Studies of Organophosphorus Selenides by Heteronuclear Magnetic Triple Resonance

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A heteronuclear magnetic selective triple resonance technique for the determination of chemical shifts in incomplete spin systems is described and applied to the measurement of ^{77}Se chemical shifts in organophosphorus selenides. The results indicate that the dipolar form makes a major contribution to the phosphorus–selenium bond, but π-bonding between phosphorus and selenium is also important. The ^{31}P–^{77}Se spin coupling constants are negative and can be interpreted in terms of the inductive effect of the substituents of the phosphorus atom.

EVIDENCE from various sources indicates that in uncharged molecules of the type R_3PE ($E = O$ or S) there are contributions to the resonance hybrid from the canonical forms (I) and (II), but the relative importance of

$R_3P{=}E$ (I) $R_3P^+{-}E^-$ (II)

these is difficult to assess.[1] The nature of the phosphorus–selenium bond in organophosphorus selenides ($E = Se$) presents the same problem, although this has not previously been discussed specifically. In this paper we report measurements of ^{1}H, ^{31}P, and ^{77}Se chemical shifts and coupling constants in a range of organophosphorus selenides $R^1_2R^2PSe$ (R^1, R^2 = Me, Ph, OMe, or NMe_2) designed to give information on the bonding in these compounds.

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[1] R. F. Hudson, 'Structure and Mechanism in Organophosphorus Chemistry,' Academic Press, London, 1965, ch. 3.

The ^{31}P chemical shifts were determined by standard heteronuclear double resonance techniques[2] which could not, however, be applied to the determination of the ^{77}Se chemical shifts since ${}^{n}J$ (^{77}Se $\cdots$ H) $= 0$ for $n > 2$ in these molecules. A triple resonance technique has therefore been developed which involves simultaneous irradiation of the sample at the ^{31}P and the ^{77}Se resonant frequencies, so that perturbation of the selenium transitions gives an observable effect in the proton spectrum.[3] This is one of the first examples of the use of fully selective triple resonance experiments[4] in which all three nuclei are of different species.

Previously ^{31}P–^{77}Se coupling constants have been reported in P_4Se_3,[5] and in R_2PSeR,[6] and recently data have been obtained for five substituted triaryl[7] and some other phosphine selenides.[8,9] Phosphorus chemical shifts have been reported in a number of phosphine selenides,[9] and there are several papers on selenium chemical shifts in organoselenium compounds.[10,11]

EXPERIMENTAL

The organophosphorus selenides were made by the reaction of the appropriate tervalent phosphorus compounds with elemental selenium and were purified by distillation or recrystallisation.[12] The absence of significant spurious peaks from their proton n.m.r. spectra was used as a criterion of adequate purity.

Proton magnetic resonance spectra were recorded in frequency sweep mode at 60 MHz at 24 °C with neat liquids or concentrated solutions in dichloromethane containing *ca.* 5% Me_4Si to provide a reference signal and to actuate the field frequency locking circuits of the spectrometer. The ^{1}H–{^{31}P} double resonance experiments were performed by standard techniques with a Schlumberger FS-30 frequency synthesiser which was also used to maintain the spectrometer r.f. oscillator at 60 MHz with a precision substantially better than $\pm 0{\cdot}1$ Hz for indefinite periods. For the ^{1}H–{^{31}P, ^{77}Se} triple resonance experiments the frequency synthesiser provided r.f. energy at the ^{77}Se resonant frequency, and a simple quartz crystal oscillator system was used to generate the ^{31}P r.f. irradiating field. The overall arrangement was as shown in Figure 1, and by using audiofrequencies in the kHz range to generate the two r.f. sidebands it was possible to ensure that only one of these could correspond with any ^{31}P transition frequencies. In the unstabilised environment of our laboratory the frequency stability was *ca.* 10^{-8} for periods of several hours, and this was adequate for most experiments. In many applications the two frequency counters can be dispensed with, and the equipment then offers a very economical means of performing ordinary heteronuclear double resonance experiments. The probe of the spectrometer was modified by adding a coil system which was double tuned to accept the phosphorus and selenium resonance frequencies of 24·28 and 11·44 MHz respectively. An unforeseen complication was the fortuitous relation $2\nu({}^{31}P) + \nu({}^{77}Se) = \nu({}^{1}H)$, so that any nonlinearity in the various circuits could lead to the generation of extraneous r.f. power at or near the proton resonant frequency and so give problems of bridge balancing and saturation of the receiver preamplifier. These were avoided by restricting the power applied simultaneously at the phosphorus and selenium resonance frequencies to modest levels. This difficulty should not arise for triple resonance experiments involving many other trios of nuclei, and could have been circumvented by a scheme of time division.

