

The ratio of $\text{Na}^+:\text{B:H}^-$ is thus 1.00:1.04:0.96 indicating 1:1:1 stoichiometry. The results are summarized in Table II.

Stability of Alkali Metal Trialkylborohydrides. A. Dry Nitrogen. Solutions of lithium triethylborohydride and sodium triethylborohydride were analyzed for the hydride concentration periodically either by hydrolysis or by the *n*-octyl iodide reduction technique. The results clearly indicate that under dry nitrogen these reagents are indefinitely stable.

B. Effect of Dry Air. A 100-mL flask with a side arm was fitted with a condenser protected by a drying tube (filled with Drierite®) and flushed with dry air. Lithium triethylborohydride, 20 mL (~20 mmol) of a standard solution in THF, was introduced and allowed to stand exposed to dry air with constant stirring. At appropriate intervals, aliquots were removed and analyzed for residual hydride. Thus, in 1 h only, 6% hydride loss was observed and in 24 h 45% hydride had been destroyed.

A similar experiment was conducted with a solution of sodium triethylborohydride.

C. Effect of Air and Moisture. Lithium triethylborohydride solution (15 mL) was syringed into a 50-mL Erlenmeyer flask. The flask was covered with a lid which had an opening 0.4 in. in diameter. Periodically, aliquots were removed and analyzed for the residual hydride. The solution lost the hydride activity completely in 3 h, revealing that the THF solution of this reagent is more sensitive to moisture than dry air alone. A similar study was conducted with sodium triethylborohydride.

The results are summarized in Table V and Figure 5.

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An Ultraviolet Photoelectron Spectroscopic-Molecular Orbital Study of Some Cyclopolyphosphines

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Abstract: He(I) photoelectron spectra of the cyclotriphosphine, $(\text{C}_2\text{F}_5\text{P})_3$ (**1**), the cyclotetraphosphines $(\text{CF}_3\text{P})_4$ (**2**), $(\text{C}_2\text{F}_5\text{P})_4$ (**3**), $(t\text{-C}_4\text{H}_9\text{P})_4$ (**4**), and $(\text{C}_6\text{H}_{11}\text{P})_4$ (**5**), and the cyclopentaphosphines $(\text{CF}_3\text{P})_5$ (**6**), $(\text{CH}_3\text{P})_5$ (**7**), $(\text{C}_2\text{H}_5\text{P})_5$ (**8**), and $(n\text{-C}_3\text{H}_7\text{P})_5$ (**9**) have been measured. The technique of ultraviolet photoelectron spectroscopy (PES) has been shown to be capable of differentiating cyclopentaphosphines from other cyclopolyphosphines in the vapor phase. The trends in the observed ionization energies (IEs) of the phosphorus lone pair electrons are discussed from the standpoints of nearest neighbor and cross-ring lone pair interactions, substituent electronegativity effects, and P(3d) orbital participation. The PES assignments are based principally on MNDO molecular orbital (MO) calculations on **2** and the model compounds $(\text{PH})_3$, $(\text{PH})_4$, $(\text{CH}_3\text{P})_4$, and $(\text{PH})_5$. MO calculations of the STO-6G type have also been performed on $(\text{PH})_4$.

Ring size assessment has turned out to be one of the more contentious problems in the chemistry of the cyclopolyphosphines.³⁻⁵ X-ray crystallography has played an important role in the delineation of ring sizes and conformations in the solid state; however, to date only a small number of molecules have been investigated by this technique.⁶⁻¹¹ More recently, the advent of Fourier transform ^{31}P NMR spectroscopy has permitted the measurement of ring sizes in solution.⁴ However, the study of ring sizes in the vapor state has been much more limited. In principle mass spectrometry could be employed for this purpose. However, in practice the technique has proved unreliable because of the weakness of the parent peak, the occurrence of collision species, and the sensitivity of the results to ionizing voltage and inlet temperature.¹² In the present ar-

ticle it will be demonstrated that in certain cases UV photoelectron spectroscopy can be used to assess the ring sizes of cyclopolyphosphines in the vapor phase.¹³ The technique might be applicable to a wide variety of homocatenates which feature lone pair electrons.

