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Donor-acceptor properties of trivalent  
phosphorus and arsenic ligands

by

Larry James Vande Griend

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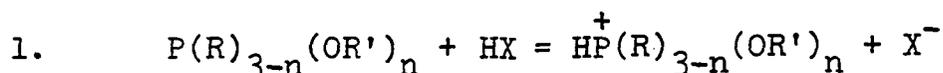
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PART I. INTERACTION OF TRIVALENT PHOSPHORUS LIGANDS WITH  
LEWIS ACIDS

## THE PROTON AS A LEWIS ACID

## Introduction

As a Lewis base, a trivalent phosphorus compound is capable of forming an adduct with a wide variety of Lewis acids including boranes, chalcogens, transition metal centers, carbonium ions and of prime importance here, the proton. The protonation of trivalent phosphorus is known to occur under acid conditions (1-5) as shown by reaction 1 where R and R' are alkyl, aryl or hydrogen and n = 0 to 3.

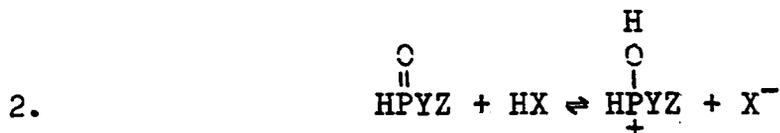


For phosphorus, a relatively weak base, it is often necessary to use a strong acid and low temperatures in order to achieve a protonated species which exchanges slowly on the nmr time scale. Although some protonated species, particularly those obtained from alkyl phosphines, can be observed in freshly prepared solutions at room temperature, dealkylation readily occurs with those compounds having alkoxy substituents (4,5).

Various acid media have been used as protonating agents for trivalent phosphorus including saturated HBr solutions of methylene chloride (1), concentrated H<sub>2</sub>SO<sub>4</sub> (2,6), ether solutions of HCl or CF<sub>3</sub>SO<sub>3</sub>H (5), trifluoroacetic acid (7), aqueous BF<sub>3</sub> solutions (6), fluorosulfuric acid (3,4) and a 1:1 ratio of HFSO<sub>3</sub>·SbF<sub>5</sub> (4). The last acid (Magic Acid) is

one of the strongest acids known. In addition, fluorosulfuric acid (4,8), sulfuric acid (6) and perchloric acid (9) have been used to study the protonation of phosphoric acids.

The resulting tetravalent species of reaction 1 can easily be observed by  $^{31}\text{P}$  and  $^1\text{H}$  nuclear magnetic resonance techniques. In the absence of additional coupling from the other substituents on phosphorus, both the  $^1\text{H}$  and  $^{31}\text{P}$  resonances for  $\text{H}-\overset{+}{\text{P}}\leftarrow$  are doublets with the same coupling constant and it is this value which is of primary interest here. All of the reported directly bonded PH coupling constants observed in protonation studies are listed in Table 1. Included are PH couplings obtained from protonated trivalent phosphorus systems as well as those observed for a protonated phosphoryl oxygen as shown in reaction 2 wherein Y and Z can be R, OR, H, or OH and R is alkyl or aryl.



Also listed in Table I are the  $^{31}\text{P}$  chemical shifts of the tetravalent species, the acid used and the temperature at which the measurement was made.

The first extensive study of the protonation of trivalent phosphorus systems was undertaken by Grim and McFarlane (1) who synthesized a variety of tertiary phosphine hydrobromides. They found that the  $^{31}\text{P}$  chemical shifts for each series of

Table 1. Chemical shifts and coupling constants for protonated trivalent phosphorus compounds

Protonated Species	Coupling Constant $^1J_{\text{PH}}^{\text{a}}$	$^{31}\text{P}$ Chemical Shift $\delta_{\text{P}}^{\text{b}}$	Acid	Temperature	Reference
$\text{HP}(\text{OCH}_3)_3^+$	827	-24.7	$\text{HFSO}_3$	-60	4
	$830 \pm 2$	-26	$\text{H}_2\text{SO}_4$	RT	2
$\text{HP}(\text{OC}_2\text{H}_5)_3^+$	811	-19.7	$\text{HFSO}_3$	-60	4
	$806 \pm 2$	-18	$\text{H}_2\text{SO}_4$	RT	2
$\text{HP}(\text{O}-\underline{1}-\text{C}_3\text{H}_7)_3^+$	796	-15.7	$\text{HFSO}_3$	-60	4
	$795 \pm 2$	-16	$\text{H}_2\text{SO}_4$	RT	2
$\text{HP}(\text{O}-\underline{n}-\text{C}_4\text{H}_9)_3^+$	812	-20.4	$\text{HFSO}_3$	-60	4
$\text{HP}(\text{OCH}_2\text{C}(\text{CH}_3)_3)_3^+$	$834 \pm 6$	-24.9	$\text{HCl}(\text{ether})$	-50	5
	810	-21.1	$\text{CF}_3\text{SO}_3\text{H}$	25	5

<sup>a</sup>In Hz.

<sup>b</sup>In ppm relative to 85%  $\text{H}_3\text{PO}_4$ .

Table 1. (Continued)

Protonated Species	Coupling Constant $^1J_{\text{P}}\text{H}$	$^{31}\text{P}$ Chemical Shift $\delta\text{P}$	Acid	Temperature	Reference
$\text{HP}(\text{OC}_6\text{H}_5)_3^+$	875	-11.7	$\text{HFSO}_3$	-60	4
	$870 \pm 2$	-10	$\text{H}_2\text{SO}_4$	RT	2
$\text{HP}(\text{OC}_6\text{H}_5)(\text{OCH}_2\text{CH}_2\text{O})^+$	$822 \pm 2$	-16	$\text{H}_2\text{SO}_4$	RT	2
$\text{HP}(\text{OH})(\text{OCH}_3)_3^+$	$744.3^c$	$-13.0^c$	$\text{CF}_3\text{CO}_2\text{H}$	RT	7
$\text{HP}(\text{OH})(\text{O}-\underline{n}-\text{C}_3\text{H}_7)_2^+$	820	-19.4	$\text{HFSO}_3$	-60	4
	804	-17.6	$\text{CF}_3\text{SO}_3\text{H}$	25	5
$\text{HP}(\text{OH})(\text{O}-\underline{1}-\text{C}_3\text{H}_7)_2^+$	812	-16.3	$\text{HFSO}_3$	-60	4
$\text{HP}(\text{OH})(\text{O}-\underline{n}-\text{C}_4\text{H}_9)_2^+$	819	-19.3	$\text{HFSO}_3$	-60	4
$\text{HP}(\text{OH})(\text{OCH}_2\text{C}(\text{CH}_3)_3)_2^+$	792	-16.6	$\text{CF}_3\text{SO}_3\text{H}$	25	5

<sup>c</sup>Probably not completely protonated. See text.

Table 1. (Continued)

Protonated Species	Coupling Constant $^1J_{\text{PH}}$	$^{31}\text{P}$ Chemical Shift $\delta\text{P}$	Acid	Temperature	Reference
$\text{HP}(\text{OH})_2(\text{O}-\underline{1}-\text{C}_3\text{H}_7)^+$	824	-17.3	$\text{HFSO}_3$	-60	4
$\text{HP}(\text{OH})_2(\text{OCH}_2\text{C}(\text{CH}_3)_3)^+$	786	-15.4	$\text{CF}_3\text{SO}_3\text{H}$	25	5
$\text{HP}(\text{OH})_3^+$	825	-19.0	$\text{HFSO}_3$	-60	4
	806.2	- <sup>d</sup>	$\text{H}_2\text{SO}_4$	RT	6
	804	- <sup>d</sup>	$\text{HClO}_4$	RT	9
$\text{HP}(\text{OCH}_3)_2(\text{C}_6\text{H}_5)^+$	$666 \pm 2$	-54	$\text{H}_2\text{SO}_4$	RT	2
$\text{HPH}(\text{OH})_2^+$	687	-36.1	$\text{HFSO}_3$	-60	4
	673.9	- <sup>d</sup>	$\text{H}_2\text{SO}_4$	RT	6
	671	- <sup>d</sup>	$\text{HClO}_4$	RT	9
$\text{HPF}(\text{OH})_2^+$	899	-15.7	$\text{HFSO}_3$	RT	8

<sup>d</sup>Not reported.

Table 1. (Continued)

Protonated Species	Coupling Constant, $^1J_{\text{PH}}$	$^{31}\text{P}$ Chemical Shift $\delta\text{P}$	Acid	Temperature	Reference
$\text{HP}(\text{OCH}_3)(\text{C}_6\text{H}_5)_2^+$	$553 \pm 2$	-56	$\text{H}_2\text{SO}_4$	RT	2
$\text{HPH}_3^+$	548	+101	$\text{HFSO}_3$	RT	3
	$546.7 \pm 0.3$	+104	$\text{H}_2\text{SO}_4$	-43	6
	$547.7 \pm 0.1$	- <sup>d</sup>	$\text{BF}_3 \cdot \text{H}_2\text{O}$	22	6
$\text{HPFH}(\text{OH})^+$	756	-39.2	$\text{HFSO}_3$	-60	8
$\text{HPH}(\text{C}_6\text{H}_5)_2^+$	519	+21.2	$\text{HFSO}_3$	RT	3
$\text{HPCl}(\text{C}_6\text{H}_5)_2^{+e}$	$561 \pm 2$	-46	$\text{H}_2\text{SO}_4$	RT	2
$\text{HPCl}_2(\text{C}_6\text{H}_5)^{+e}$	$653 \pm 2$	-41	$\text{H}_2\text{SO}_4$	RT	2

<sup>e</sup>The authors note that HCl is evolved on dissolution in  $\text{H}_2\text{SO}_4$  and suggest that the actual protonated species are  $\text{HP}(\text{OSO}_3\text{H})(\text{C}_6\text{H}_5)_2^+$  and  $\text{HP}(\text{OSO}_3\text{H})_2(\text{C}_6\text{H}_5)^+$ .

Table 1. (Continued)

Protonated Species	Coupling Constant $^1J_{PH}$	$^{31}P$ Chemical Shift $\delta P$	Acid	Temperature	Reference
$HP(CH_3)_3^+$	497	+3.2	$HFSO_3$	RT	3
	505	+2.9	$HBr(CH_2Cl_2)$	RT	1
$HP(C_2H_5)_3^+$	471	-22.5	$HFSO_3$	RT	3
	500	-19.7	$HBr(CH_2Cl_2)$	RT	1
$HP(\underline{i}-C_3H_7)_3^+$	448	-44.4	$HFSO_3$	RT	3
	455	-39.6	$HBr(CH_2Cl_2)$	RT	1
$HP(\underline{n}-C_4H_9)_3^+$	470	-13.7	$HFSO_3$	RT	3
	475	-11.9	$HBr(CH_2Cl_2)$	RT	1
	$457 \pm 10$	-12	$H_2SO_4$	RT	2
$HP(\underline{t}-C_4H_9)_3^+$	436	-58.3	$HFSO_3$	RT	3
$HP(\underline{n}-C_8H_{17})_3^+$	465	-13.0	$HFSO_3$	RT	3

 $\infty$

Table 1. (Continued)

Protonated Species	Coupling Constant $^1J_{\text{PH}}$	$^{31}\text{P}$ Chemical Shift $\delta\text{P}$	Acid	Temperature	Reference
$\text{HP}(\text{C}_6\text{H}_{11})_3^+$	445	-32.7	$\text{HFSO}_3$	RT	3
	455	-27.9	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1
$\text{HP}(\text{CH}_3)_2(\text{C}_6\text{H}_5)^+$	525	+2.1	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1
	$500 \pm 10$	+1	$\text{H}_2\text{SO}_4$	RT	2
$\text{HP}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)^+$	490	-18.3	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1
$\text{HP}(\text{n-C}_4\text{H}_9)_2(\text{C}_6\text{H}_5)^+$	490	-12.2	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1
$\text{HP}(\text{i-C}_3\text{H}_7)_2(\text{C}_6\text{H}_5)^+$	485	-32.0	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1
$\text{HP}(\text{C}_6\text{H}_{11})_2(\text{C}_6\text{H}_5)^+$	485	-20.8	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1
$\text{HP}(\text{CH}_3)(\text{C}_6\text{H}_5)_2^+$	525	+2.2	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1
$\text{HP}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2^+$	515	-8.3	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1

Table 1. (Continued)

Protonated Species	Coupling Constant $^1J_{\text{PH}}$	$^{31}\text{P}$ Chemical Shift $\delta\text{P}$	Acid	Temperature	Reference
$\text{HP}(\underline{n}\text{-C}_4\text{H}_9)(\text{C}_6\text{H}_5)_2^+$	520	-2.1	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1
$\text{HP}(\underline{1}\text{-C}_3\text{H}_7)(\text{C}_6\text{H}_5)_2^+$	510	-14.0	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1
$\text{HP}(\text{C}_6\text{H}_{11})(\text{C}_6\text{H}_5)_2^+$	510	-10.5	$\text{HBr}(\text{CH}_2\text{Cl}_2)$	RT	1
$\text{HP}(\text{C}_6\text{H}_5)_3^+$	510	-6.8	$\text{HFSO}_3$	RT	3
	$506 \pm 2$	-5	$\text{H}_2\text{SO}_4$	RT	2

phosponium compounds,  $R(C_6H_5)_2PH^+$ ,  $R_2(C_6H_5)PH^+$  and  $R_3PH^+$ , gave a linear relationship with respect to the sum of the group contributions of the organic substituents. Previous work (10) with tertiary phosphines had established the contributions each of these substituent groups made to  $^{31}P$  chemical shifts.

For the acyclic phosphine hydrobromides (1), the range of  $^1J_{PH}$  was 70 Hz, from 455 Hz for  $(C_6H_{11})_3PH^+$  and  $(i-C_3H_7)_3PH^+$  to 525 Hz recorded for  $(CH_3)_2(C_6H_5)PH^+$  and  $(CH_3)(C_6H_5)_2PH^+$ . Thus, the PH couplings for such phosphonium compounds were larger than the PH couplings of about 200 Hz found in trivalent phosphines (11). Since proton-phosphorus coupling had been found to be qualitatively related to the amount of s character in the bond (12), the rationale (1) of this phenomenon was provided by the relatively small amount of s character in the P-H bond of trivalent phosphines which have approximately  $p^3$  bonding and the larger amount of s character found in the P-H bond when phosphorus became increasingly  $sp^3$  hybridized as a result of quaternization. Grim and McFarlane (1) noted that  $^1J_{PH}$  increased with the number of phenyl groups attached to phosphorus. They also reported that dichloromethane solutions of the hydrobromides of  $P(C_6H_5)_3$ ,  $PH(C_6H_5)_2$  and  $PH_2(C_6H_5)$  did not show any  $^{31}P$  resonances. This indicated to them that these phosphines were so weakly basic that rapid proton exchange broadened the  $^{31}P$  resonance.

Prior to the work of Grim and McFarlane (1) the protolysis of  $\text{P}(\text{CH}_3)_3$  in water (13) had yielded a  $^1\text{JPH}$  value of  $515 \pm 10$  Hz whereas for  $[\text{HP}(\text{CH}_3)_3]^+[\text{Cl}^-]$  (11) it was 495 Hz with a chemical shift of +2.8 ppm. These data agree fairly well with the results of later work recorded in Table 1.

In 1967 McFarlane (14) determined from spin tickling experiments that the sign of  $^1\text{JPH}$  for  $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{PH}^+\text{Br}^-$  was positive relative to the sign of  $^1\text{J}^{13}\text{CH}$  which is positive (15).

In a study using  $\text{HFSO}_3$  as the acid, Olah and McFarland (3) showed that  $^1\text{JPH}$  is inversely related to the bulkiness of the alkyl substituents in a group of phosphines. Thus,  $^1\text{JPH}$  decreased steadily in  $\text{HPR}_3^+$  from 548 Hz to 436 Hz in the series  $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{i-C}_3\text{H}_7$  and  $\text{t-C}_4\text{H}_9$ . Their rationale was that increased bulk led to larger C-P-C angles and hence increased s character in the phosphorus bonds to the alkyl groups with a consequent decrease in s character in the bond between phosphorus and the proton. For six of the phosphonium ions another linear relationship of the chemical shifts with the sum of the group contributions for the phosphorus substituents, as described above, was found.

The next development in the protonation of trivalent phosphorus compounds was a study in which the average electronegativity of the substituents at phosphorus was varied over a wider range. McFarlane and White (2) found a significant increase in  $^1\text{JPH}$  with electronegativity for the representative

compounds  $\text{HP}(\text{C}_4\text{H}_9)_3^+$  (457 Hz),  $\text{HP}(\text{OCH}_3)(\text{C}_6\text{H}_5)_2^+$  (553 Hz),  $\text{HP}(\text{OCH}_3)_2\text{C}_6\text{H}_5^+$  (666 Hz),  $\text{HP}(\text{OCH}_3)_3^+$  (830 Hz) and  $\text{HP}(\text{OC}_6\text{H}_5)_3$  (870 Hz) in 100%  $\text{H}_2\text{SO}_4$ . These authors cautioned, however, against explaining these results solely in terms of s character changes in the phosphorus-hydrogen bond since it was felt that large changes in substituent angles would be necessary to account for the wide coupling range. An additional argument involving the effective nuclear charge placed on phosphorus by the increased electronegativity of the substituent groups was therefore invoked. A further discussion of this rationale will be taken up in the Results and Discussion section.

Olah and McFarland were the first to study the protonation of acyclic phosphites using fluorosulfuric acid (4). For the first three  $\text{HP}(\text{OR})_3^+$  species listed in Table I (also studied by McFarlane and White (2)) a decrease in  $^1\text{J}_{\text{PH}}$  is observed as R is changed from  $\text{CH}_3$  to  $\text{C}_2\text{H}_5$  to  $\text{i-C}_3\text{H}_7$ . This is reminiscent of the behavior of alkyl phosphines (3) and can be explained in the same manner, although neither report (2,4) included these arguments for phosphites. Upon warming the  $-60^\circ$   $\text{HFSO}_3$  solutions of phosphites, carbon-oxygen bonds were cleaved sequentially to form protonated phosphonic acid as the end product. This procedure made it possible to observe the nmr parameters, (Table I), for the series  $\text{HP}(\text{OCH}(\text{CH}_3)_2)_n(\text{OH})_{3-n}^+$  ( $n = 0$  to 3). It was also noted that complete fluorination

and oxidation of protonated  $P(OCH_3)_3$  eventually took place at room temperature to yield  $OPF_3$  (4).

Protonation of trialkyl phosphites and the mechanism of the first dealkylation step in the presence of HCl in ether solutions was investigated by Hudson and Roberts (5). For trineopentyl phosphite  $^1J_{PH}$  was found to be 834 Hz when protonated by HCl in a 1:6.6 phosphite/HCl ratio in ether at  $-50^\circ$  and 810 Hz when protonated by  $CF_3SO_3H$  in the same ratio at  $25^\circ$ . Although it is not concluded in their work, the lower value in the latter case probably indicates a rapid equilibrium in which the protonated phosphite is appreciably dissociated, since lower ratios of HCl to phosphite and warmer temperatures produced the same result. It is also probable that the  $^1J_{PH}$  value of 804 Hz for di-n-propyl phosphite in  $CF_3SO_3H$  at  $25^\circ C$  is indicative of incomplete protonation since  $^1J_{PH}$  for this compound in  $HFSO_3$  at  $-60^\circ C$  is 820 Hz (4). Hudson and Roberts (5) observed that  $CF_3SO_3H$ , like  $HFSO_3$ , also cleaved alkyl groups from neopentyl phosphite at  $25^\circ C$ , thus enabling them to observe the protonated di- and mononeopentyl phosphites. However, as noted for the two cases above with the same acid and temperature conditions, full protonation was probably incomplete. The kinetics of the first dealkylation will be discussed more appropriately in the Results and Discussion section.

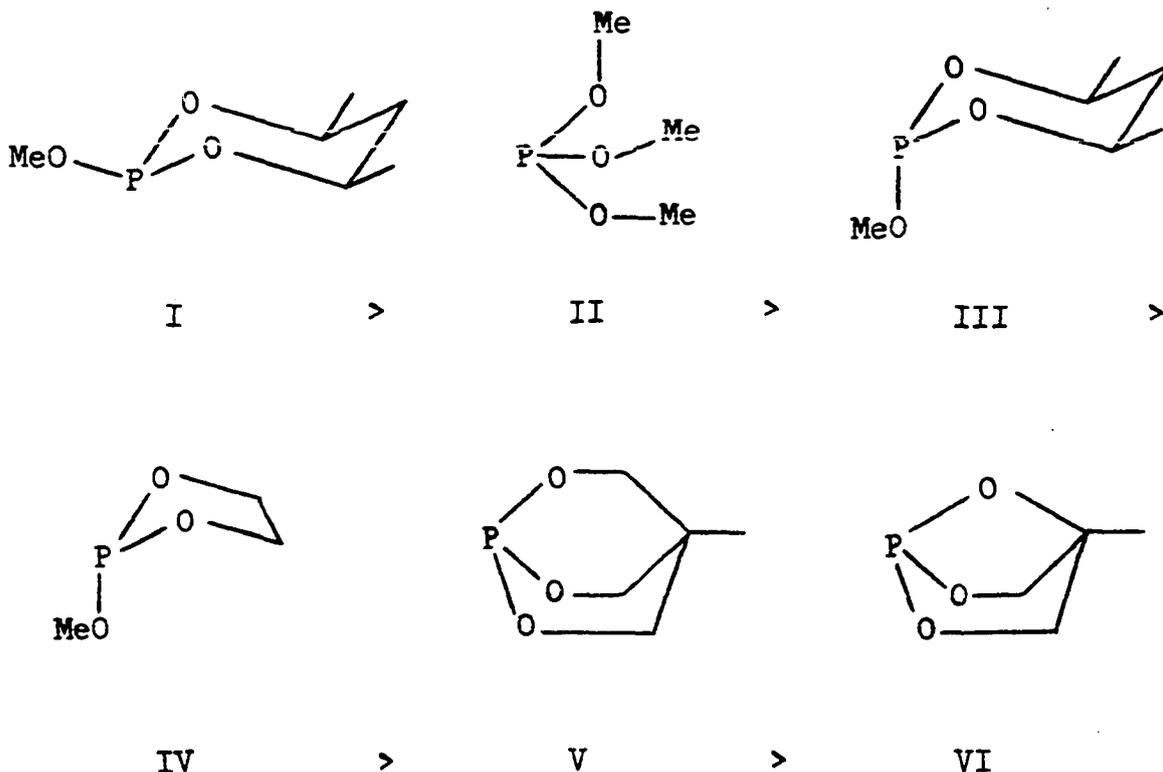
In a 10 to 1 trifluoroacetic acid/ $OPH(OCH_3)_2$  ratio at room temperature, protonation of the phosphoryl oxygen occurs

and  $^1\text{JPH}$  for  $\text{HP}(\text{OH})(\text{OCH}_3)_2$  was measured to be 744.3 Hz (7). This value is very low when compared to  $\text{H}^+\text{POH}(\text{O}-\text{n}-\text{C}_3\text{H}_7)_2$  (820 Hz) and it is reasonable to assume once again that protonation is incomplete. Since  $^1\text{JPH}$  values can be obtained by protonating the phosphoryl oxygen in hydrogen phosphonates and hydrogen phosphinates, protonated phosphonic and phosphinic acid (reaction 2) are also expected to display these couplings. Thus, Olah and McFarland (4) obtained values of 825 and 687 Hz, respectively, for  $\text{H}^+\text{P}(\text{OH})_3$  and  $\text{H}^+\text{P}(\text{OH})_2$  in  $\text{HFSO}_3$  at  $-60^\circ$ . The former value compares favorably with 827 Hz obtained for  $\text{HP}(\text{OCH}_3)_3^+$ . Protonation studies on these acids by other workers using  $\text{H}_2\text{SO}_4$  (6) and  $\text{HClO}_4$  (9), both at room temperature, resulted in lower values for  $^1\text{JPH}$  as shown in Table 1. In a later paper, Olah and McFarland (8), succeeded in obtaining  $^1\text{JPH}$  values for  $\text{HPFH}_2^+$  (756 Hz) and  $\text{HPF}(\text{OH})_2^+$  (899 Hz), thus showing that substitution of fluorine for hydrogen in  $\text{HPH}_3^+$  and for hydroxy in  $\text{HP}(\text{OH})_3^+$  increases  $^1\text{JPH}$  by 208 and 74 Hz, respectively.

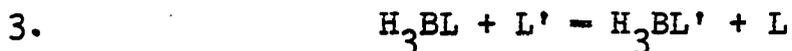
From the protonation studies described above, it is apparent that a very strong nonaqueous acid at low temperature is highly desirable to effect complete protonation and that the cold solutions retard solvolysis reactions. The very strong acid,  $\text{HFSO}_3$  (16), is greatly favored over sulfuric acid because it remains reasonably nonviscous down to  $-80^\circ$ . A still stronger acid system is a 1:1 mixture of  $\text{HFSO}_3$  and

$\text{SbF}_5$  (16) although it suffers from a minor handling disadvantage in that the volatile diluents  $\text{SO}_2$  or  $\text{SO}_2\text{ClF}$  must be condensed into the mixture to overcome viscosity increases at low temperature (17).

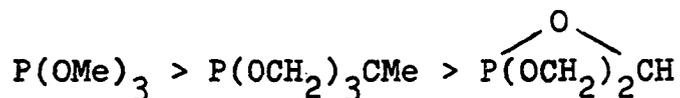
Until the present work, only one cyclic phosphite had been protonated, namely,  $\text{C}_6\text{H}_5\text{OPOCH}_2\text{CH}_2\text{O}$  (2). A more extensive study of protonated monocyclic and bicyclic phosphites seemed warranted when it was realized that the "hinge" (18,19) and orbital repulsive (20,21) effects concluded to be operative in cyclic phosphites would contribute increasingly to both the relative positive charge on phosphorus and the s character in the phosphorus lone pair. These effects are important in accounting for the decreasing basicity order:



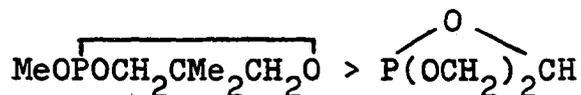
The evidence for the decrease in basicity of the phosphorus lone pair comes from several sources. Equilibrium studies (22) involving borane adducts (reaction 3) wherein a



stronger phosphorus base will displace  $\text{BH}_3$  from a weaker base have shown that the order of basicities is



and

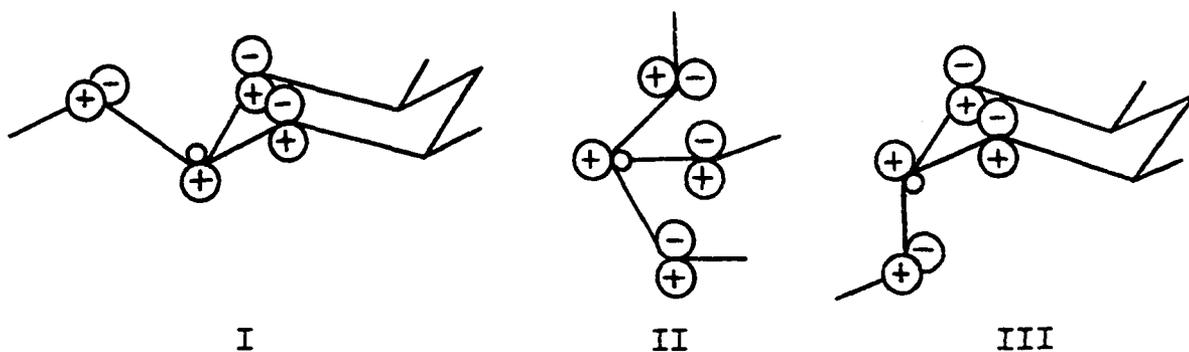


Furthermore, BH stretching frequencies of borane adducts (22, 23) show an increase for I through VI which reflects the decreasing ability of the phosphorus to rehybridize a  $\text{BH}_3$  moiety. Finally, increasingly smaller OH stretching frequency shifts found for phosphites and phosphates hydrogen bonded to phenol is indicative of lessened basicity in this series (24, see also p. 139 of this work).

Available structural data summarized for phosphites and phosphates (18,19,20) show that POC angles prefer to be about  $120^\circ$  while OPO angles tend to be approximately  $100^\circ$ . Thus, the  $\text{sp}^2$  hybridization at an alkoxy oxygen places the remaining pair of electrons in a p orbital.

The interaction of these p orbitals with the phosphorus lone pair is the basis for the orbital repulsion effect.

Their geometrical relationship (18,19,20) for phosphites I, II and III is shown with the arrangement in IV to VI approximately that of III. Thus, there are two p orbitals repelling

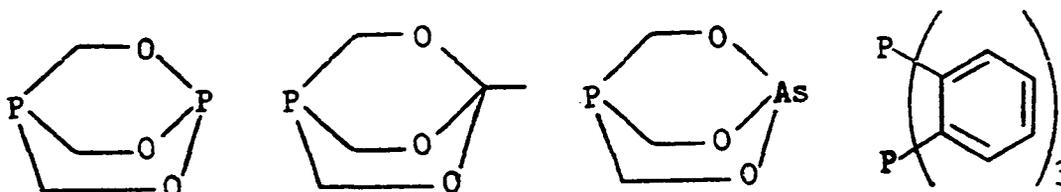


the phosphorus lone pair in I, one in II and none in III. The result is that the energy of the phosphorus lone pair decreases from I to III and the lone pair becomes less receptive to Lewis acids such as  $\text{BH}_3$  and phenol. In terms of orbital repulsion alone, the basicity of phosphites III to VI would be expected to be fairly constant. However, the "hinge" effect described next becomes important with increasing constraint and begins to play a differentiating role.

The electron pair in the p orbital on any alkoxy oxygen involved in a  $120^\circ$  POC angle is able to participate in p $\rightarrow$ d pi bonding with the phosphorus d orbitals, thereby accumulating electron density on phosphorus. However, polarization of the phosphorus lone pair by a Lewis acid opens the OPO angles which in turn brings about a decrease in the POC angles.

This has been termed the "hinge" effect by Verkade (18,19). Because of increasing constraint of the alkoxy groups from III to VI the POC angles progress toward tetrahedrality, decreasing the pi bonding in the P-O bond and thus reducing the electron density on phosphorus.

In an earlier communication (25), we reported that the bicyclic phosphite,  $P(OCH_2)_3CCH_3$ , when protonated in  $HFSO_3$  possessed an unusually large  $^1J_{PH}$  value of  $898 \pm 3$  Hz at  $-55^\circ C$  when compared to protonated acyclic phosphites. The primary goal of this work was to extend that study to a variety of protonated monocyclic and bicyclic phosphites in order to relate the  $^1J_{PH}$  values to the electronic properties of the phosphorus. Two related studies stemming from this project were the protonation of the bicyclic organophosphines shown below and the protonation of  $PF_{3-n}Cl_n$  ( $n = 0$  to  $3$ ) and



$PCl_{3-n}Br_n$  ( $n = 1$  to  $3$ ). The detection of  $HPF_3^+$  was of particular interest in view of the earlier unsuccessful attempt to protonate  $PF_3$  by others (8).

## Experimental

### Techniques and preparations

Materials Part of the fluorosulfuric acid was a gift from Research Organic/Inorganic Chemical Corporation while the remainder was purchased from Aldrich Chemical Corporation. It was always distilled prior to use ( $b_g = 50^\circ$ ; lit.  $b = 163^\circ$  at atmospheric pressure (16)). Superacid,  $\text{HFSO}_3 \cdot \text{SbF}_5$ , was obtained from the latter company sealed in vials under nitrogen and used as received. Sulfur dioxide was purchased from Matheson.

The alcohols not synthesized,  $\text{CF}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{C}(\text{CH}_2\text{OH})_3$ , were purchased from Aldrich Chemical Corporation. All alcohols were dried by vacuum distillation before use.  $\text{SbF}_3$  was purchased from Alfa. All other chemicals needed for preparations were reagent grade and used without further purification with the following exceptions.  $\text{SbCl}_5$  was always taken from a freshly opened bottle while  $\text{P}(\text{OCH}_3)_3$ ,  $\text{PCl}_3$  and  $\text{PBr}_3$  were distilled prior to use.

Spectroscopy The  $^{31}\text{P}$  data were obtained with a Bruker HX-90 spectrometer operating at 36.44 MHz in the Fourier mode. The acid solution provided the fluorine signal necessary for lock stabilization for the protonation experiments. The spectra obtained were always undecoupled. All samples were contained in 10 mm (o.d.) tubes and were transferred to a previously cooled probe. A melting point

capillary, containing the standard, was held in the center of the tube by means of a hole drilled in the bottom of a Teflon plug. The Teflon plug fitted tightly in the tube and also prevented vortex formation.

For the protonation of phosphites, the standard was 85%  $\text{H}_3\text{PO}_4$ . At or above  $-50^\circ$  this signal was reasonably sharp but at lower temperatures the signal became very broad because of viscosity. Chemical shifts below  $-50^\circ\text{C}$  were then referenced to a cursor point set on the phosphoric acid peak at a higher temperature by the computer. During any experiment involving phosphorus trihalides the probe temperature was never allowed above  $-40^\circ$  because fluorination and/or solvolysis of some samples at higher temperatures would produce explosive results. Since the signal from 85%  $\text{H}_3\text{PO}_4$  would have been too broad for most of these experiments, the standard chosen was  $\text{PCl}_3$  contained in an external capillary. However, the chemical shifts listed in Table 9 are given relative to 85%  $\text{H}_3\text{PO}_4$ . The chemical shift of neat  $\text{PCl}_3$  with respect to 85%  $\text{H}_3\text{PO}_4$  was measured at  $-219.4$  ppm in agreement with literature (26). The chemical shifts for the protonated phosphines,  $\text{P}(\text{OCH}_2)_3\text{P}$ ,  $\text{P}(\text{CH}_2\text{O})_3\text{CCH}_3$  and  $\text{P}(\text{CH}_2\text{O})_3\text{As}$ , found in Table 7 were also obtained by this method.

The protonation of the bicyclic phosphite,  $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ , reported earlier by us (25), was observed from the  $^1\text{H}$  nmr spectrum using a Varian Associates HA-100 nmr spectrometer with external TMS as a reference.

Routine  $^1\text{H}$  nmr spectra for checking the purity of the phosphorus ligands were obtained on either a Varian Associates A-60 nmr spectrometer or a Hitachi Perkin-Elmer R20-B spectrometer operating at 60 MHz. An Atlas CH-4 mass spectrometer provided the low resolution mass spectra. The remaining  $^{31}\text{P}$  spectra were obtained on the Bruker HX-90 spectrometer operating at 36.44 MHz in the Fourier mode. The lock signal in most cases was that provided by deuterium in the solvents,  $\text{CDCl}_3$  or  $\text{CD}_3\text{CN}$ . In a few instances a fluorine lock stabilization was used with the fluorine signal provided by  $\text{CFCl}_3$  (Freon 11). Chemical shifts obtained on the same compound using these two different lock stabilizations are within experimental error ( $\pm 0.2$  ppm) of each other. The infrared spectrum, calibrated with polystyrene, was recorded on a Beckman IR-4250 using sodium chloride optics.

Sample preparation      Preparation of samples for protonation of the phosphites and the phosphine,  $\text{P}(\text{o-C}_6\text{H}_4)_3\text{P}$ , was accomplished by initially cooling about 2 ml of  $\text{HFSO}_3$  at  $-78^\circ$  in the nmr tube using a Dry Ice-isopropanol slush bath. A pipet was used to add a liquid phosphite, allowing it to cool as it flowed down the inside of the tube. Solid phosphites were added in small amounts of about 20 mg. Approximately 200 mg of phosphite was used in all experiments which meant that the acid was always present in at least a ten-fold excess. Vigorous shaking while alternately warming

(about  $-40^{\circ}$ ) and cooling the heterogeneous mixture was necessary to effect solution. Severe decomposition or small explosions occurred if localized areas of heating were allowed to intensify around undissolved phosphite. For the most

constrained phosphite,  $\text{P}(\text{OCH}_2)_2\text{CMe}$ , which is a liquid at room temperature, freezing in a separate tube was first necessary, followed by breaking the solid into small pieces and depositing the latter on  $\text{HFSO}_3$  which had been frozen in liquid nitrogen. Warming to  $-78^{\circ}\text{C}$  and vigorous shaking at that temperature effected solution after about one hour.

All acid solutions of the phosphorus trihalides were maintained at  $-78^{\circ}\text{C}$  throughout preparation and handling. Sulfur dioxide, used as a diluent (17), was mixed with  $\text{HFSO}_3 \cdot \text{SbF}_5$  in 8:3 volume ratio. The gases,  $\text{PF}_3$  and the  $\text{PF}_2\text{Cl}-\text{PF}_3$  mixture, were bubbled into the acid.  $\text{PCl}_3$ ,  $\text{PBr}_3$ , the  $\text{PFCl}_2-\text{PCl}_3$  mixture and the  $\text{PCl}_3-\text{PCl}_2\text{Br}-\text{PClBr}_2-\text{PBr}_3$  mixture were added as liquids to the acid and some shaking was required to effect solution.

The phosphines,  $\text{P}(\text{CH}_2\text{O})_3\text{P}$ ,  $\text{P}(\text{CH}_2\text{O})_3\text{CMe}$  and  $\text{P}(\text{CH}_2\text{O})_3\text{As}$ , were protonated in the sulfur dioxide solution of  $\text{HFSO}_3 \cdot \text{SbF}_5$  prepared as described above. However, only 70-80 mg of each of these solid compounds was used and solution was very rapid.

Preparation of compounds

$(\text{HOCH}_2)_2(\text{HO})\text{CCH}_3$ , 2-methylglycerol      This triol

was prepared from 2-methyl-2-propene-1-ol by the method used to hydroxylate cyclohexene (27) with the modification that acetone was used for extraction. The yield of viscous liquid ( $b_{0.7} = 129-132^\circ$ ; lit.  $b_3 = 120-122^\circ$  (28)) was 55%. The proton nmr spectrum in  $\text{CD}_3\text{CN}$  shows a sharp resonance at 1.07 ppm ( $\text{CH}_3$ ) and broader resonances at 3.25 ppm (OH) and 3.42 ppm ( $\text{CH}_2$ ) integrating in a 3:3:4 ratio, respectively.

$(\text{CH}_3)_2(\text{HO})\text{CC}(\text{OH})(\text{CH}_3)_2$ , pinacol      The preparation

of this diol has been previously described (29). Purification was accomplished by recrystallization from water and vacuum distillation of the resulting hexahydrate removed the water to give the product ( $b_{30} = 94-96^\circ$ ; lit.  $b = 168-173^\circ$  at atmospheric pressure (30)).

$(\text{CH}_3)_2(\text{HO})\text{CCH}_2\text{C}(\text{OH})(\text{CH}_3)_2$ , 2,3-dimethyl-2,3-

butanediol      This diol was prepared by the action of  $\text{CH}_3\text{MgI}$  on water-free diacetone alcohol (31) with the modification that it was necessary to reflux the mixture for 12 hours to insure complete reaction. Furthermore, workup was accomplished by slow addition of aqueous ammonium chloride. Distillation of the ether layer gave a 72% yield of diol ( $b_{23} = 106-107^\circ$ ; lit.  $b_5 = 89^\circ$  (31)). A pnmr spectrum in  $\text{CD}_3\text{CN}$  displayed sharp peaks at 1.26 ppm ( $\text{CH}_3$ ) and 1.68 ppm ( $\text{CH}_2$ ) but a slightly broader peak at 4.33 (OH) integrating in a 6:2:2 ratio, respectively.

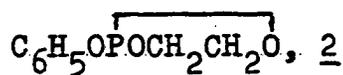
HOCH<sub>2</sub>C(OH)(CH<sub>3</sub>)<sub>2</sub>, 2-methyl-1,2-propandiol This

diol was unexpectedly prepared from 2-methyl-2-propene-1-ol according to a procedure (32) reported to yield 2-methylglycerol and although the latter compound was actually the desired product (and was subsequently synthesized as recorded above), 2-methyl-1,2-propane diol also proved to be useful for our purposes. The product was a mobile liquid distilling at 66° and 2 mm of Hg (lit.  $b_{10}$  = 80-81° (33)) in a 40% yield. A pmr spectrum in CD<sub>3</sub>CN showed a singlet at 1.11 ppm (CH<sub>3</sub>), a singlet at 3.26 ppm (CH<sub>2</sub>) and a singlet at 3.39 ppm (OH) in the correct integration ratios.

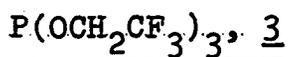
P(O)(OCH<sub>2</sub>)<sub>2</sub>CMe, 1 This phosphite formally named

4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.1]heptane was prepared by transesterification in an analogous fashion to P(O)(OCH<sub>2</sub>)<sub>2</sub>CH (34,35). In a typical preparation, a middle fraction of 2-methylglycerol was distilled into a tared reaction flask. This procedure minimized transferring the very viscous liquid. To 64 g of triol (0.61 mole) were added 78 grams (0.63 mole) of trimethyl phosphite and 50 ml of Dow Corning 550 silicon oil under a nitrogen flush. The mixture was heated to about 90°C whereupon methanol slowly distilled. After the distillation of methanol slowed considerably, the reaction flask was cooled to 50°C and 1.5 grams of NaOCH<sub>3</sub> were added. Distillation was then continued under vacuum and 59 grams (73% yield) of a colorless liquid with a b.p. of 60-65°

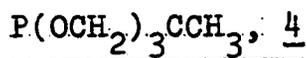
at 7-5 mm of Hg was realized. Redistillation at 46-48° and 6-5 mm of Hg resulted in pure material whose mass spectrum showed a parent ion at 134 m/e corresponding to the molecular weight. A  $^1\text{H}$  nmr spectrum in  $\text{CDCl}_3$  showed a singlet methyl resonance at 1.62 ppm and a multiplet for the methylene protons centered at 3.55 ppm.



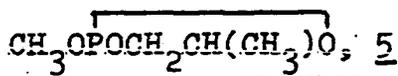
The preparation and purification of this phosphite by transesterification of triphenyl phosphite has been described (36) ( $b_{0.2-0.3} = 72-73^\circ$ ; lit.  $b_{0.3} = 73^\circ$  (36)).



The preparation and purification of this compound from  $\text{PCl}_3$  and the corresponding alcohol in the presence of a nitrogen base has been described (37) ( $b_{35} = 65^\circ$ ; lit.  $b_1 = 32-34^\circ$  (37)). A mass spectrum revealed the parent ion at 328 m/e corresponding to the calculated molecular weight.



The preparation and purification of this bicyclic phosphite has been described elsewhere (38).



The preparation of this monocyclic phosphite has been described elsewhere (39). Purification by distillation ( $b_{38} = 61-68^\circ$ ; lit.  $b_{23} = 53-59^\circ$  (39)) occurred in a temperature range because of the presence of two possible isomers (cis and trans methyl to methoxy).

Although these can be separated by gas liquid pressure chromatography (39), further separation was not carried out here.

$\text{P}(\text{OCH})_3(\text{CH}_2)_3$ , 6      This adamantane-like phosphite was prepared by Ebel (40) following a known literature procedure (38).

$\text{CH}_3\text{OPOCH}_2\text{CH}_2\text{CH}_2\text{O}$ , 7      The synthesis and purification of this six-membered ring phosphite has been described previously (41) ( $b_{21} = 64-66^\circ$ ; lit.  $b_{38} = 76-78^\circ$  (41)).

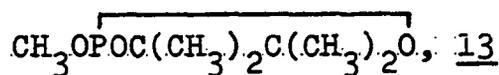
$\text{ax-CH}_3\text{OPOCH}(\text{CH}_3)_{\text{eq}}\text{CH}_2\text{CH}(\text{CH}_3)_{\text{eq}}\text{O}$ , 8      The synthesis and purification of this six-membered ring phosphite has been described previously (41).

$\text{CH}_3\text{OPOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}$ , 9      This phosphite was prepared by Rix (42) according to a known procedure (41).

$\text{eq-CH}_3\text{OPOCH}(\text{CH}_3)_{\text{eq}}\text{CH}_2\text{CH}(\text{CH}_3)_{\text{eq}}\text{O}$ , 10      The synthesis and purification of this six-membered ring phosphite has been described elsewhere (43).

$\text{CH}_3\text{OPOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ , 11      A preparation of this seven-membered ring phosphite, reported some time ago (44), involves the reaction of  $\text{CH}_3\text{OPCl}_2$  with 1,4-butanediol in the presence of pyridine, but only a 3% yield was obtained. A somewhat better method involves transesterification as reported

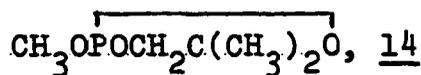
here. To about 200 ml of benzene was added 30 grams (0.33 mole) of 1,4-butanediol. Some of the benzene and any benzene-water azeotrope was then distilled away from this heterogeneous mixture to ensure the absence of water. The mixture was then cooled to 40°C after which 47 g (0.38 mole) of  $P(OCH_3)_3$  and 0.1 g of  $NaOCH_3$  were added. By vigorously stirring the mixture and slowly heating from 40° to 110°C, the methanol-benzene azeotrope and finally the remaining benzene were distilled away. Distillation was then continued under vacuum and a 13% yield of colorless liquid was realized ( $b_{9-8} = 56-57^\circ$ ; lit.  $b_{4.5-5.0} = 54-55^\circ$  (44)). The  $^1H$  nmr spectrum (neat) revealed a quintet at 1.70 ppm ( $OCH_2CH_2$ ) with  $^3J_{HCCH} = 2.4$  Hz, a doublet at 3.43 ppm ( $OCH_3$ ) with  $^3J_{POCH} = 11.2$  Hz and a complex multiplet centered at 3.86 ppm ( $OCH_2CH_2$ ) having the correct integration ratios of 4:3:4, respectively. A parent ion at 150 m/e in the mass spectrum corresponds to the molecular weight.



