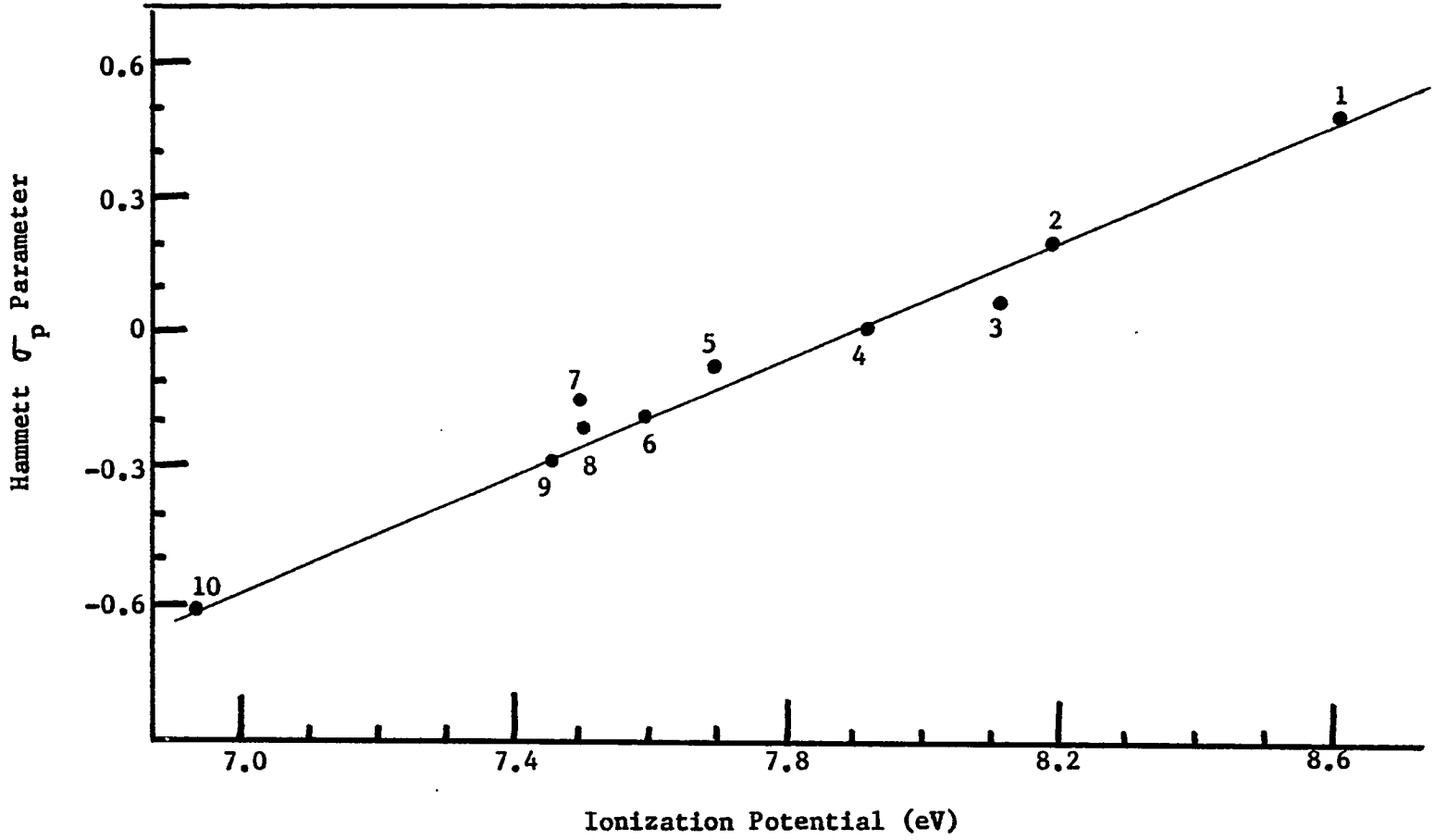
R	IP_1[b]	IP_2[b]	IP_3[b]
CF_3[c]	9.7		
F[d]	9.11(b_1)	9.82(a_2)	
Cl[c,e]	9.1(b_1)	9.7(a_2)	11.32[f]
H	9.24		
$(CH_3)_3Si$[c]	9.0[g]	9.3[g]	
CH_3[d]	8.72(b_1)	9.24(a_2)	
$(CH_3)_3C$[c]	9.0		
CH_3O[h]	8.42(b_1)	9.21(a_2)	
$(CH_3)_2N$[h]	7.45(b_1)[i]	9.00(a_2)	9.85(b_1)

[a] In electron volts. [b] Assignments in parentheses. [c] Reference 20. [d] Reference 16. [e] Reference 18. [f] Chlorine lone pair. Accompanied by a band at 11.7 eV also assigned to a chlorine lone pair. [g] Two components of the band envelope were attributed to IP_1 and IP_2 by R. A. N. McLean, Can. J. Chem., 51, 2089 (1973). [h] Reference 15. [i] Ionization apparently correlates with $(CH_3)_2N$ lone pair.

substituents, the ionizations from the a_2 and b_1 phenyl orbitals are not resolved. This is also true for the corresponding substituted benzenes. Therefore there is no evidence here that the relative energies of the a_2 and b_1 orbitals are changing much upon substitution into the phosphino system.

The phosphorus lone pair IP values appear to be a well behaved function of the electron-donating or -withdrawing nature of the substituents. A very good correlation (correlation coefficient 0.986) is observed between the Hammett σ_p parameter[21] and the lone pair IP of phosphorus (see Figure 5) for the ten compounds with para substituents. In this case, σ_p is a measure of the total effect of the substituent (both inductive and resonance) on the attached aryl ring, but excludes direct resonance interaction between the aryl system and the phosphorus atom (see page 27 for a further discussion). The inductive electron-withdrawing nature of the fluorine and chlorine atoms is indicated, but the effect is apparently partially cancelled in the para derivatives by the electron-donating resonance effect, which places charge on the ring position adjacent to the phosphorus, and causes some lowering of the lone pair IP. In the m-fluoro derivative the resonance effect is submerged, and the result is a noticeable raising of the phosphorus lone pair IP. The strong resonance effect of the p-dimethylamino and p-methoxy substituents enhances the electron density adjacent to the phosphorus, and the result is a pronounced lowering of the IP value, whereas the somewhat higher value for the m-methoxy derivative is consistent with the diminished resonance effect at the meta ring position.

Figure 5: Correlation of Ionization Potential of the Phosphorus Lone Pair with the Hammett σ_p Substituent Constant for $(p\text{-}RC_6H_4)_3P$.[a]



[a]The numbers on the points correspond with the compound numbers in Table 3.

The electron-donating effect of the alkyl groups is expected, but the lack of any change in the lone pair IP's among the ortho, meta, and para methyl derivatives should be noted. Despite the inductive effect of the $(CH_3)_3Si$ group, it appears to be only a modest electron donor, poorer than the alkyl groups. This phenomenon is well documented[22] and is believed to be due to an electron-withdrawing component in the behavior of the silicon, in which charge from the aromatic ring is delocalized into the d π orbitals of the silicon.

The results of this study show that while the effect of the substituted aryl groups on the phosphorus lone pair electrons is easily rationalized, there is little apparent effect of the phosphorus on the π orbital energies of the aryl system. This observation is independent of the nature of the aryl substituent. This would appear to rule out any substantial resonance effect between the phosphorus lone pair of electrons and the filled π orbitals of the ring, or any substantial stabilization of the phenyl π orbitals by interaction with the phosphorus d orbitals. The lack of resonance interaction is consistent with the finding of Schäfer and Schweig.[8] More generally, there is little evidence that the trivalent phosphorus acts as a significant electron donor or acceptor toward an attached aryl group.[23]

It appears that the possibility of π/P-C hyperconjugation can be eliminated since this interaction would destabilize the b_1 orbital relative to the a_2 orbital in the phosphine, and the difference between their respective IP's would be greater than in the monosubstituted benzene.

It is suggested that the correlation between the phosphorus lone pair IP values and the substituent σ^-_p values should be discussed in terms of the effect of the substituent on the energy difference between the ground state and the cationic state (analogous to the consideration of σ^-_p as measuring the effect of the substituent on the energy difference between the ground state and a charged transition state[21]). This effect is determined largely by the action of the substituent on the developing charge at the "reaction site" (here the phosphorus atom). In this case migration of electrons from the substituted aryl groups to the positive phosphorus center would result in a stabilization of the cation. Thus, not only would lower lone pair IP's result than those expected from Koopmans' Theorem,[24,25] but the magnitude of the charge migration (and therefore lowering of the IP) is related to the σ^-_p value of the substituent. The lack of deviation from the normal σ^-_p correlation, particularly on the part of the dimethylamino and methoxy substituents, argues against any enhanced resonance interaction between the substituents and the positive phosphorus center, and therefore the drift of charge would be through the P-aryl σ bond. On the other hand, the ability of the trivalent phosphorus to effect significant stabilization of the radical cation, produced by ionization from the aryl π orbitals, appears to be quite limited.

It should be noted that any correlation between phosphorus lone pair IP's and substituent σ^-_p values assumes no significant

difference in hybridization at the phosphorus among the para-substituted $aryl_3P$. Thus the effects discussed above are not extended here to a comparison between the $aryl_3P$ and other phosphines.

PART III

ULTRAVIOLET PHOTOELECTRON SPECTRA OF 4-SUBSTITUTED PYRIDINE-BORANES

Introduction

The bonding interaction of pyridine in Lewis acid-base systems has been of concern in this laboratory.[32] In view of this, we sought to study the interactions of a series of substituted pyridines in their borane adducts by pes. This study could shed some light on the question of the Lewis basicity of pyridine. The pyridine boranes form a class of complexes sufficiently volatile and stable in the gas phase to study with the use of pes.

In the only other pes study on borane complexes, Lloyd and Lynaugh[33] have reported the pes of a series of alkylamine complexes, $H_nMe_{3-n}N{\cdot}BH_3$ (n = 0 - 3). They assign the first ionization band (ca. 10 - 10.4 eV) to the BH_3 group of the complexes on the basis of observed vibrational fine structure and CNDO/2 calculations. Considering only the pyrimidal BH_3 structure, the BH_3 group gives rise to a_1 and e symmetry orbitals. The first band in the spectra is assigned to ionization from the e orbitals since the a_1 orbital contains substantial boron 2s character and must lie at a higher IP (15-19 eV[33]). The second band is assigned to the B-N bonding orbital and represents a stabilization of about 3 eV from the lone pair IP in the corresponding uncomplexed amines.

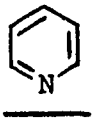
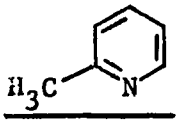
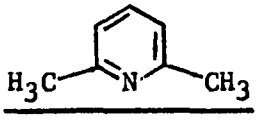
Previous evidence concerning the Lewis basicity of pyridine relative to alkylamines has not produced a satisfactory answer as to which acts as the stronger base under a variety of circumstances. The pK_a data shows that pyridine (pK_a = 5.2) is a weaker base than the saturated aliphatic amines (pK_a = 9 - 11).[34] This fact can be rationalized by considering the differences in hybridization at the

nitrogen atom in pyridine (sp^2) and the aliphatic amines (sp^3). The "lone pair" orbital with more s character will hold the pair of electrons closer to the nucleus, resulting in a reduction of the donor power of the nitrogen base. However, this data only measures basicities relative to the aqueous proton. Once other acids are used, or basicity in the gas phase is considered, the evidence indicates that this order of base strengths does not remain constant.

A recent gas phase proton affinity (PA) study by Taft and coworkers[35] shows that the proton affinity for pyridine (PA = 225 kcal) is greater than that for ammonia (PA = 207 kcal) and comparable to aliphatic amines, for example Me_2NH (PA = 225 kcal). The authors suggest that solvation effects, and in particular differential polarization of the π orbitals in the pyridinium ion, can account for these results. The positively charged proton causes the electron density of the pyridine π orbitals to shift towards the nitrogen, leading to a greater electrostatic attraction between the acid and base. This is submerged in solution where the dielectric effect of the medium causes an attenuation of polarization phenomena.[35,36]

An important factor to consider in determining base strengths towards acids other than the proton is the steric effect. Brown has shown[37] (Table 5) that, although the pK_a increases for the series pyridine < 2-picoline < 2,6-lutidine (due to inductive effects), the heats of formation (ΔH) for the corresponding complexes of BH_3, BF_3, and BMe_3 decrease in the order pyridine >

Table 5: Comparison of Pyridine, 2-Picoline, and 2,6-Lutidine with Various Reference Acids.[a]

Measurement	Acid			
pK_a	H	5.17	5.97	6.75
$-\Delta H$[b]	$\frac{1}{2}(BH_3)_2$	20.2	19.7	16.4
$-\Delta H$	BF_3	33.3	31.6	25.8
$-\Delta H$	BMe_3	21.4	16.1	No Reaction

[a]Table reproduced from reference 37. [b]$-\Delta H$ (kcal/mole) in nitrobenzene solution for reaction Base(sol) + Acid(sol) → Complex(sol).

2-picoline > 2,6-lutidine. The effect on ΔH becomes more pronounced as the steric requirements of the acid increase: $BH_3 < BF_3 < BMe_3$. He suggests that, even with borane, the steric interaction between the methyl groups on the pyridine and the acid is enough to significantly affect ΔH.

