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Modes of coordination for the phosphorylic unit

Neil Burford
Department of Chemistry, Dalhousie University, Halifax, N.S. B3H 4J3 (Canada)

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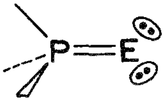
CONTENTS

A. INTRODUCTION

The coordinate bond takes on many forms and can be administered by most elements or compounds. While the acceptor can be any Lewis acidic centre, most common are complexes to metal centres. Coordination chemistry was revolutionised by the discovery of coordinative versatility for certain organic ligands. Many unsaturated systems have the ability to adopt conventional σ-complexation (Werner coordination) involving donation from a single atomic centre of a ligand, as well as π-complexation involving donation from the π-manifold of a multi-atom unit (multihapticity). Certain ligands are capable of coincident σ- and π-donation, and the distinction is often difficult. Multihapto coordination is less common for inorganic ligands, although a number of important examples have recently been reported (see, for example, ref. 1 and the references cited therein).

Derivatives of the phosphorylic unit **1** (E = NR, O, S, Se) contain an electron-rich centre (E) and represent well-characterised examples of "formally" monohapto ligands. Complexes are often illustrated with an A–E coordinate bond **2** (A = Lewis acid). However, the coordinate behaviour of the phosphorylic unit is diverse, exhibiting a variety of unusual features. An assessment of the extensive data available in the literature is presented here in an attempt to illustrate two distinct coordinative bonding modes.



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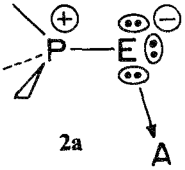

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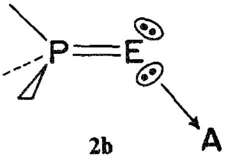

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B. PROBING THE PHOSPHORYLIC BOND

The phosphorylic bond has been extensively examined by a wide variety of techniques. Early studies involved comparison of the P—E infrared stretching frequencies of coordinated systems with those of the corresponding free bases for a series of derivatives (see, for example refs. 2–4). General observation of lower P—E stretching frequencies for the coordinated unit have been explained in terms of a lowering of the P—E bond order, as originally suggested for the P—O bond [4]. However, the magnitudes of the frequency changes associated with coordination are worthy of note. While the frequency shift for the oxophosphorylic unit is generally much less than 50 cm^{-1}, the thiophosphorylic units exhibit a more substantial ($>$ 50 cm^{-1}) change [3], implying a more dramatic electronic perturbation as a result of coordination.

Numerous NMR studies are consistent with these conclusions, but provide a further insight into the electronic structure. The triphenylphosphorylic derivatives represent the most readily available and easily handled series of compounds, and have therefore been the most extensively examined. Table 1 lists NMR data for the methylene, imino-, oxo-, thio-, and seleno-triphenylphosphoryl compounds and their conjugate acids (corresponding hydroxyphosphonium cations). Data for methylated phosphonium cations, and examples of Lewis acid complexes are also listed.

Trends in the ^{31}P chemical shifts are most striking. The second row phosphorylic systems (E$=$C, N, O) exhibit significant ^{31}P chemical shifts (29 ppm) as a result of protonation or complexation of the free base. The magnitude of the shifts varies with the nature of the Lewis acid (H^+, Me^+, $AlCl_3$, or BF_3), but the effect is consistent. In contrast, the thio- and selenophosphorylic centres show little or no adjustment in ^{31}P NMR chemical shift between the corresponding phosphorylic and phosphonium centres. ^{31}P chemical shifts are notoriously difficult to rationalise and are dependent upon a number of factors. For instance, phosphorylic systems with electron-rich substituents (RO—, R_2N—, X—) show a less pronounced deshielding response toward coordination (cf. $(MeO)_3PO$, -2.4 ppm; $(MeO)_4P^+$, 1.6 ppm) [10]. Moreover, coordination often enhances shielding of the phosphorus centre for the thio and seleno derivatives (cf. $(NMe_2)_3PS$, 82 ppm; $(NMe_2)_3PS{-}AlCl_3$, 69 ppm) [12]. As a general rule, all four substituents are manifest in the chemical shift of the phosphorus centre. Nevertheless, an isolated analysis of the P=E bond is valid in Table 1 and shows a deshielding of the phosphorus centre associated with coordination of the methylene, imino-, and oxo-phosphorylic unit.

The ^{13}C chemical shifts for the carbon nuclei of the phenyl groups are uniformly sensitive to chemical changes at the E position. Upon coordination, the ipso position is shielded, and (to a lesser extent) the para position is deshielded, while the ortho and meta positions generally show little or no effect. The observations can be rationalised in terms of simple resonance considerations, and provide evidence for π-interaction between the phenyl groups and the phosphorus centre [14].

