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SPECTROSCOPIC STUDIES OF METAL–PHOSPHORUS BONDING IN COORDINATION COMPLEXES

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CONTENTS

A. INTRODUCTION

Much controversy has surrounded the degree of pi back-bonding which may accompany sigma donation in the link connecting a phosphorus ligand to the acceptor species. Experimental evidence from a variety of sources has been interpreted either to support or to deny a substantial pi effect. A detailed analysis of all of these arguments is not within the purview of this article and it will appear elsewhere[1]. The aspects of the controversy treated herein will be restricted to evidence bearing directly on the results of our studies.

Phosphorus–acceptor bonds occur very extensively and most of the metals as well as several non-metals can be ligated with trivalent phosphorus compounds. Although zerovalent or divalent metals are generally involved, formal metallic oxidation states from −1 to +4 can be stabilized and a wide variety of coordination numbers and geometries can be found among them. Many function as hydrogenation, polymerization or oxo catalysts; lubricant additives; pesticides; fuel additives; bactericides; antioxidants and blowing agents and several contain molecular nitrogen. A forthcoming review of the coordination compounds of trivalent organophosphines[2] and organophosphites, phosphonites, phosphinites and aminophosphines[3] contains their syntheses and provides a compilation of the complexes along with their properties and uses.

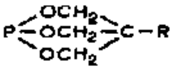
The primary objective in our investigations in this area over the past ten years has been the gathering of spectroscopic information which would permit some definite conclusions to be made regarding the nature of the phosphorus–acceptor link. Spectroscopic quantities which to varying degrees of certainty are indicative of the bonding in a phosphorus–acceptor (PA) link are the ligand field parameter $10Dq$, the stretching frequency ν(PA), the spin–spin coupling constant ${}^{1}J\mathrm{A}^{31}\mathrm{P}$ (where A is an NMR active nucleus) and $J^{31}\mathrm{PA}^{31}\mathrm{P}$, the ^{31}P and ^{1}H NMR chemical shifts, and the PA internuclear distance. The trends in these parameters will be interpreted after commenting on certain important aspects of the bonding and structure in the ligand systems.

The trivalent phosphorus ligands we chose to study varied in electronegativity in order for us to explore possible correlations of this parameter with trends in the spectroscopic quantities obtained from the complexes. The organophosphorus ligands also fell into two structural classes, namely polycyclic and acyclic. The bonding in these two types of ligands and their complexes is not identical and as will be developed later, this difference is *not* primarily the result of the reduced steric requirements of the polycyclics.

B. LIGANDS

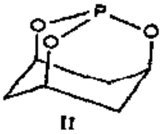
(i) Syntheses

Of particular importance in our investigations has been the use of polycyclic phosphites such as Ia, first reported by us[4,5], and II, synthesized by Stetter and Steinacker[6]. Although open-chain organophosphorus ligands are either commercially available or can be synthesized by standard techniques found in the literature, the syntheses mainly developed in our labo-


I

$P(OCH_2)_3C{-}R$

	R		R
Ia	Me	Ih	NO_2
Ib	Et	Ii	CH_2OH
Ic	*n*-Pr	Ij	C_4H_9
Id	*n*-Pentyl	Ik	C_6H_{13}
Ie	H	Il	$C_{10}H_{21}$
If	CH_2Br	Im	$C_{16}H_{33}$
Ig	Ph	In	$CH_2OOCC(Me)CH_2$


II

ratories for those of the bicyclo[2.2.2] octane[7] variety are now summarized and those reported by others will be cited for completeness.

As shown in eqns. (1)–(5), transesterification of the appropriate trialcohol with $P(OR)_3$, or HCl elimination in the presence of PCl_3, leads to phosphites Ia–Il, In and II.

$$\begin{aligned} PCl_3 + \text{trialcohol} &\xrightarrow[THF]{3\,C_5H_5N} Ia^{4}, If^{15}, Ig^{16}, II^{6} + 3\,C_5H_5N{\cdot}HCl \\ &\xrightarrow{\Delta} Ia^{13}, Ib^{14}, Ih^{10} + 3\,HCl \end{aligned} \tag{1}$$

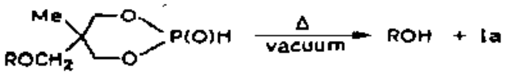
$$P(OMe)_3 + \text{trialcohol} \xrightarrow{\Delta} Ia^{8}, Ib^{9}, Ic^{10}, Id^{11}, Ie^{12}, If^{15}, II^{8} + 3\,MeOH \tag{2}$$

$$P(OEt)_3 + (HOCH_2)_3CCH_2OH \xrightarrow{\text{amine}} Ii^{9} + 3\,EtOH \tag{3}$$

$$P(OPh)_3 + (HOCH_2)_3CR \xrightarrow{OPh^-} Ii{-}Im^{17} \tag{4}$$

Yields are generally in excess of 50% and Ib is commercially available (Aldrich Chemical Company and Frinton Laboratories). Reaction of Ii with methacryl chloride forms In[9]. Reaction of $P(OPh)_3$ or $P(OBu)_3$ with the proper polyalcohol affords $P[OCH_2C(CH_2O)_3P]_3$, $O[CH_2C(CH_2O)_3P]_2$ and $P_8[(OCH_2)_3CCH_2OCH_2C(CH_2O)_2{-}H_2OCH_2C(CH_2O)_3]_3$ (ref. 18), all of which presumably contain bicyclic phosphite moieties. Bicyclic phosphite compounds of this type and of type I function as flame retardants[18,19], vinyl resin stabilizers[17,18] and antioxidants[17].

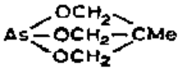
An interesting reaction resulting in a 52% yield of Ia[20] is analogous to an elimination reaction discovered earlier in which II is formed (vide infra). In the decomposition (below)[20], R can be $PhCH_2$ or H, the latter compound probably having been formed by the hydrolysis of Ia although no details were given. The hydrolysis of Ia gives two isomers of the starting material in reaction (5), both of which quantitatively dehydrate[21] in vacuum to Ia.



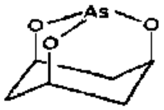
(5)

A bicyclic phosphite formulated as $P(OCH_2CH_2)_3CH$ has been claimed in a patent[22] but no details were given.

The arsenic ligands III[5] and IV[23] have been made in 38% and 59% yield respectively, using $AsCl_3$ in a reaction similar to (1). Reaction of Sb_2O_3 or Bi_2O_3 with $(HOCH_2)_3CR$ in the presence of phenol gives compounds of the type $M(OCH_2)_3CR$, where M = Sb or Bi and R = $HOCH_2$, Me or Et (ref. 24).



III



IV

Transesterification reactions (6) have been shown to give Va[25], Vb[25], Vc[12], Vd[26] and Ve[27] in good yields.

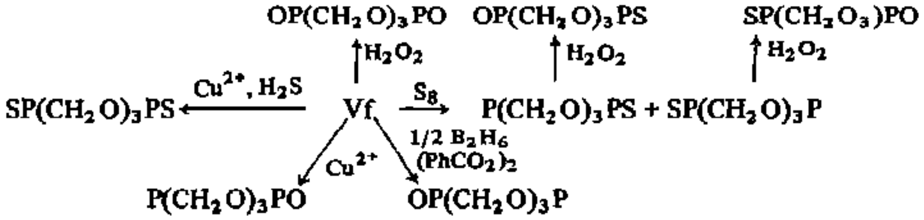
	Z in $P(CH_2O)_3Z$
Va	As
Vb	SiMe
Vc	CH
Vd	CMe
Ve	C-*n*-Bu
Vf	P

$$\begin{tikzcd}
 & \mathrm{Va} & \\
\mathrm{Vf} & (HOCH_2)_3P \arrow[l, "P(OMe)_3"'] \arrow[u, "As(OMe)_3"'] \arrow[r, "MeSi(OMe)_3"] \arrow[d, "RC(OMe)_3"'] & \mathrm{Vb} \\
 & \mathrm{Vc{-}e} &
\end{tikzcd} \qquad (6)$$

Special care must be exercised in the preparation of the trialcohol used in the synthesis of Vf if the chances of a violent side reaction are to be minimized[25]. Compounds formulated as $X(OCHR)_3Y$ where X = CR, Y = P; X = Y = P and X = P, Y = CR were mentioned in a patent[28] but no method of preparation or proof of structure was given.

It is quite remarkable that in most cases syntheses of polycyclic compounds involving trialcohols are not highly susceptible to polymer formation, and high yields are often obtained even in the absence of solvents. We have noticed, however, that crystalline samples of Ia and Ib on standing under vacuum in sealed tubes become sticky over a period of months and the oily substance formed is insoluble in ether and hydrocarbons, in which the caged phosphites are quite soluble. This suggests that cage formation is kinetically controlled whereas thermodynamically these polycyclic phosphites are unstable with respect to intermolecular transesterification in the solid state yielding polymers involving monocyclic and/or acyclic species. The highly strained phosphite $\overset{O}{\overbrace{P(OCH_2)_2CH}}$ reported to form from $P(OMe)_3$ and glycerol[29] decomposes rather easily even in vacuum unless it is stored at low temperature.

Phosphites of types I and V are easily converted to phosphate, thiophosphate or selenophosphate analogs[5,11–13,15,17,25,26,30,31] while efforts to prepare the arsenate or thioarsenate derivatives of III and IV have thus far failed. The variety of oxidation products[31] achieved from Vf is summarized in reaction scheme (7).



$$\begin{tikzcd} & OP(CH_2O)_3PO & OP(CH_2O)_3PS & SP(CH_2O_3)PO \\ SP(CH_2O)_3PS & Vf \arrow[l, "Cu^{2+}, H_2S"'] \arrow[u, "H_2O_2"'] \arrow[r, "S_8"] \arrow[dl, "Cu^{2+}"'] \arrow[d, "1/2\ B_2H_6 \ (PhCO_2)_2"] & P(CH_2O)_3PS + \arrow[u, "H_2O_2"'] & SP(CH_2O)_3P \arrow[u, "H_2O_2"'] \\ P(CH_2O)_3PO & OP(CH_2O)_3P & & \end{tikzcd}$$

(7)

Assignment of the location of the chalcogen(s) in these systems was accomplished by comparing their P—H coupling constants and ^{31}P and ^{1}H chemical shifts with those of Ia, Vd and their chalconide derivatives[30–33] which mimic quite closely the appropriate phosphorus moieties in the diphosphorus systems.

The synthesis of analogs of I and III in which the oxygens are substituted by sulfur or NMe groups (VI–IX) has been effected in high yields by converting the appropriate trialcohol to the corresponding trimercaptan[27,34] or tris-methylamine[27,35] followed by treatment with $E(NMe_2)_3$, where E = P or As.

$P(SCH_2)_3CR$
VIa, R = Me
VIb, R = *n*-Pentyl

$P[N(Me)CH_2]_3CR$
VIIa, R = Me
VIIb, R = *n*-Pentyl

$As(SCH_2)_3CMe$
VIII

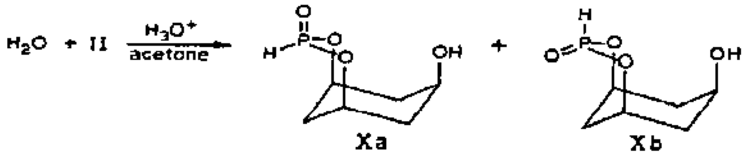
$As(NMeCH_2)_3CMe$
IX

$$E(NMe_2)_3 + (HSCH_2)_3CR \xrightarrow{\Delta} \text{VIa}^{34}, \text{VIb}^{27}, \text{VIII}^{34} + 3\ Me_2NH \qquad (8)$$

$$E(NMe_2)_3 + (MeHNCH_2)_3CR \xrightarrow{\Delta} \text{VIIa}^{34}, \text{VIIb}^{27}, \text{IX}^{35} + 3\ Me_2NH \qquad (9)$$

Compound VIa was oxidized[34] to $OP(SCH_2)_3CR$ using SO_2Cl_2 and $OP(NMeCH_2)_3CMe$ was synthesized[35] by reacting $(MeNHCH_2)_3CMe$ with $OPCl_3$. Reaction of VIa[34] and VIIa[35] with sulfur gave the expected thio derivatives.

Because one of the isomers (Xa) formed in the acid-catalyzed hydrolysis of II functions as a rather unusual trivalent phosphorus ligand for several metal ions (see later), evidence for its structure will be briefly presented.



(10)

Although the reaction is quantitative, separation and purification procedures reduce the individual yields[36] to about 30%. Both Xa and Xb dehydrate to II on heating in vacuum. Although the structures of these isomers were predicted from conclusions based on NMR and IR studies[36], the configuration of Xa was confirmed by a single-crystal X-ray investigation[37] discussed in a later section. The stereochemical implications of the hydrolysis of Ia and II to give six-membered ring phosphorus esters will not be treated here[21,38].

(ii) Dipole moments

The remarkably high dipole moments recorded in Table 1 for the bicyclic phosphites and thiophosphites compared with their open-chain analogs are most reasonably rationalized on the basis of the rigid orientation of chalcogen lone-pair density in the former structures[34,39]. Evidence for this hypothesis is that VIIa and $P(NMe_2)_3$ have very comparable moments owing to the nearly sp^2 planarity of the nitrogens in these systems (see later). The single *p* lone pair on each nitrogen in these compounds would contribute to the overall moment only if it were to pi bond with the phosphorus, in which case the slightly larger moment for VIIa may or may not be indicative of a greater tendency in this direction. Further evidence for the lone-pair orientation effect on the overall moment comes from the comparison of $MeC(OMe)_3$, 1.90 D (ref. 40) and $MeC(OCH_2)_3CMe$, 2.71 D (ref. 23) in benzene. The effect of mis-aligning the lone-pair moment of the unique bridging oxygen in $\overbrace{P(OCH_2)_2CH}^{O}$ is seen in the substantial decrease in dipole moment compared with Ia.

The high polarity undoubtedly also contributes to the relatively large lattice energy of these systems as reflected in their great tendency to be crystalline solids at room temperature in contrast to their liquid open-chain analogs[41,42]. Convincing evidence that the molecular dipole in all of these polycyclic systems is as shown by the arrow in Table 1, comes from (*a*) comparison of their dipole moments with oxidized derivatives, (*b*) the additivity of group moments, and (*c*) aromatic solvent chemical shift effects (see next section). The bond moment in an $O{=}P{\leqq}$, $S{=}P{\leqq}$ or $H_3B \longleftarrow P{\leqq}$ group is certainly in the direction of the chalcogen in the first two cases and toward the borane in the last. Thus larger dipole moments compared with the trivalent phosphorus analog Ia, 4.13 D, are observed in $OP(OCH_2)_3CMe$, 7.10 D (ref. 40), $SP(OCH_2)_3CMe$, 6.77 D (ref. 40), $H_3BP(OCH_2)_3CMe$, 8.60 D (ref. 41) and $H_3BP(OCH)_3(CH_2)_3$, 8.82 D (ref. 42). Dipole moments of this size would indeed be surprising if those of the trivalent analogs had been directed toward the hydrocarbon moiety.

TABLE 1

Dipole moments at 25° of polycyclic phosphorus compounds and open-chain analogs

Compound[a] $\overset{-\qquad\qquad +}{\longleftarrow}$	Dipole moment[b] (debye)	Solvent	Ref.
$\overset{O}{\overline{P(OCH_2)_2C}}H$	3.28	C_6H_6	[c]
$P(OCH_2)_3(CH_2)_3$	4.42	C_6H_6	23, 39
	4.51	$O(CH_2CH_2)_2O$	[d]
$As(OCH)_3(CH_2)_3$	2.89	C_6H_6	23
$P(OCH_2)_3CMe$	4.13	C_6H_6	23
$P(OCH_2)_3CPh$	4.08	CCl_4	16
$P(SCH_2)_3CMe$	3.86	CCl_4	34
$As(SCH_2)_3CMe$	3.13	CCl_4	34
$As(OCH_2)_3CMe$	2.68	C_6H_6	23 [e]
$P(NMeCH_2)_3CMe$	1.62	CCl_4	23
$P(OCH_2)_3P$	3.10	C_6H_6	[f]
$As(OCH_2)_3P$	1.58	C_6H_6	25
$MeC(OCH_2)_3P$	1.54	C_6H_5	23
$MeO\overline{POCH_2CH_2O}$	2.51	C_6H_6	[c]
$MeO\overline{POCH_2CH_2CH_2O}$	2.82	C_6H_6	[c]
$(MeO)_{ax}\overline{POCH(Me)_{eq}CH_2CH(Me)_{eq}O}$	3.6	C_6H_6	[c]
$(MeO)_{eq}\overline{POCH(Me)_{eq}CH_2CH(Me)_{eq}O}$	3.04	C_6H_6	[c]
$P(OMe)_3$	1.83	CCl_4	40
	1.90	C_6H_6	[c]
$P(SMe)_3$	1.36	C_6H_6	34
$P(NMe_2)_3$	1.21	C_6H_{12}	[g]
PMe_3	1.192	Gas	40

[a] The arrow indicates the direction of the molecular dipole in all of the compounds as written.

[b] Precision of the measurements is at least 0.05 D (cf. A.C. Vandenbroucke, R.W. King and J.G. Verkade, *Rev. Sci. Instrum.*, 4 (1968) 558).

[c] J.G. Verkade and D.W. White, unpublished observation.

[d] See ref. 127.

[e] Reference 40 contains an erroneous reference to a group of French workers as having measured this moment.

[f] F.B. Ogilvie and J.G. Verkade, unpublished observation.

[g] B.L. Laube and J.G. Verkade, unpublished result.

Owing to the rigidity and symmetry of these polycyclic systems, the group dipole moments are additive. It becomes possible, therefore, to compare the experimental moments of Va and Vf with those obtained by subtracting the contribution of a $P(CH_2)_3$ moiety, 1.19 D (ref. 25) from the moments of III and Ia, respectively. Despite the approximations inherent in this procedure[25,24], the results (1.49 D for Va and 2.94 for Vf) are quite reasonable.

An interesting aspect of the bonding in bicyclic phosphorus esters becomes apparent on examining the magnitude and direction of the MY_3 moment in molecules $M(YCH_2)_3CMe$ (ref. 34). When the H—C bond moments and the carbon—chalogen bond moments (which include half the lone-pair density on the chalcogen atoms) are subtracted from the experimental moments, group moments for the MY_3 moiety remain which include contributions from the MY bond polarity, the pnictogen lone pair and half the lone-pair density on the chalcogens. Surprisingly these group moments are directed toward the phosphorus in Ia (0.8 D) and VIa (0.5 D) whereas they point toward the chalcogens in the arsenic analogs III (0.65 D) and VIII (0.2 D) as would be expected on electronegativity grounds. The same is true for the MY_3 portion of the pairs II, Vb—Vf and their arsenic analogs IV, Va respectively. If the anomalous PO_3 and PS_3 moments in Ia and VIa were due primarily to the directionality of the chalcogen lone pairs, their magnitudes would be reversed on electronegativity grounds assuming that the moment of a second quantum level sp^3 lone-pair orbital on oxygen is smaller than that of a similar orbital on sulfur in the third quantum level. It would appear then that appreciable sp^2 character resides in the oxygen of bicyclic phosphites which favors drift of electron density from the unhybridized filled *p* orbital on each oxygen into available *d* orbitals on phosphorus and a consequent elevation of the PO_3 moment in the direction of phosphorus. This effect would appear to be substantially less in VIa. It should be noted that the remaining lone pair on each oxygen under these conditions is of the sp^2 type and its contribution is 25% less (from geometrical considerations) than that of two sp^3 oxygens, assuming similar density distributions. Thus the PO_3 moment in the direction of the oxygens should be *increased* instead of decreased in progressing from an sp^3 to an sp^2 oxygen unless electron drift to phosphorus takes place via the unhybridized *p* orbital. Moreover, without such pi bonding, the chalcogen lone pair in the unhybridized *p* orbital would not contribute to the moment in either direction because of the geometry of its charge distribution relative to the molecular axis. It should not be inferred from this discussion that PO pi bonding in polycyclic phosphites exceeds that in open-chain phosphites because evidence to be presented later leads to the conclusion that it is probably nearly the same. Because of non-rigidity in the open-chain systems, the reasoning given above is not applicable to their measured moments.

(iii) NMR parameters

Selected NMR parameters[12,13,25–27,29–35,43,44] of a wide variety of polycyclic trivalent phosphorus systems and their open-chain analogs are presented in Table 2. Except for the assignment of a bonding environment (e.g. PC_3, PO_3, OPO_3, etc.), it is presently not feasible to interpret the $\delta^{31}P$ shift values in terms of bonding parameters. From a quantum mechanical viewpoint, changes in ^{31}P chemical shifts appear to be a function of three parameters[45]. For a series of trialkyl phosphites[46a], these are the change in electronegativity of the alkoxy group(s) ($\Delta\chi OR$) the change in *d*-orbital occupation number (Δn_π) and the change in the angle between the P—O bond and the phosphorus lone pair ($\Delta\alpha$). The equation is of the form[46a] $\Delta\delta = -25\Delta\chi OR - 382\Delta n_\pi + 21\ \Delta\alpha$. Changes in χOR

TABLE 2

NMR parameters of polycyclic systems [a]

Compound	δ^{31}P	Ref.	δ^{1}H [b]	J [c]	Ref.
$\overbrace{\mathrm{P(OCH_2)_2CH}}^{\mathrm{O}}$	−105	44	3.59	0.29, 3.83	29, 44
P(OCH)$_3$(CH$_2$)$_3$	−137.7	33	4.3(OCH) 3.0(OCH$_{eq}$) 1.9(OCH$_{ax}$)	+6.3	23, 33, 43
As(OCH)$_3$(CH$_2$)$_3$			4.2(OCH) 3.0(OCH$_{eq}$) 1.8(OCH$_{ax}$)		23
P(OCH$_2$)$_3$CR	−92	27, 32, 33	4.0	+2	12, 23, 26, 33
P(OCH$_2$)$_3$CPh			4.4	2.0	[d]
P(OCH$_2$)$_3$CCH$_2$Br			4.08	3.0	[e]
As(OCH$_2$)$_3$CMe			4.0		23, 43
P(OCH$_2$)$_3$PO					31
P(OCH$_2$)$_3$PS					31
P(SCH$_2$)$_3$CR	−33	27	2.9	2.1	27, 34
As(SCH$_2$)$_3$CMe			2.94		34
P(NMeCH$_2$)$_3$CR	−87	27	2.5(NCH$_3$) 2.6(NCH$_2$)	16(^3JPNCH$_3$) 3(^3JPNCH$_2$)	23, 27, 35
As(NMeCH$_2$)$_3$CMe			2.53(NCH$_3$) 2.61(NCH$_2$		35
P(OCH$_2$)$_3$P	+67(P(CH$_2$)$_3$) −90(PO$_3$)	30, 32	4.5	+8.9(^2JPCH) −37.2(^3JPP) +2.5(^3JPOCH)	25, 30, 32
As(OCH$_2$)$_3$P			4.61	+9.4(^2JPCH)	25
RC(OCH$_2$)$_3$P	+81	27, 32	4.3	+8(^2JPCH)	12, 23, 26, 27
MeSi(OCH$_2$)$_3$P			4.66	+8.9(^2JPCH)	25
SP(OCH$_2$)$_3$P	+71(P(CH$_2$)$_3$) −52(PO$_3$)	32	5.11	+7.6(^2JPCH) +7.5(^3JPOCH)	32
P(OCH$_2$)$_3$PO	−7.45(P(CH$_2$)$_3$) −85.53(PO$_3$)	31	4.60	−8.1(^2JPCH) +3.2(^3JPOCH) +140(JPP)	31
P(OCH$_2$)$_3$PS	−6.30(P(CH$_2$)$_3$) −90.49(PO$_3$)	31	4.60	−5.8(^2JPCH) +3.0(^3JPOCH) +118(^3JPP)	31
OP(OCH$_2$)$_3$P	+69.98(P(CH$_2$)$_3$) +14.25(PO$_3$)	31	5.15	+7.5(^2JPCH) +7.5(^3JPOCH) +65(^3JPP)	31
P(OMe)$_3$	−140	43	3.69	11.35	72 [e]
P(CH$_2$OH)			4.07	3.0(^2JPCH)	25
P(SMe)$_3$	−124.1 to −125.6	45	2.2	10.0	72 [e]
P(NMe$_2$)$_3$	−121.5 to −123	45	2.49	8.82	[f]

The footnotes to this Table appear at the bottom of p. 10.

brought about by stepwise substitution of two OEt groups in $P(OEt)_3$ by various OR groups lead to linear positive or negative changes in $\Delta\delta$ which range from < 1 to 6 p.p.m. Extending the above arguments, an upfield shift with respect to $P(OEt)_3$(−137 p.p.m.)[46a] is expected in Ia (−91.5 p.p.m.) since α should be greater[26] than in $P(OEt)_3$. Although the observed value would appear to confirm this hypothesis, the value of −105 p.p.m. for $\overset{O}{\overline{P(OCH_2)_2}}CH$ is not consonant with the trend inasmuch as α is expected to be greater in this compound than in Ia.

The decrease in n_π reinforces the effect of the concomitant increase in α in the above equation and the ^{31}P chemical shift of $\overset{O}{\overline{P(OCH_2)_2}}CH$ should be more shielded than that of Ia. Although the decrease in the number of carbons from $P(OEt)_3$ (six) to Ia (five) to $\overset{O}{\overline{P(OCH_2)_2}}CH$ (three) might be expected to increase the χOR term and thus tend to deshield the phosphorus in $\overset{O}{\overline{P(OCH_2)_2}}CH$ sufficiently to dominate the n_π and α terms, $P(OMe)_3$ with only three carbons has a chemical shift only 3 p.p.m. to lower field than $P(OEt)_3$. Thus the reason for the apparently anomalous trend in ^{31}P chemical shift values is not clear and may be controlled by more subtle factors. The correlation of $\delta^{31}P$ with ΔHNP values (see later) for several series of phosphines reported recently[46b] does not extend to the phosphites discussed here.

The proton chemical shift assignments are all straightforward except for the axial and equatorial protons on the CH_2 groups in II and IV. In the latter molecules greater coupling of the OCH protons to the low-field rather than the high-field $C\underline{H}_2$ absorption was observed in decoupling experiments[43]. In an unconstrained cyclohexane ring an equatorial hydrogen should be *gauche* with respect to the hydrogens of the adjacent methylene group and equally coupled to each. Because the POC and OPO angles in Ia and II are larger and smaller, respectively, than the tetrahedral angle (see later) the cyclohexane ring will be strained such as to decrease the dihedral angle formed by the methine and equatorial methylene protons, thereby increasing their predicted coupling. Thus the low-field $C\underline{H}_2$ absorption was assigned to the equatorial methylene hydrogen[43]. This assignment is substantiated by the downfield and upfield movement of the axial and equatorial CH_2 protons, respectively, when the dielectric constant of the solvent is increased[43]. This phenomenon stems from the reaction field at the dipolar solute produced by the solvent dipole while the opposite progression of the shifts arises from the different angles between the solvent electric field and the C—H

Footnotes to Table 2:

[a] ^{31}P chemical shifts are given with respect to external 85% H_3PO_4 while the ^1H values have internal TMS as reference. Because the solvent dependence of the shifts is not significant[28] except for protons when aromatic solvents are used[13] (see text), the solvents are not specified here. Values obtained in various solvents were therefore rounded off. In most instances where more than one compound is represented, the ^{31}P shifts refer to the species where R is a methyl group.

[b] Only values for the CH_2 ring protons are given unless otherwise specified. R group absorptions are typical and show no coupling to the phosphorus or ring protons.

[c] Unless otherwise specified, J refers to ^3JPYCH couplings.

[d] R. Swain, J. Mosbo and J.G. Verkade, to be published.

[e] S.C. Goodman and J.G. Verkade, unpublished results.

[f] G. Martin and G. Mavel, *C.R. Acad. Sci.*, (1962) 2095.

bond directions involved[47].

Compelling evidence for the assignment of the equatorial and axial protons in II as well as for the direction of the dipole moments in all the polycyclic systems in Table I came from a systematic investigation of aromatic solvent induced shifts (ASIS) displayed by polycyclic compounds[23]. The generally accepted model of the ASIS effect is one in which the aromatic solvent is preferentially oriented with its π electron cloud toward an electron-deficient center on a solute molecule in a time-averaged collision complex which involves one or more solvent molecules[48]. Protons in the solute which are close to the center of the ring of the aromatic solvent molecule are shielded while protons near the periphery of the aromatic ring are deshielded. The orientation effect produced by the attraction of aromatic π clouds and positive ends of solute dipoles is enhanced by mutual repulsion of the π cloud and the negative end of the solute dipole.

In addition to the strong upfield shift in benzene of the methylene protons (ca. 0.3 p.p.m.) of the bicyclic orthoformate $HC(OCH_2)_3CMe$ and the even stronger upfield shift (ca. 0.8 p.p.m.) of the methyl protons, a strong downfield shift (ca. 0.4 p.p.m.) was observed for the orthoformyl proton. Geometry and steric factors require that separate benzene molecules are involved at the two ends of the molecule and the downfield shift is in accord with the proposed model in which the benzene molecules are oriented with their relatively positive peripheries toward the negative end of a dipole in a time-averaged collision complex resulting in deshielding of the orthoformyl proton (Fig. 1). In hexafluorobenzene exactly opposite effects are observed which are interpreted in terms of a similar solvent cluster complex except that the orientations are all reversed because of the electronegativity of the fluorines (see Fig. 2).

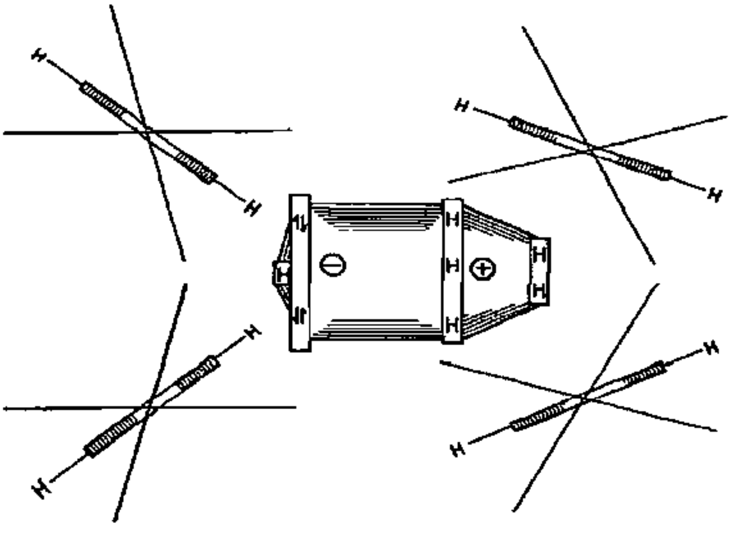


Fig. 1. Schematic representation of the interactions of the shielding and deshielding regions of benzene molecules with protons at the charged ends of dipolar bicyclic solutes.

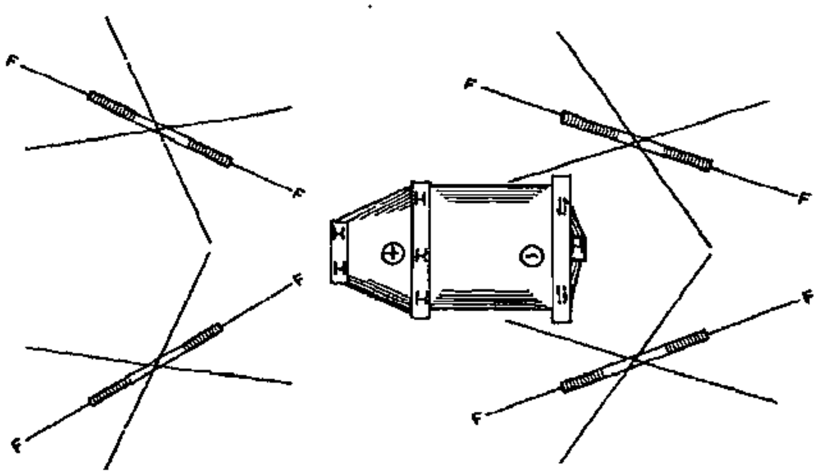


Fig. 2. Schematic representation of the interactions of the shielding and deshielding regions of hexafluorobenzene molecules with protons at the charged ends of dipolar bicyclic solutes.

These results along with similar observations on the bicyclic compounds in Table 1 strongly suggested that the direction of the dipole is on the three-fold axis of the caged molecules in Table 1 and in the direction of the pnictogen. Because the axial protons in II are more affected in aromatic solvents than the equatorial and OCH protons (which being in similar environments at the "waist" of the dipole are nearly equally shifted) the assignment of the axial and equatorial protons becomes unambiguous[23].

The ^{3}JPOCH coupling constants listed in Table 2 are rather small in bicyclic phosphites I but are three times as large in II. This is attributable to the POCH dihedral angle in II (180°) being larger[33] than in I (60°). It should be stressed, however, that the correlation between this coupling and the dihedral angle is quite crude owing to hybridization changes among the compounds presently available for study[49].

There is a remarkably large difference in $^{3}J\mathrm{PNCH_3}$(16 Hz) and $^{3}J\mathrm{PNCH_2}$(3 Hz) in VIIa, b. Constancy of the pair of doublets observed for these protons in a low temperature study[35] failed to distinguish between rapidly inverting tetrahedral nitrogens or static trigonal ones. The configuration around nitrogen in these bicyclic aminophosphines is nearly planar (see next section) and low-temperature NMR studies of the P–N rotational barrier in methylamino phosphines[50] have led to the conclusion that $^{3}J\mathrm{PNCH_3}$ is larger when the methyl group is *cis* to the phosphorus lone pair than when it is *trans*. This accords with our observation on VIIa, b in which the relationships of the $\mathrm{NCH_3}$ and $\mathrm{NCH_2}$ groups to the phosphorus lone pair are fixed *cis* and *trans* to one another, respectively, as a result of molecular constraint. It should be noted, however, that no C–N rotation is permitted in VIIa, b which probably reduces the ^{3}JPNCH coupling compared with the open-chain analogs studied[50] wherein this restriction is lifted. The increased magnitude of ^{3}JPNCH compared with ^{3}JPCH in analogous systems has been noted and the difference accounted for in terms of enhancement of ^{3}JPNCH by P–N pi bonding or alternately by the increase in *s* character in the CH bond owing to the higher electronegativity of nitrogen compared with phosphorus[51]. Caution should be used with this type of reasoning, however, since $^3JPNCH_2$ in VIIa, b is about three times smaller than $^2JPCH_2$ in cages of type V[52].

Whereas $^3JPOCH_2$, $^3JPSCH_2$ and $^3JPNCH_2$ are seen to decrease significantly from open-chain to caged systems, $^2JPCH_2$ rises drastically. It has already been pointed out that the former group of coupling constants appear to be strongly influenced by hybridization changes among several constrained molecules[49]. As will be seen later there is good reason to believe that hybridization changes upon polycyclization occur in phosphates and to a lesser extent in phosphites. Thus a narrowing of the YPY angles upon constraint would decrease the *s* character in the PY link and account for the decrease in ^3JPYCH. Although ^2JPCH would be predicted to behave similarly upon decrease of the CPC angle, Manatt et al.[53] have presented evidence which indicates that *decreasing s* character in P–C bonds results in a more *positive* ^2JPCH value.

The ligand properties of Xa in eqn. (10) and the lack of such characteristics in Xb is closely linked to their respective structures (see later). At this time the structure of Xb rests on the comparison of its NMR spectrum with that of Xa (whose configuration has been confirmed by diffraction studies[37]) and a comparison of their IR spectra in the P=O and P–H stretching regions[36]. All the data are consistent with isomerism only at phosphorus. The proton NMR spectra of Xa and Xb are very similar except for a feature unique to the PH proton absorption of Xb. Here decoupling experiments showed that coupling (1 Hz) of the PH proton occurs to one of the protons in the methylene proton region. The only methylene carbon possessing such single protons is the carbon below the PH bond. From our previous work on long range coupling constants[12] it was found that a favorable condition for coupling (1–2 Hz) over a distance of five bonds is opposing collinear C–H links. Because the P–H bond in Xb is collinear with the CH bond of the axial proton on the methylene carbon below, the configuration shown was postulated. Flipping the phosphorus portion of the boat ring to a chair form in order to obtain an equatorially disposed phosphoryl oxygen can not be ruled out, however. The resulting non-collinear HP–CH configuration could also produce an observable five-bond $^1HPOCC^1H$ coupling, although such interactions have not yet been reported.

(iv) Structure

Bond angle changes induced by polycyclization of organophosphorus compounds are revealed by solid-state X-ray diffraction studies carried out in our laboratories. Because the polycyclic phosphites have not afforded crystals suitable for X-ray analysis, it has been necessary to extrapolate structural data obtained on phosphite derivatives to phosphites. The structure of the polycyclic phosphate $OP(OCH_2)_3CMe$ derived from Ia is shown in Fig. 3. If the OPO and POC bond angles in $OP(OCH_2Ph)_2(OH)$ (ca. 104° and 120°, respectively[54]) can be assumed to be representative of strainless angles of this type, some evidence of strain is present in $OP(OCH_2)_3CMe$ in the 115° POC angles. Strain probably present

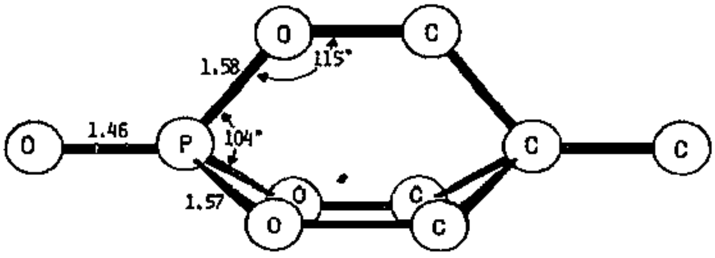


Fig. 3. The molecular configuration of $OP(OCH_2)_3CMe$.

in the hydrocarbon portion of the molecule since even adamantane possesses[55] a strain energy of 648 cal/mole. The decrease in POC angle from $OP(OCH_2Ph)_2(OH)$ to $OP(OCH_2)_3CMe$ strongly suggests that the maximal pi bonding permitted by the sp^2 oxygens in the open-chain system is reduced in the bicyclic phosphate. That pi bonding remains in these links in the constrained phosphate, however, is indicated by the 1.57 Å P–O bond length which in the revised Cruickshank bond order scale[56] would have a bond order of about 1.4. The bonding picture and strain considerations would similarly apply to $SP(OCH)_3(CH_2)_3$ (Fig. 4) wherein the pertinent bond parameters[57] very closely resemble those in $OP(OCH_2)_3CMe$.

