Fourier-transform Heteronuclear Magnetic Triple Resonance in Complex Spin Systems. Part 2.† Acyclic Ditertiary Phosphines and their Selenides

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Phosphorus–phosphorus nuclear spin–spin coupling has been studied in a series of symmetrical bis(diphenylphosphino)-compounds with aliphatic, olefinic, and acetylenic carbon groups linking the two phosphorus atoms. ^{13}C-{^1H,^{31}P} and ^{31}P-{^1H,^{77}Se} magnetic triple resonance experiments allow the signs of these coupling constants to be obtained, and in some cases prove essential for the measurement of their magnitudes. Different patterns of behaviour clearly emerge for phosphorus in the +3 and +5 oxidation states. In the diselenide series the various geminal and vicinal couplings show marked similarities in their trends to the much more extensively studied couplings J(HH) and $J(P^{Y}H)$. When, however, at least one of the phosphorus atoms possesses a lone pair of electrons the same rules no longer apply, and certain conformations (frequently the most favoured ones) apparently make an exceptionally large positive contribution to the coupling constant. Factors affecting selenium-77 shielding in the selenides and diselenides are discussed.

Many types of nuclear spin coupling constant are sensitive to molecular conformation and configuration, and in particular those involving phosphorus-31 have been used frequently to derive features of molecular geometry.[1] The primary aim of the present study is the determination of the magnitudes and signs of $^{n}J(^{31}P-^{31}P)$ (n = 2—4) for a series of ditertiary diphosphines and their mono- and di-selenides, $Ph_2P(Y)XP(Z)Ph_2$, with X, Y, and Z as designated in Table 1. Considerable effort has gone into the measurement of $^{n}J(^{31}P-^{31}P)$ in organophosphorus transition-metal complexes and in the free ligands. However, much of this work has depended on the synthesis of asymmetrical diphosphines to permit direct measurements of $J(^{31}P-^{31}P)$ from their ^{31}P spectra.[2,3] These syntheses are often lengthy and the ligands are therefore not readily available. However, the symmetrical ligands (1a), (3a), (5a), and (7a) are amongst the most commonly used in this field, and it is of considerable interest to compare the values of $J(^{31}P-^{31}P)$ in these free ligands with those in complexes where the ligand may act in a chelating, a bridging, or a monodentate fashion.[4] In addition, the co-ordination chemistry of the ligand (2a) is currently under investigation in our laboratory, and some work has also been carried out on complexes of the monoselenide (1b).[5]

Methods of determining $J(^{31}P-^{31}P)$ in symmetrical compounds using ^1H-{^{31}P} double resonance experiments were developed some years ago.[6] Their success depends upon the existence of *magnetic* inequivalence between the two chemically equivalent phosphorus nuclei, and the indirect detection of extremely weak phosphorus transitions while observing specific strong proton lines. The determination of $^{2}J(^{31}P-^{31}P)$ in this way for (1a) has been described in detail.[7] However, the complexity of the proton spectra of (2a)—(7a) means that it is very difficult or impossible to apply this method to them, and we have therefore used ^{13}C-{^{31}P,^1H} triple resonance experiments which take advantage of the spectral simplification brought about in both ^{13}C and ^{31}P spectra by broad-band proton decoupling and by the low natural abundance of carbon-13. This technique was previously described[8] in connection with the determination of the sign of $^{1}J(^{31}P-^{31}P)$ in tetramethyldiphosphine disulphide. Although the magnitude of $J(^{31}P-^{31}P)$ may be determined by inspection of the ^{31}P spectra of the monoselenides [and of the diselenides when ^{77}Se satellites ($I = \frac{1}{2}$, natural abundance 7%) are considered], additional heteronuclear triple resonance experiments of the type ^{31}P-{^{77}Se,^1H} were performed in order to determine the relative signs of the $^{31}P-^{31}P$ and $^{77}Se-^{31}P$ coupling constants. These experiments also gave the selenium-77 chemical shifts, and trends in these are discussed.

Table 1. Compound numbering for $Ph_2P(Y)XP(Z)Ph_2$

Compound number	Bridging group X
(1)	CH_2
(2)	$C=CH_2$
(3)	$-CH_2CH_2-$
(4)	*trans*-CH=CH-
(5)	*cis*-CH=CH-
(6)	$-C\equiv C-$
(7)	$-CH_2CH_2CH_2-$

Compound letter	Substituent Y	Z
(a)	Lone pair	Lone pair
(b)	Lone pair	Se
(c)	Se	Se

Results

Diphosphines.—The required $^{n}J(^{31}P-^{31}P)$ values for the diphosphines (1a)—(7a) were most readily obtained from the various AXX′ spectra given by their phenyl groups. It was usually necessary to study both the ^{13}C (A) spectra and the ^{13}C satellites in the ^{31}P (X,X′) spectra. However, for certain combinations of parameters [particularly for large values of $J(^{31}P-^{31}P)$] a full analysis was not always possible, because certain lines were too weak to be observed directly. The use of multiple resonance methods as described here can overcome these problems. In the analysis of AXX′ systems it is conventional to define the quantities $N = J(AX) + J(AX')$, $L = J(AX) - J(AX')$, and $J = J(XX')$. Typical spectra are shown schematically in Figure 1. Descriptions of the general features of such spin systems are to be found in the standard texts but it should be remembered that in the present case the difficulty of locating the very weak lines in the ^{31}P spectrum is aggravated by the presence of the very strong central peak leading to

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† Part 1 is ref. 25.