Thermochemical data on the heats of reaction of aliphatic amines and pyridine with various Lewis acids should give an insight into the strength of the B-N bond. However, consistent data under identical conditions is hard to find. Table 6 lists the heats of reaction for Me_3N and C_5H_5N with BF_3,[38] BH_3,[38] and BMe_3.[39] It should be noted that the values for the C_5H_5N complexes were obtained in nitrobenzene solution, whereas the other values were obtained in the gas phase. Brown and Horowitz[40] suggest that the different phases may have little effect on the value of ΔH, but this suggestion is open to question in light of the differences between pK_a and PA values (<u>vide supra</u>). Nevertheless, the data does show Me_3N and C_5H_5N to be comparable in basicity.

Mooney and coworkers[41] have reported the base strength of pyridine to be greater than triethylamine towards the boron trihalides (BF_3, BCl_3, BBr_3). The authors maintain that the donor ability of a base (or the acceptor ability of an acid) can be correlated with ^{11}B NMR chemical shift data. As the basicity is increased, the electron density at the boron increases, leading to a greater difference between the ^{11}B chemical shift of the complexed and free boron trihalide ($\Delta\delta$). Table 7 lists the data and shows that the $\Delta\delta$ value for C_5H_5N is consistently greater than

Table 6: Heats of Reaction (ΔH) of Me_3N and C_5H_5N with BMe_3, BH_3, BF_3.

BASE	ACID	PHASE	$-\Delta H$[a]
Me_3N	BMe_3	gas	17.6
C_5H_5N	BMe_3	gas	17.0
Me_3N	BH_3	gas	31.5
C_5H_5N	BH_3	solution[b]	32.5
Me_3N	BF_3	gas	30.9[c]
C_5H_5N	BF_3	solution[b]	32.9

[a] kcal/mole. [b] nitrobenzene solution. [c] Another value of 26.6 has been suggested (Ref.38).

Table 7: ^{11}B Chemical Shifts (δ) for $C_5H_5N \cdot BX_3$ and $Et_3N \cdot BX_3$ (X = F,Cl,Br) in Acetone Solution.[a]

X	$\delta_{complex}$[b]		δ_{acid}[b]	$\Delta\delta$[c]	
	$C_5H_5N \cdot BX_3$	$Et_3N \cdot BX_3$	BX_3	$C_5H_5N \cdot BX_3$	$Et_3N \cdot BX_3$
F	+0.3	-0.2	-9.7	+10.0	+9.5
Cl	-8.0	-10.0	-47.6	+39.6	+37.6
Br	+7.1	+5.1	-40.0	+47.1	+45.1

[a] Table taken from reference 41. [b] ppm from external Me_2OBF_3.

[c] $\Delta\delta = \delta_{complex} - \delta_{acid}$.

the value for Et_3N.

These results have been criticized because ^{11}B chemical shifts are dependent on other factors as well.[42] However, in support of the evidence, the data (Table 7) also shows that the relative acidities of the boron trihalides increase in the order $BF_3 < BCl_3 < BBr_3$, and this order is well known.[42]

Finally, Hillier and coworkers[43] measured the core electron binding energies of the boron 1s orbital in $C_5H_5N \cdot BF_3$ and $C_2H_5NH_2 \cdot BF_3$ by x-ray photoelectron spectroscopy (ESCA). The authors suggest that the absolute value of the B 1s orbital energy should reflect the donor ability of the base; the greater the donation, the more destabilized the B 1s orbital (lower binding energy). Their results for the B 1s binding energies of $C_5H_5N \cdot BF_3$ and $C_2H_5NH_2 \cdot BF_3$ are 194.5 eV and 194.8 eV, respectively. This difference of 0.3 eV, they maintain, is enough to indicate that pyridine is a better base. Although conclusions drawn from a difference of 0.3 eV with such large absolute values may be questioned, their conclusion is also supported by ab initio and semi-empirical molecular orbital calculations.[43]

The above discussion summarizes some of the previous evidence concerning the relative basicities of pyridine and aliphatic amines. Although not conclusive, the evidence does indicate pyridine to be as good a base as aliphatic amines, if not better. It should also be pointed out that in no investigation (except for the pK_a data) was pyridine found to be a weaker base than aliphatic amines.

It is possible that the hyperconjugative interaction, peculiar to the acid BH_3, can influence the apparent base strength of pyridine. This effect can be defined as a $\sigma - \pi$ interaction between the B-H σ orbitals on the acid and the π -type orbitals on the base. Hyperconjugation has been invoked to explain the existence of $OC \cdot BH_3$ and $F_3P \cdot BH_3$ and the nonexistence of $OC \cdot BF_3$, $F_3P \cdot BF_3$, and $F_3N \cdot BF_3$. Hyperconjugation provides a mechanism whereby electron density from the B-H σ bonds can be delocalized into the vacant π^* ($OC \cdot BH_3$) or 3d($F_3P \cdot BH_3$) orbitals on the base, thus stabilizing the molecule. The existence and extent of hyperconjugation in borane complexes has been a subject of some controversy over the years,[33,44,45] but it is an interaction to be considered when dealing with complexes of borane.

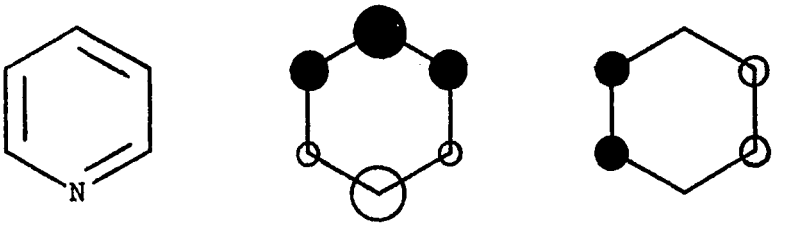
Before proceeding to the results of the present study, mention should be made of the band assignments in the pes of the uncomplexed pyridine, since the assignments have produced somewhat of a controversy over the past few years.[46,47,48] Table 8 lists the first three IP's of various uncomplexed 4-substituted pyridines. The assignment of the first two IP's has been the point in question. However, recent experimental evidence [46,47] supports the assignments of Heilbronner,[48] where the first ionization arises from the "lone pair" (n) orbital on nitrogen and the second and third ionizations from the a_2 and b_1 orbitals, respectively (Figure 6). These latter two π orbitals are derived from the degenerate e_g π orbitals (IP = 9.24 eV) of benzene and are split in the reduced symmetry of

Table 8: Vertical Ionization Potentials[a] of RC_5H_4N.

R	IP_1[b]	IP_2[c]	IP_3[d]
4-H[e]	9.60[f]	9.75	10.50
4-CH_3[e]	9.50[f]	9.60	10.05
4-$(CH_3)_3C$[e]	9.3[f]	9.5[f]	9.7
4-CF_3	10.1[f]	10.26	11.12
4-NO_2	10.4[f]	10.48	

[a] In eV. [b] Assigned to the n orbital. [c] Assigned to the a_2 orbital. [d] Assigned to the b_1 orbital. [e] References 47, 48. [f] Shoulder or overlapping band.

Figure 6: The Two Highest Occupied π Molecular Orbitals of Pyridine.[a]



b_1 a_2

[a]Based on MINDO/2 calculations from this laboratory.

pyridine ($D_{6h} \rightarrow C_{2v}$). The stabilization of both orbitals arises from the electronegative nitrogen ring heteroatom; the b_1 orbital is stabilized to a greater extent since this orbital has density at the nitrogen ring position (Figure 6). This assignment, $n(IP_1)$, $a_2(IP_2)$, and $b_1(IP_3)$, is the one we have adopted.

Assignments and Substituent Effects

The IP values of the 4-substituted pyridine-boranes are listed in Table 9. The pes of pyridine-borane shows three assignable peaks below 12 eV, and this pattern persists for most of the substituted pyridine-boranes as well. Exceptions are the methoxy derivative where IP_2 and IP_3 overlap, and those derivatives where ionization from substituent orbitals (or orbitals with significant substituent character) interfere with the assignment of IP_3. Assignments were made with the aid of a MINDO/2 calculation[49] on pyridine-borane, with appropriate parameters chosen for the calculation of the B-N, B-H, and B-C resonance integrals. Not only was the assigned order of IP's from the BH_3 group and the pyridine a_2 and b_1 π orbitals in agreement with the calculated order, but the calculated energy of stabilization of the pyridine a_2 and b_1 π orbitals upon complexation was in agreement with the experimentally found increase in the IP's. The calculated stabilizations of the a_2 and b_1 orbitals were 0.64 eV and 1.15 eV respectively, while the experimental increases were 0.88 eV and 1.38 eV respectively (Tables 8, 9, and references 48, 49). The order of energy levels from

Table 9: Vertical Ionization Potentials[a] of $RC_5H_4N \cdot BH_3$.

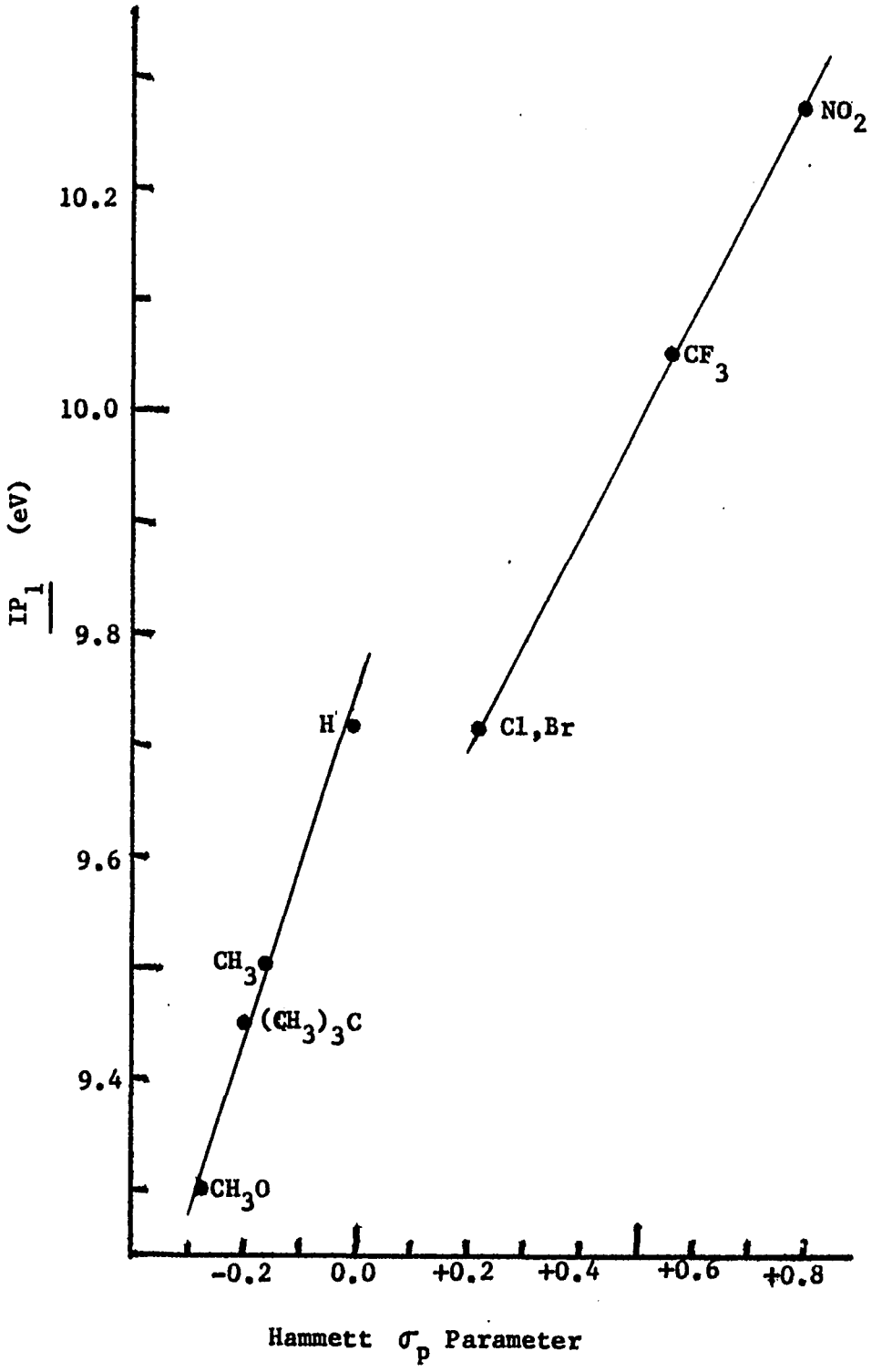
R	IP_1[b]	IP_2[c]	IP_3
4-CH_3O	9.30	10.5[d]	
4-$(CH_3)_3C$	9.45	10.30	11.21[e]
4-CH_3	9.50	10.45	11.41[e]
4-H	9.72	10.63	11.88[e]
4-Cl	9.71	10.84	11.37[f]
4-Br	9.71	10.82[g]	11.07[f]
4-CF_3	10.04	11.02	12.3[e]
4-NO_2[h]	10.27	11.25	

[a] In eV. [b] BH_3 group - see text. [c] Ring a_2 orbital - see text. [d] IP_2 and IP_3 are unresolved. The value listed is the maximum of the resulting peak. [e] Assigned to b_1 orbital, largely localized on the ring. [f] Significant admixture of halogen lone pair character. Additional bands at 12.32 (chloro compound) and 11.59 (bromo compound) also assigned to halogen lone pair. [g] Shoulder. [h] Additional IP's from 11.9-12.5 due to the NO_2 group.

calculations using the PRDDO[50] technique (partial retention of diatomic differential overlap) was also consistent with the assigned order of IP's.