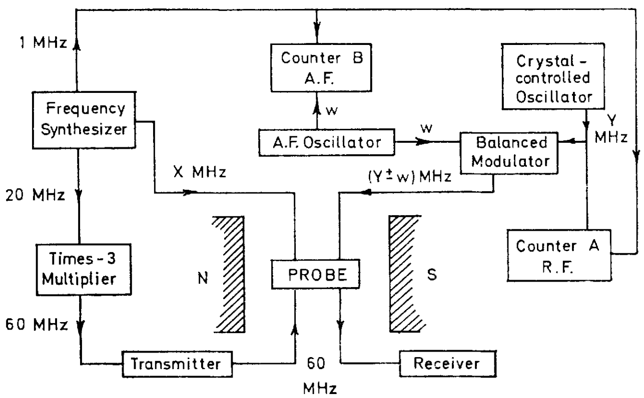

FIGURE 1 Schematic diagram of equipment used for the heteronuclear triple resonance experiments. The frequency counters A and B are needed mainly for initial setting up and can then be dispensed with for many experiments

RESULTS

The signs of the ^{31}P–H coupling constants are based on the results of ^{1}H–{^{13}C} and ^{1}H–{^{31}P} double resonance experiments performed on some of these and other related molecules.[13] It is assumed that ${}^{1}J({}^{13}C–H) > 0$. The ^{31}P chemical shifts are calculated on the basis that $\Xi({}^{31}P)$ for 85% H_3PO_4 is 40,480,790 Hz; and the ^{77}Se shifts on the basis that $\Xi({}^{77}Se)$ for Me_2Se is 19,071,520 Hz.

The only naturally occurring magnetic isotope of selenium is ^{77}Se with $I = \frac{1}{2}$ and an abundance of 7·6%, and in all but two of the compounds studied the coupling between this nucleus and protons is zero. Consequently, lines in the proton spectrum arising from molecules containing non-magnetic and magnetic selenium are exactly superposed (there appears to be a negligible ^{77}Se–^{0}Se isotope effect upon the proton shielding), and irradiation at the ^{77}Se resonant frequency has no effect upon the appearance of the proton spectrum. However, the coupling ${}^{1}J({}^{31}P–{}^{77}Se)$ is substantial, and it is therefore possible to perform independent ^{1}H–{^{31}P} decoupling experiments either upon

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[3] W. McFarlane and D. S. Rycroft, *Chem. Comm.*, 1972, 902.

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[7] R. P. Pinnell, C. A. Megerle, S. L. Mannatt, and P. A. Kroon, *J. Amer. Chem. Soc.*, 1973, **95**, 977.

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[13] W. McFarlane, *Proc. Roy. Soc.*, 1968, *A*, **306**, 185.