TABLE 1

NMR Data (δ in ppm) for triphenylphosphorylic systems[a]

Ext. ref	^{31}P 85%H_3PO_4		^{13}C TMS					^{77}Se Me_2Se	(J_{PSe})	
			ipso	ortho	meta	para				
Ph_3PCMe_2	20	[5]	133.6	133.8	128.3	130.6	[6]			
$Ph_3PCMe_2H^+$	31	[7]	117.5	133.8	130.6	134.9	[6]			
Ph_3PNPh	3	[8]	131.2	132.4	128.4	131.5	[8]			
Ph_3PNPhH^+	32	[8]	119.8	135.5	130.0	135.2	[8]			
Ph_3PO	23–29	[9]	132.8	132.1	128.5	131.8	[9]			
Ph_3POH^+	57	[9]	120.0	131.1	129.0	132.8	[9]			
Ph_3POMe^+	65	[10]								
Ph_3PO-BF_3	44	[11]	124.7	132.9	129.1	134.2	[11]			
$Ph_3PO-AlCl_3$	45	[11]	124.7	132.5	129.3	134.5	[11]			
Ph_3PS	43	[9]	133.0	132.2	128.5	131.5	[9]			
Ph_3PSH^+	43	[9]	119.3	132.6	129.8	135.2	[9]			
Ph_3PSMe^+	47	[10]								
$Ph_3PS-AlCl_3$	43	[12]	124.4	133.2	129.4	134.1	[12]			
Ph_3PSe	35	[9]	131.9	132.7	128.5	131.5	[9]	−275	(736)	[12]
Ph_3PSeH^+	37	[13]	116	130.8	133.8	137.0	[12]		(418)	[13]
Ph_3PSeMe^+	36	[10]							(465)	[10]
$Ph_3PSe-AlCl_3$	34	[12]	124.1	133.5	129.5	134.0	[12]	−190	(540)	[12]

[a] References are given in brackets.

^{77}Se NMR spectroscopy provides an additional probe of the selenophosphorylic bond. In general, coordination effects a significant deshielding of the selenium nucleus, and a decrease (100–350 Hz) in the $^1J_{PSe}$ coupling constant [15] (Table 1). In addition, there is an apparent correlation between the magnitude of the $^1J_{PSe}$ coupling constant and the narrow range observed for P–Se bond lengths. Ph_3PSe contains one of the shortest P–Se bonds (2.106(1) Å) [16] and exhibits a relatively large $^1J_{PSe}$ of 736 Hz [12] (a larger value is obtained for $(MeO)_3PSe$, 963 Hz) [15]. The novel heterocyclic cation $[\{Et_2N\}_2PSe]_2^{2+}$ contains significantly longer P–Se bonds (shortest, 2.238(3) Å), which might be considered single, and the $^1J_{PSe}$ (341 Hz) is dramatically reduced [17]. Similar $^1J_{PSe}$ values are observed for Me_2PSeMe (205 Hz) and $Me_2P(S)$-SeMe (341 Hz) [15], which are envisaged to contain P–Se single bonds, although structural data are not available. Intermediate $^1J_{PSe}$ values are observed for selenophosphorylic complexes (e.g. Ph_3PSeH^+, 418 [13]; $Ph_3PSe-AlCl_3$, 540 [12]; $(Ph_3PSe)_4Cd^{2+}$, 585 [18]; $(Bu_3PSe)_2HgCl_2$, 512 and 522 Hz [19]) consistent with an intermediate P—Se bond length (e.g. Ph_3PSe–$AlCl_3$, P—Se = 2.182(2) Å) [12], and retention of some P—Se multiple bonding.

The spectroscopic data are conclusive in that they illustrate that the electronic consequences of coordination for the phosphorylic unit are general and essentially independent of the acceptor. However, there are distinct differences in the nature of the electronic adjustments experienced by the second row (E = C, N, O) phosphorylic systems in comparison with those for the heavier (E = S, Se) phosphorylic units.

C. GEOMETRIES OF COORDINATION

Phosphorylic units **1** generally form a coordinate bond which is envisaged as a σ-donation from the E centre. The P—E—A framework (A = Lewis acid) is typically depicted as bent, **2**, with a bond angle implicating a conventional valence shell electron pair repulsion (VSEPR) geometry for the environment of E (109° **2a** or 120° **2b**, depending on the degree of P—E multiple bonding retained in the coordinated unit). Indeed, iminophosphorylic ligands conform closely to the VSEPR ideals (see, for example, ref. 20). However, chalcogenophosphorylic ligands are coordinatively flexible and behave in a much less conventional manner. Lindqvist [21] attempted a systematic assessment of the oxo-coordinate bond, including those involving phosphorylic ligands. Based on fewer than 20 structural studies (four involving P—O ligands) he recognised a wide range of bond angles at oxygen from 117° to 151°, and realised the need for more extensive and accurate experimental data. Naturally, a vast crystallographic database is now available, and Table 2 contains a representative sample of oxo-, thio- and selenophosphorylic complexes. The compounds are listed according to decreasing P—E—A bond angles, together with their P—E and E—A bond lengths. The table is not comprehensive (systems possessing substantial steric strain or involving heterocyclic constraints on the P—E—A framework have been omitted), but is intended to illustrate the wide range of observed coordination geometries for terminally bound chalcogenophosphorylic units.

It is clear from Table 2 that the range of coordination geometries is extreme. In general, the oxo complexes adopt the widest angles at the donation centre (an extreme example is illustrated in Fig. 1), while the thio and seleno complexes adopt the most acute angles at E (an example is illustrated in Fig. 2). The P—E bond length of the coordinated phosphorylic system is, in general, slightly longer than that of the free base, consistent with the lower P—E stretching frequency observed in the IR spectra of the complexes. However, the bond length adjustment resulting from coordination (0.06 Å, more than 3%) is only significant for the thio and seleno systems. The P—O bond length is remarkably constant, and the accuracy of much of the structural data available for the oxo complexes is insufficient to identify a bond length change, although it is generally in the order of <1% (0.01 Å).