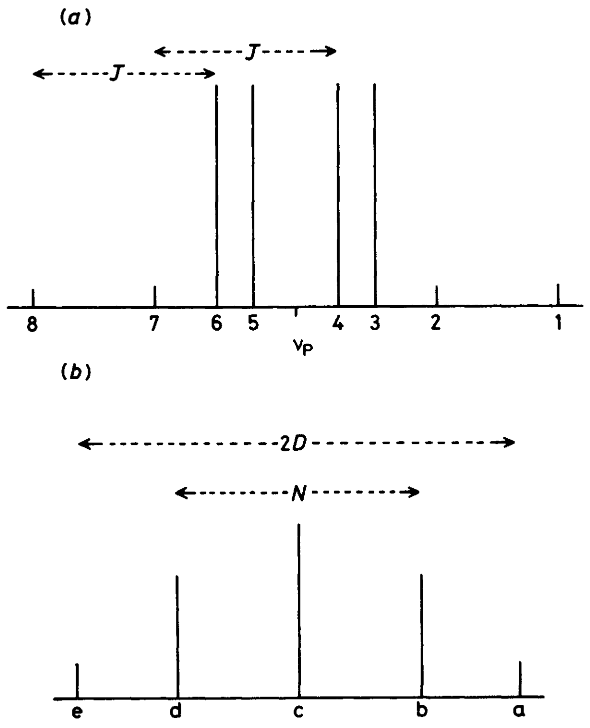


Figure 1. Schematic spectra of an AXX′ spin system appropriate to the C^2 carbons of, for example, (4a) with A = ^{13}C; X and X′ = ^{31}P. Frequency increases from right to left and the parameters used are $N = L = 20, J = 15$ Hz: (*a*) ^{31}P spectrum, (*b*) ^{13}C spectrum

Table 2. Carbon-13 n.m.r. data for the aromatic groups of compounds (1a)—(7a) and (1c)—(7c)

Compound [a]	δ(^{13}C)/p.p.m.[b]				$N(^{31}P-^{13}C)$/Hz [c]			
	C^1	C^2	C^3	C^4	C^1	C^2	C^3	C^4
(1a)	139.1	133.1	128.6	128.9	6.3	20.8	7.2	<1
(1c)	130.1	132.0	128.0	131.4	77.4 [d]	11.2	12.6	3.2
(2a)	136.0	134.4	128.5	129.0	9.2	21.4	7.8	<1
(2c)	131.8	133.2	127.8	131.5	78.6 [e]	11.2	13.2	3.0
(3a)	138.9	133.1	128.8	129.0	14.6	19.1	5.8	<1
(3c)	130.0	131.2	128.5	131.5	73.2	10.8	12.2	2.8
(4a)	137.0	133.1	128.3	128.6	8.5	19.6 [f]	7.4	<1
(4c)	130.5	131.5	128.7	131.8	78.6	10.8	12.7	2.0
(5a)	138.2	133.0	128.6	128.6	6.8	19.6	6.8	<1
(5c)	129.9	132.0	128.4	131.3	77.9 [g]	11.2	12.8	3.0
(6a)	136.2	133.0	128.9	129.3	4.9 [h]	21.5 [i]	7.8 [j]	<1
(6c)	130.0	131.1	128.7	132.2	87.6 [k]	12.5	14.0	3.3
(7a)	139.1	132.9	128.6	128.7	13.7	18.5	6.3	<1
(7c)	131.0	131.2	128.4	131.4	72.0	9.8	11.0	2.5

[a] Compounds (1a)—(7a) in CH_2Cl_2–C_6D_6 (9 : 1, v/v); compounds (1c)—(7c) in $CDCl_3$. [b] To high frequency of $SiMe_4$. [c] $N(^{31}P^{13}C^m) = |^mJ(^{31}P-^{13}C) + {}^nJ(^{31}P-^{13}C)|$: $n = m + 2$, compounds (1) and (2); $n = m + 3$, compounds (3)—(6); $n = m + 4$, compounds (7). [d] $^1J = 75.6$, $^3J = 1.8$. [e] $^1J = 79.0$, $^3J = -0.4$. [f] $^2J = 19.6$, $^5J = 0$. [g] $^1J = 78.2$, $^4J = -0.3$. [h] $^1J = 6.5$, $^4J = -1.6$. [i] $^2J = 21.3$, $^5J = 0.2$. [j] $^3J = 7.6$, $^6J = 0.2$. [k] $^1J = 88.0$, $^4J = -0.4$.

problems of dynamic range, spinning sidebands, *etc.* For this reason a full analysis is most likely to be possible when the value of L is large.