The first band in the spectra is assigned to ionization from the e orbitals of the BH_3 group (vide supra). This ionization is in the same region as the corresponding vertical IP in the spectra of the methylamine-boranes.[33] However, no vibrational fine structure on this band was observed for the pyridine complexes, whereas fine structure was observed for the methylamine complexes.[33] In the reduced symmetry of the pyridine complex, the degeneracy of the e orbitals is split, with one of the components having π symmetry suitable for interaction with the ring b_1 π orbital. However no splitting of the peak was observed, consistent with the result of the MINDO/2 calculation on pyridine-borane, which showed the splitting to be only of the order of 0.1 eV. An attempted correlation between the IP_1 values of the substituted pyridine-boranes and the σ^-_p values[21] of the substituents resulted in the two regression lines (Figure 7). The CH_3O, H, and alkyl substituents gave $IP = 1.52\ \sigma^-_p + 9.73$, with no IP value more than 0.03 eV from the regression line, while the halo, CF_3, and NO_2 substituents gave $IP = 1.02\ \sigma^-_p + 9.48$, with no IP value more than 0.01 eV from the regression line (see Figure 7). The smaller slope in the relationship involving the electron withdrawing substituents shows that their effect is clearly diminished. The presence of the electron withdrawing $>N\text{-}BH_3$ group reduces the effect of the electron withdrawing groups in the para position. Examples of this phenomenon

Figure 7: Correlation of IP_1 with the Hammett σ_p Substituent Constant for $RC_5H_4N \cdot BH_3$.

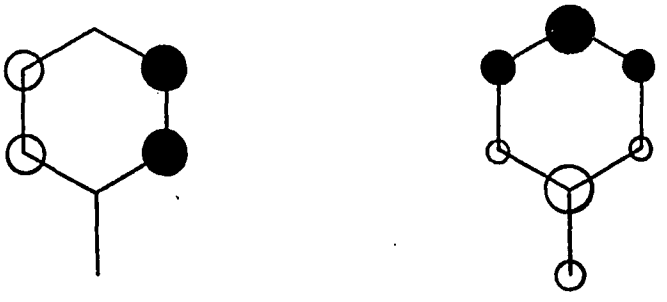


appear in the chemistry of both 4-substituted pyridines,[51] and para disubstituted benzenes.[52] The same effect was observed in an attempted correlation between the IP_1 values and the pK_a values of the corresponding substituted pyridines.

The second band in each spectrum is assigned to the ring a_2 orbital (Figure 8), with the exception of the methoxy derivative (see discussion above). The increase in IP_2 upon complexation of pyridine, 0.88 eV, is in the same range as the increases found for the alkyl, CF_3 and NO_2 derivatives, 0.75-0.9 eV. The chloro compound is not included because there is no real resolution of the first three bands in the spectrum of 4-chloropyridine.[53] The IP_2 and σ_p values are correlated by one regression line (vide infra), $IP = 0.88\,\sigma_p + 10.58$ (Figure 9), where all IP values are within 0.06 eV of the regression line, except for the t-butyl derivative (0.11 eV).

The third band in the spectra of the alkyl and CF_3 derivatives is assigned to ionization from the b_1 π orbital (Figure 8). The increase in IP_3, upon complexation of the pyridine, ranges from 1.2 eV for the CF_3 derivative to 1.5 eV for the t-butyl derivative. Moreover, the value of IP_3 is more sensitive to the substituent than the other assigned IP's (with the CF_3 group again showing a decreased electron withdrawing effect). This would be consistent with the assignment of IP_3 to an orbital with a large value at the 4-position. The results obtained with IP_3 are in contrast to the smaller increase of IP_2 upon complexation, and the smaller substituent effect. This is consistent with the assignment of IP_2 to

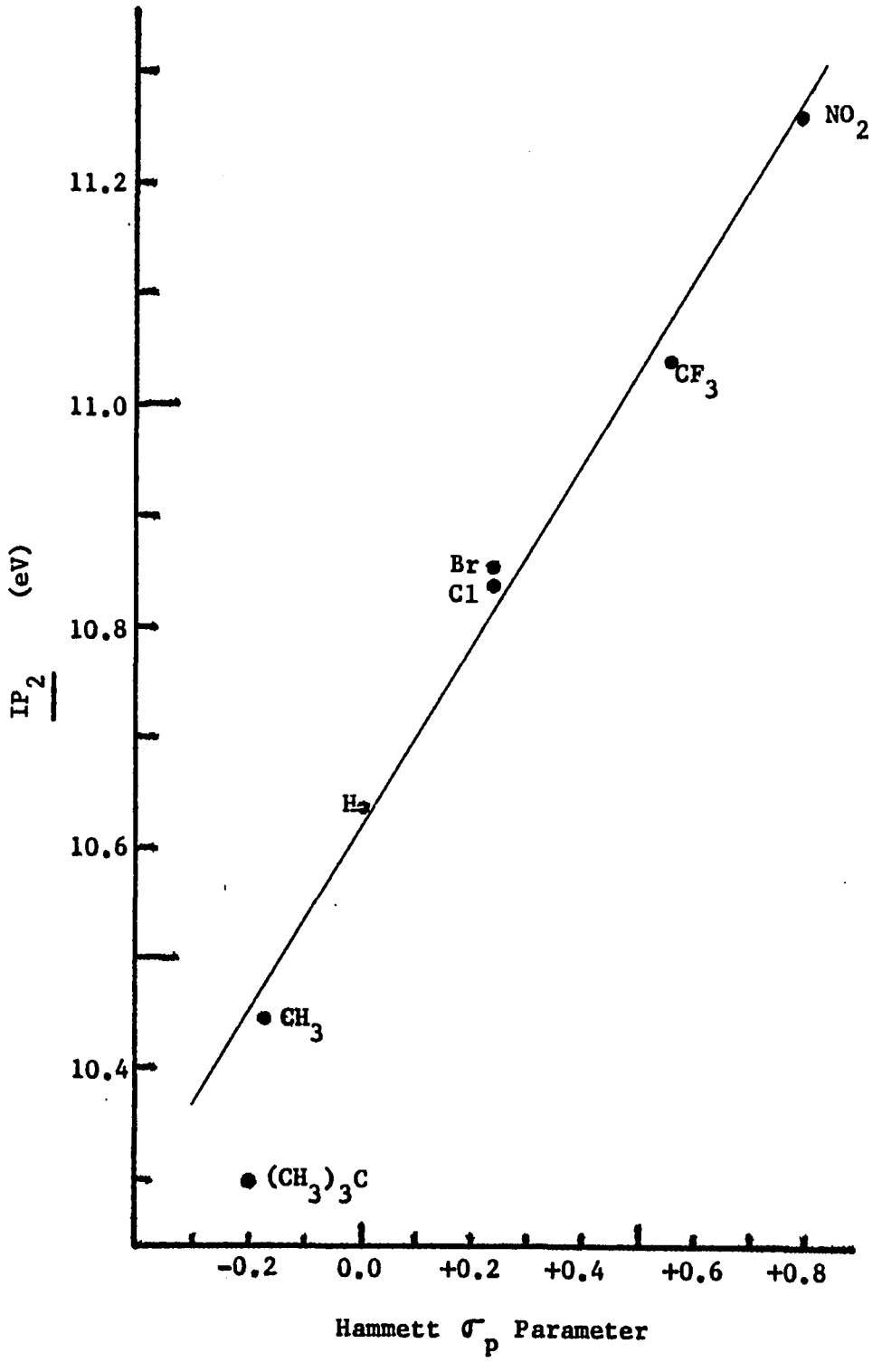
Figure 8: The Two Highest Occupied π Molecular Orbitals of $C_5H_5N \cdot BH_3$.[a]



a_2 b_1

[a]Based on MINDO/2 calculations from this laboratory.

Figure 9: Correlation of IP_2 with the Hammett σ_p Substituent Constant for $RC_5H_4N \cdot BH_3$.



the ring a_2 orbital containing a nodal plane through positions 1 and 4, with the substituent exerting only an inductive effect. The nature of the a_2 ring orbital also seems responsible for the single regression line relating IP_2 with σ_p.

One difficulty in the present study is the lack of any separately observable band due to the highest occupied a_1 orbital, which contains significant nitrogen lone pair character in pyridine and B-N bonding character in the borane complex. A reasonable estimate of the stabilization of the pyridine a_1 orbital upon complexation would place the IP from the a_1 orbital of the pyridine-boranes in the region discussed in this paper. This is based on the MINDO/2 calculation and the pes of $NH_3 \cdot BH_3$ or the alkylamine-boranes.[33] It would seem likely, therefore, that either IP_2 or IP_3 contains an unresolved component due to the a_1 orbital.

Discussion

The results of this study indicate that there is no significant interaction between the π system on pyridine and the π component of the BH_3 group orbitals. The lack of any observed splitting of the e orbitals (IP_1) suggests that the energy of the π component is not perturbed by the ring any more than the other component. The results of the MINDO/2 calculation show that the π component of the e orbitals is largely localized on the BH_3 group (80%) while the b_1 ring orbital (Figure 8) contains little BH_3 character (15%). Moreover, the lack of deviation from the σ_p correlation, particularly on the part of the methoxy substituent, argues against

any enhanced resonance interaction between the substituents and the BH_3 group.[54,55] An attempted correlation of IP_1 with σ_p^+ was unsuccessful.

A comparison of the IP's of the BH_3 e orbitals in the pyridine and methylamine[33] adducts could give an insight into the relative donor abilities of the two Lewis bases. A comparison of the corresponding B-N σ bonding IP's might be a better probe, but this orbital is not observed in the pyridine-borane spectra. The vertical IP's of the BH_3 e orbitals in the two complexes are 9.72 eV and 10.01 eV[33] for $C_5H_5N \cdot BH_3$ and $Me_3N \cdot BH_3$, respectively. These values show that the BH_3 e orbitals in the pyridine complex are of higher energy than those of the trimethylamine complex.

These results may indicate that pyridine is a better base towards borane. It donates electron density through the σ system to a greater extent, resulting in greater density in the BH_3 e orbitals, leading to a lower IP. However, this explanation is difficult to accept in view of the traditional "hybridization" concept.

An alternative explanation could be the variation in the H-B-H bond angle in the complexes. As this angle decreases (less s character) the IP would also be expected to decrease. Although the H-B-H bond angle in $Me_3N \cdot BH_3$ is known (112°),[56] unfortunately the corresponding angle in $C_5H_5N \cdot BH_3$ is not. The F-B-F bond angles for the BF_3 complexes have been measured, however. The wider angle has been found for the C_5H_5N complex (110°)[57] compared to the Me_3N complex (107°).[58] If this difference can be extended to the corresponding boranes, the pes results would be the opposite of

those expected.

The results might also be rationalized in terms of steric effects since the Me_3N could be considered the bulkier group. Although steric interaction cannot be ruled out by the present study, it seems unlikely that methyl groups attached to the nitrogen would sterically interact to any significant extent with the borane hydrogens. It is suggested, therefore, that the apparent increased basicity of pyridine in this study is due to the availability of the extra electron density contained in the π system of the ring. Polarization of the π system could shift electron density to the ring nitrogen, analagous to the polarization found in the pyridinium ion[35] (vide supra). If this polarization occurs in the ground state, the electrons in the BH_3 e orbitals should be easier to ionize on account of electron-electron repulsion. If it takes place in the radical cation, a stabilization of the cation would lead to a lower IP, i.e., Koopmans' Theorem fails. It should again be pointed out that any direct π interaction between C_5H_5N and BH_3 in the complex, even in the cation, has already been ruled out. This study cannot differentiate between polarization in the ground or cationic state, but stabilization of the cation seems more intuitively reasonable.

Comparison with Pyridine N-Oxide

The results of this study can be compared to the results of our previous work on 4-substituted pyridine N-oxides[25] (Table 10). The assignments here were originally based on SCF calculations on pyridine

Table 10: The Vertical Ionization Potentials (eV) of RC_5H_4N-O.

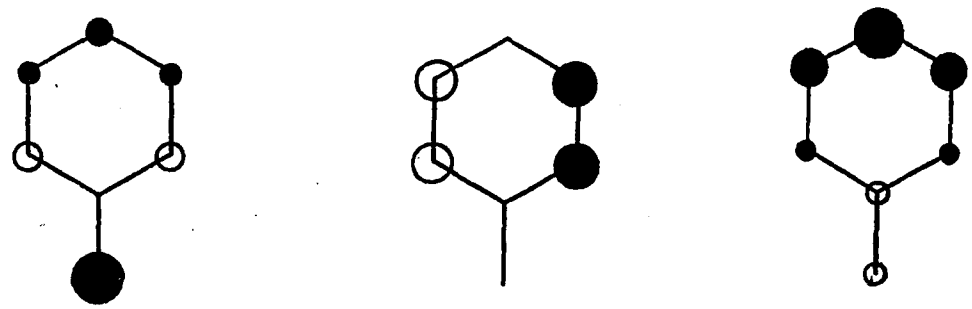
R	IP_1[a]	IP_2[b]	IP_3[c]	IP_4[d]
4-CH_3O	7.89	8.96	10.17	10.54
4-$(CH_3)_3C$	8.00	9.03	9.95	11.00
4-CH_3	8.17	9.09	10.13	11.19
4-H	8.46	9.34	10.36	11.59
4-Cl	8.51	9.48	10.61	-[e]
4-Br	8.44	9.44	-[e]	12.24
4-CF_3	8.90	9.76	10.80	12.03

[a] πO: ($3b_1$) orbital; [b] σO: (b_2) orbital; [c] πa_2 orbital; [d] π $2b_1$ orbital; [e] Halogen lone pair ionizations interfere.