Thio- and selenophosphorylic ligands often impose severe asymmetric distortions on the coordination geometries of the other ligands in the complex. For

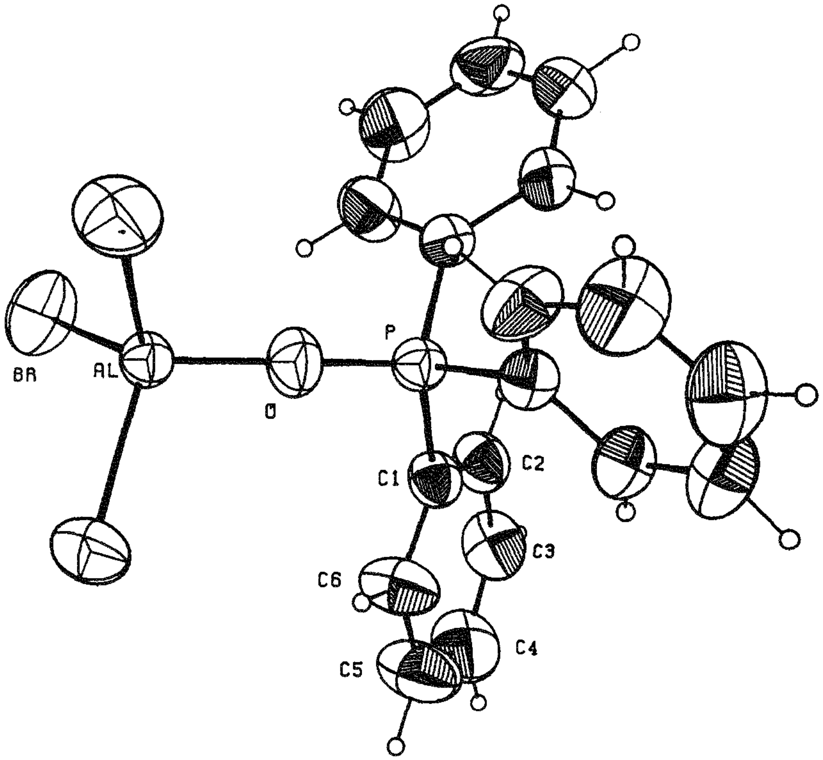


Fig. 1. A crystallographic view of $Ph_3PO-AlBr_3$.

example, the chlorine atoms of $Ph_3PS-AlCl_3$ and $Ph_3PSe-AlCl_3$ are tilted away from the phosphorus centre (as shown in Fig. 2), as if to allow a contact between the phosphorus and aluminium centres, which is within the sum of the van der Waal's radii ($Ph_3PS-AlCl_3$: P—Al = 3.538(2) Å; $Ph_3PSe-AlCl_3$: P—Al = 3.727(3), 3.706(3) Å) [12]. Similar features are reported for $Ph_3PSe-HgCl_2$ (P—Hg = 3.53 Å) [69] and $Ph_3PSe-AuCl$ (P—Au = 3.497(7) Å) [68]. While the sharp bond angles have been rationalised in terms of repulsions between non-bonding electrons on the selenium centre [68], the incipient phosphorus–metal interaction implies that the observed distortions are the result of an auxiliary bonding interaction between the acid and the phosphorus centre, and the observed geometries represent the steric limit in each case.

Complexes to aluminium centres offer an important probe into the coordination geometries in solution. The quadrupolar ^{27}Al nucleus generally gives broad lines, however, in cubic environments (octahedral or tetrahedral) the electric field gradient is zero, and sharp lines can be observed [70,71]. For example, the $AlCl_4^-$ anion often gives a sharp resonance at 102 ppm with a line width at half-height ($\Delta\nu_{1/2}$) of 3 Hz (cf. $AlMe_3(OEt_2)$ in toluene, $\Delta\nu_{1/2} = 2000$ Hz) [71]. Narrow signals are observed in

TABLE 2

P–E and E–A bond lengths (Å) and P–E–A bond angles (°) for selected phosphorylic complexes