A comparison[58] of the bond angles in the structure of $OP(OCH_2)_3CMe$ with those of $SP(OCH_2)_3P$ (Fig. 5) indicates that the principal effect of changing the CCC and CCO angles in the cage of the former to those represented by the CPC and PCO angles of the

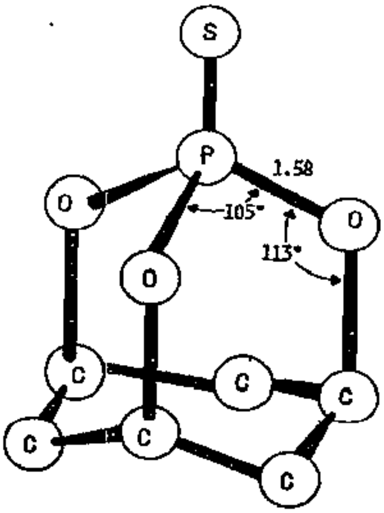


Fig. 4. The molecular configuration of $SP(OCH)_3(CH_2)_3$.

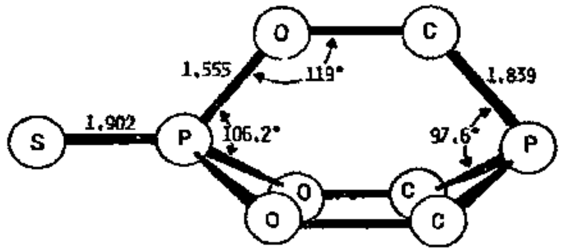


Fig. 5. The molecular configuration of SP(OCH$_2$)$_3$P.

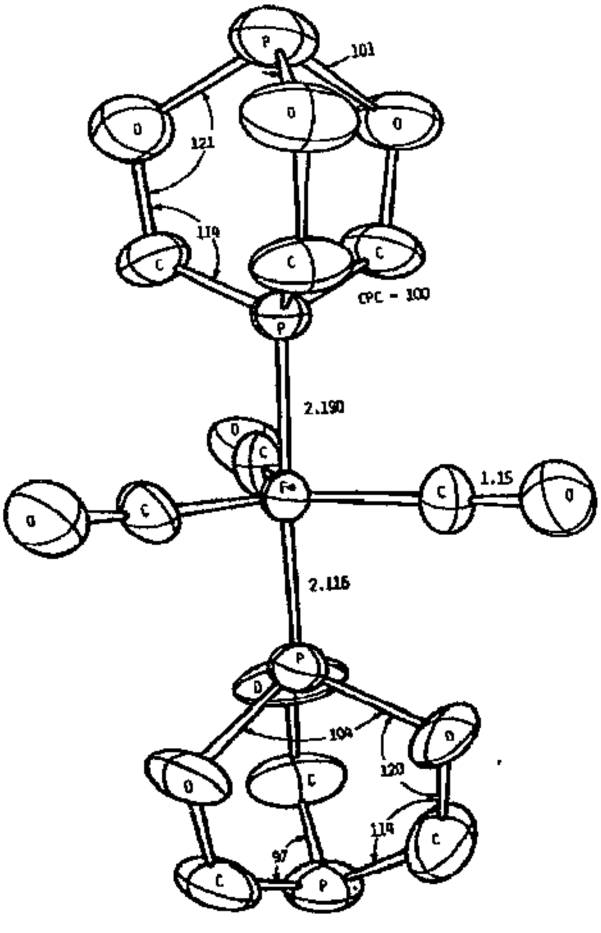


Fig. 6. The molecular configuration of *trans*-Fe(CO)$_3$ [P(OCH$_2$)$_3$P] [P(CH$_2$O)$_3$P] (ref. 59).

latter is a widening of the POC angle. Lengthening the C—C bond in the former to a C—P bond in the latter would similarly affect the POC angle. The same observation can be made on the ligated form of Vf in the structure[59] of *trans*-$P(OCH_2)_3PFe(CO)_3P(OCH_2)_3P$ shown in Fig. 6 wherein the POC angles are nearly 121°. One of the ligands in Fig. 6 is a polycyclic phosphite (i.e. $P(OCH_2)_3Z$, where $Z = Fe(CO)_3P(OCH_2)_3P$) wherein the OPO angle is 101°. The fact that this angle is 99° in the $Ag[P(OCH_2)_3CMe]_4^+$ ion[60] implies that the OPO angle in the uncoordinated Ia molecule is very likely no larger than this value. Moreover the POC angles in the $[Ag(Ia)_4]^+$ cation are 122°, making it reasonable to suppose that it will be similar in uncoordinated Ia. Thus the OPO and POC angles in Ia may resemble the OPO and POP angles in P_4O_6 (99.8° and 127.5°)[61] although the change in the OPO angle of Ia on oxidation to $OP(OCH_2)_3CMe$ would then be significantly larger than that which occurs from P_4O_6 to P_4O_{10} (OPO = 101.6°, POP = 123.5° (ref. 56)). Structural data have been reported for two open-chain phosphites in an electron diffraction study[62a]. The data obtained for $P(OCH{=}CH_2)_3$ produce error limits in the relevant parameters (3—4°) which are about twice as large as those in the other work cited. Thus it is somewhat dubious to conclude from the OPO angle (104±4°) and the POC angle (118±3°) whether or not a caged phosphite such as Ia is strained or not. The other compound studied[62a] was $P(OEt)_3$ for which the electron diffraction data yielded OPO and POC bond angles which are inconclusive for our purpose because they could vary (95—108° and 110—116°, respectively) even when a skeletal model of "the basic rotational isomer" was assumed[62a]. More accurate structural data on the *trans*-methyl mesohydrobenzoin phosphite $MeO\overline{POCHPhCHPhO}$ obtained by X-ray diffraction[62b] shows that the exocyclic POC angle is 117.5° with an average O_{exo}-PO_{endo} angle of 101°. Assuming tetrahedral CCC angles, 120° POC angles and CO and OP bond distances which are the same as in $MeO\overline{POCHPhCHPhO}$ (1.5 Å and 1.63 Å, respectively[62b]), models predict a rather strainless structure for Ia with OPO bond angles between 95 and 100°. Based on the structural data at hand it seems justifiable to conclude for Ia, then, that its geometrical reorganization on coordination results in an increase in the sp^3 character of both the phosphorus and the oxygen atoms as manifested by the increase in OPO angle and a decrease in the POC angle. While the former change is a consequence of polarization of the phosphorus lone pair, the latter comes about as a "hinge" effect because of the constraints in the molecule. This concept will be of considerable importance in the discussion of metal phosphorus bonding.

Considering the molecules represented in Fig. 5 and 6 as polycyclic phosphine derivatives of the type $P(CH_2O)_3Z$, it is noteworthy that the average of the CPC angles in both molecules (97°) is not significantly different from those found in Me_3P (98.6°, 99.1°)[63]. This gives support to the idea that polycyclic phosphites of the bicyclo[2.2.2]octane type are essentially strainless.

Structures of amino phosphines have proven worthwhile to determine because of the possibility that nitrogen or phosphorus can function as the donor site in adducts and complexes. An additional concern in our work has been the effect of coustraint on the ligating properties and structure of VIIa. Because VIIa is a liquid, an X-ray difraction study[64] was

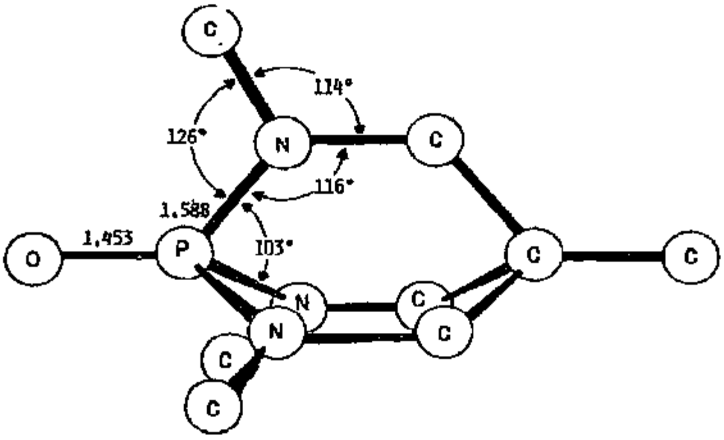
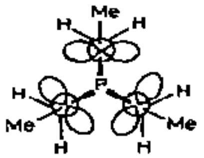


Fig. 7. The molecular configuration of $OP(NMeCH_2)_3CMe$.

carried out on its oxide $OP(NMeCH_2)_3CMe$ and the structure is depicted in Fig. 7. At first glance it would appear that P–N pi bonding is chiefly responsible for the nearly complete planarity of the nitrogens (the sum of the appropriate angles being 357°). Although pi bonding is undoubtedly a factor, steric interactions of the nitrogen methyl groups with the methylene hydrogens are also operative, viz.



Eclipsing the methyl carbons with the CH_2 protons would allow the protons to come within van der Waals radii of one another. Although the 116° $PNC(H_2)$ angles might be taken as an indication that P–N pi bonding is not maximal, the P–N distances (1.588 Å) are the shortest observed so far with the possible exception of that found[65] for the exocyclic P–N bond in $P_3N_3(NCS)_6$ (1.58 Å). Interestingly, in F_2PNMe_2 the solid-state structure[66] indicates planarity about nitrogen and a rather short P–N bond distance (1.628 Å) whereas the gas-phase electron diffraction data[67] are consistent with distortion from planarity (the sum of the CNC and PNC angles being 348°) and a significantly longer P–N bond (1.684 Å). It would seem that molecular motions permitted in the gas phase diminish the effectiveness of P–N pi bonding and/or perhaps crystal packing forces may induce planarity in the solid state.

The question of strain in VIIa is not as easily answered as in the case of Ia. An indication of strain stems from the 116° $PNC(H_2)$ average angle but the NPN average angle of 103° is rather close to the two NPN angles (100.6° and 102.8°) found[68] in $OP(NH_2)_3$. The third angle in $OP(NH_2)_3$ appears to be distorted by the extensive intermolecular hydrogen bond-

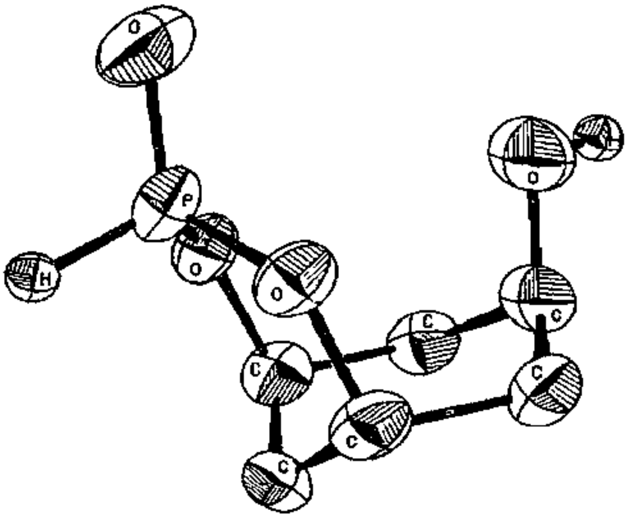
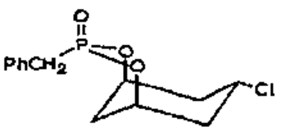
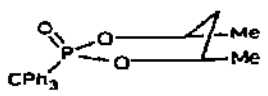


Fig. 8. The molecular configuration of isomer Xa obtained from the hydrolysis of $P(OCH)_3(CH_2)_3$.

ing present[68]. Unfortunately it is not possible to estimate the role of these hydrogen bonding interactions in establishing the PNH angles (117°) and so comparison with the PNC angle in $OP(NMeCH_2)_3CMe$ is rendered fruitless. Similarly the less-than-tetrahedral angles in the aziridine rings of $SP(NCH_2CH_2)_3$ undoubtedly influence the value[69] of the PNC angle (119°) and so it too must be disregarded as being representative of a typical value for this angle. The average NPN angle of 100° in $SP(NCH_2CH_2)_3$ is not sufficiently smaller than that in $OP(NMeCH_2)_3CMe$ (within experimental error) to conclude that constraint is responsible for the difference.

The last ligand structure to be discussed is that of Xa[37] which is represented in Fig. 8. An unusual structural feature of this ligand is the boat form of the phosphorus-containing ring. Earlier[37] it was reasoned that steric interactions inhibited flipping of the ring to the more favorable chair form. More recently, however, it has been shown that the phosphoryl oxygen in six-membered ring phosphates and phosphonates resides in the equatorial position in six compounds for which structures have been determined in the solid state[70]. The POC (122°) and OPO (108°) as well as the P—O (1.56 Å) and P=O (1.43 Å) bond lengths found for Xa compare well with those in similar systems[70]. On the basis of dipole moment and NMR studies, an analogous configuration was postulated for the bicyclic phosphonate shown below[71a,b]. In spite of the presence of 1—3 interactions involving the bulky triphenylmethyl group and the axial CH protons, the phosphoryl oxygen does not adopt an axial configuration in the monocyclic phosphonate below, although the phosphorus end of the ring is al-





most completely flattened to distort the ring from a chair to a "chaise longue" conformation[71c]. Though the reason for the strong equatorial preference of the phosphoryl oxygen is not obvious, its consistent observation in the solid state thus far and its probable dominance in solution[38,71d] raises the question of whether or not the structure shown for Xb in eqn. (10) is correct since the disposition of the P=O group was postulated to be axial. Until a molecular structure determination is carried out, the configuration shown is tentatively retained on the basis of the long range NMR coupling discussed earlier.

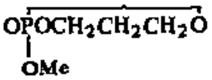
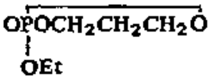
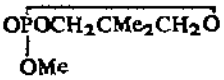
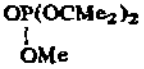
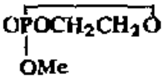
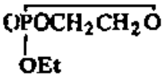
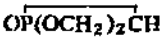
(v) P=O stretching frequencies

Despite the constancy of the phosphoryl oxygen bond lengths (ca. 1.45 Å) in the trialkyl phosphates $OP(OCH_2)_3CMe$ (ref. 37), $OP(OCH_2)_2(OMe)$ (ref. 37), $OP(OCMe_2)_2(OMe)$ (ref. 37) and $(O)(PhO)P(OCH_2)_2CH_2$ (ref. 70a) whose structures are known, there does seem to be a wide variation in P=O stretching frequencies[11,29,38,72]. From Table 3 it is seen that open-chain phosphates generally absorb in the 1260–1275 cm^{-1} region except for $OP(OMe)_3$, in which presumably a second conformer[72b,73,74] contributes another band at 1290 cm^{-1}. The six- and five-membered ring phosphates absorb from 1270–1310 cm^{-1} while the bicyclic phosphates exhibit very high frequencies between 1310 and 1340 cm^{-1}. Although there seems to be no correlation of ν(P=O) with ring size in the monocyclic compounds[72a], it is tempting to regard the rather sharp increase from open-chain phosphates to the polycyclic derivatives as reflecting to some degree a change in the bonding in the P=O link. Utilizing the conclusions drawn in the previous section concerning structural and hybridization changes upon polycyclizing an open-chain phosphate, it could be concluded that most of the increase in ν(P=O) is the result of the smaller POC angle in $OP(OCH_2)_3CMe$, since the OPO angle is not changed significantly. Thus the reduction in P–O pi bonding due to the decrease in POC angle requires the exocyclic P=O bond to increase its pi bonding to compensate. This effect would be even stronger in $\mathrm{O\overline{P(O\overset{O}{C}H_2)_2C}H}$ because of the greater constraint, and the value of ν(P=O) is indeed observed to rise noticeably.

A less conspicuous increase in ν(P=O) is observed in polycyclizing $OP(CH_2OH)_3$ (1190, 1130 cm^{-1})[75] to $OP(CH_2O)_3CH$ (1200 or 1210 cm^{-1}, $CHCl_3$)[76] which would accord with the incapability of the carbon substituents on phosphorus to pi bond to phosphorus. Consequently hybridization changes on the carbon upon constraint are far less than in the case of oxygen. Substitution of a PO or PS group for the CH moiety in $OP(CH_2O)_3CH$ as expected does not greatly alter the phosphine P=O frequency ($OP(CH_2O)_3PO$, 1220 cm^{-1}, KBr; $OP(CH_2O)_3PS$, 1215 cm^{-1}, KBr)[31] since the bridgehead angles are not changed by more than a few degrees. It is also rather interesting in this respect that the P=O frequency of the phosphate phosphorus in $OP(OCH_2)_3P$ (1300 cm^{-1}, KBr)[31] is not the same as that in $OP(OCH_2)_3PO$ (1325 cm^{-1}, KBr)[31]. It is reasonable that the latter frequency is the same as that observed for $OP(OCH_2)_3CMe$ (Nujol)[4] because the CPC angles (106° in Me_3PO)[63] are not expected to be far from the virtually tetrahedral CCC angles observed[37] in

TABLE 3

Phosphoryl oxygen stretching frequencies for trialkyl phosphates in solution

Compound	ν(P=O) (cm^{-1})	Ref.
$OP(O\text{-}n\text{-}Bu)_3$	1260	11
$OP(OEt)_3$	1261	72a
	1270, 1260	72b
$OP(OMe)_3$	1290, 1275	72b
	1290, 1274	38
 $\mathrm{O}\overline{\underset{\mathrm{OMe}}{\mathrm{P}}\mathrm{OCH_2CH_2CH_2O}}$	1312, 1279	38
 $\mathrm{O}\overline{\underset{\mathrm{OEt}}{\mathrm{P}}\mathrm{OCH_2CH_2CH_2O}}$	1290	72a
	1308	72f
 $\mathrm{O}\overline{\underset{\mathrm{OMe}}{\mathrm{P}}\mathrm{OCH_2CMe_2CH_2O}}$	1310, 1270	38
 $\mathrm{O}\underset{\mathrm{OMe}}{\mathrm{P}}\mathrm{(OCMe_2)_2}$	1290	72c
 $\mathrm{O}\overline{\underset{\mathrm{OMe}}{\mathrm{P}}\mathrm{OCH_2CH_2O}}$	1302	72d
	1302	72e
 $\mathrm{O}\overline{\underset{\mathrm{OEt}}{\mathrm{P}}\mathrm{OCH_2CH_2O}}$	1287	72a
	1301	72f
$OP(OCH)_3(CH_2)_3$	1325 [a]	72e
$OP(OCH_2)_3C\text{-}n\text{-}Pentyl$	1336 or 1320	72e
 $\mathrm{O}\overline{\mathrm{P(OCH_2)_2CH}}$	1340 [b]	29
	1355 or 1346	72e

[a] Nujol null.
[b] Solvent was not mentioned[29].

$OP(OCH_2)_3CMe$. On the other hand, the CPC angle in $OP(OCH_2)_3P$ should be close to that in $SP(OCH_2)_3P$ (98°, Fig. 5) and this reduction would permit the POC angles to open up toward 120°, thereby obligating the P=O link to participate less in pi bonding.

In contrast, the P=O stretching frequency of $OP(SCH_2)_3CMe$ (1202 or 1214 cm^{-1}, KBr)[34] compares reasonably well with that found for $OP(SEt)_3$ (1200 cm^{-1}, solution)[77]. This result is consonant with the conclusion based on dipole moment considerations[34] (vide supra) that little change occurs on polycyclizing $OP(SR)_3$. The fact that the IR spectra were measured in different media because of solubility problems makes this conclusion somewhat tenuous, however.

The P=O stretching frequency of $OP(NMeCH_2)_3CMe$ (1280 cm^{-1}, CCl_4)[78] is significantly higher than that reported[79] for $OP(NMe_2)_3$ (1208 cm^{-1}, smear). It is attractive to ascribe the higher frequency in the caged aminophosphine to the greater P=O pi bonding necessary to compensate for the loss incurred in the P–N links upon reducing the PNC angle from 120 (ref. 80) to 116°.

(vi) Basicity studies

This section will be restricted to comparisons of the affinities of open-chain and polycyclic phosphites and phosphates for protons and for lanthanide ions in the case of phosphates. Phosphorus–metal and phosphorus–boron interactions will be discussed in Sect. C.

A measure of the proton affinity of water-insoluble bases can be obtained in water–methanol mixtures by a potentiometric titration technique[81] in which the half-wave neutralization potential (ΔHNP) is measured. The higher the ΔHNP value, the weaker the base. Though the method was originally developed to measure relative basicities of phosphines, which are comparatively basic, it has been extended to include a series of phosphites including Ia[82a]. The order of decreasing basicity (ΔHNP) is: $P(OR)_3$ (520) > Ia (665) > $P(OPh)_3$ (875). This order is in agreement with the idea put forth earlier that the lone pair on phosphorus in caged phosphites is more difficult to polarize because the OPO bond angles are difficult to open toward tetrahedrality. Any widening of this angle which does occur will close the POC angles from 120° by the "hinge" effect and thus reduce pi delocalization to phosphorus, resulting in a higher positive charge on phosphorus and decreased basicity compared with open-chain analogs. Because the OH stretching frequency of phenol decreases upon hydrogen bonding with lone pair electrons, it is possible to order basicities in a series of compounds of a similar nature. The basicity order of four phosphites representative of various degrees of constraint is[82b] $MeOP(OCH_2)_2CH_2 \cong P(OMe)_3 \cong MeOP(OCH_2)_2 > P(OCH_2)_3CEt$ (Table 4). While an inductive effect may be competitive among the first three compounds, increasing constraint appears to win out in the last. It should be realized, however, that both the oxygens and the phosphorus atoms are potential protonation or hydrogen bonding sites in phosphites. Thus it is not unambiguously clear that phosphorus

TABLE 4

Phenol shifts of phosphorus compounds[a]

Compound	Δν(OH) (cm^{-1})	Compound	Δν(OH) (cm^{-1})
$P(OMe)_3$	216	$OP(OMe)_3$	263
$MeOP(OCH_2)_2CH_2$	225	$OP(OCH_2)_2CH_2(OMe)$	244
$MeOP(OCH_2)_2$	212	$OP(OCH_2)_2(OMe)$	243
$P(OCH_2)_3CEt$	136	$OP(OCH_2)_3C$-*n*-Pent	232

[a] The concentrations of phosphorus compound and PhOH are 0.01 *M* and 0.150 *M*, respectively.

basicities are being measured in either the half-wave neutralization or the phenol shift experiments. Phosphorus involvement is reasonable if the "hinge" effect actually results in an increase in basicity of oxygen because of the progression from an sp^2 toward a more basic sp^3 oxygen, provided the oxygen basicities are always less than that of phosphorus, for if the reverse were true, opposite orders would have resulted from both experiments. On the other hand, a reduction of oxygen basicity could be envisioned on constraint (despite an increase in sp^3 character) if the increase in positive charge on phosphorus due to loss in P—O pi bonding were to polarize the P—O sigma bond. Thus the results of these experiments, while consistent with the quoted basicity orders, are not definitive regarding the basic site involved. In excess acid, acyclic phosphites have been shown to protonate the phosphorus atom[82c,d] by the observation of the characteristically strong P—H coupling (~800 Hz). The highest P—H coupling to date for a protonated phosphite was recently observed for $P(OCH_2)_3CMe$ (899 Hz)[82b]. This result not only attests to the possibility of protonation of phosphorus in the phenol shift studies but also to the lowering of phosphite basicity on constraint (increased lone-pair *s* character and phosphorus positive charge). A monotonic change of $\Delta\delta^{31}P$ (the change in ^{31}P shift on protonation) with ^1JPH was postulated[82c] to arise from inductive effects, since coupling increased in the order $P(O\text{-}i\text{-}Pr)_3 < P(OEt)_3 < PhOP(OCH_2)_2 < P(OMe)_3 < P(OPh)_3$. The phosphorus atom in five-membered ring phosphites is apparently less nucleophilic than in open-chain systems as determined from several organic reactions[83a–c].

It has been shown experimentally that the lone-pair availability on the phosphoryl oxygen in caged phosphates is drastically reduced. By reversed phase chromatography techniques[83d] it was demonstrated[11] that $OP(OCH_2)_3C\text{-}n\text{-}Pent$ does not function as an extractant for trivalent lanthanum, neodymium, samarium, gadolinium and ytterbium ions under a variety of conditions, in striking contrast to the well known extractant $OP(OBu)_3$. Thus in spite of the reduced steric requirements of the caged phosphite and its much higher dipole moment (vide supra), its extraction properties are too weak to be observed. Although it was recognized that the rare earth extraction ability of organic phosphates decreased with increasing ν(P—O) values[84a], the origin of the effect in the caged phosphate has been obscure until now. Piperidinium phosphate ester association constants[84c] calculated from conductivity measurements were also found to be consistent with a decrease in phosphoryl oxygen basicity for phosphates in the order $O{=}P(O\text{-}n\text{-}Bu)_3 > (n\text{-}OctO)(O{=})P(OCH_2)_2CH_2 > O{=}P(OCH_2)_3CEt$ although no rationalization was given for the trend.

Phenol shift experiments in our laboratories have shown[72e] that basicity decreases from an open-chain to six and five-membered rings to a polycyclic phosphate (Table 4). These results can now be rather firmly rationalized on the basis of increased phosphoryl oxygen pi bonding via constraint. Although a decrease in sigma basicity toward the phosphoryl oxygen from the phosphorus would also explain the trend, the similarity of OPO angles among the series does not support this contention. The question of P=O or POC oxygen protonation again arises, however. Favoring phosphoryl oxygen involvement are the substantially higher phenol shifts encountered for phosphates than phosphites which would not be expected on inductive grounds if POC oxygens were involved in both cases. It is interesting in this respect that phosphoryl oxygens are generally more basic than the ester oxygens, which may indicate that stronger sigma polarization of phosphorus by the former type results in a higher negative charge on the phosphoryl oxygen, as has been calculated[84b].

Pi bonding in amino phosphines and amino phosphine oxides has frequently been cited as the probable cause of the relatively low basicity of the nitrogen in these compounds[86] and it has also been invoked to rationalize the increased basicity of phosphorus in amino phosphines[87a]. Even in competition reactions it has been found that phosphines form more stable "onium" salts than amines[87b], which would appear to reinforce the expectation that phosphorus can generally be expected to function as the donor site. There does appear to be an electronegativity effect in $P(NR_2)_3$ compounds, however, since the phosphorus in aminophosphines is less nucleophilic than in phosphines[87b], despite the common notion that the electron inductive effect of the Me_2N group surpasses methyl[88]. Although phosphorus coordination is observed in the majority of cases, an additional Lewis acid can sometimes be coordinated to one of the nitrogens (see Sect. C).

(vii) UV photoelectron spectra

Photoelectron spectroscopy has proven very valuable for obtaining information on the nature of through-bond and through-space orbital interactions in bicyclo[2.2.2]-octane hydrocarbons[89], $N(CH_2CH_2)_3N$ (ref. 90) and also[91] P_4. A review has appeared recently in which the natures of these interactions are analyzed[92].

Preliminary investigations on polycyclic phosphorus compounds[93] indicate that useful structural as well as electronic information can be extracted from their photoelectron spectra. The pi bonding and antibonding MO ionization potentials in $P(NMeNMe)_3P$, for instance, fall in a rather small range 3 eV), suggesting that the pi-type interactions are not very strong. This may mean that the molecule does not have C_{3v} symmetry with planar nitrogens. Following this discovery it was learned that an X-ray diffraction study had been carried out in which it was shown that indeed the Me groups on adjacent nitrogens are staggered (the sum of the angles around the nitrogens being ca. 345°)[94] and this configuration is even preserved in $SP(NMeNMe)_3PS$ (ref. 95a) and in $OP(NMeNMe)_3PO$ (ref. 95b). In all cases the PN bond lengths appear to be indicative of some pi bonding. The reason for the staggering of Me groups appears to be the presence of steric repulsions between vicinal methyl groups, since they would come well within each other's van der Waals radius in an eclipsed configuration. In contrast, $P(CCF_3CCF_3)_3P$ exhibits a photoelectron spectrum[93] which is similar to that[96] of $HC(CH{=}CH)_3CH$ except that the pi ionization potentials are somewhat higher. The splitting in the low ionization potential region of the PE spectra of $P(OCH_2)_3CMe$, $P(CH_2O)_3CMe$ and $MeC(OCH_2)_3CMe$ is consistent with through-space interactions among the oxygens as shown schematically in a view down the C_{3v} axis (see over).

(viii) Conclusions

It is quite probable that constrained phosphites of types I, II and Vf are very much like an acyclic analog in terms of bond angles and lengths. Because of oxygen lone-pair orientations, however, they are much more polar. Moreover the large PO moments in the direction of phosphorus are consistent with significant P–O pi bonding. Caged phosphines (Va–f), thiophosphites (VI) and aminophosphines (VII) probably resemble their open-chain analogs as well, although lack of data at present makes this less certain.

The contrasts in ligating character between open-chain and caged phosphorus systems (to be elaborated upon in Sect. C) become evident to some extent from comparisons of their proton affinities but chiefly from structural, infrared and basicity differences in their oxides. The main conclusion to be drawn is that polarization of the phosphorus lone pair in both caged and open-chain compounds by an acceptor results in an increase in the OPO angle but a definite decrease of the PYC angle (Y = O or N) from 120° occurs in the caged molecule because of constraints. The consequent decrease in P–O pi bonding manifests itself in three effects. (*1*) An increase in the P=O stretching frequences of oxide derivatives of caged phosphites and aminophosphines is observed because of the necessity for the P=O bond to make up the P–O pi bonding loss. (*2*) The decrease in the basicity of the phosphoryl oxygen in caged phosphates occurs for the same reason. (*3*) A decrease in proton affinity of the phosphorus is found in caged phosphites because the reduced P–O pi bonding leaves a higher positive charge on phosphorus.

There are two intriguing aspects of pi bonding which can arise in many systems but which will be illustrated here with PZ_3 systems where Z = OR or NMe_2. The first deals with the efficiency of PO or PN pi bonding as a function of the orientations of the oxygen or nitrogen lone-pair *p* orbitals with respect to one another. Thus if the POC angles were 120° in $OP(OCH_2)_3CMe$, for instance, the oxygen *p* orbitals would all lie in the same plane whereas in $OP(OCH_2Ph)_2(OH)$ this is not the case in the solid state[54] at least. A self-consistent molecular orbital calculation showed differences[97a] in the P–O pi energies in $OP(OCH_2Ph)_2$-(OH) and $MeO(O)P(OCH_2)_2$ and EHMO calculations revealed a smaller negative phosphoryl oxygen negative charge for cyclic phosphates compared with an acyclic one[84b]. A recent independent EHMO calculational comparison of P=O oxygen charges shows that they are roughly equal in $OP(OMe)_3$ and $OP(OCH_2)_2CH_2(OPh)$ while they are also about the same but smaller in magnitude[97b] in $OP(OCH_2)_2(OMe)$ and $OP(OCH_2)_3CMe$. Because of their similarity in these compounds, comparison of the P–O distances does not reveal any discernible trend. The record shortness of the P–N bond in $OP(NMeCH_2)_3CMe$, however, makes it clear that coplanarity of the nitrogen *p* orbitals does not hinder P—N pi bonding and perhaps even augments it.

The other curious facet of PZ_3 pi bonding is the possibility that an sp^3 orbital on nitrogen could pi bond with phosphorus in an aminophosphine. It has recently[98] been shown theoretically that pyramidal nitrogen can conjugate with an adjacent unsaturated system and the associated resonance interactions are about four-fifths as effective as planar nitrogen. Although it is not necessary to invoke this possibility to explain our results, it may apply to the structure[94] of $P(NMeNMe)_3P$ in which the P—N distances are comparable with those in $OP(NH_2)_3$ (ref. 68), F_2PNMe_2 (refs. 66, 67) and $\{Cu[(Me_2N)_2(O)POP(O)(NMe_2)_2]_3\}(ClO_4)_2$ (ref. 80) in spite of the non-planarity of the nitrogens.

C. COORDINATION COMPOUNDS

(i) Phosphoryl compounds

A substantial portion of Sect. B has already been devoted to this class of compounds and it may seem strange to dwell any longer on them or even to consider them as coordination compounds. In Sect. B phosphoryl systems were treated as derivatives from which essential information could be obtained concerning their trivalent parents. Throughout this section it was tacitly assumed that relatively strong pi bonding was a characteristic of the phosphoryl link. Although multiple bond character in phosphoryl compounds seems indicated by their short P=O distances and high P=O stretching frequencies, it is appropriate to justify this assumption more thoroughly at this point because in addition to the fact that the oxygen atom can be considered as an atom ligated by a trivalent phosphorus compound, the P=O bond exemplifies a system in which the coordinated species is capable of both extremely strong phosphorus lone-pair polarization as well as pi back-donation. Thus in further discussions, phosphoryl systems will frequently serve as models with which to compare coordination compounds suspected of engaging in some degree of phosphorus–acceptor pi bonding.

A detailed review[99] of the evidence for $d_\pi - p_\pi$ bonding in the P=O bond appeared some years ago in which thermodynamic, structural and spectral parameters were analyzed for their importance in multiple bonding. Only the more pertinent arguments will be summarized here and greater emphasis will be placed on more recent experiments and calculations which reflect the pros and cons of P=O pi bonding.

Contrasts of the properties of the pnictide-oxygen groups in amine and phosphine oxides have commonly been used to support the presence of $d_\pi - p_\pi$ bonding in the latter[99,100]. Thus the dissociation energies for P=O bonds lie in the 120–150 kcal/mole range, whereas they occur from 50–70 kcal/mole for N→O bonds. Weakening of the dissociation energies for N→O systems, because of the greater ionization potential of amines or interelectronic repulsions between first row elements, are considered to be of secondary importance. The P=O bond length tends to be about 0.2 Å shorter than the sum of the covalent radii whereas the N→O bond generally approximates that of the calculated single bond length. Shortening of the N→O length due to the greater electronegativity of N compared with P and hence a lowering of the N→O bond moment is discounted by the larger moments of N→O links. The surprisingly short NO bond length[101] in F_3NO of 1.15 Å, however (which is about 0.2 Å shorter than an NO single bond), is strongly indicative of the presence of appreciable p_π–p_π bonding[102]. Dipole moment increments due to the oxidation of a phosphine to a phosphine oxide ($\Delta\mu \cong 2.7$ (ref. 103) to 2.9 D (ref. 104)) are generally much smaller than those expected (4.25 D) from the proportionality presumably involving simple coordinate N→O, N→B and P→B bonds: $\Delta\mu(Me_3PO)/\Delta\mu(Me_3NO) = \Delta\mu(Me_3PBCl_3)/\Delta\mu(Me_3NBCl_3)$[99,103]. The rationalization of this result on the basis of d_π–p_π back-donation to phosphorus has been criticized, however, on the ground that even such large differences could be due to polarizability differences of the P and N atoms[105]. Furthermore, the incremental value for Me_3PO calculated from the proportionality (4.25 D), though 30% larger than the increments involved in oxidizing PPh_3 (ref. 103) or PR_3 (ref. 104) (R = Et, *n*-Pr, *n*-Bu or *n*-Pent), is indeed equal to the 4.2 D increment recently determined for the PMe_3–$OPMe_3$ pair[106].

Optical and magnetic resonance spectral studies of phosphorus compounds by and large point toward possible P=O double-bonding. The increase in ν(P=O) with increasing electronegativity of Z in OPZ_3 systems[107], with decreasing bond length[108] or with increasing force constants calculated from spectral analyses[109] is consistent with increasing bond order due to d_π–p_π involvement but measured P=O bond refractions are not[110]. Although the P=O bond is transparent in the far ultraviolet, aryl group absorptions in phosphoryl derivatives have been examined for evidence of conjugation with the P=O group. Unfortunately, conflicting interpretations of the importance of this interaction were put forth[99]. Strongly donating aromatic systems, however, greatly displace the *p* bands of aromatic phosphine oxides[99] and this effect seems to be asssociated with d_π–p_π delocalization involving only the phosphorus in the P=O group[99,111] since the orbitals on the phosphorus used by the conjugating substituents are not the same as those employed by the oxygen[112]. A plot of the nuclear quadrupole resonance frequencies of the ^{35}Cl nucleus in a series of $OPCl_2R$ compounds versus the effective electronegativity of R as calculated from ν(P=O) values[113] yields separate lines for conjugating and non-conjugating R groups[112]. Thus the conclusion drawn is that if substituents on phosphorus can conjugate with phosphorus *d* orbitals, so can a phosphoryl oxygen. Further indirect evidence of phosphorus *d* orbital participation in bonding stems from the weak interaction of the unpaired electron in anionic radicals such as $[O\dot{P}Ph_3]^-$ with the ^{31}P nucleus as indicated by their ESR spectra[114]. This was interpreted to arise from the placement of the electron in an orbital of high *d* character with enough *s* component to make coupling observable. Further splitting due to *ortho* and *para* protons on the phenyl groups was taken as evidence for the conjugation of the phenyl moieties with phosphorus *d* orbitals. The inclusion of pi bond occupation and electronic distribution in the theoretical treatment of ^{31}P chemical shifts is apparently an essential feature[45]. Whereas sigma bonds are generally composed of *s* and *p* orbitals, *d* orbitals exclusively make up the pi bonds and the two contributions to the chemical shift are then additive[45]. ^{13}C–^{1}H coupling constant measurements have also been related to pi bonding in P=O links[115]. J ^{13}C–^{1}H increases from NMe_3 (131 Hz) to NMe_4^+ (145 Hz) and $ONMe_3$ (143 Hz) owing to the increase in electronegativity (positive charge) on nitrogen which increases the *s* character in the C–H bonds. Where a sizeable increase is also noted from PMe_3 (127 Hz) to PMe_4^+ (134 Hz), the value for $OPMe_3$ (129 Hz) is indicative of only a small change in charge on the phosphorus, consistent with substantial pi feedback[115].