N-oxide by Kobinata and Nagakura,[59] calculations by Kubota,[60] and the behavior of the various IP's with different substituents. Subsequently, our assignments of IP_1 and IP_2 were shown to be in the reverse order to assignments made with the help of MINDO/2 calculations and He II (40.82 eV) excitation.[61] The results in Table 10 reflect, obviously, the corrected order. IP_1, IP_3, and IP_4 are assigned to ionizations from the three highest occupied π molecular orbitals, $3b_1(\pi O:)$, a_2, and $2b_1$, respectively (Figure 10). IP_2 is assigned to the σ lone pair on oxygen ($\sigma O:$). IP_1 arises from the overlap of the oxygen lone pair of π symmetry and the b_1 orbital of pyridine; however, this orbital is highly localized on the oxygen (Figure 10).

It is of interest to compare IP_3 of the N-oxide with IP_2 of the borane, both due to the a_2 orbital, and IP_4 of the N-oxide with IP_3 of the borane, both due to the b_1 orbital with mostly ring character (Table 11). Although the increases, Δa_2 and Δb_1 (Table 11), are smaller for the N-oxides than for the boranes, the relative stabilizations of the a_2 and b_1 orbitals in the two systems are consistent. The smaller increases upon N-oxide formation are not consistent with the calculated results on the two systems.[62] Therefore, it appears that the ionization of the ring π electrons in the N-oxide is lowered in energy through stabilization of the incipient cation by the neighboring oxygen electrons. This seems to reflect the greater availability of electron density in an oxygen lone pair p π orbital relative to the density available in the BH_3 σ bonding orbitals directed away from the ring π system.

Figure 10: The Three Highest Occupied π Molecular Orbitals of Pyridine N-Oxide.[a]



$3b_1$ a_2 $2b_1$

[a] Based on MINDO/2 calculations from this laboratory.

Table 11: The Relative Stabilizations[a] of the RC_5H_4N π Molecular Orbitals Upon N-Oxide Formation and Complexation with BH_3.

	Δa_2[b]		Δb_1[b]	
R	N-O	BH_3	N-O	BH_3
4-H	0.61	0.88	1.09	1.38
4-CH_3	0.53	0.85	1.14	1.36
4-$(CH_3)_3C$	0.45	0.8	1.3	1.51
4CF_3	0.54	0.76	0.91	1.18

[a] In eV. [b] $\Delta = IP_{complex} - IP_{base}$.

Preparation of Compounds

Pyridine-borane was obtained from the Aldrich Chemical Company and used after the removal of excess pyridine in vacuo. 4-Picoline and 4-t-butylpyridine were purchased (Aldrich) and used without further purification. 4-Trifluoromethylpyridine was a gift from Dr. W. A. Sheppard of Dupont. 4-Methoxypyridine was prepared by the reduction of 4-methoxypyridine N-oxide with PCl_3.[63] 4-Nitropyridine* was prepared by the reduction of 4-nitropyridine N-oxide with a mixture of H_2SO_4 and HNO_3.[64] 4-Chloro- and 4-bromopyridine were obtained by adding aqueous KOH to chilled solutions of the corresponding hydrochlorides and extracting the products with ether. The ether solution was dried and the solvent removed immediately before use. $BF_3 \cdot Et_2O$ was distilled at 39°C (7 mm) and stored under prepurified nitrogen.

4-Methoxypyridine N-oxide, 4-t-butylpyridine N-oxide, 4-picoline N-oxide, and pyridine N-oxide were purchased commercially. All were sublimed under vacuum. 4-Bromo- and 4-chloropyridine N-oxides were prepared from 4-nitropyridine N-oxide and the corresponding acetyl halide according to the procedure of Itai.[65] 4-Trifluoromethylpyridine N-oxide was prepared by the oxidation of 4-trifluoromethylpyridine with hydrogen peroxide in acetic acid.[66]

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*CAUTION: One should be careful not to let 4-nitropyridine come in contact with the skin since it is likely to give disagreeable burns, sometimes causing severe reddening and blistering.

All the N-oxides were dried over P_2O_5 immediately before their spectra were recorded. Transfer to the photoelectron spectrometer was done as quickly as possible.

Melting points were measured with a Thomas Hoover Capillary Apparatus. Elemental analyses were performed by Galbraith Laboratories, Incorporated, Knoxville, Tennessee 37921, and Schwarzkopf Microanalytical Laboratory, Woodside, New York 11377.

Synthesis of $RC_5H_4N \cdot BH_3$:

The substituted pyridine-boranes were prepared by the method of Mooney and Qaseem.[54] Diborane was generated by the dropwise addition of $BF_3 \cdot Et_2O$ to $NaBH_4$ in diglyme and bubbled into a stirred pentane solution of the substituted pyridine. About 5 - 10 minutes after the reaction had begun, a white precipitate of the borane complex came out of the pentane solution. The reaction was stopped after diborane bubbling had ceased. The product was filtered, washed four times with pentane, and treated under vacuum to remove the pentane. The yield is virtually quantitative. The complexes were purified by vacuum sublimation (Table 12). The compounds are all air stable except for the nitro derivative which is not only air sensitive, but unstable thermally (exploding in the sublimation apparatus!) and was used without purification. Table 12 gives the analytical data on the compounds prepared for the first time, as well as the sublimation temperatures.

In a typical synthesis, 7.1g (0.050 mole) of $BF_3 \cdot Et_2O$ was added dropwise to a mixture of 1.2g (0.032 mole) of $NaBH_4$ in 15 ml of diglyme to generate the B_2H_6. The B_2H_6 was bubbled into a solution

Table 12: Analytical Data on the Pyridine Boranes Prepared for the First Time.

Substituent	m.p.(°C)	% C		% H		% N		Approximate Sublimation Temperature[a,b]
		Calcd.	Found	Calcd.	Found	Calcd.	Found	
4-CH_3O	92-95	58.61	58.72	8.20	8.31	11.39	11.33	80
4-$(CH_3)_3C$	115-117	72.53	72.58	10.82	10.92	9.40	9.30	70
4-Br	151-152 (dec.)	34.95	35.20	4.11	4.17	8.15	7.67	80
4-Cl	140-142 (dec.)	47.15	47.21	5.54	5.49	11.00	10.97	80
4-CF_3	79-82	44.78	44.62	4.39	4.35	8.71	8.70	50
4-NO_2	ca. 133 (dec.)	43.54	43.92	5.12	4.60	20.31	20.08	--[c]

[a] °C at 0.05mm. [b] $CH_3C_5H_4N \cdot BH_3$ = 60°C. [c] Do not sublime.

of 1.86g (0.020 mole) of $4\text{-}CH_3C_5H_4N$ in 50 ml of pentane. Care was taken during the reaction to allow unreacted B_2H_6 to pass from the reaction flask, through an oil bubbler, and into a stream of running water. The entire setup was placed in a fume hood and the apparatus purged with nitrogen both before and after the reaction.

PART IV

AN INTRODUCTION TO THE STUDY OF SUBSTITUENT EFFECTS IN TRANSITION METAL CARBONYLS BY ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY

Historical

Most of the transition metal complexes that have been studied by pes have been either organometallics or metal carbonyls. These are virtually the only complexes with enough volatility to study with this technique. This discussion will focus on carbonyls, substituted carbonyls, and related compounds (excluding metal-olefin bonded complexes), and will point out some of the information available from the study of transition metal complexes with pes.

One of the main conclusions drawn from pes work on transition metal complexes has been that Koopmans' Theorem often does not correctly predict the relative IP values in the photoelectron spectrum (sometimes even failing to predict the proper order).[67,68] This fact apparently arises from the difference in relaxation energies (i.e., the stabilization of the cation through electronic rearrangement) of the orbitals localized on the metal, relative to metal-ligand and pure ligand orbitals. The greater the relaxation energy, the more stabilized is the cation. This leads to an observed IP lower than that predicted by Koopmans' Theorem. This phenomenon is evident when ground state molecular orbital calculations are carried out to interpret pes data on complexes containing filled metal d orbitals.[67] Hillier and coworkers[69] investigated the isoelectronic species $Ni(CO)_4$, $Co(CO)_3NO$, and $Fe(CO)_2(NO)_2$. The pes results are listed in Table 13. The first two ionization bands in the spectrum of $Ni(CO)_4$ exhibit an intensity ratio of 3:2, respectively. This would be expected from

Table 13: Experimental Vertical Ionization Potentials and Orbital Energies from Ab Initio and Δ SCF Calculations.[a]

Complex	Pes[b]	Ab Initio[b]	Δ SCF[b]	Assignment[c]
$Ni(CO)_4$	8.90	11.7	7.0	t_2
	9.77	13.5	7.8	e
$Co(CO)_3NO$	8.90	8.7	6.7	8e(M-L)
		12.9	6.7	$8a_1$
	9.82	14.1	7.8	7e
$Fe(CO)_2(NO)_2$	8.97	8.7	7.9	$6b_1$(M-L)
		9.1	8.1	$10a_1$(M-L)
	8.56	12.6	7.5	$6b_2$
	9.74	15.1	9.4	$9a_1$
		16.0	9.6	$3a_2$

[a] Table taken from reference 69. [b] In eV. [c] Assigned to metal d orbitals unless otherwise indicated; M-L = metal-ligand (NO) mixing.

a d^{10} configuration in a system of T_d symmetry, and is in qualitative agreement with ground state ab initio calculations which show the t_2 orbitals to be of higher energy than the e orbitals (Table 13). However, the spectrum of $Co(CO)_3NO$ also shows the same 3:2 intensity ratio, whereas the ab initio calculations predict a 2:1:2 ratio, where the order of levels is $8e > 8a_1 > 7e$, with the $8a_1$ and 7e lying close in energy. These calculations also show the two highest occupied orbitals (8e) of the nitrosyl complex contain considerable ligand (mainly NO) character, followed by the three orbitals ($8a_1$ and 7e) of mainly metal d character. In order to try to resolve the discrepancy in the $Co(CO)_3NO$ spectrum, direct calculations on the ion states were performed. The results indicate the extremely large relaxation energies associated with orbitals of mainly metal character (ca. 5 - 6 eV) relative to the other orbitals (ca. 1 - 2 eV). The values in Table 13 (ΔSCF) are the improved calculated IP's obtained by taking the difference between the molecular and ionic state electronic energies. The greater relaxation energies of the $8a_1$ and 7e orbitals in $CO(CO)_3NO$ lowers their IP and places the $8a_1$ IP in near coincidence with the 8e IP. This accounts for the 3:2 intensity ratio in the spectrum. Similar arguments were made to interpret the pes of $Fe(CO)_2(NO)_2$ (Table 13). The Δ SCF calculations give excellent agreement with the observed spectra in this region. Thus, for $Ni(CO)_4$, although the ground state calculations predicted the order of IP's found in the spectrum, the relative IP values were different than the

calculated relative energies. The Δ SCF calculations yield much better agreement, where the calculated relaxation energies for the t_2 (74% metal character) and e (90% metal character) orbitals are 4.7 and 5.7 eV, respectively.

Thus, it seems that on account of the failure of Koopmans' Theorem, determination of absolute metal d orbital energies from their IP values is of little use without Δ SCF calculations. However, if systems are chosen such that all members of a series are expected to have the same basic orbital compositions, the effects of Koopmans' Theorem deviations should, in large part, be cancelled out. Nixon[70] has used this idea to compare the bonding properties of CO and PF_3 in the corresponding Cr^0, Fe^0, and Ni^0 complexes (Table 14). It can be seen that the IP trends of the CO and PF_3 complexes parallel each other, with the PF_3 complexes having slightly larger IP's. This may indicate the higher positive charge on the central metal atom due to the stronger electron withdrawing properties of PF_3. The larger t_2 - e splitting of the d orbitals in $Ni(PF_3)_4$ than in $Ni(CO)_4$ may also indicate a slightly better π acceptor ability for the PF_3 ligand. Moreover, the phosphorus "lone pair" (σ_{ML}) IP's vary in the order $Cr(PF_3)_6 < Fe(PF_3)_5 \leqslant Ni(PF_3)_4 < Rh(PF_3)_4H \approx Pd(PF_3)_6 < Pt(PF_3)_4$. This may indicate that σ-donation increases on going from Cr to Pt in this series.[71,72] Lloyd and coworkers[72] have interpreted the pes of the series $M(PF_3)_4$, where M = Ni, Pd, Pt, in terms of the Pt complex having both the strongest σ-bonding and the strongest π-bonding interactions (Table 14).