This phosphite was

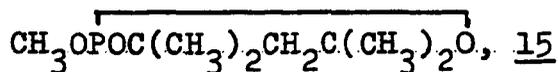
prepared as previously recorded (39) with the modification

that the intermediate  $\overline{ClPOC(CH_3)_2C(CH_3)_2O}$  was not isolated before reaction with methanol. Purification by distillation yielded the liquid product ( $b_{19} = 67^\circ$ ; lit.  $b_3 = 33^\circ$  (39)).



This phosphite was

prepared as recorded elsewhere (39) with the modification noted for phosphite 13. Distillation yielded pure product ( $b_{41} = 70-71^\circ$ ; lit.  $b_{20} = 54^\circ$  (39)).



To a mechanically

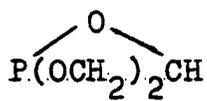
stirred solution of 27.5 g (0.200 mole) of  $\text{PCl}_3$  in ether at  $0-5^\circ\text{C}$ , was slowly added a solution of 24.6 g (0.200 mole) of diol and 35 g (0.44 mole) of pyridine in ether. After addition was complete, stirring was continued for about one hour before an ether solution of 6.4 g (0.20 mole) of methanol and 16 g of pyridine (0.20 mole) was slowly added. After this addition the ice bath was removed and stirring was continued overnight. With the use of a Schlenk apparatus, the ethereal solution was filtered from the pyridine salt and the solid was further washed with ether. Removal of the ether and distillation of the residue gave 21.5 g of the phosphite in a 56% yield. The pure colorless phosphite distilled at  $82-83^\circ\text{C}$  and 21 mm of Hg. The  $^1\text{H}$  nmr spectrum of the neat liquid showed a slightly broadened resonance at 1.34 ppm for the two pairs of chemically inequivalent methyl protons on the ring, a doublet ( $^3\text{JPOCH} = 12.1$  Hz) at 3.36 ppm for the methoxy protons and an AB pattern of an ABX system for the methylene protons centered at 2.04 ppm with the correct integration of 12:3:2, respectively, for the three types of protons. In the ABX

system where X is phosphorus,  $JAB = 14.2$  Hz,  $JAX = 3.1$  Hz,  $JBX = 0.0$  Hz and  $\delta_B - \delta_A = 33.5$  Hz. A mass spectrum revealed a parent peak at 192 m/e corresponding to the molecular weight.

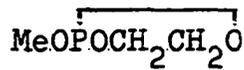
An attempt to prepare this phosphite by the transesterification of  $P(OCH_3)_3$  with the diol was not successful. Although methanol along with  $P(OCH_3)_3$  slowly distilled from the reaction mixture when heated to 110-120°C, vacuum distillation of the remaining liquid yielded a mixture of  $OP(OCH_3)_3$  and  $H(O)P(OCH_3)_2$ . The residue left in the reaction vessel which solidified upon cooling proved to be

$H(O)POC(CH_3)_2CH_2C(CH_3)_2O$ . This material after recrystallization from ether had a m.p. of 61°C and a mass spectrum revealed a parent peak at 178 m/e corresponding to the molecular weight. A  $^1H$  nmr spectrum ( $CDCl_3$ ) revealed resonances for the two different sets of methyl protons at 1.49 ppm and 1.53 ppm, a doublet at 6.98 ppm with  $^1J_{PH} = 694.0$  Hz for the proton directly bonded to the phosphorus and a broadened resonance for the methylene protons at 2.04 ppm, all in the correct integration ratios for this hydrogen phosphonate. The methylene resonance is broadened, possibly because the two protons probably represent an AB system which is almost collapsed. The outer peaks, being small in that case, are thus buried in the baseline. A  $^{31}P$  spectrum taken under proton nondecoupled conditions revealed a doublet for the phosphorus resonance centered at +6.2 ppm relative to

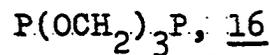
85%  $\text{H}_3\text{PO}_4$ . The value of 692.5 Hz for  $^1\text{JPH}$  compares well with that obtained from the proton nmr. When dissolved in  $\text{CCl}_4$ , an infrared spectrum revealed a phosphoryl resonance at  $1281\text{ cm}^{-1}$  with a shoulder at  $1287\text{ cm}^{-1}$ , and a P-H stretch at  $2408\text{ cm}^{-1}$  with a shoulder at  $2429\text{ cm}^{-1}$ . Thus, all of the spectroscopic parameters are consistent with the formulation as the hydrogen phosphonate but the stereochemistry at phosphorus is uncertain. The nature of the reaction resulting in this product, instead of the sought for phosphite, is not fully understood.



This compound was prepared by the transesterification of  $\text{P}(\text{OMe})_3$  with glycerine according to a modified procedure (45) ( $b_{0.50-0.75} = 40-45^\circ$ ; lit.  $b_4 = 40^\circ$  (34)).



This compound was prepared from the diol and  $\text{P}(\text{OMe})_3$  according to White (46) (b.p.  $52-53^\circ$  at 20 mm of Hg; lit.  $56-58^\circ$  at 30 mm of Hg (46)).



The preparation of this difunctional phosphorus ligand was carried out as previously described (47) with the modification that  $\text{P}(\text{OCH}_3)_3$  was reacted with  $\text{P}(\text{CH}_2\text{OH})_3$  triol in a vigorously stirred benzene suspension. After the benzene-methanol azeotrope was distilled away, the remaining benzene solution was decanted

from the insoluble polymer that had formed. Removal of the benzene under vacuum and sublimation of the residue resulted in pure product.

As(OCH<sub>2</sub>)<sub>3</sub>P, 17      The preparation of this bicyclic compound has been described elsewhere (47).

P(CH<sub>2</sub>O)<sub>3</sub>CCH<sub>3</sub>, 18      The preparation of this bicyclic phosphine has been described elsewhere (48), however, the phosphine triol used in this synthesis was prepared following a later procedure (47).

P(O-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, 19      The preparation of this triptycene phosphine has been previously described (49) (m.p. 315-317°C, lit. 323-325°C (49)).

PF<sub>3</sub>, PF<sub>2</sub>Cl and PFCl<sub>2</sub>      These phosphorus halides were synthesized by the action of SbF<sub>3</sub> on PCl<sub>3</sub> with SbCl<sub>5</sub> as a catalyst as initially described by Booth and Bozarth (50) and simplified by Holmes and Gallagher (51). However, only PF<sub>3</sub> was obtained pure by distillation. The mixed compounds, PF<sub>2</sub>Cl and PFCl<sub>2</sub>, difficult to obtain pure by redistillation, were obtained as mixtures with PF<sub>3</sub> and PCl<sub>3</sub>, respectively. Fortunately, these mixtures presented no problems in the protonation studies since the chemical shifts and couplings are very distinctive for each species.

PCl<sub>2</sub>Br and PClBr<sub>2</sub>

These phosphorus trihalides

were obtained as a mixture with PCl<sub>3</sub> and PBr<sub>3</sub> when 44 g (0.32 mole) of PCl<sub>3</sub> and 43 g (0.16 mole) of PBr<sub>3</sub> were refluxed at 100°C for 24 hrs. Distillation yielded a fraction of 15 ml with a boiling point of 98-99° at atmospheric pressure. A <sup>31</sup>P spectrum showed this to be approximately 30% PCl<sub>3</sub>, 35% PCl<sub>2</sub>Br, 25% PClBr<sub>2</sub> and 10% PBr<sub>3</sub>.

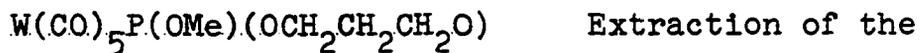
W(CO)<sub>5</sub>(phosphite) complexes

Four new complexes

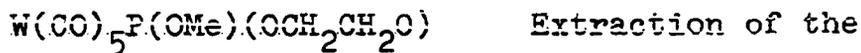
of this formulation were synthesized by the known reaction (52)  $[W(CO)_5I]NEt_4 + L + Et_3OBF_4 \rightarrow W(CO)_5L + NEt_4BF_4 + EtI + Et_2O$ . All reactions were carried out under nitrogen atmosphere using a Schlenk apparatus. The general procedure was to partially dissolve  $[W(CO)_5I]NEt_4$  in 30 ml of CH<sub>2</sub>Cl<sub>2</sub>. To this solution-suspension was added the phosphite ligand and an excess of triethyloxonium tetrafluoroborate. Stirring for 1 to 5 hrs produced an almost colorless solution indicating reaction was complete. The solvent was then removed under vacuum leaving a residue from which the product could be extracted.

In the characterization of the individual complexes described below, CDCl<sub>3</sub> was used as the <sup>1</sup>H nmr solvent. Mass spectra always revealed parent ions corresponding to the three most abundant isotopes of tungsten (mass 182, 26.4%; mass 184, 30.6%; and mass 186, 28.4%) although only the parent ion with mass 184 is mentioned specifically. Furthermore, the

fragmentation pattern showed that all of the complexes lost five carbonyls sequentially before further breakdown. The tungsten-phosphorus coupling constants are listed in Table 10 while the  $^{31}\text{P}$  chemical shifts are found in Table 23. The carbonyl stretching frequencies are found in Table 20.

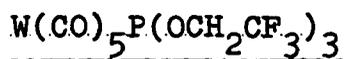


residue resulting from reacting 1.74 g (3.00 mmole) of tungsten carbonyl salt and 0.60 g of phosphite with 20 ml of hexane and cooling to  $-78^\circ$  gave 0.82 g (60% yield) of fluffy white product (m.p.  $54-55^\circ$ ). A  $^1\text{H}$  nmr spectrum showed a multiplet at 2.1 ppm ( $\text{CH}_2$ ), a multiplet at 4.1 ppm ( $\text{OCH}_2$ ) and a doublet at 3.65 ppm ( $\text{CH}_3$ ) with  $^3\text{JPOCH} = 12.0$  Hz. A mass spectrum gave a parent ion at 460 m/e corresponding to the molecular weight of the complex and a base peak at 376 m/e showing that three carbonyls are most easily lost.



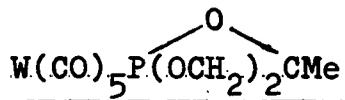
residue resulting from reacting 1.74 g (3.00 mmole) of tungsten carbonyl salt and 0.60 g (4.9 mmole) of phosphite with 20 ml of hexane and cooling to  $-78^\circ$  gave 0.93 g (69% yield) of white product (m.p.  $64-66^\circ$ ). A  $^1\text{H}$  nmr spectrum revealed a multiplet (ring  $\text{CH}_2$  protons) at 2.3 ppm and a doublet ( $\text{OCH}_3$  protons;  $^3\text{JPOCH} = 11.7$  Hz) at 3.58 ppm. A parent ion at 446 m/e in the mass spectrum corresponds to the molecular weight of the complex and a base peak at 362 m/e

shows that like the preceding monocyclic complex, loss of three carbonyls is favored.



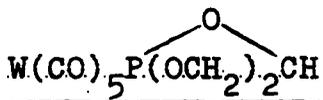
After the reaction of

0.58 g (1.0 mmole) of tungsten carbonyl salt and 0.39 g (1.2 mmole) of ligand, evaporation of the cyclohexane extractant (30 ml) resulted in an oil which was purified by distillation onto a cold finger at 70° and 0.1 mm Hg. A <sup>1</sup>H spectrum revealed a quintet centered at 4.26 ppm (<sup>3</sup>J<sub>P</sub>OCH = <sup>3</sup>J<sub>F</sub>CCH = 7.73 Hz). A mass spectrum showed a parent ion for the molecular weight of the complex at 652 m/e but a base peak at 328 m/e for the molecular weight of P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>.



Extraction of the residue

resulting from reacting 0.58 g (1.0 mmole) of tungsten carbonyl salt and 0.16 g (1.2 mmole) of P(O)(OCH<sub>2</sub>)<sub>2</sub>CMe with a 9:1 mixture of methylcyclohexane and CH<sub>2</sub>Cl<sub>2</sub> yielded 0.37 g (81% yield) of white crystals (m.p. 152-153°). A <sup>1</sup>H nmr spectrum revealed a methyl proton singlet at 1.68 ppm and a methylene multiplet at 3.85 ppm. A parent ion at 458 m/e for the molecular weight of the complex was found in the mass spectrum; however, the base peak at 318 m/e corresponds to the loss of five carbonyls.



This compound was prepared

by a route different from the four preceding complexes. A solution of diglyme (distilled from CaH<sub>2</sub>) containing 8.8 g

(25 mmole) of  $W(CO)_6$  and 2.0 (17 mmole) of  $P(O)(OCH_2)_2CH$  was heated at  $130^\circ$  for 7 hours. Formation of an undesirable black tar occurs if the solution is heated at  $160^\circ$ . The diglyme was removed under vacuum and the residue extracted with 100 ml of benzene. Addition of 50 ml of pentane to the benzene solution and cooling to  $0^\circ$  gave 5.2 g (71% yield) of crystalline product (m.p.  $153-154^\circ$ ). An  $^1H$  nmr spectrum revealed a methylene multiplet at 4.0 ppm and two smaller sets of multiplets for the bridgehead proton centered at 5.1 ppm ( $^3J_{POCH} = 23$  Hz). The mass spectrum revealed a parent ion at 444 m/e consonant with the calculated molecular weight and a base peak at 304 m/e for the loss of five carbonyls.

### Results and Discussion

This section is divided into five parts which will be discussed in order of their approximate chronological development. The original goal of this work which was to protonate acyclic, monocyclic and bicyclic phosphites, obtain their  $^1J_{PH}$  values and correlate them to variations in electronic properties, will be dealt with first. During this initial phase, difficulties in obtaining a protonated five-membered ring phosphite led to experiments with monocyclic phosphites having more extensive methyl substitution on the ring. Secondly, the isomerization that occurs at phosphorus in three of these phosphites will be discussed. Thirdly, bicyclic phosphines and the difunctional phosphorus compound,

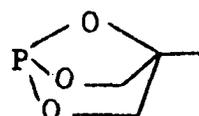
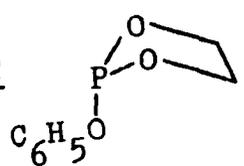
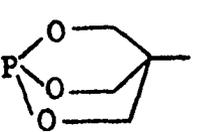
$P(OCH_2)_3P$ , were protonated in order to determine their  $^1J_{PH}$  values. Fourth is the protonation of the two phosphorus trihalide series,  $PF_{3-n}Cl_n$  ( $n = 0$  to  $2$ ) and  $PCl_{3-n}Br_n$  ( $n = 0$  to  $3$ ). Finally, the course of fluorination of several phosphites will be followed and a possible mechanism of fluorination is presented.

#### Protonation of acyclic, monocyclic and bicyclic phosphites

The synthesis of all of the trivalent precursor compounds except 1 have been reported in the literature. Compound 1 was synthesized by transesterification of  $P(OMe)_3$  with 2-methyl glycerol following a previously published procedure for the synthesis of the very similar compound,  $P(OCH_2)_2CH$ . Edmundson and Mitchell (53) reported unsuccessful attempts to synthesize 1 by the transesterification method and by the reaction of  $PCl_3$  with the triol in the presence of a nitrogen base. The synthesis of 11 was accomplished by transesterification of  $P(OMe)_3$  with the appropriate diol using a dilution technique to reduce formation of polymer, instead of reacting  $PCl_3$  with diol and methanol as reported earlier (44). The method reported in the experimental section is easier and results in a higher yield.

The initial discussion will be concerned primarily with the twelve phosphites found in Table 2. In this table is compiled nmr data for the protonated phosphites (in decreasing

Table 2. Nmr parameters of protonated phosphites in  $\text{HFSO}_3$  and their trivalent precursors

Compound	Protonated Species			Trivalent Precursor		
	$^1\text{JPH}^a$	$^3\text{JPOCH}^{a,b}$	$\delta^{31}\text{P}^c$	$^3\text{JPOCH}^d$	$\delta^{31}\text{P}^e$	$\Delta^f$
<u>1</u> 	928.8	- <sup>g</sup>	-46.1		-113.7	67.6
<u>2</u> 	913.3	8.9 quintet <sup>h</sup>	-43.9	9.11(trans) <sup>i,j</sup> 1.53(cis) <sup>i,j</sup>	-127.9	84.0
<u>3</u> $\text{P}(\text{OCH}_2\text{CF}_3)_3$	910.0	9.1 septet <sup>k</sup>	-21.4	8.0 <sup>l</sup>	-139.1	117.7
<u>4</u> 	899.2	4.5 septet <sup>m</sup>	-32.2	+2 <sup>n</sup>	-92 <sup>n</sup>	59.8
	898 ± 3 <sup>o</sup>	4.3 <sup>o</sup>				

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<sup>a</sup>Values were measured from <sup>31</sup>P spectra at -50°C unless otherwise indicated and are precise to ± 1.0 Hz.

<sup>b</sup>The multiplicity denotes fine structure on each member of the doublet separated by <sup>1</sup>JPH.

<sup>c</sup>In ppm relative to 85% H<sub>3</sub>PO<sub>4</sub>, precise to ± 0.2 ppm and measured at -50°C.

<sup>d</sup>Values in Hz measured from <sup>1</sup>H spectra.

<sup>e</sup>In ppm relative to 85% H<sub>3</sub>PO<sub>4</sub> at ambient temperature.

<sup>f</sup>Δ is the change in chemical shift from the trivalent phosphite to the protonated species.

<sup>g</sup>Inadequate solution for determining fine structure.

<sup>h</sup>The two outermost peaks were shoulders but intensities were correct for a quintet.

<sup>i</sup>Refers to the stereochemical relationship of a ring proton to an axial alkoxy group.

<sup>j</sup>Reference 54.

<sup>k</sup>Measured at -30°C. JPOCCF = 0.0 Hz.

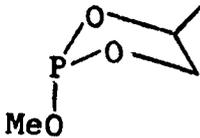
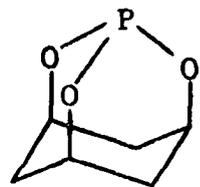
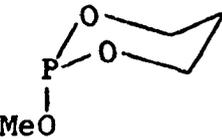
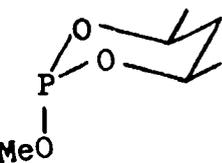
<sup>l</sup>JPOCCF = 4.5 Hz.

<sup>m</sup>Measured at -30°C.

<sup>n</sup>Reference 18.

<sup>o</sup>Reference 25. Measured at -55°C from <sup>1</sup>H spectrum where δCH<sub>2</sub> = 5.12 ppm, δCH<sub>3</sub> = 1.34 ppm and δPH = 8.01 ppm relative to external TMS.

Table 2. (Continued)

Compound	Protonated Species			Trivalent Precursor		
	$^1J_{\text{PH}}$	$^3J_{\text{POCH}}$	$\delta^{31}\text{P}$	$^3J_{\text{POCH}}$	$\delta^{31}\text{P}$	$\Delta$
<u>5a</u> 	890.4	12.8 septet <sup>p</sup>	-44.7	8 (trans) <sup>1,q</sup> 2 (cis) <sup>1,q</sup> 10.5(OMe)	-137.0	92.3
<u>6</u> 	880.3	15.0 quartet of quartet <sup>p</sup>	-40.5	+6.0 <sup>n,s</sup>	-137.7 <sup>n</sup>	97.2
<u>7</u> 	870.0	- <sup>g</sup>	-18.2	4.26(ax) <sup>t</sup> 10.40(eq) <sup>t</sup> 11.8(OMe)	-130.3	112.1
<u>8</u> 	865.0	12.8 quartet	-17.3	2.2(ax) <sup>u</sup> 11.8(OMe) <sup>u</sup>	-127.6	110.3

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<sup>p</sup>The four outermost peaks were shoulders but the intensities were correct for a septet.

<sup>q</sup>Reference 55. The specific hydroxy group was not mentioned.

<sup>r</sup> $J_{\text{POCCH}_{\text{eq}}} = 2.2 \text{ Hz}$ . Even two peaks of the set of quartets with smaller coupling.

<sup>s</sup> $J_{\text{POCCH}_{\text{eq}}} = 0.5 \text{ Hz}$  from

<sup>t</sup>Reference 57.

<sup>u</sup>Reference 41.

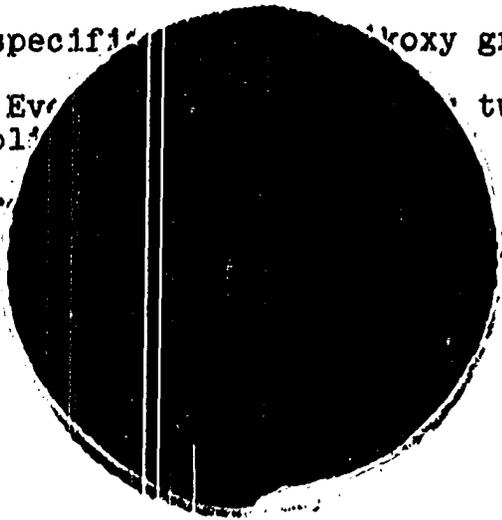
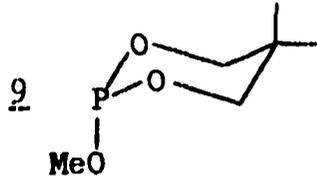
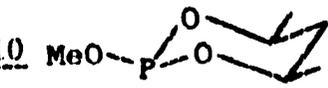


Table 2. (Continued)

Compound	Protonated Species			Trivalent Precursor		
	$^1J_{PH}$	$^3J_{POCH}$	$\delta^{31P}$	$^3J_{POCH}$	$\delta^{31P}$	$\Delta$
<u>9</u> 	861.2	11.1 sextet	-17.7	2.8(ax) <sup>u</sup> 10.8(eq) <sup>u</sup> 12 (OMe)	-122.9	105.2
<u>10</u> 	850.6	12.8 quartet	-18.2	3.1(ax) <sup>u</sup> 10.8(OMe) <sup>u</sup>	-131.9	113.7
<u>11</u> 	844.5	.. <sup>v</sup>	-28.7	11.2(OMe) <sup>w</sup>	-134.6	105.9

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<sup>p</sup>The four outermost peaks were shoulders but the intensities were correct for a septet.

<sup>q</sup>Reference 55. The specific R in the alkoxy group was not mentioned.

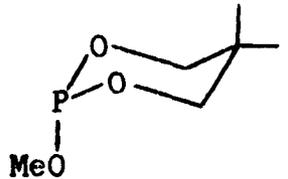
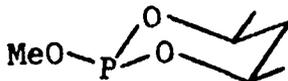
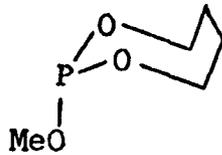
<sup>r</sup> $J_{\text{POCCH}_{\text{eq}}} = 2.2 \text{ Hz}$ . Even at  $-30^{\circ}\text{C}$  the outer two peaks of the set of quartets with smaller coupling were shoulders.

<sup>s</sup> $J_{\text{POCCH}_{\text{eq}}} = 0.5 \text{ Hz}$  from reference 56.

<sup>t</sup>Reference 57.

<sup>u</sup>Reference 41.

Table 2. (Continued)

Compound	Protonated Species			Trivalent Precursor		
	$^1J_{PH}$	$^3J_{POCH}$	$\delta^{31}P$	$^3J_{POCH}$	$\delta^{31}P$	$\Delta$
<u>9</u> 	861.2	11.1 sextet	-17.7	2.8(ax) <sup>u</sup> 10.8(eq) <sup>u</sup> 12 (OMe)	-122.9	105.2
<u>10</u> 	850.6	12.8 quartet	-18.2	3.1(ax) <sup>u</sup> 10.8(OMe) <sup>u</sup>	-131.9	113.7
<u>11</u> 	844.5	- <sup>v</sup>	-28.7	11.2(OMe) <sup>w</sup>	-134.6	105.9
<u>12</u> P(OMe) <sub>3</sub>	826.2	12.0 octet <sup>x</sup>	-24.4	11.35 <sup>n</sup>	-140.8	116.4

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<sup>v</sup>The symmetrical pattern of 16 peaks which was resolved at -20°C was not analyzed.

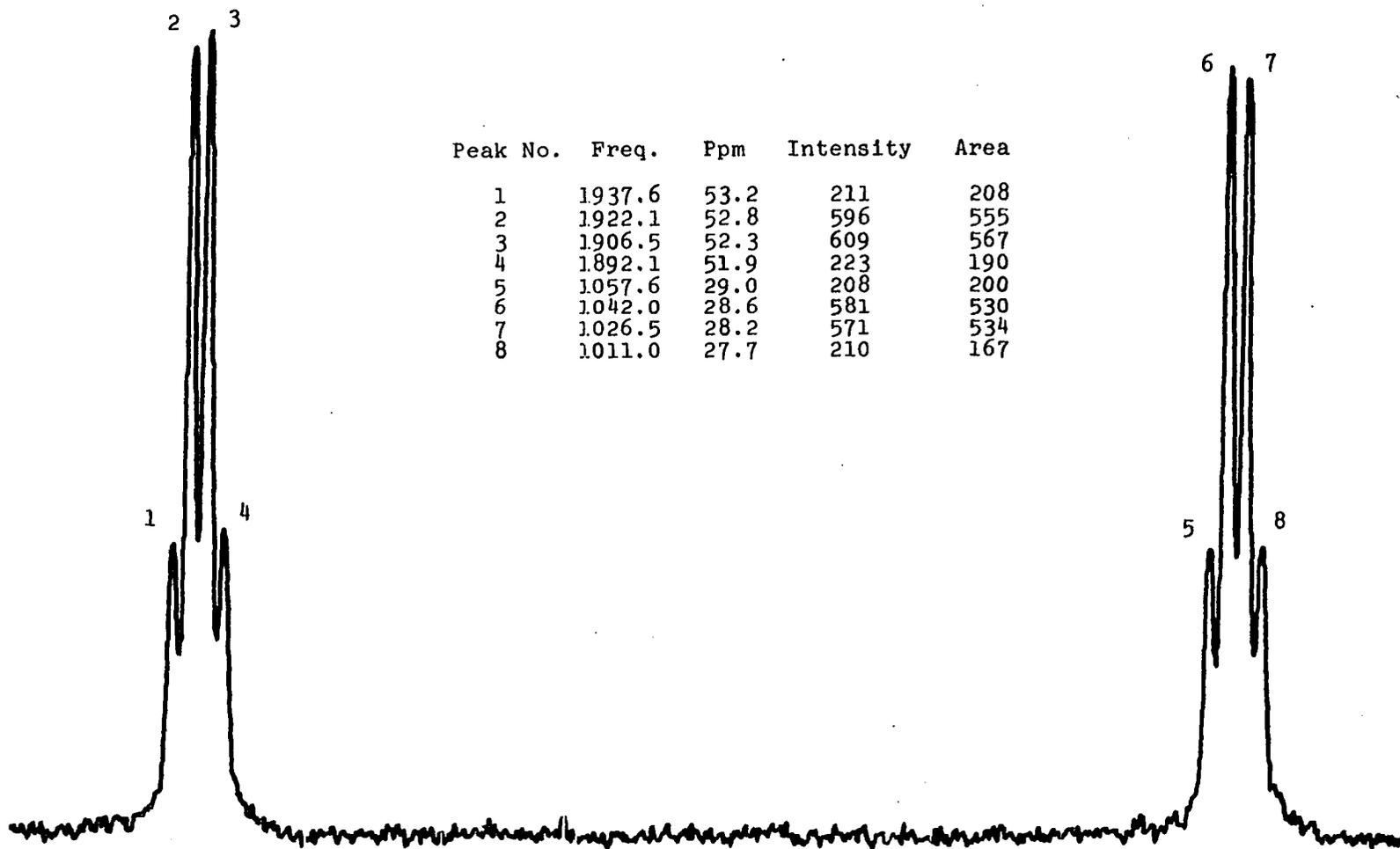
<sup>w</sup>The ring <sup>3</sup>JPOCH values have not been determined.

<sup>x</sup>Only 8 of the theoretical 10 peaks were observed.

order of  $^1\text{JPH}$ ) along with their trivalent precursors. Except for the various phosphorus-proton coupling constants for the trivalent phosphites and the second set of nmr parameters for the protonated form of compound 4 which were obtained from  $^1\text{H}$  spectral experiments, these data were taken from  $^{31}\text{P}$  spectra. Spectroscopic  $^{31}\text{P}$  and  $^1\text{H}$  parameters for the trivalent compounds, 1, 3 and 11 are reported for the first time.

All of the compounds in Table 2 were protonated using  $\text{HFSO}_3$ , and observation of  $^1\text{JPH}$  for the protonated species was made at  $-50^\circ\text{C}$ . Spectra, however, for many of the protonated phosphites were taken at several other temperatures, principally to determine possible changes in  $^1\text{JPH}$  with temperature. One problem associated with temperatures below  $-50^\circ\text{C}$  was the greater viscosity of  $\text{HFSO}_3$  (f.p. =  $-89^\circ\text{C}$  (16)), which tended to broaden the fine structure on each arm of the protonated doublet. Thus, additional fine structure parameters are reported only at higher temperatures. A typical spectrum from which  $^{31}\text{P}$  parameters were extracted is shown in Figure 1 for the protonated form of compound 6. Although the reference is phosphoric acid, this peak has been omitted so that the spectrum could be expanded sufficiently to observe fine structure visually. This spectrum shows that the phosphorus atom is protonated since it gives rise to the large doublet associated with a P-H bond while the quartet fine structure on each arm of the doublet, arising from POCH

Figure 1. The  $^{31}\text{P}$  nmr spectrum at  $-50^\circ\text{C}$  of phosphite 6 protonated in  $\text{HFSO}_3$ . The computer data (rounded off) are shown for each peak.



coupling, indicates that the cage structure has remained intact. Since this spectrum, like the others, is not proton decoupled, the chemical shift is represented by the midpoint of the doublet of quartets.

In terms of obtaining stable solutions without extensive decomposition or solvolysis, the most difficult phosphites to protonate were 1, 2 and 5, all of which contain five-membered rings. In four attempts the protonated form of  $\text{MeOPOCH}_2\text{CH}_2\text{O}$ , a liquid at  $-78^\circ$ , was not observed owing to decomposition or solvolysis. Phosphite 1 was protonated after several initial failures, but only by following a special procedure. Protonated forms of compounds 2 and 5 were somewhat easier to obtain and it is tentatively suggested that the phenoxy group in the former and the methyl group in the latter are sterically active in preventing rapid attack at the endocyclic oxygens. For the other phosphites, stable solutions were relatively easy to obtain at the low temperatures employed. These qualitative results are not too surprising since it has been found that five-membered ring phosphates hydrolyze in the presence of acid about  $10^6$  times faster than acyclic, six- or seven-membered ring phosphates (58). Release of ring strain has been postulated to account for the rapid ring opening in hydrolysis and this could well be a factor here also.

Inspection of Table 2 shows that  $^1\text{JPH}$  rises from the smallest value in  $^+\text{HP}(\text{OMe})_3$  (826.2 Hz) to the largest value for  $^+\text{HP}(\overset{\text{O}}{\text{OCH}_2})_2\text{CMe}$  (928.8 Hz), an increase of over 100 Hz.  $^1\text{JPH}$  for previously reported protonated alkyl phosphites were all smaller or only slightly larger. Thus, neo-pentyl phosphite protonated in HCl yielded  $^1\text{JPH} = 834 \pm 6$  Hz (5) and  $^+\text{HP}(\text{O}-\text{i-C}_3\text{H}_7)_3$  gave the low value of 796 Hz (4) (see the first entries in Table 1).

As mentioned in the Introduction, changes in  $^1\text{JPH}$  are related to s electron density and effective nuclear charge. For atoms which are directly bonded, Ramsey (59) and later Pople and Santry (60) found that coupling due to the Fermi contact interaction is most important. The coupling constant is then dependent not only upon the square of the s character in the bond but also upon the cube of the effective nuclear charge of either atom (61,62). The latter effect has been shown to be experimentally valid for  $^1\text{J}^{13}\text{CH}$  (62). For protonated trivalent phosphorus compounds,  $^1\text{JPH}$  has been found to increase with increasing electronegativity of the substituents at phosphorus (2). Some of the increase in  $^1\text{JPH}$  can be accounted for by the greater amount of s character in the PH bond since according to Bent's rule (63) p character would be directed toward the electronegative phosphorus substituents leaving s character to concentrate in the P-H bond. However, the electron withdrawing power of

electronegative substituents will also place a greater effective positive charge on phosphorus and McFarlane and White (2) reasoned that this could be more important in determining the magnitude of  $^1\text{JPH}$  than increases in s character in the proton-phosphorus bond.

The larger value of  $^1\text{JPH}$  found (2) for  $^+\text{HP}(\text{OPh})_3$  (870 Hz) where alkyl substituents have been replaced by more electronegative phenyl groups was consistent with the above rationale. Similarly,  $^1\text{JPH}$  becomes larger by approximately 100 Hz in going from  $^+\text{HP}(\text{OCH}_2\text{CH}_3)_3$  (806 Hz) (2) to  $^+\text{HP}(\text{OCH}_2\text{CF}_3)_3$  (910.0 Hz) since the greater electron withdrawing power of  $\text{CF}_3$  compared to  $\text{CH}_3$  must be the dominant factor here.

The remainder of the phosphites in Table 2, however, all have alkyl substituents and differ mainly in the constraint of the alkoxy moieties. Consider first of all the phosphites 12, 10, 8, 5, 4 and 1, the protonated forms of which experience an approximate monotonic rise in  $^1\text{JPH}$  from 826.2 to 928.8 Hz. As reviewed in the Introduction the basicity order for these phosphites when the Lewis acid is  $\text{BH}_3$  or phenol is 10 > 12 > 8 > 5 > 4 > 1. Thus, except for the reversal of 10 and 12, the decreasing basicity parallels the increase in  $^1\text{JPH}$  obtained from the protonated forms. Orbital repulsion effects (20,21) predict that  $^1\text{JPH}$  should have increased from 10 to 12 to 8 since the phosphorus lone pair becomes less polarizable, leaving increased s character in the P-H bond. On the other hand, the increase in  $^1\text{JPH}$  from 8 to 5 to 4 to 1 is consonant

with the "hinge" effect (18,19) which increases the effective nuclear charge placed on phosphorus as electron delocalization from alkoxy oxygen to phosphorus becomes less efficient. Although it has been concluded (20) from structural evidence that the "hinge" effect apparently does not operate from acyclic to six-membered ring phosphites and that electron pair repulsion can explain basicity trends for 10, 12 and 8 when the Lewis acid is  $\text{BH}_3$  or phenol, it is suggested here that this effect becomes operative for 10 and 8 when the Lewis acid is a proton. Since the proton is a more effective Lewis acid, it can induce greater tetrahedrality of the phosphorus substituents in polarizing the lone pair, thereby activating the "hinge" effect and closing the ring POC angles. Supporting evidence for this contention is obtained from the structural study (64) of the borane adduct of 8 wherein the average OPO and POC angles are  $104.3^\circ$  and  $119.5^\circ$ , respectively. Thus, while decreased nuclear charge is responsible for the smaller  $^1\text{JPH}$  value for protonated 12 compared to that of 10 and 8, the difference of 14.4 Hz in  $^1\text{JPH}$  for the last two protonated species can still result from orbital repulsion effects superimposed on the hinge effect.

Preliminary CNDO/2 calculations performed by Buck and Pennings (65) lend general support to the above arguments and the results of their study on six phosphites are summarized in Table 3 (except for columns 4, 8 and 10). Under the heading of "lone pair" is a quantity related to the total

Table 3. Results of CNDO/2 calculations for phosphites compared to  $^1J_{PH}$  for protonated phosphites

Phosphite	POC Angle (°)	$\rho_P$	$\rho_{P3}$	$\rho_O$	Lone pair	% s character in lone pair	Available s electrons	$\Delta E_{H^+}$	$^1J_{PH}$
<u>12</u>	119	+0.361	0.047	-0.246	2.152	38.3	0.824	-0.3776	826.2
<u>10<sup>a</sup></u>	113	+0.371	0.051	-0.256	2.150	38.3	0.823	-0.3560	850.6
<u>8<sup>a</sup></u>	113	+0.395	0.061	-0.264	2.138	38.4	0.821	-0.3530	865.0
<u>5<sup>b</sup></u>	112	+0.402	0.065	-0.265	2.140	38.7	0.828	-0.3605	890.4
<u>4</u>	114	+0.409	0.068	-0.285	2.127	37.6	0.800	-0.3641	899.2
<u>1</u>	112 <sup>c</sup>	+0.477	0.109	-0.302	2.088	39.7	0.829	-0.3132	928.8
	113 <sup>c</sup>			-0.276					

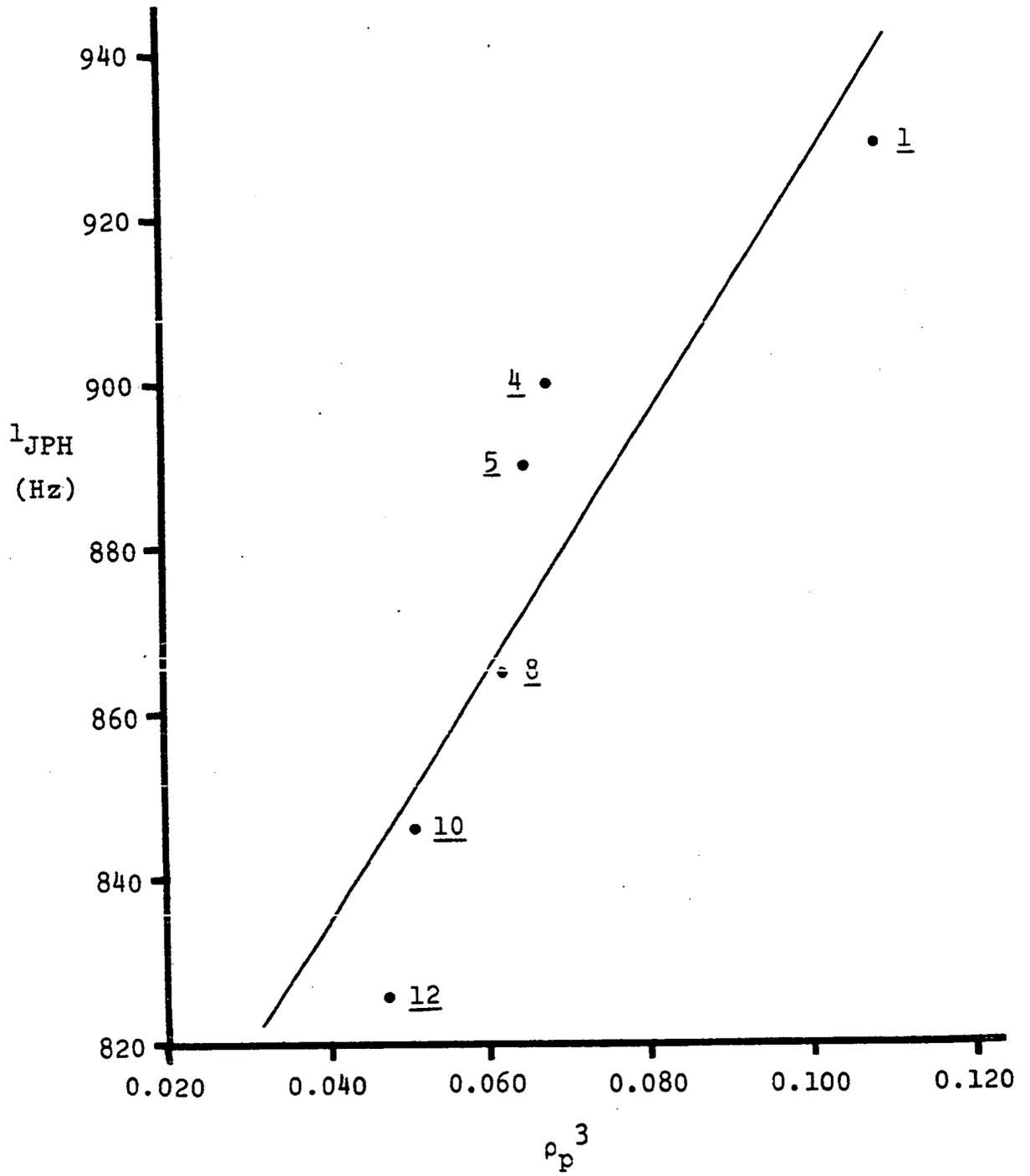
<sup>a</sup>CNDO/2 calculations were done on these phosphites with the stereochemistry as indicated in Table 2, but without the methyl substitutions on the 4 and 6 positions.

<sup>b</sup>As in (a) calculations were done without a methyl substituent at position 4.

<sup>c</sup>The smaller and larger angles are for the five- and six-membered rings in this bicyclic phosphite, respectively.

electron density in the phosphorus lone pair. If this is multiplied by the percent of s character in the lone pair, the result should be related to the available s electron density. The trend in this quantity is rather erratic, however, and a least-squares analysis of the square of this quantity plotted against  $^1\text{JPH}$  yields the very poor correlation coefficient of 0.08. Comparison of  $\rho_p^3$ , the cube of the net positive charge on the phosphorus atom, with  $^1\text{JPH}$  reveals a much better linear correlation with  $^1\text{JPH}$  (Figure 2) which obeys the equation,  $y = 1495.9x + 776.7$ , with a correlation coefficient of 0.90. An attempt to correlate the product of  $s^2$  and  $\rho_p^3$  (giving both quantities equal weight) with  $^1\text{JPH}$  was again poorer having a correlation coefficient of 0.88. It is tentatively concluded, therefore, that the cube of the effective nuclear charge is the dominant factor in determining the magnitude of the phosphorus-proton coupling in these systems. Calculation of  $\Delta E_{\text{H}^+}$ , the energy difference between the unprotonated phosphite and the protonated species, shows a gradual decrease upon constraint for this parameter. This is reasonable since the more highly constrained systems would be expected to have a higher energy before protonation. As observed, the charge on the alkoxy oxygens,  $\rho_o$ , is expected to increase with constraint, since decreased p $\rightarrow$ d pi bonding restricts delocalization of the electron density. It is probable that protonation occurs on the alkoxy oxygen but fast exchange prevents observation of any POH coupling due to this phenomenon.

Figure 2. The plot of  $^1\text{JPH}$  for protonated phosphites 1, 4, 5, 8, 10 and 12 versus the cube of the calculated positive charge on the trivalent phosphorus atom.



The protonation of the seven-membered ring phosphite, 11, resulted in a  $^1\text{JPH}$  value intermediate between protonated acyclic phosphites and protonated six-membered ring phosphites. Since the protonated species of 11 can more easily adopt the geometry of the protonated acyclic phosphites, this is not unexpected.

In addition to  $^1\text{JPH}$  obtained for protonated 10 and 8, two other six-membered phosphites were protonated, namely 9 and 7, both of which adopt the stereochemistry of a chair conformer for the ring with a predominantly axial methoxy group at phosphorus (41). It is not surprising, therefore, that  $^1\text{JPH}$  for protonated 7, 8 and 9 are within a 9 Hz range with 7, which has no methyl ring substituents, exhibiting the largest value. Since the ring methyl substituents of 8 and 9 would be expected to contribute to the basicity of phosphorus by the inductive effect, they should have the smaller protonated coupling values.

Prior to this work, the protonation of  $\text{PhOPOCH}_2\text{CH}_2\text{O}$  was reported by McFarlane and White (2) in 100%  $\text{H}_2\text{SO}_4$  at room temperature with  $^1\text{JPH} = 822 \pm 2$  Hz and a  $^{31}\text{P}$  chemical shift of -16 ppm. However, this value when compared to  $(\text{MeO})_3\text{PH}^+$  (826.2 Hz) was suspect for two reasons. Both the influence of the more electronegative phenoxy group on  $^1\text{JPH}$  and the behavior of this parameter upon molecular constraint predicts a much higher value. For this reason the protonation of

$\overline{\text{PhOPOCH}_2\text{CH}_2\text{O}}$  was re-examined in  $\text{HFSO}_3$  at  $-50^\circ\text{C}$  and the larger  $^1\text{JPH}$  value of 913.3 Hz with a shifted  $\delta^{31}\text{P}$  value ( $-43.9$  ppm) was obtained confirming the prediction. It is also satisfying to note that this coupling was larger than that of the

890.4 Hz resulting from protonated  $\overline{\text{MeOPOCH}_2\text{CHMeO}}$ , showing that where ring constraint was constant, the electronic nature of the exocyclic moiety independently influences  $^1\text{JPH}$  in the expected manner. The erroneous  $^1\text{JPH}$  value reported earlier (2)

for  $\overline{\text{PhOPOCH}_2\text{CH}_2\text{O}}$  may have corresponded to a ring-opened species (e.g.,  $\text{PhO(H)P(OCH}_2\text{CH}_2\text{OH)(OSO}_3\text{H)}^+(\text{SO}_3\text{H)}^-$ ) since data was obtained at room temperature. Support for this idea is provided by our observation that in  $\text{HFSO}_3$  at  $-20^\circ\text{C}$  severe decomposition of the phenoxy five-membered ring phosphite was evident from the appearance of additional peaks.

The  $^1\text{JPH}$  value of 899.2 Hz for  $^+\text{HP(OCH}_2)_3\text{CMe}$ , obtained from  $^{31}\text{P}$  nmr data, confirmed the value of  $898 \pm 3$  Hz obtained for the same protonated species from  $^1\text{H}$  nmr experiments reported by us in an earlier communication (25). In the stronger acid system  $\text{HFSO}_3 \cdot \text{SbF}_5$  diluted with  $\text{SO}_2$  (17) at  $-60^\circ\text{C}$   $^1\text{JPH}$  was 895.6 Hz with a  $^{31}\text{P}$  chemical shift of  $-31.8$ . The similarity of  $^1\text{JPH}$  for this phosphite in these acids of different strength indicates complete protonation is occurring in both cases. However, one experiment in which  $\text{P(OCH}_2)_3\text{CMe}$  was dissolved in a 30% solution of trifluoroacetic acid in

acetonitrile resulted in a single resonance at -91.8 ppm, which is the same as that seen in hydrocarbon solvents. This indicates that no protonation has occurred at phosphorus in this medium.

Comparison of  $^1\text{JPH}$  obtained from  $^+\text{HP}(\text{OCH}_2)_3\text{CMe}$  and  $^+\text{HP}(\text{OCH})_3(\text{CH}_2)_3$  (derived from precursor phosphite 6) shows that this value is nearly 20 Hz lower in the latter species. These results concur with an earlier study (66) where it was shown that 6 is more basic than 4 toward boron acids.