Calculations based on bonding theory have also been carried out and their validity tested with experimental parameters in some cases. Ab initio computations[116] on PCl_3 and $OPCl_3$ with Slater-type orbitals give orbital energies which compare favorably with vertical ionization potentials measured from PE spectra when phosphorus *d* orbitals are included. Furthermore, when PCl_3 complexes to oxygen, the phosphorus $3s$ and $3p_\sigma$ populations decrease greatly, whereas a large increase in the $3p_\pi$ and $3d_\pi$ densities occurs, with the latter exceeding the former. Substantial $3d_\pi$ bonding has also been calculated[117a–d,118] for OPF_3 by ab initio[117a,b,118], non-empirical valence bond[119] and CNDO[120a,b] methods. Although inclusion of such a component brings the calculated dipole moment closer to the experimental value[118,120a,b], SCF–LCAO[121] and CNDO[120a,b] calculations show that bond angles around second-row atoms are virtually independent of *d* orbital inclusion. The larger pi bonding and smaller sigma bonding calculated[117d] for the P=O bond in OPF_3 compared with OPH_3 is rationalized by the higher electronegativity of the fluorine atoms compared with the protons, which places a higher positive charge on the phosphorus. The small change in positive charge on phosphorus from PF_3 to OPF_3 was interpreted as reflecting about equal sigma donation and pi acceptance on the part of phosphorus. A problem arises in the ab initio calculations[122] of $OPMe_3$, which indicate that the charge on phosphorus in PMe_3 is unaltered on oxide formation, yet the calculated dipole moment increase (ca. 2 D) is only half of the experimental[104] increment (4.2 D). Ab initio calculations on PO, PO^- and PO_2^- systems also show a lowering of the ground state and a rise in overlap population when *d* orbitals are included[123a,b]. Extended Hückel MO calculations including *d* orbitals reveal[102] trends in P=O bond length which look more realistic and overlap populations which resemble those obtained from ab initio studies.

The preponderance of theoretical evidence, then, supports a degree of P=O pi bonding which is chemically significant in that it rather severely affects electronic distributions and energies[102,120a,124]. On the other hand, the role of *d* orbitals in determining bond angles seems minimal at best[102,120a]. It is reasonable to conclude that whereas in many cases outer *d* orbitals lie too high in energy and are too diffuse for efficient overlap[125], there are valence state configurations in which highly electronegative ligands can sufficiently contract the phosphorus $3d$ orbitals for overlap with a pi electron base[126a–d], in this case oxygen. Having hopefully established an experimentally and theoretically reasonable case for ligand–acceptor pi bonding in phosphoryl systems, we now turn our attention to some coordination compounds which will be compared with phosphoryl compounds in a number of instances.

TABLE 5

Boron adducts of phosphorus and arsenic ligands

Adduct[a]		Properties	Ref.
Base	Acid		
$\mathrm{P(OCH)_3(CH_2)_3}$	$\mathrm{BH_3}$	M.p. 247–251°, air stable	41
$\mathrm{P(OCH)_3(CH_2)_3}$	$\mathrm{B_3H_7}$	Dec. 270°, air stable	41
$\mathrm{P(OCH)_3(CH_2)_3}$	$\mathrm{BMe_3}$	Dissociable solid	41
$\mathrm{P(OCH)_3(CH_2)_3}$	$\mathrm{BF_3}$	Decomposes easily	41
$\mathrm{P(OCH_2)_3CMe}$	$\mathrm{BH_3}$	M.p. 199°, air stable	127
$\mathrm{P(OCH_2)_3CMe}$	$\mathrm{BD_3}$	Air stable	127
$\mathrm{P(OCH_2)_3CMe}$	$\mathrm{B_3H_7}$	Dec. 167°	127
$\mathrm{P(OCH_2)_3CMe}$	$\mathrm{BMe_3}$	Solid, dissociates	127
$\mathrm{P(OCH_2)_3CMe}$	$\mathrm{BF_3}$	Hydrolyzes easily	127
$\overset{O}{\overline{\mathrm{P(OCH_2)_2CH}}}$	$\mathrm{BH_3}$	Decomposes easily	72e
$\mathrm{As(OCH)_3(CH_2)_3}$	$\mathrm{BH_3}$	No reaction	85
$\mathrm{As(OCH)_3(CH_2)_3}$	$\mathrm{BMe_3}$	No reaction	85
$\mathrm{P(NMeCH_2)_3CMe}$	$\mathrm{BH_3}$[b]	M.p. 74–76°, sublimes in vacuum	35
$\mathrm{P(NMeCH_2)_3CMe}$	$\mathrm{2BH_3}$	Dec. 120°, sublimes in vacuum	35, 85
$\mathrm{OP(NMeCH_2)_3CMe}$	$\mathrm{BH_3}$	Stable to dissociation at room temp.	35
$\mathrm{SP(NMeCH_2)_3CMe}$	$\mathrm{BH_3}$	Stable to dissociation at room temp.	35
$\mathrm{As(NMeCH_2)_3CMe}$	$\mathrm{BH_3}$[b]	Decomposes rapidly at room temp.	85
$\mathrm{As(NMeCH_2)_3CMe}$	$\mathrm{2BH_3}$	Decomposes slowly at room temp.	85
$\mathrm{As(NMeCH_2)_3CMe}$	$\mathrm{BMe_3}$	Dissociates slowly	85
$\mathrm{As(NMeCH_2)_3CMe}$	$\mathrm{2BF_3}$	Dissociates slowly	85
$\mathrm{P(CH_2O)_3CMe}$	$\mathrm{BH_3}$	Stable in air	26
$\mathrm{P(CH_2O)_3CMe}$	$\mathrm{BMe_3}$	No reaction	26
$\mathrm{P(CH_2O)_3CMe}$	$\mathrm{2BF_3}$	Unstable to dissociation and hydrolysis	26, 85
$\mathrm{P(CH_2O)_3CMe}$	$\mathrm{BBr_3}$	Decomposition prevents isolation	85
$\mathrm{P(OCH_2)_3P}$	$\mathrm{BH_3}$[b]	Stable in air	31
$\mathrm{P(OCH_2)_3P}$	$\mathrm{2BH_3}$	Hydrolyzes easily	31
$\mathrm{MeO\overline{POCH_2CH_2O}}$	$\mathrm{BH_3}$	Stable liquid	72e
$\mathrm{MeO\overline{POCH_2CMe_2CH_2O}}$	$\mathrm{BH_3}$[d]	Stable solid	72e
$\mathrm{MeO\overline{POCH_2CH_2CH_2O}}$	$\mathrm{BH_3}$	Stable liquid	72e
$\mathrm{(MeO)_{ax}\overline{POCH_2C(Me)_{ax}\text{-}(CH_2Cl)_{eq}CH_2O}}$	$\mathrm{BH_3}$	Stable liquid isomer mixture	128
$\mathrm{(MeO)_{ax}\overline{POCH_2C(Me)_{eq}\text{-}(CH_2Cl)_{ax}CH_2O}}$	$\mathrm{BH_3}$	Stable liquid isomer mixture	128
$\mathrm{(MeO)_{ax}\overline{POCH(Me)_{eq}\text{-}CH_2CH(Me)_{eq}O}}$	$\mathrm{BH_3}$	M.p. 76–77.5°, stable	72e
$\mathrm{(MeO)_{eq}\overline{POCH(Me)_{eq}\text{-}CH_2CH(Me)_{eq}O}}$	$\mathrm{BH_3}$	Stable liquid, mixture with preceding isomer	72e

TABLE 5 (continued)

Adduct[a]		Properties	Ref.
Base	Acid		
$P(OMe)_3$	BH_3[d]	Stable liq., b.p. 86°/23 mm	72e, 129
$P(OMe)_3$	BMe_3	Dissociates	43
$P(OEt)_3$	BH_3[d]	Stable liq., b.p. 39°/0.4 mm	129
$P(O\text{-}i\text{-}Pr)_3$	BH_3[d]	Stable liq., b.p. 42–43°/0.1 mm	129
$P(O\text{-}n\text{-}Bu)_3$	BH_3[d]	Stable liq., b.p. 83–55°/0.15 mm	129
$P(OPh)_3$	BH_3[d]	M.p. 54°	130
$P(OC_6H_{11})_3$	BH_3[d]	M.p. 69°	129
$P(NH_2)_3$	BH_3	Solid	131
$P(NMeH)_3$	BH_3	M.p. 30.5–31.0	132
$P(NMe_2)_3$	BH_3[d]	M.p. 32.5	35, 133
	BMe_3	Dissociates	134
	BEt_3	Dissociates	134
$OP(NMe_2)_3$	BH_3	Dissociates	35
$SP(NMe_2)_3$	BH_3	No reaction	35

[a] The formulation of the adduct as shown is meant to imply nothing about the site(s) of attachment of the acid. This will be discussed in the appropriate sections of the text. In all cases the base was reacted with excess Lewis acid (B_2H_6, B_4H_{10}, BX_3 or BR_3) at room temperature or below unless otherwise indicated. It is noted under the properties column if no adduct formed. [b] B_2H_6/Base = 0.5. [c] B_2H_6/Base = 1.0. [d] Base + BH_4^- + CO_2.

(ii) Boron adducts

1. Nature of the adducts

In contrast to phosphines or arsines, in which a boron Lewis acid has no choice but to attach to the pnictogen, compounds such as phosphites, arsenites, amino phosphines and amino arsines possess additional lone pair density on oxygen or nitrogen atoms. Table 5 contains pertinent data regarding the formation of adducts of the latter type made in our laboratories[26,31,35,41,72e,85,127,128]. Others [129–134] have been included for which useful comparisons can be made in later sections.

Phosphite and amino phosphine borane adducts can be made by depolymerizing B_2H_6 or by replacing a hydride on the BH_4^- anion[3]. In our syntheses listed in Table 5, stoichiometries were checked by analyses, molecular weight measurements or by plotting the vapor pressure of the Lewis acid versus the mole ratio of reactants and noting the break in the curve. The latter technique was particularly useful in the case of easily dissociable adducts. It was also found that the BMe_3 adduct of Ia could be used as a superior source of pure BMe_3 when allowed to dissociate[41].

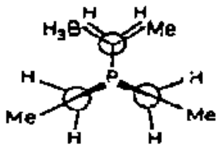
In addition to the possibility of multiple coordination sites in the ligands shown in Table 5, evidence has been put forth both for and against the involvement of pi bonding from the BH_3 moiety to *d* orbitals on phosphorus. Although a more detailed discussion of this problem will occur elsewhere[1], results bearing on our work will be included in subsequent paragraphs.

2. NMR spectral parameters

^{31}P, ^{11}B and ^{1}H NMR spectral studies conducted on the polycyclic[26,31,35,41,72e,85] and acyclic ligand[41,72e,135–138] boron adducts are most helpful in assigning the site(s) of coordination on the ligand. Phosphorus coordination is expected only to shift the ligand ^{1}H spectra downfield by the inductive effect. It might also be expected that a change in the phosphorus to ligand–proton coupling would be observed. Large ^{11}B–^{31}P couplings are also predicted if phosphorus is the basic site and these should register in the ^{31}P and ^{11}B spectra. Comparison of the relevant data in Tables 2 and 6 satisfactorily shows that phosphorus is bonded in the adduct. Coordination to oxygen would not give such large ^{11}B–^{31}P coupling and in the absence of exchange, the OCH protons would not remain equivalent. That exchange among oxygens is not occurring is indicated by the observation of ^{11}B–^{31}P and ^{31}P–B–^{1}H coupling. The reason for the equivalence in ^{1}JBP and ^{1}JBH values in Table 6 is not presently understood.

Several lines of evidence point to phosphorus as the donor site in 1:1 adducts of amino phosphines. ^{31}P, ^{11}B and ^{1}H NMR data similar to that presented in Table 6 for phosphites have been interpreted in terms of P–B bonds in $P(NMe_2)_3$ adducts of BH_3 and HEt_2B (ref. 139) and in $P_4(NMe)_6$–BH_3 compounds[140]. The presence of ν(BH) bands in the 2400–2500 cm^{-1} has been concluded to be characteristic of PBH_3 systems whereas NBH_3 groups yield ν(BH) frequencies in the 2230–2400 region[141].

Evidence gathered from ^{1}H NMR spectra is summarized in Table 7 showing that a nitrogen atom in the polycyclic aminophosphine VIIa can behave as an electron pair donor after prior occupation of the phosphorus by a borane, oxygen or sulfur. Thus the CH_2 proton resonances become a complex multiplet while three doublets[142] are expected for the NCH_3 hydrogens on the basis of the schematic structure shown here.



Contrastingly, $OP(NMe_2)_3$ forms a 1:1 adduct in which preservation of the NCH_3 proton NMR doublet suggests that either rapid exchange of the BH_3 group is occurring among the nitrogens or that the phosphoryl oxygen (which is more basic than in $OP(NMeCH_2)_3CMe$) coordinates to the borane. The lack of a borane complex with $SP(NMe_2)_3$ is explicable on the latter hypothesis since the donor properties of a thiophosphoryl sulfur are expected to be slight in this case.

Although evidence for di-adduct formation in aminophosphines such as $P(NMe_2)_2Bu$ and $P(NMe_2)Bu_2$ could not be found[141], $P(NMe_2)Me_2$ apparently forms $H_3BP(NMe_2BH_3)Me_2$ quite easily[143]. From infrared studies, B–N bonding is also indicated

TABLE 6

NMR parameters[a] of boron adducts of phosphites

Adduct	$\delta^{31}P$[b]	$\delta^{11}B$[c]	$^1J_{BP}$	δBCH $\delta B\underline{H}$[d]	$^1J_{BH}$	$\delta PC\underline{H}$ $\delta PNC\underline{H}_2$ or $\delta POC\underline{H}$[d]	$^2J_{PCH}$ $^3J_{PNCH_2}$ or $^3J_{POCH}$	Ref.
$H_3B\overline{P(O\overset{O}{C}H_2)_2CH}$				0.61	102	3.9–5.5	[h]	72e
$H_3BP(OCH)_3(CH_2)_3$	−117	+60.5	97.6	0.23	97.6	4.88	12.5	41
$Me_3BP(OCH)_3(CH_2)_3$	−128	+32.3	[e]	−0.25		4.38	6.7	41
$F_3BP(OCH)_3(CH_2)_3$	−138	+20.0	[e]	[f]		4.33	[e]	41
$H_3BP(OCH_2)_3CMe$	− 97	+62.1	96.0	0.31	96.0	4.30	4.2	41
$Me_3BP(OCH_2)_3CMe$	− 91	+10.2	[e]	−0.03		3.98	2.2	41
$F_3BP(OCH_2)_3CMe$	− 93	+20.2	[e]	[g]		3.95	2.0	41
$H_3BP(OCH_2)_3P$	+ 66.25[i]			0.50	100	4.97	9.0[j] 5.5[k]	31
$H_3BP(OCH_2)_3PBH_3$						4.98	0[j] 5.9[k]	31
$H_3B\underset{OMe}{\overline{POCH_2CH_2O}}$				0.3	92	4.04–4.61[l] 3.68[m]	 11.4	72e
$H_3B\underset{OMe}{\overline{POCH_2CH_2CH_2O}}$				0.3		3.8–4.6[l] 3.69[m]	 11.0	72e
$H_3BP(OMe)_3$	−118	+63.8	97.2	0.33	97.2	3.67	10.9	41, 72e
$H_3BP(OEt)_3$	−113.5							135
$H_3BP(O\text{-}i\text{-}Pr)_3$	−115	+44.45[n]	99.5					136

[a] Upfield and downfield chemical shifts for ^{31}P and ^{11}B nuclei are prefaced with a positive and negative sign, respectively. The opposite convention is used for protons. [b] With respect to external 85% H_3PO_4. [c] With respect to external $B(OMe)_3$. [d] With respect to internal $SiMe_4$. [e] Not observed because of probable exchange. [f] $\delta^{19}F = 146$ with respect to internal $FCCl_3$. [g] $\delta^{19}F = 143$ with respect to internal $FCCl_3$. [h] Solution of spectrum in progress. [i] This chemical shift represents the PC_3 phosphorus. [j] $^2J_{PCH}$. [k] $^3J_{POCH}$. [l] CH_2 multiplet. [m] OCH_3 doublet. [n] With respect to external Me_2OBF_3.

in the 1:1 adduct $P(NMe_2BF_3)F_2$ but in the BH_3 mono-adduct of this ligand B–P bonding is likely[144]. ^{19}F NMR studies are consistent with di-adducts of the type $2BF_3 \cdot OP(OMe)_3$ and $2BF_3OP(NMe_2)_3$ in which it is believed possible for one of the oxygens or nitrogens attached to the methyl groups to coordinate in addition to the phosphoryl oxygen[145].

It is attractive to conclude that reduced N–P pi bonding in the polycyclic aminophosphine borane, oxide or sulfide (see Sect. B) is responsible for the increased basicity of the nitrogens compared with $OP(NMe_2)_3$ or $SP(NMe_2)_3$, with the result that one of the nitrogens becomes tetrahedral on coordination to a BH_3 group. The easy formation of $H_3BP(NMe_2BH_3)Me_2$ supports this conclusion in that the lack of electronegative substituents on phosphorus in the ligand prevents the nitrogen from significantly pi bonding with phosphorus. Involvement of more than one nitrogen in adduct formation in the compounds in Table 7 is probably electronically rather than sterically inhibited. Models do not permit an unambiguous conclusion on this point[35] but it is reasonable that breakage of one N–P pi bond in forming an N–B link will strengthen the remaining two. The NMR data on the polycyclic aminoarsine BH_3 and BF_3 adducts also show clear evidence for an N–B bond. The lack of such behavior with BMe_3 could well be sterically determined. The isolation of the crystalline compound $H_3BP(NMe_2)_3 \cdot HCl$ is not inconsistent with the above reasoning since the strongly Lewis acidic proton is evidently able to coordinate to a nitrogen but another BH_3 group is not[35].

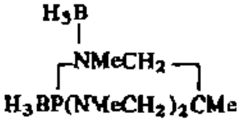
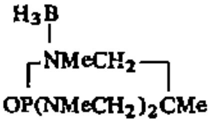
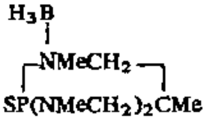
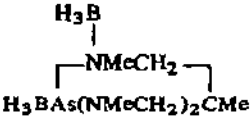
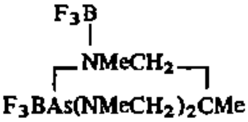
Borane coordination to phosphorus in $H_3BP(CH_2O)_3CMe$ is shown by the simple doublet for the CH_2 protons and the ^2JPCH coupling constant of 0.8 Hz typical for coordinated phosphorus[26]. Moreover, $MeC(OCH_2)_3CMe$ does not react[85] with B_2H_6. In contrast, both $P(CH_2O)_3CMe$ and $HC(OCH_2)_3CMe$ reacted with at least two moles of BF_3, but facile decomposition prevented further characterization of the products[85].

The absence of consistent trends in the ^{11}B and ^{31}P chemical shifts and the constancy of ^1JBP and ^1JBH values in Table 6 preclude interpretation in terms of bonding arguments[146]. A clue as to the nature of the boron–phosphorus bond in BH_3 adducts of I and II does present itself in a study[8, 147] of the variation of ^3JPOCH with the chemical shift of the OCH proton in a series of the type $AP(OCH_2)_3CMe$ and $AP(OCH)_3(CH_2)_3$. The linear rise of ^3JPOCH with the downfield movement of the chemical shift shown in Figs. 9 and 10 for the two phosphites is easily rationalized on the basis of an increase in *s* character in the P–O bonds and a rise in phosphorus *s* density owing to an increase in electronegativity of the A moiety. When A = oxygen or sulfur, however, the NMR parameters give points which fall off the line in a manner suggesting that pi density feedback to phosphorus from the chalconide abnormally shields the protons by a mesomeric inductive effect extending into the ring oxygens. Since the BH_3 adducts in Figs. 9 and 10 are part of a linear plot involving non-pi bonding acids such as carbonium ions, the bromonium ion and BF_3, the foregoing results imply that pi feedback from the BH_3 group is at least small compared with a chalconide.

A similar linear correlation is not observed[8] for $P(OMe)_3$ or $P(OEt)_3$ and ^3JPOCH varies less than 1 Hz from 10 and 7 Hz, respectively. The reason for this is not apparent at this

TABLE 7

NMR parameters of boron adducts of aminophosphine derivatives

Adduct	$\delta\,^1H(CH_2)$[a]	$\delta\,^1H(NCH_3)$[a]	$^3JPNCH_3$	Ref.
$H_3BP(NMeCH_2)_3CMe$	2.81 [b]	2.51	14	35
 $\overset{H_3B\text{—}NMeCH_2}{H_3BP(NMeCH_2)_2CMe}$	2.90–3.60 [c]	2.64 2.74 2.78	13 12 12	35
 $\overset{H_3B\text{—}NMeCH_2}{OP(NMeCH_2)_2CMe}$	3.10–3.80 [c]	2.76 2.79	12 11	35
 $\overset{H_3B\text{—}NMeCH_2}{SP(NMeCH_2)_2CMe}$	3.14–3.90 [c]	2.74 2.85 2.87	14 14 13	35
$H_3BP(NMe_2)_3$		2.63	9.2	137
 $\overset{H_3B\text{—}NMeCH_2}{H_3BAs(NMeCH_2)_2CMe}$	1.40–2.97 [c]	2.55 2.78 3.07		85
$Me_3BAs(NMeCH_2)_3CMe$	2.6	2.54		85
 $\overset{F_3B\text{—}NMeCH_2}{F_3BAs(NMeCH_2)_2CMe}$	2.7 [c]	2.50 2.63 3.03		85

[a] With respect to internal Me_4Si. [b] $^3JPNCH_2$ = 5.0 Hz. [c] Broad absorption.

time but the structural and hence electronic flexibility of open-chain systems is undoubtedly a factor. It is possible, for instance, that the changes in *s* character which dominate the coupling are not on phosphorus but on oxygen. In caged phosphites the "hinge effect" causes the oxygen bonding orbitals to increase in *s* character as the electronegativity of the

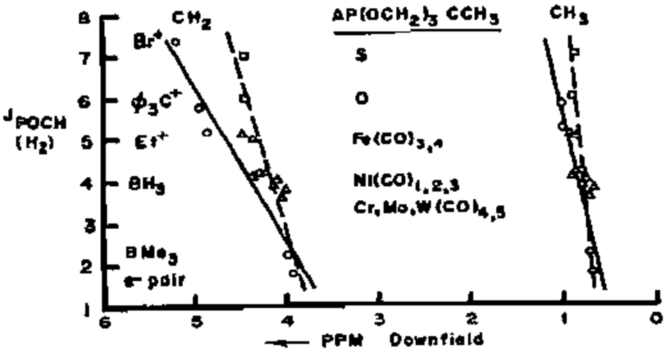


Fig. 9. Plot of ^3JPOCH vs δC$\underline{H}_2$ for P(OCH$_2$)$_3$CMe and its adducts and complexes.

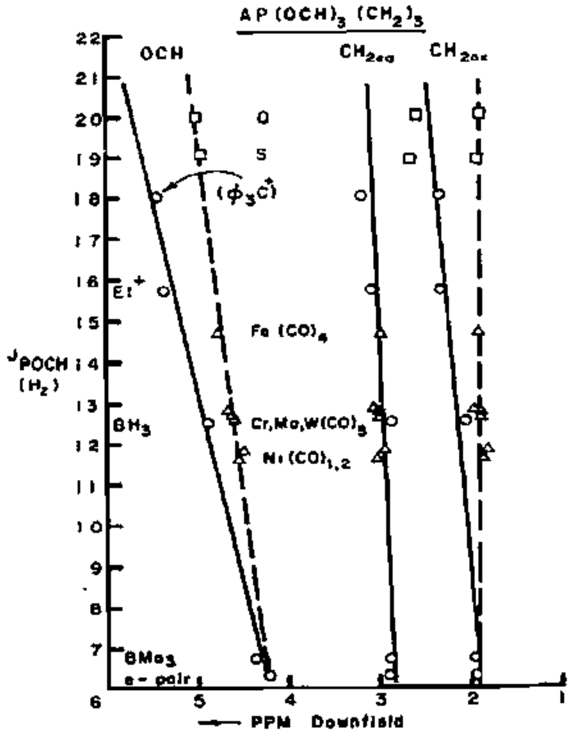


Fig. 10. Plot of ^3JPOCH vs. δC$\underline{H}$ for P(OCH)$_3$(CH$_2$)$_3$ and its adducts and complexes.

A group increases while in open-chain systems the POC angle need not change appreciably. While constancy of ^3JPNCH within 0.2 Hz of an average value of 9.3 Hz is observed[137] in AP(NMe$_2$)$_3$ where A = BH$_3$, BH$_2$Cl, BHCl$_2$, BCl$_3$, it is noteworthy that ^1JBP and ^1JBH are curvilinear and nearly linear, respectively, with δ^1H, δ^{11}B and δ^{31}P (Fig. 11). Here, increasing electron withdrawal by A produces shielding of the phosphorus and deshielding of the boron nucleus and methyl proton. It is demonstrated in this series that the signifi-

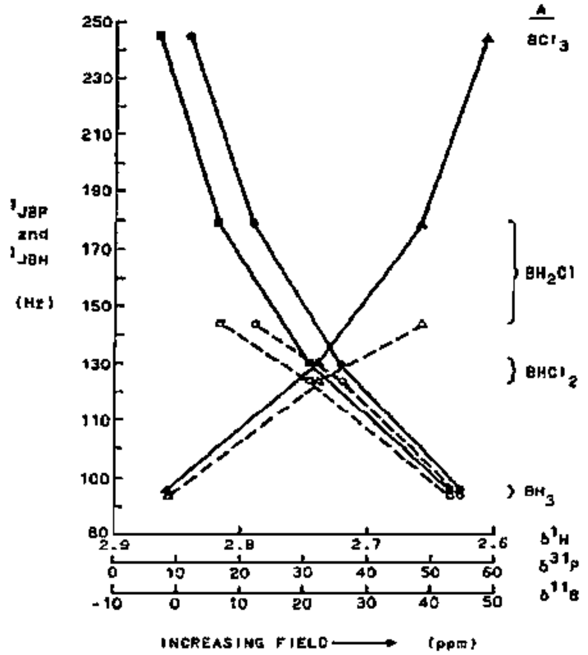


Fig. 11. Plot of (——) ^{1}JBP and (– – –) ^{1}JBH vs. $\delta\,^{1}$H (circles), $\delta\,^{31}$P (triangles) and $\delta\,^{11}$B (squares) for AP$(NMe_2)_3$ systems (taken from the data of ref. 137).

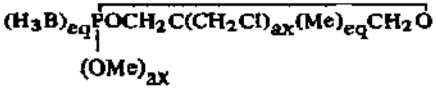
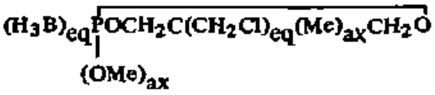
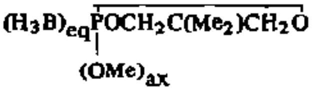
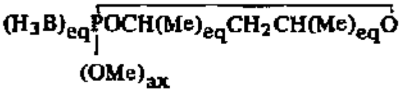
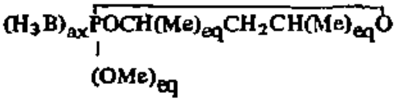
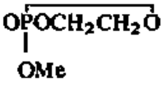
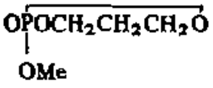
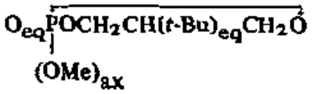
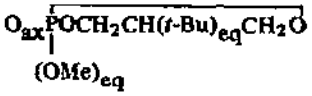
cant changes in *s* character registered in the rising ^{11}B–^{31}P and ^{11}B–^{1}H coupling take place around boron. Although the electronic environment of phosphorus is also changing (as manifested by the comparatively large ^{31}P chemical shifts), any *s* character change as reflected in the ^{31}POC^{1}H coupling seems to be completely attenuated by the nitrogens.

3. Dipole moments

Dipole moments indicate high polarities for the boron adducts (Table 8). Comparison of a variety of BH_3 adducts[41, 72c, 127, 128] and phosphates[39, 40, 72c, 148] leads to the firm conclusion that the P–B link is substantially more polar than the P=O link in comparable compounds. In view of the larger electronegativity of oxygen and its higher lone-pair density compared with the BH_3 group, it is tempting to regard this result as a strong indication that pi back-donation lowers the P=O moment. Using the comparison $\Delta\mu$(phosphate)/$\Delta\mu(Me_3NO)$ = $\Delta\mu(H_3B$-phosphite)/$\Delta\mu(Me_3NBH_3)$ (where $\Delta\mu$ is the increment in dipole moment upon forming the oxide or BH_3 link) it is found that the experimental $\Delta\mu$(phosphate) values are 65% of those calculated for the caged derivatives of I and II whereas this percentage for the six-membered rings and open-chain systems ranges from 55 to 80%. The variation in the latter values is probably related to conformational differences among the YPOC dihedral angles (Y = lone pair, O, BH_3) in the derivatives from which the dipole

TABLE 8

Dipole moments at 25° of borane and oxide compounds of phosphorus

Compound	Dipole moment[a] (debye)	Solvent	Ref.
 $H_3BP(OCH_2)_2CH$	6.25	C_6H_6	72e
$H_3BP(OCH)_3(CH_2)_3$	8.82	$O(CH_2CH_2)_2O$	41
$H_3BP(OCH_2)_3CMe$	8.60	$O(CH_2CH_2)_2O$	127
 $(H_3B)_{eq}POCH_2C(CH_2Cl)_{ax}(Me)_{eq}CH_2O$ $(OMe)_{ax}$	6.01	C_6H_6	72e
 $(H_3B)_{eq}POCH_2C(CH_2Cl)_{eq}(Me)_{ax}CH_2O$ $(OMe)_{ax}$	5.21	C_6H_6	72e
 $(H_3B)_{eq}POCH_2C(Me_2)CH_2O$ $(OMe)_{ax}$	6.07	C_6H_6	72e
 $(H_3B)_{eq}POCH(Me)_{eq}CH_2CH(Me)_{eq}O$ $(OMe)_{ax}$	6.28	C_6H_6	72e
 $(H_3B)_{ax}POCH(Me)_{eq}CH_2CH(Me)_{eq}O$ $(OMe)_{eq}$	5.89	C_6H_6	72e
$H_3BP(OMe)_3$	4.07	C_6H_6	72e
$OP(OCH)_3(CH_2)_3$	7.46		*b*
$OP(OCH_2)_3CMe$	7.10	$O(CH_2CH_2)_2O$	39
	7.29	C_6H_6	146
 $OPOCH_2CH_2O$ OMe	4.47	C_6H_6	72e
 $OPOCH_2CH_2CH_2O$ OMe	5.55	C_6H_6	72e
 $O_{eq}POCH_2CH(t\text{-}Bu)_{eq}CH_2O$ $(OMe)_{ax}$	5.63	C_6H_6	72e
 $O_{ax}POCH_2CH(t\text{-}Bu)_{eq}CH_2O$ $(OMe)_{eq}$	5.08	C_6H_6	72e
$OP(OMe)_3$	3.18	C_6H_6	40

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[a] Precision is ± 0.05 debye unless otherwise specified. [b] Because of insolubility of the compound, this value was estimated by adding the difference in moments for Ia and $OP(OCH_2)_3CMe$ to 4.51, the moment for II.

moments are taken for the crude calculation. The effects of lone-pair orientation are also again evident in that the moments increase in the series open-chain < six-membered ring < bicyclo-[2.2.2] octane ≅ adamantane derivatives in both the phosphate and BH_3 series. Similarly "over-constraint" in the highly strained ring sytems $H_3B\overline{P(O\overset{O}{C}H_2)_2C}H$ and $(MeO)(O)\overline{POCH_2CH_2O}$ apparently destroys to some extent the ability of the oxygen lone pairs to add vectorially along the molecular dipole axis as well as they can in the bicyclo-[2.2.2] octane and six-membered ring analogs, respectively, and so the overall moments are lowered. The same effect can be seen in Table 1 for the analogous phosphites.

It is assumed in the proportionality used in the previous paragraph that P—B pi bonding is at least much less than that in a P=O link. There is some evidence, however, that there is a reduction in polarity in H_3BPPh_3 (4.79 D) compared with Cl_3BPPh_3 (7.03 D) beyond that expected on sigma bonding alone[149]. Using[150] a correction for the BH and BCl moments based on CH_4 and $HCCl_3$, zero and 1.18 D were subtracted from the moments of the BH_3 and BCl_3 adducts, respectively. The remainders are then crudely representative of the $BPPh_3$ moments in both[149]. Assuming that the PPh_3 contribution in each is not very different, it is clear that the BP moment is less polar in the BH_3 adduct and pi bonding may be responsible[149].

The melting points of the BH_3 adducts span a rather wide range from $H_3BP(OMe)_3$ (liquid) to the five- and six-membered ring phosphite adducts (liquids or relatively low-melting solids) to $H_3BP(OCH_2)_3CMe$ (199°)[127] to $H_3BP(OCH)_3(CH_2)_3$ (247–251°)[41]. Although lower symmetry is undoubtedly partially responsible for the lower lattice energies of the non-caged species, the effect of dipole–dipole interactions seems to become evident in the caged adducts since increasing melting point parallels the increase in polarity[41]. A similar phenomenon can be noted for the parent phosphites I and II and the oxides[4,6] (Tables 1 and 5). The origin of the higher moment for $H_3BP(OCH)_3(CH_2)_3$ is not clear. A greater induction effect due to the larger number of carbons compared with $H_3BP(OCH_2)_3CMe$ is not likely to be totally responsible since the difference in moment between Ia and Ig (Table 1) is negligible. Small bonding changes in the two cages probably play a role here.

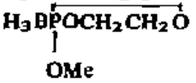
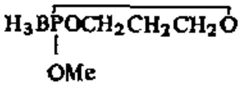
4. Infrared data

Boron–phosphorus stretching frequencies have been assigned[42, 72e, 151, 152a,b] in a range of compounds (Table 9) but relatively little can be concluded from them because of the absence of consistent trends. Coupling effects are undoubtedly a factor here since the 750–900 cm^{-1} region is quite rich in absorptions in the phosphite adducts. A similar conclusion was reached[153] after assigning boron–phosphorus modes in borane adducts of PMe_3, $P(NMe_2)F_2$ and $P(NMe_2)_2F$.

The trend in boron–hydrogen frequencies seems to correlate reasonably well with the basicities of the phosphites as paralleled by the phenol shifts of the phosphates (vide supra). Thus the higher asymmetric and lower symmetric[42, 154] ν(BH) values increase as the basicities decrease in the order[155] $P(OMe)_3$ > $Me\overline{OPOCH_2CH_2O}$ ≅ $Me\overline{OPOCH_2CH_2CH_2O}$ > $\overline{P(OCH_2)_3C}Me$ > $\overline{P(O\overset{O}{C}H_2)_2C}H$.

TABLE 9

Infrared data for boron adducts of phosphorus compounds

Adduct	ν(BP)[a]	Ref.	ν(BH), ν(BD)[b]			Ref.
			Asym.	Sym.	Weighted average	
 $H_3B\overbrace{P(OCH_2)_2CH}^{O}$			2433	2380	2415	72e
$H_3BP(OCH)_3(CH_2)_3$	860	42	2400	2350[a]	2383	42
$D_3BP(OCH)_3(CH_2)_3$	848	42	1827	1719[a]	1791	42
$H_7B_3P(OCH)_3(CH_2)_3$	868	42	2470	2350[a]		42
$Me_3BP(OCH)_3(CH_2)_3$	833	42				
$F_3BP(OCH)_3(CH_2)_3$	854	42				
$H_3BP(OCH_2)_3CMe$	855	42	2400	2355[a]		42
			2415	2366	2399	72e
$D_3BP(OCH_2)_3CMe$	844	42	1810	1705[a]	1775	42
$H_7B_3P(OCH_2)_3CMe$	855	42	2510	2400[a]		42
$Me_3BP(OCH_2)_3CMe$	811	42				
$F_3BP(OCH_2)_3CMe$	869	42				
 $H_3B\underset{OMe}{\overbrace{POCH_2CH_2O}}$			2410	2363	2394	72e
 $H_3B\underset{OMe}{\overbrace{POCH_2CH_2CH_2O}}$			2411	2364	2395	72e
$H_3BP(OMe)_3$	799	42	2402	2362	2389	72e
$D_3BP(OMe)_3$	759	42	1795	1691[a]	1760	42
H_3BPH_3	572	149	2399	2392	2397	152b
H_3BPF_3	607[c]	150	2455	2385[c]	2432	152a
H_3BPPh_3	608[a]	149	2440	2330[a, d]	2403	149
D_3BPPh_3			1820	1755[a, d]	1798	149
H_3BPMeH_2	581[e]	152b	2386	2344[e]	2355	152b
D_3BPMeH_2	533[e]	152b	1802	1730[e]	1778	152b
H_3BMe_2H	575[e]	152b	2366	2346[e]	2359	152b
D_3BMe_2H	518[e]	152b	1795	1742[e]	1777	152b
H_3BEtH_2	562[e]	152b	2385	2348[e]	2373	152b
D_3BEtH_2	507[e]	152b	1802	1704[e]	1769	152b
H_3BEt_2H	573[e]	152b	2368	2341[e]	2359	152b
D_3BEt_2H	511[e]	152b	1785	1733[e]	1768	152b
H_3BCO			2434	2380[e]	2412	152a

[a] Measured in solid state or polar solvents such as $CHCl_3$, CH_2Cl_2 and CH_3CN. [b] Measured in CCl_4 or C_6H_6 unless otherwise specified. [c] Liquid. [d] Estimated from spectra shown in ref. 149. [e] Low temperature glass.

The BD frequencies are in agreement with this order in cases where they were measured. The increase in ν(BH) with decreasing basicity can be ascribed to the rise in *s* character of the boron as it progresses from a more sp^3 configuration toward sp^2. Indeed the weighted average of the BH stretching modes linearly correlate with ^1JBH in a variety of boron compounds and borane adducts containing oxygen and nitrogen donors[154]. Unfortunately, the lack of precision in several of our ^1JBH values and their small range (see Table 6) do not permit a similar correlation to be made although the points generated by the coupling and the weighted average of the BH frequencies (Table 9) corroborate the linear correlation in which no phosphorus–boron adducts were present[154]. Similarly the ν(BH) data for H_3BPH_3 and H_3BPF_3 in Table 9 in conjunction with their ^{11}B–^1H coupling constants (103 Hz (ref. 151) and 107 Hz (ref. 156)) help verify the correlation[154] although inclusion of all data on phosphorus compounds tends to alter the slope of the line slightly.

The gross infrared features of the phosphite–borane adducts do not allow much speculation on the electronic nature of the BP bond. Inasmuch as there is general agreement, however, that H_3BCO possesses the capability of BC pi bonding, it is extremely noteworthy that the BH stretching frequencies for this compound and for $H_3B\overbrace{P(OCH_2)_2C}^{O}H$ are the same to within experimental error. It is also interesting in this regard that force field calculations on H_3BPH_3 and H_3BPF_3 give PB bond orders of 0.78 and 0.92, respectively[157]. Since the BH frequency increase from H_3BPH_3 to H_3BPF_3 (Table 9) is in accord with the expectation that PF_3 is less polarizable than PH_3, the larger bond order in the PF_3 adduct is consistent with the possibility that pi feedback from the BH_3 group is more pronounced when electronegative phosphorus substituents are present.