Table 14: Vertical Ionization Potentials (eV) of Selected Carbonyls and Related Transition Metal Complexes.[a]

Complex	IP_1	IP_2	IP_3	IP_4
$Ni(CO)_4$[b]	8.90(t_2)	9.77(e)		
$Co(CO)_3NO$[b]	8.90(e, a_1)	9.82(e)		
$Fe(CO)_2(NO)_2$[b]	8.56(b_2)	8.97(a_1, b_1)	9.74(a_1, a_2)	
$Cr(CO)_6$[c]	8.40(t_{2g})			
$Cr(PF_3)_6$[d]	9.0 (t_{2g})	12.7 (σ_{ML})		
$Fe(CO)_5$[e]	8.60(e)	9.86(e)		
$Fe(PF_3)_5$[d]	8.9 (e)	10.2 (e)	13.0 (σ_{ML})	
$Ni(PF_3)_4$[f]	9.69(t_2)	10.74(e)	13.17(σ_{ML})	
$Pd(PF_3)_4$[f]	9.9 (t_2)	12.2 (e)	13.7 (σ_{ML})	
$Pt(PF_3)_4$[f]	9.83(t_2)	12.45(e)	14.54(σ_{ML})	
$Rh(PF_3)_4H$[d]	9.7 (e)	11.8 (e)	13.7 (σ_{ML})	
$Mn(CO_5)H$[g]	8.85(e)	9.14(b_2)	10.55(σ_{ML})	
$Mn(CO)_5CH_3$[g]	8.65(e)	9.12(b_2)	9.49(σ_{ML})	

Complex	IP_1	IP_2	IP_3	IP_4
$Mn(CO)_5SiH_3$[g]	8.99(e)	9.38(b_2)		
$Mn(CO)_5GeH_3$[g]	8.90(e)	9.26(b_2)		
$Mn(CO)_5SiMe_3$[g]	9.0 (e)	9.3 (b_2)		
$Mn(CO)_5SiF_3$[h]	9.8 (e, b_2)	10.4 (σ_{ML})		
$Re(CO)_5SiH_3$[g]	9.1 (e) 8.9 sh[i]	9.5 (b_2)	9.6 (σ_{ML})	
$Re(CO)_5GeH_3$[g]	9.13(e) 8.9 sh[i]	9.4 (b_2)	9.6 (σ_{ML})	
$Co(CO)_4H$[g]	8.90(e)	9.90(e)	11.5 (σ_{ML})	
$Co(CO)_4SiH_3$[g]	8.85(e)	9.90(e)		
$Co(CO)_4GeH_3$[g]	8.80(e)	9.80(e)		
$Mn(CO)_5CF_3$[j]	9.17(e)	9.51(b_2)	10.53(σ_{ML})	
$Mn(CO)_5Cl$[j]	8.87(e)	9.5 (b_2)	10.46(e_L)	11.08(σ_{ML})
$Mn(CO)_5Br$[j]	8.83(e)	9.5 (b_2)	10.14(e_L)	10.79(σ_{ML})
$Mn(CO)_5I$[j]	8.40) (e_L) 8.71)	9.65(b_2, e)		10.36(σ_{ML})
$Re(CO)_5Cl$[j]	9.06(e)	9.91(b_2)	10.83(e_L)	11.23(σ_{ML})

Complex	IP_1	IP_2	IP_3	IP_4
$Re(CO)_5Br$[j]	8.83, 9.06 (e_L)	9.94(b_2)	10.52(e)	10.90(σ_{ML})
$Re(CO)_5I$[j]	8.36, 8.78 (e_L)	9.71(b_2)	10.02(e)	10.44(σ_{ML})
$Re(CO)_5H$[j]	8.89, 9.15 (e)	9.51(b_2)	10.47(σ_{ML})	
$Re(CO)_5CH_3$[j]	8.71, 8.93 (e)	9.51(b_2, σ_{ML})		
$Cr(CO)_6$[c]	8.40(t_{2g})			
$Mo(CO)_6$[c]	8.50(t_{2g})			
$W(CO)_6$[c]	8.56(t_{2g}) 8.30sh[i]			
$Cr(CO)_5NH_3$[k]	7.56(e)	7.85(b_2)		
$Cr(CO)_5NMe_3$[k]	7.45(e)	7.76(b_2)	10.57(σ_{ML})	
$Cr(CO)_5PH_3$[k]	7.90 sh (e)	8.03(b_2)	11.43(σ_{ML})	
$Cr(CO)_5PMe_3$[k]	7.58 sh (e)	7.72(b_2)	10.00(σ_{ML})	
$Cr(CO)_5CNMe$[k]	7.61 sh (e)	7.77(b_2)		
$W(CO)_5NH_3$[k]	7.75(e) 7.54 sh[i]	8.06(b_2)		

Complex	IP_1	IP_2	IP_3	IP_4
$W(CO)_5NHMe_2$[k]	7.62(e) 7.41 sh[i]	7.95(b_2)	11.14(σ_{ML})	
$W(CO)_5NMe_3$[k]	7.62(e) 7.41 sh[i]	7.96(b_2)	10.75(σ_{ML})	

[a]Assignments are in parentheses adjacent to IP value; assignments are metal d orbitals unless otherwise indicated: σ_{ML} = metal - ligand (non - CO) σ orbital; e_L = e orbitals of halides. [b]Reference 69. [c]Reference 82. [d]Reference 70. [e]Reference 97. [f]Reference 72. [g]Reference 73. [h]Reference 74. [i]Shoulder due to spin-orbit splitting. [j]Reference 75. [k]Reference 83.

Cradock, et. al.[73,74] have interpreted the pes of the series $Mn(CO)_5L$ (L = SiH_3, GeH_3, $SiMe_3$, SiF_3) and $Re(CO)_5L$ (L = SiH_3, GeH_3) in terms of the absense of (d $\longrightarrow$ d) π-bonding. Both the e and b_2 levels of the above complexes are stabilized from the levels in the hydride and methyl complexes (Table 14) and they suggest that only σ-bonding is involved, since (d $\longrightarrow$ d) π-bonding should stabilize only the e orbitals. Similar conclusions, i.e., no π-bonding, were drawn from the pes of $Co(NO)_4L$ (L = H, SiH_3, GeH_3).[73]

There appears to be somewhat of a trans-Atlantic controversy between Hillier's group in England and Fenske's group in the United States over the assignments of the low IP region of the pes of $Mn(CO)_5L$, where L = CF_3, Cl, Br, I.[67,75,76] Both groups have agreed on the assignments of the pes of $Mn(CO)_5H$ and $Mn(CO)_5CH_3$. The ordering of IP's has been found to be $e < b_2 < a_1$ where the e and b_2 orbitals are the metal d orbitals and the a_1 is the σ_{ML} orbital. Fenske and Hall[76] originally assigned the pes of $Mn(CO)_5CF_3$ as $e \approx a_1 < b_2$ on the basis of approximate molecular orbital calculations. However, this assignment was made on a spectrum which was very poorly resolved. It exhibited an ionization band with a shoulder centered at 9.2 eV and a higher band centered at 10.3 eV. Lloyd and coworkers[75] pointed out that Fenske's assignments would mean a splitting of at least 1 eV for the metal d orbitals, substantially higher than for any other $Mn(CO)_5L$ species (Table 14), as well as an almost constant IP for the a_1 orbital in the methyl and perfluoromethyl derivatives. In light of these suggestions, and the subsequent availability of the data in Table 14 (as well as a more

clearly resolved spectrum[67]) it appears that Fenske has revised his original assignments to $e < b_2 < a_1$, to agree more closely with expected trends.[67] Further evidence for these orbital assignments comes from the corresponding spectra of the Re analogs,[75,77] where ionization from the metal e orbitals is accompanied by a low IP shoulder due to spin-orbit splitting. This splitting (ca. 0.3 eV) aids in pes assignments. Lloyd[75] and Hall[77] found that for $Re(CO)_5H$ and $Re(CO)_5CH_3$, the first band is split by about 0.3 eV, thus yielding good evidence that this ionization arises from the metal e orbitals (Table 14).

The discrepancy between the assignments of the $Mn(CO)_5L$ (L = Cl, Br, I) may not be so easy to resolve, however. Fenske and coworkers[67,78] have assigned the order of IP's in these complexes to be $e(L) < a_1(\sigma_{ML}) < e(M) < b_2(M)$ on the basis of approximate molecular orbital calculations[79] and intensity considerations. Lloyd and coworkers[75] have concluded that the order of IP's is not constant for these complexes. Although they find that the second and fourth ionizations are consistently due to the b_2 and a_1 orbitals, respectively, the overall order for $Mn(CO)_5I$ is $e(L) < b_2(M) < e(M) < a_1(\sigma_{ML})$, whereas the first and third ionizations are interchanged in $Mn(CO)_5Br$ and $Mn(CO)_5Cl$. These assignments were made primarily with the use of spectra obtained from He II (40.82 eV) excitation. It has been shown[80,81] that ionization bands arising from orbitals with strong halogen p character decrease significantly in intensity compared to the corresponding bands in the He I spectra, whereas intensity changes in bands due to metal d levels are much smaller,

and sometimes in the reverse direction. Lloyd found IP_2 actually increased in intensity in the He II spectrum leading to the e(M) assignment; IP_4 decreased in intensity for the three complexes under He II excitation, resulting in the a_1 assignment. IP_1 decreased in intensity for the iodide complex, whereas IP_3 showed this behavior in the bromide and chloride complexes, resulting in the different overall assignments. The behavior of the analogous Re complexes follows that of the Mn complexes, except for $Re(CO)_5Br$ which is assigned the same sequence as the iodide complexes. These results seem to be in agreement with the work of Hall[77] who arrived at similar conclusions using spin-orbit splitting parameters. The question of assignments of the Group VII B pentacarbonyls has overshadowed any substantial study of chemical bonding in these systems. Table 15 summarizes most of the available data on the metal d levels for the $Mn(CO)_5L$ derivatives. It can be seen that the e and b_2 IP's are a reasonably well behaved function of the electronegativity of L (with an apparent increase in electronegativity of GeH_3, SiH_3, and $SiMe_3$).[73,74] The separation of the two metal levels (Δ) seems to reflect the degree of mixing with the e levels of L. Thus L = H yields the smallest Δ (0.29 eV), whereas the halides exhibit the largest Δ (ca. 0.65 eV). These figures appear to support Cradock's[73,74] suggestion of no significant ($d \rightarrow d$) π-bonding between Mn and Si or Ge.

Unambiguous assignments have been made for the pes of the hexacarbonyls of Cr, Mo, and W. The spectra show ionization bands around 8.5 eV (Table 14) and no other ionization until above 13 eV.

Table 15: Vertical Ionization Potentials (eV) of $Mn(CO)_5L$.[a]

L	e		b_2	$\Delta (b_2 - e)$
H	8.85		9.14	0.29
CF_3	9.17		9.51	0.34
CH_3	8.65		9.12	0.47
Cl	8.87		9.5	0.63
Br	8.83		9.5	0.67
I	-	9.65[b]	-	-
SiH_3	8.99		9.38	0.39
GeH_3	8.90		9.26	0.36
$SiMe_3$	9.0		9.3	0.30
SiF_3	-	9.8[b]	-	-

[a] Taken in part from reference 75. [b] b_2, e not resolved.

Lloyd and coworkers[82] have assigned the first ionization band to the t_{2g} level (d^6 configuration) of the metal atoms. This band exhibits spin-orbit splitting (ca. 0.25 eV) in the case of the tungsten derivative. One trend that can be observed in the spectra is the increase in intensity of IP_1 as the central metal atom gets larger. This "heavy atom effect" has been observed before,[72] but the origin of such an effect still appears to be a mystery.

Lloyd and Hillier[83] also investigated the pes of the mono-substituted derivatives of $Cr(CO)_6$ and $W(CO)_6$ with substituents NH_3, NMe_3, PH_3, PMe_3, CNMe, and $NHMe_2$ (Table 14). They observed a destabilization of the metal d orbitals as well as a splitting of the d levels into the expected e and b_2 components. The magnitude of the splitting of the Cr d orbitals varied with the donor atom: ca. 0.30 eV for ligands with the nitrogen donor, and ca. 0.15 eV for ligands with the phosphorus donor. Intensity considerations show the e level to have a lower IP than the b_2 level, whereas ab initio calculations reverse this order in the ground state. However, the calculations show the e orbitals to have greater metal character than the b_2 orbital, i.e., larger relaxation energy. Thus, the pes observations can be rationalized in terms of the inaccuracies in Koopmans' Theorem. Although the splitting could be explained in terms of σ-donation and π-acceptance, the failure of Koopmans' Theorem prohibits such a discussion in situations with such small differences. There is also observed, in most of the spectra, a clearly resolved ionization due to the a_1 (σ_{ML}) orbital. In the

case of the PMe_3 and NMe_3 derivatives, the IP's of the donor "lone pair" orbitals are stabilized by 1.37 eV and 2.08 eV, respectively, from the uncomplexed ligand. This appears to indicate that the amine is more tightly bound to the Cr,,consistent with the calculations on the PH_3 and NH_3 complexes.

Results and Discussion

In order to determine if substituent effects could be observed in the pes of transition metal complexes, we investigated some monosubstituted derivatives of $Cr(CO)_6$ and $Mo(CO)_6$ (Table 16). From the above discussion, assignments should be comparatively simple to make, since the spectra ought to yield clearly resolved metal d orbital ionization bands as well as (hopefully) resolved σ_{ML} ionization bands. The complexes investigated are listed in Table 16, with their corresponding IP's and assignments. In addition, the "lone pair" orbital IP's are listed for the uncomplexed ligands (IP_L). All the compounds listed are reasonably volatile and sufficiently stable in the gas phase (see experimental section) for study with pes.

IP_1 is assigned to the metal d orbitals. In the reduced symmetry of $M(CO)_5L$ (C_{4v}), the metal t_{2g} levels of $M(CO)_6$ would be expected to split into b_2 and e components, the latter of which has the correct symmetry for π interaction with the ligand, L. A low IP shoulder is observed on these bands with L = PR_3, whereas a clear splitting of this band is observed for L = $S(CH_3)_2$ and

Table 16: Vertical Ionization Potentials (eV) of $M(CO)_5L$ and L.

Complex	IP_1[a]	$\overline{IP}_1$[b]	IP_2[c]	IP_3	IP_L[d]	ΔL[e]
$Cr(CO)_5P(C_2H_5)_3$	7.55 (7.40)		9.67	11.14[f]	8.31	1.36
$Cr(CO)_5P(CH{=}CH_2)_3$	7.66 (7.56)		9.60	10.31[g], 10.80[f]	8.48	1.12
$Cr(CO)_5P(CH_3)_3$[h]	7.72 (7.58)		10.00	-	8.63[h]	1.37
$Cr(CO)_5S(C_2H_5)_2$	7.45, 7.65	7.55	9.71	11.51[i]	8.47	1.24
$Cr(CO)_5S(CH{=}CH_2)_2$	7.65	7.65	9.46	-	8.42	1.04
$Cr(CO)_5S(CH_3)_2$	7.59, 7.79	7.69	10.00	12.08[i]	8.70	1.30
$Cr(CO)_5S(CH_3)(CH_2Cl)$	7.86	7.86	10.27	-	9.17	1.10
$Mo(CO)_5P(C_2H_5)_3$	7.75 (7.60)		9.63	11.11[f]	8.31	1.31
$Mo(CO)_5P(CH{=}CH_2)_3$	7.73 (7.58)		9.52	10.28[g], 10.78[f]	8.48	1.04

[a]Assigned to the metal e and b_2 levels; numbers in parentheses are shoulders assigned to the b_2 level. [b]Midpoint of first ionization band for sulfide derivatives (see text). [c]Assigned to the metal-ligand σ bonding orbital. [d]IP of lone pair in uncomplexed ligand. [e]$\Delta L = IP_2 - IP_L$. [f]Assigned to the P-C σ bond. [g]Assigned to the C-C π bond. [h]Reference 83. [i]Assigned to the S-C σ bond.