An additional facet of interest in the cyclopolyphosphines relates to the nature of the bonding. Following the discovery that cyclopolyphosphines exhibit intense ultraviolet spectra a model was suggested in which circumannular delocalization of phosphorus lone pair electrons is achieved by 3d orbital participation.¹⁴ It has been found that PES data have a bearing both on this postulate and also on the question of cross-ring interactions. As an interpretational aid we have performed MNDO (modified neglect of diatomic overlap) molecular

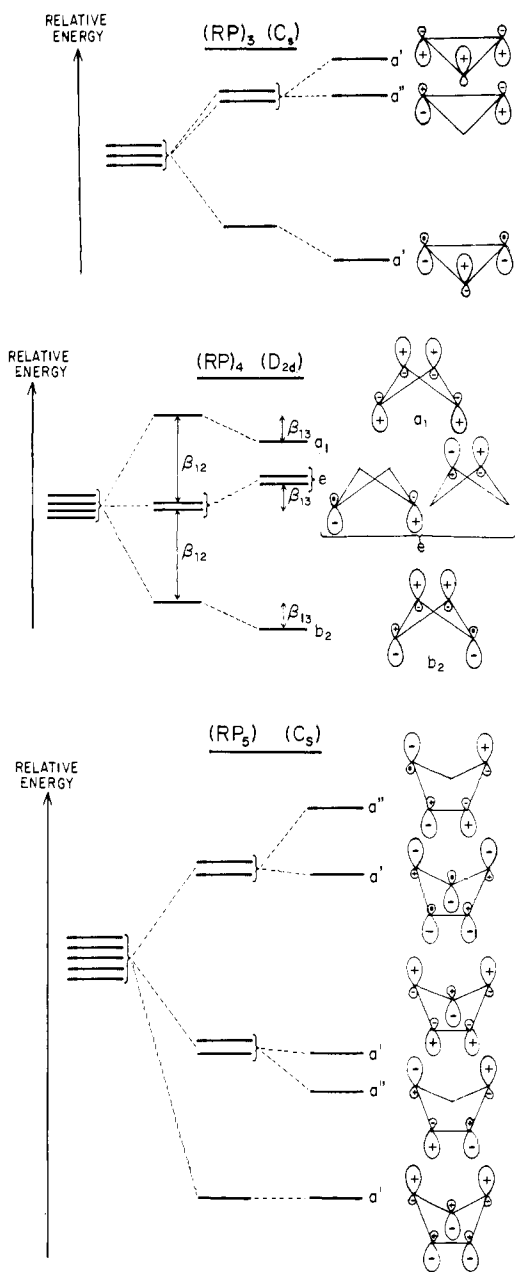


Figure 1. Symmetry-adapted lone pair molecular orbitals for three-, four-, and five-membered phosphorus rings.

orbital (MO) calculations¹⁵ on $(CF_3P)_4$ and the model compounds $(PH)_3$, $(PH)_4$, $(CH_3P)_4$, and $(PH)_5$. Ab initio (STO-6G)¹⁶ MO calculations have also been performed on $(PH)_4$. Previous theoretical work¹⁷ on cyclopolyphosphines was limited to extended Hückel calculations on $(PH)_3$ and $(PH)_4$.

Results and Discussion

X-ray crystallographic studies have established that cyclophosphines adopt D_{2d} skeletal geometry in the solid state.^{7,10,11} Strictly speaking, the cyclophosphines are devoid of symmetry because of the wide scatter of P-P bond distances and P-P-P bond angles.^{6,8} However, x-ray analysis of $(C_6H_5P)_5$ revealed that the ring was close to possessing mirror symmetry.⁸ Furthermore, the phosphorus nuclei of $(RP)_5$ species constitute AA'BB'C spin systems which implies at least a C_s molecular geometry on a time average basis.^{4,18} The point group C_s will therefore be assumed for the cyclophosphines. No structural data are available for the cyclophosphines; however, it is safe to predict a C_s ground state