5. Enthalpy data

Heats of association were measured[41,127] on $Me_3BP(OCH_2)_3CMe$ (−14.4 kcal/mole) and $Me_3BP(OCH)_3(CH_2)_3$ (−15.9 kcal/mole) for the reaction

$$\text{Phosphite (solid)} + BMe_3\ \text{(gas)} \rightleftharpoons Me_3B.\text{Phosphite (solid)} \qquad (11)$$

These values are very close to that obtained for Me_3BPMe_3 (−16.47 kcal/mole[158a]) and not far from the one measured for F_3BPMe_3 (−18.9 kcal/mole[158a]). In spite of the weaker basicity of bicyclic phosphites compared with phosphines, the comparable heats of association with BMe_3 may reflect the reduction of steric requirements of the bicyclic phosphites compared to PMe_3.

The heat of association of H_3BPF_3 has been evaluated at −24.9 kcal/mole[158c]. The rather high value of this enthalpy could represent a partial stabilizing contribution from BP pi bonding. Such a consideration gains merit from the fact that F_3BPH_3 is very highly dissociated[158a].

Phosphite II appears to be somewhat stronger as a base than Ia but both are significantly weaker than Me_3N in a reaction analogous to (11) for which $\Delta H_{\text{assoc}} = -25.1$ kcal/mole (ref. 127). From a normal coordinate analysis of I_3BPI_3, a best fit of the infrared spectrum was obtained[158b] assuming a force constant of 1.0 mdyne/Å. Using a plot of force constant versus association energy for a variety of molecules, an extrapolated value of −16 kcal/mole was predicted[158b] for I_3BPI_3 and the good agreement with those found for our caged phosphite Me_3B adducts is not unreasonable.

This rise in the heats of association for the borane adducts of $PPhH_2$ (−31.2 kcal/mole), PPh_2H (−34.1 kcal/mole) and PPh_3 (−37.6 kcal/mole) according to

$$\text{Base (soln)} + BH_3\ \text{(gas)} \rightleftharpoons H_3B{\cdot}\text{Base (soln)} \qquad (12)$$

has been ascribed[149] to less reorganization energy toward tetrahedrality for the base and greater ease of phosphorus charge neutralization by mesomeric induction as the number of phenyls increases. The latter is substantiated by a downfield chemical shift in the phenyl proton NMR spectra along the series[149]. Evidence for a detectable pi effect in triaryl phosphine boranes comes from a comparison of enthalpy data for a series of alkyl and aryl boranes and BF_3 adducts[159]. Heats of association for the BF_3 adducts, viz.

$$\text{Base (soln)} + BF_3\ \text{(gas)} \rightleftharpoons F_3B{\cdot}\text{Base (soln)} \qquad (13)$$

became less exothermic with increasing aryl substitution and decreased linearly with the sums of the Taft polar substitution constants as expected on inductive grounds. The same correlation for the BH_3 adducts, however, produced a change in slope of the line when alkyl groups were replaced by aryls. The enhanced stabilization in the aryl phosphine boranes is about 4 kcal/mole and is attributable to BP pi bonding originating from the BH_3 group[159].

6. Displacement reactions

Although entropy effects render evaluations of Lewis basicities from equilibrium constant data dangerous, a series of very similar bases such as phosphites measured with respect to a common acid should be relatively free of changes in entropy. By integrating NMR absorptions for equilibrated benzene solutions containing the species

$$H_3B{\cdot}\text{Phosphite} + \text{Phosphite}' \rightleftharpoons H_3B{\cdot}\text{Phosphite}' + \text{Phosphite} \qquad (14)$$

The following order of basicities toward BH_3 was established: $P(OMe)_3 > P(OCH_2)_3CMe > \overline{P(O\overset{O}{C}H_2)_2CH}$ and $MeO\overline{POCH_2CMe_2CH_2O} > \overline{P(O\overset{O}{C}H_2)_2CH}$. The observation that $P(OCH_2)_3CMe$ is incapable of displacing BH_3 from H_3BNMe_3 while $P(OCH)_3(CH_2)_3$ is partially able to do so[41,127] shows that II is a stronger base than Ia. All of these results are entirely in accord with conclusions drawn previously in this review regarding the decrease in phosphorus basicity upon augmenting the "hinge effect" by greater constraint of the alkoxy groups.

Displacement reactions in solution using the bifunctional phosphorus ligand $P(OCH_2)_3P$ yield the order[31] $PBu_3 > P(OCH_2)_3P > P(CH_2Cl)_3$. It is quite interesting that the phosphite phosphorus is more basic than the phosphine phosphorus in the caged ligand Vf and the phosphite phosphorus in Vf is more basic than $P(CH_2Cl)_3$, which is opposite to electronegativity arguments in both cases. It was also found[31] that $P(CH_2O)_3CMe >$

$P(CH_2O)_3PBH_3$ and $P(CH_2O)_3As > P(CH_2O)_3PBH_3$. Here the large dipole moment of $P(CH_2O)_3PBH_3$, estimated[160] to be about 7.4 D in the direction of the borane group, weakens the basicity of the phosphine phosphorus at the positive end of the dipole. This dipolar-inductive effect is weaker for the bases with which the borane bicyclic base is compared; their moments are almost five times smaller (Table 1).

7. *Structural data*

Phosphorus–boron bonding occurs in all the BH_3 adduct structures thus far analyzed and the separation of these atoms decreases in the series $H_3BP_2Me_4BH_3$ (1.951 Å)[161], H_3BPH_3 (1.93 Å)[162a], H_3BPH_2Me (1.906 Å)[162b], H_3BPMe_3 (1.901 Å)[162b], $H_3BP(NH_2)_3$ (1.887 Å)[163], $F_3PBH_2BH_2PF_3$ (1.848 Å)[164], H_3BPF_2H (1.832 Å)[162b] and H_3BPF_3 (1.836 Å)[158c]. In the adduct shown in Fig. 12, the BP distance (1.879 Å)[165] falls close to that in $H_3BP(NH_2)_3$ and it appears that electronegativity effects strongly influence the BP bond lengths.

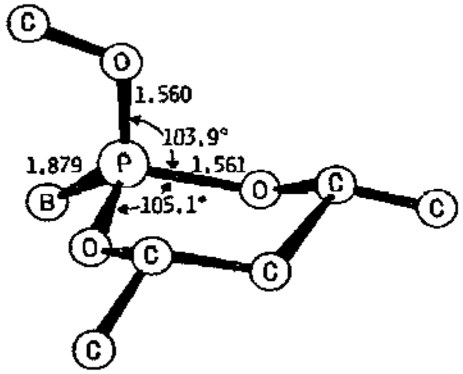
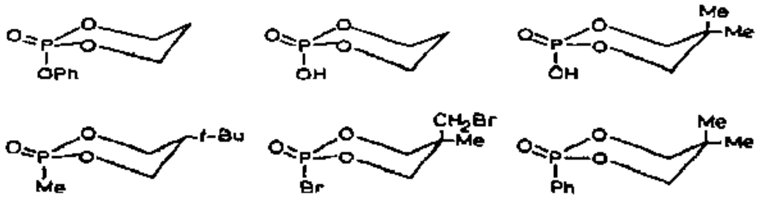
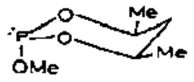


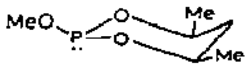
Fig. 12. The molecular configuration of $BH_3(MeO)P(OCHMe)_2CH_2$.

Although the question of BP pi bonding is not resolved, the fact that the PO distances (1.55–1.57 Å) are very close to the analogous ones in the phosphoryl structures below[70a–e] might be taken as weak evidence that some pi bonding must occur in the BP link.



An interesting feature of the structure in Fig. 12 is that the precursor phosphite can exist[166] as the two isomers


XI


XII

For the structural study, the H_3B adduct was formed from the thermodynamically stable isomer[165] XI. Because phosphorus inversion on adduct formation at low temperature is unlikely, the thermodynamically more stable isomer contains an axial methoxy group and an equatorial lone pair.

8. Ab initio calculations

Photoelectron spectra in conjunction with ab initio calculations show that the major changes in orbital populations on forming the H_3BPF_3 complex are a decrease in the phosphorus $3s$ by 0.32 electron and an increase in the $3d$ by 0.18 electron[167]. The total contribution to the BP pi population ($2p_\pi$–$3d_\pi$ and $2p_\pi$–$3p_\pi$) is much smaller[167] (0.08) than that of the sigma (0.57). Similarly, it has been calculated[168] that phosphorus $3d$ orbital participation in overlap population in the hypothetical OPH_3 is much greater (0.272) than in H_3BPH_3 (0.034).

From the theoretical and experimental evidence discussed here, it seems quite likely that the BH_3 group can participate in pi bonding with phosphorus as was first postulated over fifteen years ago to account for the unusual stability of phosphinoborines[169]. It does seem, however, that the pi contribution to the BP coordinate link is small compared with that in a phosphoryl bond.

(iii) Metal complexes

1. Nature of the complexes

A compilation of all of the $P(OR)_3$ and $P(NMe_2)_3$ complexes which have been reported in the literature would comprise well over a thousand compounds[3]. Even if the list were restricted to polycyclic phosphite complexes, over three hundred compounds would have to be included[3]. Since the chemical and spectroscopic bases for the formulations and stereochemical assignments of the complexes as well as their syntheses are included in another review[3], they will be omitted for the most part here.

The spectroscopic studies discussed below were generally carried out on complexes containing polycyclic phosphorus ligands, although in some cases open-chain ligands were also used. The complexes studied contained metals in oxidation states from zero to plus three and possessed various stereochemistries. Thus metal carbonyls of the type $M(CO)_5L$, *cis*- and *trans*-$M(CO)_4L_2$ (where M = Cr, Mo or W), $Fe(CO)_4L$, *trans*-$Fe(CO)_3L_2$ and $Ni(CO)_{4-x}L_x$ ($x = 1$ to 4) were employed[26,170–175]. Also investigated were zero through trivalent species such as PdL_4 (ref. 173), PtL_4 (ref. 173), MnL_4^{2+} (refs. 36, 176), FeL_4^{2+} (refs. 36, 176), CoL_5^+ (refs. 15, 177–180), $[CoL(NO_3)_2]^-$ (ref. 179), CoL_6^{3+} (refs. 177–180), NiL_5^{2+} (refs. 177–180), *trans*-$NiL_3(CN)_2$ (ref. 181), *cis*- and *trans*-MX_2L_2 (where

M = Pd or Pt)[175,182,183], CuL_4^+ (refs. 179, 182), AgL_4^+ (ref. 182), ZnL_4^{2+} (ref. 176) and CdL_4^{2+} (ref. 176). Some highlights concerning the stereochemical features are discussed in the following paragraphs.

The metal carbonyl phosphite complexes are colorless but the phosphine analogs are pale yellow[26,175]. Some rather subtle steric and electronic factors appear to govern formation of *cis* and *trans* isomers. Whereas *trans* isomers of II are made with all three Group VIB metals[171,172], the only *trans* isomer of Ia which could be isolated was that of chromium[170,172] while molybdenum and tungsten gave *cis* isomers. Models indicate that Ia is slightly less bulky than II (Fig. 13) but it may be that the difference in steric requirement is sufficient to force a *trans* configuration for Ia only in the case of the smallest metal. *Cis* isomers can be made for all three metals with both Ia and II[172]. By merely substituting a propyl chain for the methyl group in Ia, *cis* complexes of tetracarbonyl molybdenum and tungsten can be formed but now the *cis* chromium analog seems to be synthetically forbidden[172]. A bizarre illustration of the questionability of steric arguments is the ease of the isomerization of *cis*-$Mo(CO)_4[P(NMe_2)_3]_2$ to the *trans* form in striking contrast to the remarkable stability of the *cis* $P(NMePh)_3$ analog[184].

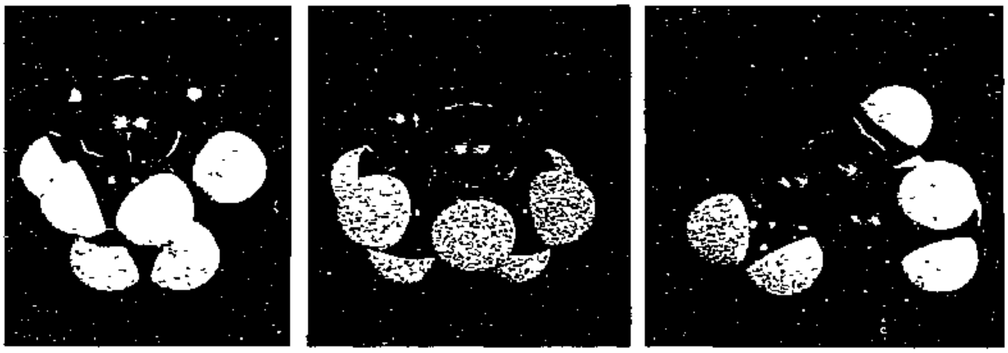
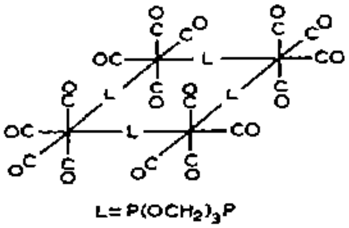


Fig. 13. Models showing the geometrical properties of $P(OCH_2)_3CMe$, $P(OCH)_3(CH_2)_3$ and $P(OMe)_3$.

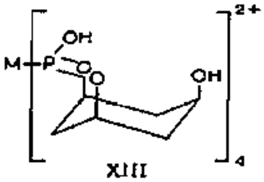
Carbonyl complexes containing two different monodentate ligands are relatively rare. As was observed earlier[185], the synthesis of such compounds can be complicated by formation of several other products. Thus the preparation of *cis*- and *trans*-$Mo(CO)_4LL'$ (L = Ib, L′ = $P(OMe)_3$) involved the isolation (by column chromatography) of *cis*- and *trans*-$Mo(CO)_4L'_2$ and *trans*-$Mo(CO)_4L_2$ as well[186]. Other mixed complexes made were *cis*- and *trans*-$Mo(CO)_4LL''$ and *trans*-$Fe(CO)_3LL''$ where L″ = $P(NMe_2)_3$ (ref. 186).

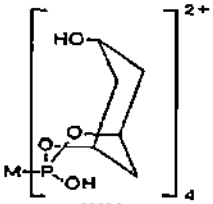
The difunctional ligand $P(OCH_2)_3P$ possesses two donor sites and its geometry permits linkage isomerism and metal bridging. Complexes of the type $(OC)_5MP(OCH_2)_3P$ and $(OC)_5MP(OCH_2)_3PM(CO)_5$ (M = Cr, Mo and W)[32], $(OC)_4FeP(OCH_2)_3P$ (ref. 32), $(OC)_4FeP(CH_2O)_3P$ (ref. 32), $(OC)_4FeP(OCH_2)_3PFe(CO)_4$ (ref. 32), *trans*-$P(OCH_2)_3PFe(CO)_3P(OCH_2)_3P$ (ref. 59) and *cis*-$P(OCH_2)_3PMo(CO)_4P(CH_2O)_3P$ (ref. 174) have been characterized. The complex $[(OC)_5WP(OCH_2)_3PMe]BF_4$ containing a quaternized ligand has also been reported[32] and preliminary results[174] indicate the existence of the

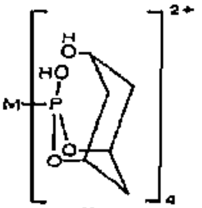


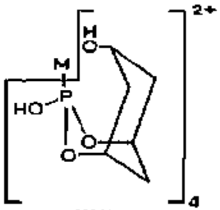
square molybdenum polymer shown below. Polymers of iron and nickel also occur[174].

When Xa is allowed to react with hydrated divalent Mn, Fe, Ni, Zn or Cd ions, complexes of the type ML_4^{2+} are formed in which the PH and P=O stretching bands of the free ligand have disappeared[176]. These results suggest the formation of an MP bond. Of the two structures below, XIII seems more reasonable since only migration of a proton to the phosphoryl oxygen is involved whereas XIV involves oxygen insertion into a P–H bond. Although there is no reason to expect inversion at phosphorus, XV cannot be ruled out but XVI would appear to be sterically crowded.


XIII


XIV


XV


XVI

In surprising contrast, isomer Xb does not react with metal ions. Both isomers dehydrate in the presence of Cu^{2+} and reduce it to give $Cu(II)_4^+$; the green $Ni(Xa)_4^{2+}$ easily disproportionates on heating to give[176] the yellow $Ni(II)_5^{2+}$. Whether the differences in behavior of Xa and Xb are premarily steric or electronic in origin is not certain at this time. Contrary to a recent statement in the literature[187], however, phosphorus–metal bonds do exist between $H(O)P(OR)_2$ ligands and class (a) metals, in our case divalent manganese and iron.

Electronic factors are certainly responsible for the lack of isolable complexes of $H(O)P(OMe)_2$ with these ions[188]. Other reported examples of metal complexation of $H(O)P(OR)_2$ or $H(O)P(OPh)_2$ in the "enol" form via the phosphorus are thus far confined to zerovalent metal carbonyl derivatives, monovalent copper and divalent platinum[3]. While

$B_{10}H_{11}$ also coordinates $H(O)P(OEt)_2$ in the enol form, apparently BCl_3 does so via the phosphoryl oxygen in the keto form[3].

Cobalt(II) ions undergo dismutation[177–180] to a monovalent and trivalent species in the presence of phosphites according to eqn. (15).

$$2\,Co^{2+} + 11\,L \rightarrow CoL_5^{+} + CoL_6^{3+} \qquad (15)$$

The yellow cobalt(I) and pale yellow to colorless cobalt(III) complexes are best isolated as the BF_4^- salts since one of the trivalent cobalt perchlorate derivatives is explosive[3,179]. When cobalt(II) nitrate is allowed to react with $P(OMe)_3$, $[CoL_5][CoL(NO_3)_2]$ can be isolated and the novel cobalt(I) anion can also be obtained as the azure blue tetraphenylarsonium salt[179]. In view of the marked proclivity of the coordinated nitrate ion to behave in a bidentate fashion[179], the complex anion is probably a five-coordinate species. Nitrates of the CoL_6^{3+} species tend to be unstable with respect to decomposition while $[CoL_5]NO_3$ compounds are not[179].

Phosphites react with nickel(II) to give five-coordinate compounds which are isoelectronic with the monovalent cobalt systems[177–180,189] and presumably are also isostructural (vide infra). The nickel complexes of the caged phosphites can be reduced to zerovalent NiL_4 complexes in aqueous base[180].

$$NiL_5^{2+} + 2\,HCO_3^- \rightarrow NiL_4 + H_2O + O{=}L + CO_2 \qquad (16)$$

This preparative reaction is similar to the non-aqueous scheme reported for tetrakis-trialkyl phosphite nickel compounds[190] except that the five-coordinate species were not isolated.

Square-planar palladium(II) complexes of easily solvolyzed phosphorus ligands can be made conveniently by a metathetical reaction using *trans*-dichlorobis(benzonitrile)palladium(II)[175,183].

The somewhat strange ability of nitrate to complete with $P(OMe)_3$ for metal coordination sites, made evident in the $[CoL(NO_3)_2]^-$ ion, is again observed[179] in $[AgL_2NO_3]$. The lack of such competitive behavior in the case of polycyclic phosphites may be related to their stronger ligand fields[179] (see next section).

2. *Ultraviolet spectral studies*

Calculation of *Dq* values from the UV–visible spectra of complexes is relatively straightforward in the case of highly symmetrical complexes[191] and the diamagnetic CoL_6^{3+} phosphite complexes of O_h symmetry yield valuable information on the nature of the cobalt–phosphorus bond. In addition to the two charge-transfer bands at about 39,500 and 44,500 cm^{-1} ($\epsilon \cong 10^3$), two bands at lower energy (ca. 30,500 cm^{-1}, $\epsilon \cong 10^3$ and 35,500 cm^{-1}, $\epsilon \cong 10^2$) can be assigned[178–180] to the spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively, depicted in Fig. 14. Because neither of the two weaker spin-forbidden transitions were observed, the ratio of the Condon–Slater integrals F_2/F_4 in the simultaneous equations (17) and (18) for the strong-field case was taken[192] to be 10 on the reasonable assumption that it would be between that of $Co(en)_3^{3+}$ (9.3) and $Co(CN)_6^{3-}$ (11) (refs. 193, 194).

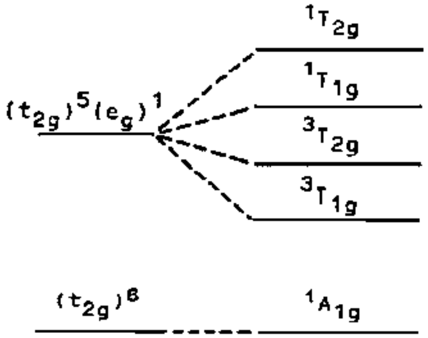


Fig. 14. Energy levels for a d^6 ion in a strong octahedral field.

$$\Delta E(^1T_{1g} - {}^1A_{1g}) \cong -35F_4 + 10Dq \tag{17}$$

$$\Delta E(^1T_{2g} - {}^1A_{1g}) \cong 16F_2 - 115F_4 + 10Dq \tag{18}$$

The results in Table 10 imply that the ligand field splitting decrease from Ia to $P(OMe)_3$ and that surprisingly the bicyclic phosphite is quite comparable to cyanide ion in the field strength it displays toward trivalent cobalt.

The high ligand field splitting caused by phosphites is not explicable in terms of sigma donor character since they are weaker bases toward protons and Group III Lewis acids than amines which have very much lower Dq values even if they can chelate (e.g.[193] 2,320 cm^{-1} for $Co(en)_3{}^{3+}$). Metal-to-phosphorus pi bonding is very attractive to postulate as the main source of extra stability of the $^1A_{1g}$ level as is predicted by ligand field theory[195].

TABLE 10

Ligand field parameters for octahedral cobalt(III) complexes

Ligand	Dq[a] (cm^{-1})	β	$\Delta E(^1T_{2g}-{}^1T_{1g})$ (cm^{-1})
CN^-	3480[b]	0.37[b]	6410[b]
$P(OCH_2)_3CMe$	3290	0.28	5000
$P(OCH_2)_3CEt$	3270	0.22	5800
$P(OCH)_3(CH_2)_3$	3225	0.13	2300
$P(OMe)_3$	3080	0.19	3300

[a] The values quoted here for the phosphites differ slightly from those given in previous publications[178-180] because the value F_2/F_4 was assigned a more conservative value rather than using the one for $Co(CN)_6{}^{3-}$ (see text)[178-180]. The spectra and the band positions were obtained by Gaussian analysis. [b] H.B. Gray and N.A. Beach, *J. Amer. Chem. Soc.*, 85 (1963) 2922.

While negative evidence must be viewed with caution, the absence of $CoL_6{}^{3+}$ complexes where L is PR_3 may be attributable to the relatively poor pi bonding capability of the phosphorus (i.e. R is insufficiently electronegative) in spite of its higher sigma basicity. At the other extreme $Co(PF_3)_6{}^{3+}$ may be unstable because the phosphorus is not sufficiently basic to neutralize properly the charge on the metal so that electron density from the metal is unable to delocalize into the highly acidic pi orbitals on phosphorus. The intermediate sigma donor and pi acceptor ability of phosphites may thus be responsible for their very high position in the spectrochemical series for cobalt(III) complexes, viz.

$CN^- > P(OR)_3 > en > NH_3 > H_2O > CO_3{}^{2-}$

The decline in Dq in the order Ia ≅ Ib > II > $P(OMe)_3$ may reflect a rise in ligand–ligand repulsions in the same order as might be expected from their increasing steric requirements (Fig. 13). It is tempting to ascribe part of the decrease in Dq from caged phosphites to $P(OMe)_3$ to a fall in pi acid strength (owing to the "hinge" effect) which overrides an augmentation in sigma donor strength for which evidence was presented earlier in this review.

A measure of the interelectronic repulsion in the complexes can be gained from the ratio $\beta = (F_2 - 5F_4)/B_{\text{ion}}$ where B_{ion} is 1100 cm^{-1} for cobalt(III)[193]. Although no consistent trends are found among the β values or the differences in energy between the ${}^1T_{2g}$ and ${}^1T_{1g}$ excited states (Fig. 14)[178] for the phosphites, both nephelauxetic criteria suggest that the cyano complex entails more electronic repulsion on the metal (less covalent binding) than the phosphite complexes.

Stable cobalt(I) complexes containing monodentate ligands are rare. Besides the pentakisphosphite cobalt(I) cations described in the previous section, only the $Co(CNMe)_5{}^+$ and $Co(CNPh)_5{}^+$ species have been characterized[196a,b]. In contrast, the pentacyanocobaltate(I) anion has only been detected in solution[197a,b]. The pentakis-phosphite nickel(II) cations[179] and the pentacyano nickelate(II) anion[198] are isoelectronic with the cobalt(I) complexes and presumably isostructural. The similarity of the UV–visible spectra of the cobalt(I) and nickel(II) phosphite compounds (Table 11) is consistent with this idea as are the trigonal bipyramidal configurations found for $Co(CNMe)_5{}^+$ (ref. 196b) and $Ni(II)_5{}^{2+}$ (ref. 199) (see Sect. 9).

The one-electron spin-allowed ligand field transition of lowest energy in a d^8 complex of D_{3h} symmetry is $(e'')^4(e')^4 \rightarrow (e'')^4(e')^3a_1$ (see Fig. 15)[200]. In all the complexes for which assignments have been made[200], the extinction coefficients of the observed spectral band of lowest energy are relatively large (ca. 10^3). A significant number of spectral data on trigonal bipyramidal nickel(II) phosphine complexes is most consistently interpreted, however, if the lowest energy band in their spectra is assigned to the $e' \rightarrow a'$ d–d transition[201]. The high intensity of this band has been ascribed to a large admixture of higher configurations by odd crystal field components[201] and to covalency effects[202].

If the data in Table 11 are regarded with the above considerations in mind, the low energy bands (24,800–27,400 cm^{-1}, $\epsilon \cong 10^3$) of the nickel complexes (assigned to the $e' \rightarrow a'$ ligand field transition) lie considerably higher in energy than those found for complexes

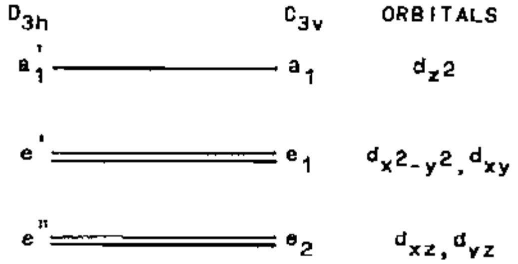


Fig. 15. Energy levels for a d^8 complex in D_{3h} and C_{3v} symmetry.

of the type $[\mathrm{NiLX}]^+$, where L is a tetradentate phosphine tripod ligand[201] (ca. 17,000 cm^{-1}). This is not unreasonable in view of the higher ligand field expected for five phosphites than for four phosphines and a halogen. Comparing the relative energies of the cobalt(I) and nickel(II) complexes of the same phosphite indicates that the cobalt(I) ligand field splittings appear to be somewhat greater. This may be a consequence of the larger ligand field stabilization due to pi bonding which might be expected to be slightly larger for a smaller positive charge on the metal[203]. It is also seen from the low-energy transitions in Table 11 that the ligand field strength of $\mathrm{P(OMe)_3}$ is smaller than those of the caged phosphites and this accords with the conclusion reached earlier for the octahedral cobalt(III) complexes.

TABLE 11

Spectral parameters of pentakis-phosphite cobalt(I) and nickel(II) complexes

	Band maxima (cm^{-1})	ϵ (l/mole.cm)	Ref.
$\mathrm{Co[P(OCH_2)_3CMe]_5^+}$	28,600	1.1×10^3	180
	43,500	1.0×10^4	
$\mathrm{Co[P(OCH_2)_3CEt]_5^+}$	28,600	1.4×10^3	180
	45,400	1.3×10^4	
$\mathrm{Co[P(OCH)_3(CH_2)_3]_5^+}$	29,300	1.4×10^3	180
	43,500	1.5×10^4	
$\mathrm{Co[P(OMe)_3]_5^+}$	26,200	1×10^3	179
	39,600	1.6×10^4	
	43,500	1.3×10^4	
$\mathrm{Ni[P(OCH_2)_3C(CH_2)_4Me]_5^{2+}}$	27,300	2.6×10^3	179
$\mathrm{Ni[P(OCH)_3(CH_2)_3]_5^{2+}}$	27,400	2.1×10^3	179
$\mathrm{Ni[P(OMe)_3]_5^{2+}}$	24,800	2.5×10^3	179
	40,200	1.6×10^4	

Inasmuch as only one spin-permitted band is expected in D_{3h} symmetry[201], the more intense bands at higher energy observed in the nickel(II) phosphite complexes are probably of the charge-transfer type.

When nickel(II) cyanide is treated with phosphorus ligands, both four- and five-coordinate complexes of the type $NiL_5(CN)_2$ and $NiL_2(CN)_2$ are formed[181,202,204–208]. Trigonal-bipyramidal structures of D_{3h} symmetry generally have been assigned on the basis of the single observed cyanide stretching frequency[181,202,204a]. Although the solid-state molecular structures obtained for the compounds

$NiL_3(CN)_2$
(L=PPh(OEt)$_2$)
Ref. 209 a

$PPhMe_2$
Ref. 209 b


(R=Me,Et)
Ref 210

support the *trans* relationship of the cyanide groups, distortion from an idealized trigonal-bipyramidal geometry (which in some cases is severe) can be observed (see later). The reported[207] dipole moment of $Ni(PBu_3)_3(CN)_2$ (2.44 D) is inconsistent with D_{3h} symmetry as are the two low-energy maxima observed[202] in the electronic spectrum of $Ni(PPh_2Me)_3(CN)_2$.

Despite the above difficulties, the low-energy band in $NiL_3(CN)_2$ has been assigned to the $e' \rightarrow a'$ *d–d* transition in D_{3h} symmetry[202,204]. If the spectral assignments are correct, inclusion of our data in such an analysis indicates that all of the ligands (which are of the type $P(OPh)_3$ (ref. 181), $P(OR)_3$ (refs. 181, 204a), $PPh_{3-x}(x = 1 \text{ or } 2)$[204a], $PPhMe_2$ (ref. 202) and $P(C_6F_5)Me_2$ (ref. 202)) yield a low-energy band between 22,500 and 24,600 cm^{-1} with that of $Ni(CN)_5{}^{3-}$ being[204a] at 23,800. Because of solubility problems, only a broad band at 27,400 cm^{-1} could be seen[181] in *trans*-$Ni[P(OCH_2)_3CMe]_3(CN)_2$, which could possibly have a low-energy component in the 24,000 cm^{-1} region. Thus the low-energy band in these systems does not appear to be very sensitive to variations in ligand field strength. Electronic and steric factors governing spectrally detected dissociation equilibria of the type[202,204a,205,206]

$$NiL_3X_2 \rightarrow NiL_2X_2 + L \tag{19}$$

are not understood[181].

The lowest-energy band in $Ni[P(OEt)_3]_4$ (42,000 cm^{-1}, $\epsilon = 2.2 \times 10^3$), $Ni[PPh(OEt)_2]_4$ (30,000 cm^{-1}, $\epsilon = 1.8 \times 10^3$), $Pd[PPh(OEt)_2]_4$ (32,300 cm^{-1}, $\epsilon = 1.7 \times 10^3$) and $Cu[PPh(OEt)_2]_4{}^+$ (36,800 cm^{-1}, $\epsilon = 0.8 \times 10^3$) have been assigned to a combination of two transitions emanating from two metal 3*d* states ($(2e)^4$ and $(3t_2)^6$) to a π^* state ($4t_2$) on the ligand[211]. Although the lower energy transition in the nickel complexes might have been expected with $P(OEt)_3$ because of the greater electronegativity of an OEt group compared with Ph, the higher energy transition in the $P(OEt)_3$ complex is ascribed to electronic repulsions in the $d^9\ (\pi^*)^1$ state which would be more intense with lone pairs on three oxygens. Equilibrium studies show that $PPh(OEt)_2$ replaces $P(OEt)_3$ in the nickel complex to give $Ni[PPh(OEt)_2]_4$ and it was concluded[211] from this and the spectral results that metal–

phosphorus pi bonding is more extensive with $PPh(OEt)_2$. It is difficult to rationalize within this theoretical framework the analogous ultraviolet spectral data obtained earlier in our laboratories for $Ni[P(OCH_2)_3CMe]_4$ (34,500 cm^{-1}, $\epsilon = 1.9 \times 10^4$), $Ni[P(OCH_2)_3CEt]_4$ (41,00 cm^{-1}, $\epsilon = 2.4 \times 10^5$) and $Ni[P(OCH)_3(CH_2)_3]_4$ (45,000 cm^{-1}, $\epsilon = 2.7 \times 10^4$) since the variation in this charge-transfer energy is so large for such a structurally similar triad of ligands. Consistent with $3d \rightarrow \pi^*$ charge transfer, however, is the 47,000 cm^{-1} band ($\epsilon \cong 10^3$) observed in $Cu[P(OCH_2)_3CMe]_4^+$ and the absence of an observable absorption for the silver(I) analog[177] since the energy gap is expected to increase as the 3*d* metal orbitals are stabilized by increasing charge. The question of the relative importance of steric and electronic effects is still open, for extensive ligand exchange equilibria studies[212] are consistent with a dominance of steric size, rather than electronic factors, in determining the stabilities of NiL_4 complexes.

It was noted years ago that substitution of a piperidine in *trans*-$Pt(piperidine)_2Cl_2$ by PPr_3 or $P(OMe)_3$ resulted in an increase in energy of the $d \rightarrow d$ spin-allowed transition from 31,750 cm^{-1} ($\epsilon = 78$) to 32,600 cm^{-1} ($\epsilon = 303$) and 33,400 cm^{-1} ($\epsilon = 319$), respectively[213]. These bands were assigned to $d_{xy} \rightarrow d_{x^2-y^2}$ transition which could be taken as a measure of the average crystal field splitting power of the ligands. The dominant source of the larger separation between these orbital energies for $P(OMe)_3$ compared with PPr_3 was postulated[213, 214] to be the stabilizing effect of the pi acidity of the ligand on the d_{xy} orbital which is greater in the case of $P(OMe)_3$. The drastic increase in energy in the lowest transition observed for *cis*-$Pt[P(OCH_2)_3CMe]_2Cl_2$ (40,000 cm^{-1}, $\epsilon = 1165$) is not unexpected then in view of the fact that now two phosphites of very high ligand field strength are attached to platinum. In the approximation of pure *d* orbitals, the fact[175] that the bicyclic phosphite complex is *cis* is not relevant. The *d–d* band in *cis*-$Pd(1a)_4Cl_2$ occurs at 43,500 cm^{-1} ($\epsilon = 3400$)[177].

3. ^{31}P chemical shifts

While the nature of ^{31}P chemical shifts has been elucidated theoretically[215], the interplay of factors (e.g. the imbalance of the σ-bonds due to electronegativity effects, the degree of *d* orbital occupation and geometrical symmetry deviations) has not yet permitted a quantitative interpretation of experimentally observed shifts. Thus chemical shift relationships do not reflect phosphorus electron density changes in a simple manner and empirical correlations of such shifts to other parameters appear to break down when a larger range of compounds is studied. These problems have been reviewed recently in some detail[216]. Recent efforts to correlate ^{31}P chemical shifts upon coordination, with $\delta^{31}P$ of the free ligand have met with success for a variety of complexes, however[217a].

Because of the formidable barriers to interpreting ^{31}P trends, our activity in the area has been restricted to establishing some caveats on generalizing too broadly regarding the origins of such trends in a limited number of coordination compounds of varying geometry. It had been postulated[217b] that the increasing upfield shift in several metal complexes with respect to free ligand ($P(OEt)_3$ and $P(OMe)_3$) could be interpreted in terms of increased shielding of the phosphorus nucleus by electron drift from the alkoxy oxygens as the metal

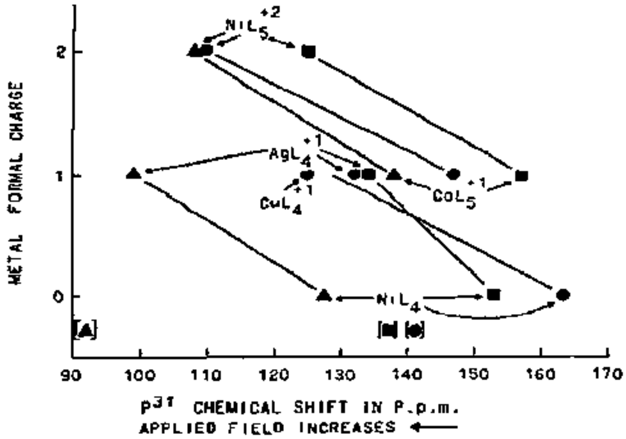


Fig. 16. Plot of ^{31}P chemical shift of complexes of $P(OCH_2)_3CR$ (▲), $P(OCH)_3(CH_2)_3$ (■) and $P(OMe)_3$ (●) against charge on the metal. The points in brackets represent the chemical shifts of the free ligands.

charged increased. There are several serious limitations on this postulate in attempting to extend it to polycyclic phosphite complexes or even other complexes of $P(OMe)_3$. From the data in Table 11 (depicted graphically in Fig. 16) it is seen that on the basis of the above postulate, several inconsistencies occur[218]. (*1*) It is unexpected that the ^{31}P shift of $[Co(P(OMe)_3)_5]NO_3$ is found at lower field than the ligand. (*2*) It is unexpected that without exception all ^{31}P shifts for complexes of $P(OCH_2)_3CR$ are found downfield of the free ligand. Even a formally dipositive metal charge seems incapable of producing a net upfield shift. (*3*) The shifts for AgL_4^+ and NiL_5^{2+} ($L = P(OCH_2)_3CR$) are reversed. (*4*) The shifts for NiL_4 and CoL_5^+ ($L = P(OCH_2)_3CR$) are reversed. (*5*) The ^{31}P resonance of CoL_5^+ is downfield of the free ligand $P(OCH)_3(CH_2)_3$.

It is apparent from Fig. 16 that the changes on coordination of these ligands are not constant nor do they act in the same direction. Furthermore, comparisons of ^{31}P shifts for variously charged complexes can be more meaningfully made in systems which are both isostructural and isoelectronic[218]. In such complexes all other variations which alter ^{31}P shifts (phosphorus hybridization changes from one complex to another, ligand–ligand interactions and magnetic anisotropies, etc.) are minimized.