species containing magnetic selenium or upon species containing non-magnetic selenium. Examples of this type of experiment performed on trimethyl selenophosphate (7) are shown in Figure 2(b) in which the two sharp lines arising from molecules $(\mathrm{MeO})_3\mathrm{P}^{77}\mathrm{Se}$ can be seen clearly when the main doublet [arising from $(\mathrm{MeO})_3\mathrm{P}^{0}\mathrm{Se}$] is collapsed by irradiation at the centre of the ^{31}P resonance. Figure 2(b) is actually two superposed traces obtained respectively with and without simultaneous irradiation at the ^{77}Se resonance frequency, and their identical appearance confirms that $J(^{77}\mathrm{Se}\cdots\mathrm{H}) = 0$. The ^{31}P spectrum will have ^{77}Se satellites separated by $\pm\frac{1}{2}J(^{31}\mathrm{P}{-}^{77}\mathrm{Se})$ from the central resonance, and irradiation at either of these frequencies can collapse up to 3·8% of the total proton intensity into a line at the centre of the double according to the amplitude of the irradiating r.f. field. This is illustrated in Figure 2(c) and (d) and the difference between the two values of $\nu(^{31}\mathrm{P})$ needed to do this gives $|^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se})|$ to ± 10 Hz. In cases where the phosphorus spectrum is very complex or broad this is the limit of the precision that can be achieved as quite high amplitudes of $\nu(^{31}\mathrm{P})$ are needed, but if the phosphorus spectrum is a simple multiplet as in $(\mathrm{MeO})_3\mathrm{PSe}$ or $\mathrm{Me_3PSe}$ higher precision can be attained by using weaker irradiating fields. By a partial decoupling technique similar to that used in a study [14] of dimethyl phosphite it was possible to determine the positions of the spaces *between* the transitions of the binomial decets in the ^{31}P spectra of $\mathrm{Me_3PSe}$ and $(\mathrm{MeO})_3\mathrm{PSe}$ to $\pm 0{\cdot}2$ Hz and hence to measure $|^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se})|$ to $\pm 0{\cdot}3$ Hz. This is illustrated in Figure 3. The foregoing approach is better than the alternative one of studying variations in the heights of the two main signals in the proton spectrum which occur as the ^{77}Se satellites in the ^{31}P spectrum are irradiated, because the relevant changes can be masked by relatively small random variations in the strength of the signal from molecules containing non-magnetic selenium.

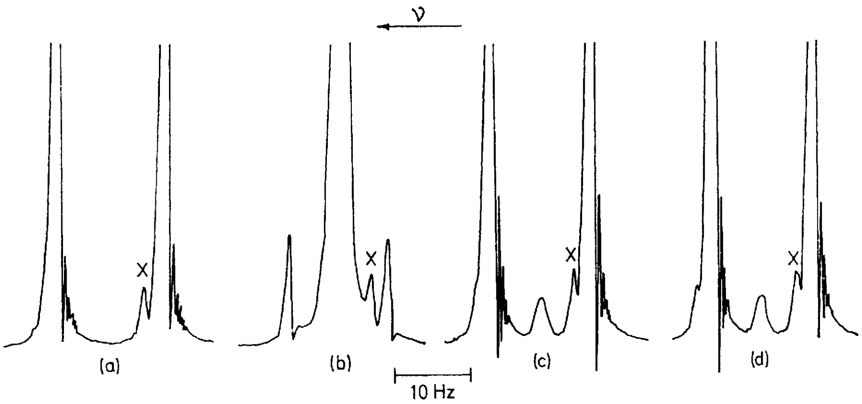

FIGURE 2 ^{31}P Decoupling experiments performed upon trimethyl selenophosphate, $(\mathrm{MeO})_3\mathrm{PSe}$. (a) Normal single resonance proton spectrum at 60 MHz. The peak marked × is due to an impurity present in low concentration. (b) With irradiation at the centre of the phosphorus spectrum to achieve decoupling in molecules containing non-magnetic selenium nuclei and to reveal the signals arising from molecules containing ^{77}Se. (c) With irradiation at a ^{31}P frequency 481·5 Hz [*i.e.*, $\frac{1}{2}{}^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se})$] higher than in (b) to decouple $^3J(^{31}\mathrm{P}\cdots\mathrm{H})$ in half the molecules containing ^{77}Se. (d) With irradiation at a frequency 481·5 Hz lower than in (b) to decouple $^3J(^{31}\mathrm{P}\cdots\mathrm{H})$ in the other half of the molecules containing ^{77}Se

