Ambidentate Nucleophiles. Part 3.[1] Reactions of Phosphoroselenoates with Molecular Halides: The Use of ^1J(PSe) as a Structural Diagnostic

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Sodium *OO'*-di-isopropyl phosphoroselenoate, Na[SeOP(OPr^i)$_2$] (Na[L]), reacts with molecular halides of carbon, silicon, germanium, tin, phosphorus, arsenic, and sulphur to give derivatives ML$_n$. Comparison of the values of ^1J(PSe) in the products with those in a number of model compounds indicates that *O*-bonded isomers M[OP(OPr^i)$_2$-Se] are formed in LCOPh and PL$_3$, that Se-bonded isomers M[SePO(OPr^i)$_2$] are formed in LC$_2$H$_5$, SiMe$_3$L, GePh$_3$L, SnPh$_3$L, AsL$_3$, LSO$_2$Ph, and L$_2$, while SnMe$_3$L, SnPh$_2$L$_2$, and SnPhL$_3$ probably contain bidentate L. The esters P(OR)$_3$Se (R = Me or Et) are inert to reaction with molecular halides. The compound P(OEt)$_3$Se is a much weaker base than PPh$_3$Se which itself is much weaker than PPh$_3$O.

In a previous paper[2] the reactions of the (1,3) ambidentate nucleophile sodium *OO'*-di-isopropyl phosphorothioate, Na[SOP(OPr^i)$_2$], with some halides of Group 4 were described. The halides of silicon, germanium, and tin(IV) give the thermodynamically more stable *O*-bonded thione species P(OR)$_2$(OX)S (R = Pr^i): phosphorus halides give the thermodynamic *O*-isomer[3] and sulphur halides the thermodynamic *S*-bonded thiol isomer,[4] but, while halogenoalkanes yield the thermodynamic *S*-isomer,[5] acyl halides give[6] the *O*-isomer P(OR)$_2$(OCOR')S and methyl chloroformate yields[7] a mixture of isomers.

The present paper describes the reactions of the analogous sodium *OO'*-di-isopropyl phosphoroselenoate, Na[SeOP(OPr^i)$_2$], and of the related neutral triesters P(OR)$_3$Se with some simple halides of carbon, silicon, germanium, tin, phosphorus, arsenic, sulphur, and selenium: the only previously reported reactions of such species with halides are those with PCl(O)(OEt)$_2$ to give a product,[8] subsequently shown by i.r.[9] and n.m.r. spectroscopy[3c] to be the *O*-bonded selenone isomer (EtO)$_2$P(O)OP(OEt)$_2$Se, and with halogens to yield[4] [(RO)$_2$POSe]$_2$, whose structures were not investigated.

EXPERIMENTAL

Red selenium was prepared by sulphite reduction of selenium(IV) oxide in aqueous hydrochloric acid; reaction[10,11] with phosphites P(OR)$_3$ (R = Me, Et, Pr^i, or Ph) yielded the phosphoroselenoates P(OR)$_3$Se. Sodium dialkyl phosphoroselenoates were prepared[4] by reaction of red selenium with sodium dialkyl phosphites; although their preparation is much less easy than that of the analogous phosphorothioates, this method was found to be more satisfactory than either the hydrolysis[12] or the aminolysis[13] of the triesters P(OR)$_3$Se.

Reactions of Na[SeOP(OPr^i)$_2$] *with Molecular Halides.*—Solutions of the halide (5.0 mmol) and of the stoicheiometric quantity of the sodium salt were mixed with stirring in chloroform or nitromethane: with EtI, PhCOCl, SiMe$_3$Cl, GeBrPh$_3$, SnMe$_3$Cl, SnPh$_3$Cl, SnPh$_2$Cl$_2$, SnPhCl$_3$, PCl$_3$, AsCl$_3$, and PhSO$_2$Cl a white precipitate of sodium halide formed either at room temperature or on reflux (1—6 h). The mixtures were filtered and centrifuged, and the solvent was removed to afford almost quantitative yields of products: microanalytical data are recorded in Table 1.

TABLE 1

Microanalytical data (%) for derivatives of L [= PO(OPr^i)$_2$Se]

	Found		Calc.	
	C	H	C	H
LC$_2$H$_5$	35.3	6.8	35.2	7.0
LCOPh	44.5	5.4	44.7	5.5
SiMe$_3$L	34.3	6.9	34.1	7.3
GePh$_3$L	52.7	5.4	52.6	5.3
SnMe$_3$L	26.6	5.9	26.5	5.7
SnPh$_3$L	48.6	5.1	48.5	4.9
SnPh$_2$L$_2$	37.7	4.9	37.9	5.0
SnPhL$_3$	30.6	5.0	31.1	5.1
PL$_3$	28.4	5.8	28.3	5.6
AsL$_3$	26.7	5.3	26.8	5.3
LSO$_2$Ph	37.4	4.8	37.4	5.0

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With bromine[4] the dimeric product $[(Pr^iO)_2POSe]_2$ was formed. When the halide was Se_2Cl_2 the precipitation of sodium chloride was accompanied by copious deposition of red selenium, and the phosphorus-containing product was again $[(Pr^iO)_2POSe]_2$. With SCl_2, decomposition occurred, chlorine was evolved, and an orange solid was precipitated whose mass spectrum contained only ions of composition $[Se_xS_y]^+$ ($x = 0$, $y = 1$—8; $x = 1$, $y = 1$—7; $x = 2$, $y = 1$—6; $x = 3$, $y = 1$—4; $x = 4$, $y = 2$—4; $x = 5$, $y = 1$ or 3; $x = 6$, $y = 0$).