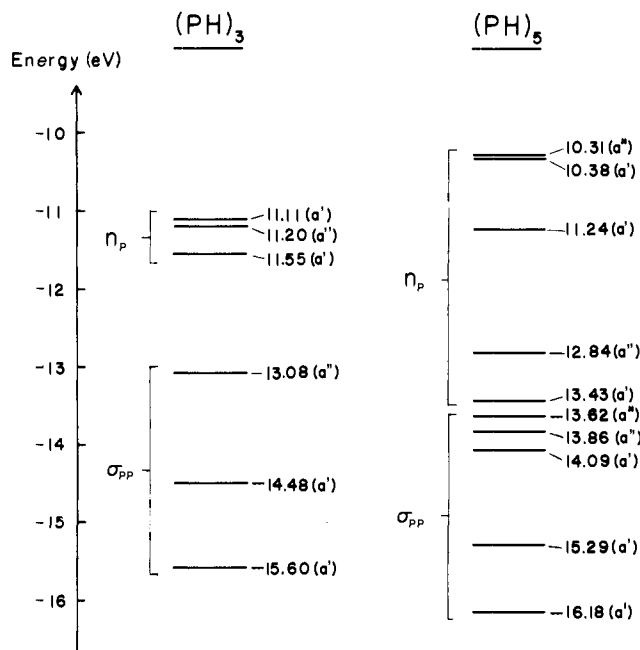


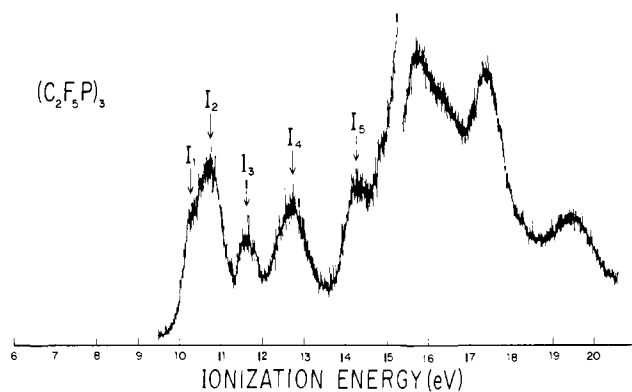
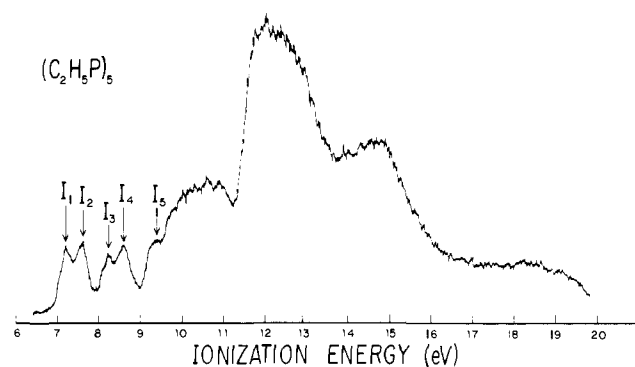
Figure 2. The valence molecular orbitals of predominantly phosphorus 3p character of $(PH)_3$ and $(PH)_5$ computed by the MNDO method. Eigenvalues in eV. n_p signifies predominantly phosphorus lone pair molecular orbitals; σ_{pp} signifies predominantly P-P σ bonds.

geometry since this conformation would minimize the steric interactions among the three substituents.

One of the intriguing features of UV photoelectron spectroscopy is the experimental demonstration of the interactions between, e.g., lone pairs of electrons.¹⁹ Indeed, it is this aspect which is responsible for the possible stereochemical utility of PES data. The symmetry-adapted combinations of phosphorus lone pair electrons for three-, four-, and five-membered phosphorus rings are displayed in Figure 1. The qualitative sequencing of the lone-pair MOs has been arrived at on the basis of the nodal rule,¹⁹ viz., the more nodes the less stable the MO. Secondary interactions have been allowed to take place among some of the MOs of the same symmetry, leading to the final sequencing shown in Figure 1. For example, in the cyclophosphine an interaction takes place among the two MOs of a' symmetry. Several such interactions are possible in the larger $(RP)_5$ system and it is difficult to be definitive about their relative magnitudes without MO calculations. For the more symmetrical cyclophosphines the situation is slightly different. The primary interactions are of the nearest-neighbor (β_{12}) type, and nodal rule considerations lead to the initial sequence depicted in Figure 1. Transannular (β_{13}) interactions are then introduced. Inspection of the forms of the MOs (Figure 1) indicates that the β_{13} interactions are bonding in the a_1 and b_2 MOs, but antibonding in the e MO.

The phosphorus-phosphorus σ bonds, σ_{pp} , span the irreducible representations $2a' + a''$ and $3a' + 2a''$ in the three- and five-membered rings, respectively, while the σ_{pp} MOs of the cyclophosphines transform as $a_1 + e + b_1$. Previous PES studies^{13,20} have shown that electron ejection from P-P σ bonds occurs at relatively low energy; hence it is possible that these ionizations protrude into the phosphorus lone pair region. In order to explore this possibility it was decided to perform MNDO¹⁵ molecular orbital calculations on $(CF_3P)_4$ and the model compounds $(PH)_3$, $(PH)_4$, $(CH_3P)_4$, and $(PH)_5$. Ab initio (STO-6G)¹⁶ MO calculations were also performed on $(PH)_4$ as a cross-check of the MNDO calculations. Both methods yielded the same sequence of orbital energies.