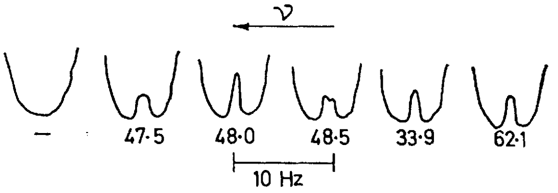

FIGURE 3 ^{31}P Selective decoupling experiments used to give accurately the positions of the lines of the ^{77}Se satellites in the ^{31}P spectrum of $(\mathrm{MeO})_3\mathrm{PSe}$. The region between the lines of the strong doublet in the proton spectrum is shown, and the numbers are the phosphorus irradiation frequencies in Hz *minus* 24,288,200·0 Hz. Optimum collapse is attained when the irradiating frequency is set on the spaces between the transitions. Thus 48·0 Hz represents the (vacant) centre of the binomial decet, and 33·9 and 62·1 Hz correspond to the adjacent spaces

The ^{77}Se spectrum of each of the compounds examined except (15) and (16) is a simple doublet of separation $^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se})$ (= several hundred Hz) and irradiation at the frequency of either of the two lines has no effect upon the proton spectrum because $J(^{77}\mathrm{Se}\cdots\mathrm{H}) = 0$ and ^{77}Se transitions associated with different proton spin states are degenerate.[4] However, such irradiation does split the transitions of the phosphorus spectrum in accordance with the normal spin tickling rules,[15] and consequently when a simultaneous $^1\mathrm{H}{-}\{^{31}\mathrm{P}\}$ tickling experiment is being performed as in Figure 4(b) the former resonance condition in the phosphorus spectrum is destroyed and the perturbed line in the proton spectrum will be split as shown in Figure 4(c)—(e). That is, the splitting in the phosphorus spectrum which is produced by irradiating the selenium resonance is ' transferred ' (with diminished magnitude) to the proton spectrum as in the double resonance experiments of Freeman and Gestblom.[16] Thus the positions of the two lines in the selenium spectrum, and hence the ^{77}Se chemical shift, can be determined to $\pm 0{\cdot}5$ Hz by $^1\mathrm{H}{-}\{^{31}\mathrm{P},^{77}\mathrm{Se}\}$ triple resonance experiments as shown in Figure 4(c)—(e).

In fact, the behaviour normally observed is somewhat

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[14] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 1148.

[15] R. Freeman and W. A. Anderson, *J. Chem. Phys.*, 1962, **37**, 2053.

[16] R. Freeman and B. Gestblom, *J. Chem. Phys.*, 1967, **47**, 1472.

more complicated than that outlined above because irradiation of the phosphorus transitions also splits the lines of the selenium spectrum, and so for most of the molecules examined two pairs of ^{77}Se frequencies were found. The values of $|^1J(^{31}P-^{77}Se)|$ determined from the separations of these pairs agreed within experimental error with those determined by the $^1H-\{^{31}P\}$ experiments described earlier, and the splitting within the pairs was $\gamma(^{31}P)B_2/2\pi$. This was normally 40—150 Hz owing to the complexity of the phosphorus spectrum except in Me$_3$PSe and (MeO)$_3$PSe for which it was possible to use values of only 8 Hz.

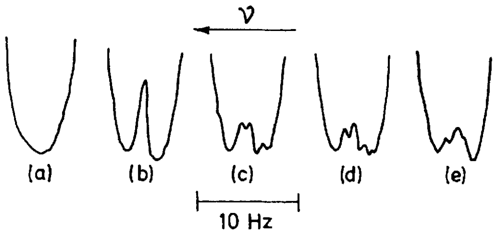

FIGURE 4 $^1H-\{^{31}P,^{77}Se\}$ Triple resonance experiments used to give accurate ^{77}Se line positions for (MeO)$_3$SPe. (a) Region between the components of the strong doublet in the proton spectrum with no irradiation. (b) With simultaneous irradiation at 24,288,248 Hz, corresponding to the centre of one of the ^{77}Se satellites in the phosphorus spectrum. (c) As for (b) but in addition with irradiation at a frequency 0·5 Hz below a line position in the selenium spectrum. (d) As for (c) but with selenium frequency set on resonance. (e) As for (c) but with selenium frequency set 0·5 Hz above exact resonance