The phenyl groups in compounds (1a)—(7a) all give rise to rather similar ^{13}C spectra, as summarised in Table 2. For C^2, C^3, and C^4 it is a good approximation to take $N = L = J(AX)$ since one of the coupling constants, $J(AX')$, will always involve coupling over at least four bonds and will therefore be small. For example, in three cases where a full analysis was possible it was found that $|^5J(C^2P)| < 0.2$ Hz [in (4a) and (6a)] and $|^6J(C^2P)| < 0.3$ Hz [in (7a)]. It can therefore be seen that the best opportunity of detecting the D lines will be provided by the ^{13}C resonances of the *ortho*-carbons since these have the largest values of N (and hence of L) of *ca.* 20 Hz. Equally, the ^{13}C satellites arising from these carbons will provide the best hope of measuring $J(^{31}P-^{31}P)$ directly from the ^{31}P spectrum. For compounds with $|J(^{31}P-^{31}P)| < 20$ Hz it was indeed possible to measure this coupling in this way. In addition, the D lines could be found in the ^{13}C spectrum of the C^2 resonance of (3a) and the assumption $N = L$ allowed a value of $^3J(^{31}P-^{31}P)$ to be obtained (which was subsequently verified by multiple resonance).

For (1a), (2a), and (5a), none of the required weak lines could be detected in the ^{13}C or ^{31}P spectra even after extended accumulation times, so that $^{13}C-\{^{31}P,^1H\}$ triple resonance experiments had to be used to locate lines 1 and 8 indirectly, by observing the effects of ^{31}P irradiation on the N lines (b and d) of the C^2 resonance. Levels of the irradiating r.f. (radiofrequency) field, B_2, appropriate to tickling experiments were used, although the low transition probabilities of the irradiated transitions meant that rather higher levels were required than in the case of first-order spectra,[9] and care was taken to avoid simultaneous perturbations due to off-resonance irradiation of the strong inner lines (3—6) in the ^{31}P spectra. These experiments also gave the sign of $J(^{31}P-^{31}P)$ relative to that of N as explained previously.[8] Irradiation of line 1 perturbs either line b or line d: if line b is perturbed then N and J have the same sign, if line d is perturbed, then the signs are opposite. A series of separate $^{13}C-\{^1H\}$ experiments using low-power continuous-wave unmodulated proton irradiation demonstrated that in this class of compounds the signs of $N(^{31}P-^{13}C^2)$ [effectively $^2J(^{31}P-^{13}C)$] and $^3J(^{31}P-H)$ were the same, and N is therefore positive in agreement with earlier results on, for example, triphenylphosphine.[10]

Similar $^{13}C-\{^{31}P,^1H\}$ experiments gave the signs of $J(^{31}P-^{31}P)$ in (3a), (4a), and (6a), although here the experiments were rather easier since the precise frequencies for irradiation were known beforehand and only the level of B_2 had to be adjusted. For (7a), J was found to be small and it was not possible to resolve the line separations a–b and d–e. Consideration of the

Table 3. Carbon-13 n.m.r. data for bridging groups

Bridging group	Compound [a]	$\delta(^{13}C)$ [b]	$J(^{31}PY^{13}C)$/Hz [c]	Y
$-CH_2-$	(1a)	28.5	−22.9	l.p.
	(1b)	34.6	−31.5	l.p.
			+47.6	Se
	(1c)	37.8	36.0	Se
$>C'=C''H_2$	(2a)	148.4 (C′), 135.5 (C″)	36.4, 8.1	l.p.
	(2b)	142.6 (C′), 144.2 (C″)	−44.0, 5.0	l.p.
			+50.6, <1	Se
	(2c)	144.1 (C′), 154.6 (C″)	44.9, 3.9	Se
$-(CH_2)_2-$	(3a)	24.4	(±) 16.1, (∓) 16.1 [d]	l.p.
	(3b)	21.2, 28.9	15.6, 19.3	l.p.
			2.4, 47.6	Se
	(3c)	25.9	(+) 50.5, (−) 0.8 [e]	Se
trans-C=C	(4a)	142.2	(±) 20.1, (∓) 18.9 [f]	l.p.
	(4b)	152.5, ?	26.4, ?	l.p.
			0, ?	Se
	(4c)	142.1	(+) 61.0, (+) 5.4 [e]	Se
cis-C=C	(5a)	146.7	15.6 [g]	l.p.
	(5b)	149.6, 139.6	−23.4, +23.8	l.p.
			1.2, 73.6	Se
	(5c)	136.6	(+) 69.5, (−) 3.1 [e]	Se
$-C\equiv C-$	(6a)	107.7	(±) 16.3, (±) 2.3 [f]	l.p.
	(6b)	108.3, 97.6	15.9, 4.0	l.p.
			27.8, 127.3	Se
	(6c)	97.3	(+) 112.3, (−) 10.7 [e]	Se
$-C'H_2C''H_2C'H_2-$	(7a)	29.7 (C′), 22.7 (C″)	12.2, 12.2 (C′)	l.p.
			17.1 (C″)	l.p.
	(7c)	31.7 (C′), 17.2 (C″)	50.0, 12.2 (C′)	Se
			<2 (C″)	Se