The MNDO calculations on $(PH)_3$ and $(PH)_5$ (Figure 2) indicate that in both molecules all the phosphorus lone pair

Figure 3. He(I) PE spectrum of $(C_2F_5P)_3$ (1).Figure 4. He(I) PE spectrum of $(C_2H_5P)_5$ (8).Table I. Minimum Energy and Experimental^a Geometry for $(CF_3P)_4$ Computed by the MNDO Method

	Minimum energy	Exptl
d_{PP}	2.049 Å	2.213 Å
d_{PC}	1.848 Å	1.867 Å
$\angle PPP$	85.05° ^b	84.7°
$\angle PPC$	109.1°	97.8°

^a Reference 7. ^b Average value.

MOs (n_p) are at lower IE than the σ_{pp} MOs. Furthermore, there is a satisfactory agreement between the computed sequences of lone pair MOs and those deduced on the foregoing qualitative arguments. The PE spectra of $(C_2F_5P)_3$ (1) and the cyclopolyphosphines $(RP)_5$, R = CF_3 , C_2H_5 , $i-C_3H_7$ (6–9) can therefore be assigned using Figures 1 and 2 and assuming the validity of Koopmans' theorem.²¹ In the PE spectrum of $(C_2F_5P)_3$ (1) (Figure 3), peaks I_1 , I_2 , and I_3 are assigned to the ionization of lone pair MOs of symmetry a' , a'' , and a' , respectively, while peaks I_4 and I_5 are attributed to electron ejection from σ_{pp} MOs of symmetry a'' and a' , respectively. Presumably the third σ_{pp} (a') ionization is obscured beneath the P–C bond ionizations.

All the cyclopentaphosphines exhibit essentially similar PE spectra. In each case except $(CF_3P)_5$, where ionization from the most stable a' lone pair MO overlaps somewhat with a σ_{pp} ionization, five peaks of approximately the same intensity appear in the low IE region (Figure 4). These are assigned to the ionization of phosphorus lone pair MOs of symmetries a'' , a' , a' , a'' , and a' in order of increasing IE. The σ_{pp} peaks are overlapped badly. This is unfortunate, since, as demonstrated for the polysilanes, the higher lying σ MOs can be useful for conformational analysis.²²

The cyclohexaphosphines present a more complex case for spectral assignment. Basically, this arises because the σ_{pp} MO ionizations protrude into the phosphorus lone pair region. In

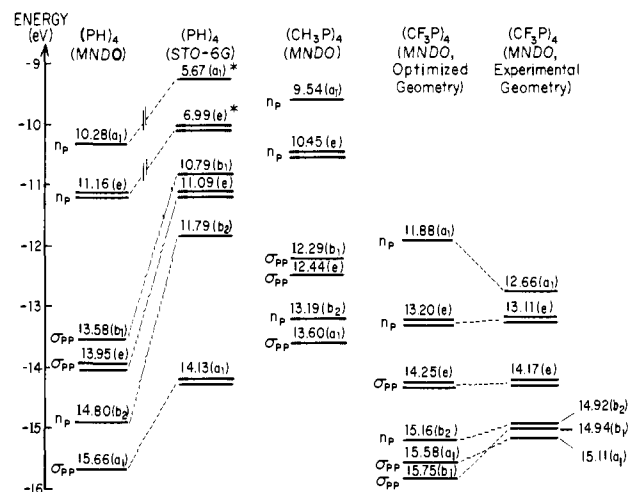
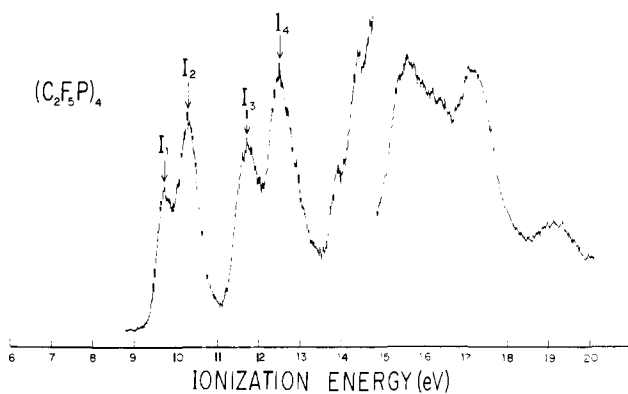


Figure 5. The valence molecular orbitals of predominantly phosphorus 3p character of various cyclotetraphosphines computed by the MNDO and STO6G methods.