Spectra for all of the protonated phosphites except 5 were taken at several temperatures in the range  $-80^\circ$  to  $0^\circ$ . The chemical shifts for all of the protonated species did not change more than  $\pm 0.3$  ppm with temperature and there appeared to be no consistent trend in this small variation. Likewise  $^{31}\text{P}-^1\text{H}$  couplings did not vary in any consistent manner except that resolution was always best at the highest temperature before rapid decomposition and/or solvolysis occurred.

However, a noticeable increase in  $^1\text{JPH}$  with decreasing temperature was always observed. The extremes of these variables as well as the slope of the resulting linear relationship are recorded in Table 4. It is possible in systems where there is exchange of nuclei between two different sites to determine the rate of exchange by appropriate formulas if coalescence of chemical shifts and/or spin multiplets can

Table 4. Variation of  $^1\text{JPH}$  for protonated phosphites with temperature

Phosphite	Temperature		$^1\text{JPH}^a$		$\Delta J/\Delta T \times 10$
	High	Low	Low	High	
<u>1</u>	-20	-80	921.1	935.5	2.4
<u>2</u>	-40	-80	911.1	915.5	1.1
<u>3</u>	-20	-80	906.7	914.4	1.3
<u>4</u>	-10	-70	894.2	900.6	1.1
<u>6</u>	-10	-80	876.7	883.3	0.9
<u>7</u>	-30	-70	865.6	874.4	2.2
<u>8</u>	0	-80	859.5	868.4	1.1
<u>9</u>	-20	-80	857.8	864.5	1.1
<u>10</u>	-20	-80	847.3	855.6	1.4
<u>11</u>	-20	-80	842.3	846.7	0.7
<u>12</u>	-20	-70	824.2	827.0	0.6

<sup>a</sup>Each value is precise to  $\pm 1.0$  Hz.

be observed (67). Such collapse can be brought about by varying concentration or temperature. In these protonated phosphites, collapse of the PH doublet, possibly expected at the high temperature extreme and resulting from rapid intermolecular exchange of the proton, was not observed. However, the slope,  $\frac{\Delta J}{\Delta T}$ , does divide into distinct ranges; 0.6-0.7 for 11 and 12, 2.2-2.4 for 1 and 7 and 0.9-1.4 for the remainder. Since it is reasonable that this slope should become larger as Lewis basicity decreases, the results for all except 6 and 7 are consonant with the basicity trends noted earlier.

The discussion will now center on  $^3\text{JPOCH}$  and other longer range couplings. Unfortunately, resolution prevented observation of couplings which were smaller than about 2 Hz so that some spectra did not exhibit all of the expected spin multiplicity. For two protonated phosphites, 1 and 7, no fine structure could be resolved.

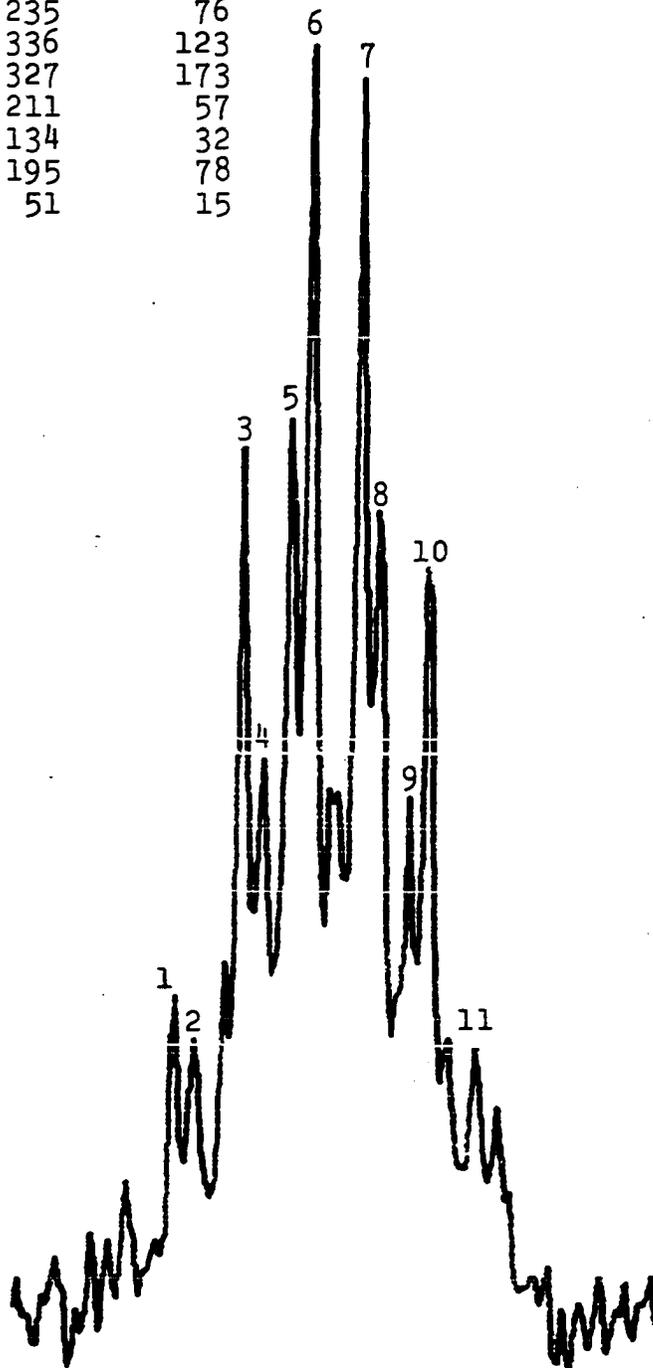
For the protonated acyclic phosphites, 3 and 12,  $^3\text{JPOCH}$  changed little from the trivalent form. However, the septet on each half of the doublet for protonated 3, measured at  $-30^\circ$  where resolution was best, showed that  $^3\text{JPOCCF}$  was  $0.0 \pm 1.0$  Hz which represents a significant decrease from the absolute magnitude of 4.5 Hz in the trivalent phosphite.

A symmetrical pattern of 16 peaks (Figure 3) was observed at  $-20^\circ$  for each half of the doublet of protonated 11. Unfortunately, second order coupling effects and the lack of a

Figure 3. The  $^{31}\text{P}$  nmr spectrum at  $-20^\circ\text{C}$  showing the expanded downfield region of the resonance of phosphite 11 protonated in  $\text{HFSO}_3$ . The computer data (rounded off) obtained for eleven of the peaks are shown.

58b

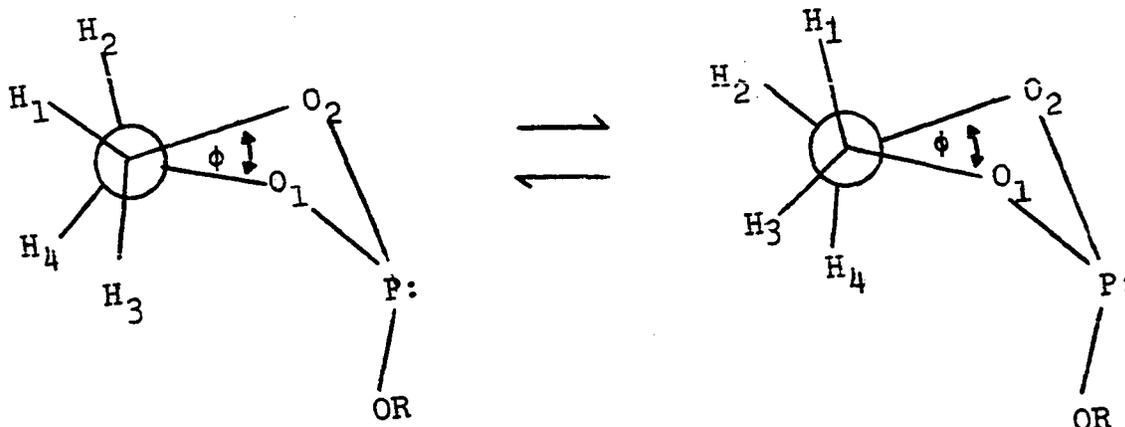
Peak No.	Freq.	Ppm	Intensity	Area
1	1499.2	41.1	80	22
2	1494.8	41.0	68	19
3	1482.6	40.7	227	105
4	1477.1	40.5	144	34
5	1470.4	40.4	235	76
6	1464.8	40.2	336	123
7	1452.6	39.9	327	173
8	1448.2	39.7	211	57
9	1440.4	39.5	134	32
10	1436.0	39.4	195	78
11	1418.2	38.9	51	15



computer program to analyze an eight spin system (LAOCOON III is limited to seven spins) prevents reporting the three possibly different  $^1\text{JPOCH}$  values.

For the protonated six-membered ring phosphites 8, 9 and 10, which presumably retain the chair form of the ring, three-bond coupling from phosphorus to the axial proton is less than 2 Hz and was unresolved. Thus, 8 and 10 show the expected quartet arising from phosphorus coupling to the methoxy protons ( $^3\text{JPOCH} = 12.8$  Hz in both). In protonated 9 coupling from phosphorus to the methoxy protons and to the ring equatorial protons is apparently the same within limits of this experiment so that a sextet is observed. In all three protonated phosphites,  $^3\text{JPOCH}$  is similar to the same values found in the unprotonated phosphite.

From the analysis of nmr parameters, five-membered ring phosphites have been proposed (55,68,69) to prefer two twist envelope conformations with the exo alkoxy group in the axial position on phosphorus as shown below. The dihedral angle,  $\phi$ ,



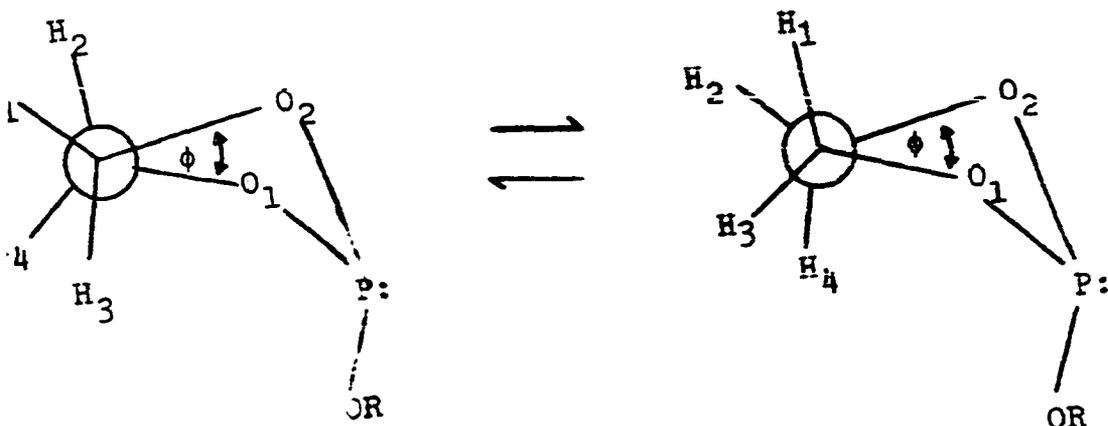
formed by  $O_1-C_1-C_2-O_2$  was calculated by the Karplus relation (70) to be  $\sim 30^\circ$ . A recent X-ray structural study on trans-methyl meso-hydrobenzoin phosphite,  $\text{MeOPOCHPhCHPhO}$ , confirms this conformation and  $\phi$  was found to be  $35.0^\circ$  (71). In this conformation phosphorus couplings to protons anti ( $H_1, H_2$ ) and syn ( $H_3, H_4$ ) are about 9 Hz and 2 Hz, respectively (Table 2). With the alkoxy group axial, protonation is assumed to have occurred at the equatorial position of 2. If the POCH couplings had remained approximately the same in the protonated species, a triplet with broadened peaks would be expected because the resolution was not adequate to define the smaller coupling. Observation of a quintet, however, indicates the phosphorus coupling to the syn and anti protons are approximately equal. Oxidation of 2 to the phosphate,  $\text{C}_6\text{H}_5\text{O}(\text{O})\text{POCH}_2\text{CH}_2\text{O}$ , does result in syn and anti couplings which are similar (72) (9.05 and 12.36 Hz, respectively) even though the dihedral angle probably has not changed since  $\phi$  in  $\text{MeO}(\text{O})\text{POCHPhCHPhO}$  is  $32.8^\circ$  (71). Thus, with respect to these couplings the protonated species and the phosphate are similar.

Complications arose with phosphite 5 because two isomers are formed in its synthesis (39). Assuming that the OMe group is axial in both cases, isomer 5a is formed in preference to 5b in a 60:40 ratio (39). The preference to

puter program to analyze an eight spin system (LAOCOON III limited to seven spins) prevents reporting the three possibly different  $^1J_{\text{POCH}}$  values.

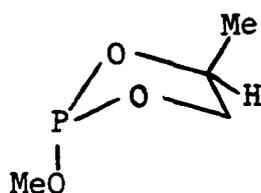
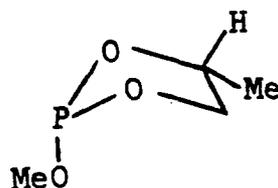
For the protonated six-membered ring phosphites 8, 9 and 10 which presumably retain the chair form of the ring, the  $^1J_{\text{POCH}}$  value for the axial bond coupling from phosphorus to the axial proton is less than 2 Hz and was unresolved. Thus, 8 and 10 show the expected quartet arising from phosphorus coupling to the equatorial protons ( $^3J_{\text{POCH}} = 12.8$  Hz in both). In protonated 9 the coupling from phosphorus to the methoxy protons and to the equatorial protons is apparently the same within limits of this experiment so that a sextet is observed. In all three protonated phosphites,  $^3J_{\text{POCH}}$  is similar to the same values found in the unprotonated phosphite.

From the analysis of nmr parameters, five-membered ring phosphites have been proposed (55,68,69) to prefer two twist envelope conformations with the exo alkoxy group in the axial position on phosphorus as shown below. The dihedral angle,  $\phi$ ,



formed by  $O_1-C_1-C_2-O_2$  was calculated by the Karplus relation (70) to be  $\sim 30^\circ$ . A recent X-ray structural study on trans-methyl meso-hydrobenzoin phosphite,  $MeO\overbrace{POCHPhCHPhO}$ , confirms this conformation and  $\phi$  was found to be  $35.0^\circ$  (71). In this conformation phosphorus couplings to protons anti ( $H_1, H_2$ ) and syn ( $H_3, H_4$ ) are about 9 Hz and 2 Hz, respectively (Table 2). With the alkoxy group axial, protonation is assumed to have occurred at the equatorial position of 2. If the POCH couplings had remained approximately the same in the protonated species, a triplet with broad peaks would be expected because the resolution of the peaks would not define the smaller coupling. Observations of the spectrum of 2 indicate the phosphorus coupling constants are approximately equal. The spectrum of the phosphate,  $C_6H_5O(O)\overbrace{POCH_2CH_2O}$ , does not show anti couplings which are similar (72) (9. Hz and 2 Hz, respectively) even though the dihedral angle probably has not changed since  $\phi$  in  $MeO(O)\overbrace{POCHPhCHPhO}$  is  $32.8^\circ$  (71). Thus, with respect to these couplings the protonated species and the phosphate are similar.

Complications arose with phosphite 5 because two isomers are formed in its synthesis (39). Assuming that the OMe group is axial in both cases, isomer 5a is formed in preference to 5b in a 60:40 ratio (39). The preference to

5a5b

form 5a apparently results from a minimization of steric interactions. Assuming that the ratio of the two isomers does not change on protonation, the nmr parameters reported in Table 3 are for the protonated species of the dominant 5a isomer. From the discussion on the conformation of five-membered ring phosphites, protonation of 5a, like 2, is most likely equatorial and support for this is found on comparing the chemical shifts of protonated 5a and 2 which are both about  $-44$  ppm. Unfortunately, the inner members of the doublet of protonated 5a and 5b overlap and since 5b is not the dominant isomer, the nmr parameters for the latter cannot be reported with great certainty ( $^1J_{PH} = 865 \pm 25$  Hz,  $\delta^{31}P = -22.6 \pm 2.0$ ). Speculation on the stereochemistry of protonated 5b will be reserved for the next section after better defined data for other phosphites is introduced. Observation of a septet for 5a indicates that like 2, the syn and anti POCH couplings for the protonated phosphites are similar.

A significant increase in  $^3\text{JPOCH}$  is seen for protonated bicyclic phosphites, 4 and 6, and in  $^4\text{JPOCCH}_{\text{eq}}$  for the latter. A comparison of these parameters with those found in other adducts is found in Table 5. Previously, it had been concluded (38) that the rise in  $^3\text{JPOCH}$  for  $\text{AP}(\text{OCH}_2)_3\text{CMe}$  and  $\text{AP}(\text{OCH})_3(\text{CH}_2)_3$  resulted from the increase in s character in the P-O bonds as the phosphorus lone pair became polarized to a greater degree by the rising Lewis acidity of the acceptor group. The linear correlation (38) of  $^3\text{JPOCH}$  and the chemical shift of the methylene protons of adducts of 4 (not including  $\text{OP}(\text{OCH}_2)_3\text{CMe}$ ) cannot be extended to include  $^+\text{HP}(\text{OCH})_3\text{CMe}$  since  $\text{HFSO}_3$  rather than  $\text{CH}_3\text{CN}$  was the solvent. It should be noted, however, that in  $\text{AP}(\text{OCH}_2)_3\text{CMe}$ ,  $\text{A} = \text{BH}_3$  and  $\text{H}^+$  seem to polarize the lone pair to about the same extent, while in  $\text{AP}(\text{OCH})_3(\text{CH}_2)_3$ ,  $\text{H}^+$  and  $\text{Et}^+$  comparably polarize this lone pair as indicated by the similarities in the POCH couplings. This probably reflects the greater basicity of the lone pair in the latter phosphite (66). Actually,  $\text{H}^+$  is expected to polarize the lone pair in both phosphites to a larger extent than either the ethyl or triphenylmethyl carbonium ions owing to its larger charge to size ratio. The reason for this apparent anomaly is presently unclear. The value of  $^4\text{JPOCCH}_{\text{eq}}$  in protonated phosphite 6 is about the same as in the corresponding phosphate. This increase in coupling over that of the parent phosphite can be ascribed to a through-bond

Table 5. Coupling constants for bicyclic phosphite derivatives

A	$^3J_{\text{POCH}}$ AP(OCH <sub>2</sub> ) <sub>3</sub> CMe	$^3J_{\text{POCH}}$ AP(OCH) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	$^4J_{\text{POCCH}}^{\text{a}}$ AP(OCH) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	Reference
Lone pair	1.8	6.3	0.5 <sup>b</sup>	38
B(Me) <sub>3</sub>	2.2	6.7		38
BH <sub>3</sub>	4.2	12.5		38
H <sup>+</sup>	4.4	15.0	2.2	This work
Et <sup>+</sup>	5.2	15.7		38
Ph <sub>3</sub> C <sup>+</sup>	5.8	18.0		38
O	7.0	20.0	2 <sup>b</sup>	38
Br <sup>+</sup>	7.2			73

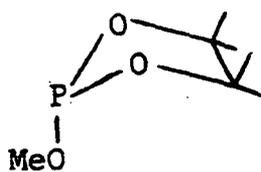
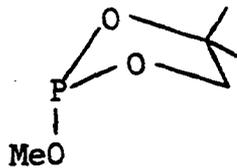
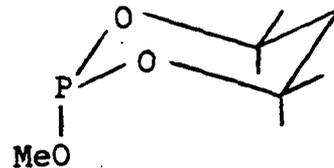
<sup>a</sup>Coupling is to the axial proton.

<sup>b</sup>Reference 56.

coupling mechanism (56) and it probably arises mainly from increased s character in the bonds and a higher positive charge on phosphorus as discussed above for three-bond coupling.

Protonation of monocyclic phosphites having extensive ring substitution

In an effort to protonate a monocyclic five-membered ring phosphite which in contrast to  $\text{MeOPOCH}_2\text{CH}_2\text{O}$  did not decompose in  $\text{HFSO}_3$  and which did not possess overlapping peaks as did the protonated isomers 5a and 5b, pinacol phosphite, 13, was chosen. Surprisingly, the  $^{31}\text{P}$  spectrum of 13 freshly

131415

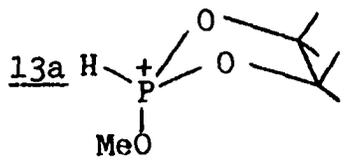
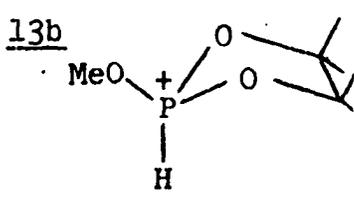
protonated in  $\text{HFSO}_3$  at  $-50^\circ$  and below showed not one but two sets of doublets of quartets indicating the presence of two protonated species. Furthermore, the spectrum changed with time and/or higher temperatures until only one species remained. Following this discovery, phosphites 14 and 15 were protonated and found to exhibit the same behavior. The nmr data for these protonated species and their parent

phosphites are found in Table 6. It should be noted that for all three phosphites the protonated species which became dominant (13b, 14b and 15b) have substantially smaller  $^1\text{JPH}$  values than 13a, 14a and 15a by 25.2 Hz, 35.2 Hz and 17.7 Hz, respectively.

As already noted, five-membered ring phosphites prefer the twist-envelope conformation and six-membered ring phosphites prefer the chair conformation (41) with the methoxy group axial in both systems. Thus, it is reasonable to suppose that initial protonation of 13, 14 and 15 occurs at equatorial lone pair. Furthermore, it is suggested that the later appearing (higher temperature) isomers arise from protonation of the axial lone pair since these couplings are expected to have smaller values owing to the greater polarizability of the axial lone pair. Support for this contention arises from the protonation of the ring-locked phosphites 8 and 10 which have  $^1\text{JPH}$  values of 865.0 Hz and 850.6 Hz (a difference of 14.4 Hz) for equatorial and axial protonation, respectively.

It has been shown by others that inversion of five-membered ring phosphites is very slow (74,75) and the same is true for six-membered ring phosphites (76,77). Thus, it is unlikely that phosphorus inversion is responsible for the appearance of axially and equatorially protonated phosphites 13-15 since then the ring-locked phosphite 8 should also

Table 6. Nmr parameters of phosphites 13, 14 and 15 and their protonated species in  $\text{HFSO}_3$

Compound	Protonated Species <sup>a</sup>			Trivalent Precursor		
	$^1\text{JPH}^b$	$^3\text{JPOCH}^{b,c}$	$\delta^{31}\text{P}^d$	$^3\text{JPOCH}^e$	$\delta^{31}\text{P}^d$	$\Delta^f$
<u>13a</u> 	856.4	13.4 quartet	-40.2	12.3	-148.9	108.7
<u>13b</u> 	831.2	12.2 quartet	-20.4	12.3	-148.9	

<sup>a</sup>All values obtained from  $^{31}\text{P}$  spectra at  $-50^\circ$  except for 14a at  $-60^\circ$ .

<sup>b</sup>In Hz.

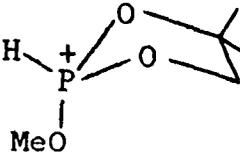
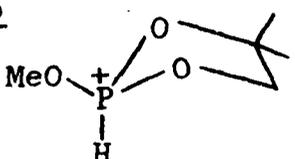
<sup>c</sup>The multiplicity denotes fine structure on each member of the doublet separated by  $^1\text{JPH}$ .

<sup>d</sup>In ppm relative to 85%  $\text{H}_3\text{PO}_4$ .

<sup>e</sup>In Hz. Obtained from  $^1\text{H}$  spectra.

<sup>f</sup> $\Delta$  is the change in chemical shift from the trivalent phosphite to the protonated species.

Table 6. (Continued)

Compound	Protonated Species			Trivalent Precursor		
	$^1\text{JPH}$	$^3\text{JPOCH}$	$\delta^{31}\text{P}$	$^3\text{JPOCH}$	$\delta^{31}\text{P}$	$\Delta$
<u>14a</u> 	882.2	12.2 sextet <sup>g</sup>	-44.8	13.5(trans) <sup>h,i</sup> 0.3(cis) <sup>h,i</sup> 10.6(OMe)	-143.8	99.0
<u>14b</u> 	847.8	12.8 6.4 quartet of triplets <sup>j</sup>	-20.8	13.5(trans) <sup>h,i</sup> 0.3(cis) <sup>h,i</sup> 10.6(OMe)	-143.8	

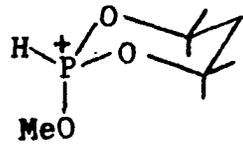
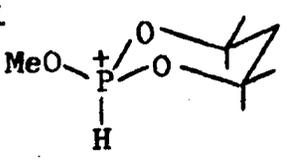
<sup>g</sup>Outer four peaks were shoulders.

<sup>h</sup>Refers to the stereochemical relationship of a ring proton to an axial alkoxy group.

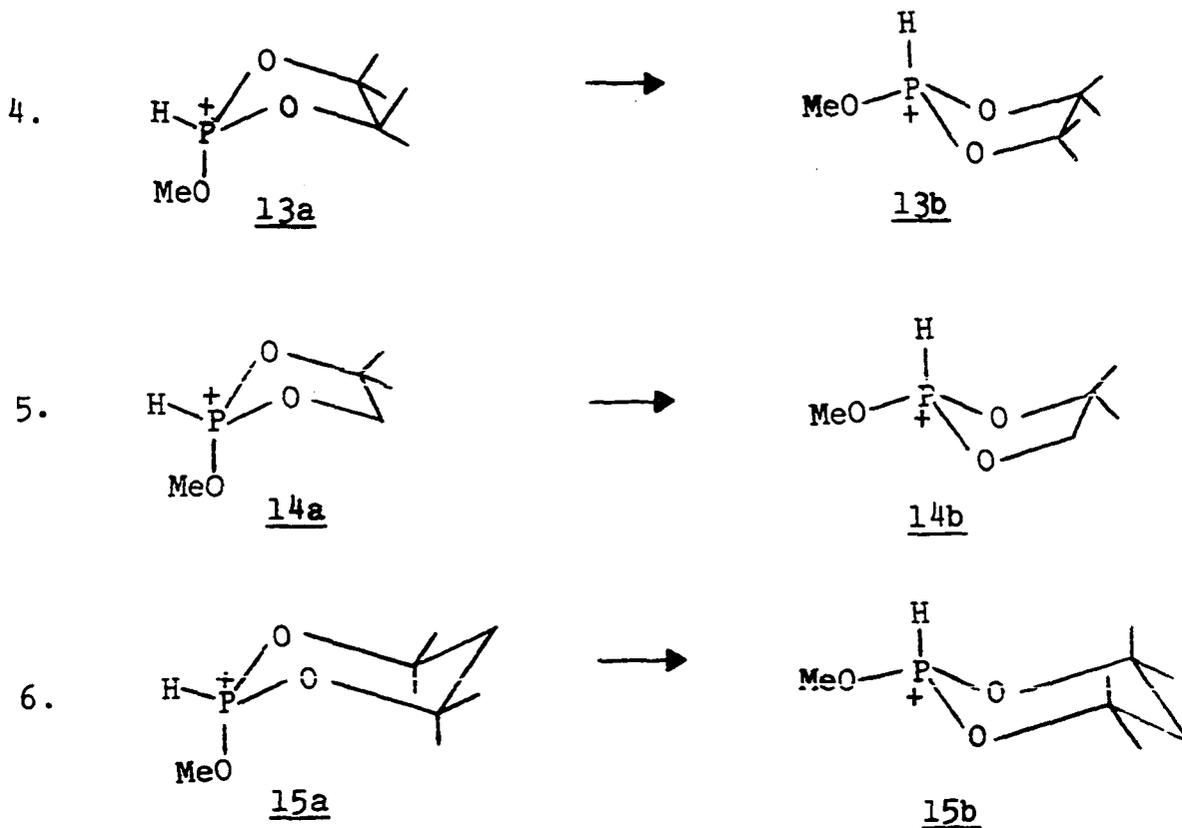
<sup>i</sup>Reference 55. The specific R in the alkoxy group was not mentioned.

<sup>j</sup>Resonance actually consisted of 9 peaks because some of the 12 peaks were coincident.

Table 6. (Continued)

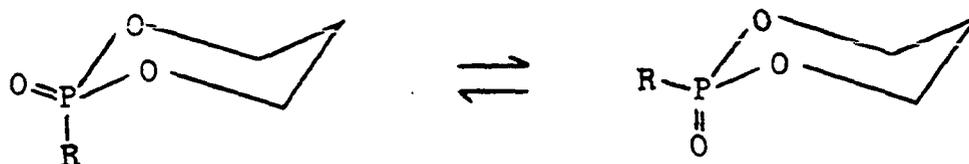
Compound	Protonated Species			Trivalent Precursor		
	$^1J_{PH}$	$^3J_{POCH}$	$\delta^{31}P$	$^3J_{POCH}$	$\delta^{31}P$	$\Delta$
<p><u>15a</u></p> 	850.6	12.8 quartet	-15.7	12.1	-128.9	113.2
<p><u>15b</u></p> 	832.9	12.6 quartet	-20.5	12.1	-128.9	

have displayed protonated forms of 8 and 10. In fact an acid solution of 8 at all temperatures (even at  $-20^{\circ}$  for 20 minutes) showed no presence of protonated 10 which would be expected from an inversion process occurring at phosphorus. Acid solutions of 13, 14 and 15, on the other hand, which had both isomeric forms at temperatures lower than  $-40^{\circ}$ , were converted in about 20 minutes at  $-40^{\circ}$ , to the b isomers. It is more plausible, therefore, that the conformational rearrangements indicated in reactions 4, 5 and 6 are occurring.



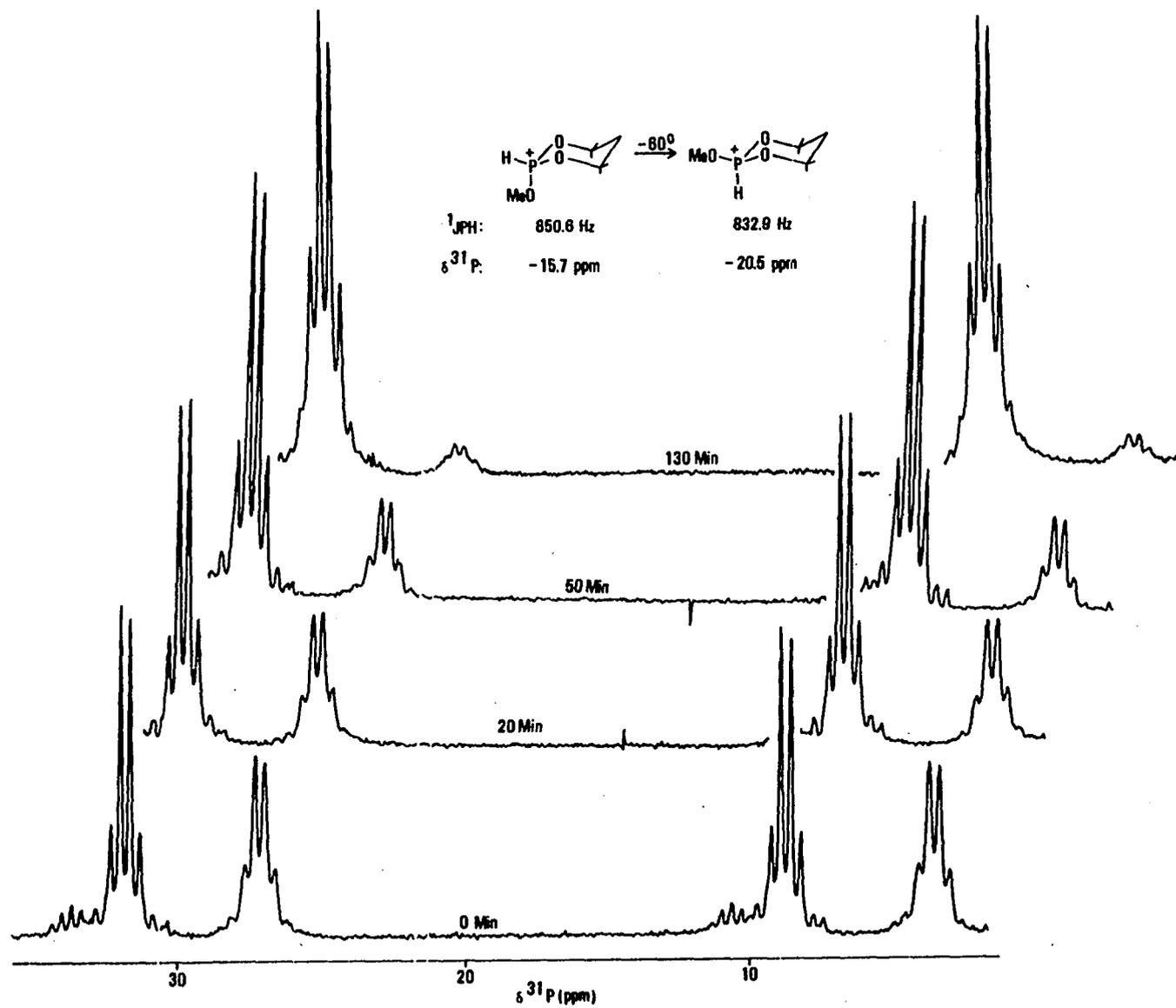
The rearrangement represented by reactions 4-6 appears to be irreversible. When a sample of 15 in fluorosulfuric acid, converted to the protonated form 15b, was held at  $-80^{\circ}$  for

70 minutes in the nmr probe, there was no hint of isomer 15a reappearing. Another sample of 15 in acid initially revealed 40% of 15a and 60% of 15b at  $-60^\circ$  as shown by the bottom spectrum in Figure 4. By keeping this sample at  $-60^\circ$  in the nmr probe and taking nmr spectra at time intervals of 20 and 50 minutes, the amount of isomer 15a is seen to decrease until after 130 minutes essentially all is converted to isomer 15b. In other protonation experiments wherein spectral observance was begun at low temperatures followed by increasing the temperature by  $10^\circ$  intervals, conversion to the b isomers for all three protonated phosphites was 90-100% complete in 20 minutes at  $-40^\circ$ , the length of time needed for data collection at each temperature. Furthermore, only b isomers were present at  $-20^\circ$ . These observations contrast previous nmr and infrared solution studies (20,78) which have shown the presence of rapid conformational equilibria involving the 2-substituted 1,3,2-dioxaphosphorinan-2-ones shown below (R =  $\text{CPh}_3$ , OMe, t-OBu, Me, Et, Br and other neutral groups).



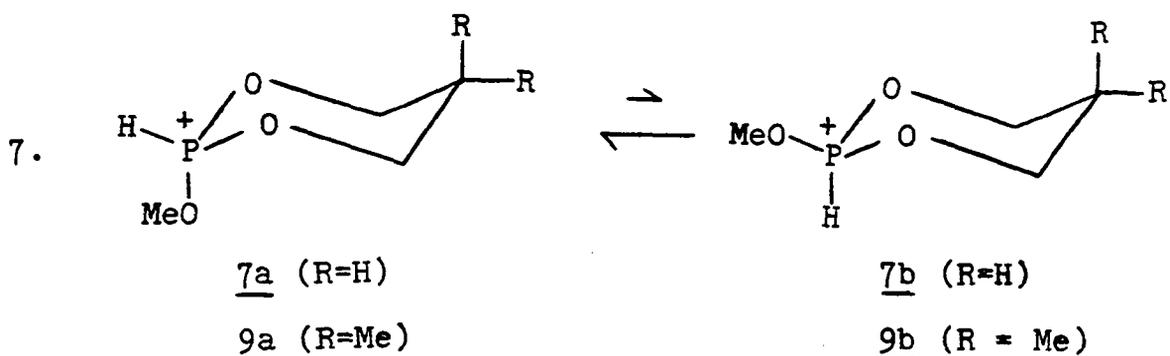
Similar equilibria involving five-membered ring systems are not known.

Figure 4. The  $^{31}\text{P}$  nmr spectra of 15 in fluorosulfuric acid at  $-60^\circ$  showing the conversion of 15a to 15b with time



The driving force for the irreversible rearrangement from equatorial to axial protonation could stem from two sources. One is the greater basicity of an axial lone pair, and it is likely that the proton, being a highly polarizing Lewis acid, prefers this coordination site. Secondly, there is syn-axial steric interaction of the axial methoxy group with the ring methyl groups. Evidence that the latter is a reasonable postulate is provided by the comparison of the crystal structures of methyl ethylene phosphate (79) and methyl pinacol phosphate (80). The methoxy group in the former bisects the OPO angle and is under the ring while in the latter structure the methoxy group is under the phosphoryl oxygen because of steric crowding by the staggered methyls of the pinacol ring (80). Further evidence that steric interaction is probably the principal cause of the conformational change comes from a comparison of the protonated phosphites 7, 8 and 10. Although there is a small inductive effect (5.0 Hz) when comparing  $^1\text{JPH}$  of protonated 7 (870.0 Hz) and 8 (865.0 Hz), their similarity probably means that the former is protonated equatorially as has already been shown for protonated 8. However, a solution of protonated 7 allowed to rise to  $-30^\circ$  in one experiment (a temperature at which 13a, 14a and 15a are readily converted to their b isomers) showed no evidence of a smaller PH coupling comparable to that of axially protonated 10. A similar

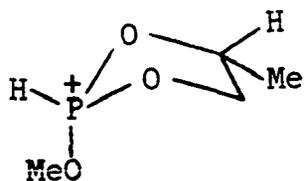
experiment in which an acid solution of 9 was allowed to rise to  $-20^\circ$  revealed the absence of any detectable axially protonated form as judged by the large  $^1\text{JPH}$  value of 861.2 Hz. Thus, while the a isomers of 13, 14 and 15 are formed first, the b isomers are thermodynamically favored on steric grounds. It is also reasonable to conclude that protonated 7 and 9 prefer conformation a in spite of the greater basicity of the axial phosphorus lone pair in 7b and 9b. Electron



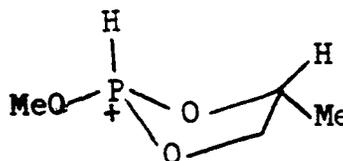
repulsion rather than steric effects may well dominate here in that the highly polar P-H sigma bonding orbital experiences less electron repulsions from the ring oxygen p orbitals when it is equatorially directed.

The chemical shifts of 13a (-40.2 ppm) and 14a (-44.8 ppm) are about 20 ppm downfield of their isomeric counterparts, 13b and 14b, but reasonably close to those of the protonated phosphite 2 (-43.9 ppm) and 5a (-44.7 ppm). The striking similarity of these chemical shifts is again in agreement with equatorial protonation for all four. As noted in the previous discussion,  $\delta^{31}\text{P}$  for protonated 5b was

-22.6  $\pm$  2.0 ppm which is close to the analogous chemical shifts of 13b (-20.4 ppm) and 14b (-20.8 ppm). Since trivalent 5b has been suggested (39,69,81) to have the ring methyl syn to the methoxy group which could involve steric interaction, it is probable that the observed protonated form of 5b possesses an axial proton. The equatorially protonated



5b (eq H<sup>+</sup>)



5b (ax H<sup>+</sup>)

form of 5b was not observed, possibly because its chemical shift and coupling would be expected to be very similar to that of protonated 5a and therefore masked by the peaks of this dominant isomer. It is also possible that conversion to the axially protonated form of 5b was already complete since nmr data on the acid solution of 5 was first collected at -50°.

Although the chemical shifts of five-membered ring phosphites protonated equatorially have <sup>31</sup>P chemical shifts 20 ppm downfield of axially protonated species, the analogous shifts for 15a and 15b differ by only 4.8 ppm. Furthermore, the shift of 15a is downfield from 15b in marked contrast to the reverse in five-membered ring phosphites. The reason

for this reversal is not understood but it is consistent with the  $^{31}\text{P}$  shifts of protonated 10 (-18.2 ppm, equatorial protonation) and protonated 8 (-17.3 ppm, axial protonation), although the difference in these phosphites is only 0.9 ppm.

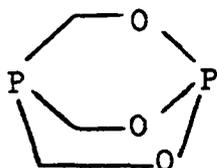
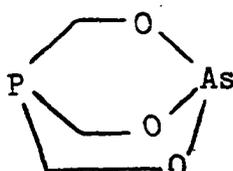
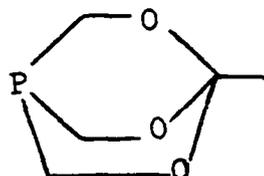
The inductive effect of the ring methyl groups in decreasing  $^1\text{JPH}$  is quite dramatic. One methyl group in protonated 5a yields  $^1\text{JPH} = 890.4$  Hz, two methyls in 14a lead to  $^1\text{JPH} = 882.2$  Hz and  $^1\text{JPH}$  for 13a with four ring methyl substituents yields  $^1\text{JPH} = 556.4$  Hz. Similarly,  $^1\text{JPH}$  for protonated 7 (870.0 Hz, no ring methyls) is larger than  $^1\text{JPH}$  for 15a (850.6 Hz) which has four methyl substituents in the 4 and 6 ring positions.

The  $^3\text{JPOCH}$  coupling to the methoxy protons for the a and b isomers of 13 and 15 are little changed from the parent phosphites. Furthermore, each half of the protonated doublet of 14a is a septet showing that all  $^3\text{JPOCH}$  couplings are similar, an observation which has been noted for other equatorially protonated phosphites in the previous section. However, 14b, which is axially protonated, shows each member of the larger doublet to be a quartet of triplets wherein phosphorus to methoxy proton coupling is twice as large as phosphorus to ring methylene proton coupling.

#### Protonation of phosphines

Three bicyclic alkyl phosphines were also subjected to protonation studies. However, two of these, 16 and 17, are

bifunctional Lewis bases in having phosphorus and arsenic,

161718

respectively, at the other bridgehead position. The conditions under which these molecules were protonated and their nmr parameters are listed in Table 7.

In the course of the phosphite protonation studies described earlier, 16 was also dissolved in  $\text{HFSO}_3$ . Since fluorosulfuric acid was thought to be an acid of sufficient strength to protonate both phosphorus bridgeheads, it came as a surprise to find that only the phosphite phosphorus was protonated. Protonation of the phosphine phosphorus was ruled out since comparison of nmr parameters for  $\text{HP}^+(\text{OCH}_2)_3\text{P}$  ( $^1\text{JPH} = 901.1 \text{ Hz}$  and  $\delta^{31}\text{P} = -23.2 \text{ ppm}$ ) and  $\text{HP}^+(\text{OCH}_2)_3\text{CMe}$  ( $^1\text{JPH} = 899.2 \text{ Hz}$  and  $\delta^{31}\text{P} = -32.2 \text{ ppm}$ ) show great similarity. Furthermore, the resonance at +54.7 ppm, though shifted downfield from the phosphine resonance of +67 ppm in  $\text{P}(\text{OCH}_2)_3\text{P}$ , is still reasonable for an unprotonated phosphine. Protonation at only the phosphite phosphorus seemed unusual since Reetz (82) has shown that acyclic phosphites are poorer

Table 7. Nmr data for protonated bicyclic alkyl phosphines and their trivalent precursors

		$^1J_{PH}^{a,b}$	$\delta^{31}P^c$	$^1J_{PH}^{a,d}$	$\delta^{31}P^c$	$^3J_{PP}^a$	$J^e$	Conditions
<u>16</u>	$P(OCH_2)_3P$		$-90^f$		$+67^f$	$-37.2^f$	$2.5(POCH)^f$ $8.9(PCH)^f$	DMSO at RT
	$HP^+(OCH_2)_3P$	901.1	-23.2		+54.7	46.6	5.6(POCH) 8.9(PCH)	HFSO <sub>3</sub> at $-50^\circ$
	$HP^+(OCH_2)_3PH^+$	1007.8	-28.9	698.2	+20.2	156.3		HFSO <sub>3</sub> ·SbF <sub>5</sub> ·SO <sub>2</sub> at $-70^\circ$
<u>18</u>	$P(CH_2O)_3CMe$				$+81^f$		8(PCH) <sup>f</sup>	
	$HP^+(CH_2O)_3CMe$			635.7	+25.5			HFSO <sub>3</sub> ·SbF <sub>5</sub> ·SO <sub>2</sub> at $-70^\circ$
<u>17</u>	$P(CH_2O)_3As$				+65.7		9.4(PCH) <sup>f</sup>	CDCl <sub>3</sub> at RT
	$HP^+(CH_2O)_3As$			589.5	-0.3			HFSO <sub>3</sub> ·SbF <sub>5</sub> ·SO <sub>2</sub> at $-70^\circ$

<sup>a</sup>Precise to  $\pm 2.0$  Hz.

<sup>b</sup>Refers to coupling at the protonated phosphite.

<sup>c</sup>Relative to 85% H<sub>3</sub>PO<sub>4</sub>. Precise to  $\pm 0.3$  ppm.

<sup>d</sup>Refers to coupling at the protonated phosphine.