[a] Diphosphines in $CH_2Cl_2–C_6D_6$ (9 : 1, v/v), mono- and di-selenides in $CDCl_3$. [b] In p.p.m. to high frequency of $SiMe_4$. [c] Relative signs of coupling constants, arising from spectral analysis, are given in parentheses; if a sign has been determined by multiple resonance, no brackets are used. [d] $|^1J| = |^2J|$, but of opposite sign; assignment uncertain. [e] Quoted as $^1J,^2J$. [f] Quoted as $^1J,^2J$, but assignment uncertain. [g] $|^1J + {}^2J|$.

energy-level diagram [8] for the AXX′ spin system shows that, in the case where N and J are of the same sign, irradiation of the ^{31}P line at highest frequency will affect both lines d and a, and thus the failure to resolve the N lines from the D lines makes the determination of the relative signs of N and J impracticable in this case.

Once $J(^{31}P–^{31}P)$ is known it is frequently possible to analyse also the AXX′ spin systems given by the bridging carbons, and thus obtain J(AX) and J(AX′) for these. However, unambiguous assignments are not always possible since, for diphosphines, $^1J(^{31}P–^{13}C)$ and $^2J(^{31}P–^{13}C)$ commonly have similar magnitudes. Carbon-13 chemical shifts and coupling constants for these bridging groups are given in Table 3.

Diselenides.—The analysis of ^{77}Se satellite patterns as AXX′ spectra (A = ^{77}Se, X,X′ = ^{31}P) has been dealt with previously [11] so we confine ourselves here to a description of the $^{31}P-\{^{77}Se,^1H\}$ multiple resonance experiment necessary to obtain the sign of J. There are similarities to the experiments described in the last section (with the difference that here X is observed and A is irradiated) and the experiments could be treated in the same way by reference to the energy-level diagram.[8] However, the relative magnitudes of the parameters [large $^1J(^{31}P–^{77}Se)$, *ca.* 750 Hz; small $^nJ(^{31}P–^{77}Se)$, *ca.* 1 Hz] make it possible to treat the problem in first-order terms. Figure 2 shows typical ^{77}Se and ^{31}P spectra in schematic form.

The 'outer' ^{77}Se satellites (lines 1, 2, 7, and 8) may be thought of as arising essentially from $^{31}P(X)$ with an effective chemical shift of $\nu_P \pm \frac{1}{2} \cdot {}^1J(^{31}P–^{77}Se)$, and the 'inner' satellites are then resonances of P(X′) with effective chemical shifts of $\nu_P \pm \frac{1}{2} \cdot {}^nJ(^{31}P–^{77}Se)$ which will be very close to ν_P.

In general, observations of the outer ^{77}Se satellites in the

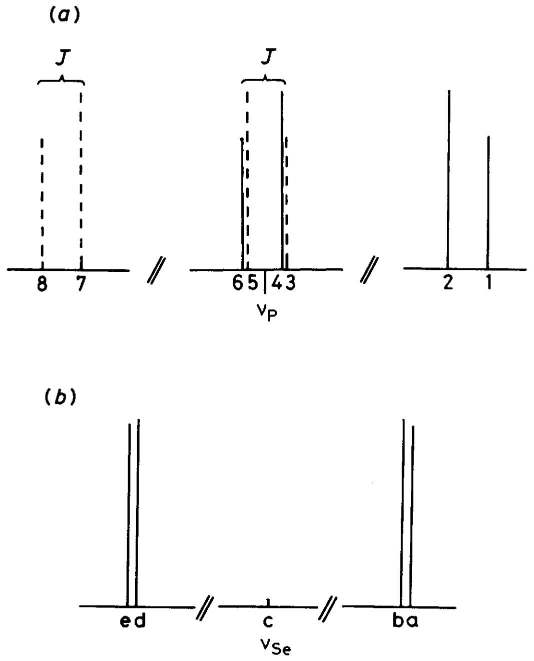


Figure 2. Schematic spectra of an AXX′ spin system appropriate to, for example, (4c) with A = ^{77}Se; X and X′ = ^{31}P. Frequency increases from right to left and the parameters used are $N = -749$, $L = -751$, $J = 60$ Hz: (*a*) ^{31}P spectrum with transitions associated with one spin state of ^{77}Se shown by broken lines, (*b*) ^{77}Se spectrum