Figure 6. He(I) PE spectrum of $(C_2F_5P)_4$ (3).

turn, this is a consequence of the greater interactions between the phosphorus lone pairs in P_4 rings (Figure 1). The following assignments are based primarily on MNDO MO calculations on $(CF_3P)_4$ and the model compounds $(PH)_4$ and $(CH_3P)_4$. In each case the starting geometry for the D_{2d} skeleton was based on the x-ray crystal structure data⁷ for $(CF_3P)_4$. Several iterations were then performed, resulting in the minimum energy geometry shown in Table I. The eigenvalues of interest are shown in Figure 5. It is apparent immediately that the sequence of MOs is sensitive to the electronegativity of the cyclotetraphosphine substituent. The most obvious variation is the stabilization of the b_1 σ_{pp} MO upon replacing H or CH_3 by CF_3 . Furthermore, the b_1 MO is quite sensitive to geometric changes as may be seen by comparing the eigenvalues of $(CF_3P)_4$ at the crystallographic and minimum energy structures (Figure 5). The a_1 MO is also sensitive to changes in geometry; however, it remains the highest occupied MO in both structures. It is, therefore, necessary to interpret the PE spectra of the perfluoroalkyl species $(CF_3P)_4$ (2) and $(C_2F_5P)_4$ (3) in a slightly different manner than those of the alkylated compounds ($t-C_4H_9P$)₄ (4) and $(C_6H_{11}P)_4$ (5). Thus, for 2 and 3 (Figure 6) peaks I_1 and I_2 are assigned to the ionization of phosphorus lone pair MOs of symmetries a_1 and e , respectively, while peak I_3 is attributed to electron elimination from the σ_{pp} MO of symmetry e . The large peak I_4 is assigned to the overlap of ionizations from the b_2 phosphorus lone pair MO and the a_1 and b_1 σ_{pp} MOs. Note that the MNDO calculations place these three MOs very close in energy. Furthermore, the relative intensities of the peaks are in qualitative accord with the total

Table II. He(I) PES Data for Cyclopolyphosphines^a

	Cyclotriphosphines						
	$\overline{IE}_1(a')$	$\overline{IE}_2(a'')$	$\overline{IE}_3(a')$	$\overline{IE}_4(a'')$	$\overline{IE}_5(a')$	\overline{IE}_n	
(C ₂ F ₅ P) ₃ (1)	10.39	10.83	11.69	12.76	14.42	10.97	
	Cyclotetraphosphines						
	$\overline{IE}_1(a_{1,nP})$	$\overline{IE}_2(e,nP)$	$\overline{IE}_3(e,\sigma_{PP})$	$\overline{IE}_4(b_{2,nP} + a_{1,\sigma_{PP}} + b_{1,\sigma_{PP}})$	\overline{IE}_n	β_{12}	β_{13}
(CF ₃ P) ₄ (2)	10.18	10.58	12.38	12.89	11.06	1.35	0.48
(C ₂ F ₅ P) ₄ (3)	9.99	10.48	11.95	12.65	10.90	1.33	0.42
	$\overline{IE}_1(a_{1,nP})$	$\overline{IE}_2(e,nP)$	$\overline{IE}_3(b_{1,\sigma_{PP}} + e,\sigma_{PP})$	$\overline{IE}_4(b_{2,nP})$	\overline{IE}_n	β_{12}	β_{13}
	(<i>t</i> -C ₄ H ₉ P) ₄ (4)	7.39	7.85	9.27	9.99	8.27	1.30
(C ₆ H ₁₁ P) ₄ (5)	7.28	7.83	9.15				
	Cyclopentaphosphines						
	$\overline{IE}_1(a'')$	$\overline{IE}_2(a')$	$\overline{IE}_3(a')$	$\overline{IE}_4(a'')$	$\overline{IE}_5(a')$	\overline{IE}_n	
(CF ₃ P) ₅ (6)	9.79	10.13	10.71	11.21	12.1	10.8	
(CH ₃ P) ₅ (7)	7.58	7.93	8.69	9.01	9.76	8.59	
(C ₂ H ₅ P) ₅ (8)	7.41	7.74	8.40	8.74	9.51	8.36	
(<i>n</i> -C ₃ H ₇ P) ₅ (9)	7.26	7.61	8.30	8.61	9.45	8.25	

^a Vertical ionization energies in eV.

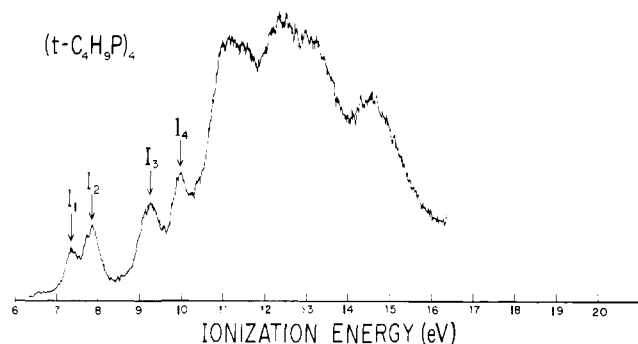


Figure 7. He(I) PE spectrum of (*t*-C₄H₉P)₄ (4).

orbital degeneracies.²³ As with **2** and **3** the first two PES peaks of **4** (Figure 7) and **5** are ascribed to the ionization of n_p MOs of symmetry a_1 and e . Peak I_3 is assigned to the ionization of the b_1 and e σ_{PP} MOs on the basis of the MO calculations and the relative orbital degeneracies.²³ Finally, peak I_4 is assigned to the ionization of the b_2 phosphorus lone pair MO.