4. C–O stretching frequencies

The possible origin of the trend toward higher CO stretching frequencies and force constants in metal carbonyl complexes of phosphorus ligands as the electronegativity of the phosphorus substituent rises has claimed the attention of numerous investigators. Consider, for example, the energies (or force constants) of the CO bands in $Mo(CO)_5PY_3$, where an increase in the order $Y = Me < OMe < Cl$ is observed. Using a simple force field analysis this result has been interpreted as stemming from the increasing electronegativity of Y which acts primarily to depopulate the CO antibonding orbitals and thus strengthen the CO bond[219].

Correlation of ν(CO) values or their associated force constants with σ^* polarity constants has led to the alternate explanation that the falling σ basicity of the phosphorus ligand (as Y increases in electronegativity) is the dominant effect responsible for depletion of the CO antibonding orbitals, a process which is brought about by the increasing charge on the metal tending to concentrate electron density in the MC bonds[220]. In yet another study[221], it was concluded from a comparison of the dipole moment derivatives of the E and T_{1u} modes that there is the same or less M to CO pi electron transfer in $M(CO)_5L$ complexes in the case when L is an electronegative phosphorus ligand as when L is a carbonyl group. Thus no increase in pi bonding in the M–C link is experienced as CO is displaced by a poorer pi bonding ligand[221]. In further contrast to the conclusion cited earlier[219], it was also noted that increases in ν(CO) values with increasingly electronegative phosphorus ligands are caused by weakening of the MC sigma bond (owing to decreasing electron density on the metal) and not by an increase in the MC pi bond[221].

Because the pi acidity of a phosphorus ligand parallels its decreasing basicity, the concomitant increases in CO frequencies or force constants do not by themselves support or deny increasing metal–phosphorus pi bonding. The data in Tables 12–17 do demonstrate, however, that as expected: (*a*) caged ligands produce higher ν(CO) values than open-chain analogs in analogous complexes; (*b*) that although the order in CO frequencies caused by caged phosphites and thiophosphites is not the same in all cases for analogous complexes, both cause higher ν(CO) values than caged aminophosphines; (*c*) statement (*b*) also applies to the open-chain analogs; (*d*) $P(OCH)_3(CH_2)_3$ complexes possess somewhat lower CO frequencies than $P(OCH_2)_3CR$ analogs; and (*e*) $As(OCH_2)_3CMe$ raises the CO frequencies above $P(OCH_2)_3CMe$. Although comparison of force constants is more valid than a frequency trend[219], these conclusions accord well with the expected differences in either basicity or pi bonding among the ligands. Force constant calculations[27] based on a simple force field model[219] also corroborate these conclusions for $W(CO)_5L$ complexes but the total ranges of the two CO force constants are only 0.3 and 0.4 mdyne/Å. Since the errors are at least[219] ±0.1 mdyne/Å, more precise ordering of the ligands considered here is unwarranted. Statement (*a*) above implies that the hinge effect is operative not only in caged phosphites but also in caged thiophosphites and aminophosphines. The origin of the exalted CO frequencies in the case of caged ligands could be either decreased sigma basicity or increased pi acidity or a combination of the two, for it will be recalled that both changes are expected to result from the "hinge" effect.

The caged ligands $P(CH_2O)_3CR$ and $P(CH_2O)_3P$ each possess a $P(CH_2O)_3$ moiety which confers some rather curious aspects on the carbonyl infrared region. In Table 12 it is found, for instance, that although not surprisingly the CO frequencies in Group VI complexes of $P(CH_2O)_3CMe$ are less than those of $P(OCH_2)_3CR$, they are rather close to those of $P(SCH_2)_3CMe$ and $P(OMe)_3$. This implies that the oxygens in the $P(CH_2O)_3$ system are capable of exerting a sizeable electron-withdrawing effect which renders the phosphorus effectively the same as that in the latter two ligands. Although the iron complexes in Table 15 exhibit higher frequencies for $P(OMe)_3$ than $P(CH_2O)_3CMe$ as perhaps expected, those

TABLE 12
ν(CO) assignments in $M(CO)_5L$ complexes

	$A_1^{(2)}$	B_1	$A_1^{(1)}$	E	$E(^{13}C)$	Medium	Ref.
$Cr(CO)_5P(OCH_2)_3CMe$	2082	[a]	1995	1960	[a]	$CHCl_3$	170
$P(NMeCH_2)_3CMe$	2066	[a]	1980	1942	[a]	$CHCl_3$	[b]
$Mo(CO)_5P(OCH_2)_3CMe$	2085	[a]	2001	1962	[a]	$CHCl_3$	170
$As(OCH_2)_3CMe$	2090	2060	[a]	1965	[a]	C_6H_6	85
$W(CO)_5P(OCH_2)_3CMe$	2084	[a]	1993	1958	[a]	$CHCl_3$	170
$P(OCH_2)_3C$-*n*-Pent	2085.5	1989.0	1963.5	1958.0	1928.0	C_6H_{12}	27
$P(SCH_2)_3C$-*n*-Pent	2081.0	1990.5	1965.0	1959.5	1930.5	C_6H_{12}	27
$P(CH_2O)_3C$-*n*-Bu	2079.0	1983.0	1965.5	1951.5	1921.5	C_6H_{12}	27
$P(NMeCH_2)_3C$-*n*-Pent	2071.5	[a]	1949.0	1943.0	1914.0	C_6H_{12}	27
$Cr(CO)_5P(OCH)_3(CH_2)_3$	2077	[a]	1995	1955	[a]	CH_2Cl_2	171
$Mo(CO)_5P(OCH)_3(CH_2)_3$	2076	[a]	1995	1955	[a]	CH_2Cl_2	171
$W(CO)_5P(OCH)_3(CH_2)_3$	2084	[a]	1991	1953	[a]	CH_2Cl_2	171
$Cr(CO)_5P(OCH_2)_3P$	2077	[a]	[a]	1951	[a]	CH_2Cl_2	32
$(OC)_5CrP(OCH_2)_3PCr(CO)_5$	2073	[a]	[a]	1956	[a]	CH_2Cl_2	32
$Mo(CO)_5P(OCH_2)_3P$	2077	[a]	[a]	1948	[a]	CH_2Cl_2	32
$(OC)_5MoP(OCH_2)_3PMo(CO)_5$	2078	[a]	[a]	1951	[a]	CH_2Cl_2	32
$W(CO)_5P(OCH_2)_3P$	2085	[a]	[a]	1948	1907	CH_2Cl_2	32
$(OC)_5WP(OCH_2)_3PW(CO)_5$	2077	[a]	[a]	1948	[a]	CH_2Cl_2	32
$[W(CO)_5P(OCH_2)_3PMe]BF_4$	2085	[a]	[a]	1947	1912	CH_2Cl_2	32
$Cr(CO)_5P(OMe)_3$	2073.4	1985.2	1963.0	1948.0	[a]	$C_{16}H_{34}$	[c]
$N(CH_2CH_2)_3CH$	2062	[a]	1905	1925	[a]	C_6H_{12}	172
$P(NMe_2)_3$	2055	[a]	1978	1932	[a]	[d]	[e]
$Mo(CO)_5P(OMe)_3$	2082	[a]	1997	1970	[a]	C_6H_{14}	221
$P(NMe_2)_3$	2066	[a]	1983	1938	[a]	[d]	[e]
$N(CH_2CH_2)_3CH$	2067	[a]	1901	1925	[a]	C_6H_{12}	172
$W(CO)_5PF_2$	2103	[a]	2007.0	1983.0	1952.0	C_6H_{12}	27
$P(OPh)_3$	2083.0	[a]	1965.0	1957.5	[a]	C_6H_{12}	27
$P(OMe)_3$	2080.5	1988.0	1951.1	1936.2	[a]	$C_{16}H_{34}$	[c]
$P(OEt)_3$	2078.0	[a]	1959.0	1944.5	[a]	C_6H_{12}	27
$P(SMe)_3$	2062.0	[a]	1946.0	1939.5	[a]	C_6H_{12}	27
$P(NMe_2)_3$	2070.0	1971.0	[a]	1940.5[f]	1902.6	C_6H_{12}	27
				1931.5	[a]		
PPh_3	2072.0	[a]	1947.5	1942.0	[a]	C_6H_{12}	27
PBu_3	2067.5	[a]	1941.0	1934.0	[a]	C_6H_{12}	27
$NH_2C_6H_{11}$	2071.0	[a]	1916.5	1929.0	[a]	C_6H_{12}	27
$N(CH_2CH_2)_3CH$	2062	[a]	1900	1912	[a]	C_6H_{12}	172

[a] Not observed. [b] J.R. Pipal and J.G. Verkade, to be published. [c] R. Mathieu, M. Lenzi and R. Poilblanc, *Inorg. Chem.*, 9 (1970) 2030. [d] Halocarbon. [e] See footnote *e* of Table 14. [f] Split *E* mode.

TABLE 13

ν(CO) assignments in *cis*-$M(CO)_4L_2$ complexes

	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2	Medium	Ref.
$Cr(CO)_4[P(OCH_2)_3CMe]_2$	2043	1950	1925	[a]	CH_2Cl_2	172
$[P(SCH_2)_3CMe]_2$	2033	1957	1931	[a]	$CHCl_3$	[b]
$[As(OCH_2)_3CMe]_2$	2065	1962	1955	[a]	CH_2Cl_2	172
$Mo(CO)_4[P(SCH_2)_3CMe]_2$	2045	1965	1945	[a]	$CHCl_3$	[b]
$[P(SCH_2)_3C\text{-}n\text{-}Pent]_2$	2045	1965	1945	[a]	$CHCl_3$	[b]
$[P(OCH_2)_3CMe]_2$	2038	1945	1923	[a]	CH_2Cl_2	172
$[P(NMeCH_2)_3CMe]_2$	2028	1934	1912	1890	$CHCl_3$	[c]
$W(CO)_4[P(OCH_2)_3CMe]_2$	2045	1950	1924	[a]	CH_2Cl_2	172
$[P(SCH_2)_3CMe]_2$	2041	1976	1927	[a]	$CHCl_3$	[b]
$Cr(CO)_4[P(OCH)_3(CH_2)_3]_2$	2043	1950	1929	[a]	CH_2Cl_2	172
$Mo(CO)_4[P(OCH)_3(CH_2)_3]_2$	2050	1957	1934	[a]	CH_2Cl_2	172
$W(CO)_4[P(OCH)_3(CH_2)_3]_2$	2053	1950	1927	[a]	CH_2Cl_2	172
$Cr(CO)_4[P(OCH_2)_3P]_2$	2037	1946	1924	[a]	CH_2Cl_2	32
$Mo(CO)_4[P(OCH_2)_3P]_2$	2048	1954	1938	[a]	CH_2Cl_2	174
$[P(OCH_2)_3P][P(CH_2O)_3P]$	2044	1955	1938	[a]	CH_2Cl_2	174
$Mo(CO)_4[P(OCH_2)_3CEt][P(NMe_2)_3]$	2031	1930	1913	[a]	$CHCl_3$	186
$[P(OCH_2)_3CEt][P(OMe)_3]$	2048	1961	1944	1935	C_6H_{12}	186
$Cr(CO)_4[P(OMe)_3]_2$	2026	1947	1939	1913	$C_{16}H_{34}$	[d]
$[P(NMe_2)_3]_2$	2015	1945	1930	1900	[d]	[f]
$(PMe_3)_2$	2000	1890	1876	1858	C_6H_{12}	175
$Mo(CO)_4[P(SMe)_3]_2$	2045	1955	2045	[a]	$CHCl_3$	[b]
$[P(OMe)_3]_2$	2037	1945	1926	1921	[e]	[g]
$[P(CH_2Cl)_3]_2$	2032	1952	1932	1928	C_6H_{12}	175
$(PMe_3)_2$	2024	1930	1901	1879	C_6H_{12}	175
$[P(NMePh)_3]_2$	2125	1933	1911	[a]	$CHCl_3$	184
$[P(NMe_2)_3]_2$	2012	1908	1894	1880	$CHCl_3$	186, [c]
$W(CO)_4[P(OMe)_3]_2$	2034.6	1947.2	1939.3	1914.5	$C_{16}H_{34}$	[f]
$(PMe_3)_2$	2012	1912	1893	1865	C_6H_{12}	175
$[P(NMe_2)_3]_2$	2004	1876	1866	1690	[e]	[f]

[a] The B_1 and B_2 bands are unresolved and both modes probably contribute to the band listed under B_1.

[b] F.B. Ogilvie and J.G. Verkade, to be published.

[c] See footnote *b* of Table 12.

[d] See footnote *c* of Table 12.

[e] Hydrocarbon.

[f] R. Mathieu and R. Poilblanc, *C.R. Acad. Sci., Ser. C*, 264 (1967) 1053.

[g] R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.*, (1962) 1301.

TABLE 14

ν(CO) assignments in *trans*-$M(CO)_4L_2$ complexes

	A_{1g}	B_{1g}	E_u	Medium	Ref.
$Cr(CO)_4[P(SCH_2)_3C$-*n*-Pr$]_2$	[a]	[a]	1935	$CHCl_3$	[b]
$[P(OCH_2)_3CMe]_2$	[a]	[a]	1915	CH_2Cl_2	172
$[P(NMeCH_2)_3CMe]_2$	[a]	1938	1887	$CHCl_3$	[c]
$[P(OCH)_3(CH_2)_3]_2$	[a]	[a]	1926	CH_2Cl_2	172
$Mo(CO)_4[P(NMeCH_2)_3CMe]_2$	[a]	1949	1905	$CHCl_3$	[c]
$[P(OCH)_3(CH_2)_3]_2$	[a]	[a]	1932	CH_2Cl_2	172
$W(CO)_4[P(NMeCH_2)_3CMe]_2$	[a]	1938	1894	$CHCl_3$	[c]
$[P(OCH)_3(CH_2)_3]_2$	[a]	[a]	1924	CH_2Cl_2	172
$Mo(CO)_4[P(OCH_2)_3CEt][P(NMe_2)_3]$	[a]	[a]	1910	$CHCl_3$	186
$[P(OCH_2)_3CEt][P(OMe)_3]$	[a]	[a]	1932	$CHCl_3$	186
$Cr(CO)_4[P(OMe)_3]_2$	[a]	1967	1918	[d]	[e]
$[P(SMe)_3]_2$	[a]	[a]	1925	$CHCl_3$	[b]
$[PMe_3]_3$	[a]	[a]	1876	C_6H_{12}	175
$[P(NMe_2)_3]_2$	[a]	[a]	1868	[f]	[g]
$Mo(CO)_4[P(OMe)_3]_2$	2045	1973	1923	C_6H_{14}	221
$[P(NMe_2)_3]_2$	[a]	[a]	1885	[f]	[g]
$W(CO)_4[P(OMe)_3]_2$	[a]	[a]	1915	$C_{16}H_{34}$	[h]
$[P(NMe_2)_3]_2$	[a]	[a]	1870	[f]	[g]

[a] Not observed. [b] See footnote *b* of Table 13. [c] See footnote *b* of Table 12. [d] Hydrocarbon. [e] G.C. Faber and G.R. Dobson, *Inorg. Chem.*, 7 (1968) 584. [f] Halocarbon. [g] R.B. King, *Inorg. Chem.*, 2 (1963) 936. [h] See footnote *c* of Table 12.

recorded in Table 16 for nickel carbonyl derivatives tend to be larger for $P(CH_2O)_3CMe$ with respect to $P(OMe)_3$ and variable for $P(CH_2O)_3As$ and $P(CH_2O)_3SiMe$. These observations, coupled with the fact that $P(CH_2O)_3CMe$ does not react with BMe_3 (Table 5) whereas $P(OMe)_3$ forms a stable adduct[43] with this sigma acceptor, strongly suggest that (*a*) the sigma basicity of the phosphorus in $P(OMe)_3$ may be significantly enhanced by pi donation from the oxygens, and (*b*) that since $P(CH_2O)_3CMe$ is an even weaker base than $P(OMe)_3$, its pi acid character is at least as great as that of $P(OMe)_3$ and perhaps even greater in view of the fact that carbon cannot pi bond. Triphenyl phosphine is widely held to be a good pi acid and it is interesting that the ν(CO) values in $W(CO)_5P(CH_2O)_3C$-*n*-Bu are higher than those of the PPh_3 analog.

The PC_3 and PO_3 phosphorus atoms in $P(OCH_2)_3P$ are unexpectedly similar in their effect on the CO frequencies in Group VI metal carbonyls. Thus only three bands were observed in bridged complexes of the type $(OC)_5MP(OCH_2)_3PM(CO)_5$ and furthermore these bands were close to those observed for the corresponding $M(CO)_5P(OCH_2)_3P$ complex (Table 12). Similarly the linkage isomers *cis*-$Mo(CO)_4[P(OCH_2)_3P]_2$ and *cis*-$Mo(CO)_4$-$[P(OCH_2)_3P]$ possess spectra which resemble one another closely (Table 13). In iron com-

TABLE 15

ν(CO) assignments in $Fe(CO)_4L$ and *trans*-$Fe(CO)_3L_2$ complexes

	$A_1^{(2)}$	$A_1^{(1)}$	E	Medium	Ref.
$Fe(CO)_4P(OCH_2)_3CMe$	2065	1996	1965	$CHCl_3$	170
$P(NMeCH_2)_3CMe$	2053	1976	1942	$CHCl_3$	[a]
$As(OCH_2)_3CMe$	2125	2005	1980	CCl_4	85
$P(OCH)_3(CH_2)_3$	2065	1993	1962	CH_2Cl_2	171
$P(OCH_2)_3P$	2068	1991	1954	CH_2Cl_2	32
$P(CH_2O)_3P$	2065	1993	1946	CH_2Cl_2	32
$(OC)_4FeP(OCH_2)_3PFe(CO)_4$	2068	1999	1963	CH_2Cl_2	32
$Fe(CO)_4P(CH_2O)_3CMe$	2059	1988	1949	CH_2Cl_2	26
$P(OMe)_3$	2063	1994	1964	C_6H_{12}	[b]
$P(NMe_2)_3$	2041	1969	1930	[c]	[d]

	E'	Medium	Ref.
trans-$Fe(CO)_3[P(OCH_2)_3CMe]_2$	1933	$CHCl_3$	170
$[P(CH_2O)_3CMe]_2$	1904	CH_2Cl_2	26
$[P(NMeCH_2)_3CMe]_2$	1890	$CHCl_3$	[a]
$[P(OCH)_3(CH_2)_3]_2$	1926	CH_2Cl_2	171
$[P(OCH_2)_3P][P(CH_2O)_3P]$	1927	$CHCl_3$	59
$[P(OMe)_3]_2$	1923 1914	C_6H_{12}	[b]
$[P(NMe_2)_3]_2$	1871	[c]	[d]
$[P(OCH_2)_3C\text{-}n\text{-}Pr][P(NMe_2)_3]$	1899	C_6H_{12}	186

[a] See footnote *b* of Table 12. [b] J.D. Cotton and R.L. Heazlewood, *Aust. J. Chem.*, 22 (1969) 2673. Splitting of the *e* and *e'* modes in the mon- and bis-trimethyl phosphite compounds is observed. [c] Halocarbon. [d] See footnote *g* of Table 14.

plexes (Table 15) decreased resemblances are noted since the linkage isomers $Fe(CO)_4$-$P(OCH_2)_3P$ and $Fe(CO)_4P(CH_2O)_3P$ and the bridged complex $(OC)_4FeP(OCH_2)_3PFe(CO)_4$ do display distinguishable spectra.

Some miscellaneous carbonyl frequency comparisons which are not unexpected but are worthy of comment close this section. Complexes containing two different ligands (Tables 13–16) possess CO frequencies which lie between those of the analogous complexes containing two identical ligands. Quinuclidine ($N(CH_2CH_2)_3CH$) seems to be a better base than $NH_2C_6H_{11}$ in $W(CO)_5L$ (Table 12) and $P(NMe_2)_3$ a better one than $P(NMePh)_3$ in *cis*-$Mo(CO)_4L_2$ (Table 13). Finally, the increase in positive charge on the metal in *trans*-$Co(CO)_3[P(OCH_2)_3CMe]_2^+$ (2063 cm^{-1})[222] probably serves to depopulate the CO antibonding pi orbitals and raise ν(CO) compared with the neutral *trans* iron analog (Table 15).

TABLE 16

ν(CO) assignments in $Ni(CO)_{4-x}L_x$ complexes

	A_1	E	Medium	Ref.
$Ni(CO)_3P(OCH_2)_3CMe$	2090	2021	$CHCl_3$	170
$P(OCH)_3(CH_2)_3$	2086	2018	CH_2Cl_2	171
$P(CH_2O)_3As$	2082	2005	$CHCl_3$	[a]
$P(CH_2O)_3SiMe$	2079	2002	$CHCl_3$	[a]
$P(OMe)_3$	2079	2010 2003	[b]	[c]
	A_1	B_1	Medium	Ref.
$Ni(CO)_2[P(OCH_2)_3CMe]_2$	2048	1994	$CHCl_3$	170
$[P(OCH)_3(CH_2)_3]_2$	2044	1896	CH_2Cl_2	171
$[P(CH_2O)_3CMe]_2$	2030	1978	CH_2Cl_2	26
$[P(CH_2O)_3SiMe]_2$	2030	1975	$CHCl_3$	[a]
$[P(CH_2O)_3As]_2$	2022	1970	$CHCl_3$	[a]
$[P(CH_2O)_3As][P(OCH_2)_3CMe]$	2039	1973	$CHCl_3$	[a]
$[P(OMe)_3]_2$	2024	1976	$C_{16}H_{34}$	[d]
	A_1		Medium	Ref.
$NiCO[P(OCH_2)_3CMe]_3$	1997		$CHCl_3$	170
$[P(OCH)_3(CH_2)_3]_3$	1979		CH_2Cl_2	171
$[P(CH_2O)_3CMe]_3$	1971		CH_2Cl_2	26
$[P(OMe)_3]_3$	1963		$C_{16}H_{34}$	[d]

[a] J. Rathke and J.G. Verkade, to be published. [b] Hydrocarbon. [c] M. Bigorgne and H. Zelwer, *Bull. Soc. Chim. Fr.*, (1960) 1986. The *e* mode is split. [d] G.R. Van Hecke and W. de W. Horrocks, *Inorg. Chem.*, 5 (1966) 1960.

5. M–P stretching frequencies

Metal–phosphorus stretching modes ranging from 98 to 463 cm^{-1} have been assigned with more or less certainty for over 150 metal complexes containing a variety of phosphorus ligands[1]. Table 18 contains Raman and infrared data obtained for phosphite complexes[172, 173, 223–230] and the values are generally in the low end of the range. Prior to the extensive study[172] of the far IR region of fifteen metal complexes of caged phosphites in 1968, the only other ν(MP) assignment reported for a metal–phosphite complex ($Ni[P(OMe)_3]_4$) was based on the presence of a strongly polarized Raman band at 178 cm^{-1} attributed to the completely symmetric A_1 mode in T_d symmetry[223,225]. The assignments of ν(MP) bands in the caged phosphite complexes were arrived at from the arguments[172,173,230]

TABLE 17

ν(CO) assignments for $Mn(CO)_{4-x}L_xX$ complexes[a]

	$A_1^{(2)}$	$A_1^{(1)}, B_1$	B_2	Ref.
cis-$Mn(CO)_4[P(OCH_2)_3C$-*n*-Pr]Cl	2110	2028	1972	*b*
$[P(OCH_2)_3C$-*n*-Pr]Br	2105	2020	1980	*b*
$[P(OCH_2)_3CMe]Br$	2110	2029	1985	*b*
[P(O-*n*-Bu)$_3$]Br	2105	2016	1972	*c*
$[P(OPh)_3]Br$	2101	2020	1972	*d*
$[P(OCH_2)_3C$-*n*-Pr]I	2105	2020	1984	*b*
$[P(OCH_2)_3CMe]I$	2103	2023	1993	*b*
$[P(NMe_2)_3]Br$	2083	2000	1942	*b*
	2076	2013	1961	
		2000	1953	*e*
			1946	
$[P(NMe_2)_3]I$	2083	2000	1942	*b*
	2080	2017	1975	
		2006	1968	*e*
			1962	

	A_1	B_1	A_1'	Ref.
sym[f]-*mer*-$Mn(CO)_3[P(OCH_2)_3C$-*n*-Pr]$_2$Br	2061	2000	1946	*b*
[P(O-*n*-Bu)$_3$]$_2$Br	2049	1969	1927	*g*
$[P(OMe)_3]_2Br$	2058	1976	1890	*b*
$[P(OPh)_3]_2Br$	2070	2000	1949	*g*
$[P(OMe)_3]_2I$	2045	1965	1942	*b*
$[P(OPh)_3]_2I$	2056	1991	1948	*h*
$[P(NMe_2)_3]_2Cl$	2024	1946	1887	*b*
$[P(OPh)_3]_2Cl$	2051	1973	1931	*i*
$[P(NMe_2)_3]_2Br$	2020	1938	1901	*b*

	A'_a, A''	A'_b	Ref.
fac[j]-$Mn(CO)_3[P(OCH_2)_3CMe]_2Cl$	2060, 2005	1921	*b*
$[P(OCH_2)_3C$-*n*-Pr]$_2$Br	2061, 2000	1946	*b*
$[P(OMe)_3]_2Br$	2052, 1975	1939	*k*
[P(O-*n*-Bu)$_3$]$_2$Br	2037, 1969	1927	*g*
$[P(OPh)_3]_2Br$	2053, 2000	1949	*g*
$[P(OCH_2)_3CMe]_2I$	2054, 2000	1959	*b*

TABLE 17 (continued)

[a] All spectra were obtained in $CHCl_3$ except where indicated otherwise. The assignments for the *cis* complexes are based on the approximation that they are of C_{2v} symmetry.

[b] See footnote *b* of Table 13.

[c] R.J. Angelici and F. Basolo, *Inorg. Chem.*, 2 (1963) 728.

[d] R.J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, 84 (1962) 2495.

[e] R.B. King and T.F. Korenowski, *J. Organometal. Chem.*, 17 (1969) 95. The splitting of the low-field band could arise from conformational isomers of the ligand. The spectrum was obtained in cyclohexane.

[f] The mutually *trans* phosphites are symmetrically related (i.e. *cis*) to the halide.

[g] R.J. Angelici, F. Basolo and A.J. Poë, *J. Amer. Chem. Soc.*, 85 (1963) 2215. The spectra were obtained in $Cl_2C_2H_4Cl_2$.

[h] R. Ugo and F. Bonati, *J. Organometal. Chem.*, 8 (1967) 189. The spectrum was obtained in CH_2Cl_2.

[i] B.L. Booth and R.N. Haszeldine, *J. Chem. Soc. A*, (1966) 157.

[j] The phosphorus ligands and X are mutually *cis*.

[k] P.M. Treichel and J.J. Benedict, *J. Organometal. Chem.*, 17 (1969) P37.

which follow taken in toto. (*a*) The far IR spectrum of $Ni[P(OCH_2)_3CMe]_4$ consists of only six bands, five of which are attributable to vibrational modes of the ligand while it seemed reasonable to assign the sixth at 157 cm^{-1} to the F_2 mode in T_d symmetry. (*b*) The observance of a strong Raman band at 146 cm^{-1} in $Ni[P(OCH_2)_3CMe]_4$ assignable to the A_1 mode. (*c*) The five expected M–C and M–C–O bands for $Ni(CO)_2[P(OCH_2)_3CMe]_2$ could be observed in the 656–377 cm^{-1} region allowing the bands at 155 and 144 cm^{-1} to be ascribed to the infrared-active A_1 and B_2 modes in C_{2v} symmetry. (*d*) A comparison of the far IR spectra of *cis*-$Cr(CO)_4[P(OCH_2)_3CMe]_2$ with that of the $As(OCH_2)_3CMe$ analog showed that a band at 181 cm^{-1} assigned to overlapped A_1 and B_2 M–P modes in the phosphite complex was conspicuously absent in the arsenite analog. (*e*) The assignment of the single IR-active M–P asymmetric stretch in *trans*-$Cr(CO)_4[P(OCH)_3(CH_2)_3]_2$ is substantiated by the appearance at higher energy of the expected three M–C and M–C–O modes. (*f*) As expected, two bands are observed for *cis*-$W(CO)_4[P(OCH_2)_3CMe]_2$ in the 180 cm^{-1} region which can be assigned to the A_1 and B_2 IR-active ν(MP) modes. The small separation between these bands (3 cm^{-1}) makes it likely that their overlap in the remaining *cis* complexes prevents their resolution.

The bands assigned to M–P vibrations in the caged phosphite complexes often do not have observable bands below them, and when they are present they are at least 20 and usually 30 or more wave number units to lower energy. The high-frequency side of the M–P band is clear for at least 150 cm^{-1} and usually for more than 200 cm^{-1}. Thus the M–P modes may be relatively free of coupling to other motions in the complex and it becomes reasonable to examine trends as a potential source of metal–phosphorus bonding information.

Previously[172] it was concluded that from the available infrared data on $Ni(CO)_{4-x}$-$[P(OCH_2)_3CMe]_x$ the increase of x from 1 to 4 was accompanied by a rise in M–P frequency (Table 18). With the recent acquisition of the Raman spectrum of the complex where $x = 4$, however, this conclusion becomes somewhat less tenable (143, $x = 1$; 155,

TABLE 18

ν(MP) assignments for metal phosphite complexes [a]

Compound	ν(MP) (cm^{-1})	Mode	No. of bands Expected	Observed	Ref.
$Cr(CO)_5P(OCH_2)_3CMe$	164	A_1 (C_{4v})	1	1	172
$Mo(CO)_5$	195	A_1 (C_{4v})	1	1	172
$W(CO)_5$	180	A_1 (C_{4v})	1	1	172
cis-$Cr(CO)_4[P(OCH_2)_3CMe]_2$	181	A_1, B_2 (C_{2v})	2	1	172
cis-$Mo(CO)_4$	201	A_1, B_2 (C_{2v})	2	1	172
	198 [b, c]	A_1, B_2 (C_{2v})	2	1	229
cis-$W(CO)_4$	185	A_1, B_2 (C_{2v})	2	1	172
cis-$Cr(CO)_4[P(OCH)_3(CH_2)_3]_2$	182	A_1, B_2 (C_{2v})	2	1	172
cis-$Mo(CO)_4$	200	A_1, B_2 (C_{2v})	2	1	172
cis-$W(CO)_4$	181, 178	A_1, B_2 (C_{2v})	2	2	172
trans-$Cr(CO)_4[P(OCH_2)_3CMe]_2$	190	A_{2u} (D_{4h})	1	1	172
trans-$Mo(CO)_4\{P(OCH_2)_3C$-*n*-$Pr\}_2$	226	A_{2u} (D_{4h})	1	1	172
trans-$W(CO)_4$	204	A_{2u} (D_{4h})	1	1	172
trans-$Cr(CO)_4\{P(OCH)_3(CH_2)_3\}_2$	198	A_{2u} (D_{4h})	1	1	172
trans-$Mo(CO)_4$	237	A_{2u} (D_{4h})	1	1	172
trans-$W(CO)_4$	202	A_{2u} (D_{4h})	1	1	172
$Fe(CO)_4P(OCH_2)_3CMe$	169	A_1 (C_{3v})	1	1	172
trans-$Fe(CO)_3[P(OCH_2)_3CMe]_2$	192	A_2'' (D_{3h})	1	1	172
$Ni(CO)_3P(OCH_2)_3CMe$	143	A_1 (C_{3v})	1	1	172
$Ni(CO)_2[P(OCH_2)_3CMe]_2$	155, 144	A_1, B_2 (C_{2v})	2	2	172
$Ni(CO)[P(OCH_2)_3CMe]_3$	157, 151	A_1, E (C_{3v})	2	2	172
$Ni[P(OCH_2)_3CMe]_4$	157	F_2 (T_d)	1	1	172, 173
	157 [b, c]	F_2 (T_d)	2	2	229
	146 [b, c]	A_1 (T_d)			
Pd	192	E (C_{3v})	3	2	173
	142	A_1 (C_{3v})			
Pt	191	E (C_{3v})	3	2	173
	160	A_1 (C_{3v})			
	191 [b, c]	E (C_{3v})	3	3	229
	158 [b, c]	A_1 (C_{3v})			
	148 [b, c]	A_1 (C_{3v})			
$Ni\{P(OCH)_3(CH_2)_3\}_4$	162	F_2 (T_d)	1	1	172, 173
Pd	193	E (C_{3v})	3	2	173
	145	A_1 (C_{3v})			
Pt	194	E (C_{3v})	3	2	173
	170	A_1 (C_{3v})			
$Ni(CO)_3P(OMe)_3$	240 [d]	A_1 (C_{3v})	1	1	224
	242 [e]	A_1 (C_{3v})	1	1	228
	242 [b, f]	A_1 (C_{3v})	1	1	228

TABLE 18 (continued)

Compound	ν(MP) (cm^{-1})	Mode	No. of bands Expected	No. of bands Observed	Ref.
$Ni(CO)_2[P(OMe)_3]_2$	243^e	A_1 (C_{2v})	2	1	228
	$242^{b,f}$	A_1 (C_{2v})	2	1	228
$Ni(CO)\{P(OMe)_3]_3$	$239^{b,f}$	A_1 (C_{3v})	2	1	228
$Ni[P(OMe)_3]_4$	$178^{b,g}$	A_1 (T_d)	2	1	223, 225
	$180^{b,c}$	A_1 (T_d)	2	1	229
$Ni[P(OEt)_3]_4$	335	$F_2{}^h$ (C_{3v})	3	2^i	227
	305	$F_2{}^h$ (C_{3v})			
	210	A_1 (C_{3v})			
	$169^{b,c}$	A_1 (T_d)	2	1	229
	335^j	$F_2{}^h$ (C_{3v})	3	2^i	227
	302^j	$F_2{}^h$ (C_{3v})			
	226^j	A_1 (C_{3v})			
Pd	335	$F_2{}^h$ (C_{3v})	3	2^i	227
	290	$F_2{}^h$ (C_{3v})			
	200	A_1 (C_{3v})			
Pt	332	$F_2{}^h$ (C_{3v})	3	2^i	227
	290	$F_2{}^h$ (C_{3v})			
	215	A_1 (C_{3v})			
	335^j	$F_2{}^h$ (C_{3v})	3	2^i	227
	300^j	$F_2{}^h$ (C_{3v})			
	212^j	A_1 (C_{3v})			
trans-$Pt_2Cl_4[P(OEt)_3]_2$	361	B_u (C_{2h})	1	1	226
trans-Pd_2Cl_4	364	B_u (C_{2h})	1	1	226
trans-Pd_2Br_4	354	B_u (C_{2h})	1	1	226
$\{Ag[P(OCH_2)_3CMe]_4\}ClO_4$	112	F_2 (T_d)	1	1	173
$\{Cu[P(OCH_2)_3CMe]_4\}ClO_4$	132	F_2 (T_d)	1	1	173

[a] All spectra were obtained in Nujol using an infrared spectrometer unless otherwise indicated.
[b] Raman data.
[c] Spectrum taken on crystals.
[d] Medium not specified.
[e] Solution (solvent not specified).
[f] Liquid phase.
[g] Hexadecane solution.
[h] Assigned as split F_2 mode.
[i] One of the modes (F_2) is split.
[j] Benzene solution.

144, $x = 2$; 157, 151, $x = 3$; 157, 146, $x = 4$). It is perhaps more realistic to examine weighted averages of these frequencies in order to take into account their degeneracies. If we assume that the symmetric mode when $x = 3$ is higher than the asymmetric vibration as is experimentally the case when $x = 4$ (Table 18) the weighted averages are 143 ($x = 1$), 150 ($x = 2$), 155 ($x = 3$), 154 ($x = 4$). If these frequencies reflect bonding changes, their generally increasing order can be rationalized by making the reasonable assumption that phosphites are poorer pi bonding ligands than CO. The pi electron density deposited on the metal by a departing CO group is not completely engaged in pi bonding to the phosphorus which takes its place. Successive substitutions force the phosphorus atoms to pi bond to a greater extent as CO groups are replaced because of electron accumulation on the metal and hence the NiP frequency rises. The augmenting electron density on the metal on CO substitution is also reflected in the lowering of the force constants for the CO stretching mode[172,228]. Supporting the idea that phosphorus–nickel pi rather than sigma effects are dominating the rise in ν(NiP) as x increases is the expectation that ν(NiP) would decrease with increasing x if the basicity of phosphorus were important. Thus the metal would become less acidic as electron density accumulated on the nickel. Because only the A_1 modes for the $Ni(CO)_{4-x}[P(OMe)_3]_x$ are available no trends can be discussed. It is worthy of observation, however, that in the analogous $P(OCH_2)_3CMe$ complexes, the A_1 mode is lower in energy which could reflect, at least in part, the mass difference of the ligands.

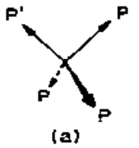
As with the nickel complexes, ν(MP) increases from mono- to disubstituted octahedral complexes of $P(OCH_2)_3CR$ (Table 18). In all cases, this increase is greater in the *trans* than in the *cis* compounds and the same trend occurs in the $P(OCH)_3(CH_2)_3$ analogs. The same reasoning given for the rise in ν(NiP) on CO substitution is felt to apply here. Because carbonyl groups are undoubtedly more strongly pi bonding ligands than phosphites, their depleting effect on the pi density available to the phosphite is expected to be greater when oriented *trans* to a phosphite than in a *cis* orientation. This stems from the fact that *trans* ligands share two d_π orbitals whereas those *cis* to each other share only one. Hence the stronger M–P pi bond and higher-frequency M–P stretch is expected for the *trans* isomers. Pi effects of phosphorus ligands are "symmetry factored" from sigma influences[219] and so force constant calculations on the CO modes in these compounds should complement the ν(MP) data. Although all the CO modes are not available[172], the bands which have been observed are quite close to those of the analogous molybdenum $P(OMe)_3$ complexes[219]. As expected, the latter possess k_1 and k_2 values, both of which are larger in the monosubstituted derivative than k_1 and k_2 in the *cis*, and k_2 in the *cis* is larger than k_2 in the *trans*.

If these trends are reflections of changing M–P bond order in the Group VI complexes, the results are consistent with dominant MP pi bonding effects and they militate strongly against arguments based solely on sigma-donor properties of phosphorus ligands. If the latter effect were dominant, a decrease in ν(MP) would have been expected from mono- to disubstitution and no significant change in ν(MP) from the *cis* to the *trans* isomer would have been predicted.