Table 4. Phosphorus-31 and ^{77}Se n.m.r. data

Compound [a]	J(PP)/Hz	$\delta(^{31}P)$ [b]	$\delta(^{77}Se)$ [c]	^{1}J(PSe)/Hz	^{n}J(PSe)/Hz [d]
(1a)	+125	−21.6			
(1b)	+84.8	−27.3, 30.9 [e]	−289.3	−725.1	+14.3
(1c)	−17.3	25.1	−240.0	−744.4	−2.6
(2a)	+98	−3.9			
(2b)	+91.9	−14.6, 39.2 [e]	−277.4	−752.4	<1
(2c)	+25.0	38.4	−235.2	−756.9	−2.9
(3a)	+33.6	−13.2			
(3b)	(+) 49.3 [f]	−14, 36.4 [e]	(−358.8) [g]	−749.3	(0) [g]
(3c)	+64.7	35.9	−352.3	−730.4	+0.9
(4a)	+13.4	−8.4			
(4b)	(+) 18.3 [f]	−7.1, 29.6 [e]	−335.8	−758.0	<1
(4c)	+60.3	28.6	−324.7	−750.9	+0.5
(5a)	+105.5	−23.1			
(5b)	+23.8	−29.0, 20.9 [e]	−249.7	−751.6	+19.3
(5c)	+19.5	22.6	−277.8	−735.2	+0.4
(6a)	−6.1	−32.3			
(6b)	6.6 [f]	−33.4, 5.7 [e]	−226.4	−761.1	<1
(6c)	+5.3	7.5	−237.6	−774.9	0
(7a)	1.0 [f]	−17.5			
(7b)	1.5 [f]	−18.9, 33.2 [e]	−354.0	−741	0
(7c)	0	33.3	−341.8 [h]	−723 [h]	0

[a] Phosphines in CH_2Cl_2–C_6D_6 (9 : 1, v/v); monoselenides in C_6H_6–C_6D_6 (9 : 1, v/v); diselenides in $CDCl_3$. [b] In p.p.m. to high frequency of 85% H_3PO_4. [c] In p.p.m. to high frequency of $SeMe_2$. [d] n = 3, 4, or 5 depending on the compound. [e] Quoted as $\delta(^{31}P^{III})$, $\delta(^{31}P^{V})$. [f] Sign not determined. [g] From ref. 39 (measured in CH_2Cl_2). [h] In C_6H_6 δ(Se) = −353.7 p.p.m.; ^{1}J(PSe) = −738.5 Hz.

^{31}P spectrum permits comparison of $J(^{31}P-^{31}P)$ with $^{n}J(^{31}P-^{77}Se)$, using $^{31}P-\{^{77}Se\}$ tickling experiments, whilst the inner satellites must be observed in order to compare $^{1}J(^{31}P-^{77}Se)$ with $J(^{31}P-^{31}P)$. Often, analysis alone can yield the relative signs of $^{1}J(^{31}P-^{77}Se)$ and $^{n}J(^{31}P-^{77}Se)$ and then, strictly speaking, only one of these experiments in necessary. It is well established [11] that the sign of $^{1}J(^{31}P-^{77}Se)$ is negative in this type of compound, hence these experiments give the absolute sign of $J(^{31}P-^{31}P)$.

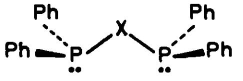
Monoselenides.—In compounds with $^{n}J(^{31}P-^{77}Se)$ non-zero the sign of $J(^{31}P-^{31}P)$ could be obtained by standard $^{31}P-\{^{77}Se,^{1}H\}$ multiple resonance techniques for an AMX spin system (A = $^{31}P^{III}$, M = $^{31}P^{V}$, X = ^{77}Se). In the event that $^{n}J(^{77}Se-^{31}P)$ = 0, $^{13}C-\{^{31}P,^{1}H\}$ experiments were carried out for some of the compounds, and the sign of $J(^{31}P-^{31}P)$ was compared with that of a $J(^{31}P-^{13}C)$ of known sign, for example, $^{1}J(^{31}P^{V}-^{13}C)$ which may be reliably taken as positive.[12]

Discussion

^{2}J(PCP) *Coupling.*—The results given in Table 4 permit the comparison of values of the geminal phosphorus–phosphorus coupling constant for the three classes of compound and show how these are affected by a change in the hybridisation of the intermediate carbon atom from sp^3 to sp^2. When one of the phosphorus atoms possesses a non-bonding pair of electrons the coupling constant is found to be positive both for sp^3 and for sp^2 carbon, although there is some reduction in magnitude accompanying conversion of one phosphorus to the P^{V} oxidation state. When both phosphorus atoms are P^{V} further reduction in magnitude of $^{2}J(^{31}P-^{31}P)$ occurs, but there is also a sign inversion on going from sp^3 carbon (J negative) to sp^2 (J positive). This behaviour is reminiscent of the pattern found for ^{2}J(HCH) which changes from negative to positive when, for example, methane is compared with ethylene,[13] and also for $^{2}J(^{31}P^{V}-CH)$ where J is again negative for saturated carbon [12] but positive for ethylenic carbon.[14] The results for $^{2}J(^{31}P^{V}-CH)$ and $^{2}J(^{31}P^{V}C^{31}P^{V})$ suggest that a similar mechanism [15] may be involved in the two cases.