The PES data for all the cyclopolyphosphines considered here are summarized in Table II. The average lone pair ionization energies, \overline{IE}_n , are computed straightforwardly for the three- and five-membered rings; for the cyclotetraphosphines orbital degeneracies must be considered, vis.

$$\overline{IE}_n = \frac{IE_{a_1} + 2(IE_e) + IE_{b_2}}{4}$$

The β_{12} and β_{13} interaction parameters for the cyclotetraphosphines have been computed according to the splitting diagram in Figure 1.

Some specific stereochemical and bonding aspects of the cyclotetraphosphines are now considered.

1. Ring Sizes. As indicated above PES can be used as a diagnostic tool for the measurement of ring sizes in the vapor phase. In particular, the spectra of the five-membered rings are differentiated easily from those of the three- and four-membered rings since the first five bands, which correspond to ionization of the phosphorus lone pair MOs, are clearly resolved and of virtually equal intensity (except for (CF₃P)₅, vide supra).

The confusion surrounding the C₂F₅P ring system has been discussed elsewhere.⁴ On the basis of ³¹P NMR data it has been argued that the C₂F₅P ring system exists at three- and four-membered rings in solution.⁴ The present results confirm this argument and indicate that the three- and four-membered rings persist in the vapor phase. Our claim to the synthesis of the first three-membered phosphorus ring is therefore substantiated.²⁴

The ethyl-,²⁵ *n*-propyl-,²⁵ and *n*-butyl-^{25,26}substituted cyclopolyphosphines were originally believed to be tetrameric in solution; however, subsequent ³¹P NMR studies⁴ revealed that all three compounds are, in fact, pentameric in solution. The present data confirm that these compounds exist as five-membered rings in the vapor phase. Our conclusion regarding the degree of polymerization of the CF₃- and C₆H₁₁-substituted rings agrees with x-ray crystallographic data for these molecules in the solid state.^{6,7,10} There does not appear to have been any doubt about the ring sizes of (CH₃P)₅ and (*t*-C₄H₉P)₄.

The first ionization energies, \overline{IE}_1 , and average phosphorus lone pair ionization energies, \overline{IE}_n , are also indicative of ring size for a given substituent. Thus, for the CF₃P and C₂F₅P ring systems the \overline{IE}_1 and \overline{IE}_n values increase with decreasing ring size. Similar trends have been noted in the first ionization energies of, e.g., cycloalkanes²⁷ and cyclopolysilanes.^{22a}

2. Nearest-Neighbor and Transannular Interactions. Four-membered rings, having high symmetry, are convenient cases for evaluating nearest-neighbor (β_{12}) and transannular (β_{13}) interactions. Both types of interactions are expected to be dependent on substituent electronegativities and the details of the ring stereochemistry. Structural data exist for only three cyclotetraphosphines: (CF₃P)₄ (**2**),⁷ (C₆H₁₁P)₄ (**5**),¹⁰ and (C₆F₅P)₄.¹¹ The P-P bond distances and cross-ring P...P distances in **5** are very slightly larger than those in **2**, owing, presumably, to the larger steric bulk of the C₆H₁₁ substituents. Unfortunately, it is impossible to evaluate the β_{12} and β_{13} parameters for **5** because of overlapping of the PES peaks. However, the observed trends in the β_{12} and β_{13} parameters in **2**, **3**, and **4** can be attributed (in part at least) to changes in the steric bulk of the substituents.

3. Electronegativity Effects. It is well known that localized MOs, such as lone pair electrons on neutral Lewis bases, are quite sensitive to the nature of the substituents. Since photo-

Table III. Mean Phosphorus Lone Pair Ionization Energies (eV)^{a,b}

	(RP) ₅	trans-R ₄ P ₂ ^c	R ₃ P ^d
R = CH ₃	8.59	8.71	8.60
R = CF ₃	10.8	11.44	11.70