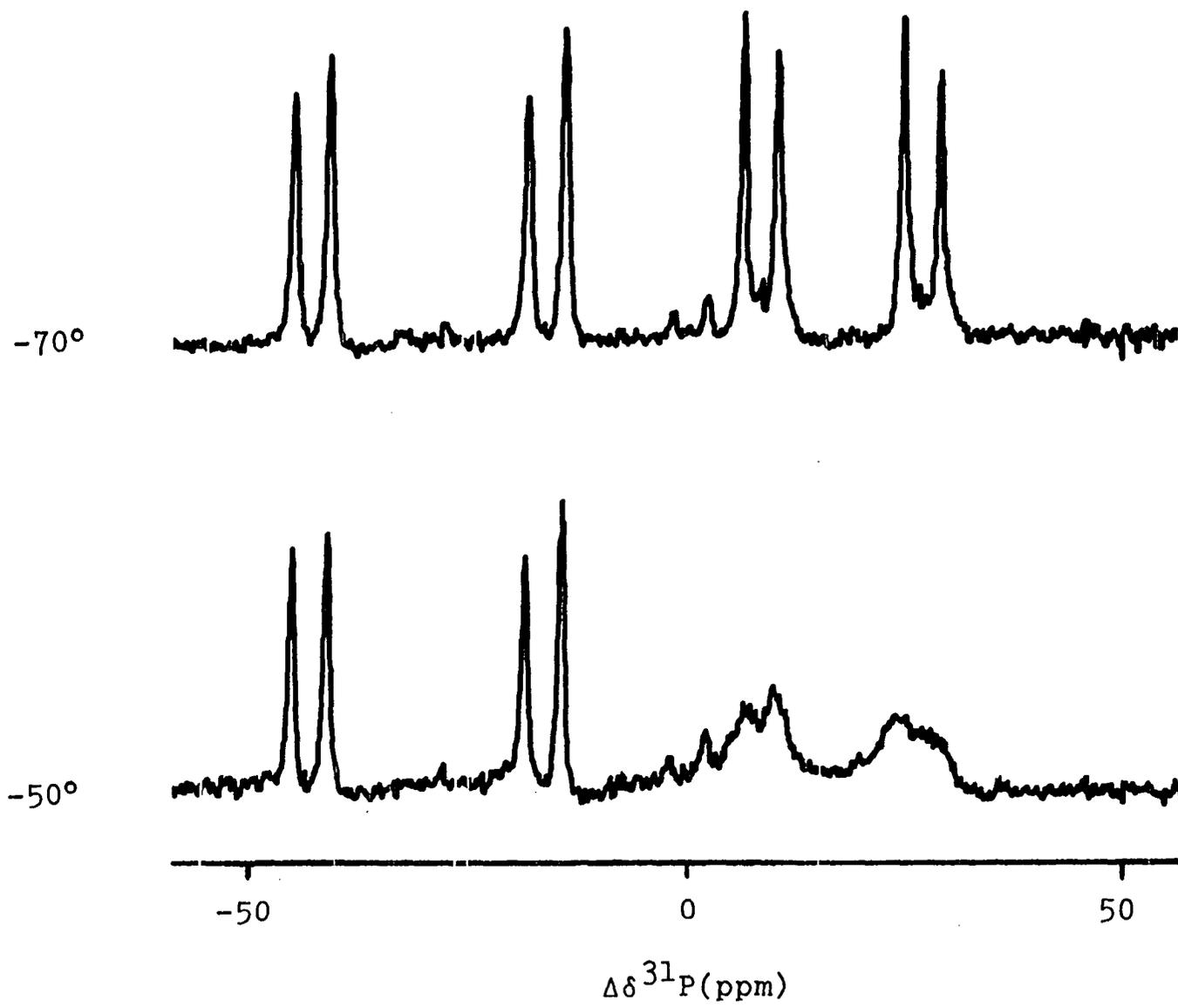
<sup>e</sup>Coupled nuclei are referred to in parentheses.

<sup>f</sup>Reference 18.

donors toward  $\text{BH}_3$  than acyclic phosphines. However, protonation of both phosphorus moieties was successful in the stronger acid system  $\text{HFSO}_3 \cdot \text{SbF}_5$  diluted with  $\text{SO}_2$  at  $-70^\circ$  (Compare  $H_o$  of  $\text{HFSO}_3 \cdot \text{SbF}_5$  (19.5 (est.)) and  $\text{HFSO}_3$  (15.07) (83)). Figure 6 shows the two sets of doublets as expected for this diprotonated molecule. Fine structure due to methylene proton coupling to phosphorus is not observed. Upon raising the temperature to  $-50^\circ$ , broadened resonances for the phosphine phosphorus arise because of rapid exchange of the proton at this site, while the coupling parameters ( $^1\text{JPH}$  (phosphite) and  $^3\text{JPP}$ ) and the chemical shifts of both protonated atoms remain essentially the same. This again reveals the poorer acceptor strength of the phosphine lone pair compared to the phosphite lone pair.

The behavior of the proton in seeking the lone pair of the phosphite phosphorus is not unique since  $\text{BH}_3$  and  $\text{CH}_3^+$  also prefer coordination at this site (84). The dipolar effect (84) previously invoked to rationalize coordination of these Lewis acids at the  $\text{P}(O)_3$  phosphorus can also explain the observed protonation behavior. Although the phosphine phosphorus may be more basic, there is a large dipole (3.10 D) in the phosphite phosphorus direction (47) which demands charge neutralization. Coordination of  $\text{H}^+$  fulfills this requirement but also diminishes electron density at the  $\text{P}(\text{CH}_2)_3$  phosphorus by an inductive effect. Consequently, a

Figure 5. The  $^{31}\text{P}$  nmr spectra of  $\text{P}(\text{OCH}_2)_3\text{P}$  in  
 $\text{HFSO}_3 \cdot \text{SbF}_5 \cdot \text{SO}_2$  at  $-70^\circ$  and  $-50^\circ$



stronger acid is needed to quaternize the phosphine phosphorus, making  $\text{HP}^+(\text{OCH}_2)_3\text{PH}^+$  the first known diphosphonium salt of 16.

Protonation of  $\text{P}(\text{CH}_2)_3$  in  $\text{HP}^+(\text{OCH}_2)_3\text{P}$  dramatically increases  $^1\text{JPH}$  at the phosphite end by over 100 Hz to the value of 1007.8 Hz, the highest known P-H coupling for any type of phosphite. Since the protonated phosphine in  $\text{HP}^+(\text{OCH}_2)_3\text{PH}^+$  should structurally mimic the tetrahedral bridgehead carbon in  $\text{HP}^+(\text{OCH}_2)_3\text{CMe}$  reasonably well ( $^1\text{JPH} = 899.2$  Hz), the 1007.8 Hz coupling is even more surprising. This large value of  $^1\text{JPH}$  in the diprotonated species can be ascribed to the accumulation of a second positive charge on the molecule.

Phosphine phosphorus protonation of  $\text{P}(\text{CH}_2\text{O})_3\text{As}$ ,  $\text{P}(\text{CH}_2\text{O})_3\text{CMe}$  and  $\text{P}(\text{CH}_2\text{O})_3\text{PH}^+$  is characterized by a downfield  $^{31}\text{P}$  chemical shift characteristic of protonated acyclic phosphines (3) and by the appearance of the doublet in the  $^{31}\text{P}$  nmr due to proton-phosphorus coupling. Surprisingly,  $^3\text{JPCH}$  couplings for the above phosphines were not observed, which suggests that these couplings are near zero as was found for the bis-borane adduct of 16 and the borane adduct of 18 (84). Another factor which may have contributed to the unobservability of this coupling is insufficient resolution ascribable at least in part to the poorer lock stabilization by  $\text{HFSO}_3 \cdot \text{SbF}_5$  which contains several different fluorine species (16) compared to  $\text{HFSO}_3$ .

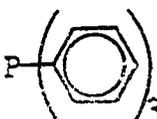
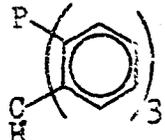
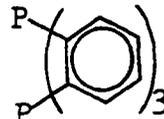
The protonated phosphines in Table 7 all have  $^1\text{JPH}$  values larger than any protonated acyclic phosphine (1-3) and these couplings are comparatively larger than the  $^1\text{JPH}$  value of 497 Hz found for  $\text{Me}_3\text{PH}^+$  formed in fluorosulfuric acid (3). This general augmentation may arise from the presence of electronegative oxygens two bonds away from the phosphorus atom, which inductively place a greater amount of positive charge on phosphorus compared to other phosphines which have only hydrocarbon substituents. For the bicyclic phosphines the larger value of  $^1\text{JPH}$  for  $\text{HP}^+(\text{CH}_2\text{O})_3\text{CMe}$  (635.7 Hz) compared to  $\text{HP}^+(\text{CH}_2\text{O})_3\text{As}$  (589.5 Hz) probably is the result of increased s character in the P-H bond brought about by the larger size of arsenic compared to carbon. In the absence of structural data for an arsenite, the FAsF angle ( $96.0 \pm 0.2^\circ$ ) in  $\text{AsF}_3$  (85) can be compared to the FCF angle ( $108^\circ$  average) in  $\text{CH}_3\text{CF}_3$  (86). Assuming tetrahedral angles at oxygen and carbon and assuming that the FAsF and FCF angles are similar to OAsO and OCO angles, respectively, framework molecular models show a smaller CPC angle in  $\text{P}(\text{CH}_2\text{O})_3\text{CMe}$  than in  $\text{P}(\text{CH}_2\text{O})_3\text{As}$ . Thus, more s character is placed in the P-C bonds and less s character in the P-H bond for the latter compound upon protonation. It is also possible that replacement of arsenic with the more electronegative carbon for E in  $\text{HP}^+(\text{CH}_2\text{O})_3\text{E}$  may increase the relative positive charge on phosphorus and thus augment  $^1\text{JPH}$ . The largest known  $^1\text{JPH}$  value for a protonated

phosphine found in  $\text{HP}^+(\text{CH}_2\text{O})_3\text{PH}^+$  is undoubtedly also the result of the accumulation of two positive charges, as was suggested earlier to account for the exceedingly large  $^1\text{JPH}$  value for the phosphite end of the molecule.

Three bond P-P coupling for a number of derivatives of  $\text{P}(\text{OCH}_2)_3\text{P}$  have been measured (87) and found to range from -37.2 Hz in  $\text{P}(\text{OCH}_2)_3\text{P}$  to +151.3 Hz in  $\text{SP}(\text{OCH}_2)_3\text{PO}$ . Comparison of  $^3\text{JPP}$  found in  $\text{HP}^+(\text{OCH}_2)_3\text{P}$  (46.6 Hz) and  $\text{HP}^+(\text{OCH}_2)_3\text{PH}^+$  (156.3 Hz) with  $[\text{CH}_3\text{P}^+(\text{OCH}_2)_3\text{P}]\text{BF}_4$  (+46.2 Hz),  $[\text{P}(\text{OCH}_2)_3\text{P}^+\text{CH}_3]\text{BF}_4$  (+114.6 Hz) and  $\text{SP}(\text{OCH}_2)_3\text{PO}$  indicate that the signs of  $^3\text{JPP}$  for the protonated species should also be positive. Thus,  $^3\text{JPP}$  increases in magnitude by 83.8 Hz from 16 to  $\text{HP}^+(\text{OCH}_2)_3\text{P}$  and by 109.7 Hz from  $\text{HP}^+(\text{OCH}_2)_3\text{P}$  to  $\text{HP}^+(\text{OCH}_2)_3\text{PH}^+$ . This rise can be attributed to increases in the effective nuclear charge placed on the phosphorus atoms as monoprotection and diprotection occur and also to increases in the s character first in the P-O and then the P-C bonds brought about by hybridization changes as each phosphorus atom is quaternized.

Protonation of diphosphatriptycene, a bicyclic triphenyl phosphine derivative, was also accomplished and the nmr results are compared in Table 8 along with nmr data for two similar compounds. Unlike  $\text{P}(\text{OCH}_2)_3\text{P}$ , diphosphatriptycene was easily protonated at both phosphorus bridgeheads as indicated by the lack of a parent phosphine resonance at higher field.

Table 8. Nmr data for protonated phenyl phosphines and their trivalent precursors.

Compound	$^1J_{\text{PH}}^{\text{a}}$	$\delta^{31}\text{P}^{\text{b}}$	Temp	$\delta^{31}\text{P}^{\text{b}}$	$\Delta^{\text{c}}$	Reference
<u>21</u> 	510	-6.8	RT	+5.4	-12.2	3
<u>20</u> 	571	+23.3	-60	+64.8	-41.5	88
<u>19</u> 	639.2	+20.1	-50	+43.1	-23.0	This work

<sup>a</sup>Precise to 1.0 Hz.  $\text{HFSO}_3$  was the protonating acid.

<sup>b</sup>Relative to 85%  $\text{H}_3\text{PO}_4$ . Precise to  $\pm 0.3$  ppm.

<sup>c</sup> $\Delta$  is the change in chemical shift from the trivalent phosphine to the protonated species.

Thus, the protonation of the parent phosphine to give  $\text{HP}^+(\text{O-C}_6\text{H}_4)_3\text{PH}^+$  with the weaker acid  $\text{HFSO}_3$  (compared to  $\text{HFSO}_3 \cdot \text{SbF}_5$ ), like the formation of the dicarbonium salt  $\text{MeP}^+(\text{CH}_2\text{CH}_2)_3\text{P}^+\text{Me}$  (89), indicates that the dipolar effect (84) is of smaller consequence for these symmetrical compounds.

There is a small temperature dependence of  $^1\text{JPH}$  for protonated diphosphatriptycene and phosphatriptycene. In the temperature range  $0^\circ$  to  $-80^\circ$ ,  $^1\text{JPH}$  for the former species goes from 625.9 Hz to 642.0 Hz, while in the latter species  $^1\text{JPH}$  ranges from 551 Hz to 571 Hz as the temperature decreases from  $+67^\circ$  to  $-60^\circ$  (87).

From a comparison of  $^2\text{JPH}$  obtained from the methyl phosphonium salt of triphenylphosphine and phosphatriptycene, Jongasma, de Kleijn and Bickelhaupt (90), have concluded that the former and latter P-Me bonds have less and more than 25% s character, respectively. They also concluded that the P-H bond in protonated phosphatriptycene ( $^1\text{JPH} = 568$  Hz) has more than 25% s character compared to  $\text{PH}_4^+$  ( $^1\text{JPH} = 548$  Hz (3)) which has  $\text{sp}^3$  hybridization. Thus, the increase in  $^1\text{JPH}$  from  $\text{Ph}_3\text{PH}^+$  (510 Hz) to  $\text{HC}(\text{O-C}_6\text{H}_4)_3\text{PH}^+$  (571 Hz) to  $\text{HP}^+(\text{O-C}_6\text{H}_4)_3\text{PH}^+$  (639.2 Hz) seems to reflect an increase in s character in the P-H bond. However, comparison of the  $^{31}\text{P}$  chemical shifts of the trivalent phosphines (employing the argument that higher upfield shifts result from more s character in the lone pair) suggests that s character diminishes in the lone

pair from phosphatriptycene to diphosphatriptycene to tri-phenylphosphine. While this apparently contradicts the s character trend in the P-H bond, the anomaly can be resolved by considering that the double positive charge on  $\text{HP}(\text{O-C}_6\text{H}_4)_3^+$  compared to the single positive charge for the other two protonated phosphines contributes strongly to  $^1\text{JPH}$ .

#### Protonation of phosphorus trihalides

In the protonation studies of phosphites, it was noted that slow decomposition and/or solvolysis of some phosphites led to the formation of  $\text{PF}_3$  as a major fluorinated product. A similar fluorinating ability of fluorosulfuric acid has been reported (4,8) wherein phosphonic and phosphinic acids have been converted to  $\text{PF}_3$  and  $\text{OPF}_3$  in addition to a number of fluorinated intermediates. This is not unusual since  $\text{HFSO}_3$  is a known fluorinating agent for converting inorganic salts, oxides and oxy acids to inorganic fluorides (91).

Although phosphites and phosphines are easily protonated by  $\text{HFSO}_3$ , there was no indication in this work from the  $^{31}\text{P}$  spectrum that  $\text{PF}_3$ , a weaker base, was protonated by  $\text{HFSO}_3$  as it formed via the decomposition of phosphites. Olah and McFarland (8) have described the room temperature  $^{19}\text{F}$  nmr spectrum of a  $\text{PF}_3\text{-HFSO}_3$  solution which consisted of a doublet of doublets ( $^1\text{JPH} = 987 \text{ Hz}$ ,  $^2\text{JHPF} = 94 \text{ Hz}$ ) tentatively assigned to  $\text{HPF}_3^+$ , although corroboration could not be obtained from  $^1\text{H}$  or  $^{31}\text{P}$  spectral data. These authors also reported that

when  $\text{PF}_3$  was dissolved in a 1:1 mole ratio of  $\text{HFSO}_3 \cdot \text{SbF}_5$  (Magic Acid), the  $^{19}\text{F}$  spectrum showed only phosphorus oxy-fluoride as a rapidly exchanging system.

In spite of the above negative results, it is now possible to report  $^{31}\text{P}$  spectral evidence (Table 9) for the formation of  $\text{HPF}_{3-n}\text{Cl}_n^+$  ( $n = 0$  to 3) and  $\text{HPCl}_{3-n}\text{Br}_n^+$  ( $n = 1$  to 3). The phosphorus trihalides have been found to be readily soluble in  $\text{HFSO}_3 \cdot \text{SbF}_5$  using  $\text{SO}_2$  as diluent. Complete protonation was ensured by keeping the acid to phosphorus ratio in the range of five to ten to one and by keeping the samples colder than  $-50^\circ$ . Although these values were obtained at  $-70^\circ$ , protonation can easily be observed over a range of temperatures. In the range from  $-50$  to  $-80^\circ$ ,  $\delta^{31}\text{P}$  and  $^1\text{JPF}$  remain quite constant while  $^1\text{JPH}$  values increase about 4 Hz.

That all of the phosphorus trihalides are protonated at phosphorus is shown by the appearance of a doublet with a large coupling constant (800-1200 Hz) corresponding to  $^1\text{JPH}$ . Figure 6 displays the  $^{31}\text{P}$  nmr spectrum of the  $\text{HPF}_3^+$  ion which exhibits the expected doublet of quartets while Figure 7 shows a  $^{31}\text{P}$  nmr spectrum having four doublets corresponding to the  $\text{HPCl}_3^+$ ,  $\text{HPCl}_2\text{Br}^+$ ,  $\text{HPClBr}_2^+$  and  $\text{HPBr}_3^+$  ions. The doublet due to  $\text{HPBr}_3^+$  in Figure 7 is of low intensity because the precursor phosphorus trihalide mixture contained only 10%  $\text{PBr}_3$ . However,  $\text{PBr}_3$  was protonated in a separate experiment confirming the assignment in Figure 7.

Table 9.  $^{31}\text{P}$  nmr parameters for  $\text{HPX}_3^+$  and  $\text{PX}_3$ 

Compound	Z = H <sup>+</sup>			Z = lone pair		
	$^1\text{JPH}^a$	$^1\text{JPF}^a$	$\delta^{31}\text{P}^{b,c}$	$^1\text{JPF}^d$	$\delta^{31}\text{P}^c$	$\Delta\delta^{31}\text{P}^e$
$\text{ZPF}_3$	1190.6	1279.3	-16.2 dq	1410 <sup>f</sup>	-97.0 q	80.8
$\text{ZPF}_2\text{Cl}$	1068.9	1272.8	-66.4 dt	1380 <sup>g</sup>	-176 t <sup>g</sup>	109.6
$\text{ZPFCl}_2$	979.5	1254.9	-92.0 dd	1326 <sup>h</sup>	-224 d <sup>h</sup>	132.0
$\text{ZPCl}_3$	911.1		-86.9 d		-219.4 s <sup>i</sup>	132.5
$\text{ZPCl}_2\text{Br}$	875.6		-61.7 d		-224.6 s <sup>i</sup>	162.9
$\text{ZPClBr}_2$	841.2		-31.7 d		-227.4 s <sup>i</sup>	195.7
$\text{ZPBr}_3$	809.8		+3.0 d		-227.7 s <sup>i</sup>	230.7

<sup>a</sup>Precise to  $\pm 1.0$  Hz. Measured at  $-70^\circ$ .

<sup>b</sup>Precise to  $\pm 0.2$  ppm. Because 85%  $\text{H}_3\text{PO}_4$  is frozen at  $-70^\circ$ ,  $\text{PCl}_3$  was used as an external standard. All chemical shifts, however, are reported relative to 85%  $\text{H}_3\text{PO}_4$  for convenience.

<sup>c</sup>dq = doublet of quartets, dt = doublet of triplets, dd = doublet of doublets, q = quartet, t = triplet, d = doublet and s = singlet.

<sup>d</sup>In Hz.

<sup>e</sup> $\Delta\delta^{31}\text{P}$  is the change in chemical shift upon protonation ( $\delta^{31}\text{P}(\text{HPX}_3^+) - \delta^{31}\text{P}(\text{PX}_3)$ ).

<sup>f</sup>Reference 92.

<sup>g</sup>Reference 93.

<sup>h</sup>Reference 94.

<sup>i</sup>These chemical shifts match closely those assigned in reference 95.

Figure 6. The  $^{31}\text{P}$  nmr spectrum of  $\text{HPF}_3^+$  at  $-70^\circ$

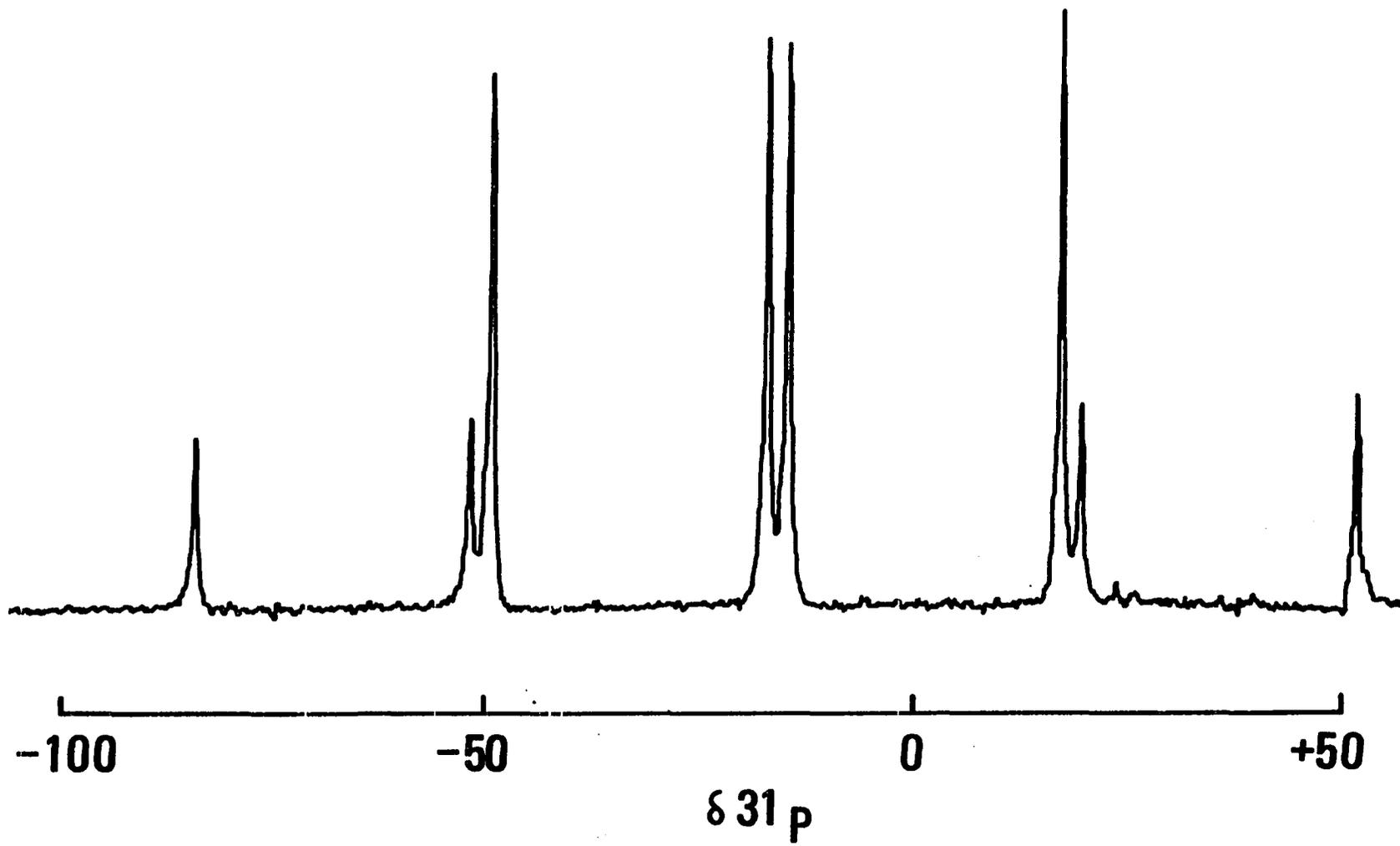
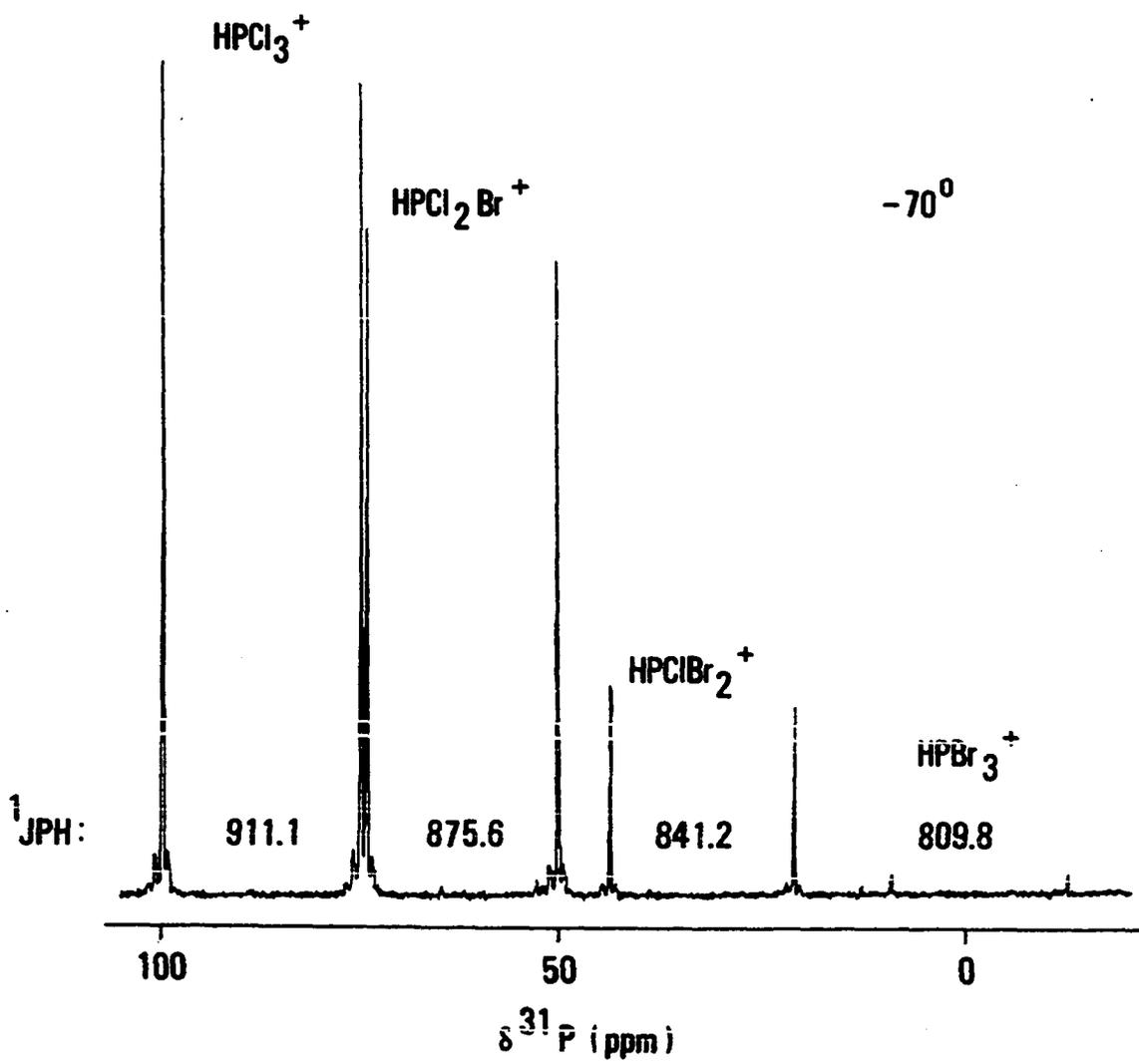


Figure 7. The  $^{31}\text{P}$  nmr spectrum of  $\text{HPCl}_3^+$ ,  $\text{HPCl}_2\text{Br}^+$ ,  
 $\text{HPClBr}_2^+$  and  $\text{HPBr}_3^+$  at  $-70^\circ$



The  $^1\text{JPH}$  value of 1190.6 Hz for the  $\text{HPF}_3^+$  cation is the largest reported for these nuclei and can be attributed to a strong Fermi contact interaction (59,60) induced by the high degree of s character in the P-H bond and to substantial nuclear charge on phosphorus; both effects stemming from the large electronegativity of fluorine. There is a dramatic linear drop in  $^1\text{JPH}$  with the sum of the halogen electronegativities which is ascribable to the accompanying decrease in s character of the protonated phosphorus lone pair. This is illustrated in Figure 8 which shows a plot of  $^1\text{JPH}$  with the sum of the Pauling electronegativities (96) including the point for  $\text{PH}_4^+$  ( $^1\text{JPH} = 548 \text{ Hz (3)}$ ). The equation for the least squares line,  $^1\text{JPH} = 118.3(\text{E.N.}) - 230.0$ , has an excellent correlation coefficient of 0.998.

McFarlane and White (2) were the first to report a linear correlation between  $^1\text{JPH}$  obtained from protonated phosphorus compounds and the corresponding values of  $^1\text{JWP}$  observed in  $\text{LW}(\text{CO})_5$  complexes. From this relationship they concluded that  $^1\text{JWP}$  was also dominated by changes in the effective nuclear charge of the coupled nuclei. Earlier we were able to include the point for  $\text{P}(\text{OCH}_2)_3\text{CMe}$  in this correlation (25). With the protonation of phosphorus trihalides, this relationship can now be extended even further. Values of  $^1\text{JPH}$  and  $^1\text{JWP}$  are collected in Table 10 and plotted in Figure 9. A calculation of a least-squares line for these

Figure 8. Plot of  $^1\text{JPH}$  obtained from  $\text{HPX}_3^+$  ions versus  
the sum of Pauling electronegativity of the  
X substituents

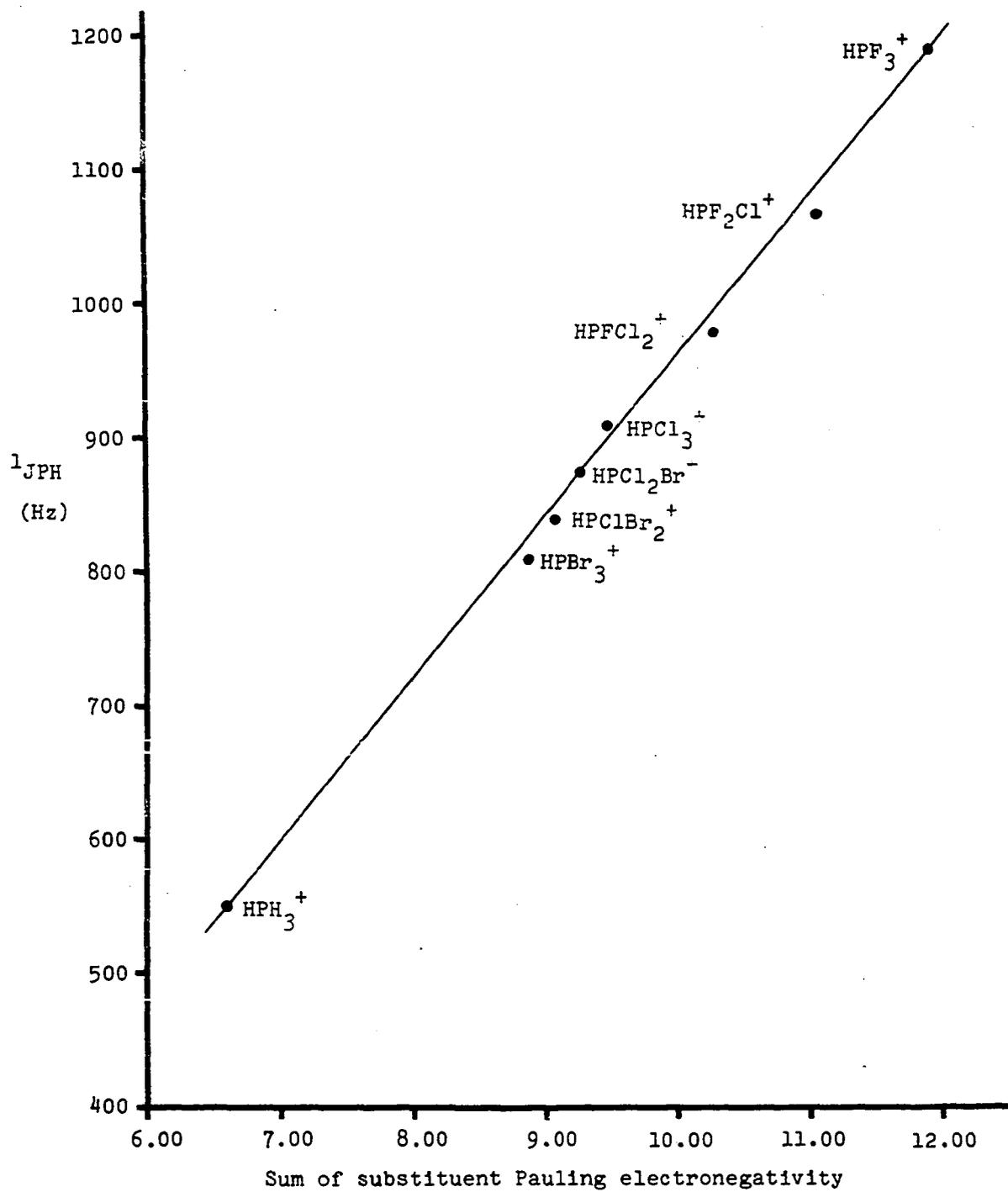


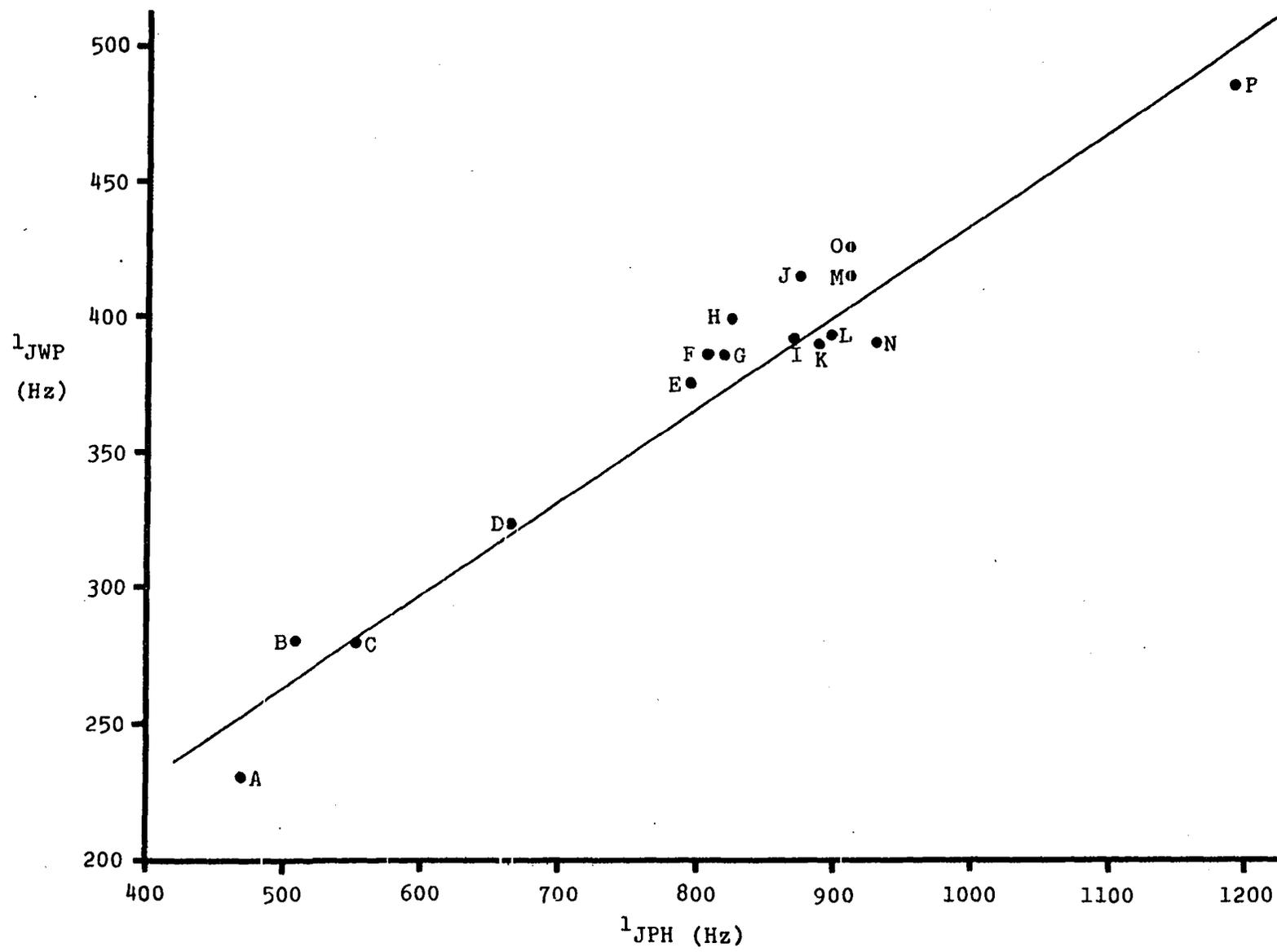
Table 10. Tabulation of  $^1\text{JWP}$  (Hz) and  $^1\text{JPH}$  (Hz) values

Letter	Ligand	$^1\text{JPH}$	Reference	$^1\text{JWP}$	Reference
A	$\text{P}(\underline{n}\text{-Bu})_3$	470	3	227.0	97
B	$\text{P}(\text{Ph})_3$	510	3	280	100
C	$\text{POMe}(\text{Ph})_2$	553	2	280	100
D	$\text{P}(\text{OMe})_2\text{Ph}$	666	2	323	100
E	$\text{P}(\text{O}-\underline{1}\text{-Pr})_3$	796	4	378	100
F	$\text{P}(\text{OEt})_3$	811	4	391	100
G	$\text{P}(\text{O}-\underline{n}\text{-Bu})_3$	812	4	390	100
H	$\text{P}(\text{OMe})_3$	826.2	This work	398	100
I	$\text{POMe}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{O})$	870.0	This work	390.6	This work
J	$\text{P}(\text{OPh})_3$	875	4	415.5	97
K	$\text{POMe}(\text{OCH}_2\text{CHMeO})^a$	890.4	This work	388.4	This work
L	$\text{P}(\text{OCH}_2)_3\text{CR}^b$	899.2	This work	393	98
M	$\text{P}(\text{OCH}_2\text{CF}_3)_3$	910.0	This work	415.0	This work
N	$\text{P}(\text{O})(\text{OCH}_2)_2\text{CMe}$	928.8	This work	390.6	This work
O	$\text{PCl}_3$	911.1	This work	426	99
P	$\text{PF}_3$	1190.6	This work	485	98

<sup>a</sup>The methyl substituent was on the ring carbon only when  $^1\text{JPH}$  was measured.

<sup>b</sup>R is methyl for  $^1\text{JPH}$  and n-butyl for  $^1\text{JWP}$ .

Figure 9. Plot of  $^1\text{JPH}$  obtained from the protonation of trivalent phosphorus compounds versus  $^1\text{JWP}$  obtained from  $\text{W}(\text{CO})_5\text{L}$  complexes



points led to the equation  ${}^1J_{WP} = 0.34({}^1J_{HP}) + 95.2$ , with a correlation coefficient of 0.97. Thus, the extended linearity of this plot reinforces the concept that both couplings are dominated by regular s character changes in the sigma bond and in the effective nuclear charge on the nuclei. Since the bond between phosphorus and a proton can have only sigma bond character, the linear relationship between  ${}^1J_{PH}$  and  ${}^1J_{WP}$  suggests strongly that the latter coupling must be largely dependent on sigma bond character. Thus, the rise in  ${}^1J_{WP}$  with increased electronegativity of substituents attached to phosphorus, ascribed to W-P pi bonding (100) is undoubtedly incorrect.

Previously it was determined (98) from a series of  $LW(CO)_5$  complexes wherein  $L = P(XY)_3CR$  ( $XY = CH_2O, SCH_2, NMeCH_2$  and  $OCH_2$ ) that a linear correlation existed between  ${}^1J_{WP}$  and the electronegativity of  $XY$ . Later, a slightly different correlation was found (99) when  $L = PF_3, PCl_3, PBr_3$  and  $PI_3$ . As part of this work, complexes were made where

L varied in constraint from  $\overline{MePOCH_2CH_2CH_2O}$  to  $\overline{MeOPOCH_2CHMeO}$

to  $P(\overset{O}{\diagup}OCH_2)_2CMe$  and measurement of  ${}^1J_{WP}$  from the satellite lines in the  ${}^{31}P$  spectrum arising from  ${}^{183}W$  (14.3% abundant) gave values of 390.6 Hz, 388.4 Hz and 390.6 Hz, respectively. Comparison of these values with those where  $L = P(OMe)_3$  (398 Hz) (100) and  $P(OCH_2)_3CC_5H_{11}$  (393 Hz) (98) showed no

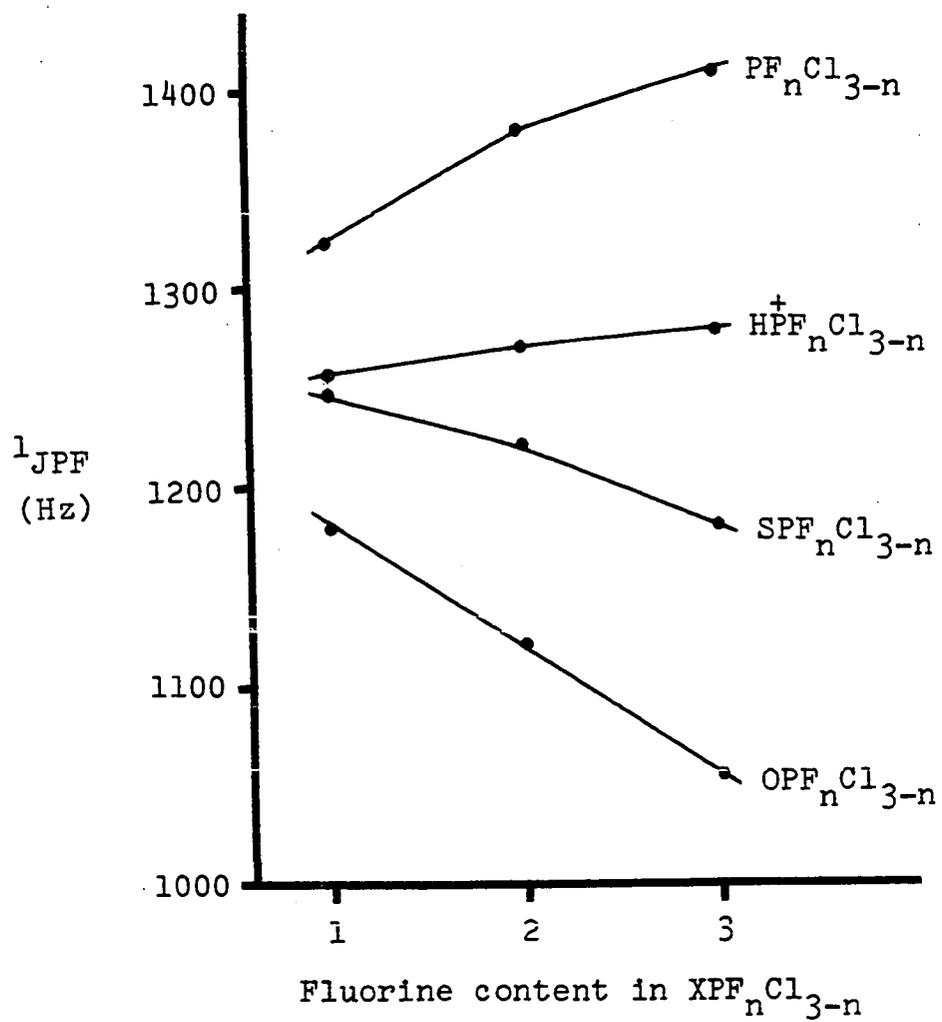
regular variation with constraint as found in  $^1\text{JPH}$  for protonated phosphites. The reason for this is presently obscure. However, when the points for these phosphites are included among the variety of other ligands in Figure 9, their anomalous behavior does not seriously influence the linear relationship.

The upfield shift of the  $^{31}\text{P}$  resonance of each phosphorus trihalide upon protonation is consistent with the upfield shift behavior for protonated phosphites. The furthest downfield  $^{31}\text{P}$  shifts occur for  $\text{HPFCl}_2^+$  (-92.0 ppm) and  $\text{HPCl}_3^+$  (-86.9 ppm) and then progress upfield with increased fluorine content in  $\text{HPF}_n\text{Cl}_{3-n}^+$  ( $n = 1$  to 3) and with increased bromine content in  $\text{HPCl}_{3-n}\text{Br}_n^+$  ( $n = 0$  to 3). While it might be expected that an increase in the number of fluorine substituents for  $\text{HPF}_n\text{Cl}_{3-n}^+$  ( $n = 1$  to 3) should deshield the  $^{31}\text{P}$  nucleus by virtue of increased electronegativity, fluorine is also able to participate in p $\rightarrow$ d pi bonding with phosphorus more readily than chlorine. Thus, increased pi bonding afforded by successive fluorine substitution actually increases phosphorus shielding to produce an upfield shift as has been noted for  $\text{PF}_n\text{Cl}_{3-n}$  ( $n = 1$  to 3) (101). The upfield trend from  $\text{HPCl}_3^+$  (-86.9 ppm) to  $\text{HBr}_3^+$  (+3.0 ppm) is tentatively explained here in terms of the increased shielding expected from the decreased electronegativity of Br compared to Cl. Previously, this argument (101) has only been applied

when comparing the upfield shift of  $\text{PI}_3$  (-178 ppm) to that of  $\text{PCl}_3$  (-219.4 ppm) and  $\text{PBr}_3$  (-227.7 ppm). It is to be noted, however, that the  $^{31}\text{P}$  shift of  $\text{PBr}_3$  is actually downfield from that of  $\text{PCl}_3$ . An upfield trend on bromine substitution is again found (102) in the pentavalent series:  $\text{PCl}_4^+$  (-87.3 ppm),  $\text{PCl}_3\text{Br}^+$  (-50.1 ppm),  $\text{PCl}_2\text{Br}_2^+$  (-9.7 ppm),  $\text{PClBr}_3^+$  (+34.6 ppm) and  $\text{PBr}_4^+$  (+81.0 ppm).