$S(C_2H_5)_2$. The splitting was not resolved for L = $S(CH{=}CH_2)_2$ and $S(CH_3)(CH_2Cl)$. The IP_1 values for $M(CO)_5L$ are ca. 1 eV lower than the corresponding IP in $M(CO)_6$. This observation is to be expected, and is caused by the increased σ-donation of L relative to CO. The shape of IP_1 in the phosphine derivatives is virtually identical to the shape of IP_1 in $Cr(CO)_5PH_3$.[83] Thus, the peak maximum is assigned to the e orbitals and the low IP shoulder to the b_2 orbital of the metal. Note again that the calculations[83] on $Cr(CO)_5PH_3$ predict the reverse ordering of the d orbitals, but the observed spectrum is easily rationalized in terms of a deviation from Koopmans' Theorem. Once again, this deviation prohibits conclusions concerning the effect of σ-donation and π-acceptance on the relative d orbital energies.

The splitting of the d orbital band in the $S(CH_3)_2$ and $S(C_2H_5)_2$ derivatives yields maxima of almost equal intensity. Moreover, the splitting is unresolved for the $S(CH{=}CH_2)_2$ and $S(CH_3)(CH_2Cl)$ compounds. Therefore, no unambiguous assignments of the b_2 and e levels could be made. The midpoints of the first ionization bands for the sulfide complexes are also recorded for comparative purposes in Table 16.

IP_2 is assigned to the metal-ligand σ-bonding orbital. The IP_2 values represent a stabilization of ca. 1 - 1.4 eV for the "lone pair" in the uncomplexed ligand (ΔL). The assignments of IP_1 and IP_2 are consistent with the work of Lloyd.[83]

IP_3 is assigned to the P-C or S-C σ-bonding orbitals in the ligands PR_3 and SR_2, in accordance with assignments made for the

free ligands.[12,84,85] The $P(CH{=}CH_2)_3$ complex shows an additional band in this region, which may be assigned to the C-C π orbitals of the vinyl groups.

The trends in the behavior of the first two IP's in the spectra of the $M(CO)_5L$ derivatives appear to be a combined function of the donor ability of the R groups in PR_3 and SR_2, as well as the C-P-C and C-S-C bond angles. As the donor ability of L increases, the electron density around the central metal atom (M) increases. This leads to a destabilization of the metal d levels, i.e., lower IP. However, the donor ability of the ligand is not only a function of the donor ability of R, but also of the bond angle about the donor atom. As the C-P-C (or C-S-C) bond angle decreases, the "lone pair" orbital on P (or S) increases in s character, leading to a more tightly held pair of electrons. This effect would obviously decrease the entire donor nature of the ligand, L.

For the Cr complexes, the d orbital ionizations (IP_1) appear to be a reasonably well-behaved function of the donor nature of the groups attached to the sulfur or phosphorus, except for the methyl group. The methyl group in both the sulfide and phosphine complexes gives rise to IP_1's which appear to be too high on the basis of its donor nature alone. Moreover, the trends in the d orbital IP's, upon variation of the substituent on either sulfur or phosphorus, parallel each other almost exactly (Table 16). It is suggested that the apparently lowered electron donating nature of the methyl ligands is a consequence of the lower C-P-C and C-S-C angles. These angles are known for the uncomplexed ligands: 99° for both

$S(CH_3)_2$[85] and $P(CH_3)_3$.[4] Unfortunately, the corresponding angles in the ethyl and vinyl molecules are not known, but these latter values should be larger due to steric factors. The importance of the C-P-C bond angle is evident by comparing the lone pair IP's of the uncomplexed ligands $P(CH_3)_3$ and $P(CH{=}CH_2)_3$ (IP_L, Table 16). Though the methyl is a better donor than the vinyl, this fact is apparently more than compensated for in the smaller bond angle. Thus, if these angle differences persist upon complexation, the trend in d orbital IP's is readily explained by the amount of charge transfer between the ligand and the metal, being in the order $P(CH_3)_3 < P(CH{=}CH_2)_3 < P(C_2H_5)_3$.

The stabilizations of the donor "lone pair" orbitals, ΔL, in both the methyl and ethyl derivatives of the complexes are of comparable value. This may indicate that the C-P-C (or C-S-C) angle in the methyl derivatives opens to a somewhat greater extent than the corresponding angle in the ethyl compounds. This would counteract the inherent poorer donor ability of the methyl group relative to the ethyl. The lower ΔL values for the $P(CH{=}CH_2)_3$ and $S(CH_3)(CH_2Cl)$ derivatives is a consequence of their inherently greater withdrawing abilities, thus inhibiting the transfer of charge from the ligand to the metal.

Experimental Discussion

A STUDY OF THE VARIOUS REACTION PATHWAYS TO MONOSUBSTITUTED DERIVATIVES OF THE GROUP VI B HEXACARBONYLS

Of the various pathways available to $M(CO)_5L$, where M = Cr or Mo and L = substituted phosphine or sulfide, the first attempted preparation was by the direct reaction[86,87] of the hexacarbonyl with L. This reaction had been reported by Bigorgne and Poilblanc[86] to yield mostly the monosubstituted derivative of $Mo(CO)_6$ with $P(C_2H_5)_3$. However, in our hands this synthesis led mainly to the disubstituted product.

Another attempted synthetic route was via a photochemical reaction, using ultraviolet radiation of various wavelength ranges. Two methods were tried by this route. The first was the irradiation of a solution of $Cr(CO)_6$ in THF to form the $Cr(CO)_5 \cdot THF$ complex, followed by the addition of $P(C_2H_5)_3$ which displaces the THF to form $Cr(CO)_5P(C_2H_5)_3$.[88]. The second route attempted was the irradiation of a solution of $Cr(CO)_6$ and $P(C_2H_5)_3$ in CH_2Cl_2 to form the monosubstituted complex directly.[89] The first route led to large amounts of disubstitution, while the second route led to monosubstituted product in yields too small to be of use.

These failures led us to consider another route to the synthesis of $M(CO)_5L$. Recently, Connor and coworkers[90] reported the synthesis of $M(CO)_5L$, (M = Cr, Mo, W and L = any conventional donor such as phosphine or sulfide) from the halopentacarbonyl-

metallate salt, $R_4N^+[M(CO)_5X]^-$ (R = Me or Et; M = Cr, Mo, W; X = Cl, Br, I). The salt is prepared from the corresponding $M(CO)_6$ and $R_4N^+X^-$ according to the displacement reaction:[91]

$$M(CO)_6 + R_4N^+X^- \longrightarrow R_4N^+[M(CO)_5X]^- + CO\uparrow .$$

The salt and ligand, L, are reacted together in the presence of a Lewis acid (e.g., $Et_3O^+BF_4^-$) to give the monosubstituted product:

$$R_4N^+[M(CO)_5X]^- + L + Et_3O^+BF_4^- \longrightarrow M(CO)_5L + R_4N^+BF_4^- + Et_2O + EtX.$$

One of the basic problems in this synthesis is the inability to satisfactorily determine the purity of the halopentacarbonylmetallate salt. Abel and coworkers[91] report the salts to be slightly air and light sensitive. They found solution IR to give inconsistent spectra due to slow decomposition, and their IR spectra were therefore obtained from KBr discs. However, these spectra give only very broad peaks. The salt does not melt, but decomposes over a wide range (e.g., 134-143°C for $Et_4N^+[Mo(CO)_5Br]^-$). Elemental analysis gave somewhat unsatisfactory results for one sample of $Et_4N^+[Cr(CO)_5Br]^-$ (calcd: C = 38.82%, H = 5.02%; Found: C = 40.14%, H = 4.74%). There are also procedural difficulties. Since the salts are air and light sensitive (particularly when wet or in solution), the synthesis and purification steps must be performed under the darkest possible conditions in an inert atmosphere. When dry, the salts can be handled in the atmosphere for short periods of time. The halopentacarbonylmetallate salts used were $Et_4N^+[M(CO)_5X]^-$, where M = Cr or Mo and X = Cl or Br.

In the preparation of $M(CO)_5L$ from $Et_4N^+[M(CO)_5X]^-$, if $Et_3O^+BF_4^-$ is used as the acid, it should be freshly prepared[92] and stored under dry Et_2O. We originally used a commercial sample of $Et_3O^+BF_4^-$ in CH_2Cl_2 solution; this is believed to have caused much of our initial difficulties in this synthesis.

All of the phosphine derivatives were purified by vacuum sublimation (60 - 70°C) onto a cold finger, chilled with dry ice-acetone. The sublimation was done as quickly as possible because the complexes decompose if left at elevated temperatures for long periods of time. A second sublimation was sometimes necessary to minimize the amount of disubstituted product. The $Mo(CO)_5P(C_2H_5)_3$ was found to be the only phosphine complex prepared with no trace of impurities (either from disubstitution or excess hexacarbonyl). The other phosphine complexes had traces of the disubstituted product.

No molybdenum derivatives with sulfide ligands could be isolated because of their high instability. Though disubstitution was not found to be a problem in the synthesis of the Cr sulfide derivative, excess hexacarbonyl was a problem. The $Cr(CO)_5S(CH_3)_2$ and $Cr(CO)_5S(C_2H_5)_2$ were purified by vacuum sublimation (ca. 30°C) onto a cold finger. These complexes were found to be free of impurities. However, both $Cr(CO)_5S(CH{=}CH_2)_2$ and $Cr(CO)_5S(CH_3)(CH_2Cl)$ were found to contain significant amounts of hexacarbonyl. Vacuum treatment of $Cr(CO)_5S(CH_3)(CH_2Cl)$ at 30°C/0.001 mm, minimized the amount of hexacarbonyl present, but did not eliminate it. Since $Cr(CO)_5S(CH{=}CH_2)_2$ and $Cr(CO)_6$ both sublime at the same temperature,

this technique could not be used for the vinyl compound. Crystallization attempts also proved fruitless. Thus, the pes of both of these complexes have bands due to $Cr(CO)_6$.

The purity of all of these complexes was determined by IR and mass spectroscopy as well as elemental analyses of the complexes prepared for the first time (Table 17). The $M(CO)_5PR_3$ derivatives gave rise to four observable bands in the CO-stretching region of the infrared spectrum (ca. 2065, 1945, 1935, and 1910 cm^{-1}). The first two bands have been assigned[93] to the two A_1 vibrations while the intense absorbtion at 1945 cm^{-1} was assigned to the E mode. The weak band ca. 1910 cm^{-1} is of unknown origin. It does not appear to be due to disubstitution, since its intensity relative to the E band of the monosubstituted species remained constant whenever bands due to disubstitution appeared (i.e., bands below 1900 cm^{-1}). The $Cr(CO)_5SR_2$ derivatives gave rise to two observable bands (ca. 2060 and 1940 cm^{-1}). The former is due to the $A_1(1)$ mode, while the latter is due to the unresolved combination of the E and $A_1(2)$ modes. An extra peak at 1980 cm^{-1} in the $S(CH{=}CH_2)_2$ and $S(CH_3)(CH_2Cl)$ derivatives indicated the presence of $Cr(CO)_6$.[93] Mass spectra were also very indicative of the purity of the metal carbonyls. These spectra are dominated by groupings of peaks 28 mass units apart, corresponding to loss of successive CO's. Peaks above the molecular ion, $M(CO)_5L^+$, could readily be assigned to $M(CO)_4L_2^+$ on the basis of their mass numbers. The presence of $M(CO)_6$ could easily be detected from the presence of the $M(CO)_6^+$ ion.

Table 17: Analytical Data on $M(CO)_5L$.

Compound	M.P. (°C)	% C		% H	
		Calcd.	Found	Calcd.	Found
$Mo(CO)_5P(C_2H_5)_3$	oil	37.31	37.29	4.27	4.23
$Mo(CO)_5P(CH{=}CH_2)_3$	oil	37.95	38.39	2.61	2.93
$Cr(CO)_5P(C_2H_5)_3$	25 - 29	42.58	42.77	4.88	5.15
$Cr(CO)_5P(CH{=}CH_2)_3$	oil	43.43	43.40	2.99	2.78
$Cr(CO)_5S(CH_3)_2$ [a]	11 - 14				
$Cr(CO)_5S(C_2H_5)_2$ [b]	oil				
$Cr(CO)_5S(CH_3)(CH_2Cl)$	oil	29.13	29.43	1.75	1.80

[a] M.p. of 9° reported in reference 98. [b] Reference 99.