It is generally accepted that in P^{V} compounds the phosphorus hybridisation is close to sp^3, whereas for P^{III} the electrons in the 3s orbital are of fairly low energy and the hybridisation is closer to p^3. The negative values for most one-bond reduced coupling constants involving P^{III} are usually attributed to this low energy.[16] Theoretical calculations [17] of $^{1}J(^{31}P-^{13}C)$ and $^{2}J(^{31}PCH)$ using the Finite Perturbation method have been quite successful for phosphonium salts, phosphine oxides, and sulphides, but not for phosphines themselves. This may partly be due to neglect of conformational effects on coupling constants, specifically the experimentally well established influence of the lone pair –P–C–H dihedral angle (φ) on $^{2}J(^{31}P^{III}CH)$. It has been found [18,19] that for both sp^3 and sp^2 intermediary carbon, large positive values of the coupling are associated with values of φ = 0°, whereas small (possibly negative) couplings arise when φ = 180°.

Discussion of geminal $^{2}J(^{31}P^{III}X^{31}P^{III})$ coupling constants has mostly been concerned with the diphosphinoamines (X = NR) and has considered the contribution to the observed values from conformations such as I, II, and III.[20,21]



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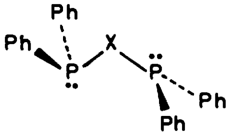

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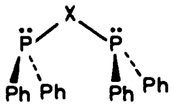
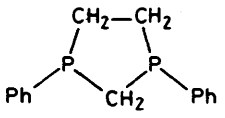


III

It has been shown convincingly, by a combination of X-ray and low-temperature n.m.r. studies,[22] that conformation II is associated with low (negative) values of $^{2}J(^{31}P-^{31}P)$, whereas I gives rise to large positive values. Conformer II tends to predominate when X carries a bulky group (R = Pr^i or Bu^t), presumably as a result of steric interaction between R and the other phosphorus substituents in conformer I.

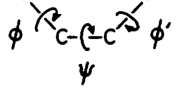
There is also much evidence that $^2J(^{31}PC^{31}P)$ shows the same sort of angular variation as $^2J(^{31}PCH)$ and $^2J(^{31}PN^{31}P)$; for example, the different values of $^2J(^{31}P-^{31}P)$ found [23] in the *meso* and *rac* isomers of $CH_2(PMePh)_2$ can be explained in this way, and we have also found [24] very small values (2 and 6 Hz) of $^2J(^{31}P-^{31}P)$ for both isomers of IV in which φ may be expected to be greater than 90°. The large positive values of $^2J(^{31}P-^{31}P)$ found for (1a) and (2a) therefore suggest that conformer I is a major contributor. It is noteworthy in this connection that in $CH(PPh_2)_3$ it is not geometrically possible for all three phosphorus–phosphorus relationships simultaneously to have the conformation I, and this is reflected in a smaller value of $^2J(^{31}P-^{31}P)$ in this molecule.[25]



IV

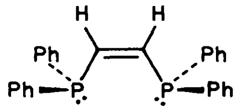
The fairly high positive values of $^2J(^{31}P-^{31}P)$ found for (1b) and (2b) may be taken as evidence that conformer I (with one lone pair replaced by selenium) is also important in the monoselenides. We have in fact noted [26] even greater values of $^2J(^{31}P^{III}C^{31}P^{V})$ in selenium derivatives of $(Ph_2P)_2CHCH_2$-PPh_2 in which the conformational imbalance is probably more marked than in (1b). When the intervening atom is sp^2 hybridised nitrogen rather than carbon the $(^{31}P^{III}X^{31}P^{III})$ couplings are somewhat larger [21,22] [*e.g.* $N(PPh_2)_2Me$, 280 Hz; NH-$(PPh_2)_2$, 175 Hz; *cf.* (2a), 98 Hz] but for $(P^{III}X^{31}P^{V})$ coupling the values are rather similar (80—90 Hz). An interpretation [27] of this is that large positive values of $^2J(^{31}P^{III}X^{31}P^{III})$ are favoured when the phosphorus–phosphorus distance is small, and the known shortening of the P–N bonds together with the narrowing of the PNP angle to less than 120° in the phosphinoamines [22] will lead to the P · · · P distance being shorter in this class of compounds than in (2a).