Signs of P-F coupling have been determined to be negative for a number of  $\text{P}^{\text{III}}$  and  $\text{P}^{\text{IV}}$  systems (103) and since all P-F couplings are large, all are believed to be negative. It is probable then that the signs of P-F coupling for the protonated phosphorus trihalides listed in Table 9 are also negative. Using the  $^1\text{JPF}$  values found in Table 9 and those reported for  $\text{XPF}_n\text{Cl}_{3-n}$  ( $n = 1$  to  $3$ ) where  $\text{X} = \text{O}$  (92) and  $\text{S}$  (104,105), a plot can be constructed (Figure 10) of  $^1\text{JPF}$  with fluorine content in  $\text{XPF}_n\text{Cl}_{3-n}$ . It is apparent that P-F couplings are displaced in a positive direction from their trivalent precursors upon coordination of a fourth group. This can be explained by the increase in s character in the P-F bond as hybridization at phosphorus changes from approximately  $\text{p}^3$  to  $\text{sp}^3$ . Increase in the s character in a bond between coupled nuclei is predicted by the Pople and Santry model (60) for spin-spin interactions to result in a more positive coupling constant and this has been found to be true for C-H, C-F and P-C couplings (60). The slight increase

Figure 10. Plot of  $^1\text{JPF}$  found in  $\text{XPF}_n\text{Cl}_{3-n}$  ( $n = 1$  to  $3$   
and  $X = \text{lone pair, H}^+, \text{O}$  or  $\text{S}$ ) versus  
fluorine content



in  $^1\text{JPF}$  in the negative direction for the protonated series as fluorine content increases is consistent with a decreasing amount of s character in the P-F bond resulting from Bent's rule (63). The smaller range of P-F coupling (14.4 Hz) compared to the trivalent series (84 Hz) possibly indicates that the geometry around the former species is relatively constant. An explanation for the decrease in  $^1\text{JPF}$  as fluorine content increases for the oxide and sulfide series remains obscure, however.

Although  $\text{HFSO}_3$  is a very strong acid ( $\text{H}_0 = 15.07$  (83)), it is incapable of protonating  $\text{PF}_3$  formed from the fluorination of phosphites. Thus our nmr parameters at  $-50^\circ$  of  $\text{PF}_3$  ( $\delta^{31}\text{P} = 104.0$  ppm,  $^1\text{JPF} = 1402.7$  Hz) obtained by this reaction agree very well with those of Olah and McFarland (8) and were checked in this work by independently synthesizing  $\text{PF}_3$  (51) and observing its spectrum in  $\text{HFSO}_3$  ( $\delta^{31}\text{P} = -104.3$  ppm,  $^1\text{JPF} = 1402.7$  Hz). These parameters in nonacidic media are  $\delta^{31}\text{P} = -97$  ppm and  $^1\text{JPF} = 1410$  Hz (92). Furthermore, the  $^{31}\text{P}$  nmr spectrum of  $\text{PF}_2\text{Cl}$  in  $\text{HFSO}_3$  ( $\delta^{31}\text{P} = -176.1$  ppm,  $^1\text{JPF} = 1376.1$  Hz) indicated no protonation as revealed by the similar values obtained in nonacidic media ( $\delta^{31}\text{P} = -176$ ,  $^1\text{JPF} = 1380$  Hz (93)), while  $\text{PCl}_3$  would not dissolve in  $\text{HFSO}_3$  even after vigorous shaking, a procedure that produced immediate solubility in  $\text{HFSO}_3 \cdot \text{SbF}_5$ . Olah and McFarland reported a doublet (987 Hz) in the  $^{19}\text{F}$  spectrum of  $\text{PF}_3$  in  $\text{HFSO}_3$  at room

temperature but because  $^1J_{PF}$  in both  $PF_3$  and  $HPF_3^+$  exceeds 1250 Hz, it is highly unlikely that this value is that for  $HPF_3^+$ . Moreover, a sign reversal allowing an intermediate coupling value at the higher temperature (where proton exchange is more likely) is not probable since all PF coupling constants are believed to be negative (103). These authors also observed no protonation of  $PF_3$  in the stronger acid  $HFSO_3 \cdot SbF_5$  ( $H_o = 19.5$  (est.) (83)) at room temperature but only an exchanging system involving  $OPF_3$ . In contrast we found that  $PF_3$  was protonated in  $HFSO_3 \cdot SbF_5 \cdot SO_2$  even though the use of  $SO_2$  as a diluent is reported to lower the acidity of Magic Acid slightly (106). In the present work temperatures below  $-50^\circ C$  were employed which may have assisted nmr observation of protonation by slowing proton exchange. In the previous report (8) the operating temperature was not stated. That a low temperature is critical for successful protonation is supported by the observation of extensive peak broadening at  $-50^\circ$ .

From the doublet of quartets expected for  $HPF_3^+$  (Figure 6), it is known that solvolysis of P-F bonds did not occur. However, the fluorination of phosphites probably involves a solvolyzed intermediate possessing the  $POSO_2F$  moiety and the possibility of solvolyzed P-Cl and P-Br bonds among the other trihalides had to be considered. Solvolysis of P-Cl bonds in the  $PF_{3-n}Cl_n$  series yielding  $PF_{3-n}(OSO_2F)_n$  systems is ruled

out, however, because the  $\text{PCl}_3\text{-PCl}_2\text{Br-PCl}_2\text{Br-PBr}_3$  mixture would be expected to provide only one rather than four doublets for protonated species (Figure 7). Thus, owing to the greater lability of bromine only  $\text{HP}(\text{OSO}_2\text{F})_3^+$  would be formed in this mixture as well as with the pure  $\text{PCl}_3$  sample. Detection of the solvolyzed species via the three-bond POSF coupling is not necessarily feasible since it is apparently not observed in the  $^{19}\text{F}$  nmr spectra of  $\text{OPF}_n(\text{OSO}_2\text{F})_{3-n}$  where  $n = 0$  to 2 (107) or in the  $^{31}\text{P}$  nmr spectrum of  $\text{SPF}_2(\text{OSO}_2\text{F})$  (108). It would be somewhat surprising, however, if this coupling were also fortuitously near zero in the trivalent analogues. Solvolysis of only the more weakly bound bromines is not as easily dismissed although the following argument strongly militates against such a process. It is reasonable to suppose that the  $\text{OSO}_2\text{F}$  group in  $\text{P}(\text{OSO}_2\text{F})_3$  is more electronegative than Br in  $\text{PBr}_3$ , since the  $\text{P=O}$  stretching frequency in  $\text{OP}(\text{OSO}_2\text{F})_3$  (107) (which increases from 1261 in  $\text{OPBr}_3$  to 1290 in  $\text{OPCl}_3$  to 1415  $\text{cm}^{-1}$  in  $\text{OPF}_3$  (109,110)) is close to that of  $\text{OPF}_3$ . The plot of Figure 8 would then be altered in an unexpected way in that the  $\text{HPCl}_{3-n}(\text{OSO}_2\text{F})_n^+$  ( $n = 1$  to 3) series would lie on a negative slope which would not intersect the  $\text{HPCl}_3^+$  point.

Further supporting the lack of solvolysis in these protonation experiments is the observation that the  $^{31}\text{P}$  spectra of  $\text{HPCl}_3^+$  and  $\text{HPBr}_3^+$  change markedly above  $-50^\circ$ . In

one experiment a sample of  $\text{PCl}_3$  in the acid solution prepared at  $-78^\circ$  was held at  $-40^\circ$  in the nmr probe for 20 minutes. The probe temperature was then lowered to  $-70^\circ$  and the spectrum revealed peaks corresponding to equal amounts of  $\text{HPCl}_3^+$  and  $\text{HPFCl}_2^+$  and a smaller amount of  $\text{HPF}_3^+$ , but no  $\text{HPF}_2\text{Cl}^+$  was evident. These observations are consistent with an increase in the fluorination rate as successive replacement of Cl occurs (50). Thus, while  $\text{HPFCl}_2^+$  can be observed, the amount of  $\text{HPF}_2\text{Cl}$  is too small to be seen since fluorination to  $\text{HPF}_3^+$  takes place immediately. In addition to the above peaks, a strong singlet at  $-88.7$  ppm has tentatively been assigned to  $\text{PCl}_4^+$  (the reported  $\delta^{31}\text{P} = -87.3$  ppm (102)). A repeat of the above temperature cycle on the same sample gave a spectrum showing only  $\text{PCl}_4^+$  and  $\text{HPF}_3^+$  in about the same ratio as the previous spectrum. A sample of  $\text{PBr}_3$  was noted to undergo a similar reaction in that a peak was observed even at  $-70^\circ$  at  $+80.5$  ppm which has been tentatively assigned to  $\text{PBr}_4^+$  ( $\delta^{31}\text{P}$  of  $\text{PBr}_4^+$  is  $+81.0$  ppm (102)). While no peaks were present which could be assigned to  $\text{HPFBr}_2^+$ ,  $\text{HPF}_2\text{Br}^+$  or  $\text{HPF}_3^+$  species, there was a resonance which appeared to be an AB quartet (JAB =  $489.8$  Hz, inner peak separation of  $3569.8$  Hz, and centered at  $-103.9$  ppm). The exact nature of the species responsible for this resonance is not clear but it may well involve a P-P bond.

In Tables 2, 6, 8, 9 and 11 a quantity has been listed under  $\Delta$ , defined as the chemical shift change from the

trivalent phosphorus compound to the protonated species. This quantity is positive for phosphites and phosphorus trihalides (upfield shift upon protonation) and negative for phosphines (downfield shift upon protonation) with only one exception (Compound 26, Table 11). McFarlane and White (2) have suggested a monotonic relationship (correlation coefficient of 0.93) between  $^1\text{JPH}$  and  $\Delta$  for nine protonated phosphorus compounds with different substituent electronegativities which are indicated in Figure 11 as solid triangles. Their erroneous value for  $\overline{\text{PhOPOCH}_2\text{CH}_2\text{O}}$  is not included. They suggested that since  $\Delta$  increases with  $^1\text{JPH}$ ,  $\Delta$  could also be related to the basicity of the trivalent precursor. However, when points from this work and the literature are included (Figures 11 and 12) it can be seen that the value of the McFarlane-White relationship is highly dubious. The only apparent linear relationships occur for the two negative slopes for the phosphorus trihalides (Figure 12).

#### Fluorination of phosphites

Since the primary intent of dissolving phosphites in  $\text{HFSO}_3$  was to obtain  $^1\text{JPH}$  values, the present section dealing with phosphite fluorination is not necessarily exhaustive in detail. While the action of  $\text{HFSO}_3$  as a fluorinating agent for converting inorganic salts, oxides and hydroxy compounds into fluorides has been studied (91), of particular interest

Table 11. Tabulation of  $^1\text{JPH}$  and  $\Delta$ 

Compound	$^1\text{JPH}^a$	$\Delta^b$	Reference
22 $\text{PH}_3$	548	-137.0	3
23 $\text{PMe}_3$	497	-59.0	3
24 $\text{PEt}_3$	471	-41.7	3
25 $\text{P}(\underline{\text{i}}\text{-Pr})_3$	448	-25.1	3
26 $\text{P}(\underline{\text{t}}\text{-Bu})_3$	436	+3.6	3
27 $\text{P}(\underline{\text{n}}\text{-Bu})_3$	457	-44	2
28 $\text{P}(\underline{\text{n}}\text{-Oct})_3$	465	-45.5	3
29 $\text{P}(\underline{\text{c}}\text{-Hex})_3$	460	-26	2
30 $\text{PPh}_2$	519	-19.5	3
31 $\text{PMe}_2\text{Ph}$	500	-45	2
32 $\text{PEt}_2\text{Ph}$	490	-34.2	1
33 $\text{P}(\underline{\text{n}}\text{-Bu})_2\text{Ph}$	490	-38.4	1
34 $\text{P}(\underline{\text{i}}\text{-Pr})_2\text{Ph}$	485	-22.0	1
35 $\text{P}(\underline{\text{c}}\text{-Hex})_2\text{Ph}$	485	-18.3	1
36 $\text{PMePh}_2$	525	-25.8	1
37 $\text{PEtPh}_2$	515	-20.3	1
38 $\text{P}(\underline{\text{n}}\text{-Bu})\text{Ph}_2$	520	-19.2	1
39 $\text{P}(\underline{\text{i}}\text{-Pr})\text{Ph}_2$	510	-13.8	1
40 $\text{P}(\underline{\text{c}}\text{-Hex})\text{Ph}_2$	510	-14.9	1
41 $\text{P}(\text{OMe})\text{Ph}_2$	553	+59	2
42 $\text{P}(\text{OMe})_2\text{Ph}$	666	+104	2
43 $\text{P}(\text{OEt})_3$	806	+121	2
44 $\text{P}(\text{O-}\underline{\text{i}}\text{-Pr})_3$	795	+122	2
45 $\text{P}(\text{O-}\underline{\text{n}}\text{-Bu})_3$	812	+117.4	4
46 $\text{P}(\text{O-}\underline{\text{neo}}\text{-Pent})_3$	834	+114.1	5
47 $\text{P}(\text{OPh})_3$	870	+118	2

<sup>a</sup>In Hz.<sup>b</sup>In ppm.

Figure 11. Plot of  $^1\text{JPH}$  versus  $\Delta$  for phosphites  
and phosphines

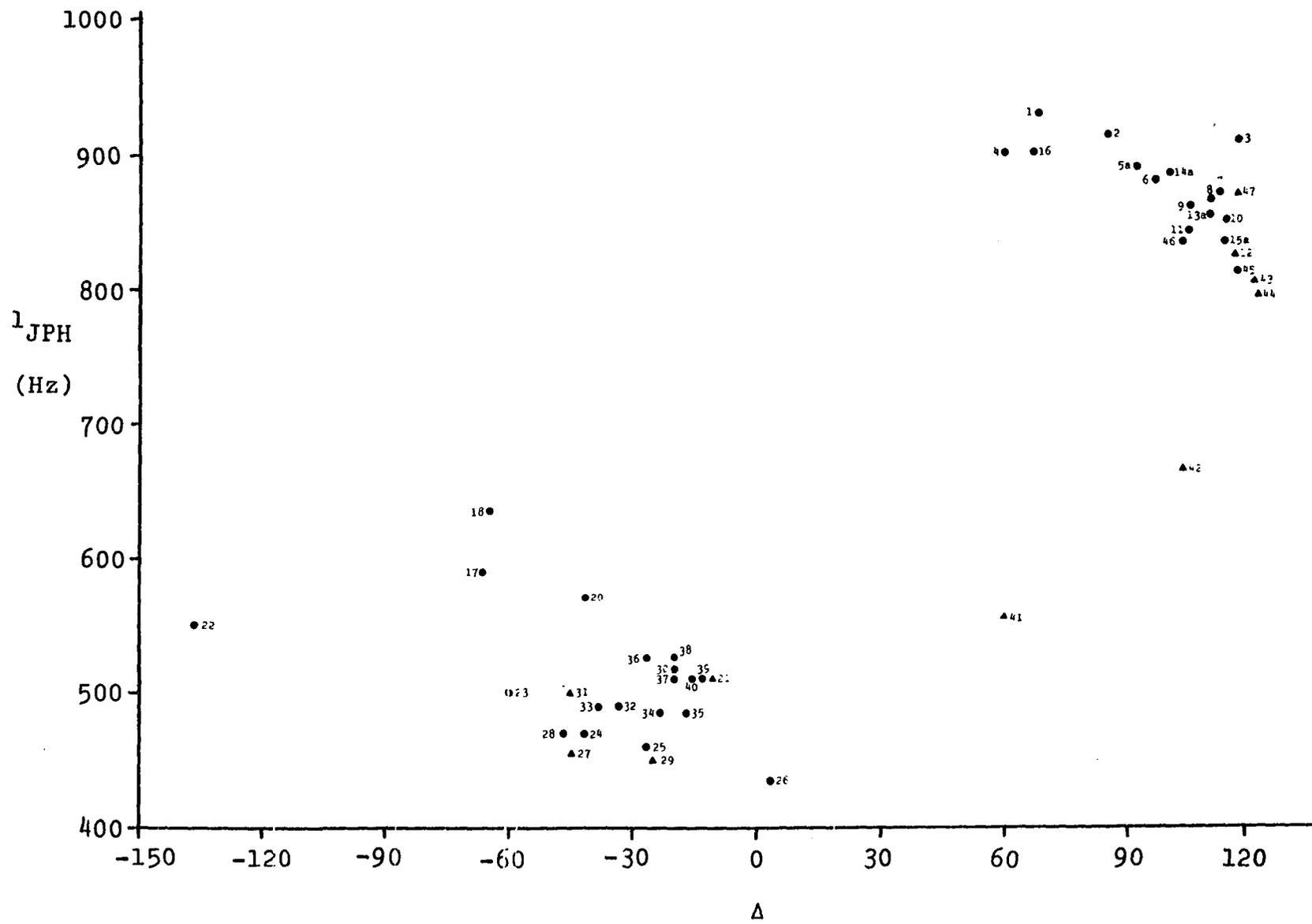
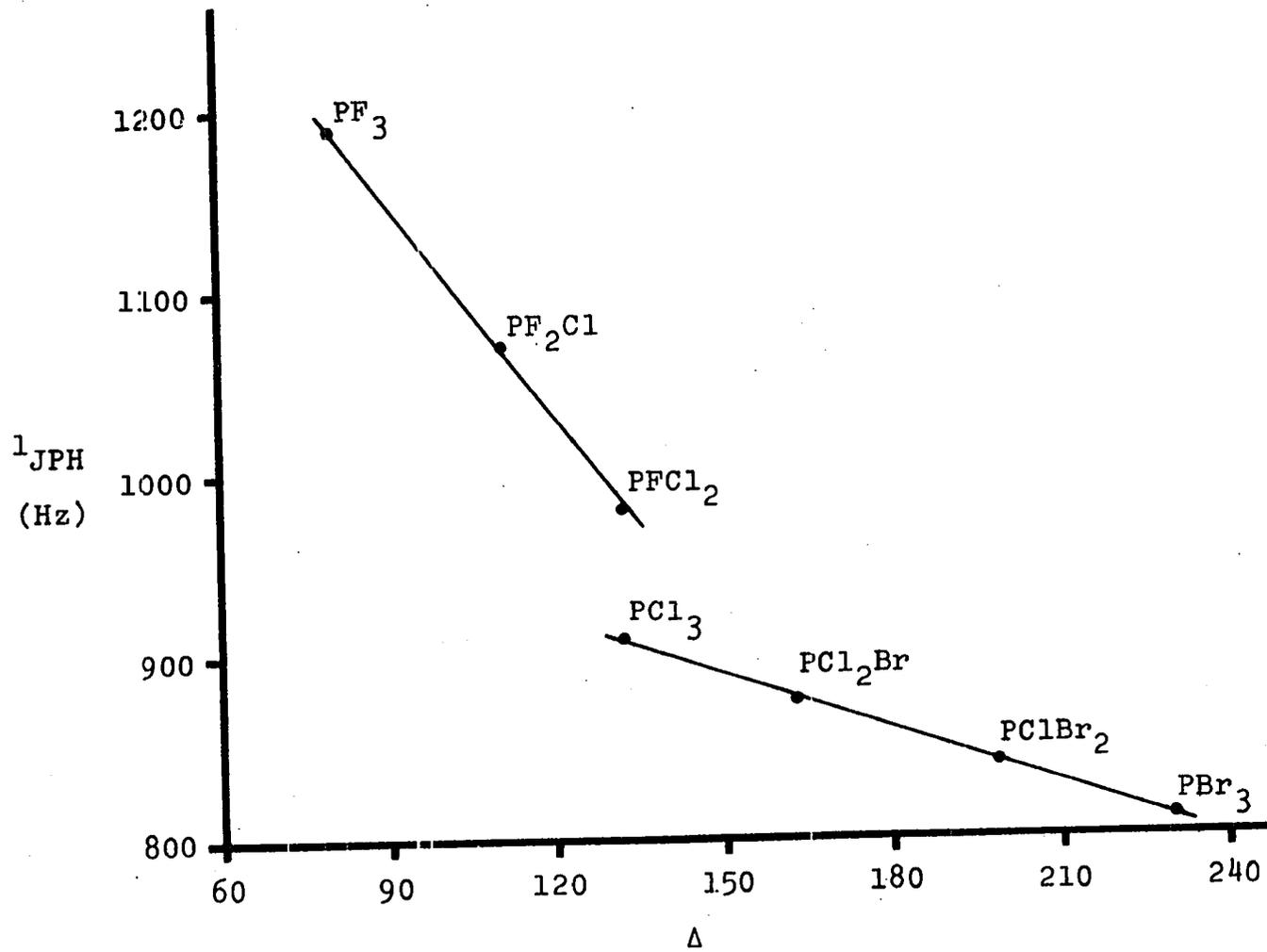


Figure 12. Plot of  $^1J_{PH}$  versus  $\Delta$  for phosphorus trihalides



here is the addition of ice cold fluorosulfuric acid to  $P_4O_{10}$  which results in an 80% yield of  $OPF_3$  (111). In a study of the protonation of phosphonic and phosphinic acids in  $HFSO_3$ , the formation of  $PF_3$  and  $OPF_3$  followed the observation of a variety of intermediate fluorophosphorus compounds (8).

For a number of compounds protonated in this work,  $PF_3$  was noted as a product when solutions were warmed to ca.  $-20^\circ$ . The parent phosphites which gave this product include 2, 3, 4, 5, 6 and 16. The thiophosphite (112),  $P(SCH_2)_3CMe$ , affords a complicated  $^{31}P$  pattern in addition to peaks for  $PF_3$ . The phosphites 1 and 14 underwent fluorination at only two and one P-O bond, respectively, and did not give  $PF_3$  while the two phosphites having four methyl substituents on the ring, 13 and 15, seemed to be quite stable.

A spectrum of a  $HFSO_3$  solution of  $P(OCH_2)_3CMe$ , which had been kept in a Dry Ice chest for two days, showed the presence of protonated phosphite, the quartet due to  $PF_3$  ( $^1J_{PF} = 1402.7$  Hz,  $\delta^{31}P = -104.0$  ppm) and a quartet due to an appreciable quantity of  $OPF_3$  ( $^1J_{PF} = 1057.6$  Hz,  $\delta^{31}P = +37.7$  ppm; lit.  $^1J_{PF} = 1060$  Hz,  $\delta^{31}P = +36.6$  ppm (8)).

Although no other resonances were observed, it is possible that a peak for protonated phosphonic acid ( $\delta^{31}P = -19.0$  ppm (4)) could be masked by the upfield arm of the phosphite doublet at  $\delta^{31}P = -19.7$  ppm. On the other hand, all other acid solutions of protonated phosphites which also

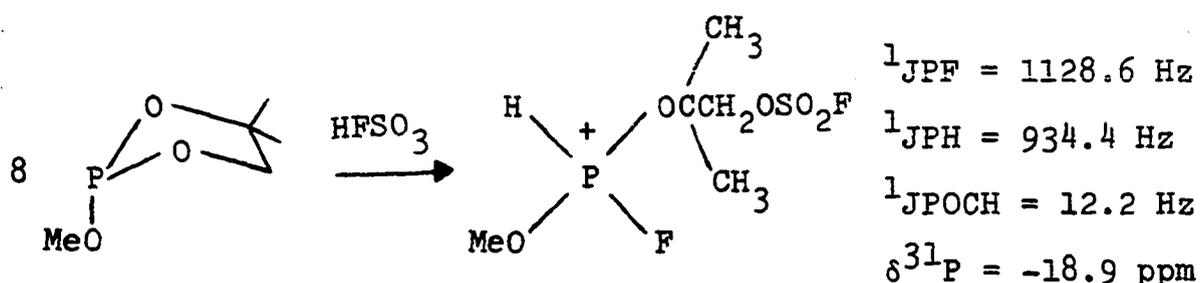
contained  $\text{PF}_3$  revealed no protonated phosphonic acid. These observations contrast the report (4) that warming a  $\text{HFSO}_3$  solution first resulted in the formation of protonated phosphonic acid followed by  $\text{OPF}_3$  after 8 days.

Engelbrecht (91) has proposed a general mechanism for fluorination which was adapted by others (8) for the reaction of hydroxy phosphoryl compounds in  $\text{HFSO}_3$ . Hudson and Roberts (5) have investigated the mechanism of dealkylation of tri-alkyl phosphites by  $\text{HCl}$  and found that their results were consistent with rapid reversible protonation followed by slow nucleophilic displacement of an alkyl group by  $\text{HCl}_2^-$  or  $\text{HCl}$ . Thus, it is probable that the fluorination of phosphites by  $\text{HFSO}_3$  also involves initial protonation followed by nucleophilic attack of a second acid molecule at the alkoxy oxygen. The intermediates in such a solvolysis reaction should be  $\text{P}(\text{OR})_n(\text{OSO}_2\text{F})_{3-n}$  ( $n = 0$  to  $2$ ). That such intermediates could easily lose  $\text{SO}_3$  to form a P-F bond is supported by the observation (107) that  $\text{OP}(\text{OSO}_2\text{F})_3$  decomposes at  $100^\circ$  to yield  $\text{SO}_3$  and  $\text{OPF}_n(\text{OSO}_2\text{F})_{3-n}$  ( $n = 1$  to  $3$ ). Since intermediate fluorinated species were observed only in special cases (see below), continued solvolysis after formation of one P-F bond must also be enhanced by fluorine substitution (50). Finally, the oxidizing agent  $\text{SO}_3$  is responsible for the formation of  $\text{OPF}_3$  (8).

Generally, fluorination occurred only with the most constrained phosphites in the present work but substitution

of methyl groups on the carbon adjacent to the alkoxy oxygen in 13 and 15 rendered these phosphites quite resistant. A plausible explanation is that attack by  $\text{HFSO}_3$  is sterically hindered by the methyl groups. This hypothesis is further substantiated by the fluorination behavior of two other phosphites discussed below.

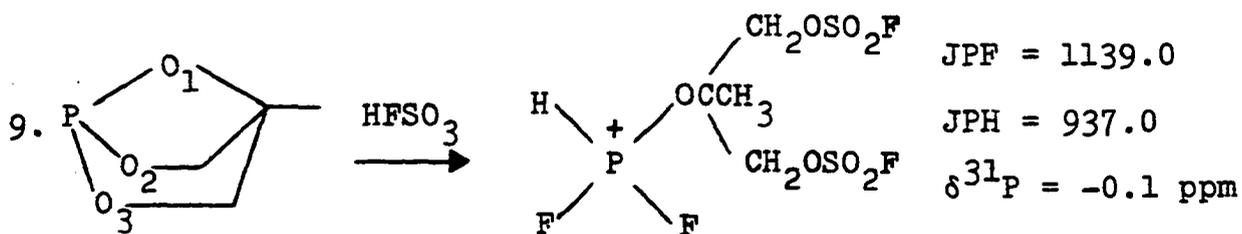
Consider first of all the following reaction which apparently occurs. At  $-20^\circ\text{C}$  the appearance of peaks in the



$^{31}\text{P}$  spectrum other than those for the protonated phosphite signalled the onset of fluorination. After stabilizing the solution at  $-60^\circ\text{C}$  a  $^{31}\text{P}$  spectrum revealed a doublet of doublets of quartets for a species which accounted for approximately 20% of the phosphorus. Overall the doublet of doublets were of equal intensity and the quartet members had a 1:3:3:1 intensity ratio. This, along with the nmr parameters, indicates that fluorination took place at the side of the ring which was not sterically protected. Attack at the other side would have resulted in a sextet pattern for each pair of doublets assuming similar  $^3J_{\text{POCH}}$  values for the

methyl and methylene protons. Since  $^1\text{JPH}$  and  $\delta^{31}\text{P}$  for  $\text{HP}^+(\text{OMe})_3$  are 826.2 Hz and -24.4 ppm, respectively, the corresponding values for the above species are reasonable considering the effect of the fluorine on increasing the magnitude of  $^1\text{JPH}$ . Furthermore, the  $^1\text{JPF}$  value of 1128.6 Hz lies almost midway between the  $^1\text{JPF}$  value of  $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{F}$  (980 Hz) (113) and  $(\text{CH}_3\text{O})_2\text{PF}$  (1210 Hz) (113) in the same way that this coupling in  $\text{HPF}_2^+\text{Cl}$  (1272.8 Hz) lies between that of  $\text{OPF}_3$  (1080 Hz) (92) and  $\text{PF}_3$  (1410 Hz) (92).

Whereas the monocyclic phosphite was monofluorinated, the constrained bicyclic phosphite shown is difluorinated:



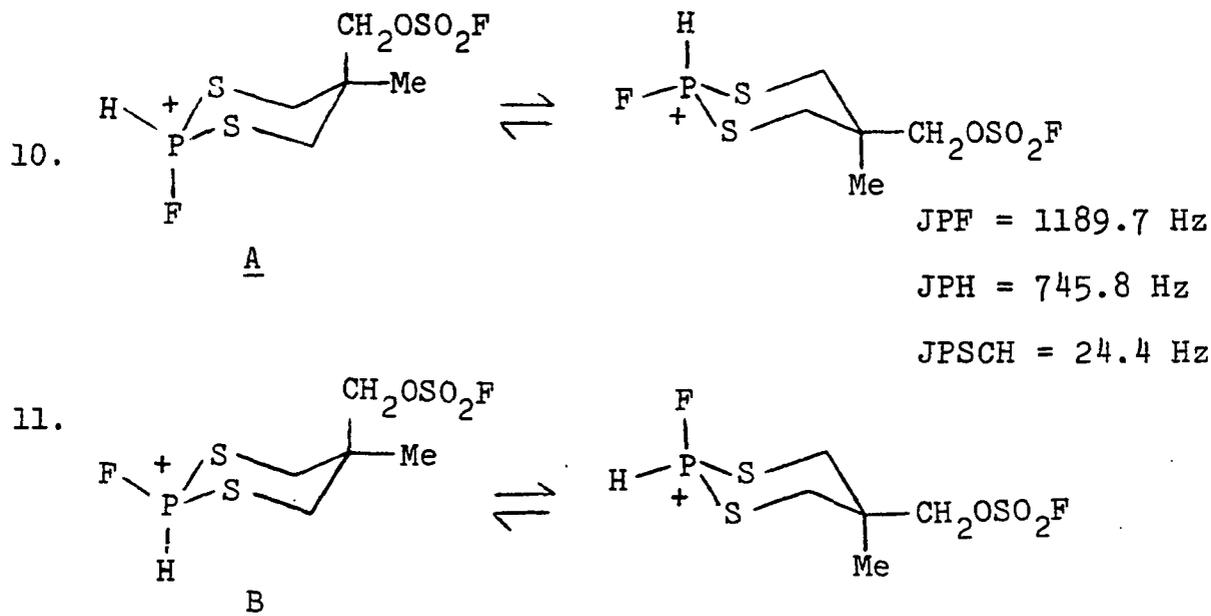
At  $-20^\circ\text{C}$  the bicyclic phosphite was about 95% difluorinated and the  $^{31}\text{P}$  spectrum showed a well-defined doublet of triplets whose large separations precluded POCH coupling. It is somewhat surprising that initial attack was either at  $\text{O}_2$  or  $\text{O}_3$  since relief of strain would be realized by attack at  $\text{O}_1$ .

Although the reason for this mode of attack is not entirely clear, perhaps the methyl tail sterically inhibits attack. After two fluorines have been substituted at

phosphorus, it is again reasonable to conjecture that  $\text{HPF}_3^+$  is not formed because the bulky tertiary carbon group prohibits attack by the fluorosulfate anion. While the chemical shift of the final species is possibly lower than expected, it is not entirely unreasonable since the chemical shift for  $\text{HPF}_3^+$  is only -15.8 ppm. The couplings, however, are puzzling. The  $^1\text{JPF}$  coupling, as assigned, lies between that of  $\text{CH}_3\text{OP}(\text{O})\text{F}_2$  (1008 Hz) (113) and  $\text{CH}_3\text{OPF}_2$  (1275 Hz) (26). However, the  $^1\text{JPH}$  value is only 2.6 Hz higher than the  $^1\text{JPH}$  value for the monosubstituted fluorine compound just discussed. The reason for this abnormally low value (assuming the assignments are correct) is not understood.

While the protonated form of  $\text{P}(\text{OCH}_2)_3\text{CCH}_3$  was easily detected by nmr techniques, this was not the case for the sulfur analogue,  $\text{P}(\text{SCH}_2)_3\text{CCH}_3$ . In several attempts this thiophosphite was slowly dissolved in  $\text{HFSO}_3$  at low temperatures but the bicyclic structure apparently did not survive. Besides the peaks corresponding to the formation of unprotonated  $\text{PF}_3$  (which always accumulated with time and warmer temperatures) and an unassigned broadened singlet at -181.5 ppm, there was a pattern of two complicated multiplets centered at -129.2 ppm and -132.0 ppm with the latter slightly greater in intensity. Each pattern was a doublet of doublets of 1:4:6:4:1 quintets with identical couplings and have tentatively been assigned to the two isomers A and B. Both

isomers are probably in rapid equilibrium with their flipped



conformers which could account for the identical coupling constants. It is not possible to assign chemical shifts to the isomers with the information available. The  $^1\text{JPF}$  coupling is again reasonable when compared to that of 1114 Hz in  $(\text{MeS})_2\text{PF}$  (114). The large size of the  $^3\text{JPSCH}$  value is surprising considering the small value of 2.1 Hz for the parent bicyclic thiophosphite (112). Unfortunately, no  $^3\text{JPSCH}$  values are known for monocyclic thiophosphites. However,  $^3\text{JPSCH}$  rises from 9.9 Hz in  $\text{P}(\text{SMe})_3$  to 15.6 Hz in  $\text{O}=\text{P}(\text{SMe})_3$  (115) and considering that this coupling is already 12.3 Hz in  $(\text{MeS})_2\text{PF}$  (114), protonation of the thiofluorophosphite in Equations 10 and 11 may dramatically increase the coupling. It is not known if the  $^1\text{JPH}$  coupling is reasonable since protonation of the thiophosphorofluorodites have not been reported.

## BORON AND OXYGEN AS LEWIS ACIDS

## Introduction

The synthesis of borane adducts of phosphites allows two convenient measurements to be made of the basicity of the phosphorus lone pair. The first is the infrared measurement of the B-H stretching frequency and the second is the magnitude of the B-P spin-spin coupling constant.

Watanabe and Nagasawa (116) have discussed a linear correlation between the weighted average of  $\nu_{\text{BH}}$  and  $^1J^{11}\text{BH}$  for an extensive series of boron compounds. Others (117) have found that this correlation is even better when limited only to borane adducts of oxygen, sulfur, nitrogen and phosphorus. That such a correlation should exist has been discussed in terms of s character in the boron-hydrogen bond (116,117). The isovalent hybridization rule of Bent (63) predicts that the B-H bond strength should be proportional to the s character of boron in that bond. It is reasonable that this should be true for the B-H stretch since the C-H stretching force constants are also dependent on the hybridization of the carbon orbitals (118). Depending on the donation of electron density from a Lewis base to  $\text{BH}_3$ , the hybridization of the boron valence orbitals will range from  $sp^2$  to  $sp^3$ .

The magnitude of  $^1J_{\text{PB}}^{11}$  can also be a measure of basicity, and Cowley and Damasco (119) have found that

increased coordinate bond strength leads to an increase in  ${}^1\text{JP}^{11}\text{B}$  (18 to 97.2 Hz) for fifteen borane adducts possessing a wide range of phosphorus substituent electronegativities. Similarly, an empirical correlation (120) between  ${}^1\text{JP}^{11}\text{B}$  and dative bond strength is evident for the borane adducts of each of the phosphine series  $\text{F}_{3-n}\text{H}_n\text{PBH}_3$ ,  $\text{Me}_{3-n}\text{H}_n\text{PBH}_3$  and  $\text{F}_2\text{XPBH}_3$  ( $x = \text{F}, \text{Cl}, \text{Br}$ ). Correlations were absent if the phosphine ligands belonged to different series (120). Although the determination of the sign of  ${}^1\text{JP}^{11}\text{B}$  has not been made, arguments have been presented which indicate that it is positive (119,120).

The strength of hydrogen bond formation is also indicative of basicity. In 1937 Badger and Bauer (121) proposed a linear relationship between the strength of the hydrogen bond and the shift in the infrared frequency of an OH functional group upon complexation to a base. This shift,  $\Delta\nu(\text{OH})$ , usually reported in  $\text{cm}^{-1}$ , is defined as the difference in position between the "free" OH stretching band and the band due to the hydrogen bonded species,  $\text{OH}---\text{Base}$ , which is displaced to a lower frequency.

In a study on the hydrogen bonding of phenol and eighteen organophosphorus compounds, Aksnes and Gramstad (122) were able to show linear correlations of the logarithms of association constants at  $20^\circ$  and  $50^\circ$  with  $\Delta\nu(\text{OH})$ . From this it was possible to obtain linear relationships of  $\Delta\nu(\text{OH})$  with the free energy, enthalpy and entropy of this equilibrium reaction.

Based upon available enthalpy data for hydrogen bonding of phenol to bases and phenol shifts for thirty-three nitrogen and oxygen donors, an empirical relation,  $-\Delta H(\text{kcal/mole}) = 0.016\Delta\nu(\text{OH}) + 0.63$ , was found for these parameters (123). Significantly, fourteen of eighteen organophosphates studied by Aksnes and Gramstad (122) were found to obey this equation within the error limit of  $\pm 0.5$  kcal. In other papers (124, 125) Drago and Epley were able to improve this relationship obtaining the equation  $-\Delta H = 0.0103\Delta\nu(\text{OH}) + 3.08$  when more accurate thermodynamic data were obtained by calorimetry methods instead of spectrophotometric studies. This equation has subsequently been used (126) to obtain enthalpy values for other nitrogen and oxygen donors by measuring only  $\Delta\nu(\text{OH})$ . However, with donor systems having different functional groups care must be taken to sufficiently prove the correlation of enthalpy with  $\Delta\nu(\text{OH})$  before it can be used on a predictive basis. For instance,  $\Delta\nu(\text{OH})$  values obtained for sulfur donors cannot be used in the above equation to accurately predict enthalpies of adduct formation (127).

Hydrogen bonding studies have not only included a large number of bases but have also utilized a wide variety of acids other than phenol. These have included acids stronger than phenol (1,1,1,3,3,3-hexafluoro-2-propanol (128)), weaker than phenol (t-butyl alcohol (129)), a variety of

substituted phenols (*p*- $\text{t-C}_4\text{H}_9\text{C}_6\text{H}_4\text{OH}$ , *p*- $\text{ClC}_6\text{H}_4\text{OH}$  and *m*- $\text{CF}_3\text{C}_6\text{H}_4\text{OH}$  (125)) and the alcohol,  $\text{CF}_3\text{CH}_2\text{OH}$  (130). Linear correlations of  $\Delta\nu(\text{OH})$  with enthalpies of formation have been found for all of these acid-base interactions.

It was deemed desirable to rank many of the phosphites subjected to protonation in the present work with respect to basicity order. To this end borane adducts have been synthesized for measurement of their  $^1\text{JP}^{11}\text{B}$  and  $\nu(\text{BH})$  values and hydrogen bonding studies of phenol with selected phosphates and phosphites have been carried out. The procedure for obtaining  $\Delta\nu(\text{OH})$  values, published earlier by us (24) is amended so that lower concentrations of phenol are employed.

## Experimental

### Techniques and preparations

Materials All materials used were reagent grade.

The 1 molar solution of borane in tetrahydrofuran was purchased from the Aldrich Chemical Company. Nitrogen dioxide was obtained from the Matheson Company. Trimethyl phosphate, 58, was purchased from Pfaltz and Bauer, Inc., and distilled before use. Phenol, used in the hydrogen bonding experiments, was dried by azeotropic distillation with  $\text{CCl}_4$  and the residual solvent was removed under vacuum. The 87.8 atom per cent  $^{18}\text{O}$ -enriched water used in the phosphoryl stretching frequency study was obtained from Bio-Rad Laboratories.

Spectroscopy and procedures      Proton nmr spectra for checking the purity of compounds were obtained with the Hitachi-Perkin-Elmer R20b spectrometer or with a Varian Associates A-60 spectrometer. An Atlas CH-4 mass spectrometer provided mass spectra.

The  $^{31}\text{P}$  nmr data for the borane adducts were collected on the Bruker HX-90 spectrometer operating at 36.44 MHz in the Fourier mode. An approximate 1:1 mixture of  $\text{CD}_3\text{CN}$ , which provided the deuterium lock signal, and  $\text{CH}_3\text{CN}$  was the solvent for the data reported in Table 12. The P-B coupling constants were obtained from white noise decoupled spectra. A Beckman IR-4250 provided the infrared spectra for the B-H stretching frequency region of the borane adducts. A cell path length of 0.2 mm was normally used for the adducts which were readily soluble in  $\text{CCl}_4$  while a 3.2 mm path length was used for the last five adducts in Table 12. A scale expansion of four times the normal width was used and the band at  $2851.5\text{ cm}^{-1}$  of polystyrene provided calibration.

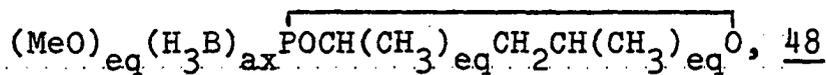
In the phenol shift experiments a 0.015 molar stock solution of phenol was prepared to which appropriate amounts of base were added. The concentrations of base (phosphite and phosphate) employed were 0.0012, 0.0060, 0.0150, 0.0400 and 0.1000 molar. In addition, a higher concentration of 0.5000 was used for phosphites. For both types of base the two lowest concentrations were made by appropriate dilution

of the 0.015 molar solution. Infrared hydrogen bonding shifts were obtained on a Beckman IR-4250 spectrometer. Because of the dilute phenol solutions it was necessary to use a cell path length of 3.2 mm between sodium chloride plates. Calibration was accomplished by the  $2851.5\text{ cm}^{-1}$  band of polystyrene. A scale expansion of twice the normal operating condition was used to obtain all data. A spectrum of the stock phenol solution revealed a flat baseline at wavelengths lower than the "free" OH peak located at  $3619.5\text{ cm}^{-1}$ , indicating that self-association of phenol would not compete with the base.

The  $^{13}\text{C}$  nmr data were obtained with the Bruker HX-90 spectrometer operating in the Fourier mode at 22.636 MHz. The solvent was  $\text{CD}_3\text{CN}$  and the nitrile carbon, located at 2650.0 Hz downfield from tetramethylsilane, was used as a reference although chemical shifts are reported relative to the carbon in TMS. The gated decoupling technique was used to determine  $^{13}\text{C}$ -H coupling while white noise decoupled spectra provided  $^{31}\text{P}$ - $^{13}\text{C}$  couplings.

The infrared spectra for determining phosphorus-chalcogen stretching frequencies (Table 14) were taken with the Beckman IR-12 spectrometer using the polystyrene calibration at  $1601.8\text{ cm}^{-1}$ . The Raman spectrum of  $^{16}\text{OP}(\text{OCH}_2)_3\text{CMe}$  was obtained on a solid sample contained in a capillary using a Jarrell-Ash 25-400 laser spectrometer operating with the  $5145\text{ \AA}$  line of argon.

Preparations Two methods were used to prepare borane adducts. In Method A (131) carbon dioxide was bubbled through a tetrahydrofuran mixture of sodium borohydride and the trialkylphosphite. However, an easier procedure (Method B) is to add slowly a stoichiometric amount of one molar borane solution in tetrahydrofuran to a THF solution of trialkylphosphite kept at room temperature. Method B has the advantage that the product can be distilled after removal of the THF or recrystallized directly from the THF solution, whereas Method A requires acid hydrolysis of borate salts. Most trialkyl phosphates were prepared by  $\text{NO}_2$  oxidation of the phosphite dissolved in  $\text{CCl}_4$  as described by Cox and Westheimer (132) and modified elsewhere (46).



This

compound while previously obtained (46) in a mixture with compound 50 (see below) was prepared isomerically pure. Method A was used with the modification that the reaction vessel was cooled in an ice bath at 0-5°C. After normal workup, distillation of the residue at 85-90°C and 0.1 mm of Hg gave an 81% yield of a colorless liquid. A  $^1\text{H}$  nmr (neat) showed a methyl doublet at 1.29 ppm ( $^3\text{JHCCH}_3 = 6.0$  Hz), a methylene multiplet at 1.85 ppm, a methoxy doublet at 3.59 ppm ( $^3\text{JPOCH} = 11.2$  Hz) and a methinyl multiplet at 4.54 ppm. A mass spectrum revealed a parent ion at 178 m/e corresponding to the molecular weight.

$\text{H}_3\text{BP}(\text{OCH}_3)_3$ , 49 This compound was prepared by Method A ( $b_8 = 62-63^\circ$ ; lit.  $b_{23} = 86^\circ$  (131)).

$(\text{MeO})_{\text{ax}}(\text{H}_3\text{B})_{\text{eq}}\overline{\text{POCH}(\text{Me})_{\text{eq}}\text{CH}_2\text{CH}(\text{Me})_{\text{eq}}\text{O}}$ , 50 This compound was prepared by Method A (m.p. =  $77-78^\circ$ ; lit. m.p. =  $76-77.5^\circ$  (64)).

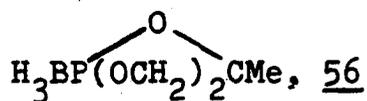
$(\text{MeO})(\text{H}_3\text{B})\overline{\text{POCH}_2\text{CH}_2\text{CH}_2\text{O}}$ , 51 This compound (46) was prepared by Method B ( $b_{1.4} = 91-95^\circ$ ).