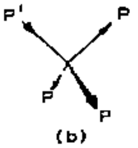
In 1969, an infrared examination of the series $M[P(OEt)_3]_4$ (M = Ni, Pd, Pt) resulted in a report[227] in which it was concluded that the two bands in the 340–290 cm^{-1} region belonged to a split F_2 mode and a band in the 220–190 cm^{-1} range could be assigned to an A_1 species due to deviation from T_d symmetry (Table 18). In a later study carried out in our laboratories[173] it was pointed out that at least one of the bands in the 340–290 region could well be a ligand band since a broad but reproducible absorption at 330 cm^{-1} was found for uncomplexed $P(OEt)_3$. Moreover, the band at 210 cm^{-1} reported earlier[227] for $Ni[P(OEt)_3]_4$ could not be observed in the infrared[173] or in the Raman[230] spectrum. However, the Raman spectrum did reveal[230] a strong band at 169 cm^{-1} which seems likely to arise from the A_1 vibration of an undistorted tetrahedron. Furthermore, the position of this band is more in line with the same Raman bands seen in the spectrum of the $P(OCH_2)_3CMe$ (146 cm^{-1})[230] and $P(OMe)_3$ analogs (178 cm^{-1})[223,225]. It is interesting that this symmetric mode increases for the NiL_4 series in the order $P(OCH_2)_3CMe <$ $P(OEt)_3 < P(OMe)_3$ and for the $Ni(CO)_3L$ series in the order $P(OCH_2)_3CMe$ (143 cm^{-1}) $< P(OMe)_3$ (240 cm^{-1}) (Table 18). Although a mass effect would certainly explain the increase in frequency from a $P(OEt)_3$ or a $P(OCH_2)_3CMe$ to a $P(OMe)_3$ complex, the substantial increase from a $P(OCH_2)_3CMe$ (mol.wt. 148) to a $P(OEt)_3$ (mol.wt. 166) complex cannot be rationalized in the same way. It is possible, however, that the rigid caged ligand has an effectively higher mass than the flexible open-chain phosphites. Thus the oscillation of the phosphorus against the metal may be more hindered by the rather stiff alkoxide cage in $P(OCH_2)_3CMe$ whereas it experiences more freedom when bonded to alkoxy chains which are more susceptible to bending and rotational motions. Whether the decrease in sigma basicity of the caged ligand contributes to a lowering of ν(NiP) here is not clear, for the better pi accepting capabilities of the ligand may compensate.

The $M[P(OCH_2)_3CMe]_4$ complexes (M = Pd, Pt) are not as straightforward as the nickel analog in that additional bands in the M–P region are suggestive of distortion from T_d symmetry. In the platinum complex, for instance, three bands are observed in the M–P stretching region of the Raman spectrum and two of these bands are also seen in the infrared spectrum[173]. If all of these absorptions are associated with M–P modes, the spectra are consistent with the idea that the platinum complex is distorted from T_d toward C_{3v} symmetry. The intense 158 cm^{-1} Raman band could then be represented by the motion shown in (a) below while the less intense 148 cm^{-1} absorption might involve compensating bond polarizability changes, as shown in (b).

The E mode in C_{3v} symmetry could then be represented by the 191 cm^{-1} band which



(a)



(b)

is both IR- and Raman-active. The similarity of the IR spectrum of the Pd analog is indicative of a similar distortion from tetrahedrality. It should be recognized that there is chemical evidence for suggesting that three of the M—P bonds may be different from the fourth in Pt^0 complexes[231]. The fact that a very similar IR spectrum is also obtained for the $Pt[P(OCH)_3(CH_2)_3]_4$ complex seems fortuitous if only a solid-state site symmetry effect obtains in the Pt and Pd(caged phosphite)$_4$ complexes.

The M—P F_2 species in the $Cu[P(OCH_2)_3CMe]_4^+$ and silver(I) analog appears at a distinctly lower energy than the F_2 mode in the nickel(0) complexes or for any of the modes in the palladium(0) complexes, respectively, in spite of the nearly identical masses involved in the third- and fourth-row metal pairs[173]. Moreover, the positive charge on the Group I metals might have been expected to increase rather than decrease ν(MP) because of the increase in M—P bond polarity. It is tentatively suggested that the weak sigma basicity of caged phosphites may result in a subordination of this effect to a substantial weakening of M—P pi bonding from the zerovalent to monovalent d^{10} complexes arising from the contraction of the metal d orbitals upon increasing the positive charge.

6. *Ligand atom chemical shifts and intraligand coupling*

Since ^{31}P chemical shifts of coordinated phosphorus nuclei have been discussed in Sect. C(iii)3 we will consider here shifts of ligand ^1H and ^{13}C atoms as well as the NMR behavior of the uncoordinated ^{31}P nucleus in complexes of $P(OCH_2)_3P$.

Although the available proton chemical shift data[3] are not always consistent with the idea that downfield shifts on coordination are expected on inductive grounds for organophosphorus ligands, the general order[184] of the δ^1H values is: L $<$ zerovalent metal complexes of L $<$ divalent Pd and Pt complexes of L $<$ L-sulfide $<$ L-oxide $<$ RL$^+$, where L = PMe_3, $P(CH_2Cl)_3$, $P(NMe_2)_3$ and $P(OMe)_3$. It is conceivable that the generally increased deshielding of these protons is a result of the increase in electronegativity of the fourth group on phosphorus and the dominance of this effect over any tendency toward back donation from metal moieties and chalconides. The presence of several discrepancies[184] in these trends admits of the possibility of one or more subtle influences which may override the inductive effect.

Polycyclic ligands have thus far exhibited proton chemical shifts which are better behaved in that the trend is always: L $<$ zerovalent metal complexes of L $<$ divalent metal complexes of L $<$ L-chalconides $<$ RL$^+$, where L = $P(OCH_2)_3CR$ (ref. 184), $P(OCH)_3(CH_2)_3$ (ref. 171), $P(CH_2O)_3CMe$ (ref. 184), $P(OCH_2)_3P$ (ref. 32) and $P(NMeCH_2)_3CMe$ (ref. 232). The rigidity of these ligands may be responsible for the greater sensitivity of their protons to inductive effects inasmuch as those on open-chain ligands will experience bond anisotropy changes if ligand conformational changes take place on coordination.

The ^{13}C chemical shifts for several open-chain ligands recorded in Table 19 appear to be sensitive to inductive effects, although no consistent correlations are apparent at this time. The trend among $P(OMe)_3$ systems is not unreasonable except that the order in the ligand and the zerovalent molybdenum complexes seems reversed. The ^{31}P chemical shift

TABLE 19

^{13}C chemical shifts and couplings

	$\delta\,^{13}C$ [a]	*J*PC	*J*PH	^1JCH	Ref.
$Mo(CO)_5P(OMe)_3$	−31.24	− 2.3	+ 11.6	+146.8	242
cis-$Mo(CO)_4[P(OMe)_3]_2$	−31.29	− 3.1 [e]	+ 11.6 [e]	+144.9	242
trans-$Mo(CO)_4[P(OMe)_3]_2$	−31.44	− 1.7 [e]	+ 11.6 [e]	+144.4	242
$P(OMe)_3$	−33.0	+ 10.0	+ 10.0	+146.0	[b]
cis-$PdCl_2[P(OMe)_3]_2$	−35.05	− 3.7 [e]	+ 12.9	+148.5	242
$OP(OMe)_3$	−39.0	− 5.8	+ 10.5	+147.0	[b]
$SP(OMe)_3$	−39.5	− 5.6	+ 12.9	+148.1	[b]
$[MeP(OMe)_3]BF_4$	−48.47 [c]	− 17.8 [c]	+ 11.4 [c]	+153.0 [c]	242
	+14.59 [d]	+132.4 [d]	− 17.8 [d]	+140.9 [d]	242
$SePMe_3$	−8.0	+ 48.5	− 13.0	+130.5	[b]
$SPMe_3$	−7.6	+ 56.1	− 13.0	+129.3	[b]
cis-$Mo(CO)_4(PMe_3)_2$	−5.58	[e]	− 6.3	+129	242
PMe_3	−1.8	− 13.6	+ 2.7	+126.9	[b]
trans-$PdI_2(PMe_3)_2$	−0.25	[e]	~ − 10.0	+130.4	242
$[MePMe_3]I$	+3.9	+ 55.5	− 15.4	+132.5	[b]
$OP(NMe_2)_3$	−16.82	+ 2.2	+ 9.30	+136.2	242
$P(NMe_2)_3$	−26.94	+ 19.4	+ 8.8	+133.5	242

[a] Chemical shifts with respect to glacial $^{13}CH_3COOH$ as an external standard. [b] W. McFarlane, *Proc. Roy. Soc., Ser. A*, 306 (1968) 185. These values given with respect to $CH_3{}^{13}COOH$ in this reference were corrected by subtracting 158 p.p.m. to obtain them relative to $^{13}CH_3COOH$. [c] $PO^{13}C$ carbon. [d] $P^{13}C$ carbon. [e] See Sect. C(iii)8.

of the uncoordinated phosphorus in $P(OCH_2)_3P$ (Table 20) seems to be fairly insensitive to coordination of the other phosphorus except in the case of $[MeP(OCH_2)_3P]BF_4$, where the PC_3 phosphorus is rather strongly deshielded.

The intraligand coupling constants are in many cases amenable to interpretation in terms of hybridization changes induced by coordination of phosphorus. ^2JPOC for $P(OMe)_3$ is seen from Table 19 to decrease from a positive value in the free ligand to negative values upon coordination in the order L > complexes of L > chalconides of L > MeL^+. A somewhat similar trend is seen to occur for the two-bond coupling ^2JPCH for PMe_3, which also becomes negative upon coordination in the order L > *cis*-$Mo(CO)_4L_2$ > *trans*-PdI_2L_2 > L-chalconide > MeL^+. Evidence for this type of behavior of ^2JPCH has also been discussed by others[233–235]. Although no ^2JPNC coupling constants were actually measured for $P(NMe_2)_3$ complexes, it is probable[236] that they lie between those for the free ligand (+ 19.4 Hz) and its oxide (+ 2.2 Hz), which would be in agreement with the ^2JPOC and ^2JPCH trends just given. Thus increased electron withdrawal at the acidic coordination site seems to induce a decrease in this coupling, as suggested earlier by others in the case of PR_3 derivatives[237].

TABLE 20

NMR data for $P(OCH_2)_3P$ derivatives

	^{2}JPH	^{3}JPH	^{3}JPP	$\delta^{31}PO_3$	$\delta^{31}PC_3$
$P(OCH_2)_3P$	+8.9	+2.5	− 37.2	− 89.78	+66.99
$(OC)_5CrP(OCH_2)_3P$	+8.5	+5.3	− 3.0	−154.47	+68.57
$(OC)_5CrP(OCH_2)_3PCr(CO)_5$	(+)2.0	(+)5.6	+ 66.1	−155.52	− 8.21
$(OC)_5MoP(OCH_2)_3P$	+8.8	+5.0	− 4.6	−130.82	+68.60
$(OC)_5MoP(OCH_2)_3PMo(CO)_5$	+2.1	+5.2	+ 63.7	−130.97	+18.94
$(OC)_5WP(OCH_2)_3P$	+8.5	+5.3	− 0.4	−109.09	+68.75
$(OC)_5WP(OCH_2)_3PW(CO)_5$	(+)	+5.5	+ 73.8	−108.37	+36.34
$[(OC)_5WP(OCH_2)_3Me]BF_4$	−5.6	+6.1	+143.2	−113.00	− 2.98
cis-$(OC)_4Cr[P(OCH_2)_3P]_2$	(+)8.4	(+)5.3	− 2.4	−157.21	+68.52
cis-$(OC)_4Mo[P(OCH_2)_3]$-	+8.5	+5.2	− 6.0	−133.3	+69.3
$[P(CH_2O)_3P]$ [b]	+2.6	+2.6	+ 20.0	− 88.0	+13.1
$(OC)_4FeP(OCH_2)_3P$	+8.5	+6.1	+ 8.6	−157.44	+71.38
$(OC)_4FeP(CH_2O)_3P$	(+)0.4	(+)2.8	+ 47.1	− 87.37	−22.42
$(OC)_4FeP(OCH_2)_3PFe(CO)_4$	(+)0.4	+6.2	+ 95.3	−160.40	−22.06
trans-$(OC)_3Fe[P(OCH_2)_3P$-	+8.7	+6.2	+ 9.0	−161.3	+68.0
$[P(CH_2O)_3P]$ [c]	0.9	2.8	[c]	[c]	[c]
$[MeP(OCH_2)_3P]BF_4$	+8.5	+6.6	+ 46.2	− 51.03	+59.80
$[P(OCH_2)_3PMe]BF_4$	−5.4	+3.1	+114.6	− 89.58	− 2.56
$OP(OCH_2)_3PO$	−8.2	+8.3	+139.1	+ 18.17	− 5.48
$SP(OCH_2)_3PO$	−9.0	+8.2	+151.3	− 49.28	− 5.50
$SP(OCH_2)_3P$	+7.6	+7.5	+ 48.1	− 52.06	+70.89
$OP(OCH_2)_3P$ [b]	+7.5	+7.5	+ 65	+ 14.25	+69.98
$P(OCH_2)_3PS$ [b]	−5.8	+3.0	+118	− 90.49	− 6.30
$P(OCH_2)_3PO$ [b]	−8.1	+3.2	+140	− 85.53	− 7.45
$SP(OCH_2)_3PS$ [b]	−5.4	+8.6	+150	− 49.28	− 3.91

[a] All data taken from ref. 32. [b] See ref. 31. [c] See ref. 59.

The increase in ^{1}JCH values generally parallels the decreases in the ^{2}JPC and ^{2}JPH coupling for a given ligand. This seems reasonable on the basis of the isovalent hybridization hypothesis, which in the present case states that when the carbon substituent becomes more electronegative through phosphorus coordination, its bond to the carbon gains *p* character. This in turn results in an accompanying increase in C—H bond *s* character. An increase in ^{1}JCH is also seen for a given compound as the substituent on carbon is changed from P to N to O since the electronegativity increases in this order also. The idea that hybridization is solely responsible for the observed trends has been criticized[238], however, and the importance of the effective nuclear charge on carbon in considering C—H coupling has been pointed out. A molecular orbital treatment[239a] also takes into account both the effects of changes in *s* character and nuclear charge on carbon, and sign changes in ^{1}JPC and ^{2}JPH have been ascribed to the dominance of an indirect Fermi contact term whose sign depends on whether *s* or *p* orbitals are primarily used in bonding[239b].

As noted previously (Sect. C(ii)2) increases in ^3JPOCH are not significant upon coordination of $P(OMe)_3$ to BH_3 or carbonium ions which is also true in the case of transition metal complexes (Table 19). Caged phosphites, however, have been observed to exhibit sizable increases in this coupling upon adduct formation with sigma-bonding Lewis acids (Sect. C(ii)2). Because proton coupling is believed to be dominated by the Fermi contact term[216,240], however, the proton chemical shifts and POCH coupling in complexes containing pi donor acids might correlate differently from those in compounds containing only non-pi-donating acids. In Sect. C(ii)2 the linear correlation of ^3JPOCH with the proton chemical shifts in the adducts $AP(OCH_2)_3CMe$ and $AP(OCH)_3(CH_2)_3$ (Figs. 9 and 10) were accounted for[8] by the variation in strength of the Lewis acid A which proportionately polarized the phosphorus lone pair toward an sp^3 state by increasing its *s* character. If indeed the coupling interaction involves mainly changes in *s* character around phosphorus and little or no pi contribution, then it could be argued that for Lewis acids of equal strength, the acceptor which could also function as a pi donor would manifest proton shifts to higher field than the acid which could function only as a sigma acceptor. In other words, as shown in Figs. 9 and 10, when A = oxygen, sulfur or a transition metal fragment, a new correlation is generated in which the chemical shift is the result of both sigma electron withdrawal and pi electron donation by A while the coupling constant reflects mainly the changes in sigma electron density on phosphorus. It is not too surprising that the chalcogens appear to be better pi donors (i.e. greater upfield proton NMR shifts relative to non-pi-bonding acids) than the transition metal moieties. A similar plot for $AP(OCH_2)_3P$ derivatives shown in Fig. 17 also shows a linear correlation for the pi bonding acids. The only non-pi-bonding acids (H_3C^+ and Ph_3C^+) are seen to lie off the line in the expected direction.

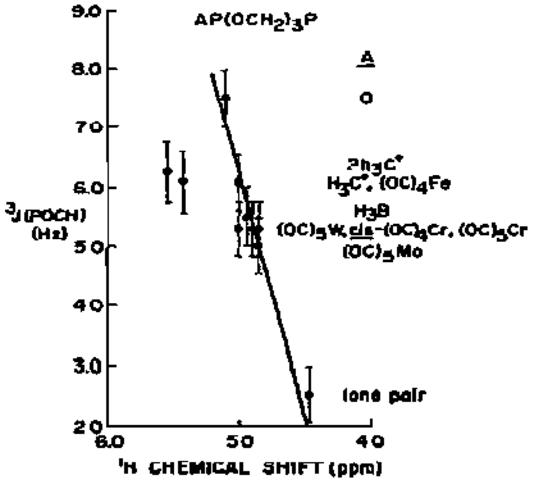


Fig. 17. Plot of ^3JPH vs. the CH_2 proton chemical shift for $AP(OCH_2)_3P$ compounds.

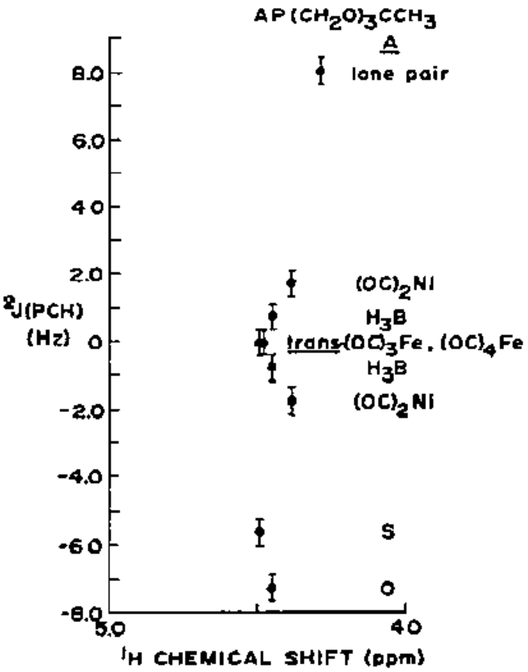


Fig. 18. Plot of ${}^2J$PH vs. the C$\underline{H}_2$ proton chemical shift for AP$(CH_2O)_3$CMe compounds (data taken from ref. 26).

There is ample evidence from internuclear double resonance experiments[32,184,236,241,242] that, as in P$(OMe)_3$ derivatives, the sign of ${}^3J$PH in caged phosphite systems is positive.

An examination of the points on the graph shown in Fig. 18 reveals that although the range of ${}^2J$PH values for AP$(CH_2O)_3$CMe systems is quite large (16 Hz), the chemical shift range is quite small (~0.5 p.p.m.). The coupling constants for the nickel carbonyl and borane derivatives were too small to determine their signs with any certainty and so no attempt was made to draw a straight line through the collection of points. In any case, the correlation would appear to be reasonably linear. The analogous plot for AP$(CH_2O)_3$P derivatives shown in Fig. 19 is similar to that in Fig. 18 with the added feature that, as expected, the point for the non-pi-bonding acid CH_3^+ lies away from the trend of the pi-bonding acids.

The variation in the ${}^2J$PH, ${}^3J$PH and ${}^3J$PP coupling constants in P$(OCH_2)_3$P as a function of the acceptor on the phosphorus is entirely consistent with the caged-ligand "hinge effect" discussed earlier. An interpretation of the trends in these couplings for the compounds in Table 20 is facilitated by their division into three classes: class A, YP$(OCH_2)_3$P; class B, P$(OCH_2)_3$PY, and class C, YP$(OCH_2)_3$PY. Here Y can be an electron pair, a metal fragment, a carbonium ion or a chalcogen. For each class, plots have been constructed of ${}^3J$PP vs. ${}^3J$PH (Fig. 20) and ${}^3J$PP vs. ${}^2J$PH (Fig. 21). It should be noted that for each of the class C compounds, Y is the same Lewis acid except in $(OC)_5$WP$(OCH_2)_3$P$^+$Me and SP$(OCH_2)_3$PO.

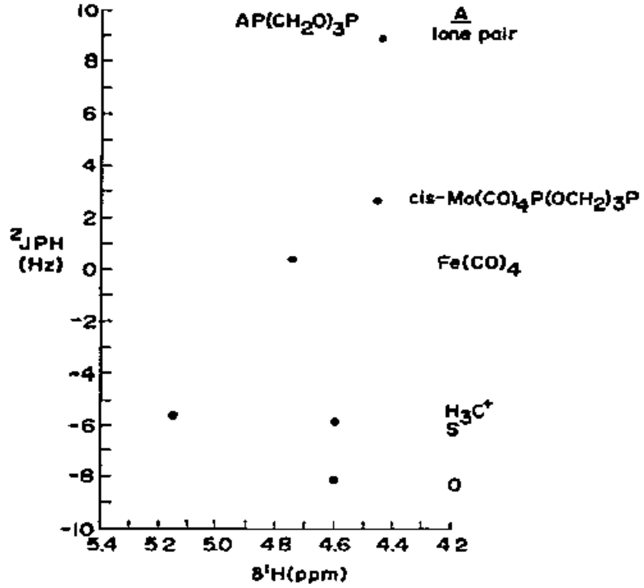
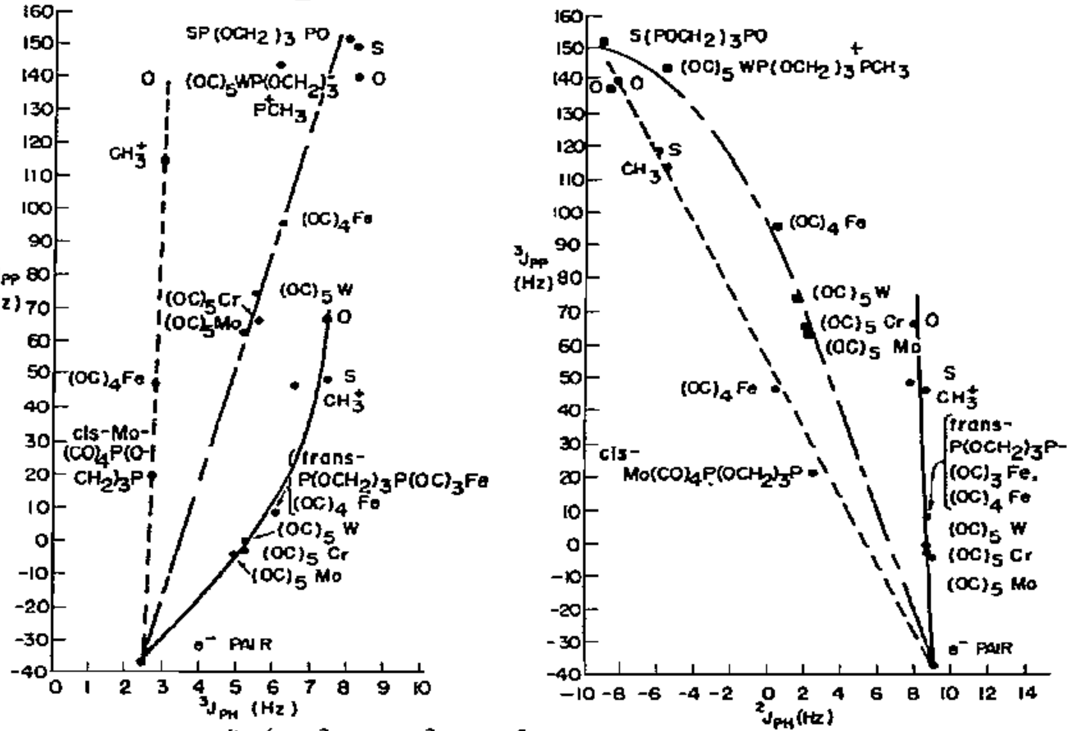


Fig. 19. Plot of ^{2}JPH vs. the C$\underline{H}_2$ proton chemical shift for AP(CH$_2$O)$_3$P compounds.



Figs. 20 and 21. Plot of ^{3}JPP′ vs. ^{3}JPH and ^{3}JPP vs. ^{2}JPH, respectively, for (———) YP(OCH$_2$)$_3$P, (– – –) P(OCH$_2$)$_3$PY and (— — — —) YP(OCH$_2$)$_3$PY, where the Y groups are those indicated adjacent to each point.

From Fig. 20 it is seen that ^3JPH increases substantially (~5 Hz) in positive magnitude for classes A and C, but only slightly (~0.5 Hz) for class B as the Lewis acidity of Y increases in the order electron pair < methyl < chalcogen. This is not unexpected in view of the increase in *s* character in the internal P—O bonds of the ligand and the rise in effective positive charge on the nuclei of the cage (particularly the coordinated PO_3 phosphorus), which would accompany an increase in Lewis acidity of Y. The very much smaller rise in ^3JPH in the class B compounds might stem from the fact that the PC_3 phosphorus is coordinated to Y and this donor site is more remote from the POCH bond system through which ^3JPH is transmitted. Extension of the explanation given for the rise in ^3JPH in the class A and C compounds to the very small rise in the class B compounds must be viewed with some caution, because of the small range of this parameter in the latter compounds (~0.5 Hz) and the error in the measurements (0.1—0.2 Hz).

Figure 21 reveals that over a range of about 15 Hz ^2JPH becomes negative upon increasing the Lewis acidity for classes B and C, whereas a range of less than ca. 1 Hz is noted for the compounds in class A. Experimental evidence from NMR studies has already been cited which strongly suggested a sign change for this coupling constant in a similar series of compounds of $P(CH_2O)_3CMe$, but absolute signs could not be determined. The data obtained for the $P(OCH_2)_3P$ systems firmly support the postulate of a sign change in ^2JPH.

Values of ^2JPH for all the memebers of class A fall between +7.6 and +8.9 Hz. It has been found[243] that there is a correlation which can be made in a large variety of phosphines between ^2JPH and the dihedral angle made by a plane containing the P, C and H atoms, and the plane containing the C—P bond and the three-fold axis of the PC_3 bond system. The expected value of ^2JPH for the class A compounds and $P(CH_2O)_3CCH_3$ according to such a plot, is +5 Hz, which is somewhat below the +7.6 to +8.9 Hz we observe for the former and the +8.0 Hz for the latter[244]. The reason for the small rise in ^2JPH with rising electron-withdrawing power of the Y group in the class A compounds is not apparent at this time.

The values and signs of the vicinal ^3JPP couplings for the compounds in Table 20 represent the first systematic study of this coupling interaction. Figures 20 and 21 show that this coupling constant increases markedly from negative to positive values as the Lewis acidity of the Y group increases in the order: electron pair < metal carbonyl fragment < methyl < chalcogen for each class of compounds. This trend parallels those discussed above for the rise in ^2JPH and ^3JPH, and the same arguments based on effective nuclear charge and hybridization changes in the bicyclic portion of these systems used to interpret the latter results are felt to apply here. It is interesting that ^3JPP is more sensitive to coordination of the PC_3 phosphorus than the PO_3 phosphorus. This may arise from the greater polarizability of a more basic phosphine phosphorus lone pair by the Lewis acid moiety. Polarizing both phosphorus lone pairs (class C) augments the ^3JPP coupling over that in analogous compounds in classes A and B as expected. Although no theoretical basis for vicinal $^{31}P—^{31}P$ couplings has been put forth, the data suggest that ^3JPP values become more positive with increasing *s* character and effective nuclear charge in the ligand.

For carbonyl complexes of $P(OCH_2)_3P$, experimental values of ^3JPP can be used to predict ^3JPP interactions in new compounds because of their additivity[31]. Hence ^3JPP for $(OC)_4FeP(OCH_2)_3P$ is +8.6 Hz which is an increase of 45.8 Hz over that of the ligand. For the linkage isomer $(OC)_4FeP(CH_2O)_3P$, ^3JPP is +47.1 Hz and Δ^3JPP = +84.3 Hz. Δ^3JPP for $(OC)_4FeP(OCH_2)_3PFe(CO)_4$ is +132.5 Hz, which is close to the sum of the Δ^3JPP values of the linkage isomers (130.1 Hz). Similarly Δ^3JPP calculated for $[(OC)_5WP(OCH_2)_3PMe]^+$ is 188.6 Hz compared with the experimentally obtained value of 180.4 Hz. The additivity of Δ^3JPP seems to hold reasonably for $SP(OCH_2)_3PS$ (166 Hz calculated compared with 150 Hz experimental) but the calculated values increasingly exceed the experimental ones in proceeding from $SP(OCH_2)_3PO$ to $OP(OCH_2)_3PO$ by 37 and 66 Hz, respectively, for reasons which are not clear at this time. It is possible that a disproportionate increase in pi bonding occurs upon formation of the $YP(OCH_2)_3PY$ system when Y is a chalcogen, with a resultant shift of electron density to phosphorus which decreases its positive nuclear charge and hence lowers ^3JPP. It is perhaps more likely that molecular constraints for some reason prevent both phosphorus atoms in $YP(OCH_2)_3PY$ from achieving the bond angle configurations (and hence the same degree of *s* character) which they can in $YP(OCH_2)_3P$ and $P(OCH_2)_3PY$.

It remains to consider the possibility of a "through-space" ^{31}P–^{31}P spin–spin coupling involving the phosphorus non-bonding orbital lobes which lie inside the bicyclic structure along the three-fold axis of the molecule. The distance between the phosphorus atoms is probably at least 2 Å, which would seem to militate against such a mechanism. Moreover it would be difficult to see how this coupling could rise positively with the increasing Lewis acidity of Y as observed, inasmuch as the phosphorus non-bonding hybrid lobe(s) would be expected to lose *s* character. A larger effect on the PH coupling constants of the uncoordinated phosphorus atoms in classes A and B might also have been expected. It therefore seems that a through-space coupling mechanism need not presently be invoked. The observation that quaternizing the uncoordinated phosphorus in $(OC)_5WP(OCH_2)_3P$ with a carbonium ion did not visibly alter the CO stretching frequencies in the complex indicates that the interaction of the phosphorus lobes inside the cage, if any, was not sufficient to allow inductive effects to change the donor properties of the P coordinated to tungsten. Photoelectron spectral work along with calculations[90,92] on $N(CH_2CH_2)_3N$ strongly suggests that the interaction of the nitrogen lone pairs occurs through three sets of bonds rather than through space. The uncommonly large[32] ^3JPP values for $P(OCH_2)_3P$ and its derivatives also indicate a through-bond mechanism involving the three sets of bridge bonds[32].

7. *Tungsten–phosphorus coupling constants*

Although metal–phosphorus coupling constants have been measured for a variety of metals[216], the present discussion will be restricted to those results which are germane to our investigations[27,245,246]. Coupling constants are most conveniently discussed using MO theory[239a] in which the coupling of directly bonded atoms arises almost entirely from the Fermi contact interaction between nuclear spins and *s* orbital electron spins. In the following expression for ^1JAB, α_A and α_B are the magnetogyric ratios of the nuclei, β is the Bohr magneton, S_A and S_B are the valence state *s* orbitals of the atoms, the $|S(0)|$ terms are the magnitudes of these orbitals, $\Delta^3E_{i\rightarrow j}$ are the triplet excitation energies and *c* is the coefficient of an occupied or unoccupied molecular orbital.

$$
{}^1J\mathrm{AB} = \alpha_A\alpha_B \frac{\hbar}{2\pi}\frac{256\pi^2}{9}\beta^2\, |S_A(0)|^2\, |S_B(0)|^2 \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{unocc}} ({}^3\Delta E_{i\rightarrow j})^{-1}\, c_{iS_A} c_{jS_A} c_{jS_B} c_{iS_B} \tag{19}
$$

Because of the low symmetry of the $(OC)_5WL$ (C_{4v}) complexes of concern here, the mixing of other metal orbitals with the *s* becomes more complicated. Since the energies of the molecular orbitals are not known for these complexes, the precise form of the coupling theory cannot be utilized and we must be content for the present to seek trends among complexes containing a variety of ligands.

Table 21 is a tabulation of the $(OC)_5WL$ complexes and their ^1JWP coupling constants which form the basis for the conclusions given in the following paragraphs. The trend in coupling constants parallels the electronegativity changes of the phosphorus substituents, as illustrated in the plots in Fig. 22. The electronegativities used were those of the atom bound to phosphorus with no correction being made for atoms *beta*, *gamma*, etc. to phosphorus. It is remarkable that the correlation coefficients for the Pauling, Sanderson and Allred–Rochow electronegativity scales for both sets of ligands depicted in Fig. 22 exceed

TABLE 21
^1JWP coupling constants in $(OC)_5WL$ complexes

L	^1JWP (Hz)	Ref.
(1) PF_3	485	27
(2) PCl_3	426	245
(3) PBr_3	398	245
(4) PI_3	334	245
(5) $P(OPh)_3$	415	248
(6) $P(OMe)_3$	398	247
(7) $P(OCH_2)_3C$-*n*-Pent	393	27
(8) $P(OEt)_3$	391	247
(9) $P(O$-*n*-$Bu)_3$	390	247
(10) $P(O$-i-$Pr)_3$	378	247
(11) $P(OMe)_2Ph$	323	247
(12) $P(NMeCH_2)_3C$-*n*-Pent	318	27
(13) $P(NMe_2)_3$	297	247
(14) $P(NEt_2)_3$	296	247
(15) $P(OMe)Ph_2$	280	247
(16) $P(SCH_2)_3C$-*n*-Pent	276	27
(17) PPh_3	280	247
(18) $PBuPh_2$	250	247
(19) $PMePh_2$	245	247
(20) $PEtPh_2$	240	247
(21) $P(i$-$Pr)Ph_2$	240	247
(22) $P(t$-$Bu)Ph_2$	240	247
(23) PBu_2Ph	235	247
(24) $P(CH_2O)_3C$-*n*-Bu	234	27
(25) PBu_3	227	248

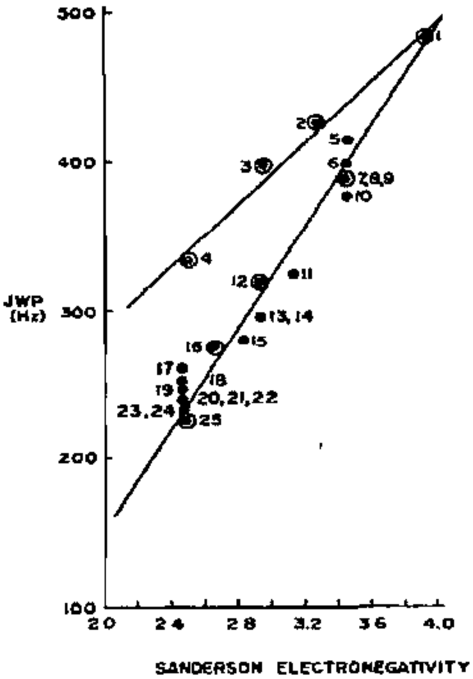


Fig. 22. Plot of $^{1}J^{83}\mathrm{W}-^{31}\mathrm{P}$ vs. the Sanderson electronegativity of the ligand (see text) in a series of $\mathrm{W(CO)_5L}$ complexes where L is the compound correspondingly numbered in Table 21. The circled points were used to draw the least-squares lines.

TABLE 22

Correlation coefficients of ^{1}JWP vs. electronegativity for $\mathrm{(OC)_5WL}$ complexes[245]

L	Electronegativity scale	Correlation coefficient
$\mathrm{PBu_3}$, $\mathrm{P(CH_2O)_3C}$-*n*-Bu	Sanderson	0.996
$\mathrm{PO_3Y}$, $\mathrm{PS_3Y}$, $\mathrm{P(NMe)_3Y}$, $\mathrm{PF_3}$	Pauling	0.983
(Y = $\mathrm{(CH_2)_3C}$-*n*-Pr or $\mathrm{(CH_2)_3C}$-*n*-Pent)	Allred–Rochow	0.961
$\mathrm{PI_3}$, $\mathrm{PBr_3}$, $\mathrm{PCl_3}$, $\mathrm{PF_3}$	Sanderson	0.995
	Pauling	0.941
	Allred–Rochow	0.949

0.941 (Tables 22)[245]. The four caged ligands and PF_3 in the first group of ligands in Table 22 were chosen for inclusion in the calculation of the correlation coefficients and to establish the least-squares line in Fig. 22 because they minimized possible coupling changes induced by steric effects of the phosphorus substituents. Tributyl phosphine was included when it was found that its coupling was only slightly different from $P(CH_2O)_3C$-*n*-Bu and this similarity indicated that electronic effects beyond the alpha atom on the phosphorus substituent as well as general steric effects were not very important. Indeed the rest of the ligands[27,247,248a] generate points which are reasonably close to this line. Interestingly, phenyl carbon atoms do not appear to be grossly different in electronegativity from alkyl carbon atoms.

A clear explanation for the presence of two slopes in Fig. 22 cannot be given at this time. Although it might be thought that substituent atoms in different families of the Periodic Table generate points which fall on different slopes, this does not appear to be the case with oxygen and sulfur, the points for which lie on the same line as those for fluorine, nitrogen and carbon.

Insofar as coupling between directly bonded atoms is generally agreed to occur through bonding orbitals having *s* character, the correlation with electronegativiry can be explained without invoking pi bonding. It has been argued that the replacement of a group X attached to a carbon by a more electronegative group Y results in less *s* character in the C–Y bond than in the C–X bond[249]. It has been further pointed out[250] that atomic *s* character is concentrated in orbitals which are directed toward the most electropositive substituents. For our $LW(CO)_5$ complexes, the above arguments appear to be applicable since the $W(CO)_5$ moiety serves as the most electropositive substituent on phosphorus in each of the complexes, and as the remaining substituent groups on phosphorus are replaced by more electronegative ones, the *s* character should increase in the tungsten–phosphorus bond, as will the positive nuclear charge on phosphorus.