Experimental

Chromium hexacarbonyl and molybdenum hexacarbonyl were purchased from the Strem Chemical Company and used without further purification. Tetraethylammonium bromide and tetraethylammonium chloride were purchased from the Aldrich Chemical Company and dried over phosphorus pentoxide before use. Triethylphosphine was purchased (Aldrich) and stored under prepurified nitrogen. Trivinylphosphine was prepared from vinyllithium and phosphorus trichloride according to the method of Seyferth and Weiner,[94] and stored under prepurified nitrogen. Dimethyl sulfide and chloromethyl methyl sulfide were purchased (Aldrich), as well as diethyl sulfide (Pfaltz and Bauer), and used without further purification. Divinyl sulfide was prepared from β,β'-dibromodiethyl sulfide* according to the method of Ruigh and Erickson.[95] The β,β'-dibromodiethyl sulfide was prepared from thiodiglycol and hydrogen bromide according to the method of Burroughs and Reid.[96] Triethyloxonium borofluorate was prepared from $Et_2O \cdot BF_3$ and epichlorohydrin according to the method of Meerwein,[92] and stored under dry ether. Ether and tetrahydrofuran were distilled over lithium aluminum hydride before use. Diglyme, methylene chloride, and chloroform were stored over molecular sieves.

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*CAUTION: β,β'-dibromodiethyl sulfide is extremely irritating to the skin, causing severe reddening and blistering.

All reactions and subsequent purification steps were performed in an atmosphere of prepurified nitrogen. Infrared (IR) spectra were recorded in hexane solution (unless otherwise indicated). IR spectra were measured with Perkin-Elmer 247 and Beckman 20A Infrared Spectrophotometers. Mass spectra were measured with a Varian CH-5 Single Focus Mass Spectrometer. Melting points were measured with a Thomas Hoover Capillary Apparatus. Elemental analyses were performed by Galbraith Laboratories, Incorporated, Knoxville, Tennessee 37921, and Schwarzkopf Microanalytical Laboratory, Woodside, New York 11377.

Attempted Synthesis of $Mo(CO)_5P(C_2H_5)_3$ by the Direct Reaction of $Mo(CO)_6$ and $P(C_2H_5)_3$:

A reaction flask was fitted with a reflux condenser and an outlet to an oil bubbler to monitor the evolution of CO. $Mo(CO)_6$ (2.69g, 0.010 mole) was dissolved in 50 ml of 1,2-dimethoxyethane and heated to 90°C (reflux temperature) in order to achieve complete solution of the solid. $P(C_2H_5)_3$ (0.60g, 0.0050 mole) was added quickly to this stirred blue solution. The solution was heated at 90°C, and CO evolved slowly as the solution turned from blue to green. After one hour, CO evolution ceased. The flask was allowed to stand at room temperature for 3.5 hours. A green solution resulted, along with a white solid (excess $Mo(CO)_6$), and a small amount of black material. The solution was poured off and the solvent removed under vacuum to give a mixture of a green paste and white solid. The

green paste was dissolved in a minimal amount of pentane, withdrawn from the white solid, and cooled to -50°C. More white solid precipitated from this solution. The solution was again separated from the solid and the solvent removed under vacuum to give the green paste once more. The IR spectrum (Nujol) of the paste indicated a mixture containing largely $Mo(CO)_4[P(C_2H_5)_3]_2$, with some $Mo(CO)_6$ and $Mo(CO)_5P(C_2H_5)_3$ present.

Attempted Photochemical Synthesis of $Cr(CO)_5P(C_2H_5)_3$ (I):

A typical synthesis is described here. $Cr(CO)_6$ (0.68g, 0.0031 mole) was dissolved in 250 ml of THF. The stirred solution was irradiated for 8 hours with a Hanovia lamp No. 654A. Aliquots were removed at various intervals and IR spectra taken to monitor the progress of the reaction. A yellow solution was produced. Although the spectra indicated the reaction to have taken place, the product appeared to be the disubstituted compound, $Cr(CO)_4(THF)_2$. $P(C_2H_5)_3$ (0.34g, 0.0029 mole) in 5 ml of THF was added to the above solution and stirred for 2 hours. After removal of the solvent, IR and mass spectral analyses of the residual product indicated the predominance of the disubstituted compound.

Attempted Photochemical Synthesis of $Cr(CO)_5P(C_2H_5)_3$ (II):

$Cr(CO)_6$ (1.88g, 0.0084 mole) and $P(C_2H_5)_3$ (0.45g, 0.0038 mole) were dissolved in 250 ml of $CHCl_3$. The solution was irradiated for 1.5 hours (Hanovia lamp No. 654A) to give a dark green solution. The

volume was reduced to 25 ml under vacuum yielding a green liquid and some solid. Addition of hexane dissolved the green liquid which was separated from the solid by filtration. Removal of the solvent under vacuum yielded just enough of a yellow liquid for an IR spectrum. The IR indicated the monosubstituted product.

A change of the solvent from $CHCl_3$ to cyclohexane produced the disubstituted product.

Typical Synthesis of $Et_4N^+[M(CO)_5X]^-$:

This reaction must be carried out under the darkest possible conditions. A mixture of 5.00g (0.023 mole) of $Cr(CO)_6$, 2.45g (0.012 mole) of $Et_4N^+Br^-$, and 100 ml of diglyme was put into a reaction flask fitted with a condenser and an outlet attached to an oil bubbler. The condenser was necessary to catch any $Cr(CO)_6$ which sublimed; the $Cr(CO)_6$ could be pushed back into the reaction mixture by means of a glass rod. The mixture was stirred and heated at 120°C until CO evolution ceased (ca. 2.5 hours). This gave a dark orange solution. The hot solution was filtered in an inert atmosphere and then cooled to room temperature. Approximately 100 ml of petroleum ether (b.p. = 36 - 55°C) was added, and the $Et_4N^+[Cr(CO)_5Br]^-$ precipitated from the solution. The solution was filtered off and the salt washed three times with petroleum ether in an inert atmosphere. The salt was dried under vacuum to remove the petroleum ether, then treated at 50°C at 0.001 mm to remove any excess $Cr(CO)_6$.

YIELD: 4.0g (85%) of the yellow compound.

Typical Synthesis of $M(CO)_5PR_3$:

$Et_4N^+[Cr(CO)_5Br]^-$ (1.25g, 0.0031 mole) was dissolved in 40 ml of CH_2Cl_2 and $P(C_2H_5)_3$ (0.53g, 0.0045 mole) was added to the stirred solution, followed by the immediate addition of $Et_3O^+BF_4^-$ (0.69g, 0.0036 mole) in 10 ml of CH_2Cl_2. The original dark yellow solution became lighter in color within one minute. Stirring was continued for 5 minutes and the volatiles were removed under vacuum. The $Cr(CO)_5P(C_2H_5)_3$ was extracted from the residue with three washings of hexane (ca. 45 ml total). The hexane was removed under vacuum, yielding a green liquid.

YIELD: 0.57g (59%).

Short path sublimation at 60°C onto a cold finger (dry ice-acetone) gave a yellow solid (m.p. = 25 - 29°C). IR and mass spectra indicated the monosubstituted product with a slight amount of disubstituted impurity.

Typical Synthesis of $Cr(CO)_5SR_2$:

$Et_4N^+[Cr(CO)_5Br]^-$ (0.91g, 0.0023 mole) was dissolved in 15 ml of CH_2Cl_2 and $S(CH_3)_2$ (0.14g, 0.0023 mole) was added to the stirred solution, followed by the immediate addition of $Et_3O^+BF_4^-$ (0.43g, 0.0023 mole) in 5 ml of CH_2Cl_2. The solution became lighter in color within 2 minutes. After stirring for 10 minutes, the

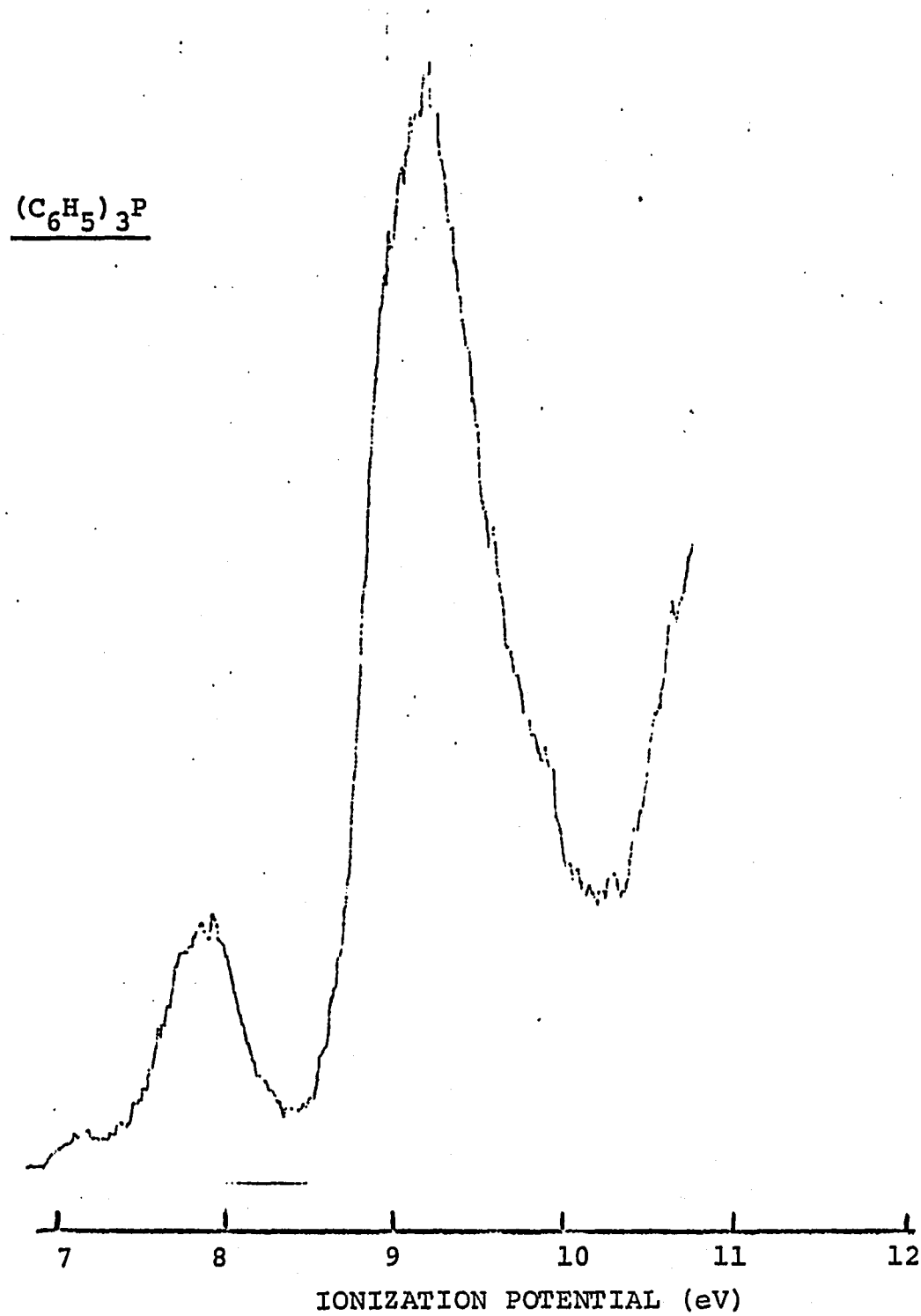
volatiles were removed under vacuum (ca. 6 mm). The $Cr(CO)_5S(CH_3)_2$ was extracted from the residue by repeated washings with a 50:50 solution of hexane-ether (ca. 50 ml total). The solvent was removed under vacuum (ca. 6 mm), yielding a yellow liquid.

YIELD: 0.34g (60%).

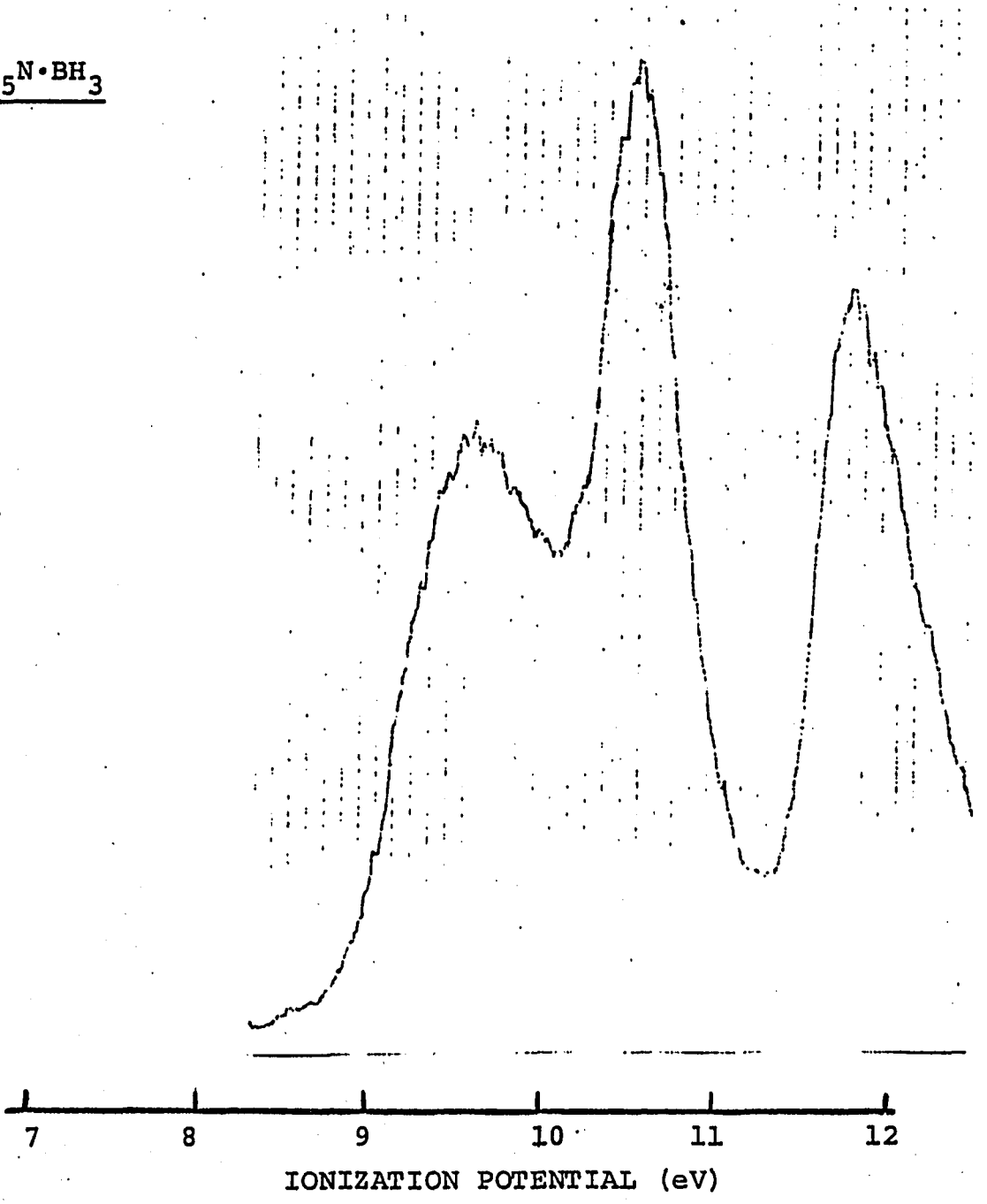
Short path sublimation at 30°C onto a cold finger yielded a yellow solid which melted as the surface of the cold finger warmed to room temperature (m.p. = 11 - 14°C). Mass spectroscopic analysis indicated the monosubstituted product with no observed disubstituted impurity.