$(\text{MeO})(\text{H}_3\text{B})\overline{\text{POCH}_2\text{CH}_2\text{O}}$ , 52 This compound (46) was prepared by Method B ( $b_{0.5} = 83-85^\circ$ ). The liquid solidifies upon cooling.

$\text{H}_3\text{BP}(\text{OCH}_2)_3$ , 53 This compound was prepared by Method A (m.p. =  $248-252^\circ$  (decomposition); lit. m.p. =  $247-251^\circ$  with decomposition (56)).

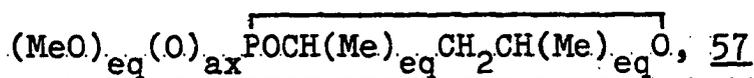
$\text{H}_3\text{BP}(\text{OCH}_2)_3\text{P}$ , 54 This compound (84) was prepared by Method A (m.p.  $235-238^\circ$  with decomposition).

$\text{H}_3\text{BP}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$ , 55 This compound was prepared by Method A (m.p. =  $132-134^\circ$ ). A  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ) showed a methylene doublet at 4.3 ppm ( $^3\text{JPOCH} = 4.5$  Hz) and an  $\text{A}_3\text{B}_2$  pattern at 1.1 ppm for the ethyl group.



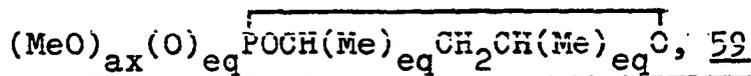
This viscous liquid adduct

was prepared by Method B. An attempted distillation at a temperature over 100° and at 1.2 mm of Hg resulted in decomposition and a fire. Fortunately, however, this compound is sufficiently pure without distillation since its <sup>1</sup>H nmr revealed only the expected methyl resonance at 1.69 ppm and a multiplet for the methylene protons at 4.0 ppm. A mass spectrum of this adduct run as a solid (no heat applied) revealed the parent ion at 148 m/e corresponding to the molecular weight.



This

phosphate was prepared by N<sub>2</sub>O<sub>4</sub> oxidation (43) (b<sub>0.4</sub> = 105°; lit. b<sub>0.2</sub> = 86° (43)).



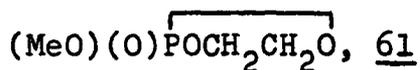
This

phosphate was prepared by NO<sub>2</sub> oxidation and was recrystallized from diethyl ether (43) (m.p. = 58-59°; lit. m.p. = 57-58° (43)).

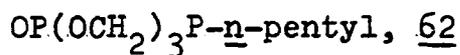


This phosphate was

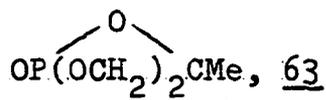
prepared by NO<sub>2</sub> oxidation (46) (b<sub>0.15</sub> = 106-107°; lit. b<sub>0.4</sub> = 115-118° (46)).



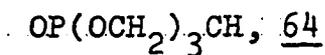
The synthesis of this phosphate by  $\text{NO}_2$  oxidation has been described (46) ( $b_1 = 99-100^\circ$ ; lit.  $b_{0.6} = 93-95^\circ$  (46)).



The synthesis of this phosphate by oxidation of the phosphite with hydrogen peroxide has been described (133) (m.p. =  $134-136^\circ$ ; lit. m.p. =  $134-137^\circ$  (133)).

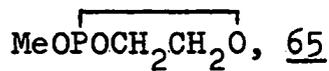


This phosphate was prepared by  $\text{NO}_2$  oxidation with the modification that the phosphite was dissolved in  $\text{CH}_2\text{Cl}_2$ . After the solvent and excess  $\text{NO}_2$  were removed under vacuum, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ , diethyl ether was added to the cloud point and the solution was cooled to  $-78^\circ$ . The yield of colorless material (m.p. =  $92-94^\circ$ ), based on 9.8 g of phosphite, was 9.9 g (90%). A  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ) showed a methyl singlet at 1.65 ppm and a methylene multiplet at 4.3 ppm. A mass spectrum showed a parent ion at 150 m/e corresponding to the molecular weight of the compound.

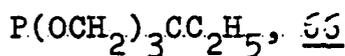


This phosphate was prepared by  $\text{NO}_2$  oxidation with the modification that the small amount of phosphite (less than 0.5 g) was dissolved in  $\text{CDCl}_3$ . After removal of the solvent the product was purified by dissolving

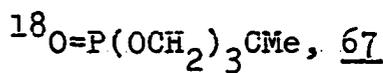
in  $\text{CH}_2\text{Cl}_2$ , adding ether to the cloud point and cooling to  $0^\circ$ . This compound was characterized only by  $^{31}\text{P}$  nmr.



The preparation of this phosphite has been previously described (46) ( $b_{40} = 56-57^\circ$ ; lit.  $b_{30} = 56-58^\circ$  (46)).



This compound was prepared according to a previous procedure (38).



A solution of 0.296 grams (2.00 mmole) of freshly sublimed  $\text{P}(\text{OCH}_2)_3\text{CMe}$  in 15 ml of dry  $\text{CH}_3\text{CN}$  was cooled under a nitrogen flush to  $0-5^\circ$ . To this was added 40  $\mu\text{l}$  (2.00 mmole) of  $\text{H}_2^{18}\text{O}$  (87.8% enrichment). Immediately after this, 3.2 ml of a  $\text{Br}_2\text{-CCl}_4$  solution containing 0.10 g of  $\text{Br}_2$  per ml (2.0 mmole of  $\text{Br}_2$  total) was slowly added over a period of 3 minutes. The red bromine color disappeared rapidly and left a slightly yellow solution. After solvent removal under vacuum, the residue was sublimed three times at  $150^\circ$  and less than 0.2 mm of Hg yielding 0.31 g (94%) of product. An  $^1\text{H}$  nmr spectrum showed a methylene doublet at 4.48 ppm ( $^3\text{JPOCH} = 6.3$  Hz) and a methyl singlet at 0.84 ppm. A mass spectrum (AEI-MS-902 spectrometer) showed a parent ion at 166 m/e corresponding to the molecular weight.

## Results and Discussion

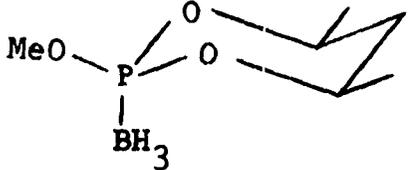
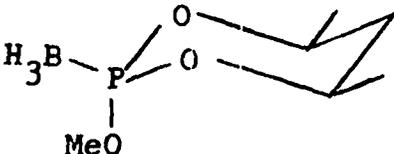
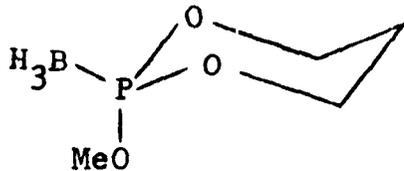
Borane adducts

The spectroscopic data for nine trialkyl phosphite borane adducts are collected in Table 12. Measurement of  $\nu(\text{B-H})$  for all of the adducts was made using the nonpolar solvent  $\text{CCl}_4$  so that comparison of values could be made in the absence of solvent effects. Comparison of stretching frequencies remeasured in this work with earlier values by White (46) shows that similar values are obtained for the asymmetric stretch but the symmetric stretch is consistently higher by 2.5 to  $14.5 \text{ cm}^{-1}$ .

Since the  $\text{BH}_3$  group has effective  $\text{C}_{3v}$  symmetry when coordinated to a phosphite, the infrared spectrum shows bands due to the symmetric ( $\text{A}_1$  mode) and asymmetric (E mode) B-H stretch. The higher energy band has been assigned to the asymmetric B-H stretch (116, 134). The weighted averages of the symmetric and asymmetric stretch ( $\nu(\text{B-H}) = \frac{1}{3}(\nu_{\text{sym}} + 2\nu_{\text{asymm}})$ ) (135) are given in Table 12 in order of increasing magnitude.

As already discussed, an increase in stretching frequency signals an increase in s character in the B-H bond. A decrease in electron density donated from phosphorus to boron can cause the hybridization at boron to vary from  $\text{sp}^3$  toward  $\text{sp}^2$ . Thus, for the phosphite borane adducts from 48 to 56,

Table 12. Spectroscopic data for trialkyl phosphite boranes

		Bands in the $\nu(\text{B-H})$ region <sup>a</sup>			<sup>31</sup> P nmr data <sup>b</sup>		
		Asymm.	Symm.	Weighted Average	Solvent	$\delta^{31}\text{P}^c$	$^1\text{JP}^{11}\text{B}^d$
<u>48</u>		2392.5 2398	2342.0 2351	2375.7	CCl <sub>4</sub> <sup>e</sup> CCl <sub>4</sub>	-109.6	108.0
<u>49</u>	H <sub>3</sub> BP(OMe) <sub>3</sub>	2397.5 2402	2352.0 2362	2382.3	CCl <sub>4</sub> <sup>e</sup> C <sub>6</sub> H <sub>6</sub>	-117.1 -118 <sup>f</sup>	103.2 97.2 <sup>f</sup>
<u>50</u>		2410.0 2410	2354.0 2358	2391.3	CCl <sub>4</sub> <sup>e</sup> CCl <sub>4</sub>	-108.5	103.2
<u>51</u>		2411.0 2411	2352.0 2364	2391.3	CCl <sub>4</sub> <sup>e</sup> CCl <sub>4</sub>	-110.6	103.9

<sup>a</sup>Positions are accurate to  $\pm 0.5 \text{ cm}^{-1}$ . The asymmetric and symmetric bands have strong and medium intensities, respectively.

<sup>b</sup>The solvent was a 1:1 mixture of  $\text{CD}_3\text{CN}$  and  $\text{CH}_3\text{CN}$ .

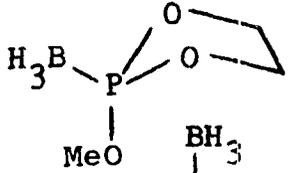
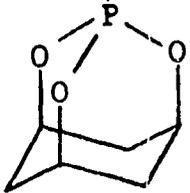
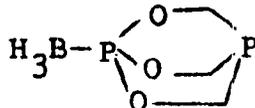
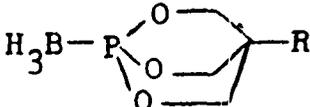
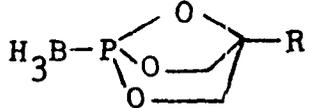
<sup>c</sup>Precise to  $\pm 0.2$  ppm. Relative to 85%  $\text{H}_3\text{PO}_4$ .

<sup>d</sup>Precise to  $\pm 1.0$  Hz except for 50 and 56 ( $\pm 2.0$  Hz).

<sup>e</sup>Reference 46.

<sup>f</sup>Reference 18.

Table 12. (Continued)

	Bands in the $\nu(\text{B-H})$ region				$^{31}\text{P}$ nmr data		
	Asymm.	Symm.	Weighted Average	Solvent	$\delta^{31}\text{P}$	$^1\text{JP}^{11}\text{B}$	
<u>52</u>		2412.0 2410	2354.0 2363	2392.7	$\text{CCl}_4$ $\text{CCl}_4^e$	-127.4	94.0
<u>53</u>		2418.0	2358.5	2398.2	$\text{CCl}_4$	-117.1 -117 <sup>f</sup>	96.2 97.6 <sup>f</sup>
<u>54</u>		2417.5	2360.0	2398.3	$\text{CCl}_4$	-89.8 <sup>g</sup>	97.3
<u>55</u>		2421.5 2415	2363.5 2366	2402.2	$\text{CCl}_4^h$ $\text{C}_6\text{H}_6^{e,1}$	-97.6 <sup>h</sup> -97 <sup>f,1</sup>	91.4 <sup>h</sup> 96.0 <sup>f,1</sup>
<u>56</u>		2432.5 2433	2365.5 2380	2410.2	$\text{CCl}_4^i$ $\text{C}_6\text{H}_6^{e,j}$	-126.8 <sup>i</sup>	63.3 <sup>i</sup>

The  $\delta^{31}\text{P}$  of the phosphine end is +66.0 ppm.

$^{\text{h}}\text{R}$  is ethyl.

$^{\text{i}}\text{R}$  is methyl.

$^{\text{j}}\text{R}$  is hydrogen.

the general increase in  $\nu(\text{BH})$  reflects the decreased capability of the phosphite to act as a Lewis base.

The rationale for the basicity order of the parent phosphites of the adducts 48, 49, 50, 51, 52, 55 and 56 has already been discussed in terms of the "hinge" (18, 19) and "orbital repulsion" (19, 20) effects and these arguments will not be repeated here. It is interesting to note that 50 and 51, both six-membered ring borane adducts, have similar asymmetric and symmetric stretching frequencies as well as identical weighted averages.

Comparison of boron and the proton as Lewis acids reveals several anomalies owing to the enhanced polarizing power of the proton. One of these, the different order of base strengths of the parent phosphites of 48 and 49 to these acids has been rationalized on this basis earlier. The values of  $\nu(\text{B-H})$  in 52 and 53 show that the adamantane-like phosphite is the weaker base toward boron. In contrast, the  $^1\text{JPH}$  values obtained from the protonated phosphites show that  $\text{MeOPOCH}_2\text{CH}_2\text{O}$  is the weaker base toward the proton. This behavior possibly reflects the decreased polarizability of a five-membered ring phosphite compared to the adamantane-like phosphite containing four six-membered rings owing to greater strain in the former.  $^1\text{JPH}$  values for monoprotonated  $\text{P}(\text{OCH}_2)_3\text{P}$  (901.1 Hz) and  $\text{P}(\text{OCH}_2)_3\text{CMe}$  (899.2 Hz) are about

equal within experimental error. However, comparison of  $\nu_{\text{avg}}(\text{BH})$  found in 54 and 55 indicates that  $\text{P}(\text{OCH}_2)_3\text{P}$  is a slightly better base toward  $\text{BH}_3$ .

An attempt was also made to determine any possible relationship between  $^1\text{JP}^{11}\text{B}$  obtained from borane adducts and the basicity of the parent phosphite. Under proton decoupled conditions the  $^{31}\text{P}$  spectrum of a borane adduct consists of a quartet due to the  $3/2$  spin of  $^{11}\text{B}$  superimposed on a broad resonance due to  $^{10}\text{B}$  coupling to phosphorus. Although  $^{10}\text{B}$  also has a spin of  $3/2$ , the broadening results from the larger quadrupole moment of  $^{10}\text{B}$ . The  $^{31}\text{P}$  data for the borane adducts using acetonitrile as solvent is tabulated in Table 12. In general there is a trend toward a smaller P-B coupling for the borane adducts as  $\nu_{\text{avg}}(\text{BH})$  increases but the range is only 16.6 Hz from 48 (108.0 Hz) to 55 (91.4 Hz). On the basis of this small range it was surprising that  $^1\text{JP}^{11}\text{B}$  for 56 was 63.3 Hz. Thus, a least squares analysis on the points generated by a plot of  $\nu_{\text{avg}}(\text{BH})$  and  $^1\text{JP}^{11}\text{B}$  gave a somewhat poor correlation coefficient of 0.83. Omission of the point for 56 gave only a small improvement (0.85). A better relationship is found between  $^1\text{JPH}$  and  $\nu_{\text{avg}}(\text{BH})$  (correlation coefficient of 0.90) in spite of the different behaviors of  $\text{H}^+$  and  $\text{BH}_3$  as Lewis acids. There is no apparent trend in  $\delta^{31}\text{P}$  for the borane adducts.

Although the  $^1\text{H}$  nmr spectrum ( $\text{CDCl}_3$ ) of 56 showed pure adduct as indicated by the absence of peaks due to the parent

phosphite, the  $^{31}\text{P}$  spectrum (white noise decoupled with acetonitrile as solvent) revealed a peak at  $-113.4$  ppm due

to  $\text{P}(\text{OCH}_2)_2\text{CMe}$  in addition to the quartet for the adduct.

Unfortunately, the extreme sharpness of the former peak and the broadness of the latter one do not permit accurate integration but it is estimated that the peak due to

$\text{P}(\text{OCH}_2)_2\text{CMe}$  accounts for less than 5% of the phosphorus nuclei.

This may explain why the parent phosphite was not detected in the  $^1\text{H}$  nmr spectrum.  $^{31}\text{P}$  spectra of 56 in  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  showed a decreased amount of free phosphite. When 1.00 mmole of  $\text{BH}_3 \cdot \text{THF}$  was added to 1.35 mmole of 56 in acetonitrile, the phosphite peak was still present. After

adding 1.50 mmole of  $\text{P}(\text{OCH}_2)_2\text{CMe}$  to 1.35 mmole of 56 in  $\text{CH}_3\text{CN}$ , a  $^{31}\text{P}$  spectrum shows that the adduct is still present.

These results indicate that the borane adduct is slightly more dissociated in the polar solvent acetonitrile and this is

not unexpected in view of the poor basicity of  $\text{P}(\text{OCH}_2)_2\text{CMe}$ .

However, exchange of  $\text{BH}_3$  is not rapid enough to cause line broadening and the  $^{31}\text{P}$  shift of the free phosphite at  $-113.4 \pm 0.2$  ppm is in excellent agreement with the  $-113.7$  ppm for pure phosphite under all of the above conditions.

### Phosphates and phosphites

The strength of intermolecular hydrogen bonding between phenol and oxygen or nitrogen bases can be measured by phenol OH band shifts in infrared spectra since frequency separations ( $\Delta\nu(\text{OH})$ ) have been correlated with hydrogen bonding enthalpies (123, 124, 125). It is necessary, however, that an inert solvent such as  $\text{CCl}_4$  or cyclohexane be used and that values of  $\Delta\nu(\text{OH})$  be determined at low donor concentrations with extrapolation to infinite dilution if possible (136). Furthermore, the concentration of phenol should be low enough to prevent self-association which could compete with the desired phenol-base interaction (123, 124). In our earlier work (24) the phenol concentration (0.15 m) was not sufficiently low to eliminate self-association completely which resulted in large changes in  $\Delta\nu(\text{OH})$  at low base concentrations. With a concentration of 0.015 m in phenol, however, self-association is not observed. Fortunately, our earlier findings concerning the basicity orders of phosphates and phosphites are not altered.

The data obtained on six phosphates over a range of concentrations are shown in Table 13 and are plotted in Figure 13. It was not possible to obtain any data on

$\text{OP}(\text{OCH}_2)_2\text{CMe}$  because of its very low solubility in  $\text{CCl}_4$ .

Since the phosphoryl group in phosphates has been shown to participate in hydrogen bonding (122, 137), these data show

Table 13. Hydrogen bonding shifts,<sup>a</sup>  $\Delta\nu(\text{OH})$ , of phenol in  $\text{CCl}_4$  at various phosphate concentrations

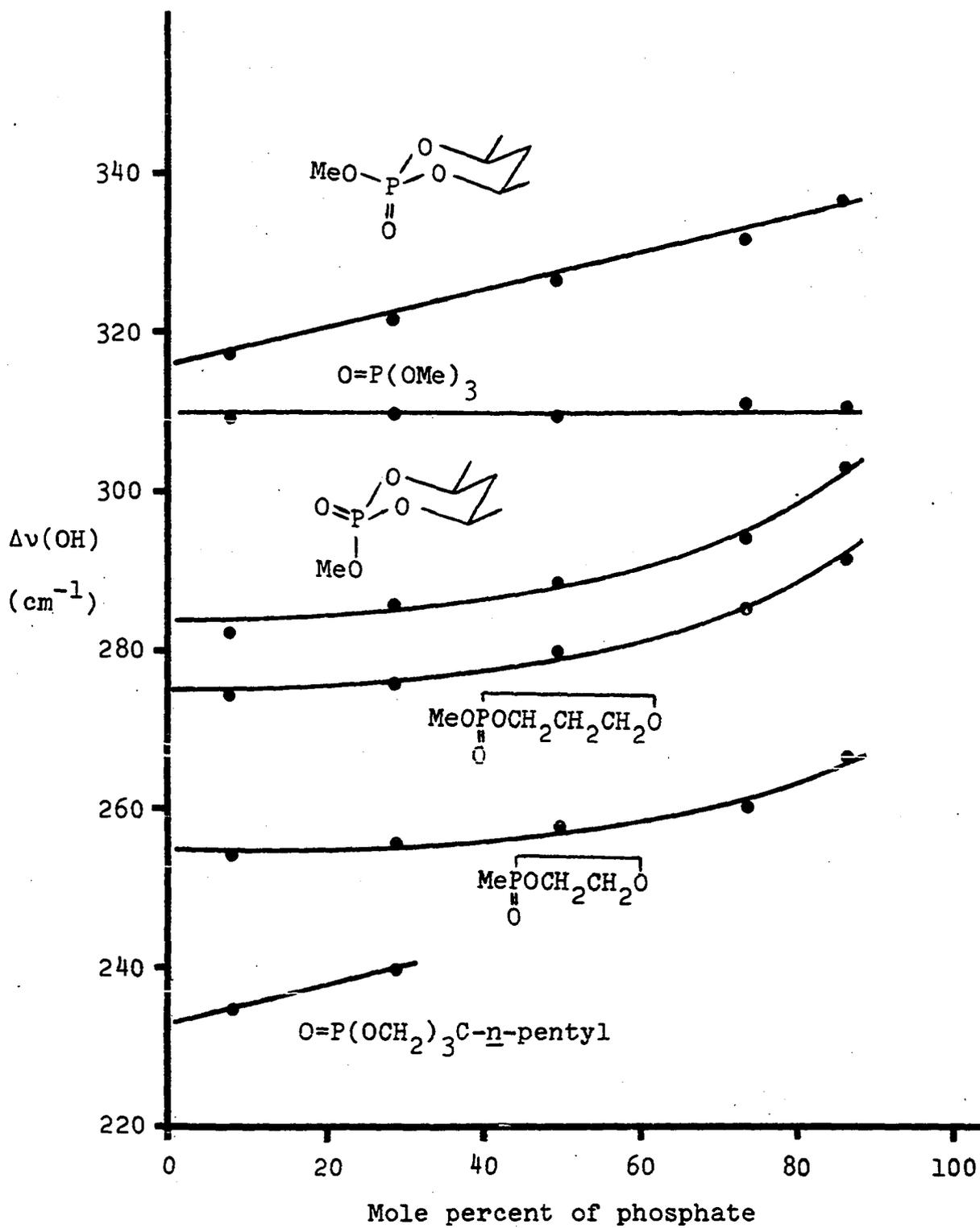
Conc. of Phosphate	Mole Percent <sup>b</sup>	<u>57</u>	<u>58</u>	<u>59</u>	<u>60</u>	<u>61</u>	<u>62</u>
0.0012	7.4	317.5	309.5	282.5	274.5	254.5	237.0
0.0060	28.6	322.0	310.0	286.0	276.0	255.5	240.0
0.0150	50.0	327.0	309.5	288.5	280.5	258.5	— <sup>c</sup>
0.0400	72.7	332.0	311.0	294.5	285.5	260.5	— <sup>c</sup>
0.1000	87.0	336.5	311.0	303.5	293.5	267.5	— <sup>c</sup>

<sup>a</sup>Values are accurate to  $\pm 1.5 \text{ cm}^{-1}$ .

<sup>b</sup>This represents the mole percent of phosphate with respect to the total moles of phosphate and phenol. Phenol concentration is constant at 0.015 molar.

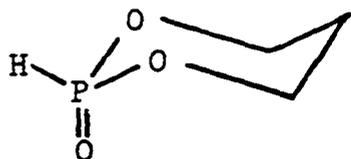
<sup>c</sup>This phosphite was not completely soluble at this concentration.

Figure 13. Plot of  $\Delta\nu(\text{OH})$  for phenol versus mole percent of phosphate in  $\text{CCl}_4$ .

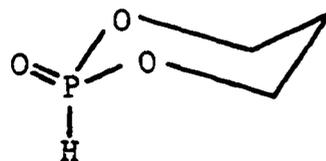


that the phosphoryl oxygen decreases in basicity from 57 to 62. Extrapolation of the curves in Figure 13 yields  $\Delta\nu(\text{OH})$  at infinite dilution and these values are tabulated in Table 14 and compared to  $\nu(\text{P}=\text{O})$ . The  $\Delta\nu(\text{OH})$  trend toward smaller values roughly parallels the upward progression of  $\nu(\text{P}=\text{O})$  in these systems. The increase in  $\nu(\text{P}=\text{O})$  has been rationalized on the basis of increased pi bonding from the phosphoryl oxygen to the phosphorus d orbitals (18) which in turn decreases the electron density on the phosphoryl oxygen and thus accounts for the drop in  $\Delta\nu(\text{OH})$ . Furthermore, the decrease in  $\Delta\nu(\text{OH})$  from 57 to 62 parallels the decreasing basicity of the phosphorus lone pair as revealed by both the increase in  $\nu(\text{BH})$  (Table 12) and by the increase in  $^1\text{JPH}$  (Table 2). For the points generated by  $\Delta\nu(\text{OH})$  versus  $\nu(\text{BH})$  and  $\Delta\nu(\text{OH})$  versus  $^1\text{JPH}$ , the correlation coefficients are 0.95 and 0.93, respectively.

Comparison of the present  $\Delta\nu(\text{OH})$  values with those obtained in other work suggests that the former are reasonable. Using 2,4,5 trichlorophenol,  $\Delta\nu(\text{OH})$  values have been obtained for the two isomeric hydrogen phosphates shown below



$$\Delta\nu(\text{OH}) = 345 \text{ cm}^{-1}$$



$$\Delta\nu(\text{OH}) = 315 \text{ cm}^{-1}$$

Table 14. Tabulation of  $\Delta\nu(\text{OH})$  of phenol at infinite dilution of phosphate and P=O stretching frequencies for trialkyl phosphates in solution

Compound	$\Delta\nu(\text{OH})^a$	$\nu(\text{P=O})^a$	Solvent <sup>b</sup>	Reference <sup>c</sup>
<u>57</u>	316	1271, 1289	$\text{C}_6\text{H}_6$	138
<u>58</u>	310 304 $\pm$ 2 <sup>d</sup> 315 <sup>e</sup>	1271, 1290	$\text{CCl}_4$	78
<u>59</u>	284	1304	$\text{CCl}_4$	138
<u>60</u>	276 276 $\pm$ 2 <sup>d</sup>	1279, 1312	$\text{CCl}_4$	78
<u>61</u>	255 257 $\pm$ 2 <sup>d</sup>	1302	$\text{CCl}_4$	24
<u>62</u>	233 230 $\pm$ 5 <sup>d</sup>	1327	$\text{CHCl}_3$	This work
<u>63</u>		1346, 1354	$\text{CH}_2\text{Cl}_2$	This work

<sup>a</sup>In  $\text{cm}^{-1}$ .

<sup>b</sup>Solvent for  $\nu(\text{P=O})$ .

<sup>c</sup>Reference for  $\nu(\text{P=O})$ .

<sup>d</sup>Reference 46.

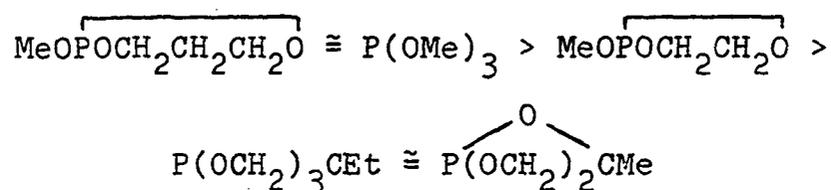
<sup>e</sup>Reference 122.

(139). The difference in  $\Delta\nu(\text{OH})$  obtained for these two isomers ( $30 \text{ cm}^{-1}$ ) is the same for 57 and 59. Using phenol as the acid, values of  $\Delta\nu(\text{OH})$  for  $(\text{EtO})(\text{O})\overline{\text{POCH}_2\text{CH}_2\text{O}}$  and  $(\text{EtO})(\text{O})\overline{\text{POCH}_2\text{CH}_2\text{CH}_2\text{O}}$  are  $270$  and  $280 \text{ cm}^{-1}$ , respectively (140). That these values are larger than their methoxy counterparts 61 ( $255 \text{ cm}^{-1}$ ) and 60 ( $276 \text{ cm}^{-1}$ ) can perhaps be attributed to the greater inductive effect of the ethyl group. Other values of  $\Delta\nu(\text{OH})$  previously obtained for four compounds are found in Table 14 and agree very well with the present results.

Although it has been shown previously that hydrogen bonding of phenol does take place at the phosphoryl oxygen (122), it is possible that this interaction could also be occurring at the alkoxy oxygens. In fact, asymmetry and sometimes a small shoulder on the broad peak due to hydrogen bonding was noted with all phosphates at all concentrations.  $\Delta\nu(\text{OH})$  for this second peak is estimated to range from  $120$  to  $200 \text{ cm}^{-1}$  which would be reasonable for the decreased basicity expected for the alkoxy oxygens.

Since hydrogen bonding studies of phenol with phosphates apparently reflect the basicity of the phosphoryl oxygen, it was desirable to determine the donor strength of the phosphorus lone pair in phosphites by this same method. Experimentally, however, infrared spectra of phosphites

dissolved in phenol- $\text{CCl}_4$  showed two bands due to hydrogen bonding. The data obtained on five phosphites are shown in Table 15 and are plotted in Figure 14. It is seen that each phosphite possesses two sets of  $\Delta\nu(\text{OH})$  values, one falling in the 150 to 190  $\text{cm}^{-1}$  range and the other in the 250 to 320  $\text{cm}^{-1}$  range. It is recognized immediately that these could be due to hydrogen bonding occurring at both the phosphorus and alkoxy oxygen. In any case, the trend in both ranges indicates that the order of hydrogen bonding and presumably basicities is roughly:



Although this basicity trend is supported by B-H stretching frequencies presented earlier, it is disturbing that the  $\Delta\nu(\text{OH})$  trend is the same in both regions. Both the CNDO/2 calculations (Table 3) and the "hinge" and "orbital" effects predict that negative charge should accumulate on alkoxy oxygens as phosphorus basicity decreases. Thus, the region which measures hydrogen bonding to the alkoxy oxygens should exhibit the reverse order of  $\Delta\nu(\text{OH})$  values. It is possible that the band at lower  $\Delta\nu(\text{OH})$  for the phosphites is due to hydrogen bonding at the alkoxy oxygen since such a lower

Table 15. Hydrogen bonding shifts,  $\Delta\nu(\text{OH})$ , of phenol in  $\text{CCl}_4$  at various phosphite concentrations<sup>a</sup>

Conc. of Phosphite	Mole Percent <sup>b</sup>	<u>12</u>	<u>7</u>	<u>65</u>	<u>66</u>	<u>1</u>
0.0012	7.4	— <sup>c</sup>				
0.0060	28.6	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>	152 ± 2	148 ± 5
0.0150	50.0	180 ± 10	184 ± 10	164 ± 5	155 ± 2	150 ± 5
0.0400	72.7	180 ± 5	182 ± 5	164 ± 5	157 ± 2	154 ± 2
0.1000	87.0	181 ± 2	179 ± 5	162 ± 2	159 ± 2	157 ± 2
0.5000	97.1	178 ± 2	171 ± 2	159 ± 2	165 ± 2	— <sup>d</sup>
0.0012	7.4	277 ± 5	278 ± 5	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>
0.0060	28.6	281 ± 2	281 ± 5	267 ± 5	— <sup>c</sup>	251 ± 5
0.0150	50.0	284 ± 2	285 ± 2	266 ± 5	— <sup>c</sup>	251 ± 2
0.0400	72.7	289 ± 2	295 ± 2	263 ± 5	— <sup>c</sup>	255 ± 2
0.1000	87.0	295 ± 2	300 ± 2	263 ± 5	254 ± 5	263 ± 2
0.5000	97.1	307 ± 2	314 ± 2	266 ± 5	257 ± 5	— <sup>d</sup>

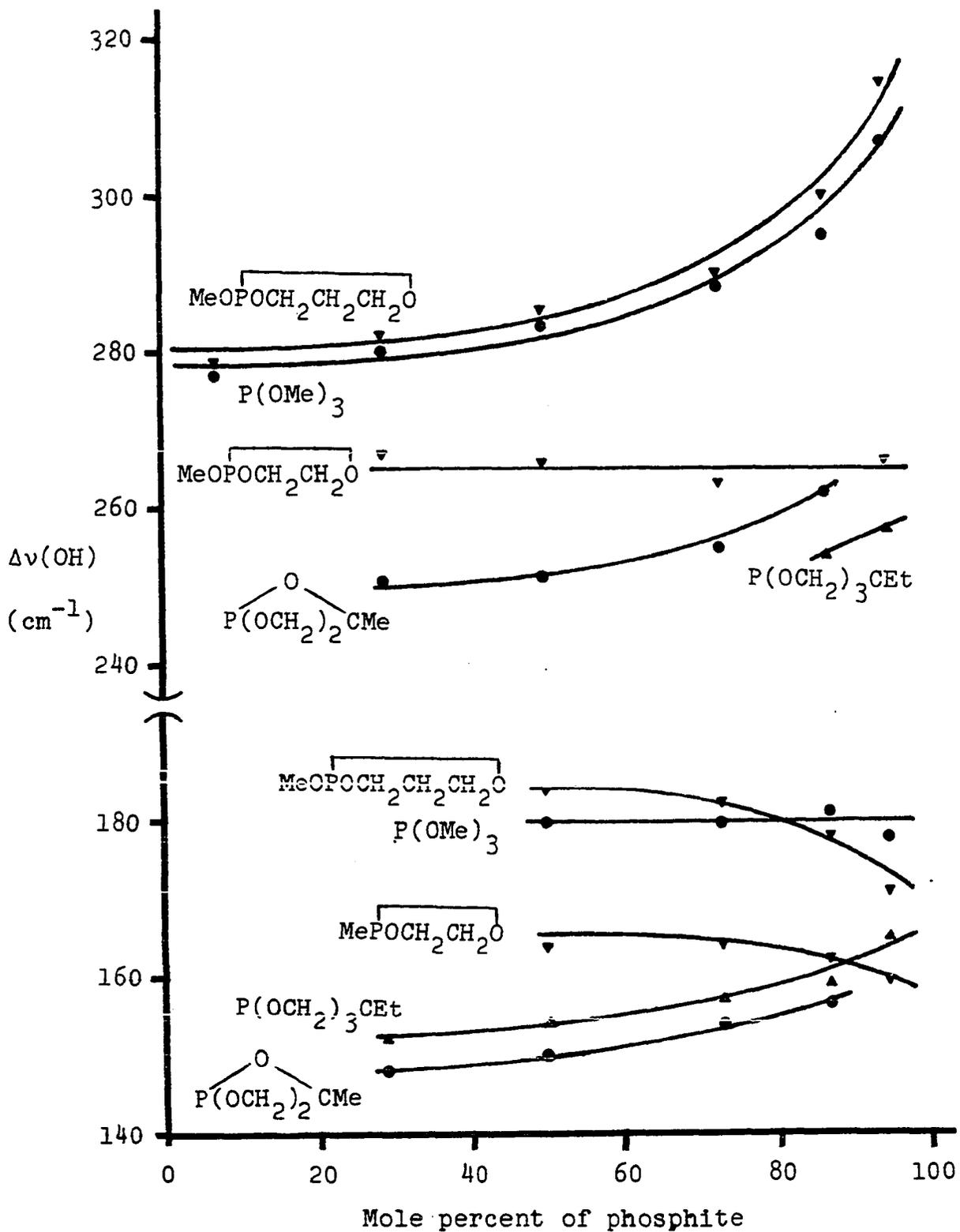
<sup>a</sup>Values in  $\text{cm}^{-1}$ .

<sup>b</sup>This represents the mole percent of phosphite with respect to the total moles of phosphite and phenol. Phenol concentration is constant at 0.015 molar.

<sup>c</sup>Too weak to be located accurately.

<sup>d</sup>Insufficiently soluble.

Figure 14. Plot of  $\Delta\nu(\text{OH})$  for phenol versus mole percent of phosphite in  $\text{CCl}_4$ .



$\Delta\nu(\text{OH})$  value was also observed for phosphates but further work is necessary to clarify this point. The presence of the second band was not apparent in our earlier work (24) because of the higher phenol concentration and poorer resolution.

Presented in Table 16 are  $\delta^{31}\text{P}$  values for bicyclic phosphites and phosphates. From quantum mechanical considerations, Mark and Van Wazer (141) have proposed that  $^{31}\text{P}$  chemical shift changes in trialkyl phosphites can be estimated from the equation  $\Delta\delta = -25\Delta\chi_{\text{OR}} - 382\Delta n_{\pi} + 21\Delta\alpha$ , where  $\Delta\chi_{\text{OR}}$  is the change in electronegativity in the P-O bond,  $\Delta n_{\pi}$  is the change in pi electron density in the d orbitals and  $\Delta\alpha$  is the change in the angle between the P-O bond and the phosphorus lone pair. Verkade (18) has shown that while this equation correctly predicts the  $^{31}\text{P}$  shift of  $\text{P}(\text{OCH}_2)_3\text{CMe}$  (-91.5 ppm) to be upfield from  $\text{P}(\text{OEt})_3$  (-137 ppm) because  $\Delta\alpha$  is expected to be larger in the former compound, the chemical

shift of  $\text{P}(\text{OCH}_2)_2\text{CH}$  (-105 ppm) is not consonant with this trend since  $\Delta\alpha$  should be largest for this compound. This

anomaly is compounded by the chemical shift of  $\text{P}(\text{OCH}_2)_2\text{CMe}$  (-113.7 ppm) in which Me has been substituted for H but no change in  $\Delta\alpha$  should have occurred. The inductive effect of the methyl group would be expected to decrease  $\chi_{\text{OR}}$  and produce an upfield shift from -105 ppm. While this reasoning can be

Table 16.  $^{31}\text{P}$  chemical shifts for bicyclic phosphites and phosphates

Compound	$\delta^{31}\text{P}^a$	Reference
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{P}(\text{OCH}_2)_2\text{CMe} \end{array}$	-113.7	This work
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{P}(\text{OCH}_2)_2\text{CH} \end{array}$	-105	18
$\text{P}(\text{OCH}_2)_3\text{CMe}$	-91.5	18
$\text{P}(\text{OCH}_2)_3\text{CH}$ (56)	-96.2	This work
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{OP}(\text{OCH}_2)_2\text{CMe} \end{array}$	-16.2	This work
$\text{OP}(\text{OCH}_2)_3\text{CMe}$	+7.97	142
$\text{OP}(\text{OCH}_2)_3\text{CH}$	+8.0	This work

<sup>a</sup>In ppm relative to 85%  $\text{H}_3\text{PO}_4$ .

used to explain the upfield shift of  $P(OCH_2)_3CMe$  (-91.5 ppm) compared to  $P(OCH_2)_3CH$  (-96.2 ppm) it fails again for  $P(OCH_2)_3C-n\text{-pentyl}$  (-92.8 ppm) (98). Furthermore, a change in chemical shift when Me (+7.97 ppm) is replaced by H (+8.0 ppm) in  $OP(OCH_2)_3CR$  is not observed. At present, no complete explanation of the above data is apparent.

Recently, an empirical correlation has been made between phosphate  $^{31}P$  chemical shifts and OPO bond angles (143).

This relationship included the point for  $OP(OCH_2)_3CMe$  for which structural data has shown the OPO angle to be  $103.7^\circ$

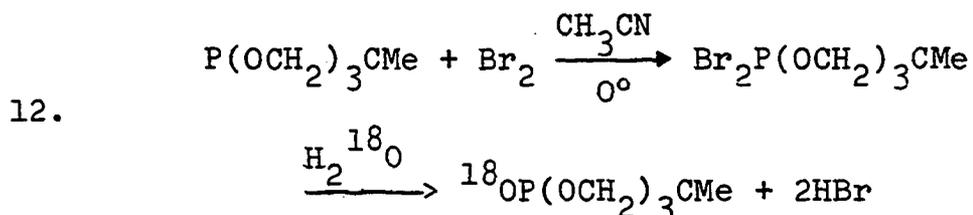
(144). Unfortunately, structural data for  $OP(OCH_2)_2CMe$  is not available but since the above correlation should have some predictive value, the chemical shift of -16.2 ppm for this compound allows an anticipated average OPO angle of  $99^\circ$ . That this angle should be smaller than in  $OP(OCH_2)_3CMe$  is reasonable in view of the increased constraint.

For many phosphates two infrared bands separated by less than  $40\text{ cm}^{-1}$  fall in the  $P=O$  stretching frequency region (24) making assignment of this mode impossible. White (46) has devoted an extensive discussion to this phenomenon and has examined this region for  $O=P(OMe)_3$  and  $O=P(OCH_2)_3CC_5H_{11}$  in a number of solvents at various concentrations but could make no unambiguous assignment. In addition, the complexing of iodine or phenol to the phosphoryl

oxygen of  $\text{O}=\text{P}(\text{OCH}_2)_3\text{C}-\underline{\text{n}}-\text{C}_5\text{H}_{11}$  in solution does not produce sufficient spectral changes to facilitate assignment.

White (46) reasoned that Fermi resonance was probably the cause for one of the bands in the phosphoryl region but noted that a conclusion could be reached most easily if substitution of  $^{18}\text{O}=\text{P}$  for  $^{16}\text{O}=\text{P}$  resulted in a single shifted band.

The incorporation of oxygen-18 into  $^{18}\text{OP}(\text{OCH}_2)_3\text{CMe}$  has been accomplished by reaction 12 which was accidentally

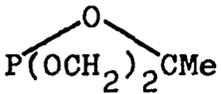
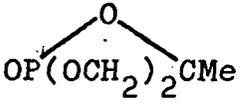
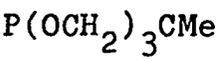
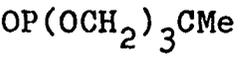


discovered (73) to occur if the acetonitrile used in making the bromine adduct contained traces of water. An infrared spectrum ( $\text{CHCl}_3$ ) of  $^{16}\text{OP}(\text{OCH}_2)_3\text{CMe}$  (145) showed bands at  $1327 \text{ cm}^{-1}$  (strong) and  $1314 \text{ cm}^{-1}$  (medium, shoulder) while  $^{18}\text{OP}(\text{OCH}_2)_3\text{CMe}(\text{CHCl}_3)$  revealed a strong new peak at  $1287 \text{ cm}^{-1}$  due to  $^{18}\text{O}=\text{P}$ . However, peaks at  $1327 \text{ cm}^{-1}$  and  $1312 \text{ cm}^{-1}$  were still evident because of 12.2%  $^{16}\text{O}$  present in the water used. Assuming that the band at  $1327 \text{ cm}^{-1}$  is due to  $^{16}\text{O}=\text{P}$ , reduced mass calculations involving only the two atoms in this group shift this band to  $1277 \text{ cm}^{-1}$  for  $^{18}\text{O}=\text{P}$  which is in fair agreement with the band at  $1287 \text{ cm}^{-1}$ . The similar intensities of the bands at  $1327$  and  $1287 \text{ cm}^{-1}$  also support the assignment of the band at  $1327 \text{ cm}^{-1}$  as the phosphoryl stretch. A Raman

spectrum of  $^{16}\text{OP}(\text{OCH}_2)_3\text{CMe}$  shows bands at  $854\text{ cm}^{-1}$  (strong) and  $462\text{ cm}^{-1}$  (strong) assigned to asymmetric P-O stretching and O=P-O deformation, respectively (146). Since the sum of these two bands is  $1316\text{ cm}^{-1}$ , it is questionable that Fermi resonance of the combination of these vibrations with the phosphoryl stretching vibration results in the band at  $1314\text{ cm}^{-1}$  as suggested by White (46), since the band at  $1314\text{ cm}^{-1}$  is only slightly shifted to longer wavelength. The possibility that the  $1314\text{ cm}^{-1}$  peak is due to a vibrational mode of the  $\text{P}(\text{OCH}_2)_3\text{CMe}$  moiety is ruled out since an infrared spectrum of  $\text{S}=\text{P}(\text{OCH}_2)_3\text{CMe}$  (145) in  $\text{CHCl}_3$  is transparent from  $1270$  to  $1340\text{ cm}^{-1}$ . It is tentatively concluded that this peak is associated with the P=O group but in a way that is not presently understood.

In order to obtain a better understanding of the nature of the bonding within bicyclic phosphorus compounds, their natural abundance  $^{13}\text{C}$  spectra were obtained. The chemical shifts and couplings are summarized in Table 17. Assignment of chemical shifts was made by first obtaining spectra under nondecoupled conditions which revealed the multiplicities due to the larger C-H coupling (125-160 Hz) at the methylene carbon (triplet), the bridgehead carbon (singlet) and the methyl carbon (quartet). The smaller C-H couplings over two and three bonds were also obtained from these spectra. However,

Table 17.  $^{13}\text{C}$  nmr data for bicyclic phosphites and phosphates<sup>a</sup>

Compound	Methylene carbon		Bridgehead carbon		Methyl carbon	
	$\delta^{13}\text{C}$ $^2\text{JPOC}$	$^1\text{JCH}$ $^3\text{JCCCH}$	$\delta^{13}\text{C}$ $^3\text{JPOCC}$	$^2\text{JCCH}$	$\delta^{13}\text{C}$ $^4\text{JPOCCC}$	$^1\text{JCH}$ $^3\text{JCCCH}$
<u>1</u> 	71.5 0	152.6 --- <sup>b</sup>	83.6 5.1 <sup>c</sup>	— <sup>b</sup>	13.6 8.8 <sup>d</sup>	128.5 2.1 <sup>e</sup>
<u>63</u> 	77.5 3.7	157.0 --- <sup>b</sup>	80.8 17.6 <sup>c</sup>	4.8 <sup>f</sup>	15.5 10.3 <sup>d</sup>	129.6 1.7 <sup>e</sup>
<u>4</u> 	71.4 0	150.3 5.2 <sup>h</sup>	31.7 22.8	2.2 <sup>g</sup>	15.6 4.4	127.4 ~1
<u>68</u> 	78.6 5.9	157.4 --- <sup>i</sup>	33.7 38.2	— <sup>i</sup>	11.2 0	128.0 --- <sup>i</sup>

<sup>a</sup>The solvent was CD<sub>3</sub>CN. Chemical shifts are precise to ± 0.1 ppm and are referenced relative to TMS. Coupling constants are precise to ± 1.0 Hz.