Employing the assumption that metal–carbonyl pi bonding is influenced by other ligands present in the complex, the carbonyl stretching frequencies have been used in a variety of ways to infer the pi-bonding capacity of the ligand. The values of raw frequency data have been used to compare pi-bonding character, especially from values of the $A_1{}^1$ mode which stem from the CO group *trans* to L. As $A_1{}^1$ stretching frequency values increase for a given series of ligands, the C–O bond order should increase as a result of increased pi-bonding in the metal–phosphorus link. Other workers[247] have plotted the *E* mode stretching frequencies of a number of $LW(CO)_5$ complexes vs. ${}^1JWP$ values and have observed a straight-line correlation between these two parameters. As they were unable to assign the $A_1{}^1$ mode for all of the complexes because of overlap with the *E* mode, the *E* mode was used as a reasonable approximation, since the $A_1{}^1$ and the *E* modes have very similar stretching frequencies. Although there is a general increase in the *E* mode carbonyl stretching frequency with the value of ${}^1JWP$, the linear correlation coefficient (0.79) is rough in view of the relatively small errors in the two parameters. It should be noted, however, that the range in these parameters defined by the $(C_4H_9)_3P$ and $(C_6H_5)_3P$ complexes was much smaller for the much better linear correlation observed by other workers[249]. The $A_1{}^1$ mode was observed for all but three of the complexes and reasonable estimates could be made for two of these unobserved peaks (Table 12). The correlation coefficient of 0.70 for the plot of the $A_1{}^1$ mode against ^1JWP did not represent any improvement. Although force constants are more reliable than raw frequency data for bonding interpretations, values of k_1 (CO stretching force constant *trans* to L) plotted vs. $^{183}W-^{31}P$ coupling constants revealed a large decrease in the correlation coefficient (0.51). This result suggests that the increase of $^{183}W-^{31}P$ coupling at best only roughly parallels the rising pi-acceptor properties of the phosphorus ligand.

Correlations of ^1JWP with $\Delta\sigma$ and $\Delta\pi$ (parameters representing the sigma and pi bonding capacities of a ligand which are calculated[251] from carbonyl force constant data) were attempted[27]. The low correlation coefficient for the $\Delta\pi$ parameter (0.35) strongly suggested that $^{183}W-^{31}P$ coupling is not dependent on pi bonding. The order of decreasing sigma-donating capacity ($\Delta\sigma$) of the complexed phosphorus compounds is: $P(C_4H_9)_3 >$ $P(SCH_3)_3 > P(OC_2H_5)_3 > P(CH_2O)_3CC_4H_9 > P(C_6H_5)_3 > P(N(CH_3)CH_2)_3CC_5H_{11} >$ $P(OC_6H_5)_3 > P(SCH_2)_3CC_5H_{11} > PF_3 > P(OCH_2)_3CC_5H_{11}$. Some of the orders are somewhat unexpected on electronegativity grounds but it is possible that "normal" basicity orders are not necessarily operative when the ligand is complexed to a transition metal[251]. If indeed $^{183}W-^{31}P$ coupling occurs through orbitals having *s* character, a better correlation with $\Delta\sigma$ than with $\Delta\pi$ might have been expected, since increasing *s* character of the phosphorus lone pair in the complex should parallel its decreasing sigma-donating character. The low correlation coefficient[27] of $^{183}W-^{31}P$ coupling with $\Delta\sigma$ (0.55) could arise from the small range in $\Delta\sigma$ values for these phosphorus ligands (+0.01 to −0.34) and the large standard deviation (0.12) in the correlation compared with the acknowledged error[251] (0.12) in the $\Delta\sigma$ evaluation.

The following tentative conclusions are drawn from these studies. (*a*) Increases in the electronegativity of the phosphorus ligand account very well for the rise in $^{183}W-^{31}P$ coupling constants in $W(CO)_5L$ complexes. (*b*) Although greater ligand electronegativity is expected to raise the pi-acceptor capacity of the ligand, the rise in $^{183}W-^{31}P$ coupling can be explained quite well without invoking pi bonding as a coupling mechanism.

More recently[248b], the increase in ^1JWP with decreasing WP distance from $(PhO)_3$-$PW(CO)_5$ (411 Hz, 2.309 Å) to *trans*-$[(PhO)_3P]_2W(CO)_4$ (480 Hz, 2.252 Å) has been cited as support for an increase in pi bonding upon substitution. Independent of any pi effect, however, the increase in coupling may stem from electronegativity reduction occasioned by the better sigma basicity of the phosphite relative to CO.

Unfortunately the only copper–phosphorus coupling constants published are those reported by us[246] on the $Cu[P(OMe)_3]_4^+$ and $Cu[P(OEt)_3]_4^+$ cations ($J^{63}Cu^{31}P = 1190 \pm$ 30 Hz and 1210 ± 30 Hz, respectively) and so a comparison of trends is not yet possible. Although the published spectrum[246] did not show complete resolution of the two four-line spectra expected for the ^{63}Cu and ^{65}Cu isotopes each having spin 3/2, more recent efforts[242] have shown that all eight lines can be seen and the observed ratio of the $^{65}Cu-^{31}P$ couplings is 1.07, in agreement with the value of 1.071 calculated from magnetogyric ratios.

8. *Interligand couplings, particularly* $^2JPMP'$

Ever since it was discovered[252] that identical proton-bearing phosphorus ligands, when mutually *trans* in a complex, yielded proton NMR spectra exhibiting a "triplet" while the normal doublet was observed for *cis* systems, this NMR criterion for stereochemistry has become widely adopted[3]. Because the spin–spin interaction of the chemically equivalent but magnetically non-equivalent phosphorus nuclei influences the appearance of the proton spectra of such $X_nAA'X_n'$ spin systems, $^2JPP'$ data which can be extracted from the spectra for a variety of ligands in a given complex are useful in elucidating the nature of the metal–phosphorus bond. The solution of these spectra in most cases is not trivial and it would seem that $^2JPP'$ values for complexes containing two chemically different phosphorus ligands would provide basically the same information with the advantage that the data could easily be obtained from the AX or AB ^{31}P NMR spectra. There are several reasons why complexes of identical phosphorus ligands are more useful. (*1*) Mixed-ligand complexes are more difficult to synthesize and so they are vastly out-numbered by those with identical phosphorus ligands. (*2*) The concentrations (ca. 30%) required for ^{31}P spectroscopy are higher than for ^{1}H NMR studies unless accumulation facilities are available. (*3*) It is not possible to apportion the coupling constants between the two chemically different phosphorus atoms in mixed-ligand complexes, and the data only become useful for interpretation when $^2JPP'$ values are known for the analogous compounds in which both ligands are identical.

Analysis of the ^{1}H spectrum of an $X_nXX'X_n'$ system via the equations[253] worked out for the general case in which the interligand H–H′ coupling (JXX') is zero leads to an evaluation of the intraligand coupling JPH (JAX) and the interligand interactions JPH' (JAX'), JPP' (JAA'). The general features of the X spectrum which appear in Fig. 23 include a sharp doublet of separation N centered at the proton chemical shift as well as $2n$ pairs of lines occurring symmetrically about δ^1H with spacings S given by:

$$S = [\Psi^2L^2 + JAA'^2]^{1/2} \pm [(\Psi-1)^2L^2 + JAA'^2]^{1/2} \tag{20}$$

where $L = [JAX - JAX']$ and Ψ is an integer[253] between 1 and n. The intensity of this portion of the spectrum is evenly divided between the N doublet and the $2n$ pairs of lines. These $2n$ pairs of lines may be divided into two sets, the so-called "inner" and the "outer" lines given by the difference and sum, respectively, in eqn. (20). For the typical case in which values of $L/JAA' < 1$, these designations refer to the lines which occur between and outside the members of the N doublet, respectively. Only the first outer pair of lines is represented in Fig. 23. It has also been shown[253] that the intensity of the outer lines is quite small compared with that of the inner lines.

As the value of JAA' increases for a particular value of N and L, the frequency distribution of the inner and outer lines changes. The separation between the first inner line and the first outer line remains JAA', but the intensity of the outer line decreases as JAA' increases. Hence it becomes experimentally quite difficult to find this line for $JAA' > 100$ Hz at realizable concentrations for compounds whose protons are not directly bound to phosphorus. As JAA' increases, the separations of the inner lines becomes smaller until for $JAA' \gg L$ the

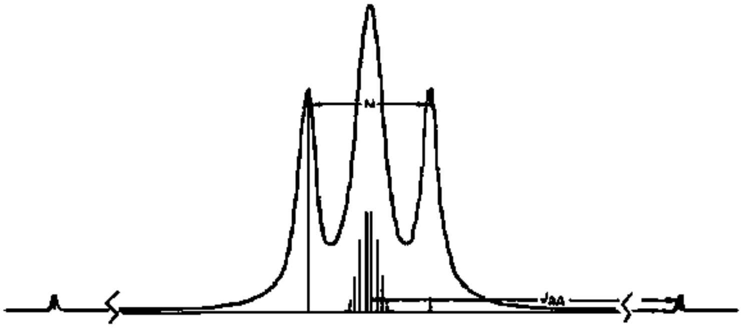


Fig. 23. Schematic diagram showing the apparent triplet for the X part of an $X_6AA'X_6'$ system arising from overlap of the inner lines when $JAA' \gg L$. The intensity of the first pair of outer lines has been exaggerated.

spectrum appears as an apparent triplet. The distribution of the frequencies and intensities of these inner lines determines the band shape of the portion of the spectrum between the *N* doublet. Only in rare cases can the fine structure due to the inner lines be resolved for organophosphorus ligand sytems, and so only the envelope of these resonances is generally observed.

Although it is in principle possible to calculate $^2JAA'$ (i.e. $^2JPP'$) from the ^{31}P spectra using equations developed for the AA′ portion of the spectrum[254], the complexity of the spectra and solubility considerations render this method impractical for most ligands.

Before discussing the *J*PP′ data, the methods we have employed to obtain the constants and their signs will be briefly described. In the event that the first pair of outer lines in the XX′ spectrum can be found, it is possible to determine the value of *J*AA′ directly ($^2JPP'$ in our application), since the separation between either of these lines and the most intense inner line is *J*AA′. Under these conditions, relatively precise values of *J*PP′ (0.3 to 3%) can be obtained[184]. In one case (Fig. 24) sufficient fine structure has been observed to allow calculation of *J*AA′ from inner line separations and the agreement with that calculated from the outer line positions was good[236]. Although direct observation of the outer pair is not rare among the PR_3, $P(OMe)_3$ and $P(NR_2)_3$ complexes we have studied[184], it is more prevalent in PH_3 and PF_3 metal compounds[184,216,255]. In the latter, ^1JPH and ^1JPF couplings are greater and larger separations of the lines are produced (eqn. (20)).

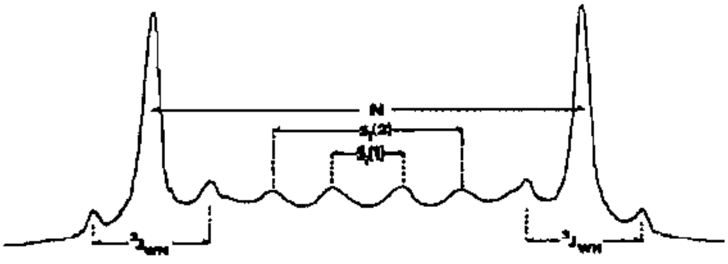


Fig. 24. ^1H NMR spectrum of *cis*-$W(CO)_4(PMe_3)_2$ showing the resolved fine structure. The low-intensity outer bands which were observed are not shown.

The first attempt to obtain $^2JPP'$ from ^1H NMR spectra which did not exhibit the outer pair of lines was an effort at computer simulation of experimental spectra consisting only of the deceptively simple triplet whose middle member had a fair range in width[170,171]. Not only was JXX' assumed to be zero but contributions from JAX' were also considered negligible. Both assumptions have been shown to be valid for the complexes of $P(OCH_2)_3CMe$ studied[184,236]. Using ^3JPH, a line-width parameter estimated from the doublet peaks and estimates of $^2JPP'$ as input data in a computer program, a best fit could be obtained visually. Independent measurements of $^2JPP'$ in complexes show, however, that results based on line-shape analysis alone are to be viewed with suspicion[184]. The assumption made in computer fitting that the line shapes are pure Lorentzian is probably invalid in most cases because: (*a*) slow passage conditions are not obtained; (*b*) paramagnetic impurities could be present which broaden the lines; (*c*) intermolecular exchange could be taking place[256]; (*d*) each transition in theory can have its own transverse relaxation time[257]; (*e*) off-diagonal elements of the relaxation matrix can cause overlapping lines to give band shapes which are not simply sums of Lorentzian lines[257a], and (*f*) some form of intramolecular motion may result in incomplete averaging of $^2JPP'$[184,258]. Although factors (*a*)–(*c*) can be ruled out with some assurance in the complexes studied[184], (*d*) and (*e*) cannot, and indeed temperature studies indicate[184] that (*f*) may apply in several complexes of $P(NMe_2)_3$.

When feasible, the method of choice for obtaining $^2JPP'$ is that of spin-tickling in which the ^{13}C satellite resonances of the proton spectrum are observed while irradiating in the ^{31}P region. In such an experiment[259] the ^{31}P resonance for the molecules containing one ^{13}C nucleus appears as two AB patterns because of the two spin states of ^{13}C. Because of the presence of the ^{13}C nucleus in one of the phosphorus-containing moieties, the two phosphorus nuclei are no longer chemically equivalent and so the AB coupling ($^2JPP'$ in this case) may be determined from the AB spectrum. If for either of the spin states of ^{13}C, the higher frequency weak intensity band is shown to be connected to the higher frequency line of the appropriate ^{13}C satellite, then $^2JPP'$ has the same sign as N; otherwise their signs are opposite. Thus if the sign of JPH is known and JPH' is small, the sign of $^2JPP'$ is determined[236]. By an additional spin-tickling experiment[236] the sign of N can be related to that of ^1JCH, which is known to be positive.

$^2JPP'$ values in mixed ligand complexes are obtained directly from the AB or nearly AX ^{31}P spectra[186]. For each proton-bearing ligand, the proton region displays a doublet which is simple or perturbed, depending upon the size of $^2JPP'$ and the chemical shift difference of the phosphorus nuclei. If $^2JAB \ll (\nu_A - \nu_B)$, then no perturbation is observed, as is the case for *trans*-$Mo(CO)_4[P(OCH_2)_3CEt][P(OMe)_3]$. If $^2JAB \cong (\nu_A - \nu_B)$, then a perturbation occurs; and if $^2JAB \gg (\nu_A - \nu_B)$, apparent triplets would be produced in the proton spectrum. The observation that the proton doublets are not split by the phosphorus on the other ligand is good evidence that ^5JPH is zero in these compounds. Thus the assumption that ^5JPH is negligible in analogous systems wherein both ligands are the same is validated.

The relatively large number of $^2JPP'$ values collected in Tables 23–25 along with the

TABLE 23

^2JPP' values in *cis*-disubstituted complexes

	^2JPP' (Hz)	Method [a]	Ref.
$Cr(CO)_4(PH_3)_2$	−26.2	A	255, [b]
$[P(SCH_2)_3CMe]_2$	~ 0	F	242
$(PMe_3)_2$	−36 ± 1	A	236
$(PH_3)(PPh_3)_2$	33.0	E	255
$(PBu_3)(PH_3)$	38.5	B	[c]
$[P(OCH_2)_3CMe]_2$	70 ± 10	D	170, 171, 184
$[P(NMe_2)F_2]_2$	62 ± 2	B	[d]
$[P(CCl_2H)F_2]_2$	67 ± 0.5	B	[m]
$[P(CCl_3)F_2]_2$	67 ± 1	B	[d]
$(PF_3)_2$	78 ± 1, 77.0	B, B	262, [e]
$[EtN(PF_2)_2]$	78.5 ± 0.5	B	260
$Mo(CO)_4(PH_3)_2$	18.3, −18.9	A, C	[c, m]
$(PMe_3)_2$	−29.7 ± 0.1	A	236
$(PBu_2Ph)(PPh_3)$	21	E	[f]
$(PPh_2H)_2$	~19	A	[g]
$(PNMe_2)_2$	12.4 ± 0.2	A	236
$[P(NMePh)_3]_2$	18.2 ± 0.2	A	[h]
$[P(SCH_2)_3CMe]_2$	30 ± 10	D	242
$[P(SMe)_3]_2$	35 ± 10	D	242
$[P(NMe_2)_3][P(OCH_2)_3CEt]$	39 ± 3	E	186
$[P(OMe)_3]_2$	−40.5 ± 1	A	236
$[P(OMe)_3][P(OCH_2)_3CEt$	48 ± 3	E	186
$[P(OCH_2)_3C\text{-}n\text{-}Pr]_2$	50 ± 10	D	170, 171, 184
$[P(NMe_2)F_2]_2$	38 ± 2	B	261
$[P(NEt_2)F_2]_2$	38 ± 2	B	261
$[P(CF_3)_2F]_2$	41.0 ± 1	B	261
$[P(CH_2Cl)F_2]_2$	42.5 ± 0.5	B	261
$[P(CCl_2H)F_2]_2$	47.5 ± 0.5	B	[m]
$[P(CCl_3)F_2]_2$	−48.0 ± 0.5	B	261
$[P(CF_3)F_2]_2$	48.5 ± 1	B	261
$(PF_3)_2$	55.0 ± 0.2	B	262
$[EtN(PF_2)_2]$	+121.0	B	260
$W(CO)_4(PH_3)_2$	13.4	A	255
$[P(SCH_2)_3CMe]_2$	~ 0	F	242
$[P(SMe)_3]_2$	~ 0	F	242
$[PMe_3]_2$	−25.0 ± 0.1	A	184
$[P(OCH_2)_3C\text{-}n\text{-}Pr]_2$	35 ± 5	D	170, 171, 184
$[P(NMe_2)F_2]_2$	21.1 ± 1.0	B	[d]
$[P(CH_2Cl)F_2]_2$	34.6 ± 0.8	B	[d]

TABLE 23 (continued)

	$^{2}JPP'$ (Hz)	Method[a]	Ref.
$W(CO)_4[P(CCl_2H)F_2]_2$	37.0 ± 0.5	B	*m*
$[P(CCl_3)F_2]_2$	37.6 ± 0.8	B	*d*
$(PF_3)_2$	38 ± 1, 41	B, B	262, *d*
$[EtN(PF_2)_2]$	155.3 ± 0.6	B	260
$PdCl_2(PMe_3)_2$	8	A	*i*
$Br_2(PMe_3)_2$	1.0 ± 1	A	*j*
$Cl_2(PMe_2H)_2$	0 ± 1	A	263
$Br_2(PMe_2H)_2$	2	A	263
$Cl_2[P(OMe)_3]_2$	+79.9 ± 0.2	A	236
$Cl_2[P(OCH_2)_3C\text{-}n\text{-}Pent]_2$	65 ± 10	D	170, 171, 184
$PtCl_2(PMe_2H)_2$	0 ± 1	A	263
$Br_2(PMe_2H)_2$	0	A	263
$I_2(PMe_2H)_2$	0	A	263
$Cl_2[P(NMe_2)_3]_2$	~ 0	F	184
$Cl_2(PMe_3)_2$	< 5, 18.9	G, A	*i, j*
$Br_2(PMe_3)_2$	16.2	A	*j*
$I_2(PMe_3)_2$	14.0	A	*j*
$Cl_2[P(OMe)_3]_2$	10 ± 2, 18.3 ± 0.1	D, A	184, 258
$Br_2[P(OMe)_3]_2$	8.8 ± 0.1	A	258
$I_2[P(OMe)_3]_2$	~ 0, 5.0 ± 0.1	F, A	184, 258
$Cl_2[P(OCH_2)_3C\text{-}n\text{-}Pent]_2$	35 ± 10	D	184
$I_2[P(OCH_2)_3C\text{-}n\text{-}Pent]_2$	14 ± 5	D	184
$Cl_2[P(OPh)_3][PBu_3]$	20.0	E	266
$Cl_2[P(NR_2)_2F]_2$	25–37	A	*k*
$Me_2[P(OPh)_3][PBu_3]$	*l*	E	266
$MeCl[P(OPh)_3][PBu_3]$	23.3	E	266

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[a] Methods of obtaining values of $^{2}JPP'$ are: separation of inner and outer lines in the ^{1}H spectrum (A); separation of inner and outer lines in the ^{19}F spectrum (B); double resonance techniques (C); computer simulation of the band shape (D); direct observation of the ^{31}P spectrum (E); perturbation of main doublet was not observed, thus $^{2}JPP'$ must be undetectably small (F); estimated from line width (G), and solution of spectrum from theoretical considerations (H).

[b] J.F. Nixon, private communication.

[c] E. Moser, E.O. Fischer, W. Bathelt, W. Gretner, L. Knauss and E. Louis, *J. Organometal. Chem.*, 19 (1969) 377.

[d] Unpublished results cited in ref. 216.

[e] T.R. Johnson, R.M. Lynden-Bell and J.F. Nixon, *J. Organometal. Chem.*, 21 (1970) P15. [f] S.O. Grim, D.A. Wheatland and P.R. McAllister, *Inorg. Chem.*, 7 (1968) 161. [g] Calculated from spectrum in J.G. Smith and D.J. Thompson, *J. Chem. Soc. A*, (1967) 1694. [h] R.D. Bertrand, private communication.

[i] R. Goodfellow, *J. Chem. Soc. D*, (1968) 114. [j] D.A. Duddell, J.G. Evans, P.L. Goggin, R.J. Goodfellow, A.J. Rest and J.G. Smith, *J. Chem. Soc. A*, (1969) 2134. [k] J.F. Nixon and M.D. Sexton, *J. Chem. Soc. D*, (1969) 827. [l] Not resolved in ^{31}P spectrum. [m] R.M. Lynden-Bell, J.F. Nixon, J. Roberts and J.R. Swain, *Inorg. Nucl. Chem. Lett.*, 1 (1971) 1187.

TABLE 24
$^2JPP'$ values in *trans*-disubstituted complexes

	JPP' (Hz)	Method [a]	Ref.
$Cr(CO)_4[P(SCH_2)_3CMe]_2$	~0	F	242
$[P(SMe)_3]_2$	~0	F	242
$(PMe_3)_2$	-28.5 ± 1	A	236
$(PBu_3)(PPh_3)$	25	E	[b]
$(PBu_3)[P(OPh)_3]$	30	E	[b]
$[P(NMe_2)_3]_2$	-17 ± 5	C	236
$[P(OMe)_3]_2$	-15.0 ± 0.1	A	236
$[P(OCH_2)_3CEt]_2$	9 ± 3	D	170, 171, 184
$(PF_3)_2$	34 ± 1, 34.0 ± 0.5	B, B	262, [c]
$Mo(CO)_4(PBu_3)(PPh_3)$	50	E	[b]
$(PBu_2Ph)(PPh_3)$	49	E	[b]
$(PBu_3)[P(OPh)_3]$	112	E	[b]
$[P(NMe_2)_3]_2$	$+101 \pm 1$	A	236
$[P(NMe_2)_3][P(OCH_2)_3CEt]$	141 ± 3	E	186
$[P(OMe)_3]_2$	$+162 \pm 5$	C	236
$[P(OMe)_3][P(OCH_2)_3CEt]$	185 ± 3	E	186
$[P(OCH_2)_3C\text{-}n\text{-}Pr]_2$	210 ± 30	D	170, 171, 184
$(PF_3)_2$	312 ± 1	B	262
$W(CO)_4(PBu_3)(PPh_3)$	65	E	[b]
$(PBu_3)[P(OPh)_3]$	120	E	[b]
$(PBu_2Ph)[P(OPh)_3]$	112	E	[b]
$[P(NMe_2)_3]_2$	$+81 \pm 5$	C	236
$[P(OCH_2)_3C\text{-}n\text{-}Pr]_2$	140 ± 25	D	170, 171, 184
$(PF_3)_2$	315 ± 1	B	262
$Fe(CO)_3[P(NMe_2)_3]_2$	$+65 \pm 10$	C	236
$[P(NMe_2)_3]_2[P(OCH_2)_3C\text{-}n\text{-}Pr]$	183 ± 1	E	186
$[P(OCH_2)_3CEt]_2$	300 ± 40	D	170, 171, 184
$PdCl_2(PMe_2H)_2$	515	A	263
$Br_2(PMe_2H)_2$	516	A	263
$PdI_2(PMe_3)_2$	$+572 \pm 5$	C	236
$I_2(PMe_3)(PEt_3)$	565	E	[d]
$I_2(PBu_3)(PMe_2Ph)$	551	E	[e]
$I_2(PBu_3)[P(OPh)_3]$	758	E	[e]
$I_2(PMe_2Ph)[P(OPh)_3]$	829	E	[e]
$Cl_2[PPh_2(CF_3)]_2$	1100 ± 50	D	257, [b]
$PtCl_2(PMe_2H)_2$	515	A	263
$Br_2(PMe_2H)_2$	462	A	263
$I_2(PMe_2H)_2$	447	A	263
$Cl_2(PEt_3)_2$	90	G	[f]
$[P(OPh)_3][PBu_3]$	709	E	266

TABLE 24 (continued)

	JPP′ (Hz)	Method [a]	Ref.
$Pt[OP(OR)_2]_2(PR_3)_2$	37.2–38.1 [g]	E	266
$PtCl[OP(OR)_2](PR_3)_2$	18.0–28.9 [g]	E	266

[a] See footnote *a* of Table 23. [b] See footnote *f* of Table 23. [c] See footnote *e* of Table 23. [d] A. Pidcock, *Chem. Commun.*, (1968) 92. [e] See footnote *i* of Table 23. [f] W. McFarlane, *J. Chem. Soc. A*, (1967) 1922. This value is considered to be too low [216,263]. [g] This is *cis* coupling.

limited number of known signs for this coupling make it possible to note some trends and to draw some conclusions concerning their origins[184,186,216,236,260–266]. The magnitude of ^2JPP′ will be shown to depend on four factors which are discussed sequentially: (*a*) the stereochemistry of the complex; (*b*) the metal atom; (*c*) the ligands present other than phosphorus, and (*d*) the nature of the phosphorus ligand.

The repeated observation in a variety of systems that ^{31}P—^{31}P coupling constants of *trans*-oriented ^{31}P nuclei are large and are characterized by apparent triplets in the ^1H spectrum while *cis* coupling constants are small, leaving the JAX doublet unperturbed, has served as a criterion for determining the geometrical relationships of phosphorus ligands in many complexes[3,252,267]. However, considerable caution should be taken in using this criterion in assigning such stereochemistries. Many *cis* complexes have appreciable phosphorus—phosphorus coupling and from preliminary data[242] it appears that the magnitudes of ^2JPP′ in *cis* and *trans* manganese complexes of the type $Mn(CO)_3L_2X$ (X = H, Cl, Br, I) are not very different (Table 25). Indeed, in chromium complexes the magnitude of ^2JPP′ is even greater in *cis* compounds than in *trans* (Tables 23 and 24). It should be pointed out that weak ^{31}P—^{31}P coupling can lead to apparent triplets when JAX is small. Thus the conclusion that there is "strong" ^{31}P—^{31}P coupling in *fac*-$Mn(CO)_3[P(OCH_2)_3CMe](MeCO)$ (ref. 268), π-$C_5H_5Rh[P(OCH_2)_3CMe]_2$ (ref. 269) and in π-$C_5H_5Rh[P(OMe)_3]_2$ (ref. 269), because the proton resonance appears as a triplet, is not necessarily correct. Support for such caution in interpretation is found in the very low coupling calculated for *fac*-$Mn(CO)_3$-$(PhCO)[P(OCH_2)_3CMe]_2$ and the intermediate coupling found in π-$C_5H_5Mn(CO)[P(OCH_2)_3$-$CMe]_2$, both of which also display proton "triplets" (Table 25). Qualitative evidence for unusually small ^{31}P—^{31}P coupling between *trans* phosphorus ligands in manganese complexes is found in *sym-mer*-$MnX(CO)_3(PMe_2Ph)_2$ systems[270a,b] (where X = Cl or Br) and the rhenium analogs. The ^1H resonances of the methyl groups appear as a "triplet" in the latter while the central portion of the "triplet" is much broader in the former despite very similar separations of the main doublet in all cases. It is reasonable that ^2JPP′ for π-$C_5H_5Mn(CO)[P(OCH_2)_3CEt]_2$ is quite comparable with the values obtained for most of the *facial* manganese systems in view of the *cis* relationship of the phosphorus nuclei (Table 25).

TABLE 25

^2JPP′ values for miscellaneous complexes

	^2JPP′ (Hz)	Method[a]	Ref.
mer-$\mathrm{Mo(CO)_3(PEt_3)_3}$	≤ 15[p]	E	b
$\mathrm{[P(OMe)_3]_3}$	47[p]	E	b
$\mathrm{[P(OEt)_3]_3}$	51[p]	E	b
fac-$\mathrm{Mo(CO)_3(PPhF_2)_3}$	−43.0 ± 1.0	H	264
$\mathrm{P(OPh)_2F}$	−51.0 ± 1.6	H	264
$\mathrm{P(OPh)F_2}$	−55.2 ± 1.0	H	264
$\mathrm{(PF_3)_3}$	−56.0 ± 0.5	H	264
fac-$\mathrm{Mn(PhCO)(CO)_3[P(OCH_2)_3CEt]_2}$	5 ± 2	D	c
$\mathrm{H(CO)_3(PF_3)_3}$	125 ± 1	B	242
$\mathrm{Br(CO)_3[P(OMe)_3]_2}$	140 ± 20	D	242
$\mathrm{Br(CO)_3[P(OCH_2)_3C}$-*n*-$\mathrm{Pr]}$	110 ± 20	D	242
sym-mer-$\mathrm{MnI(CO)_3[P(OMe)_3]_2}$	170 ± 30[p]	D	242
$\mathrm{H(CO)_3(PF_3)_2}$	155 ± 1[p]	B	242
π-$\mathrm{C_5H_5Mn(CO)[P(OCH_2)_3CMe]_2}$	120 ± 20	D	242
$\mathrm{Fe(CO)_3(PF_3)_2}$	98 ± 1	B	d
$\mathrm{RuCl_2(CO)_2(PMe_2H)_2}$[e]	308 ± 1	A	263
$\mathrm{RuCl_2(CO)_2(PMe_2H)_2}$[f]	229 ± 1	A	263
trans-$\mathrm{RhCl(CO)(PMe_2H)_2}$	321 ± 1	A	263
$\mathrm{Br(CO)(PMe_2H)_2}$	329 ± 1	A	263
$\mathrm{I(CO)(PMe_2H)_2}$	337 ± 1	A	263
$\mathrm{RhCl_3(CO)(PMe_2H)_2}$[g]	495 ± 1	A	263
mer-$\mathrm{RhCl_3(PPr_3)_3}$	22 ± 3	E	h
$\mathrm{(PBu_3)_3}$	21 ± 3	E	h
$\mathrm{[PEt_2Ph]_3}$	30 ± 8	E	h
sym-mer-$\mathrm{RhCl_3(PBu_3)_2[P(OPh)_3]}$	30.3[p]	E	i
trans-$\mathrm{IrCl_3(CO)(PMe_2H)_2}$[f]	386 ± 1	A	263
$\mathrm{Br_3(CO)(PMe_2H)_2}$[f]	390 ± 1	A	263
trans-$\mathrm{NiI_2(PMe_2H)_2}$	355	A	263
$\mathrm{Ni(CO)_2[P(NMe_2)_3]_2}$	~0	F	184
$\mathrm{Ni(CO)_2[P(OMe)_3]_2}$	10 ± 3	A	j
$\mathrm{Ni(CO)_2[P(OCH_2)_3CMe]_2}$	~0	F	184
$\mathrm{Ni(CO)_2[P(CF_3)_3]_2}$	~0	F	k
$\mathrm{Ni(CO)_2[P(NMe_2)F_2]_2}$	~0	F	l
$\mathrm{Ni(CO)_2[P(NEt_2)F_2]_2}$	~0	F	l
$\mathrm{Ni(CO)_2(PF_3)_2}$	38 ± 1	B	262
$\mathrm{Ni[P(CF_3)_2F]_4}$	<5	B	265
$\mathrm{Ni(C_6H_4O_2PF)_4}$	17.7 ± 0.2	B	265
$\mathrm{Ni[P(CH_2Cl)F_2]_4}$	12 ± 5	B	265
$\mathrm{Ni[P(CCl_3)F_2]_4}$	21 ± 1	B	265

TABLE 25 (continued)

	JPP' (Hz)	Method [a]	Ref.
$Ni[P(NMe_2)F_2]_4$	≪10	B	265
$Ni[P(CF_3)F_2]_4$	≪5	B	265
$Ni(PF_3)_4$	3 ± 1	B	265
$PdCl[OP(OPh)_2][HOP(OPh)_2]Pr_3$	600–630 [m]	E	266
$PtCl[OP(OPh)_2][HOP(OPh)_2Pr_3$	539–547 [m]	E	266
	33.0–35.8 [n]		
	23.4–23.9 [o]		
$[PtCl[P(OPh)_3](PBu_3)]Cl$	24.0	E	266

[a] See footnote *a* of Table 23. [b] M. Lenzi and R. Poilblanc, *C. R. Acad. Sci., Ser. C*, 263 (1966) 674. [c] B.L. Booth, M. Green, R.N. Haszeldine and N.P. Woffenden, *J. Chem. Soc. A*, (1969) 920. [d] This value apparently represents a time-average-value coupling from intramolecular exchange[262]. [e] All pairs of identical ligands are mutually *cis*[263]. [f] All pairs of identical ligands are mutually *trans*[263]. [g] The phosphorus ligands are *trans* as well as two of the halides[263]. [h] S.O. Grim and R.A. Ference, *Inorg. Nucl. Chem. Lett.*, 2 (1966) 205. [i] See footnote *d* of Table 24. [j] Calculated from the spectrum given in R. Mathieu and R. Poilblanc, *C. R. Acad. Sci., Ser. C*, 265 (1967) 388. [k] See footnote *i* of Table 23. [l] See footnote *d* of Table 23. [m] Coupling between PR_3 and $HOP(OR)_2$. [n] Coupling between $HOP(OR)_2$ and $OP(OR)_2$. [o] Coupling between PR_3 and $OP(OR)_2$. [p] *Cis* coupling.

With the exception of some chromium and manganese compounds, ^{31}P–^{31}P coupling constants are generally larger in *trans* compounds than in their *cis* isomers. This appears to be true especially with palladium and platinum systems.

The nature of the metal atom plays a definite role in determining the magnitude of $^2JPP'$. The most extensively studied series with the same stereochemistry consists of Group VI complexes. The data show that the ordering of size for *cis* coupling is Cr > Mo > W. For *trans* coupling there appears to be no order other than that the $^2JPP'$ values in Mo and W complexes are much larger than in their Cr analog. From the few results for other groups, it is difficult to infer meaningful trends.

From the limited data available, the other ligands in a given complex appear to affect the value of $^2JPP'$ relatively slightly. Results for compounds in which only the halides are varied suggest that $^2JPP'$ increases in magnitude from I to Cl.

The most significant factor affecting ^{31}P–^{31}P coupling appears to be the electronegativity of the substituents on phosphorus. Figures 25 and 26 are plots of the $^2JPP'$ values found in Tables 23 and 24 vs. a crude estimate of the overall Pauling electronegativity of the substituent groups on the phosphorus ligands (see Sect. C(iii)7). Where ligands contained two different substituents (e.g. $PNMe_2F_2$ or $P(CF_3)F_2$), the overall electronegativity was estimated by taking a weighted mean of the electronegativities of the three atoms bound to phosphorus. For mixed ligand complexes (e.g. *trans*-$Mo(CO)_4[P(OCH_3)_2CC_2H_5]$-$[P(NMe_2)_3]$), the average of the electronegativities of the two ligands was used[271]. Although

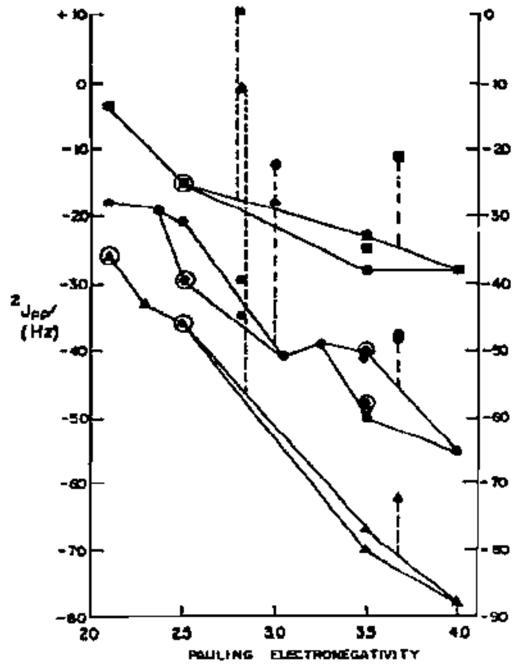


Fig. 25. A plot showing the progression of $^2JPP'$ for *cis*-$M(CO)_4L_2$ (where M = Cr (▲), Mo (●) or W (■)) as a function of the electronegativity of the ligand. The left ordinate applies to the Cr and Mo complexes and the right to W systems.

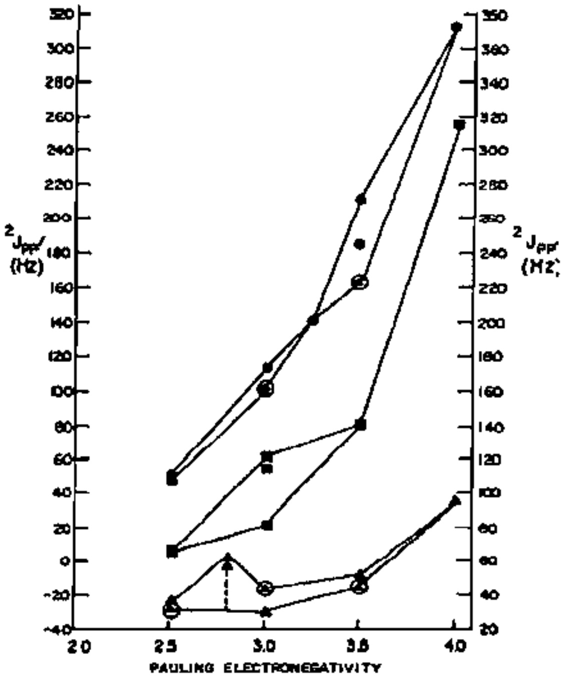


Fig. 26. A plot showing the progression of $^2JPP'$ for *trans*-$Mo(CO)_4L_2$ (where M = Cr (▲), Mo (●) or W (■)) as a function of the electronegativity of the ligand. The left ordinate applies to the Cr and Mo complexes and the right to the W systems.

these estimates are admittedly quite crude, three rather interesting features become apparent in Figs. 25 and 26. Firstly, when the known signs are taken into account (circled points), it is clear that the overall progression of $^2JPP'$ with electronegativity in the *trans* chromium complexes parallels that of the molybdenum and tungsten systems. Secondly, $^2JPP'$ appears to increase positively with electronegativity in the *trans* complexes while in the *cis* systems it is seen to increase negatively. Thirdly, the points connected to the *cis* curves by dotted lines appear to lie anomalously far off the main progression in most instances. These points represent ligands containing NR_2 and SR groups and it is not clear at this time why some complexes containing these moieties depart so noticeably from the trends set by the variety of other ligands.