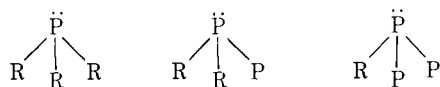
^a Vertical ionization energies in eV. ^b See text for the method of computing mean lone pair IEs. ^c For PES data for (CH₃)₄P₂ and (CF₃)₄P₂, see A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and M. C. Padolina, *J. Am. Chem. Soc.*, **96**, 2648 (1974). ^d For PES data (CH₃)₃P and (CF₃)₃P, see S. Elbel, H. Bergmann, and W. Ensslin, *J. Chem. Soc., Faraday Trans. 2*, **70**, 555 (1974); A. H. Cowley, M. J. S. Dewar, and D. W. Goodman, *J. Am. Chem. Soc.*, **97**, 3653 (1975).

electron spectroscopic peaks represent the differences of energy between the molecular ground state and the several radical cation states it is obvious that for a given ionization one must discuss the relative stabilization of both the ground state and its conjugate radical cation. Increases of substituent electronegativity generally result in pronounced increases in the lone pair IEs due, presumably, to preferential stabilization of the lone pair MO in the molecular ground state. When, however, the substituent electronegativities are similar, as with, e.g., alkyl groups, it is usual to ascribe the changes of lone pair IE to the ability of the alkyl group to stabilize the positive charge of the appropriate radical cation state.²⁸ The sequence of average lone pair ionization energies ($\bar{I}E_n$) observed here, viz., CF₃ > C₂F₅ > CH₃ > C₂H₅ > n-C₃H₇ > t-C₄H₉, is similar to those observed for other catenated systems such as hydrazines²⁹ and disulfides.³⁰ The same trend is also evident for each of the individual lone pair IEs for both the cyclotetraphosphines and cyclopentaphosphines.

4. Phosphorus-Phosphorus p_π-d_π Bonding. A π component to the P-P bond was postulated initially to account for the UV spectra of cyclopolyposphines.¹⁴ It was hoped that PES data might provide some new insights into the question of p_π-d_π bonding.

From a simplistic point of view phosphorus lone pair energies can be considered to be a function of (a) substituent electronegativities, (b) X-P-X bond angles, and (c) conjugative effects. Substituent electronegativity effects have been discussed above. The familiar Walsh argument³¹ predicts that diminution of, e.g., X-P-X bond angles leads to more s character in the phosphorus lone pair and vice versa. In turn, increased s character leads to lone pair stabilization. Conjugation between the phosphorus lone pair and vacant 3d (or 4p) orbitals would be manifested by an increase in the lone pair IE of a catenated phosphine compared to the corresponding monophosphine.

Structurally, tertiary phosphines, diphosphines, and cyclopolyposphines are related by the replacement of R groups by P atoms, viz.



In the case of R = CH₃ electronegativity effects will play a very minor role because the electronegativities of the CH₃ group and the P atom are very similar.³² Furthermore, the available structural data³³ on (CH₃)₃P, (CH₃)₄P₂, and (CH₃)₅P show that there is very little variation in X-P-X bond angles in these compounds. Significantly, the mean lone pair IEs of these compounds (Table III) are also very close. It therefore appears that conjugative effects are not significant in the polyphosphines (CH₃)₄P₂ and (CH₃)₅P. In the case of the CF₃ analogues electronegativity effects dominate since there is a pronounced increase in mean IE as P atoms are replaced by CF₃ groups. [The average X-P-X bond angles in these compounds are in the order (CF₃)₄P₂ > (CF₃)₃P > (CF₃)₅.]³⁴ However,

while the present PES data can be explained satisfactorily without invoking vacant P(3d) orbital participation, it is obvious that small conjugative interactions are not excluded rigorously.

Experimental Section

All the compounds employed in this study were prepared and purified according to literature methods.⁴ Since they are air and moisture sensitive all manipulations were performed in vacuum systems or under an inert atmosphere.

All PES data were recorded on a Perkin-Elmer Model PS-18 photoelectron spectrometer using a He(I) source (21.22 eV). When elevated temperatures were necessary to obtain suitable spectra, the direct inlet heated probe was used. The spectra were calibrated with argon (15.759-eV line) and xenon (12.130-eV line), used as internal standards. Resolution was maintained between 20 and 40 meV for the argon line. The ionization energy values reported are the band maxima unless otherwise noted.