^3J(PCCP) *Coupling*.—Studies of vicinal P–H [28] and P–C [29] coupling make it reasonable to expect a Karplus type of dependence of $^3J(^{31}PCC^{31}P)$ coupling on dihedral angle ψ, defined as in V, and this is indeed so for the $^3J(^{31}P^{V}CC^{31}P^{V})$ coupling; for example, for the ethylenic derivatives (4c) and (5c) it is found that $J_{trans} > J_{cis}$. For the ethane derivative (3c) the value of $^3J(^{31}P-^{31}P)$ is even greater than in the *trans*-ethylene compound (4c). This is rather surprising if the observed coupling constant in (3c) is a result of averaging over different conformations [*cf.* vicinal (H,H) coupling, in ethane and ethylene [13]] and suggests that there is a preponderance of the conformer with phosphorus atoms mutually *trans* in (3c).

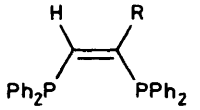


V

In the diphosphines the ' conventional ' dependence of coupling constant on dihedral angle [28] does not hold, as demonstrated by the result $J_{cis}(5a) \gg J_{trans}(4a)$. This can be accounted for in terms of lone-pair (l.p.) orientation effects (*i.e.* the lone pair ⁻P–C–C dihedral angles φ and φ′, see V) and has previously been observed [30,31] experimentally for the coupling $^3J(^{31}PCCH)$. By analogy with these results it is to be expected that large positive values of $^3J(^{31}P-^{31}P)$ will arise when the angles φ and φ′ are both small. Therefore a conformation such as VI seems most likely for (5a) (^3J = 105 Hz). Molecular models suggest that the need to minimise interactions between the phenyl groups is responsible for the adoption of this conformation, but in the *trans* isomer, (4a), the two diphenylphosphino-groups are sufficiently far apart to allow essentially free rotation about the two olefin C–P bonds. Direct measurements of ^{31}P spectra have allowed other workers [32] to obtain the magnitude of $^3J(^{31}P-^{31}P)$ for unsymmetrical compounds of type VII. $|^3J(^{31}P-^{31}P)|$ was found to be >100 Hz for R = Ph or CF_3 but it was only 37 Hz for R = Bu^t. The reduction in the latter case may be explained by steric interactions between the bulky alkyl group and the phenyl substituents causing a twisting of the lone pair out of the PCCP plane.



VI



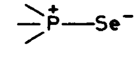
VII

Compound (6a) with an acetylenic linkage provides a rare example of a negative $^3J(^{31}PCC^{31}P)$ although other cases are known,[33] these also involving trivalent phosphorus atoms in a rigid framework. $^3J(^{31}PCCH)$ has also been found to change from negative to positive in acetylenic phosphorus compounds when the oxidation state of phosphorus increases from three to five.[34] In all the compounds examined here [except (5)] $^3J(^{31}P-^{31}P)$ becomes more positive when each phosphorus is bound to selenium, which is consistent with an increased Fermi-contact contribution to the coupling arising from greater *s* character of the phosphorus hybrid orbitals in the P^V oxidation state.

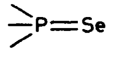
^4J(PCCCP) *Coupling*.—This coupling was found to be very small in (7a)—(7c) thus confirming previous work [2] on unsymmetrical compounds, and supporting the idea that ' backbone ' contributions [2] can be neglected in discussions of phosphorus–phosphorus coupling in transition-metal complexes of (7a) where there is a six-membered chelate ring.

However, a small five-bond $^{31}P-^{31}P$ coupling has been measured [35] in which all the intervening atoms were saturated carbon atoms, and it is reasonable to expect that further long-range couplings will be observed in the future, especially in certain rigid systems where particular geometrical relationships prevail.

^{77}Se *Chemical Shifts and Coupling Constants*.—The ^{77}Se chemical shifts of phosphine selenides occur at the extreme high-shielding end of the selenium chemical shift range.[36] This has been attributed [36] to major contributions from the polar structure VIII since high shielding is known [37] also to be associated with the presence of negatively charged selenium. In previous discussions [36] stress has been laid on the electro-



VIII



IX

negativity and π-bonding ability of the other phosphorus substituents and their influence on the relative importance of canonical forms VIII and IX. The substituents in the present series of compounds are all of rather similar electronegativity, yet a large spread (*ca.* 100 p.p.m.) of ^{77}Se chemical shifts is still observed. In an earlier study[23] we found a 17 p.p.m. difference in ^{77}Se chemical shift between the *meso* and *rac* forms of $CH_2(SePMePh)_2$ and this difference can presumably be attributed to conformational rather than electronic (substituent) effects since other parameters, such as $^1J(^{77}Se-^{31}P)$, which are known[36] to depend on hybridisation and effective nuclear charge, were identical for the two isomers.