N.m.r. parameters of organophosphorus selenides

	Compound [a]	$^2J(^{31}P\cdots{}^1H)$ ($\pm$0·2 Hz)	$^3J(^{31}P\cdots{}^1H)$ ($\pm$0·2 Hz)	$\delta(^1H)$/p.p.m.[b]		$J(^{31}P-^{77}Se)$/ Hz	$\Xi(^{77}Se)$ [e]/Hz	$\delta(^{77}Se)$ [f]/ p.p.m.	$\Xi(^{31}P)$ [e]/Hz	$\delta(^{31}P)$ [f]/ p.p.m.
				c	*d*					
1	Me$_3$PSe [g]	−13·2	—	1·94	—	−684 ± 2	19,067,041 ± 9	−234·9 ± 0·5	40,481,114·1 ± 0·8	+8·01 ± 0·02
2	Me$_2$PhPSe [h]	−13·2	—	2·12	—	−710 ± 10	19,066,338 ± 9	−271·7 ± 0·5	40,481,400 ± 4	+15·1 ± 0·1
3	MePh$_2$PSe [g]	−13·2	—	2·33	—	−725 ± 10	19,066,236 ± 17	−277·0 ± 0·9	40,481,693 ± 9	+22·3 ± 0·2
4	Ph$_3$PSe [i]	—	—	—	—	−735·5 [j]	—	—	40,482,172 ± 17	+34·1 ± 0·4
5	Me$_2$(MeO)PSe [k]	−13·0	+15·0	2·03	3·57	−768 ± 2	19,067,316 ± 9	−218·6 ± 0·5	40,484,441 ± 4	+90·2 ± 0·1
6	Me(MeO)$_2$PSe	−14·5	+14·4	1·95	3·66	−861·0 ± 0·5	19,066,049 ± 9	−268·9 ± 0·5	40,484,932·7 ± 0·4	+102·3 ± 0·1
7	(MeO)$_3$PSe	—	+14·3	—	3·68	−963·0 ± 0·5	19,063,966 ± 4	−396·1 ± 0·2	40,483,925·6 ± 0·4	+77·46 ± 0·01
8	(MeO)$_2$PhPSe	—	+14·4	—	3·60	−876 ± 4	19,065,409 ± 5	−320·4 ± 0·3	40,484,737·3 ± 1·7	+97·51 ± 0·04
9	(MeO)Ph$_2$PSe [g]	—	+14·4	—	3·68	−810 ± 10	19,066,250 ± 17	−276·3 ± 0·9	40,484,303·3 ± 1·7	+86·79 ± 0·04
10	Me$_2$(Me$_2$N)PSe [g]	−12·8	+14·9	1·99	2·48	−720 ± 10	19,066,192 ± 9	−279·4 ± 0·5	40,483,179 ± 9	+59·0 ± 0·2
11	Me(Me$_2$N)$_2$PSe	−13·0	+12·8	1·90	2·52	−767 ± 4	19,065,284 ± 17	−327·0 ± 0·9	40,484,047·3 ± 0·8	+80·5 ± 0·02
12	(Me$_2$N)$_3$PSe [g]	—	+11·7	—	2·36 [l]	−805 ± 2	19,064,544 ± 9	−365·8 ± 0·5	40,484,100·5 ± 0·5	+81·78 ± 0·02
13	(Me$_2$N$_2$)PhPSe	—	+12·7	—	2·47	−790 ± 10	19,064,464 ± 9	−370·0 ± 0·5	40,484,191 ± 9	+84·0 ± 0·2
14	(Me$_2$N)Ph$_2$PSe [g]	—	+15·4	—	2·44 [l]	−760 ± 10	19,064,182 ± 9	−384·8 ± 0·5	40,483,686·5 ± 1·7	−71·55 ± 0·04
15	Ph$_2$HPSe [g]	+461·2 [m]	—	7·955 [n]	—	−740 ± 10	19,064,869 ± 9	−348·7 ± 0·5	40,481,018·4 ± 1·7	+5·64 ± 0·04
16	(EtO)$_2$HPSe [h]	+630·6 [m]	—	8·35 [n]	—	−860 ± 10	19,066,608 ± 9	−257·5 ± 0·5	40,483,638·6 ± 1·7	+70·37 ± 0·04
17	F$_2$HPSe [o]	+691·2 [m]	—	9·19 [n]	—	−1046	—	−170	—	+74·2