<sup>b</sup>The resonance was too complex because of overlapping peaks to determine this coupling.

<sup>c</sup>This value includes a contribution due to <sup>2</sup>JPOC coupling.

<sup>d</sup>This value includes a contribution due to <sup>3</sup>JPOCC coupling.

<sup>e</sup>This coupling resulted in a triplet but assignment to axial or equatorial proton coupling cannot be made.

<sup>f</sup>A sextet due to equivalent CCH<sub>3</sub> and CCH<sub>eq</sub> or CCH<sub>ax</sub> coupling.

<sup>g</sup>A decet due to equivalent CCH<sub>3</sub> and CCH<sub>2</sub> coupling.

<sup>h</sup>An octet due to equivalent CCCH<sub>3</sub> and CCCH<sub>2</sub> coupling.

<sup>i</sup>Insufficient resolution. Coupling probably near zero.

phosphorus to carbon couplings were determined from spectra obtained under proton decoupled conditions.

The  $^1\text{JCH}$  couplings found in Table 17 are typical values for methyl and methylene groups (147). The  $^1\text{JCH}$  couplings at the methylene carbon in the two phosphites are only slightly smaller (5-7 Hz) than the same couplings in their respective phosphates. This coupling behavior is also exhibited from triethyl phosphite to triethyl phosphate (Table 18). Those values of  $^3\text{JCCCH}$  and  $^2\text{JCCH}$  coupling, which could be determined, are also typical (147).

Inspection of Table 17 shows that couplings from phosphorus to the different carbons vary widely. It is mildly surprising that  $^2\text{JPOC}$  is zero in both phosphites since this coupling is 11.3 Hz in triethyl phosphite (Table 18). However, in the phosphates 63 and 68 the absolute magnitudes of  $^2\text{JPOC}$  found to be 3.7 and 5.9 Hz, respectively, compare well with  $^2\text{JPOC}$  in triethyl phosphate (5.8 Hz) and also with  $^2\text{JPCC}$  found for the two bicyclic phosphine oxides in Table 19. Moreover,  $^2\text{JPOC}$  has been found to be  $\leq 10$  Hz in the bicyclic compound  $\text{P}(\text{OCH}_2)_3\text{P}$  (148).

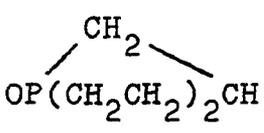
Within each compound in Table 17, P-C(bridgehead) coupling is always larger than P-C couplings over two or four bonds. For compounds 4 and 68 the phosphorus to bridgehead carbon coupling is also larger than the analogous coupling in 1 and 63 even though a two bond coupling path is

Table 18.  $^{13}\text{C}$  nmr data for triethyl phosphite and triethyl phosphate<sup>a</sup>

Compound	<u>Methylene carbon</u>		<u>Methyl carbon</u>	
	$\delta^{13}\text{C}$ $^2\text{JPOC}$	$^1\text{JCH}$	$\delta^{13}\text{C}$ $^3\text{JPOCC}$	$^1\text{JCH}$
<u>69</u> $\text{P}(\text{OCH}_2\text{CH}_3)_3$	58.4 +11.3	+142.8	17.7 +4.9	+126.0
<u>70</u> $\text{OP}(\text{OCH}_2\text{CH}_3)_3$	64.2 -5.8	+146.2	16.7 +6.8	+125.3

<sup>a</sup>This data was obtained from reference 149. The chemical shifts are in ppm and the couplings in Hz.

Table 19.  $^{13}\text{C}$  nmr data for bicyclic phosphine oxides<sup>a</sup>

Compound	Methylene carbon		Bridgehead carbon	
	$\delta^{13}\text{C}$	$^2\text{JPCC}$	$\delta^{13}\text{C}$	$^3\text{JPCCC}$
<u>71</u> 	28.6	4	27.4	35 <sup>b</sup>
<u>72</u> $\text{OP}(\text{CH}_2\text{CH}_2)_3\text{CH}$	27.4	5	22.3	47

<sup>a</sup>This data was obtained from reference 150. The chemical shifts are in ppm and the couplings in Hz.

<sup>b</sup>Includes a contribution from PCC coupling.

involved in the latter two compounds. It has also been found that phosphorus to carbon bridgehead coupling is large in the phosphine oxides 71 (47 Hz) and 72 (35 Hz) (Table 19). From the coupling information in the bicyclic phosphine oxides, Wetzel and Kenyon (150) have concluded that the high  $^3\text{JPCCC}$  value in  $\text{OP}(\text{CH}_2\text{CH}_2)_3\text{CH}$  indicates that the coupling between bridgehead atoms in  $\text{OP}(\text{CH}_2\text{CH}_2)_2\text{CH}$  is due to the vicinal coupling path even though a two bond coupling path is available in the last compound. They proposed that the three bond couplings might be large as a result of the dihedral angle of  $0^\circ$  in the vicinal coupling pathway analogous to the Karplus relationship found in other systems (151). Thus, it may be that the large values of  $^3\text{JPOCC}$  in 4 (22.8 Hz) and 68 (38.2 Hz) are also the result of this special geometrical relationship involving three coupling paths. In considering the smaller bridgehead couplings in 63 (17.6 Hz) compared to 68 (38.2 Hz), it is well to note that in pentavalent phosphorus compounds POC and POCC couplings are negative and positive, respectively (149). Thus, the two bond POC coupling appears to be cancelling some of the coupling magnitude due to POCC coupling in 63. By assuming equal coupling for each POCC path in 68 with a similar magnitude for this interaction in 63,  $^2\text{JPOC}$  in 63 is calculated to be -7.8 Hz. This value is comparable to that found in  $\text{OP}(\text{OCH}_2\text{CH}_3)_3$  (-5.8 Hz (149)).

Because POC and POCC couplings have both been found to be positive in acyclic phosphites (149), the small value of 5.1 Hz in 1 cannot be explained by partial cancellation nor is any other explanation obvious. It is possible that the sign of phosphorus to bridgehead coupling is negative in 1. The rise in bridgehead coupling from 1 to 63 (17.7 Hz) and from 4 to 68 (20.6 Hz) can probably be attributed to an increase in s character in the P-O bonds owing to quarterization of the phosphorus.

The four bond coupling  ${}^4J_{\text{POCCC}}$  has been found to be zero in 68 and 4.4 Hz in 4. Thus, for these two compounds the coupling per pathway is 0 and 1.5 Hz. In view of these small values, the larger couplings from phosphorus to the methyl carbon in 1 (8.8 Hz) and 63 (10.3 Hz) can be mainly attributed to the POCC pathway.

## ZERO VALENT TRANSITION METALS AS LEWIS ACIDS

## Introduction

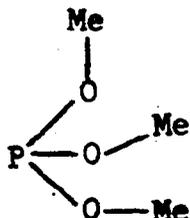
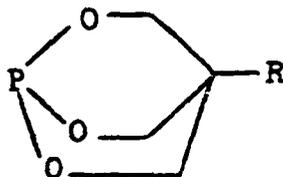
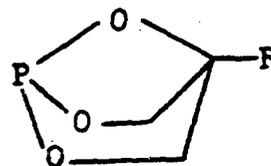
The nature of the metal phosphorus bond in transition metal complexes has been a continual subject of interest, particularly over the importance of sigma and pi contributions. While much effort has been directed at measurements of the infrared stretching frequency of the carbonyl moiety in substituted metal complexes (152) and determining its relationship to the donor-acceptor properties of the phosphorus ligand, an additional probe into the nature of the metal phosphorus bond has been the study of M-P stretching frequencies (153-156).

The strength of the C-O bond in metal carbonyl complexes is generally accepted to be related to two bonding modes of the carbonyl group to the metal center (152). Firstly, the carbon lone pair electrons interact in a coordinate fashion with an empty metal orbital to form a sigma bond. Secondly, a metal ligand pi bond results when filled metal d orbitals interact with low energy vacant antibonding pi orbitals of the carbonyl group. It has been argued (157, 158) that changes in the C-O force constants and stretching frequencies in  $M(CO)_5L$  complexes are a function only of the pi accepting ability of L. As metal-phosphorus pi bonding becomes stronger in  $M(CO)_5PY_3$  because of electronegativity increases

in Y, there is a depletion of electron density from the C-O antibonding orbitals through the metal d orbitals resulting in an increase in the C-O force constants. Others (155, 159, 160), however, maintain that changes in  $\nu_{CO}$  are related only to the inductive ability of the phosphorus ligand. Thus, the lower donor capacity of  $PF_3$  compared to  $PR_3$  reduces the negative charge on the metal and decreases the electron density in the M-C-O pi system.

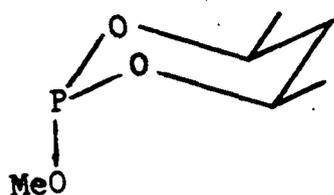
Since carbonyl stretching data can lead to ambiguous conclusions concerning the sigma and pi character of the M-P bond, a real test of the strength of the M-P bond (in the absence of coupling effects) is to measure its stretching frequency. Bicyclic phosphites lend themselves to this kind of study since ligand vibrational modes are absent in the lower infrared energy region. Thus, for suitable metal complexes of 73 the M-P stretching frequencies have been recorded and are compared to those obtained for the phosphite 4 (153, 154).

The synthesis of zero valent transition metal complexes incorporating the acyclic phosphite  $P(OMe)_3$  (159, 161-164) and the bicyclic phosphite  $P(OCH_2)_3CR$  (98, 165) has included

124 (R=Me)73 (R=Me)  
73 (R=H)

$\text{Ni}(\text{CO})_{4-n}\text{L}_n$  ( $n=2$  or  $3$ ),  $\text{Fe}(\text{CO})_{5-n}\text{L}_n$  ( $n=1$  or  $2$ ),  $\text{M}(\text{CO})_5\text{L}$  ( $\text{M}=\text{Cr}, \text{Mo}, \text{W}$ ) and cis- $\text{Mo}(\text{CO})_4\text{L}_2$ . Carbonyl stretching frequency data obtained from complexes substituted with 4 display the same or higher values than analogous complexes substituted with 12. Thus, the enhanced ligating properties of the bicyclic phosphite 4 toward transition metals has been attributed to its stronger pi bonding ability. In view of the apparent increase in pi bonding with constraint, which is accompanied by a reduction in sigma basicity, a study of substituted metal complexes of 1 or 69 seemed desirable.

Intermediate donor-acceptor properties to the acyclic and bicyclic phosphites should be exhibited by monocyclic systems. This has been shown to be true for the phosphite  $\text{C}_6\text{H}_5\text{OP}(\text{OCH}_2)_2\text{CMe}_2$  in some  $\text{Ni}(\text{O})$  and  $\text{Pt}(\text{O})$  complexes (166). Furthermore, on the basis of nmr evidence the conformation of the ligand was proposed to be in the chair form with an axial phenoxy group. This same conclusion concerning stereochemistry has been reached for complexes of  $\text{Mo}(\text{CO})_5\text{L}$  wherein L is  $\text{XP}(\text{OCH}_2)_2\text{CMe}_2$  ( $\text{X}=\text{Cl}, \text{R}, \text{OR}, \text{SR}$  or  $\text{NR}_2$ ) (167). Although the preferred conformation of six-membered ring phosphites is the chair form with an axial alkoxy group, isomerism at phosphorus has been demonstrated for the ring-locked isomeric phosphites 8 and 10 by synthesizing both the  $\text{BH}_3$  (23) and oxygen adducts (138). For the first time, ligand isomerism with 8 and 10 is now shown in a transition metal complex.

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## Experimental

### Techniques and preparations

Materials The metal carbonyls  $M(\text{CO})_6$  ( $M=\text{Cr}$ ,  $\text{Mo}$  and  $\text{W}$ ) were obtained from the Pressure Chemical Company.  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$  were purchased from A. D. Mackay, Inc. and Alfa, Inc., respectively. The solvents benzene, ethylbenzene, acetonitrile and diglyme were dried by distillation from  $\text{CaH}_2$  while methylcyclohexane, cyclohexane and heptane were dried over molecular sieves.

Spectroscopy Carbonyl stretching frequencies were measured from spectra of solutions obtained on a Beckman IR-12 double beam spectrometer using sodium chloride optics. Calibration was provided by the  $1601.8 \text{ cm}^{-1}$  band of polystyrene. A Beckman IR-11 grating spectrometer provided the far infrared spectra. All complexes were milled with Nujol and sufficient material was placed between two polyethylene films (0.038 mm thick) to obtain spectra of reasonable intensity. Proton, phosphorus and carbon-13 nmr spectra were

obtained as described in previous sections. Mass spectra were obtained on an Atlas CH-4 spectrometer. Laser Raman spectra were also recorded as previously described. Analyses were carried out by Schwarzkopf Microanalytical Laboratory.

Preparations All reactions were carried out under a dry nitrogen atmosphere.

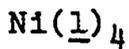
$\text{Ni}(\text{CO})_2(\underline{73})_2$  Liquid nitrogen was used to condense 5 ml of  $\text{Ni}(\text{CO})_4$  (37 mmole) into the reaction vessel. After the  $\text{Ni}(\text{CO})_4$  was warmed to and held at  $0^\circ\text{C}$  by means of an ice bath, a solution of 3.5 g (29 mmole) of 73 dissolved in 10 ml of benzene was slowly added over 15 minutes while stirring magnetically. After the evolution of CO had slowed considerably, the mixture was stirred an additional four hours at room temperature. The solution was then filtered and 80% of the benzene was removed under vacuum. Addition of ether precipitated 5.2 g of white product which was purified by dissolving in acetonitrile and adding ether (m.p. =  $154\text{--}156^\circ$  with decomposition). A mass spectrum showed a small parent ion at 355 m/e for the molecular weight of the complex. A  $^1\text{H}$  nmr in  $\text{CD}_3\text{CN}$  showed a multiplet for the methylene protons at 4.9 ppm and a doublet ( $^3\text{JPOCH} = 23$  Hz) of triplets ( $^2\text{JHCH} = 3$  Hz) at 5.24 ppm. Analysis: Calcd. for  $\text{C}_8\text{H}_{10}\text{O}_8\text{NiP}_2$ : C, 27.07%; H, 2.82%; Ni, 16.55%. Found: C, 27.00%; H, 2.88%; Ni, 16.97%.

Ni(CO)(73)<sub>3</sub> To 1.0 g (3.3 mmole) of Ni(CO)<sub>2</sub>(73)<sub>2</sub>

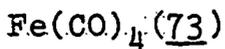
dissolved in 50 ml of dry acetonitrile was added 0.5 g (4.2 mmole) of 73. After four hours of gentle reflux, the mixture was filtered, 80% of the solvent was removed under vacuum and ether was added which precipitated 1.3 grams of white product. Recrystallization was accomplished by dissolving the material in acetonitrile, adding ether to the cloud point and cooling to 0° (m.p. = ca. 240° with decomposition). A <sup>1</sup>H nmr (CD<sub>3</sub>CN) showed a methylene multiplet at 3.85 ppm and a broadened doublet for the bridgehead proton (<sup>3</sup>JPOCH = 24 Hz). A mass spectrum did not reveal a parent ion corresponding to the molecular weight of the complex. Analysis: Calcd. for C<sub>10</sub>H<sub>15</sub>O<sub>10</sub>NiP<sub>3</sub>: C, 26.86%; H, 3.36%. Found: C, 25.81%; H, 3.53%.

Ni(73)<sub>4</sub> To 1 g (2.8 mmole) of Ni(CO)<sub>2</sub>(73)<sub>2</sub>

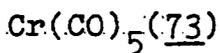
dissolved in 50 ml of acetonitrile was added 1.4 g (11.6 mmole) of 73. After the mixture was heated at a gentle reflux for 18 hours the solution was filtered and one-half of the solvent was removed under vacuum. Addition of ether caused formation of 1.3 g of white product which can be recrystallized from a minimum amount of hot acetonitrile (m.p. = ca. 315° with decomposition). Because of its limited solubility, a <sup>1</sup>H nmr could not be obtained. Analysis: Calcd. for C<sub>12</sub>H<sub>20</sub>O<sub>12</sub>NiP<sub>4</sub>: C, 26.73%; H, 3.71%; Ni, 10.90%. Found: C, 26.41%; H, 3.99%; Ni, 10.63%.



To a solution of 2.33 g (17.4 mmole) of  $\text{P}(\text{OCH}_2)_2\text{CMe}$  in 25 ml  $\text{CH}_2\text{Cl}_2$  was added 0.68 g (4.1 mmole) of  $\text{Ni}(\text{CH}_2=\text{CH}-\text{CN})_2$  (168) in small aliquots. After stirring for one hour, the slightly yellow solution was filtered through Celite. Addition of ether to the cloud point and cooling to  $-78^\circ$  yielded 2.04 g of white crystals which darkened above  $300^\circ$  but did not melt. A proton nmr ( $\text{CDCl}_3$ ) showed a methyl singlet at 1.59 ppm and a methylene multiplet at 3.75 ppm whose downfield half was broadened. Analysis: Calcd. for  $\text{C}_{16}\text{H}_{28}\text{O}_{12}\text{NiP}_4$ : C, 32.28%; H, 4.75%. Found: C, 32.46%; H, 4.76%.



A mixture of 2.0 ml (15 mmole) of  $\text{Fe}(\text{CO})_5$  and 1.2 g (10 mmole) of 73 in 50 ml of ethylbenzene was refluxed gently for 7 hours. After cooling, the solution was filtered and the volume reduced to 5 ml. Addition of pentane and cooling to  $-78^\circ$  produced 0.24 g of yellow product. The compound can be sublimed at  $90^\circ$  and less than 0.2 mm of Hg (m.p. =  $108^\circ$ ). A  $^1\text{H}$  nmr spectrum ( $\text{CD}_3\text{CN}$ ) revealed a methylene multiplet at 4.15 ppm and a doublet of triplets for the bridgehead proton at 5.40 ppm ( $^3\text{JPOCH} = 24$  Hz). A strong peak at 288 m/e in the mass spectrum corresponds to the molecular weight of the complex.



A mixture of 4.0 g (18 mmole) of  $\text{Cr}(\text{CO})_6$  and 2.2 g (18 mmole) of 73 in 75 ml methylcyclohexane

was refluxed for 18 hours. After cooling and filtering off unreacted  $\text{Cr}(\text{CO})_6$ , the methylcyclohexane was removed under vacuum to leave 1.8 g (32% yield) of crude product which was purified by sublimation at 90-100° and less than 2 mm of Hg. The white product melted at 150-152°. A  $^1\text{H}$  nmr spectrum ( $\text{CDCl}_3$ ) showed a methylene multiplet at 3.95 ppm and a multiplet for the bridgehead proton at 5.1 ppm ( $^3\text{JPOCH} = 22$  Hz). A mass spectrum showed a parent ion at 312 m/e corresponding to the molecular weight of the complex.

$\text{Mo}(\text{CO})_5(\underline{73})$  A mixture of 2.6 g (10 mmole) of  $\text{Mo}(\text{CO})_6$  and 1.0 g (8.4 mmole) of 73 in 50 ml benzene was refluxed for 20 hours. After cooling, the benzene was removed under vacuum. The residue was fractionally sublimed to remove unreacted  $\text{Mo}(\text{CO})_6$  and then 1.8 g (60% yield) of colorless product was sublimed at 80-90° and 1 mm of Hg (m.p. = 143-144° with decomposition). A  $^1\text{H}$  nmr spectrum ( $\text{CDCl}_3$ ) revealed a methylene multiplet at 3.9 ppm and a doublet of triplets for the bridgehead proton ( $^3\text{JPOCH} = 22$  Hz). A parent ion at 356 m/e in the mass spectrum corresponds to the molecular weight of the complex.

$\text{cis-Mo}(\text{CO})_4(\underline{73})_2$  A mixture of 0.80 g (2.6 mmole) of  $\text{Mo}(\text{CO})_4\text{C}_7\text{H}_8$  (169) ( $\text{C}_7\text{H}_8 = \text{norbornadiene}$ ) and 0.80 g (6.7 mmole) of 73 were stirred in 40 ml of cyclohexane. After the initial yellow color disappeared (2 minutes), pentane was

added to precipitate the product. Recrystallization by dissolving the material in  $\text{CHCl}_3$ , adding pentane and cooling to  $-78^\circ$  yielded 0.65 g of white compound (m.p.  $200-201^\circ$  with decomposition). A  $^1\text{H}$  nmr spectrum ( $\text{CD}_3\text{CN}$ ) showed a methylene multiplet at 3.9 ppm and a resonance at 5.2 ppm for the bridgehead proton exhibiting the expected virtual coupling which had a separation of 23 Hz between the doublet of triplets. A mass spectrum revealed a parent ion at 448 m/e corresponding to the molecular weight of the complex.

$\text{trans-Fe(CO)}_3(\underline{73})_2$       A mixture of 0.93 g (4.0 mmole) of  $\text{Fe(CO)}_3\text{C}_7\text{H}_8$  (169) ( $\text{C}_7\text{H}_8$  = cycloheptatriene) and 1.50 g (12.5 mmole) of 73 in 50 ml diglyme was refluxed gently for 6 hours. After the volume was reduced by 75%, addition of ether and cooling produced 0.7 g of a yellow solid (m.p. =  $175^\circ$  with decomposition). A  $^1\text{H}$  nmr spectrum ( $\text{CD}_3\text{CN}$ ) revealed a methylene multiplet at 5.0 ppm and a multiplet for the virtually coupled bridgehead proton at 5.25 ppm (outer peak separation = 24 Hz). A mass spectrum showed a parent ion at 380 m/e.

$\text{Mo(CO)}_5(\underline{8})$       A mixture of 1.3 g (5.0 mmole) of  $\text{Mo(CO)}_6$  and 0.66 g (4.0 mmole) of 8 was refluxed in 50 ml heptane for 4 hours. After the solution was filtered and one-half of the solvent was removed under vacuum, cooling to  $-78^\circ$  caused formation of 1.3 g of colorless product. The compound can be recrystallized from pentane (m.p. =  $51-52^\circ$ ).

A  $^1\text{H}$  nmr spectrum ( $\text{CDCl}_3$ ) showed a methyl doublet at 1.27 ppm ( $^3\text{JHCCH} = 6$  Hz), a methylene multiplet at 1.65 ppm, a methoxy doublet at 3.60 ppm ( $^3\text{JPOCH} = 12.5$  Hz) and a methinyl multiplet at 4.5 ppm. Parent ions centered at 400 m/e confirm the molecular weight of the complex.

$\text{cis-Mo(CO)}_4(\underline{8})_2$  To a solution of 0.60 g (2.0 mmole) of freshly prepared  $\text{Mo(CO)}_4\text{C}_7\text{H}_8$  (169) ( $\text{C}_7\text{H}_8 =$  norbornadiene) in 25 ml dry cyclohexane was added 0.80 g (4.9 mmole) of 8. The yellow color disappeared within a few minutes and after an additional one-half hour of stirring the solution was filtered. Half of the solvent was removed under vacuum and upon cooling the remaining solution, 0.88 g of white solid was collected which after recrystallization from a 1:10 mixture of chloroform-pentane with cooling to  $-78^\circ$  melted sharply at  $76^\circ$ . A  $^1\text{H}$  nmr spectrum revealed a doublet for the methyl groups at 1.28 ppm ( $^3\text{JHCCH} = 6.2$  Hz), a methylene multiplet at 1.65 ppm, a methoxy doublet showing virtual coupling at 3.72 ppm (main doublet separation = 12.2 Hz) and a methinyl multiplet at 4.6 ppm. The mass spectrum showed parent ions in the proper isotopic ratios centered at 536 m/e as expected for the molecular weight of the complex.

$\text{cis-Mo(CO)}_4(\underline{10})_2$  Using the same procedure and amounts of reactants as in the preparation of  $\text{cis-Mo(CO)}_4(\underline{8})_2$  it was noticed that the yellow color of the norbornadiene

complex persisted for about one hour. The melting point of the 0.76 g of product after recrystallization was 99-100°. A  $^1\text{H}$  nmr spectrum showed a methyl doublet at 1.33 ppm ( $^3\text{JHCCH} = 6.2$  Hz), a multiplet pattern for the methylene protons at 1.7 ppm different from that observed in cis-Mo(CO) $_4$ (8) $_2$ , a methoxy doublet showing virtual coupling at 3.72 ppm (outer peak separation of 12.2 Hz) and a methinyl multiplet at 4.6 ppm. The same parent ion pattern was noted as for the isomeric complex.

## Results and Discussion

### Carbonyl frequencies

All of the metal carbonyl complexes containing the ligand  $\text{P}(\text{OCH}_2)_2\text{CH}$ , 73, were characterized by their physical properties,  $^1\text{H}$  nmr spectra and mass spectra or elemental analysis.

The  $\nu_{\text{CO}}$  absorptions of complexes of 73 are listed in Table 20 along with those values obtained from analogous complexes containing  $\text{P}(\text{OMe})_3$  and  $\text{P}(\text{OCH}_2)_3\text{CR}$ . Comparison of this data shows that these absorptions rise from  $\text{P}(\text{OMe})_3$  to  $\text{P}(\text{OCH}_2)_3\text{CR}$  to  $\text{P}(\text{OCH}_2)_2\text{CH}$  demonstrating the same ligand order discussed earlier. It has already been shown via the protonation, boron adduct and phenol shift studies that the donor power of phosphorus decreases upon constraint. However,

Table 20. Carbonyl stretching frequencies of metal carbonyl complexes substituted with phosphites

Compound	$\nu_{\text{CO}}^{a,b}$					Solvent	Reference
	$A_1^2$	$B_1$	$A_1^1$	E	$E(^{13}\text{C})$		
$\text{Cr}(\text{CO})_5(\underline{12})$	2073.4	1985.2	1963.0	1948.0	— <sup>c</sup>	$\text{C}_{16}\text{H}_{34}$	163
$\text{Cr}(\text{CO})_5(\underline{4})$	2082 w	— <sup>c</sup>	1995 sh	1960 vs	— <sup>c</sup>	$\text{CHCl}_3$	165
$\text{Cr}(\text{CO})_5(\underline{73})$	2085 w	— <sup>c</sup>	1984 m	1972 s	1942 vw	$\text{CDCl}_3$	This work
$\text{Mo}(\text{CO})_5(\underline{12})$	2082 w	1997 vw	1970 m	1956 vs	— <sup>c</sup>	$\text{C}_6\text{H}_{12}$	159
$\text{Mo}(\text{CO})_5(\underline{4})$	2085 w	— <sup>c</sup>	2001 sh	1962 vs	— <sup>c</sup>	$\text{CHCl}_3$	165
$\text{Mo}(\text{CO})_5(\underline{73})$	2091 w	— <sup>c</sup>	1988 m	1978 s	1946 w	$\text{C}_6\text{H}_{12}$	This work

<sup>a</sup>Frequencies are in  $\text{cm}^{-1}$ .

<sup>b</sup>w = weak, vw = very weak, m = medium, s = strong, vs = very strong, sh = shoulder.

<sup>c</sup>Not observed.

Table 20. (Continued)

Compound	$\nu_{\text{CO}}$					Solvent	Reference
	$A_1^2$	$B_1$	$A_1^1$	E	$E(^{13}\text{C})$		
$\text{W}(\text{CO})_5(\underline{12})$	2080.5	1988.0	1951.1	1936.2	— <sup>c</sup>	$\text{C}_{16}\text{H}_{34}$	163
$\text{W}(\text{CO})_5(\underline{4})^{\text{d}}$	2085.5	1989.0	1963.5	1958.0	1928.0	$\text{C}_6\text{H}_{12}$	98
$\text{W}(\text{CO})_5(\underline{73})$	2091 w	— <sup>c</sup>	1982 m	1971 s	1940 w	$\text{C}_6\text{H}_{12}$	This work
$\text{W}(\text{CO})_5(\underline{1})$	2090 w	— <sup>c</sup>	1982 m	1972 s	1941 w	$\text{C}_6\text{H}_{12}$	This work
$\text{W}(\text{CO})_5(\underline{7})$	2084 w	1995 w	1966 m	1955 s	1934 w	$\text{C}_6\text{H}_{12}$	This work
$\text{W}(\text{CO})_5(\underline{65})$	2080 w	1996 w	1969 m	1962 s	1933 vw	$\text{C}_6\text{H}_{12}$	This work
$\text{W}(\text{CO})_5(\underline{3})$	2089 w	2003 w	1985 m	1959 s	— <sup>c</sup>	$\text{C}_6\text{H}_{12}$	This work
		$A_1^2$	$A_1$	$B_1$	$B_2$		
$\text{cis-Mo}(\text{CO})_4(\underline{12})_2$		2037	1945	1926	1921	Hydrocarbon	162
$\text{cis-Mo}(\text{CO})_4(\underline{4})_2$		2049 vw	1984 sh	1940 vs	— <sup>c</sup>	$\text{CHCl}_3$	165
$\text{cis-Mo}(\text{CO})_4(\underline{73})_2$		2061 w	1980 sh	1959 vs	— <sup>c</sup>	$\text{CDCl}_3$	This work

<sup>d</sup>The bicyclic ligand had a pentyl group on the bridgehead carbon.

Table 20. (Continued)

Compound	$A_1^2$	$A_1^1$	E	Solvent	Reference
$\text{Fe}(\text{CO})_4(\underline{12})$	2063 s	1994 s	1964 vs 1952 vs <sup>e</sup>	$\text{C}_6\text{H}_{12}$	161
$\text{Fe}(\text{CO})_4(\underline{4})$	2065 s	1996 vs	1965 vs	$\text{CHCl}_3$	165
$\text{Fe}(\text{CO})_4(\underline{73})$	2078 m	2006 s	1984 vs	$\text{C}_6\text{H}_{12}$	This work
			$E'$		
<u>trans</u> - $\text{Fe}(\text{CO})_3(\underline{12})_2$		1923 vs	1914 vs <sup>f</sup>	$\text{C}_6\text{H}_{12}$	161
<u>trans</u> - $\text{Fe}(\text{CO})_3(\underline{4})_2$		1933 vs		$\text{CHCl}_3$	165
<u>trans</u> - $\text{Fe}(\text{CO})_3(\underline{73})_2$		1962 vs		$\text{CDCl}_3$	This work

<sup>e</sup>The E mode is split into two bands.

<sup>f</sup>The E' mode is split into two bands.

Table 20. (Continued)

Compound	A <sub>1</sub>	B <sub>1</sub>	Solvent	Reference
Ni(CO) <sub>2</sub> ( <u>12</u> ) <sub>2</sub>	2024	1970	C <sub>16</sub> H <sub>34</sub>	164
Ni(CO) <sub>2</sub> ( <u>4</u> ) <sub>2</sub>	2048 s	1994 vs	CHCl <sub>3</sub>	165
Ni(CO) <sub>2</sub> ( <u>73</u> ) <sub>2</sub>	2068 s	2018 vs	CDCl <sub>3</sub>	This work
	A <sub>1</sub>			
Ni(CO)( <u>12</u> ) <sub>3</sub>	1963		C <sub>16</sub> H <sub>34</sub>	164
Ni(CO)( <u>4</u> ) <sub>3</sub>	1997 vs		CHCl <sub>3</sub>	165
Ni(CO)( <u>73</u> ) <sub>3</sub>	2017 vs		CDCl <sub>3</sub>	This work

phosphoryl stretching frequencies show an increase with constraint of alkoxy groups which has been attributed to increased pi bonding in the P=O link (18). Enhancement of the pi acidity of the phosphorus d orbitals has been rationalized as a means to compensate for the reduction in P-O pi bonding resulting from more tetrahedral POC angles (18). It is, therefore, not possible to decide whether to ascribe the higher  $\nu_{\text{CO}}$  values to the decreased basicity or increased pi acidity of phosphorus or both. Although the reduced steric interaction of ligand with the metal carbonyls could also account for the above trend if pi bonding were the dominant factor, it is more likely that the rise in  $\nu(\text{CO})$  is a consequence of the sigma and pi electronic changes stemming from the "hinge" effect.

Previously, only a metal complex of  $\text{P}(\text{OCH}_2)_2\text{CEt}$  had been reported (170). Based on  $^{51}\text{V}$  nmr and infrared spectra on complexes of  $\text{V}(\text{CO})_5\text{L}^-$ , this constrained phosphite was concluded to have a very high ligating strength compared to 15 other ligands studied.

Table 20 also lists  $\nu_{\text{CO}}$  values for monosubstituted tungsten carbonyl complexes containing a six-membered ring phosphite, 7, and a five-membered ring phosphite, 65. These, however, are very similar and no conclusions can be drawn about their relative ligating strengths.

The preparation of  $\text{Ni}(\text{CO})_2(\underline{73})_2$  (see Experimental) was actually intended to synthesize  $\text{Ni}(\text{CO})_3(\underline{73})$  since the mole ratio of  $\text{Ni}(\text{CO})_4$  to 73 was 37:29. Another attempt to synthesize the monosubstituted product using the same procedure but a mole ratio of  $\text{Ni}(\text{CO})_4$  to 73 of 37:14 also resulted in the disubstituted product. The reason for this behavior is unclear but perhaps it is related to the greater pi acidity and/or the reduced steric requirements of phosphite 73.

Infrared data for the molybdenum carbonyl complexes of 8 and 10 are recorded in Table 21. The cis complexes are not identical because distinct differences in their infrared absorptions are noted in both  $\text{CHCl}_3$  and  $\text{C}_6\text{H}_{12}$ . Furthermore, these complexes have different melting points and  $^1\text{H}$  nmr spectra of these two complexes do not show the same chemical shifts for the methyl groups nor do the methylene multiplets have the same pattern (Figure 15). From the mass spectral results and the number and relative intensities of the infrared peaks it is clear that the complexes both have the same molecular weight and possess cis geometries. It is reasonable to conclude, therefore, that the ligands are isomeric and that the reaction proceeds stereospecifically.

Evidence for stereoretention in the reaction of 8 and 10 with  $\text{Mo}(\text{CO})_4\text{C}_7\text{H}_8$  to produce cis- $\text{Mo}(\text{CO})_4(\underline{8})_2$  and cis- $\text{Mo}(\text{CO})_4(\underline{10})_2$ , respectively, comes from a comparison of the CO stretching frequencies of the complexes and a

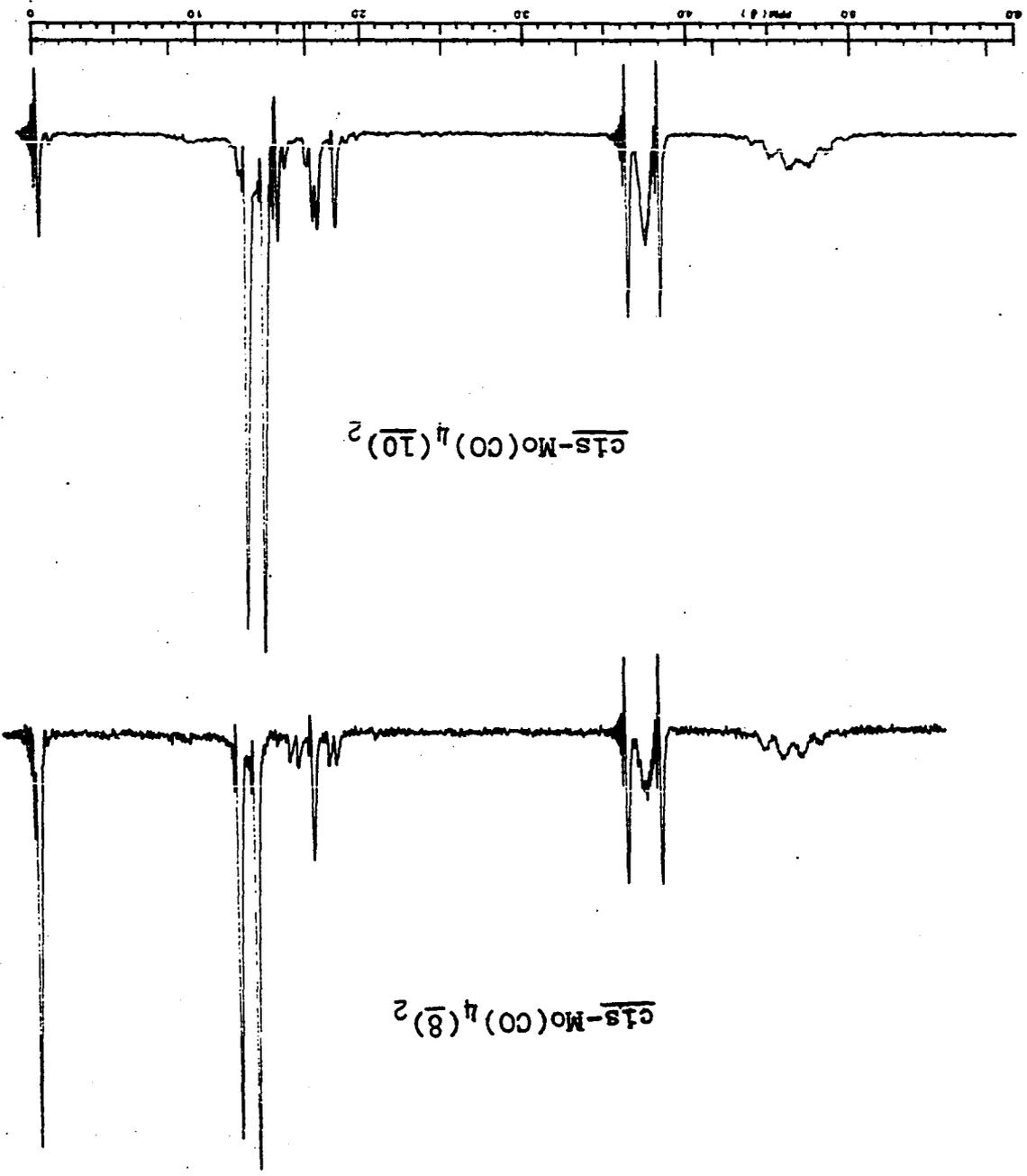
Table 21. Carbonyl stretching frequencies of metal carbonyl complexes substituted with phosphites 8 and 10

Compound	$\nu_{\text{CO}}^{\text{a,b}}$			Solvent
<u>cis</u> -Mo(CO) <sub>4</sub> ( <u>8</u> ) <sub>2</sub>	2040 w	1945 sh	1924 s	CHCl <sub>3</sub>
	2044 w	1965 m	1941 s	C <sub>6</sub> H <sub>12</sub>
<u>cis</u> -Mo(CO) <sub>4</sub> ( <u>10</u> ) <sub>2</sub>	2038 w	1942 sh	1914 s	CHCl <sub>3</sub>
	2040 w	1960 m	1931 s	C <sub>6</sub> H <sub>12</sub>
Mo(CO) <sub>5</sub> ( <u>8</u> )	2080 w	1985 sh	1956 s	CHCl <sub>3</sub>

<sup>a</sup>Frequencies are in cm<sup>-1</sup>.

<sup>b</sup>w = weak, m = medium, s = strong, sh = shoulder.

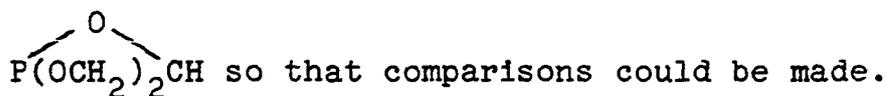
Figure 15. The  $^1\text{H}$  nmr spectra of cis- $\text{Mo}(\text{CO})_4(\underline{8})_2$   
and cis- $\text{Mo}(\text{CO})_4(\underline{10})_2$



consideration of the difference in basicity of 8 and 10. The lower sigma basicity of 8 compared to 10 toward  $\text{BH}_3$  in the stereoretentively formed adducts (23, 64) suggests that cis- $\text{Mo}(\text{CO})_4(\underline{8})_2$  should exhibit higher CO frequencies than cis- $\text{Mo}(\text{CO})_4(\underline{10})_2$  and this is verified experimentally. In view of its lower sigma basicity, phosphite 8 could conceivably be a better pi acid than 10 because of the higher positive charge likely to reside on phosphorus and this would also be consistent with the difference in CO frequencies for the complex.

#### Metal-phosphorus frequencies

A more satisfying conclusion about the importance of M-P pi bonding could stem from the study of M-P stretching frequencies and assignments of such frequencies have been made for a number of zero valent metal complexes of  $\text{P}(\text{OCH}_2)_3\text{CMe}$  (18, 152, 154). These assignments were made possible because this highly symmetrical ligand has no vibrations in the infrared region from 265 to  $100\text{ cm}^{-1}$ . In this work, assignment of  $\nu(\text{M-P})$  was sought for complexes containing the ligand



In Table 22 are listed the infrared bands found in the region from  $340$  to  $100\text{ cm}^{-1}$  for complexes of  $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{P}(\text{OCH}_2)_2\text{CH} \end{array}$ . Unfortunately, a spectrum of the ligand itself does show a weak broad band in that region at  $205\text{-}210\text{ cm}^{-1}$  which is

Table 22. Infrared bands observed in the metal-phosphorus region for two bicyclic phosphites<sup>a,b</sup>

Compound	Ligand				
	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{P}(\text{OCH}_2)_2\text{CH}, \underline{73} \end{array}$			$\text{P}(\text{OCH}_2)_3\text{CMe}^c, \underline{4}$	
Cr(CO) <sub>5</sub> L	233 w	189 s	183 m sh	179 m sh	164
Mo(CO) <sub>5</sub> L		210 s	178 s	161 s	195
W(CO) <sub>5</sub> L	220 w br	198 s	180 s	162 m	180
Fe(CO) <sub>4</sub> L	256 w br	204 s	175 s		169
Ni(CO) <sub>2</sub> L <sub>2</sub>	275 m	214 w br	176 s	138 w br	155, 141
Ni(CO)L <sub>3</sub>	295 m	243 w	182 s	166 m	157, 151
NiL <sub>4</sub>	309 m	219 w br	189 s	175 m sh	157, 156

<sup>a</sup>Frequencies in cm<sup>-1</sup>.

<sup>b</sup>W = weak, m = medium, s = strong, br = broad, sh = shoulder.

<sup>c</sup>References 18, 153 and 154.

possibly due to intraligand vibrations. Thus, coupling of this vibration with the M-P band(s) may in part account for the greater number of bands observed in this region than for analogous complexes of  $P(OCH_2)_3CMe$ .

Assignment of the M-P frequencies is difficult with the number of bands observed and the limited amount of data. However, all of the metal complexes of 73 except that of  $Mo(CO)_5L$  show a weak band in the range from 214 to 256  $cm^{-1}$  which can be attributed to the intraligand mode observed in the free ligand at 205-210  $cm^{-1}$ . Only the nickel complexes of 73 display a medium intensity band above 270  $cm^{-1}$ . While this band is displaced to higher energy with continued phosphite substitution as observed for the weighted average of the asymmetric and symmetric stretch in  $Ni(CO)_{4-x}(P(OCH_2)_3CMe)_x$  (18), two other arguments disfavor assignment of the bands above 270  $cm^{-1}$  to the Ni-P stretching mode. Firstly, the expected presence of a symmetric and an asymmetric stretching mode would not be realized since the weaker band between 214-243  $cm^{-1}$  is probably an intraligand mode. Secondly, it would be unusual if the Ni-P stretching frequencies in  $Ni(CO)_{4-x}(\underline{73})_x$  ( $x = 2, 3$  or  $4$ ) were approximately twice as large as those assigned to the Ni-P stretching frequencies in  $Ni(CO)_{4-x}(\underline{4})_x$  ( $x = 2, 3$  or  $4$ ). It is tentatively concluded that the two lower energy bands observed for each nickel complex are more appropriately assigned to M-P stretching frequencies. A raman spectrum of  $Ni(\underline{1})_4$  revealed a strong

band at  $170\text{ cm}^{-1}$  which can be assigned to the  $A_1$  vibrational mode in tetrahedral symmetry. This mode in  $\text{Ni}(\underline{4})_4$  has been observed at  $146\text{ cm}^{-1}$  (171) and measured independently here at  $152\text{ cm}^{-1}$ . For two other complexes,  $\text{Cr}(\text{CO})_5\text{L}$  and  $\text{Fe}(\text{CO})_4\text{L}$  ( $\text{L} = \underline{73}$ ), the observed infrared bands are all higher than the assigned M-P bands for the analogous complexes where L is  $\underline{4}$ . Thus, for five of the complexes of  $\underline{73}$  it appears that the M-P bond is stronger than the M-P bond in the same complexes where L is  $\underline{4}$  assuming that frequency increases with bond order in these systems. Since sigma basicity has been found to decrease from  $\underline{73}$  to  $\underline{4}$ , the increased strength of the metal-phosphorus bond may be accounted for by the greater pi acidity of the phosphorus d orbitals. Furthermore, the above results agree with the conclusion drawn earlier from phosphoryl stretching frequencies (18) that the pi accepting ability of phosphorus increases upon constraint of the alkoxy groups.

Unfortunately, for two complexes,  $\text{Mo}(\text{CO})_5(\underline{73})$  and  $\text{W}(\text{CO})_5(\underline{73})$ , the three observed bands in the metal-phosphorus region found at higher and lower energy than the assigned M-P band in the complexes of  $\underline{4}$ , do not permit any conclusions about the trend in M-P and additional data are needed to clarify this point.

In Tables 23 and 24 are found  $^{31}\text{P}$  and  $^{13}\text{C}$  nmr spectral data, respectively. These data are listed here for completeness and offers further characterization for some of the metal

Table 23.  $^{31}\text{P}$  chemical shifts for phosphite substituted metal carbonyl complexes

Compound	$\delta^{31}\text{P}^a$
$\text{Cr}(\text{CO})_5(\underline{69})$	-121 <sup>b</sup>
$\text{Mo}(\text{CO})_5(\underline{69})$	-146 <sup>b</sup>
$\text{W}(\text{CO})_5(\underline{69})$	-136 <sup>c</sup>
$\text{W}(\text{CO})_5(\underline{1})$	-140.3 <sup>b</sup>
$\text{Ni}(\underline{1})_4$	-156.2 <sup>b</sup>
$\text{Mo}(\text{CO})_5(\underline{8})$	-154.1 <sup>c</sup>
$\text{cis-Mo}(\text{CO})_4(\underline{8})_2$	-157.1 <sup>b</sup>
$\text{cis-Mo}(\text{CO})_4(\underline{10})_2$	-156.8 <sup>b</sup>
$\text{W}(\text{CO})_5(\underline{7})$	-134.2 <sup>c</sup>
$\text{W}(\text{CO})_5(\underline{65})$	-140.9 <sup>c</sup>
$\text{W}(\text{CO})_5(\underline{3})$	-138.0 <sup>c</sup>

<sup>a</sup>The chemical shifts are in ppm relative to 85%  $\text{H}_3\text{PO}_4$ .