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References and Notes

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Reactions of Metal-to-Metal Multiple Bonds. 3.¹ Addition of Nitric Oxide to Hexakis(alkoxy)dimolybdenum Compounds. Preparation and Properties of Bis(nitrosyl)hexakis(alkoxy)dimolybdenum Compounds and Structural Characterization of the Isopropoxy Derivative

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Abstract: The reactions of Mo₂(OR)₆ compounds (R = Me₃C, Me₂CH, and Me₃CCH₂) with nitric oxide yield a heretofore unrecognized class of metal nitrosyl complexes of empirical formula Mo(OR)₃NO. The latter show NO stretching frequencies at ca. 1640 cm⁻¹ and are diamagnetic, dimeric, and fluxional in solution. The compound [Mo(OPr-*i*)₃NO]₂ crystallizes in space group P $\bar{1}$ with Z = 2 and unit cell dimensions a = 10.828 (1) Å, b = 15.848 (2) Å, c = 9.885 (2) Å, α = 90.21 (2)°, β = 115.93 (2)°, γ = 82.42 (1)°, and V = 1509.4 (5) Å³. There are two crystallographically independent molecules, one centered on the origin, the other at 1/2, 1/2, 1/2, which are essentially identical in structure. Each molybdenum atom is five coordinated in a trigonal bipyramidal manner and attains only a 14-valence shell electron configuration. The nitrosyl ligands occupy terminal axial positions and the two bridging OPr-*i* groups form short bonds in equatorial positions and long bonds in axial positions which are trans to the NO ligands. The Mo-N-O units are essentially linear (178°) and the bond lengths therein are 1.754 (7) Å for Mo-N and 1.19 (1) Å for N-O. The Mo-Mo separation of 3.335 (2) Å precludes metal-to-metal bonding. The M-M triple bonds that exist in Mo₂(OR)₆ compounds are thus shown to be cleaved by the addition of two NO ligands. The electronic structure in these new nitrosyl metal complexes can be formulated so that the highest filled MO is the e level responsible for Mo to NO π bonding, made up of metal d_{xz}, d_{yz}, and NO π* orbitals. It is likely that other, similar MX₃(NO)L molecules, where M is a group 6 transition metal, X is a univalent group, and L is a two-electron donor, should be obtainable.

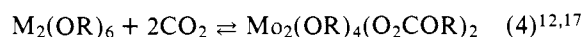
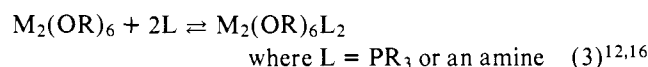
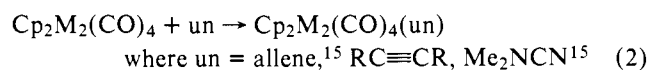
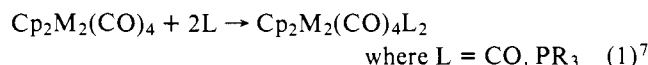
Introduction

The occurrence of compounds containing metal-to-metal multiple bonds is now a well-documented facet of transition metal chemistry.⁴ In this series we are studying the reactions of such compounds with regard to their ability (1) to undergo reactions of the type well documented in mononuclear chemistry⁵ and (2) to act as building blocks for the systematic synthesis of new cluster (polynuclear) compounds.⁶ Both have important catalytic implications.

In the compounds Cp₂M₂(CO)₄, where M = Mo or W, the formation of a metal-to-metal triple bond allows the metal atoms to achieve an 18-valence shell electron configuration.⁷ In compounds of the type M₂L₆, where M = Mo and W, L = R(alkyl),^{8,9} NR₂,^{10,11} and OR,^{12,13} which have metal-to-metal triple bonds and a central ethane-like M₂X₆ core (X = C, N, O), the metal atoms do not achieve an 18-valence shell electron configuration, even when ligand to metal π bonding is important as is the case where L = NR₂ and OR.¹⁴ The compounds Cp₂M₂(CO)₄ and M₂L₆ may be termed electronically saturated and unsaturated, respectively, and differences in their reactivity patterns may be expected. Some of these have already been observed.

All compounds containing metal-to-metal multiple bonds are inherently coordinatively unsaturated and Cp₂M₂(CO)₄

and M₂L₆ compounds react to expand the coordination number of the metal as shown:



In reactions 1 and 2, the addition of four electrons to the electronically saturated M≡M moiety reduces the M-M bond order in Cp₂M₂(CO)₄L₂ and Cp₂M₂(CO)₄(un) compounds to a single M-M bond.¹⁸ Addition of 2L (four electrons) to Mo₂(OR)₆ compounds does not reduce the M-M bond order in the adducts. The structural characterization of the dimethylamine adduct of hexakis(trimethylsiloxy)dimolybdenum, Mo₂(OSiMe₃)₂(HNMe₂)₂,¹⁶ and Mo₂(OBU-*t*)₄(O₂COBU-*t*)₂¹⁷ reveals triple bonds between two four-coordinated molybdenum atoms with Mo-Mo distances of 2.242 (1) and 2.244 (1) Å, respectively; cf.¹² Mo-Mo = 2.222 (1) Å in Mo₂(OCH₂CMe₃)₆.