[a] Examined as the neat liquid containing Me$_4$Si, unless otherwise stated. [b] Downfield from Me$_4$Si. [c] Methyl group α to phosphorus. [d] Methyl group β to phosphorus. [e] Ξ(X) is the resonant frequency of X in a magnetic field where the protons of Me$_4$Si resonate at exactly 100 MHz. [f] A positive sign indicates a downfield shift from the reference compound, Me$_2$Se for ^{77}Se and 85% aq. H$_3$PO$_4$ for ^{31}P, the Ξ-values being taken as: Ξ(^{77}Se in Me$_2$Se) = 19,071,520 Hz; Ξ(^{31}P in 85% aq. H$_3$PO$_4$) = 40,480,790 Hz. [g] CH$_2$Cl$_2$ solution. [h] Containing CH$_2$Cl$_2$. [i] CDCl$_3$ solution. [j] Ref. 7. [k] MeOH solution. [l] Referred to CH$_2$Cl$_2$ at 5·33 p.p.m. [m] Value of $^1J(^{31}P-^1H)$. [n] Chemical shift of the proton directly bound to phosphorus. [o] Data taken from D. W. W. Anderson, E. A. V. Ebsworth, G. D. Meikle, and D. W. H. Rankin, *Mol. Phys.*, 1973, **25**, 381.

In principle it should also be possible to compare the signs of $^1J(^{31}P-^{77}Se)$ and $J(^{31}P\cdots H)$ by a $^1H-\{^{31}P,^{77}Se\}$ triple resonance experiment, but in practice it was found that the values of $\gamma(^{31}P)B_2/2\pi$ needed to permit adequate selectivity were so low that the relevant weak lines split out from molecules containing ^{77}Se were always hidden by the strong signal from molecules containing non-magnetic selenium. The compounds (EtO)$_2$P(Se)H (16) and Ph$_2$P(Se)H (15) in which $^2J(^{77}Se\cdots H)$ is large enough for ^{77}Se selenium satellites to be detectable in the proton spectrum were therefore examined. $^1H-\{^{77}Se\}$ experiments showed that in each $^1J(^{31}P-^{77}Se)$ is of opposite sign to $^1J(^{31}P-H)$ which is known to be positive.[14]

DISCUSSION

Pople and Santry's molecular orbital treatment[17] of nuclear spin-spin coupling shows that the reduced coupling constant K_{AB} between a pair of directly bound nuclei A and B is given by equation (1), when the Fermi contact term is dominant, where π_{AB} is the mutual

$$K_{AB} \propto \psi^2_{ns(0)A} \cdot \psi^2_{ns(0)B} \cdot \alpha_A{}^2\alpha_B{}^2 \cdot \pi_{AB} \qquad (1)$$

polarisability of the atoms A and B and depends upon the amount of *s*-overlap in the A–B bond. We have shown that $^1K_{PSe}$ is negative in two, [(15) and (16)] of the molecules studied and the overall pattern of the results shows clearly that this is so in all cases; π_{PSe} must therefore be negative. For *large* positive (*e.g.*, $^1K_{CH}$, $^1K_{PH}$) and for *large* negative (*e.g.*, $^1K_{CF}$, $^1K_{PF}$) coupling constants it is found that variations may be ascribed mainly to changes in $\psi^2_{3s(0)P}$ and α^2 as the substituents of A and B are changed, and variations in π_{AB} are relatively unimportant. (However this is not necessarily so when $^1K_{AB}$ is small as with $^1K_{PP}$ and possibly $^1K_{PSe}$ in R$^1{}_2$PSeR^2 derivatives.) In our compounds $^1K_{PSe}$ ranges from -737 to -1038×10^{20} cm^{-3} and so is to be regarded as large. Thus the variations which are observed as the substituents of the phosphorus atom are altered will be due mainly to changes in $\psi^2_{3s(0)P}$ and $\alpha_P{}^2$. There will also be variations of the corresponding parameters for the selenium atom, but as they will be an order of magnitude less they may be ignored in a simple treatment.[18]