Compound	P–E–A	P–E	E–A	Ref
Ph_3PO		1.483(2)		22
Ph_3PS		1.950(3)		23
Ph_3PSe		2.106(1)		16
$Ph_3PO–AlCl_3$	180	1.519(4)	1.733(4)	11
$Ph_3PO–AlBr_3$	180	1.513(7)	1.736(7)	11
$Ph_3PO–GaCl_3$	180	1.49(1)	1.818(10)	11
$[Ph_3PO–CuCl]_4OCl_2$	180	1.51(2)	1.89(2)	24
$Ph_3PO–La[N(SiMe_3)_2]_3$	174.6(9)	1.52(2)	2.40(2)	25
$(Ph_3PO–)_2Ce(NO_3)_4$	173.2(4)	1.531(8)	2.216(7)	26
	169.2(5)	1.526(8)	2.222(7)	
$(Ph_3PO–)_2La(O_2)[N(SiMe_3)_2]_4$	172.6(14)	1.51(2)	2.42(2)	25
$[Ph_3PO–ReCl_2(O)Me]_2O$	171.7(3)	1.524(4)	2.115(4)	27
$(Ph_3PO–)_2Th(NO_3)_4$	170.2(11)	1.43(2)	2.37(2)	28
	170.2(10)	1.47(2)	2.33(2)	
cis-$[Ph_3PO–SmCp^*{}_2]_2(C_2H_2O_2)$	167.6(6)	1.501(10)	2.392(10)	29
	168.8(7)	1.496(11)	2.393(10)	
$(Ph_3PO–)_2UCl_4$	165.1(5)	1.524(7)	2.242(7)	30
trans-$[Ph_3PO–SmCp^*{}_2]_2(C_2H_2O_2)$	163.0(5)	1.514(7)	2.355(7)	29
	158.7(5)	1.495(8)	2.391(7)	
$(Ph_3PO–)_2NpO_2Cl_2$	167(1)	1.50(1)	2.288(15)	31
	153(1)	1.55(2)	2.261(19)	
$Ph_3PO–UO_2(Et_2NCS_2)_2$	162(2)	1.49(3)	2.34(2)	32
$Cl_3PO–MoNCl_3$	162.0(8)	1.45(2)	2.36(2)	33
	152(1)	1.45(1)	2.33(1)	
	151.6(9)	1.46(2)	2.33(2)	
	151.9(7)	1.46(1)	2.40(1)	
$Ph_3PO–Al(SiPh)_7O_{12}$	160.4(3)	1.508(4)	1.770(5)	34
$(Ph_3PO–)_2UO_2(NO_3)_2$	160.0(4)	1.505(9)	2.359(7)	31
$(Ph_3PO–)_2NpO_2(NO_3)_2$	159.1(4)	1.502(9)	2.633(8)	31
$(Ph_3PO–)_3Hg(ClO_4)$	131(1)	1.50(2)	2.31(2)	35
	160(1)	1.52(2)	2.29(2)	
	152(1)	1.50(2)	2.43(2)	
$Cl_3PO–MoCl_4(N)(C_2Cl_5)$	160.3(6)	1.426(9)	2.237(8)	36
$Ph_3PO–UO_2(MeCS_2)_2$	159(1)	1.47(2)	2.34(1)	37
$(Ph_3PO–)_2Co(NO_3)_2$	158.5(8)	1.48(1)	1.99(1)	38
$Me_3PO–SnMe_3Cl$	158(1)	1.55(3)	2.28(3)	39
$(Ph_3PO–)_2MnCl_2$	156.0(4)	1.488(6)	2.069(6)	40
$(Ph_3PO–)_2Os(OEP)$[a]	154.2(5)	1.483(8)	2.036(7)	41
$Cl_3PO–WNCl_3$	152.4(1)	1.393(5)	2.379(2)	42
	146.9(1)	1.530(3)	2.316(3)	
	146.6(1)	1.534(3)	2.286(3)	
	157.9(3)	1.517(4)	2.267(2)	
$Cl_3PO–ReCl_4(N)(C_2Cl_5)$	158.6(6)	1.434(11)	2.182(10)	43
$Ph_3PO–SnPh_3NO_3$	153(1)	1.47(2)	2.29(2)	44

TABLE 2 (*continued*)

Compound	P–E–A	P–E	E–A	Ref
$Cl_3PO–TiCl_4$	151.8(13)	1.44(2)	2.10(2)	45
$(Ph_3PO–)_2CuCl_2$	150.9(3)	1.492(4)	1.958(4)	46
$(Ph_3PO–)_2TlClBrI$	149.0(2)	1.491(4)	2.396(4)	47
	148.5(2)	1.485(4)	2.404(4)	
$Ph_3PO–Cu(ClCH_2CH_2COO)_2$	149.0(2)	1.477(3)	1.965(2)	48
$Cl_3PO–Mo(NO)Cl_3$	149.8(4)	1.439(5)	2.207(5)	49
$Cl_3PO–NbCl_5$	148.8(12)	1.45(2)	2.16(2)	50
$Ph_3PO–ReCl_3(NO)(NPPh_3)$	148.7(4)	1.502(7)	2.092(6)	51
$Cl_3PO–MoO_2Cl_2$	147.8(3)	1.457(4)	2.329(4)	52
$[Cl_3PO–SnCl_5]^-$	147.3(6)	1.46(1)	2.27(1)	53
$Cl_3PO–WCl_4(C_{10}H_{18})$	146.1(8)	1.456(12)	2.332(11)	54
$Ph_3PO–Cu(CH_3CHClCOO)_2$	146.7(4)	1.507(6)	2.095(5)	55
$Cl_3PO–SbCl_5$	145(16)	1.47(2)	2.17(2)	50
$Me_3PO–SbCl_5$	144.9(23)	1.56(4)	1.94(4)	50
$Cl_3PO–ReCl_5$	143.2(8)	1.45(1)	2.05(1)	56
$Cl_3PO–MoCl_5$	143.7(4)	1.459(7)	2.187(6)	33
$(Ph_3PO–)_2UO_2(CH_3CO_2)_2$	143(1)	1.49(4)	2.37(3)	57
$(Me_3PO–)_2Co(NO_3)_2$	139.6(1)	1.53(3)	1.92(2)	58
	133.2(1)	1.55(3)	1.95(2)	
$(Ph_3PCH)Ph_2PO–W(CO)_5$	137.1(4)	1.521(8)	2.200(7)	59
$Ph_3PO–BF_3$	134.5(2)	1.522(3)	1.516(6)	60
$Ph_3PS–NbSCl_3$	116.6(2)	2.028(5)	2.577(3)	61
	111.5(2)	2.026(6)	2.573(4)	
$Me_3PS–Cr(CO)_5$	112.5(1)	1.990(3)	2.510(2)	62
$Ph_3PS–MoOCl_3$	111.31(4)	2.041(1)	2.460(1)	63
$(Me_3PS–)_3Cu^+\ ClO_4^-$	107.2(3)	2.007(6)	2.264(5)	64
	104.3(3)	2.009(7)	2.260(6)	
	110.3(3)	1.9667(7)	2.253(5)	
$Ph_3PS–AlCl_3$	109.62(8)	2.028(2)	2.297(2)	12
$Me_2(S)PPMe_2(S)–CuCl_2$	109.5(3)	1.995(9)	2.322(7)	65
	113.1(3)	1.991(9)	2.332(7)	
$Ph_3PS–SbBr_3$	109.0(1)	1.984(3)	2.964(2)	66
$Ph_3PS–I_2$	107.0(1)	2.007(3)	2.729(2)	67
$Ph_3PSe–AlCl_3$	106.95(7)	2.182(2)	2.452(2)	12
	107.15(7)	2.181(2)	2.421(2)	
$Ph_3PSe–SbI_3$	100.8(1)	2.163(2)	2.862(1)	66
$Ph_3PSe–AuCl$	100.1(1)	2.187(5)	2.371(2)	68
$Ph_3PSe–HgCl_2$	98.1(1)	2.169(6)	2.527(3)	69