For the mono- and di-selenides (1b)—(7b) and (1c)—(7c) the compounds can be crudely divided into two classes according to whether their chemical shift is greater or less than -300 p.p.m. (A more negative chemical shift corresponds to greater shielding.) Examination of molecular models shows that in the less shielded group of compounds [(1b), (1c), (2b), (2c), (5b), (5c)] there must be considerable steric hindrance, whatever conformation is adopted, whereas in (4b), (4c), (7b), (7c), (3b), and (3c) (assuming the *trans* configuration in the latter two compounds, see above) there can be little or no crowding. Furthermore, Dean[38] has found that in the mono- and di-selenides of $Ph_2P(CH_2)_nPPh_2$ there is practically no change in $\delta(^{77}Se)$ for $n = 3$, 4, or 5. It may be that when the two Ph_2P-(Se) groups are close, as in the first set of compounds, the polar form VIII is somewhat disfavoured. Against this must be set the results for the acetylenic derivatives, (6b) and (6c), which have relatively low-field chemical shifts, although their $Ph_2P(Se)$ groups must be well separated. Clearly, the magnetic anisotropy of the acetylene group will give rise to effects an order of magnitude too small to explain the difference, which is not at present understood. Solvent effects on ^{77}Se chemical shifts have been noted[39] (see footnote *h* of Table 4), but were not studied in any detail in the present work. These are probably responsible for small differences between our results and those of Dean.[38]

Values of $^1J(^{77}Se-^{31}P)$ for the compounds studied here cover a rather narrow range (as is to be expected from the similarity of the phosphorus substituents) and do not warrant discussion. However, some interesting points emerge in connection with $^nJ(^{77}Se-^{31}P)$ $(n > 1)$. In the diselenides,[11] $^3J(^{77}Se-^{31}P)$ and $^4J(^{77}Se-^{31}P)$ are both found to be small, but these couplings can assume appreciable values in the monoselenides where they depend critically upon the precise coupling path. For example, in (1b) and (2b) the $^3J(^{77}SePC^{31}P)$ coupling drops from $+14.3$ Hz to zero when an *sp*^{2} hybridised carbon replaces an *sp*^{3} one; and in (5b) the *cis* configuration gives a $^4J(^{77}Se-^{31}P)$ coupling of $+19.3$ Hz, whereas for the *trans* configuration (4b) this coupling is zero. Such relationships should prove useful in future in the assignment of structure in polyphosphorus compounds where initial addition of selenium may take place at any one of a number of phosphorus sites.

Experimental

Ditertiary phosphines with saturated carbon linkages, compounds (1a), (3a), and (7a), were prepared from $NaPPh_2$ in liquid ammonia according to literature methods.[40] The olefinic diphosphines, (4a) and (5a), were prepared from $LiPPh_2$ in tetrahydrofuran (thf). Compound (6a) was purchased from Strem Chemicals Inc. The diselenides were prepared by the reaction of the diphosphine with two atom equivalents of elemental selenium in refluxing benzene. Monoselenides were not purified, but were examined as mixtures resulting from the reaction of the diphosphine with one equivalent of selenium. These solutions usually contained a mixture of diphosphine, monoselenide, and diselenide.

1,1-*Bis(diphenylphosphino)ethene* (2).—Triphenylphosphine (86.8 g, 0.33 mol) and lithium (4.6 g, 0.66 mol) in thf (750 cm^3) were stirred overnight under dinitrogen. The solution was treated with 2-chloro-2-methylpropane (36.5 cm^3, 0.33 mol) to remove phenyl-lithium and was then decanted, under dinitrogen, into a large dropping funnel. The resulting solution of $LiPPh_2$ was slowly added, under dinitrogen, to 1,1-dichloroethene (16.1 g, 0.165 mol) in benzene (50 cm^3). When addition was complete, dilute HCl (200 cm^3) was added, most of the thf was removed by rotary evaporator, and the organic layer was separated with ether. After removal of the solvents an oil remained which crystallised on addition of absolute alcohol. The compound (colourless air-stable crystals) was recrystallised from ethanol (*ca.* 300 cm^3). Yield, 20 g (30%); m.p. 114 °C (Found: C, 79.5; H, 5.6; P, 15.2. $C_{26}H_{22}P_2$ requires C, 78.8; H, 5.6; P. 15.6%). Diselenide: m.p. 188 °C (Found: C, 56.5; H, 4.0; P, 11.2. $C_{26}H_{22}P_2Se_2$ requires C, 56.3; H, 4.0; P, 11.2%).

Carbon-13 (15.03 MHz) and ^{31}P (24.2 MHz) Fourier-transform n.m.r. spectra were obtained with proton decoupling on a JEOL FX60 spectrometer which had been modified to accept additional ^{31}P (24.2 MHz) or ^{77}Se (11.4 MHz) continuous wave irradiating frequencies, as described previously.[8] Samples were examined as saturated solutions in methylene chloride (containing *ca.* 10% C_6D_6 for field/frequency lock), $CDCl_3$, or (for the monoselenide reaction mixtures) benzene.

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