<sup>b</sup>The solvent was  $\text{CDCl}_3$ .

<sup>c</sup>The solvent was a 1:1 mixture of  $\text{CD}_3\text{CN}$  and  $\text{CH}_3\text{CN}$ .

Table 24.  $^{13}\text{C}$  nmr data for metal complexes with phosphite substitution

Compound	Methylene		Bridgehead		Methyl	
	$\delta^{13}\text{C}^a$	$^2\text{JPOC}^b$	$\delta^{13}\text{C}^a$	$^3\text{JPOCC}^b$	$\delta^{13}\text{C}^a$	$^4\text{JPOCCC}^{b,c}$
$\text{Ni}(\underline{1})_4$	72.8	— <sup>d</sup>	81.4	— <sup>d</sup>	13.9	— <sup>d</sup>
$\text{W}(\text{CO})_5(\underline{1})^e$	74.7	5.9	84.3	— <sup>d</sup>	13.7	10.3

<sup>a</sup>Relative to the carbon-13 in TMS.

<sup>b</sup>In Hz.

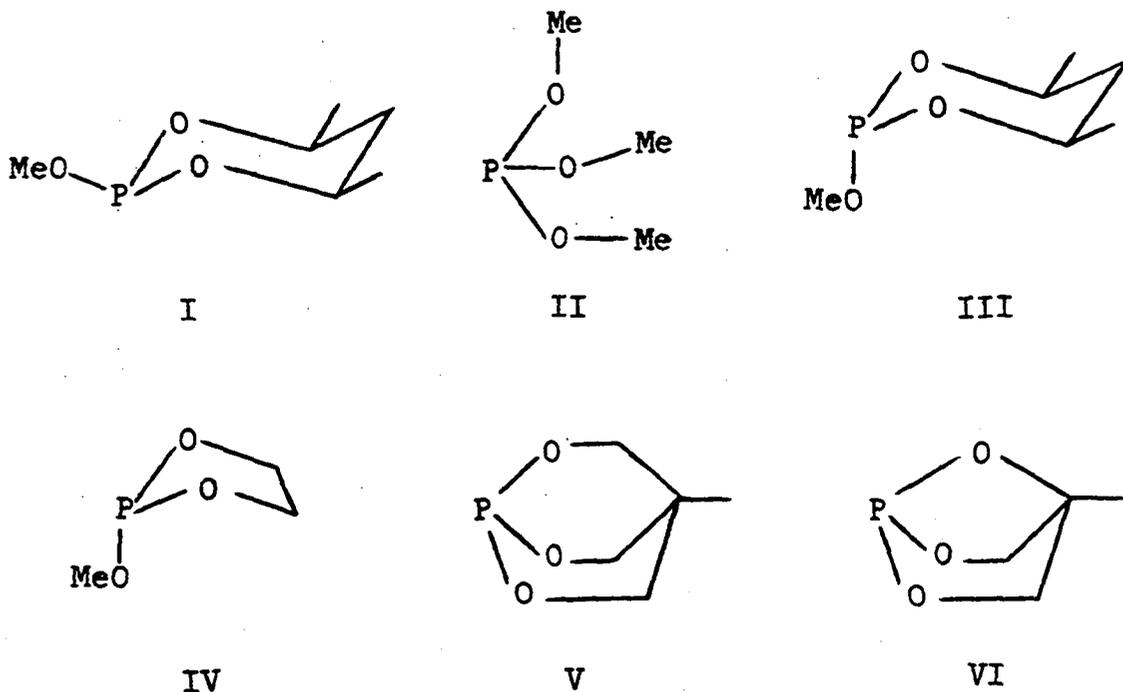
<sup>c</sup>Includes a contribution from POCC coupling.

<sup>d</sup>Not observed.

complexes discussed in this dissertation. Most of the  $^{31}\text{P}$  chemical shifts for these phosphite complexes are from 5 to 45 ppm downfield from their trivalent precursors. Only the  $^{31}\text{P}$  chemical shift of  $\text{W}(\text{CO})_5(\underline{3})$  is 1.1 ppm upfield from  $\delta^{31}\text{P}$  found in  $\text{P}(\text{OCH}_2\text{CF}_3)_3$ . The  $^{13}\text{C}$  shifts for the three types of carbon in 1 (Table 17) have changed very little upon coordination to either nickel or tungsten. In comparing phosphorus to carbon coupling in 1 and  $\text{W}(\text{CO})_5(\underline{1})$ ,  $^2\text{JPOC}$  and  $^4\text{JPOCCC}$  in the tungsten complex are similar to those found in the oxide of 1 while  $^3\text{JPOCC}$  is apparently zero, unlike the value of 17.6 Hz found in the oxide of 1. Not found in Table 24 is the  $^{13}\text{C}$  chemical shift of the cis carbonyl carbons (192.9 ppm) and  $^2\text{JPWC}$  (9.6 Hz). The  $^{13}\text{C}$  chemical shift of the trans carbonyl and its coupling to phosphorus was not observed probably owing to its low intensity. Furthermore, since  $^{183}\text{W}$  is only 14.3% abundant, its coupling to any carbon was also not observed due to the low intensity of the  $^{13}\text{C}$  peaks.

## CONCLUSIONS

The main purpose of this investigation which was to elucidate the ligating properties of the phosphites shown below to various Lewis acids has been fulfilled. The results



can be satisfactorily explained in terms of the "hinge" and orbital repulsion effects. From the rise in  $\nu(\text{BH})$  and the corresponding decrease in  $^1\text{JP}^{11}\text{B}$  found in borane adducts of I to VI, the basicity of the phosphorus lone pair toward  $\text{BH}_3$  is found to decrease. This is supported by hydrogen bonding experiments in which  $\Delta\nu(\text{OH})$  was measured on phenol solutions of the phosphites and their oxides. With phosphites two bands were observed but  $\Delta\nu(\text{OH})$  decreased for both from II to VI (no experiments were done with I) showing that the enthalpy of hydrogen bonding is reduced at phosphorus and at the alkoxy

oxygen. The phenol shift experiments with the oxides of I to VI show a more satisfying decrease in the basicity of the phosphoryl oxygen whose donor power is linked to the negative charge on the phosphorus. Values of  $^1J_{PH}$  obtained from the protonation of I to VI compliment the above basicity trend except for the reversal of I and II. This has been tentatively explained by the greater polarizing power of the proton which brings the "hinge" effect into play for I. The decreasing sigma basicity of the phosphorus lone pair from II to V to VI is accompanied by an increase in the pi acidity of the phosphorus d orbitals. Thus, the carbonyl stretching frequencies of metal carbonyl complexes reach their highest values when substituted with VI. Finally, metal-phosphorus frequencies are found to be larger in complexes of VI than in analogous complexes of V, which lends substantial support to the hypothesis of enhanced pi acidity of the phosphorus d orbitals.



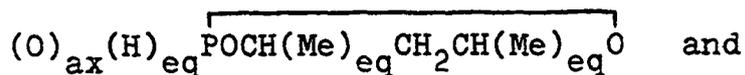
phosphanes,  $X_2PPY_2$ , where X and Y =  $CF_3$ , F, Cl or H, and  $F_2POPF_2$ . Monoprotonation should be readily achieved but diprotonation might be more difficult because of the dipolar effect discussed earlier. The cyclic phosphines,  $(CF_3P)_n$  ( $n = 4$  or  $5$ ), should also be included in this study.

While many acyclic phosphines have been protonated, attempts should be made to protonate the bicyclic phosphines  $P(CH_2CH_2)_3CR$  and  $P(CH_2CH_2)_2CH$ , the bifunctional ligand  $P(CH_2CH_2)_3P$  and a suitable derivative of phosphabenzene. In addition, four-, five- and six-membered ring monocyclic phosphines should be protonated. As in the phosphites, an upward trend in  $^1J_{PH}$  may be observed upon constraint of the alkyl groups.

The inability of the bicyclic thiophosphite,  $P(SCH_2)_3CMe$ , to remain intact upon protonation and the complexity of the  $^{31}P$  nmr spectrum prompts additional experiments. The acyclic species,  $HP^+(SMe)_nF_{3-n}$  should provide a starting point in terms of finding representative PH, PSCH and PF couplings as well as chemical shifts. The monocyclic compounds  $MeSPSCH_2CH_2S$ ,  $MeSPSCH_2CH_2CH_2S$  and  $FPSCH_2CH_2CH_2S$  should be protonated since this would aid in elucidating the nature of the species formed when  $P(SCH_2)_3CMe$  is protonated.

Since it has been found that the ring-locked phosphites, 8 and 10, display  $^1J_{PH}$  values which are indicative of

phosphorus basicity, the isomeric hydrogen phosphates,



$(O)_{eq}(H)_{eq} \overbrace{POCH(Me)_{eq}CH_2CH(Me)_{eq}}^O$  should be protonated at the phosphoryl oxygen and observation of PH coupling made.

The series,  $P(Me)_{3-n}F_n$ ,  $P(CF_3)_{3-n}F_n$  and  $P(OMe)_{3-n}F_n$ , where  $n = 0, 1$  and  $2$ , and  $P(OC_6F_5)_3$  should be protonated to determine the influence of fluorine substitution upon  $^1J_{PH}$ . This is particularly true for  $H^+PF_2OMe$  since both  $^1J_{PH}$  and  $^1J_{PF}$  would aid in the assignment of these parameters for the difluorinated product of phosphite 1.  $PF_2Br$ ,  $PFBr_2$  and  $PFClBr$  should be protonated to complete the phosphorus trihalide series and protonation of  $PX_3$  where  $X$  is any of the pseudohalides,  $CN$ ,  $NCO$  or  $NCS$ , would also be informative.

Another endeavor might be the isolation of some of the stable protonated compounds as salts using different and larger counteranions which would be nonnucleophilic. Of the phosphorus trihalides,  $(HPF_3^+)(X^-)$  would possibly be most amenable to separation since fluorination of the other ions occurs in the acid. Attempts should also be made to isolate stable salts of an acyclic, monocyclic and bicyclic protonated species. Formation of single crystals would allow an X-ray structural investigation to determine the geometries around phosphorus.

Unfortunately, in the phenol shift studies,  $\Delta\nu(\text{OH})$  was

not obtained for  $\text{OP}(\text{OCH}_2)_2\text{CMe}$  because of its limited solubility. A possible remedy would be to synthesize a derivative with a larger alkyl group at the bridgehead carbon which would lend greater solubility.

A large problem still exists in making definite assignments of M-P stretching frequencies in metal complexes of

$\text{P}(\text{OCH}_2)_2\text{CH}$ . A possible solution to this would be the synthesis

of analogous complexes incorporating the ligand  $\text{As}(\text{OCH}_2)_2\text{CR}$ . Spectra of the arsenite complexes would enable assignment of M-P bands since the M-As stretching mode should lie at lower energy.

PART II. REACTION OF ARSENITES WITH ALKYL HALIDES;  
PRELIMINARY RESULTS

## INTRODUCTION

Triesters of phosphorous acid undergo the well-known Michaelis-Arbusov reaction with aryl or alkyl halides as depicted below (172-174). If R'X is a diatomic halogen, the



reaction proceeds in the same manner (172-174) and recently the intermediate  $[\text{BrP}(\text{OCH}_2)_3\text{CMe}]^+\text{Br}^-$  formed from the reaction of  $\text{P}(\text{OCH}_2)_3\text{CMe}$  and  $\text{Br}_2$  was detected by nmr (73). The formation of a strong phosphorus oxygen double bond appears to be the driving force for reaction 13.

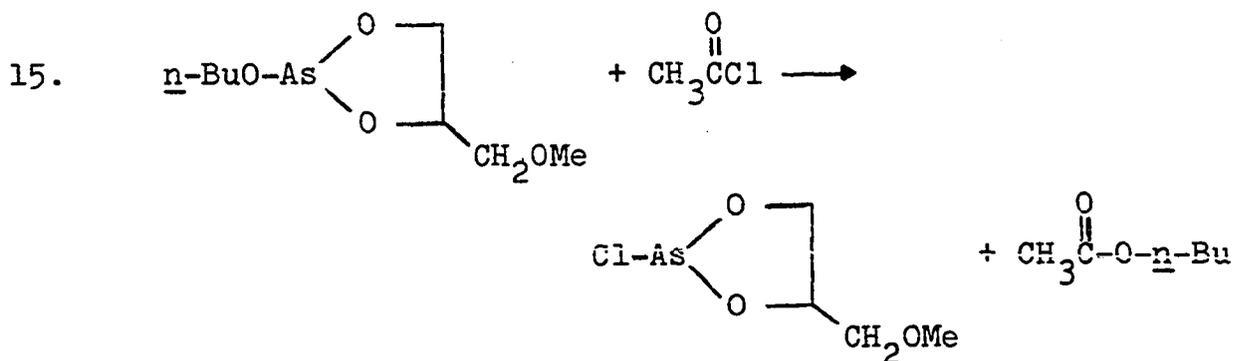
The analogous esters of arsenious and antimonous acids do not react in the above manner, but undergo an exchange reaction resulting in the formation of a pnictogen (Pn) halogen bond and an ether (Reaction 14).



The course of this reaction appears to be governed by the nucleophilic character of R'X since arsenic and antimony double bonds to oxygen are much weaker than the phosphoryl bond. In contrast to the Michaelis-Arbusov reaction, very little has been done to study the scope of reaction 14.

Dubrovina (175) has reported the only investigation of the exchange reaction involving esters of antimonous acid. For equimolar quantities of  $\text{Sb}(\text{OR})_3$  ( $\text{R} = \text{Et}, \text{Bu}$  or iso-Am) and  $\text{RX}$  ( $\text{R} = \text{Me}, \text{Et}$  or  $\text{Pr}$ ;  $\text{X} = \text{Br}$  or  $\text{I}$ ) heating at temperatures over  $150^\circ$  for about 5 hours or alternatively at  $80^\circ$  for about 30 hours was necessary to effect monosubstitution. However, equimolar quantities of  $\text{CH}_3\text{C}(\text{O})\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) reacted immediately with  $\text{Sb}(\text{OR})_3$  ( $\text{R} = \text{Me}, \text{Et}, \text{n-Pr}$  or  $\text{n-Bu}$ ) at room temperature according to reaction 14 and 2:1 ratios of the reactants gave  $\text{Sb}(\text{OR})\text{X}_2$ .

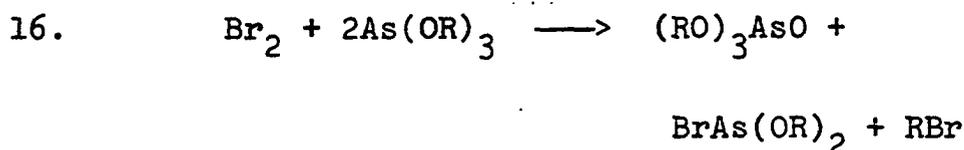
The reaction of arsenites with alkyl halide is limited to acetyl chloride. Kamai and Khisamova (176) have studied the reaction of  $\text{CH}_3\text{C}(\text{O})\text{Cl}$  with  $\text{As}(\text{OR})_3$  ( $\text{R} = \text{n-Pr}, \text{iso-Bu}, \text{n-Bu}$  and  $\text{n-Hexyl}$ ) in equimolar ratios and reported a slightly exothermic reaction giving a monosubstituted product. Also of significance, the arsenite shown below reacts without rupture



of the monocyclic ring (177).

Arsenites also react with diatomic halogen but not according to reaction 13 nor reaction 14. Instead, oxidation

of the arsenite results and the overall stoichiometry is shown in reaction 16, having been proved for R = Me, Et, n-Pr, n-Bu and n-Am (178). The proposed mechanism (178) for this reaction involves a five-coordinate intermediate,  $(RO)_3AsBr_2$ ,



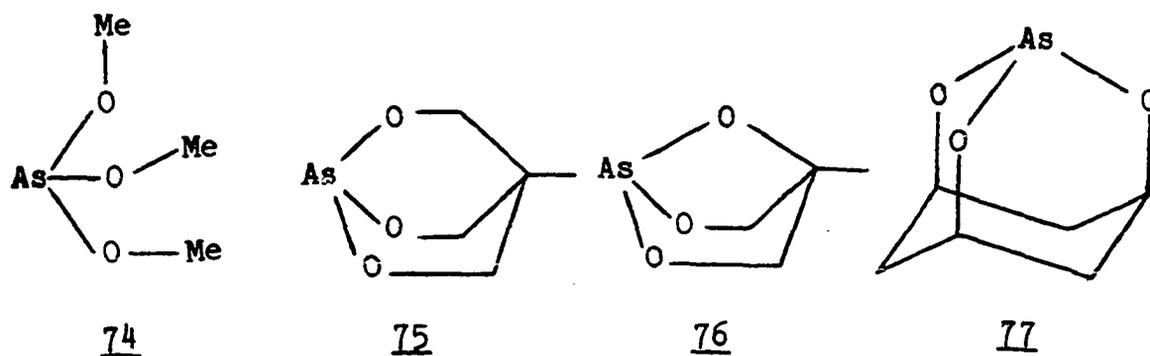
which undergoes exchange with a second alkyl arsenite to give  $BrAs(OR)_2$  and  $(RO)_3As(OR)Br$ . This second five-coordinate intermediate then eliminates alkyl bromide to give the arsenate.

Kolditz and Hass (179) have also shown that the reaction of  $X_2$  ( $X = Cl$  or  $Br$ ) with  $AsF(OR)_2$  or  $AsF_2(OR)$  ( $R = Et$ ) yields  $[As(OR)_4][AsF_6]$ . Again, the mechanism probably involves five-coordinate intermediates and exchange of alkoxy groups and halogen. However, it was suggested that the proposed intermediate  $F_3As(OR)_2$  underwent disproportionation to the final product.

Previous to the present work,  $Ph_3CCl$  had been reacted (180) with the caged arsenite,  $As(OCH_2)_3CCH_3$ , to determine if it would do so in a manner analogous to the reaction of  $P(OCH_2)_3CMe$  with  $Ph_3CCl$  which gave the Arbusov product

$Ph_3C(O)POCH_2C(CH_3)(CH_2Cl)CH_2O$  (181). However, the crystalline

product exhibited a proton nmr spectrum of phenyl (multiplet), methylene (singlet) and methyl (singlet) protons in a 15:2:1 integration ratio, respectively, indicating the cage could be intact. In this part the reaction of  $\text{Ph}_3\text{CCl}$  with the arsenites 74-77 has been explored in a preliminary manner in



order to determine whether the course of the reaction is dependent on constraint of the arsenite ester.

## EXPERIMENTAL

## Materials and Techniques

The acetonitrile used as the solvent in the following experiments was refluxed over and distilled from  $\text{CaH}_2$ . Triphenylchloromethane (Matheson Co.) and all other chemicals were reagent grade. All reactions were performed under a nitrogen blanket since arsenites are readily hydrolyzed by moisture.

The  $^1\text{H}$  nmr spectra were taken on either a Varian Associates A-60 spectrometer or a Hitachi Perkin-Elmer R20b spectrometer operating at 60 MHz. The carbon-13 spectrum was provided by a Bruker HX-90 operating at 22.636 MHz in the Fourier mode. Low resolution mass spectra were obtained on an Atlas CH-4 mass spectrometer while the high resolution mass spectra were provided by an AEI MS-902 spectrometer. The least squares iterative analysis of one nmr spectrum was accomplished with the program ITRCAL (Nicolet Instrument Corp., Madison, Wisconsin), which is based on the more familiar program LAOCOON III.

Preparations

$\text{As}(\text{OMe})_3$ , 74 The preparation of this compound by the reaction of methanol with  $\text{AsCl}_3$  in the presence of N,N-dimethylaniline was not as successful as claimed (182) since some  $\text{ClAs}(\text{OMe})_2$  was identified as a contaminant in the product. Pure  $\text{As}(\text{OMe})_3$  was prepared by adding  $\text{AsCl}_3$  to a suspension of the stronger base, NaOMe, in methanol (183).

As(OCH<sub>2</sub>)<sub>3</sub>CMe, 75 This compound was a gift from a previous member of the Verkade group, prepared according to a published procedure (145).

As(OCH<sub>2</sub>)<sub>2</sub>CMe, 76 Into a tared flask was distilled 22 grams (0.21 mole) of 2-methylglycerol. To this was added 40 grams (0.24 mole) of As(OMe)<sub>3</sub> and 40 ml of DC 550 silicone oil. This mixture was vigorously stirred with a magnetic stirring bar while being slowly heated to 85° with an oil bath. With the aid of a slow N<sub>2</sub> flush over the reaction mixture, most of the methanol was slowly distilled away. The mixture was cooled and about 0.75 grams of NaOMe were added. Distillation was then continued under vacuum until a white crystalline solid began to form in the stillhead. The product was then sublimed three times at 90-95°C onto a cold finger at less than 0.1 mm of Hg to separate it from the silicone oil. Thirty-one grams of white crystalline product in an 84% yield were realized having a melting point of 112-113°. Since this compound was prepared only once, in the same manner as the preparation for P(O)(OCH<sub>2</sub>)<sub>2</sub>CR (34, 35), it is not known whether the silicone oil or NaOMe is needed to ensure a good yield.

Low resolution mass spectra obtained by heating the sample at 160° and with no heat applied revealed only a small peak at 178 m/e corresponding to the molecular weight; however, peaks at higher mass were also observed. High resolution mass

spectra for which only the inlet path was heated showed a base peak at  $147.9505 \pm 0.0007$  m/e (calcd. 147.9506 m/e) which is consistent with the loss of an  $\text{OCH}_2$  fragment from the parent arsenite and a peak (50% intensity of the base peak) at  $299.6869 \pm 0.0015$  (calcd. 299.6880) for the  $\text{As}_4$  molecule. A peak (10% intensity of the base peak) at 396 m/e whose exact mass was not determined is the correct molecular weight for  $\text{As}_4\text{O}_6$ . These results show that extensive reorganization of the parent arsenite must take place in the mass spectrometer since elemental analysis (Spang Micro. Lab., Ann Arbor, Michigan) showed 26.72% C, 3.78% H and 43.23% As (calcd. 26.97% C, 3.97% H and 42.09% As). A carbon-13 nmr spectrum (TMS reference) showed a triplet for the methylene carbon at 72.6 ppm ( $^1\text{JCH} = 146.3$  Hz), a singlet for the bridgehead carbon at 84.7 ppm and a quartet for the methyl carbon at 14.7 ppm ( $^1\text{JPH} = 126.5$  Hz). A  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ) showed a methyl singlet at 1.52 ppm and a symmetrical methylene multiplet centered at 3.63 ppm. Analysis of the methylene region as an AA'BB' system, assigning all 24 transitions, resulted in a final rms error of 0.146. The results are summarized and compared to the phosphorus compound in Table 25.

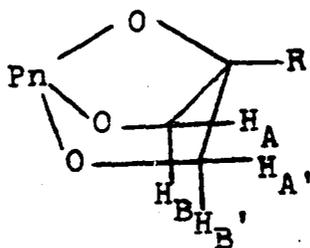


Table 25. Nmr analysis of the methylene resonance of compounds 73 and 76

Compound	Pn	R	JAA'	JBB'	JAB = JA'B'	JAB' = JA'B	$\Delta\delta_{AB}$	Reference
<u>76</u>	As	Me	3.66	-0.01	-7.87	0.43	29.72	This work
<u>73</u>	P	H	3.4	-0.25	-8.12	0.35	14.03	45

As(OCH)<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>, 77 This compound was a gift from a previous member of the Verkade group, prepared according to a published procedure (184).

### Reactions

The following reactions were allowed to proceed at room temperature using about 50 ml acetonitrile as solvent unless otherwise indicated. All solutions were magnetically stirred under a nitrogen atmosphere.

As(OMe)<sub>3</sub> and (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCl The reaction of As(OMe)<sub>3</sub> with (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCl was carried out in the ratios of 1:1, 1:2 and 1:3, respectively. For these ratios 2.79 g (10.0 mmole), 5.57 g (20.0 mmole) or 8.36 g (30.0 mmole) of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCl were added to individual solutions of 1.68 g (10.0 mmole) of As(OMe)<sub>3</sub>.

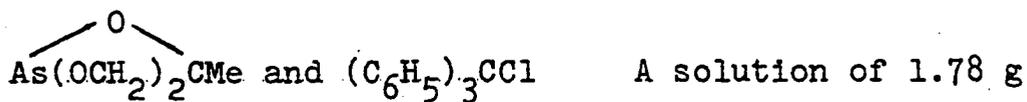
The course of each reaction was followed by nmr spectroscopy and all were essentially complete within 5 hours. The starting arsenite, As(OMe)<sub>3</sub>, and the products of the exchange reaction, As(OMe)<sub>2</sub>Cl and As(OMe)Cl<sub>2</sub>, have recorded (185) chemical shifts (all singlets) of 3.57 ppm, 3.74 ppm and 3.94 ppm, respectively, while the chemical shifts in this work taken in CH<sub>3</sub>CN are all consistently lower, being 3.51 ppm, 3.68 ppm and 3.84 ppm, respectively. The formation of the ether, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>COMe, was noted by the appearance and growth of the singlet for the methyl group at 2.95 ppm. An

authentic sample of  $(C_6H_5)_3COMe$  was made by dissolving  $(C_6H_5)_3CCl$  in methanol and allowing the product to crystallize (186). An nmr of this substance in  $CD_3CN$  showed a multiplet centered at 7.3 ppm for the phenyl protons and a singlet at 2.95 ppm for the methyl protons.

$As(OCH_2)_3CCH_3$  and  $(C_6H_5)_3CCl$  In a 1:3 ratio of reactants, a solution of 1.0 g (5.2 mmole) of  $As(OCH_2)_3CMe$  and 4.35 g (15.6 mmole) of  $(C_6H_5)_3CCl$  was stirred for several days. The white precipitate (3.0 g) was collected and was best purified by recrystallization from hot cyclohexane (m.p. 243-244°). Elemental analysis (Huffman Lab., Wheatridge, Colorado) gave 87.5% C and 6.75% H while calculated values for  $((C_6H_5)_3COCH_2)_3CCH_3$  are 87.94% C and 6.38% H. A spectrum of the triether in  $CDCl_3$  shows a broad singlet for the phenyl protons (7.17 ppm) and singlets for the methylene (3.12 ppm) and methyl (0.91 ppm) protons integrating in the correct ratio of 15:2:1, respectively. The yield for the triether is 68%.

In a 1:1 ratio a solution of 0.77 g (4.0 mmole) of  $As(OCH_2)_3CCH_3$  and 1.1 g (4.0 mmole) of  $(C_6H_5)_3CCl$  showed no reaction as indicated by pnmr spectroscopy after two hours. However, after seven hours  $(Ph_3COCH_2)_3CCH_3$  had begun to precipitate. Nmr spectroscopy showed this product was only slightly soluble in  $CH_3CN$  and that there were two peaks (3 Hz separation) centered at 4.1 ppm, possibly due to an intermediate in the reaction. After 22 hours only unreacted

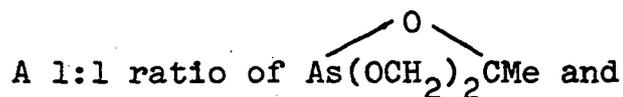
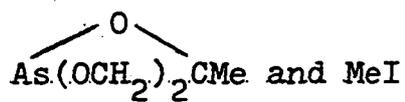
$\text{As}(\text{OCH}_2)_3\text{CCH}_3$ , a small amount of intermediate, and a small amount of triether were detected in solution. The precipitate was filtered and shown to be the triether by nmr spectroscopy and melting point. The solvent was removed from the mother liquor under vacuum but an nmr spectrum of the residue in  $\text{CCl}_4$  was unintelligible because of the broadness of the peaks.



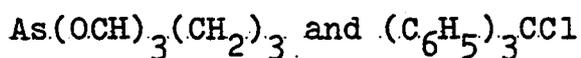
(10.0 mmole) of  $\text{As}(\text{OCH}_2)_2\text{CMe}$  and 2.79 g (10.0 mmole) of  $(\text{C}_6\text{H}_5)_3\text{CCl}$  was stirred for 8 hours during which the appearance of an AB quartet at 4.21 ppm and the disappearance of the AA'BB' pattern for the methylene protons of III at 3.58 ppm indicated the reaction was complete. Acetonitrile was removed under vacuum until the solution became cloudy and further cooling produced 3.81 grams of a white product. Recrystallization was accomplished by cooling acetonitrile or ether solutions to obtain a colorless product having a melting point of 125-127° when completely free of solvent. A mass spectrum of the recrystallized material revealed parent ions at 456 m/e and 458 m/3. This corresponds to the sum of the molecular weights of the two reactants and the isotopic ratios and molecular ions indicate the product contains one chlorine. The nmr spectrum of this compound,

$\overline{\text{ClAsOCH}_2\text{C}(\text{Me})(\text{CH}_2\text{OC}(\text{C}_6\text{H}_5)_3)\text{O}}$ , 78, in several solvents is discussed in detail in the Results and Discussion.

In a 1:3 ratio, 0.89 g (5.0 mmole) of  $\text{As}(\text{OCH}_2)_2\text{CMe}$  was reacted with 4.18 g (15.0 mmole) of  $\text{Ph}_3\text{CCl}$ . However, after 8 days, nmr spectroscopy revealed the same product as obtained in the 1:1 ratio of reactants.



MeI at room temperature for two days and the same ratio of reactants in a sealed tube at  $130^\circ$  for 10 hours failed to give any reaction as indicated by nmr spectroscopy.



A solution of 1.0 g

(4.9 mmole) of  $\text{As}(\text{OCH}(\text{CH}_2)_3)_3$  and 4.10 g (14.7 mmole) of  $(\text{C}_6\text{H}_5)_3\text{CCl}$  was stirred for 4 days, but because no precipitate had formed no reaction was assumed to have occurred. This same solution was then heated to reflux for another 4 days. The solvent was removed from an aliquot of the solution under vacuum and the pnmr spectrum of the residue, dissolved in  $\text{CCl}_4$ , showed that no reaction had occurred.

## RESULTS AND DISCUSSION

The reaction of alkyl halides with arsenites has received limited attention as evidenced by the fact that only acetyl chloride has been reacted with acyclic arsenites (176) and with only one monocyclic arsenite (177). Only mono-substitution of halide at arsenic has been observed although there was no apparent attempt to carry out further substitution. The other product of such an exchange reaction is an ether. Thus, arsenites react differently with alkyl halide than phosphites since the latter undergo the Michaelis-Arbusov reaction resulting in formation of a P=O bond and release of a different alkyl halide.

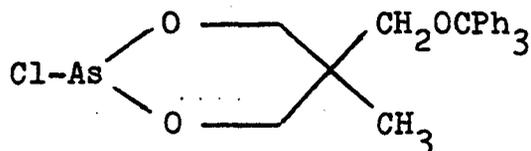
Although this work does not encompass monocyclic phosphites, it does include a complete study of  $\text{As}(\text{OMe})_3$  with different ratios of  $\text{Ph}_3\text{CCl}$ . Furthermore, the reaction of  $\text{Ph}_3\text{CCl}$  with three bicyclic arsenites,  $\text{As}(\text{OCH}_2)_3\text{CMe}$ ,  $\text{As}(\text{OCH}_2)_2\text{CMe}$ , and  $\text{As}(\text{OCH})_3(\text{CH}_2)_3$ , shows that each of them behaves uniquely.

In a 1:1 ratio of  $\text{As}(\text{OMe})_3$  and  $\text{Ph}_3\text{CCl}$ , nmr spectroscopy indicates that the reaction is complete after 3 hours by the formation of  $\text{As}(\text{OMe})_2\text{Cl}$  and  $(\text{C}_6\text{H}_5)_3\text{COMe}$  and the disappearance of  $\text{As}(\text{OMe})_3$ . No  $\text{As}(\text{OMe})\text{Cl}_2$  was detected. In the 1:2 ratio the exchange product,  $\text{As}(\text{OMe})_2\text{Cl}$ , was formed first within about one hour and  $\text{As}(\text{OMe})\text{Cl}_2$  did not appear until all of the

As(OMe)<sub>3</sub> had reacted in the first step. After this the amount of As(OMe)Cl<sub>2</sub> steadily grew at the expense of As(OMe)<sub>2</sub>Cl but the latter did not completely disappear even after 24 hours. However, the ratio of the total integration of the methoxy protons of the arsenic intermediates to the methyl protons of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>COMe indicates that all of the (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCl had reacted. In the 1:3 ratio the reaction is initially very rapid since only As(OMe)<sub>2</sub>Cl and As(OMe)Cl<sub>2</sub> were detected after 1 hour. After 4 hours only As(OMe)Cl<sub>2</sub> was present and integration showed the reaction was 80% complete. There was no further change even after 24 hours.

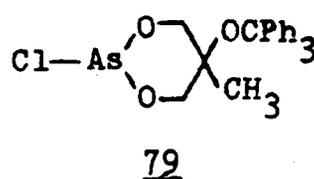
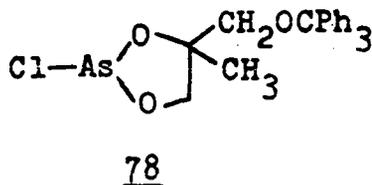
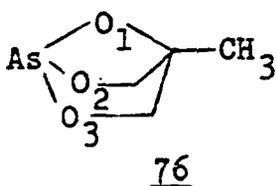
Thus, As(OMe)<sub>3</sub> reacts with Ph<sub>3</sub>CCl in an exchange reaction (172) by stepwise replacement of methoxy groups. That As(OMe)Cl<sub>2</sub> is not the sole arsenic product in a 1:2 reactant ratio of As(OMe)<sub>3</sub> to Ph<sub>3</sub>CCl can perhaps be attributed to a rapid scrambling reaction (185) which gives AsCl<sub>3</sub> (undetected by nmr) and As(OMe)<sub>2</sub>Cl.

The bicyclic arsenite, As(OCH<sub>2</sub>)<sub>3</sub>CMe, in both a 1:1 and 1:3 ratio with Ph<sub>3</sub>CCl gives the triether (Ph<sub>3</sub>COCH<sub>2</sub>)<sub>3</sub>CCH<sub>3</sub>, which was characterized by nmr spectral and elemental analysis. Since sequential substitution occurred at arsenic for acyclic arsenites, the same might have been expected for the above caged arsenite in 1:1 reactant ratios to yield the six-membered ring chloroarsenite shown. However, the triether formed in preference leaving unreacted As(OCH<sub>2</sub>)<sub>3</sub>CMe. The only

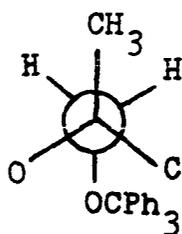


evidence for the cyclic chloroarsenite intermediate (which is tenuous at best) is the appearance of two low intensity peaks (3 Hz separation) centered at 4.1 ppm. These absorptions could be the inner peaks of an AB quartet expected for the ring methylene protons. Corresponding peaks for the other methylene protons and the methyl group could well be hidden under the analogous peaks of the triether. An attempt to isolate this intermediate was unsuccessful.

The reaction of  $\text{As}(\text{OCH}_2)_2\text{CMe}$  with  $\text{Ph}_3\text{CCl}$  in both 1:1 and 1:3 ratios, respectively, was expected to result in the formation of  $(\text{Ph}_3\text{COCH}_2)_2(\text{Ph}_3\text{CO})\text{CMe}$  analogous to the reaction of the bicyclic arsenite  $\text{As}(\text{OCH}_2)_3\text{CMe}$ . However, the crystalline compound obtained in high yield for a 1:1 ratio of reactants was revealed by a mass spectrum to contain an atom of chlorine with a molecular weight corresponding to the sum of the mass of the reactants. This evidence suggested that only one As-O bond in the bicyclic structure had been broken in an exchange reaction resulting in a monocyclic chloroarsenite. The two isomers, 78 and 79, are possible reaction products.

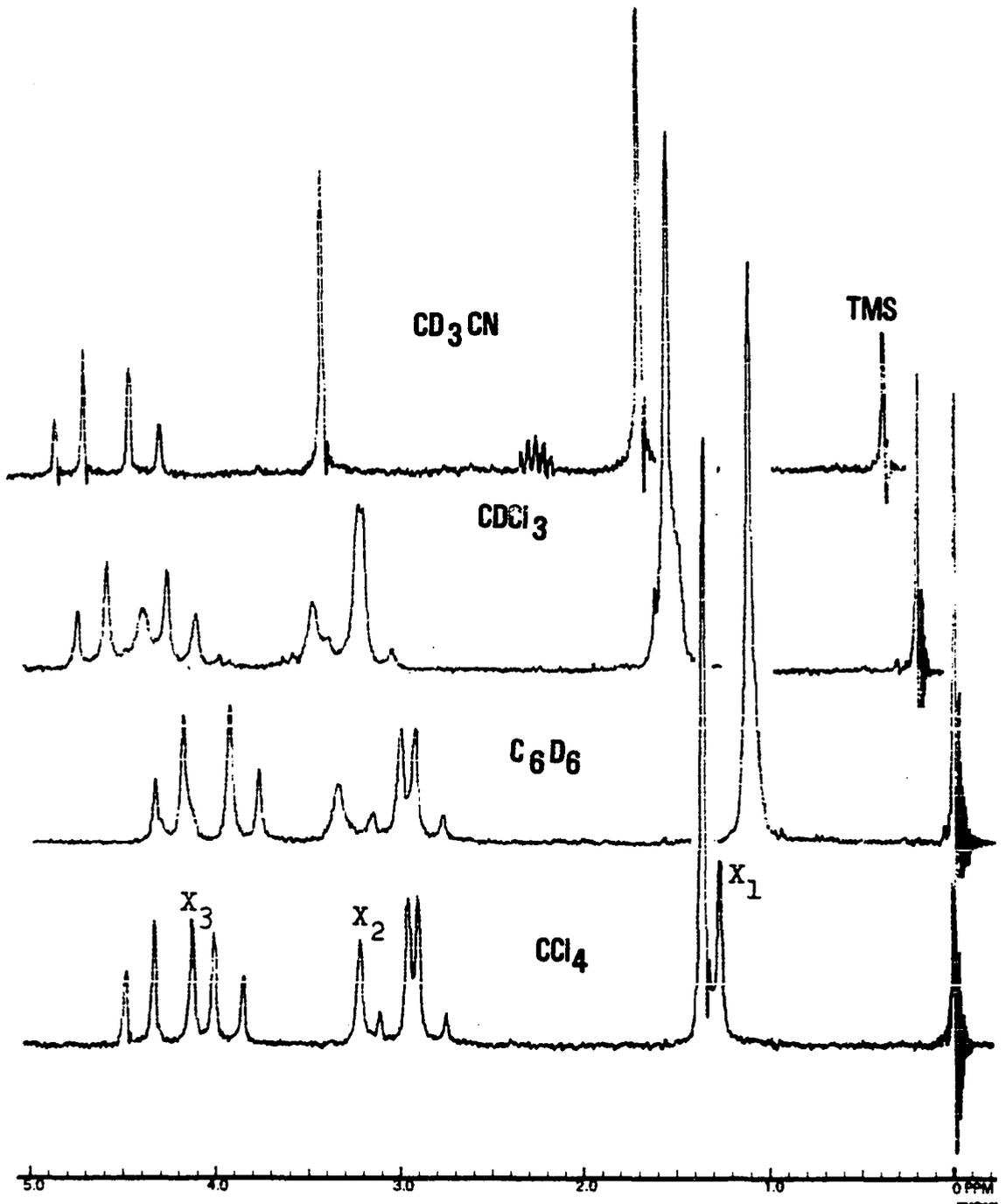


The six-membered ring chloroarsenite, 79, results from breaking the As-O<sub>1</sub> bond while 78 results if either the As-O<sub>2</sub> or As-O<sub>3</sub> bond is broken. However, a <sup>1</sup>H nmr spectrum in CD<sub>3</sub>CN (Figure 16) is only consistent with 78. The singlet at 1.31 ppm is assigned to the methyl group while the singlet at 3.04 ppm is assigned to the methylene group attached to C-4 on the basis of the chemical shift of the methylene protons in (Ph<sub>3</sub>COCH<sub>2</sub>)<sub>3</sub>CMe at 3.12 ppm. The AB quartet (<sup>2</sup>J<sub>HCH</sub> = 9.0 Hz) at 4.20 ppm is due to the ring methylene protons (compare to the methylene chemical shift of 3.63 ppm in the parent arsenite 76). The correct integration ratio of 3:2:2 for these protons is also observed. Actually, the singlet at 3.04 ppm is deceptively simple since it represents a collapsed AB quartet. In terms of a projection down the C-4 methylene carbon bond, the methylene protons are diastereotopic and are therefore nonequivalent (187, 188).



The other spectra in Figure 16 resulted when the same sample was dissolved in the indicated solvents after the previous solvent was removed under vacuum. Furthermore, each spectrum can be reproduced in any particular solvent after being dissolved in the others. The total integration of each

Figure 16. The  $^1\text{H}$  nmr spectra of 78 in  $\text{CD}_3\text{CN}$ ,  $\text{CDCl}_3$ ,  $\text{C}_6\text{D}_6$  and  $\text{CCl}_4$ . The phenyl resonance is not shown.



region remains at 3:2:2. By changing the solvent from  $\text{CD}_3\text{CN}$  to  $\text{CCl}_4$ , the methyl resonance becomes two singlets and each set of methylene resonances now shows the expected AB quartet pattern plus an extra peak. The peaks marked by  $X_1$ ,  $X_2$  and  $X_3$  are apparently related since they integrate in the ratio of 3:2:2. Intermediate changes are noted in the solvents  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$ . These nmr results are tentatively rationalized by postulating the presence of one isomer in  $\text{CD}_3\text{CN}$  arising from chlorine stereochemistry at arsenic being totally axial or equatorial. The second isomer seen in  $\text{CCl}_4$ , representing 25% of the total, could arise if the arsenic-chlorine stereochemistry is opposite. A possible mechanism allowing for the presence of two isomers is an intermolecular exchange process of the chlorines rather than inversion at arsenic since inversion barriers for arsenic are prohibitively high. Such an exchange process is postulated for 1-chloro-3,3,4,4-tetramethyl-1-phospha-2,5 dioxacyclopentane in which coalescence of the methyl resonances occurs (75). In the present case this exchange in  $\text{CCl}_4$  is slow compared to the nmr time scale since the proton resonances are reasonably sharp. The single peaks for the nonequivalent methylene protons on each methylene carbon in the postulated second isomer mean that both resonances are collapsed AB quartets. The observance of two collapsed AB quartets in the same molecule is unusual, but this behavior has been seen before

for the two AB quartets of the ABX system found in

$\text{H(O)POCH}_2\text{C(Me)}_2\text{CH}_2\text{O}$  (189) where the solvent was also  $\text{CCl}_4$ . The nmr parameters for the two isomers extracted from Figure 16 are listed in Table 26.

Table 26.  $^1\text{H}$  nmr parameters of compound 78 obtained in various solvents<sup>a</sup>

Solvent	$\delta\text{CH}_3$	$\delta\text{CH}_3(\text{X}_1)^b$	$\delta\text{CH}_2$		$\delta\text{CH}_2(\text{X}_3)^b$	
			$\delta\text{CH}_2(\text{X}_2)^b$	$\delta\text{CH}_2$		
			$\Delta_B - \Delta_A^c$	$\Delta_B - \Delta_A^c$		
			$^2\text{JHCH}$	$^2\text{JHCH}$		
$\text{CD}_3\text{CN}$	1.31		3.04		4.20 22.2 9.0	
$\text{CDCl}_3$	1.35	1.3 sh <sup>d</sup>	3.00 6.3 9.0	3.26	4.20 27.6 9.0	4.18
$\text{C}_6\text{D}_6$	1.12		2.95 10.7 9.0	3.33	4.05 22.2 9.0	
$\text{CCl}_4$	1.35	1.26	2.93 9.4 9.0	3.22	4.17 26.5 9.0	4.12

<sup>a</sup>The chemical shifts are in ppm relative to TMS. The coupling constants are in Hz.

<sup>b</sup>This peak has been assigned to a second isomer.

<sup>c</sup>This quantity is the separation in Hz between the chemical shifts of the geminal protons.

<sup>d</sup>Sh = shoulder.

It is interesting that while the reaction of 76 with  $\text{Ph}_3\text{CCl}$  does not result in a triether, neither does the 1:1 reaction yield a six-membered monocyclic chloroarsenite, even though the parent arsenite would benefit most from strain relief by such a reaction. This observation may stem from steric hindrance in that initial attack at  $\text{O}_1$  of 76 may be inhibited by the methyl group at the bridgehead carbon.

## SUGGESTIONS FOR FURTHER RESEARCH

Future reactions of arsenites with alkyl halides should be extended to include five- and six-membered ring monocyclic arsenite triesters as well as the bicyclic compounds,

$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{As}(\text{OCH}_2)_2\text{CH} \end{array}$$
 and  $\text{As}(\text{OCH}_2)_3\text{P}$ . A variety of alkyl halides and other sources of carbonium ions such as  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  and  $\text{R}_3\text{O}^+\text{BF}_4^-$  should also be explored. Attempts should be made to isolate intermediates of the reaction of  $\text{As}(\text{OCH}_2)_3\text{CMe}$  and  $\text{Ph}_3\text{CCl}$ . Possibly  $\text{As}(\text{OCH})_3(\text{CH}_2)_3$  could be made to react with  $\text{Ph}_3\text{CCl}$  under even more forcing conditions than those recorded. Finally, reaction of the As-Cl bond in 78 with an alcohol in a polar solvent ( $\text{CH}_3\text{CN}$ ) and a nonpolar solvent ( $\text{CCl}_4$ ) should be carried out in an effort to isolate and identify the two isomeric forms of 78.

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