[a] OEP = octaethylporphyrinate.

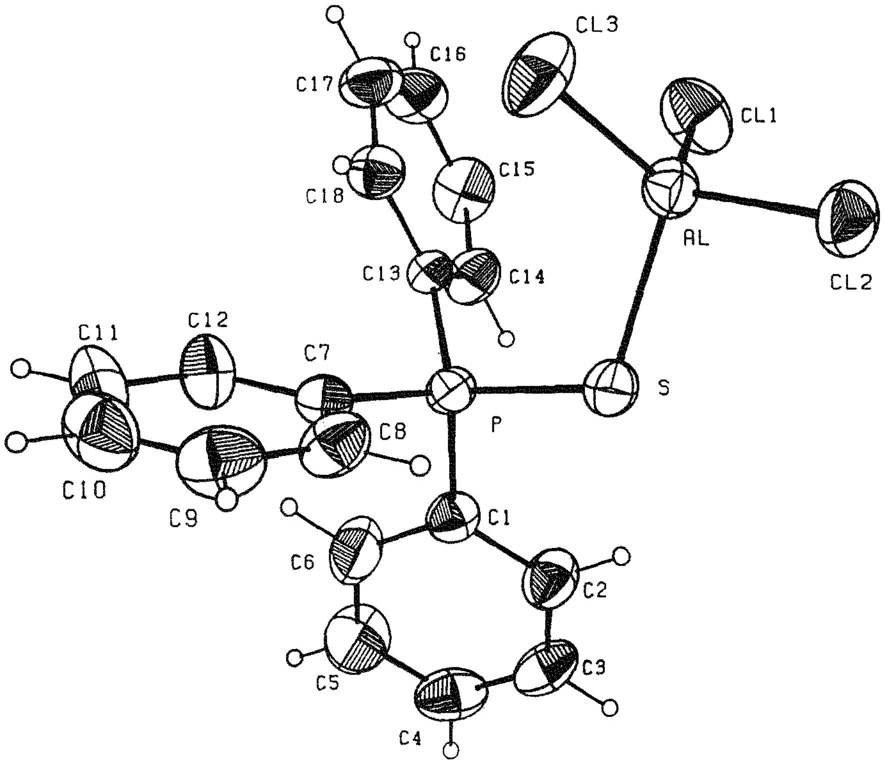


Fig. 2. A crystallographic view of $Ph_3PS{-}AlCl_3$.

the ^{27}Al spectra of $Ph_3PO{-}AlCl_3$ ($\Delta\nu_{1/2}=40$ Hz), $Ph_3PO{-}AlBr_3$ ($\Delta\nu_{1/2}=31$ Hz) and $(NMe_2)_3PO{-}AlCl_3$ ($\Delta\nu_{1/2}=18$ Hz) [11]. While the lines are not as sharp as those for a perfect tetrahedral geometry, a pseudo-tetrahedral symmetry is implied for the aluminium environment. In view of the linear solid state structures observed for these systems (vide infra), the sharp lines can be interpreted in terms of a retention of molecular C_3 symmetry in solution. The signal observed for $(NMe_2)_3PO{-}AlCl_3$ is consistent with the related solvate system $[Al(OP(NMe_2)_3)_4]^{3+}$ for which a coupling constant has been measured ($\Delta\nu_{1/2}=3$–5 Hz, $^2J_{AlP}=30$ Hz) [70,72,73].

In contrast to the oxophosphorylic complexes, ^{27}Al NMR spectra of thio- and selenophosphorylic complexes show relatively broad resonances (>200 Hz) centred at 107 ppm. While a number of factors may be responsible for the width of the signal, a non-zero electric field gradient at aluminium is a likely contributor, imposed by the pseudo-tetrahedral environment. The differing electronegativities of sulphur (or selenium) and the halogen substituents at aluminium are likely to effect such an asymmetry, although the narrow linewidth observed for the oxophosphorylic complexes appear to be independent of the substituents (cf. $Ph_3PO{-}AlCl_3$, $\Delta\nu_{1/2}=40$ Hz; $Ph_3PO{-}AlBr_3$, $\Delta\nu_{1/2}=31$ Hz; Pauling electronegativities: Cl, 3.16; Br, 2.96; O, 3.44)

[74]. Therefore, the broader lines observed for the thio and seleno derivatives can be interpreted in terms of a disruption of the molecular C_3 symmetry, consistent with the bent environment for the chalcogen observed in the solid state.