Our results show that $^1K_{PSe}$ increases as the electronegativity of the substituents of the phosphorus atom increases, and this is consistent with an increase in $\alpha_P{}^2$ for the σ component of the phosphorus–selenium bond as a result of the diversion of *s*-character from the bonds to the substituent. There may also be some increase

[17] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[18] W. McFarlane, *Quart. Rev.*, 1969, **23**, 187.

in the effective nuclear charge of the phosphorus atom which will increase $\psi^2_{3s(0)P}$ In fact the various values of $^1J(^{31}P-^{77}Se)$ can be predicted to ±10 Hz in **13** of the compounds studied using the additive substituent parameters: Me, −230; Ph, −245; Me_2N, −270; MeO, −320 Hz. These are about what would be expected on the basis of the known inductive effects of these groups. Similar behaviour has been observed[18-22] for the coupling constants $^1J(^{13}C-H)$, $^1J(^{13}C-^{19}F)$, $^1J(^{31}P-H)$, and $^1J(^{31}P-^{19}F)$. Thus $^1J(^{31}P-^{77}Se)$ can be used to assess the effective electronegativity of the substituents of the phosphorus atom (as modified by the synergic effect of any π-bonding which should not affect the Fermi contact interaction directly) in these molecules. The much narrower spread of values for $^1J(^{31}P-^{77}Se)$ (from −708 to −753 Hz) found[7] in a series a arylphosphine selenides also show trends which support this view.

Studies[11] of a wide range of organoselenium compounds have shown that the selenium chemical shift moves to lower field (*i.e.*, assumes more positive values on the sign convention used here) as the amount of withdrawal of electronic charge from selenium increases. Further, the only species which have selenium chemical shifts substantially to high field of Me_2Se are the alkyl selenide anions RSe^-, methaneselenol, and hydrogen selenide. Our present observations that the organophosphorus selenides also have very high-field selenium shifts strongly suggest therefore that the polar structure (II) (E = Se) makes a major contribution to the resonance hybrid. However, the changes in selenium shielding which occur as the electronegativity of the substituents of the phosphorus atom change cannot be accounted for simply on this basis as they are in the opposite sense to what would be expected. For example, on simple electronegativity grounds (both as assessed intuitively and as implied by the observed $^{31}P-^{77}Se$ coupling constants) Me_3PSe (1) would be expected to have a selenium chemical shift significantly to high field of that of $(MeO)_3PSe$ (7) whereas the contrary is observed.

This behaviour can be rationalised if it is assumed that the structure (I) does in fact make some contribution, and that the extent of this depends on the π-bonding ability of the other phosphorus substituents. For example in Me_3PSe (1) there is no competition for the phosphorus 3*d* orbitals and so the contribution from (I) may be quite large. As the methyl groups are replaced by ones which can form π-bonds to phosphorus the phosphorus 3*d* orbitals will be less readily available for overlap with a selenium 4*p* orbital and consequently the importance of (I) will diminish and that of (II) will increase, and the selenium atom will become more shielded. To some extent this change will be offset by the greater electronegativity of most substituents relative to the methyl group, and in the case of $Me_2(MeO)PSe$ (5) the large effective electronegativity of the methoxy-group [as indicated by its effect upon $^1J(^{31}P-^{77}Se)$] counterbalances the initial π-bonding effect. For the series $Ph_n(Me_2N)_{3-n}PSe$ (n = 0—3) it appears that the differences between the π-bonding abilities and the effective electronegativities of the two groups are small. This hypothesis accounts for the broad pattern of selenium shielding in these molecules and we conclude that a contribution from the resonance hybrid (II) is always important, and becomes more so when the phosphorus atom has π-bonding substituents. It is important to realise that this interpretation is unaffected by the question of the relative importance of the paramagnetic and the diamagnetic contributions to the selenium shielding, since it is based upon the experimental observation that increased electronic withdrawal from the selenium decreases the shielding.

The phosphorus chemical shifts are in the ranges to be expected for molecules of this type, but are of little value in the study of the phosphorus–selenium bond as they are too greatly affected directly by the changes in the three other bonds to the phosphorus atom.

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