APPENDIX

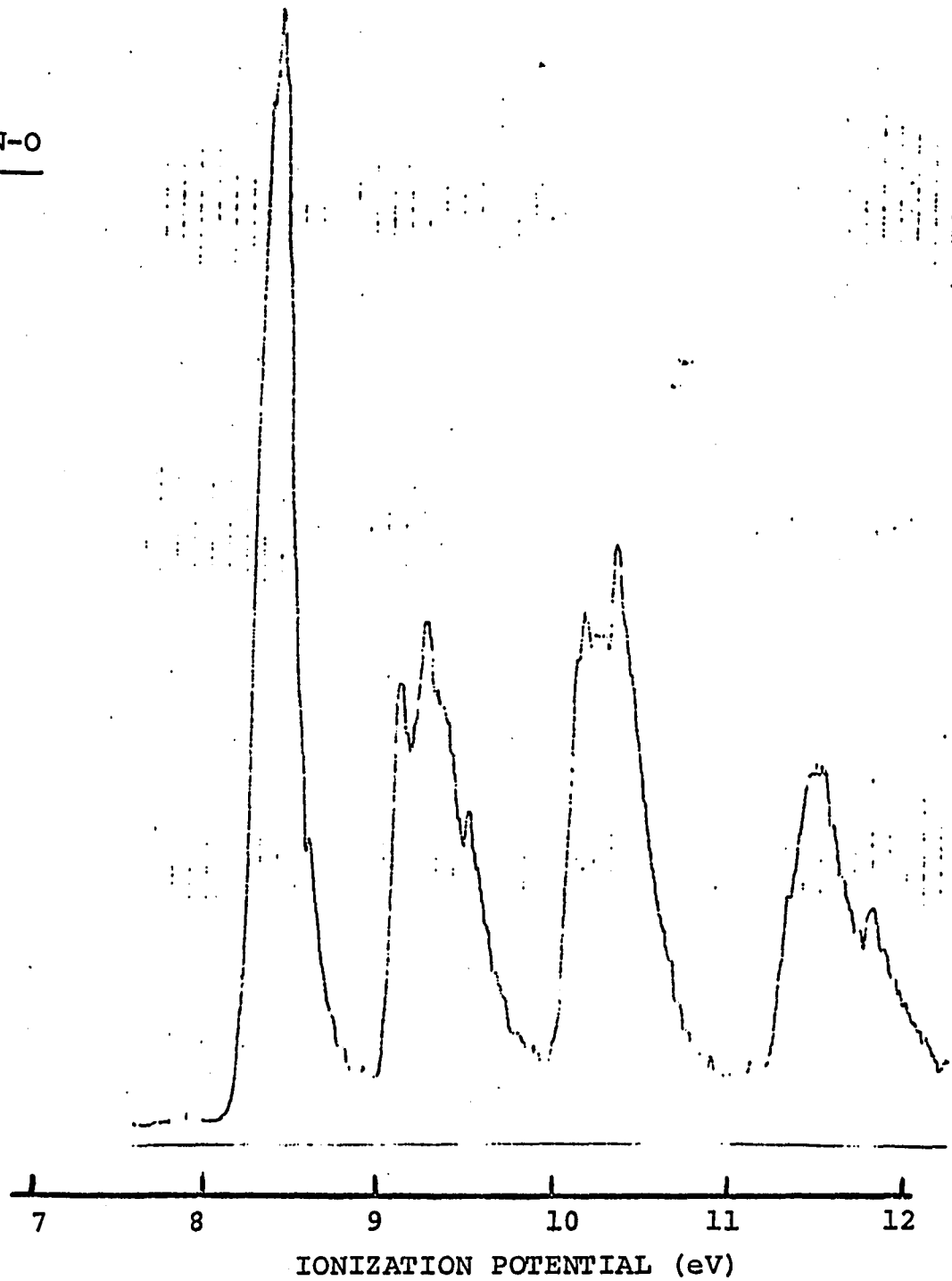
REPRESENTATIVE PHOTOELECTRON SPECTRA


$(C_6H_5)_3P$
7
8
9
10
11
12
IONIZATION POTENTIAL (eV)

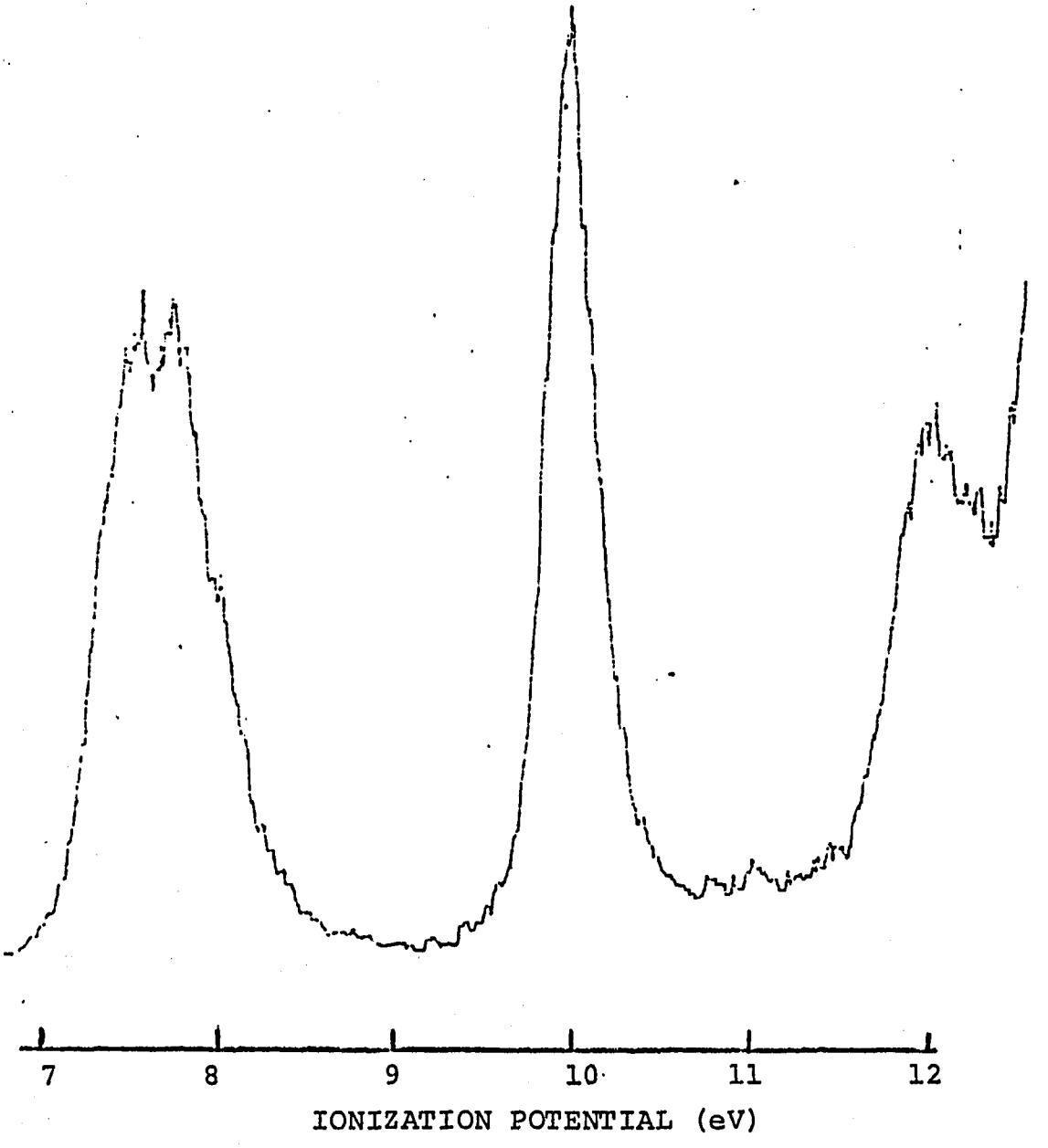
$C_5H_5N \cdot BH_3$

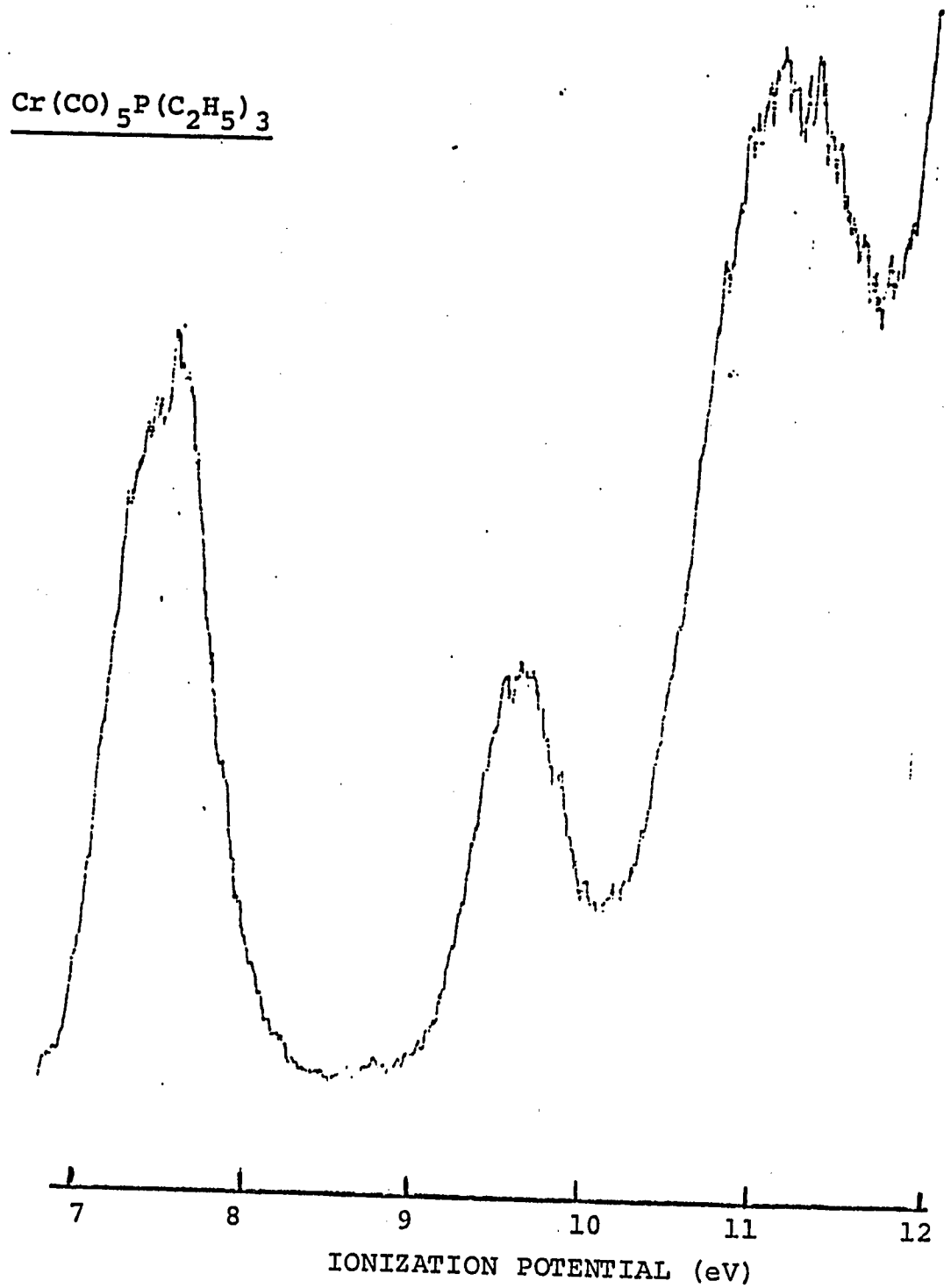


C_5H_5N-O



$Cr(CO)_5S(CH_3)_2$




Cr(CO)5P(C2H5)3
7
8
9
10
11
12
IONIZATION POTENTIAL (eV)

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