D. LINEAR ENVIRONMENTS FOR ELECTRON-RICH ATOMIC CENTRES

The electron-rich elements of the second row (N, O, F) are regularly employed to demonstrate the stereochemical presence of non-bonding lone pairs, and the utility of the VSEPR model. However, in covalent environments these elements are, in fact, uniquely electronically versatile, as illustrated by the extremely broad range of bond angles exhibited by dicoordinate oxygen in Table 2. Nitrogen and fluorine are capable of similar conformational flexibility. For example, the iminophosphoranyl anion Ph_3PN^-, and the neutral hexavalent sulphur compound F_3SN are isoelectronic with the chalcogenophosphorylic systems, and have a similar coordination behaviour. Transition metal complexes containing Ph_3PN^- are observed to adopt a wide range of P—N—M bond angles and N—M bond distances depending upon the metal (M) involved [75]. F_3SN forms coordination complexes of the type $[M(NSF_3)_4](AsF_6)_2$ with a number of transition metals, and the angle at the nitrogen donation centre is generally towards linearity (e.g. Mn—N—S, 161.1(4)°, 162.0(3)°) [76]. Similarly, complex fluoride anions such as $Sb_2F_{11}^-$ contain dicoordinate fluorine centres with angles in excess of 170° (see, for example, ref. 77).

Perhaps most fascinating are the numerous examples of linear environments for oxygen. Table 3 lists an extensive selection of compounds whose structures involve angles of greater than 170° at oxygen. Many of the compounds also exhibit short M—O bond lengths (M = metal or non-metal centre). For example, the Al—O bonds in $(C_{10}H_8NO)_2Al{-}O{-}Al(C_{10}H_8NO)_2$ (1.676(4) and 1.678(4) Å) [78] are the shortest observed to date (cf. Al—O single bond 1.78–1.80°) [103], despite the obvious steric constraints of the chelating ligands. Short Al—O bonds are also observed for the aluminium coordinated 2,6-di-*t*-butyl-4-methylphenol (BHT [104,105] or Hdbmp [106]), which usually adopts a close-to-linear coordination geometry, as in $AlMe_2(BHT)(PMe_3)$ (Al—O—C = 164.5(4)°; Al—O = 1.736(5) Å) [104] and $[AlMeCl_2(BHT)]^-$ (Al—O—C = 164.0(3)°; Al—O = 1.713(4) Å) [104], although a range of bond angles is observed. In addition, this ligand can enforce linearity on other ligands, as observed for coordinated aldehydes, ketones and esters [81,107]. However, it is interesting that the Al—O bond lengths for the carbonyl ligands are typical of single bonds [103]. Alkoxide complexes of uranium also exhibit a wide variety of angles at oxygen and a range of U—O bond lengths, suggesting that a combination of steric and electronic factors (and possibly other factors) is responsible for geometries at oxygen in these complexes.

Complexes containing linear oxygen between two transition metal centres are quite common and are considered to be a consequence of a three-centre $d\pi{-}p\pi{-}d\pi$ manifold involving π-donation of two mutually perpendicular π-type lone pairs on