Barring the possibility of unexpected sign reversals in complexes on which we were unable to perform double resonance experiments, the implied assignments of the unknown signs seem reasonable by analogy or by inference from the data on mixed complexes (Tables 23 and 24). Thus it is expected that the values of $^2JPP'$ in the mixed ligand complexes should be intermediate in value between those for the two analogous complexes in which both ligands are the same. If a sign change between complexes of $P(OCH_2)_3CR$ and

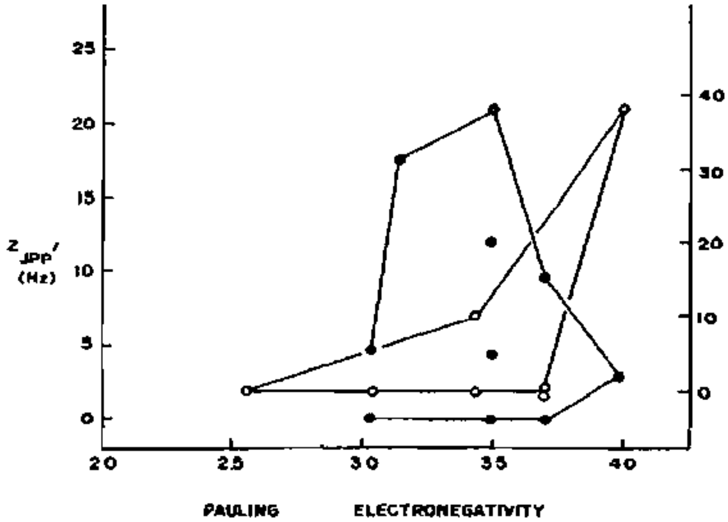


Fig. 27. A plot showing the progression of $^2JPP'$ with ligand electronegativity for $Ni(CO)_2L_2$ (○) and NiL_4 (●) complexes. The left and right ordinates apply to the NiL_4 and $Ni(CO)_2L_2$ systems, respectively.

$P(NMe_2)_3$ or $P(OMe)_3$ were occurring, the magnitudes of $^2JPP'$ in the mixed ligand complexes should be less than those in complexes in which both ligands are the same. Since the values of the mixed complexes lie between those of the latter, our assignment is probably correct.

The trends in the *cis* $^{31}P—^{31}P$ coupling in the *mer* and *fac* molybdenum complexes (Table 25) are also in line with electronegativity arguments, and not unexpectedly the magnitudes of $^2JPP'$ are in the same range as that for *cis* disubstituted molybdenum analogs. The negative sign of $^2JPP'$ in the *fac* complexes is also in accord with that found for the *cis* disubstituted systems and it is likely that the *cis* $^{31}P—^{31}P$ interaction in the *mer* compounds is also negative.

The picture is much less clear for the nickel group. The trend in $^2JPP'$ with electronegativity (Fig. 27) for the $Ni(CO)_2L_2$ systems seems to parallel to some extent that for *trans* or *cis* Group VI complexes although the sign of $^2JPP'$ here is not known. The tendency for $Ni(CO)_2L_2$ complexes to exhibit near-zero $^2JPP'$ values over a range of electronegativities is preserved in the NiL_4 complexes (Fig. 27) although no overall trend is apparent at this time. While $^2JPP'$ for *cis*-PdX_2L_2 systems seems to rise sharply to more positive values with electronegativity, the presence of a maximum is suggested in the *cis*-PtX_2L_2 series for which a greater number of ligands with intermediate electronegativities has been studied. Except for the anomalous-looking 1100 Hz value of $^2JPP'$ for one of the *trans*-PdX_2L_2 complexes, $^{31}P—^{31}P$ coupling is larger for the more highly electronegative ligand (Fig. 28).

Assuming that the Fermi contact effect dominates $^{31}P—^{31}P$ coupling, there are two factors from which the correlation of $^2JPP'$ with increasing electronegativity may arise: (*a*) an increase in the magnitude of the phosphorus valence 3*s* orbital, and/or (*b*) a decrease

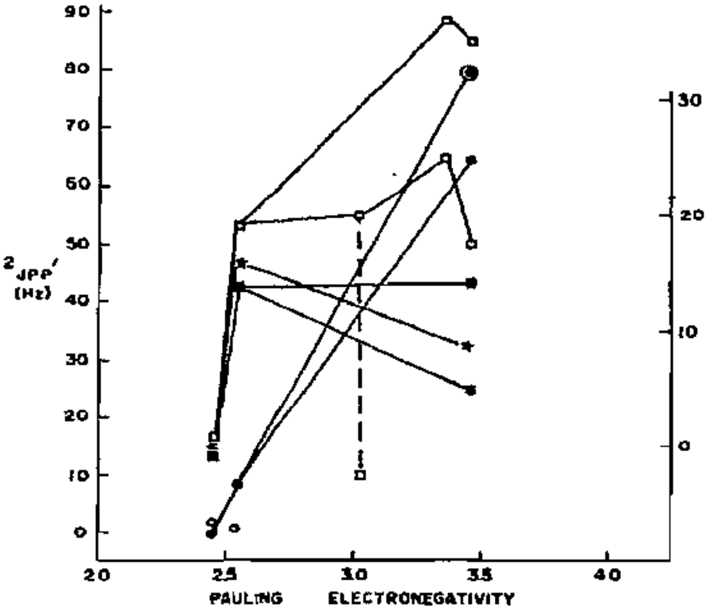


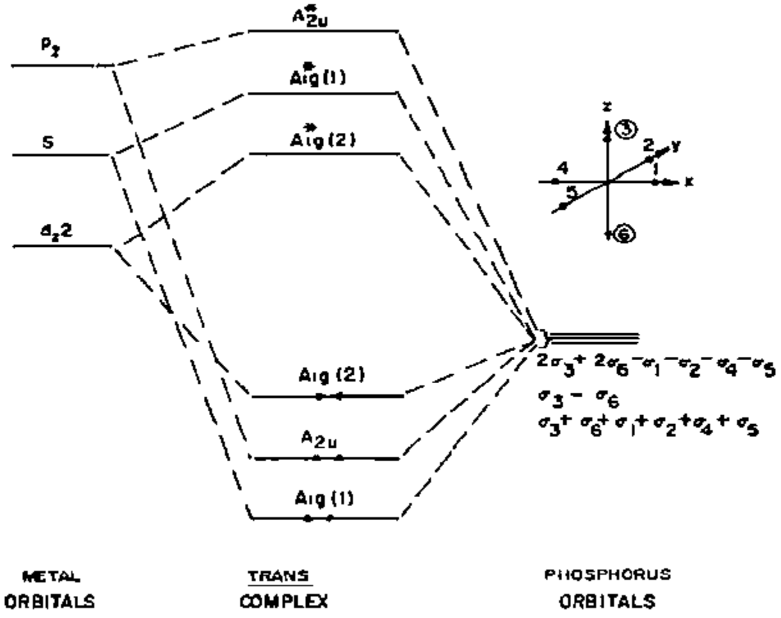
Fig. 28. A plot showing the progression of $^2JPP'$ in *cis*-$PdCl_2L_2$ (●), $PdBr_2L_2$ (○), $PtCl_2L_2$ (○), $PtBr_2L_2$ (∗) and PtI_2L_2 (■) complexes with ligand electronegativity. The left and right scales apply to the Pd and Pt complexes, respectively. The circled point is a complex for which the sign of $^2JPP'$ is known.

in the mutual polarizability of the lone pair on the phosphorus atoms. The first factor contributes[239a] to the magnitude of $^2JPP'$ (but not its sign) via the $(S_P|\delta(r_P)|S_P)$ terms in expression (21) since they represent the square of the *s* electron density at a phosphorus nucleus.

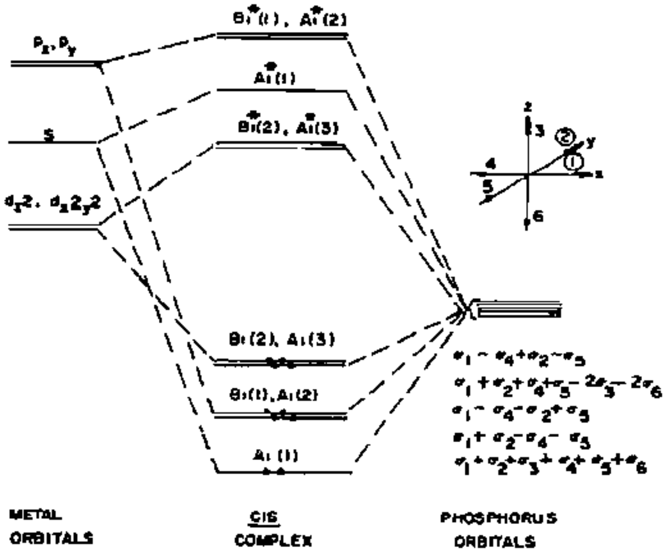
$$^2JPP' \propto -(S_P|\delta(r_P)|S_P)(S_{P'}|\delta(r_{P'})|S_{P'}) \sum_{k}^{\text{occ}} \sum_{l}^{\text{unocc}} (E_k-E_l)^{-1}\, C_{kP}C_{lP}C_{kP'}C_{lP'} \qquad (21)$$

The second factor arises[239a] from the change in the triplet excitation energy term in the summation or from variations in the LCAO coefficients (*C*) in expression (21). In valence bond terms, the polarizability of the phosphorus lone pair is related to the degree of *s* character present. The sign of $^2JPP'$ depends solely on the symmetries of the molecular orbitals involved in the dominant electronic excitation. An excitation from one orbital to another of the same symmetry (i.e. *sym→sym* or *antisym→antisym*) contributes a negative sign to $^2JPP'$ while a transition involving orbitals of opposite symmetry confers a positive sign on $^2JPP'$.

Without detailed Mo calculations on the prohibitively complicated coordination complexes studied here, prediction of the sign and magnitude of $^2JPP'$ is not possible. It is

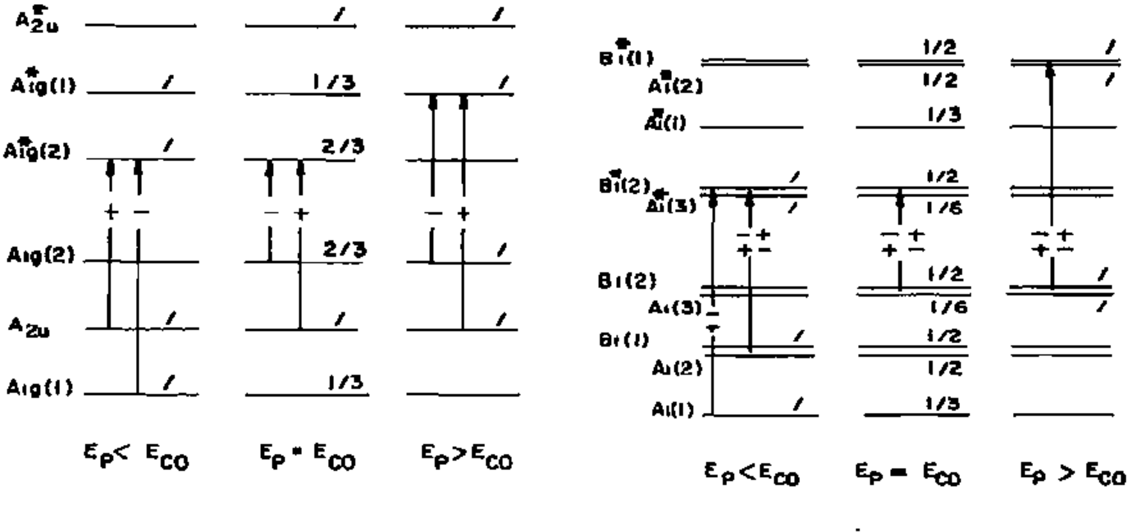


a) D_{4h} SYMMETRY



b) C_{2v} SYMMETRY

Fig. 29. Molecular orbital energy level diagrams of $M(CO)_4(PR_3)_2$ complexes in the *trans* (a) and *cis* (b) configurations. Circled points on the Cartesian axes represent the phosphorus atom locations.



a) TRANS COMPLEX

b) CIS COMPLEX

Fig. 30. Molecular orbital level arrangements and fractional phosphorus character in the appropriate orbitals for $M(CO)_4(PR_3)_2$ complexes in the *trans* (a) and *cis* (b) configurations. The signs refer to the contributions of the transitions to the overall sign of ^2JPP′.

worthwhile, however, to consider the possible origins of the signs and the trends of ^2JPP′ in the *trans* and *cis* Group VI complexes for which the greatest range of values has been obtained[272]. In Fig. 29a is depicted an MO diagram for a *trans* complex in which only the phosphorus orbitals having σ character are considered and in which the ordering of the MO levels is the same as that which is commonly accepted for complexes of O_h symmetry[193]. Because it is not known with certainty how the phosphorus "sp^3" lone-pair hybrid compares in energy with the "*sp*" lone-pair hybrid of the CO group, the three possibilities shown in Fig. 30(a) must be taken into account. Nothing quantitative is implied about the energies involved but it is assumed that the relative ordering of the levels is preserved. As the energy of the phosphorus σ orbital (E_P) changes with respect to that of the CO σ hybrid (E_{CO}), the phosphorus character (orbital coefficient) is altered in the manner shown in Fig. 30. Experiment shows that the sign of ^2JPP′ in the *trans* complex is generally positive, which would be consistent with the case where $E_P < E_{CO}$ since the transition of lowest energy ($A_{2u} \rightarrow A_{1g}^*(2)$) contributes positively to the coupling. Alternately, the case where $E_P = E_{CO}$ might equally apply if the higher energy transition ($A_{2u} \rightarrow A_{1g}^*(2)$) dominates by virtue of the greater phosphorus character in the A_{2u} level. The observation that some *trans* chromium complexes possess negative ^2JPP′ values suggests that E_P approaches or exceeds E_{CO} so that the $A_{1g}(2) \rightarrow A_{1g}^*(2)$ or $A_{1g}^*(1)$ transitions, respectively, can become dominant. As the electronegativity of the phosphorus ligand increases, the sign of ^2JPP′ in the chromium complexes changes from negative to positive. This would be expected on the ground that E_P should drop relative to E_{CO} under these conditions, allowing a transition with a positive contribution to become dominant.

The *cis* complexes (Figs. 29(b) and 30(b)) constitute a more complicated situation in that the presence of more orbitals affords an increased number of possible transitions. Of the four possible transitions among the $A_1(3)$, $B_1(2)$, $A_1{}^*(3)$ and $B_1{}^*(2)$ levels in the case where $E_P = E_{CO}$, however, the $B_1(2) \rightarrow B_1{}^*(2)$ excitation is expected to dominate both of the positively contributing transitions because of the smaller orbital coefficients associated with the latter. The experimental range of ${}^2JPP'$ values for this configuration is −12.4 to −78 Hz. The present upper limit is not far from zero and it might be possible to approach zero coupling even more closely with more electropositive phosphorus ligands, i.e. when $E_P > E_{CO}$. From the diagram in Fig. 30(b), an upper limit of zero would be predicted owing to cancellation ($E_P > E_{CO}$) and there would be no likelihood of encountering sign changes in *cis* complexes with electropositive phosphorus ligands. Although a return to zero coupling would also be predicted if E_P becomes appreciably less than E_{CO}, this may be precluded from occurring if in all of these complexes E_P remains approximately equal to or larger than E_{CO}. In both the *cis* and the *trans* complexes a numerical rise in ${}^2JPP'$ is seen as the electronegativity of the phosphorus ligand increases. This is consistent with the expected increase in the phosphorus *s* orbital coefficients and the valence *s* orbital density value at the nucleus.

Unfortunately the above considerations do not particularly clarify the reason for the general rule that ${}^2JPP'$ values for *trans*-oriented phosphorus ligands exceed those for their *cis* analogs. The nature of the exceptions to this rule exemplified by first row transition elements, such as chromium and probably manganese, is presently equally obscure.

Changes in ${}^2JPP'$ among *trans* square-planar Ru^I, Rh^I, Ir^I, Ni^{II}, Pd^{II} and Pt^{II} complexes (Table 25) have recently been rationalized assuming that variations in the singlet-to-triplet excitation energy term in expression (21) is mainly responsible[263]. It is felt[263] that the dominant transition is $B_{2u} \rightarrow A_g{}^*(2)$ (Fig. 31) which would give ${}^2JPP'$ a positive sign. Moreover, since the B_{2u} MO contains metal *d* character while the $A_g{}^*(2)$ MO is made from a metal *p* orbital, ${}^2JPP'$ might be expected to correlate inversely with the known variation in the energy of *nd* and $(n + 1)p$ atomic orbitals among the metals. This is indeed the case as the order of ${}^2JPP'$ in the *trans* square-planar compounds is $Ni^{II} < Pt^{II} < Pd^{II}$; $Ir^I < Rh^I$; and $Rh^I < Pd^{II}$ (Table 25)[263]. In extending this idea to the octahedral Ru^{II}, Rh^{III} and Ir^{III} complexes in which the phosphorus nuclei are *trans*, a similar transition is postulated and the observed order $Ir^{III} < Rh^{III}$ is as expected[263].

A rationale for the absence of a steady trend in ${}^2JPP'$ with electronegativity in NiL_4 complexes has been put forth[265]. This utilizes the MO diagram shown in Fig. 32 and the summation term in expression (21) which represents the extent to which a perturbation of the *s* orbital on one phosphorus is transmitted to the *s* orbital of the other. From Fig. 32 the expected transitions involving phosphorus nuclei are $T_2{}' \rightarrow T_2{}^*$ and/or $T_2{}' \rightarrow A_1{}^*$, depending on how close in energy the lower and upper states are. Because the molecular orbitals are not identifiable as *gerade* or *ungerade* in T_d symmetry, it is necessary to examine

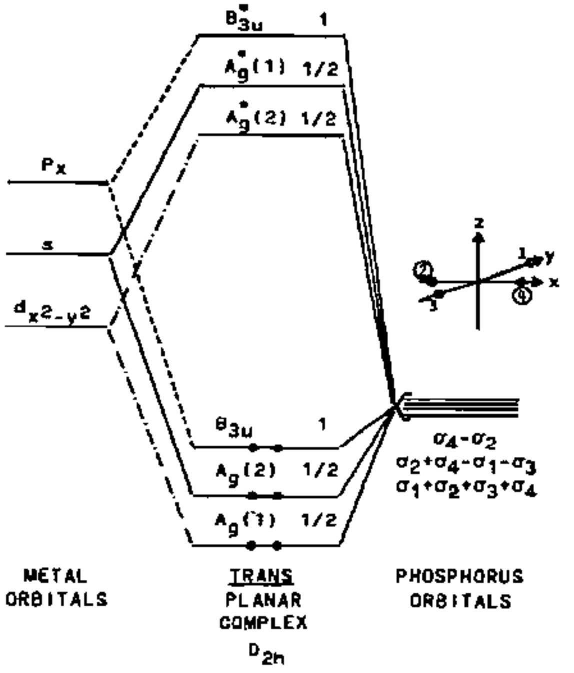


Fig. 31. Molecular orbital energy level diagram for *trans*-MX$_2$(PR$_3$)$_2$ complexes assuming that $E_P = E_X$.

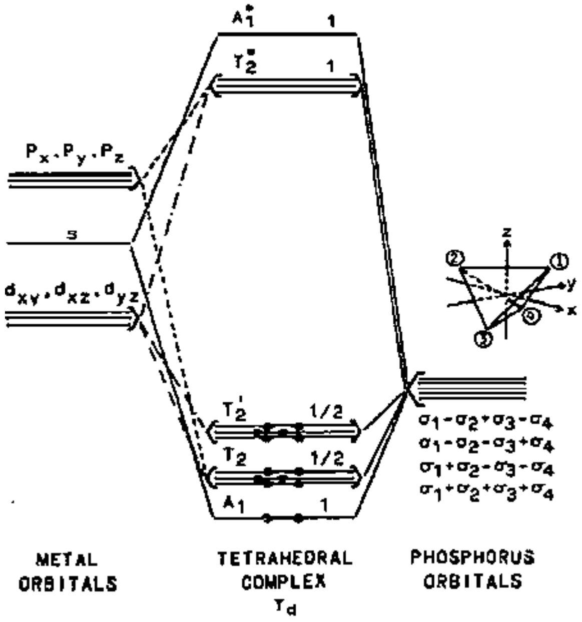


Fig. 32. Molecular orbital energy level diagram for Ni(PR$_3$)$_4$ complexes.

more closely the source of the sign of ^2JPP′. In the numerator of the summation term in expression (21) the coefficients of the ground state and excited molecular orbitals are multiplied and summed over all pairs of phosphorus atoms. The relevant ligand-orbital linear combinations for all the molecular orbitals are shown in Fig. 32. If we multiply the coefficients (as indicated in expression (21)) from any pair of identical combinations transforming as T_2, a positive sign is obtained and the expression for ^2JPP′ becomes more negative. The same procedure for any of the T_2' linear combinations and that of the $A_1{}^*$ contributes a positive sign to ^2JPP′. The overall result would be the same even if the lowest occupied MO were the A_1. Although calculations do not consistently agree on the relative order of these orbitals[273], they are probably close, which suggests that ^2JPP′ generally will not be large. A similar situation appears to be the case for the $Ni(CO)_2L_2$ complexes in which the $A_1{}'$, B_1 and $B_1{}^*$, $A_1{}'^*$ pairs may be rather close in energy (Fig. 33). Because $B_1 \rightarrow B_1{}^*$ or $A_1 \rightarrow A_1{}^*$ transitions would lead to signs which are opposite to those for $B_1 \rightarrow A_1{}^*$ or $A_1 \rightarrow B_1{}^*$ excitations, small values of ^2JPP′ could arise, as is seen in Table 25 for all but $Ni(CO)_2(PF_3)_2$, which possesses an exceptionally high coupling.

While ^2JPP′ values do seem on the whole to be interpretable in a rather general way in terms of the parameters given in expression (21), the influence of metal–phosphorus pi bonding is not in evidence. It is possible that the the presence of pi electron density has an effect[274,275] on ^2JPP′ but the data are too coarse to permit speculations on its magnitude. The question of a synergistic increase in sigma donation from phosphorus due to pi back-bonding from the metal is presently a moot one. While this effect is expected to in-

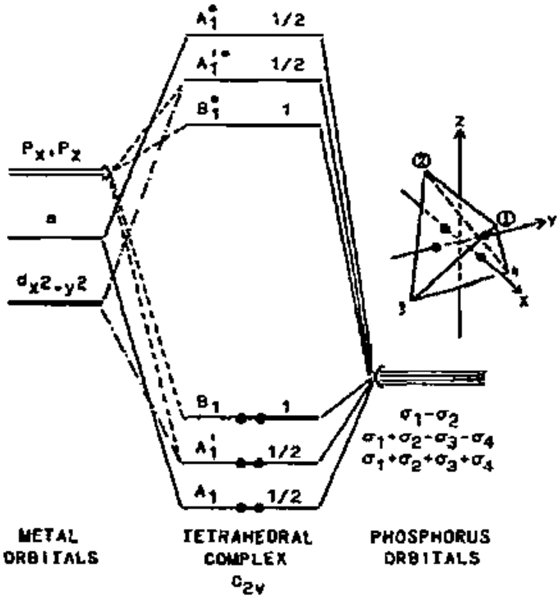


Fig. 33. Molecular orbital energy level diagram for $Ni(CO)_2(PR_3)_2$ complexes assuming that $E_P = E_{CO}$.

crease the MO coefficients in expression (21), the *s* orbital density at phosphorus and the excitation energies would decrease in a complicated fashion. In addition to pi contributions, orbital and spin dipolar effects are generally held to be negligible compared with the Fermi contact term. It should be pointed out, however, that when a more refined form of MO theory was employed, the orbital contribution in $^{19}F-C-^{19}F$ coupling dominated the contact term and was of opposite sign[276]. If $^{31}P-M-^{31}P$ coupling is susceptible to appreciable orbital contributions, present indications are that it acts in the same direction as the contact term.

9. Structural studies

In Table 26 are collected structural data obtained from X-ray and electron diffraction experiments[59,60,277–293] on complexes which contain electronegative phosphorus ligands[294]. Of particular relevance to the foregoing discussions are the caged ligand coordination compounds of Fe^0, Ni^{II} and Ag^I; the $P(OEt)_2Ph$ complex of $Ni(CN)_2$; and the chromium complex of $P(OPh)_3$.

Our observation that the Fe–P distance for the PO_3 bound ligand in *trans*-$Fe(CO)_3$-$[P(OCH_2)_3P][P(CH_2O)_3P]$ (Fig. 6) is shorter by 0.074 (4) Å than the PC_3 coordinated bicyclic could be construed to reflect the somewhat larger steric bulk of the latter ligand. There is good reason to suppose, however, that the possibly better pi-acceptor properties of the PO_3 bound donor may be partially responsible. In this regard it has been shown that the shorter Cr–P distance in $(OC)_5CrL$ when L is $P(OPh)_3$ (2.309 Å) compared with PPh_3 (2.422 Å) is accompanied by longer Cr–C bonds *trans* and *cis* to the phosphite and shorter C–O lengths in the *trans* and *cis* carbonyls as expected if the phosphite is the better pi acid[282]. The bond parameters within the two polycycles of the iron compound feature some information on the nature of the behavior of ligands upon coordination. Interestingly, all the bond lengths, the PCO and POC angles and the intraligand P–P distances are quite constant. It does appear, however, that both the OPO and CPC angles open up about 3° upon coordination of the respective phosphorus atoms to the iron. These observations accord with the prediction that *s* character will accrue in the PC and PO bonds as a result of phosphorus sigma-donation.

The Fe–P bond distance for the PO_3 bound ligand (2.116 Å) is appreciably shorter than that found in the other iron phosphite complexes in Table 26 for which structural data are available. The difference could be ascribed to the greater steric requirements of $P(OPh)_3$ and $P(OEt)_2Ph$ compared to $P(OCH_2)_3P$. However, differences in the nature of the FeP bond cannot be ruled out since $P(OPh)_3$ is apparently a poorer Lewis base toward a proton than is $P(OCH_2)_3CCH_3$, which is closely related to $P(OCH_2)_3P$ (see Sect. B (vi)). The Fe–P bond distance for the PC_3 bound ligand (2.190 Å) is also short compared with those found for $Fe(CO)_4PMe_2PMe_3$ (2.260 Å)[295] and $(OC)_3Fe(H_2CCCH_2)Fe(CO)_3PPh_3$ (2.25 Å)[296]. Again the low steric requirements of the PC_3 bound $P(OCH_2)_3P$ may be largely responsible for the short Fe–P distance but it should be realized that a rather electronegative PO_3 group is attached to the carbons of the PC_3 coordinating site, which would tend to decrease the

TABLE 266

Structural information on metal complexes of electronegative phosphorus ligands

	Average M–P distance (A)	Remarks	Ref.
$Cr(CO)_5P(OPh)_3$	2.309	Octahedral	282
$Mo(CO)_5PF_3$	2.369	Octahedral	306 [d]
cis-$Mn(CO)_4[P(OPh)_3]\{Au(PPh_3)\}$	2.27 [a]	Octahedral around manganese	284
trans-$Fe(CO)_3[P(CH_2O)_3P][P(OCH_2)_3P]$	2.116 [b] 2.190 [c]	See Sect. C(iii)9	59
cis-$FeH_2[P(OEt)_2Ph]_4$	2.128 [d] 2.150 [e]	Phosphorus array is a distorted tetrahedron and hydrogens are *cis*	279, 280
cis-$FeH_2[P(OEt)_3]_4$		Phosphorus array is a distorted tetrahedron and hydrogens are *cis*	281
π-$C_5H_5FeI\{P(OPh)_3\}_2$	2.15	Piano stool configuration	285
π-$C_5H_4FeI\{P(OC_6H_4)(OPh)_2\}[P(OPh)_3]$	2.14	One of the phosphorus ligands is bonded to the cyclopentadienyl ring via a phenyl *ortho* carbon	285
trans-$RuH_2[P(OEt)_2Ph]_4$		Phosphorus array is a distorted tetrahedron and hydrogens are *trans*	280
$HCo[P(OEt)_2Ph]_4$	2.115 eq 2.128 ax	Distorted trigonal bipyramid with hydrogen axial	278
$HCo[P(OPh)_3]_4$		Isomorphous with $Ni[P(OPh)_3]_4$ indicating tetrahedral array of phosphorus atoms	277
$HCo(PF_3)_4$	2.052	Phosphorus atoms in a distorted tetrahedral array with hydrogen probably on a face	286
$Rh[P(OMe)_3]_2BPh_4$	2.185	One of the phenyl groups is pi-bonded to the metal	287
$[(C_8H_{12})[P(OPh)_3]_2Rh]_2Cl_2$	2.14	Complex is chloro-bridged	290
$RhCl(PF_2NEt_2)_2PPh_3$	2.215 [f] 2.136 [g]	The PPh_3 and Cl groups are *cis*	292

sym-mer-$RhCl_3\{P(n\text{-}Bu)_3\}_2[P(OMe)_3]$	2.199[g]	Octahedral	283
$\overline{IrCl[P(OC}_6H_4)(OPh)_2]_2\{P(OPh)_3\}$	2.25[h]	Two of the ligands are bonded to the metal via an *ortho* phenyl carbon to give an octahedral configuration	289
$Ni[P(OCH)_3(CH_2)_3\}_5(ClO_4)_2$	2.14 2.19	Regular trigonal bipyramid with Ni–P(ax) shorter than NiP(eq)	199
$Ni(CN)_2[P(OEt)_2Ph]_3$	2.228[h]	Distorted trigonal bipyramid	209a
$Ni[PN(CH_2)_5F_2\}_4$		Tetrahedral	293
$Ni(PF_3)_4$	2.099, 2.116	Tetrahedral	288, 291
$\{Ag[P(OCH_2)_3CMe]_4\}ClO_4$	2.436	Tetrahedral	60
$Pt(PF_3)_4$	2.23	Tetrahedral	291

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[a] For $P(OPh)_3$ phosphorus. [b] For PC_3 phosphorus. [c] For PO_3 phosphorus. [d] For P *cis* to H. [e] For P *trans* to H. [f] For P *trans* to PPh_3. [g] For P *trans* to Cl. [h] Average distance.

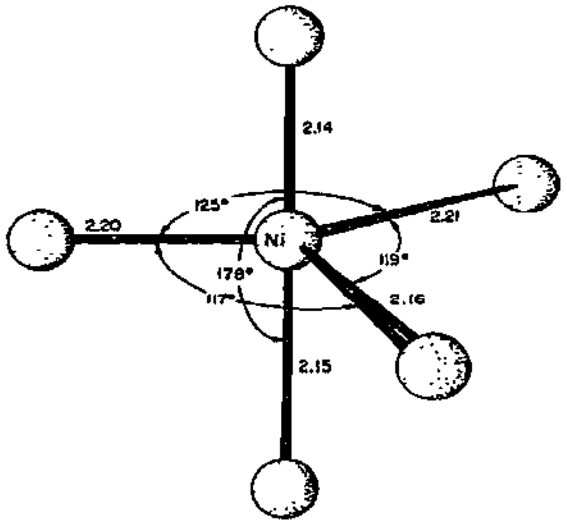

Fig. 34. The molecular configuration of the NiP_5 portion of the $Ni[P(OCH)_3(CH_2)_3]^{2+}$ cation.

sigma basicity of the coordinated phosphorus but increase its pi acidity. Infrared data have already been presented (Sect. C(iii)4) which show that carbonyl stretching frequencies are not appreciably altered in a given complex by changing the site of phosphorus coordination in $P(OCH_2)_3P$. This may be an indication that the ligand properties of the two types of phosphorus atoms are somewhat more similar than a phosphite and a phosphine possessing ordinary alkyl groups.

The configuration of the phosphorus atoms in the $Ni[P(OCH)_3(CH_2)_3]_5{}^{2+}$ cation (Fig. 34) is very nearly a perfect trigonal bipyramid and it is of singular interest that there is a compression of the Ni—P bond distance along the three-fold direction. The average nickel—phosphorus axial bond distance is 2.14 ± 0.01 Å while the average nickel—phosphorus equatorial bond distance is 2.19 ± 0.01 Å. Although the difference might be considered marginal because of the reasonably large standard deviations, similar axial contractions have been observed in other structures such as the trigonal bipyramidal $Ni(CN)_5{}^{3-}$ (ref. 297) and $CuCl_5{}^{3-}$ ions[298]. The axial contraction in the latter case was rationalized[283] in terms of electron pair repulsions, and stronger pi bonding along the axis arising from symmetry considerations[299]. The Ni—P bond lengths are within the range of values reported for similar bonds in other compounds, such as 2.18 Å in $Ni(HPPh_2)_3I_2$ (ref. 300), 2.22 Å in $Ni(PPh_3)_3(C{\equiv}CC_6H_5)_2$ (ref. 301), 2.21 Å in $Ni(TAP)CN(ClO_4)$ (TAP = $P(CH_2CH_2CH_2AsMe_2)_3$) (ref. 302), and 2.19 and 2.21 Å in $Ni(CN)_2(PPh(OEt)_2)_3$ (ref. 209a). In contrast to the pentakis caged phosphite complex, the last compound is a very distorted trigonal bipyramid. Supporting evidence for the earlier conclusion (Sect. C(iii)2) that the $Co[P(OCH_2)_3CMe]_5{}^+$ cation is isostructural with the $Ni[P(OCH)_3(CH_2)_3]_5{}^{2+}$ complex comes from an X-ray diffraction study of the $Co(CNMe)_5{}^+$ ion which was shown to be a slightly distorted trigonal bipyramid[196b].

The $Ag[P(OCH_2)_3CMe]_4^+$ cation has the expected tetrahedral configuration. The Ag–P bond distance of 2.436 Å is somewhat smaller than that for $Ag(SCN)[P(n\text{-}Pr)_3]$ (2.48 Å)[303] which also is four-coordinate owing to bridging by SCN groups.

The decrease in M–P bond lengths in Table 26 over the sum of their covalent radii ranges from about 0.05 to 0.2 Å with an average difference of approximately 0.15 Å for phosphites and $P(OEt)_2Ph$. For PF_3 and PF_2NEt_2 the range is 0.2 to 0.3 Å with an average of about 0.25 Å. It is tempting to suppose that the increased shortening of the M–P bonds from phosphites to trifluorophosphine is due to increased pi bonding which results from increased ligand electronegativity. There are two difficulties associated with this reasoning. (*a*) Complexes of trialkyl phosphines possess MP bond shortenings[63,304,305] which range from about 0.05 to 0.3 Å with an average of approximately 0.15 Å which is quite comparable with the data for the more electronegative phosphite ligands. (*b*) If increasing electronegativity does play a role in shrinking MP bond lengths, it could conceivably be accomplished by contracting the phosphorus lone pair. It may well be that steric factors render MP distances rather insensitive to pi bonding effects even if they are comparable with sigma bonding. Moreover, sigma bonding is expected to decrease with increasing electronegativity of the phosphorus which would militate against bond length shrinkage. The possible importance of synergistic enhancement of sigma bonding as a result of pi bonding is presently not known.

The suggestion that steric differences among phosphines and phosphites are important gains support from a comparison of the NiP bond lengths in $Ni(CN)_2[P(OEt)_2Ph]_3$ (2.228 Å)[209a] and the PMe_2Ph analog (2.24 Å)[209b]. The ligands in both cases probably have similar steric requirements because of the phenyl groups, in which case the MP bond lengths are unexpectedly close in view of the electronegativity difference of the ethoxy and methyl groups. It is also necessary to view with caution conclusions on bonding reached by making comparisons of shorter MP bond distances in phosphite complexes with those in analogous PEt_3 or PPh_3 complexes since evidence has been presented[306] that the steric requirements of the latter ligands are larger than $P(OMe)_3$, $P(OEt)_3$ and $P(OPh)_3$. Indeed even PMe_3 appears[212] to be comparable in bulk to $P(OPh)_3$.

In the previous two sections increases in the absolute magnitude of $^{183}W-^{31}P$ and $^{31}P-M-^{31}P$ spin–spin coupling were attributed mainly to increases in the *s* character of the phosphorus lone pair and the phosphorus *s* electron density as the phosphorus substituents became more electronegative. If the increase in *s* character in the series $PR_3 < P(OR)_3 < PF_3$ is an important influence, a concomitant reduction of the substituent–phosphorus–substituent bond angle might be anticipated. In metal complexes of the type PR_3, CPC bond angles range from 101 to 111° (refs. 63, 301, 306a–c); in $\pi\text{-}C_6H_5FeI\{P(OPh)_3\}_2$ and $[(C_8H_{12})[P(OPh)_3]_2Rh]_2Cl_2$ the OPO bond angles are 100° (ref. 285) and 99.5° (ref. 290), respectively; and in $Ni(PF_3)_4$, $(OC)_5MoPF_3$ and $Pt(PF_3)_4$ the FPF angles are 99.3° (ref. 288) or 98.4° (ref. 291), 99.5° and 98.9° (ref. 291), respectively. Although the suggestion of a trend toward smaller angles is rather slight in metal complexes, it is significantly stronger in the chalconide derivatives $ChPR_3$ (106–108°) (ref. 63), $O{=}P(OCH_2Ph)_2(OH)$

(104°) (ref. 54) and $ChPF_3$ (100.3–102.5°) (ref. 250) (where Ch is S, Se or O). It should be recalled, however, that the increase in phosphorus nuclear charge (i.e. *s* density) with electronegativity is also an important factor[238] which operates in the same direction as an *s* character rise. Thus in the event that phosphite and phosphine metal complexes are found in which OPO $\geqq$ CPC, the normal order of spin coupling could be preserved owing to the *s* density term.

CONCLUSIONS

The concept of pi back-bonding in adducts and complexes has, with varying degrees of seriousness, been referred to in the literature as "the panacea of inorganic ills"[307] and as a "noumenological"[308] occurrence (i.e. an object of purely rational apprehension as opposed to a phenomenological one). It has even inspired poetic levity[*].

Although the relative contributions of sigma and pi character to P–M bonds cannot be presently ascertained from the results described above, it appears that the ligand field and M–P stretching frequency data are most consistent with the presence of an amount of pi character sufficient to dominate the trends in Dq in the CoL_6^{3+} systems and ν(MP) in the bicyclic phosphite complexes. The observation that the coupling trends are best interpreted only on sigma inductive grounds certainly does not exclude the presence of pi character in the P–M bonds. This is reasonable inasmuch as the present theory of coupling regards the Fermi contact term as the dominant influence. Interestingly, it appears that whereas UV and IR spectroscopy and ^1H NMR chemical shifts yield information on the sum of the sigma and pi character of the P–M bond, the NMR coupling trends are indicative of the changes in its sigma character.

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