TABLE 3

Examples of systems containing linear oxygen (angle > 170°) centres

Compound	M–O–M′	M–O	O–M′	Ref
$(C_{10}H_8NO)_2$**Al–O–Al**$(C_{10}H_8NO)_2$	178.0(3)	1.676(4)	1.678(4)	78
Ph_3**Si–O–Si**Ph_3	180	1.616(1)	1.616(1)	79
$[(Me_2N)_3$**P–O–P**$(Me_2N)_3]^{2+}$	180	1.573(1)	1.573(1)	80
Ph(OMe)**C–O–Al**Me$(BHT)_2$	174(1)	1.24(1)	1.851(7)	81
$U_2(OCMe_3)_9$Terminal Me_3**C–O–U**	176(1)		2.107(10)	82
Me_3**Si–O–Mo**$(Me_3SiO)_3(HNMe_2)_2$	174.2(2)	1.539(4)	1.951(4)	83
Ph_3**Si–O–Zr**Cl_2(DME)	171(1)	1.65(2)	1.91(1)	84
Ph_3**Si–O–U**Cp_3	172.6(6)	1.62(1)	2.135(8)	85
Ph_3**Si–O–Ce**$(THF)_3(Ph_3PO)_2$	176.4(3)		2.208(4)	86
Ph_3**Si–O–Co**$(THF)_2(Ph_3SiO)$	170.7(2)	1.595(4)	1.845(4)	87
Ph_3**P–O–Al**Cl_3	180	1.519(4)	1.733(4)	11
Ph_3**P–O–Al**Br_3	180	1.513(7)	1.736(7)	11
Ph_3**P–O–Ga**Cl_3	180	1.49(1)	1.818(10)	11
$[Ph_3$**P–O–Cu**$Cl]_4OCl_2$	180	1.5(2)	1.89(2)	24
Ph_3**P–O–La**$[N(SiMe_3)_2]_3$	174.6(9)	1.52(2)	2.40(2)	25
Ph_3**P–O–Ce**$(NO_3)_4(Ph_3PO)$	173.2(4)	1.531(8)	2.216(7)	26
Ph_3**P–O–La**$(O_2)[N(SiMe_3)_2]_4(Ph_3P)$	172.6(14)	1.51(2)	2.42(2)	25
$[(Ph_3PO)ReCl_2(O)Me]_2O$				27
P–O–Re	171.7(3)	1.524(4)	2.115(4)	
Re–O–Re	180	1.847(1)	1.847(1)	
$[Cl_5$**Ru–O–Ru**$Cl_5]^{4-}$	180	1.80		88
$[Cl_5$**Re–O–Re**$Cl_5]^{4-}$	180	1.86	1.86	89
$[Cl_5$**W–O–W**$Cl_5]^{4-}$	180	1.871(1)	1.871(1)	90
$[Cl_5$**Re–O–Re** $Cl_5]^{3-}$	180	1.832(3)	1.832(3)	91
O_3**Re–O–Re** O_3	180	1.80	2.10	92
$[DDTP]_2(O)$**Mo–O–Mo**$[DDTP]_2(O)$[a]	180	1.863(12)	1.863(12)	93
$[(TEP)_2$**Fe–O–Fe**$(TEP)_2]^{4+}$[b]	172	1.77(1)	1.77(1)	94
$[(NH_3)_5$**Ru–O–Ru**$(en)_2$–O–Ru $(NH_3)_5]^{6+}$	177.2(4)	1.850(4)	1.891(4)	95
$[(CN)_4(O)$**Re–O–Re**$(O)(CN)_4]^{4-}$	180	1.915(1)	1.915(1)	96
(Py)(Phth)**Mn–O–Mn**(Phth)(Py)[c]	178	1.71	1.71	97
$OX(H_2O)(O)_2$**Mo–O–Mo**$(O)_2(H_2O)OX$[d]	180	1.876(2)	1.876(2)	98
$(XAN)_2(O)$**Mo–O–Mo**$(O)(XAN)_2$[e]	178(4)	1.85(3)	1.87(3)	99
Cl_2Cp**Ti–O–Ti**$CpCl_2$	180	1.78(3)	1.78(3)	100
$(C_7H_3O_4N)(O)_2$**Ti–O–Ti**$(O)_2(C_7H_3O_4N)$	178.1(8)	1.825(2)	1.825(2)	101
$[(NH_3)_5$**Cr–O–Cr**$(NH_3)_5]^{4+}$	180	1.821(3)	1.821(3)	102

[a] DDTP = diethyldithiophosphinate.

[b] TEP = tetraethylenepentamine.

[c] Py = pyridine; Phth = phthalocyanate.

[d] OX = oxalate.

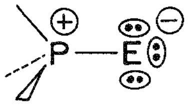
[e] XAN = xanthate.

oxygen into the dπ orbitals of the metal centres. However, a linear structure is assigned for Li_2O [108], in which lithium has no d orbitals available.

The P—O—Al linearity and short Al—O bonds (X = Cl: 1.733(4); Br: 1.736(7) Å) observed for derivatives of Ph_3P—O—AlX_3 are not a consequence of steric constraints. There is an important isoelectronic relationship between the P—O—Al backbone, the P—O—P framework of $[(Me_2N)_3POP(Me_2N)_3]^{2+}$ [80] and the Si—O—Si framework of $Ph_3SiOSiPh_3$ [79]. The P—O—P backbone of the pyrophosphate anion ($P_2O_7^{4-}$) may also be considered in this light, although linearity has been a point of much discussion [109]. Linearity for siloxanes (Si—O—Si) is well established and is interestingly unique among the Group 14 ethers [110]. Moreover, the siloxide anion is often observed to adopt a linear coordination (see Table 3). On this basis, the linearity now regularly observed for the phosphorylic unit (see Table 3) is consistent, and likely conforms to similar structural influences as those controlling the siloxy environments.

E. THE NATURE OF THE PHOSPHORYLIC BOND

The structure and chemistry of the phosphorylic compounds have long been interpreted in terms of the hypervalent Lewis structure **1**, and text books invariably describe the multiple bond as arising from an interaction of a π-type d orbital on the phosphorus centre with a p orbital on the E centre **3**. However, phosphorylic systems are also frequently illustrated as Lewis structure **4** containing polar P—E bonds, most commonly used for methylene–phosphorane ylides. Indeed, the bond polarity is instrumental in the rationale of ylide reactivity.



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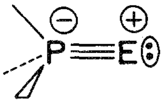

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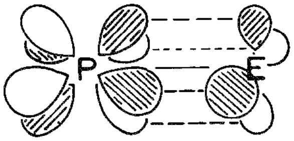

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The degree of bond polarity and the magnitude of the π-interaction has been a point of much discussion. Many theoreticians propose a significant degree of π-back donation from the E centre into the d orbitals of phosphorus [111–116] while others suggest that the best simple electronic representation is the dipolar structure **4**, with minimal π-bonding [117–119]. Irrespective of the magnitude of π-interaction between P and E, there is an important distinction to be made regarding the availability of π-electrons. The methylene–phosphorane system possesses only two π-electrons, while the imino- and chalcogenophosphorylic systems have four π-type electrons available. In this context, Wallmeier and Kutzelnigg recognised the potential for triple bond character in the phosphorylic unit [114,120]. In fact, the axial three-fold symmetry of the phosphoryl (R_3PE, C_{3v}) group imposes a degeneracy on the two π-

type d orbitals of phosphorus, as well as the two π-type p orbitals of the E centre **3**. Therefore, the common valence bond picture **1** is invalid on symmetry grounds. A more accurate model is a combination of two zwitterionic resonance structures, one involving a phosphonium centre with a P—E single bond **4** and the other a phosphoranyl system having a triple bond **5**.

From a structural viewpoint, one can envisage a linear geometry for the nitrogen centre of the iminophosphorylic system. While typical non-linear VSEPR geometries environments are generally observed for nitrogen, the potential for linearity is demonstrated by the coordination complexes of the iminophosphoranyl anion. In terms of illustration **3**, and Lewis structures **4** and **5**, the chalcogen centre of a chalcogenophosphoryl unit can be considered isolobal with the atomic centres in CO, NO^+, CN^- and N_2. The structure of the chalcogenophosphorylic system is unable to exhibit consequences of a triple P—Ch bond, nevertheless, the nature of the bond is manifest in the coordinative behaviour of the system.

F. MODES OF COORDINATION

A number of factors control the coordination geometry of a ligand, however electronic factors will dominate in sterically unrestricted systems. LePage and Wiberg [121] and others [122] have evaluated several potential modes of coordination for the organocarbonyl unit and recognised the bent σ-coordination (in the carbon trigonal plane) as the most favourable geometry, consistent with a simple VSEPR model. However, the angle of coordination (angle at oxygen) exhibits flexibility involving small energy changes and steric effects are easily accommodated by an increase in the bond angle. Indeed, the organocarbonyl unit is observed to adopt a range of coordination geometries, including π-complexation in $[Os(NH_3)_5(OCMe_2)]^{2+}$ [123]. The short Al—O bonds and close-to-linear oxygen environments enforced by sterically bulky alkoxides have been theorised to involve empty p orbitals on aluminium in the form of Al—X σ^* antibonding molecular orbitals, with the realisation that the unoccupied 3d orbitals of aluminium are of too high energy to contribute to the Al—O π-bonding [104].

The vast range of coordination geometries observed for the chalcogenophosphorylic unit (catalogued in Table 2) fall into two general categories. Oxophosphorylic systems adopt angles at oxygen ranging 140°–180°, which may be considered as "end-on" coordination, while the thio- and seleno-phosphorylic systems adopt angles ranging from 115° to 98°, considered as "side-on" geometries. Distinction between the two modes of coordination is exemplified in a variety of features:

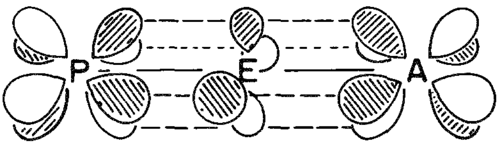
(a) There are no examples of systems exhibiting angles ranging from 115° to 135°.

(b) Coordination induces a significant ^{31}P chemical shift for the oxo-phosphorylic systems, which is not observed for the corresponding thio-and seleno- systems.

(c) The oxophosphorylic unit exhibits (IR shift and bond length increase) a less dramatic disruption of the phosphorylic bond (P—E) as a result of coordination in comparison to the corresponding thio- and seleno-phosphorylic systems.

The "end-on" coordination can be envisaged in terms of donation of the axial σ-type (in the bond axis) electron pair on oxygen (classically referred to as σ-complexation or Werner coordination). However, the linear geometry is apparently enforced by two π-interactions. Such coordination may be viewed as a six-electron donation from oxygen **6**, although the origin of the bonding electrons is of little consequence in establishing the structure of the final complex. Indeed, a useful relationship can be made to the rare phosphinocarbyne complexes, which contain a carbon–metal triple bond and a close-to-linear carbon centre [124].

The "side-on" coordination can be envisaged in terms of donation of the π-type bonding pairs (classically referred to as π-complexation). The polarisation of the π-cloud onto the chalcogen affects a stronger interaction with the acceptor and therefore precludes an equidistant (P—M is dramatically longer than E—M) π-complexation of the P—E bond. Moreover, the three-dimensional steric components of the tetracoordinate phosphorus centres likely define a steric limit for the approach of the ligand toward the metal. Tricoordinate phosphoranes (formally phosphorylic units, containing a P—E multiple bond) contain less sterically burdened phosphorylic bonds and coordinate in a more symmetric fashion, a more conventional "side-on" coordination (see, for example, ref. 125).



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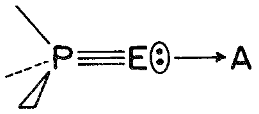

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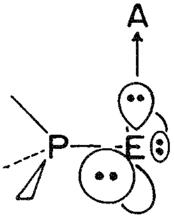

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One may conclude that the preference for σ-complexation observed by the oxophosphorylic units is a consequence of effective π-bonding between the phosphorus and oxygen centres, which renders the σ-type non-bonding electron pair most accessible for donation **7**. Phosphorus–chalcogen π-bonding is theorised to be less pronounced in the thiophosphorylic unit [113], and the electronic structure is most accurately denoted by the polar representation **3**. The experimental data is consistent in terms of the π-type bonding pairs being most available for donation **8**.

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