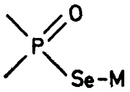
Reactions of $P(OR)_3Se$ *with Halides.*—Aliquot portions (5.0 mmol) of $P(OMe)_3Se$ were heated under reflux with stoicheiometric quantities of EtI, $PhSO_2Cl$, or $SiPh_3Cl$ in nitromethane during 6 h: after removal of solvent, examination by n.m.r. and mass spectrometry showed that no reaction had occurred; no rearrangement was observed on reflux in nitromethane with solid potassium iodide, or on passage of hydrogen chloride gas through a solution in benzene. The compound $P(OEt)_3Se$ similarly failed to react with PhCOCl and $PhSO_2Cl$. Reaction of $P(OR)_3Se$ (R = Me or Et) with an equimolar quantity of $SnCl_4(OEt_2)_2$ in diethyl ether rapidly gave the rearranged products $PO(OR)_2(SeR)$. A similar reaction using $P(OPh)_3Se$ gave almost quantitative deposition of red selenium, as did the reaction of $P(OMe)_3Se$ in dichloromethane–pentane (1 : 1) solution.

Preparation of $[PPh_3(SeEt)][BF_4]$.—Equimolar quantities (5.0 mmol) of PPh_3Se (1.70 g) and $[OEt_3][BF_4]$ (0.95 g) were mixed in dichloromethane (100 cm^3). After 1 h the mixture was poured into diethyl ether (400 cm^3) and the resulting white precipitate was filtered off and dried (Found: C, 52.3; H, 4.3. $C_{20}H_{20}BF_4PSe$ requires C, 52.6; H, 4.4%). Similarly prepared was $[PPh_3(SEt)][BF_4]$ (Found: C, 58.9; H, 4.7. $C_{20}H_{20}BF_4PS$ requires C, 58.6; H, 4.9%). Literature methods were employed for the preparation of $PO(OPr^i)_3$,[14] $SnCl_4(SePPh_3)_2$,[15] $[PdCl_2(SePPh_3)_2]$,[15] $[CdCl_2(SePPh_3)_2]$,[16] and $[HgI_2(SePPh_3)]$[15] (which by analogy with the chloride is probably dimeric). The compound $I_2{\cdot}PPh_3Se$ was prepared from the selenide and iodine,[17] and $Br_2{\cdot}PPh_3Se$ was similarly prepared (Found: C, 43.0; H, 2.8. $C_{18}H_{15}Br_2PSe$ requires C, 43.2; H, 3.0%).

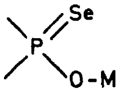
N.m.r. spectra were recorded using Varian EM-360 and HA-100 (^1H), CFT-20 (^{13}C), and XL-100 (^{31}P) instruments. Mass spectra were obtained on an A.E.I. MS902 instrument, and i.r. spectra using a Perkin-Elmer 621 spectrophotometer. Light petroleum had b.p. 40—60 °C: this, and diethyl ether, was dried over sodium wire. Halogenated solvents and nitromethane were dried over flamed-out molecular sieves.

RESULTS AND DISCUSSION

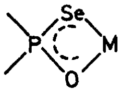
Sodium *OO'*-di-isopropyl phosphoroselenoate, Na[L], reacted with the molecular halides EtI, PhCOCl, $SiMe_3Cl$, $GeBrPh_3$, $SnMe_3Cl$, $SnPh_3Cl$, $SnPh_2Cl_2$, $SnPhCl_3$, PCl_3, $AsCl_3$, and $PhSO_2Cl$ to give derivatives ML_n which are all involatile liquids miscible with common organic solvents. The products are all stable in air, but are sensitive to heat and light, and must be stored in the dark, preferably at −30 °C: the usual decomposition mode involves loss of selenium. Spectroscopic evidence (see below) allows the assignment of selenol (1a), selenone (1b), or bidentate (1c) structures to the products.



(1a)



(1b)



(1c)

By contrast with this sodium salt, the neutral phosphoroselenoate triesters $P(OR)_3Se$ are chemically remarkably inert. No reaction, other than slight decomposition with selenium loss, was observed with EtI, PhCOCl, $PhSO_2Cl$, $SiPh_3Cl$, or HCl: these reagents had been expected to yield $PO(OR)_2(SeR')$ (R' = Et, PhCO, $PhSO_2$, $SiPh_3$, or H respectively). Similarly, $P(OMe)_3Se$ was recovered unchanged after reflux with KI, a reagent which effects[18] rearrangement of the phosphite $P(OMe)_3$ to the phosphonate $PMe(O)(OMe)_2$.

Whereas PPh_3Se reacts with $SnCl_4(OEt_2)_2$ to yield the complex $SnCl_4(SePPh_3)_2$, the ester $P(OMe)_3Se$ underwent rearrangement with this halide in diethyl ether to yield the *Se*-bonded species $PO(OMe)_2(SeMe)$. Such a rearrangement has been observed[19] previously, catalysed by boron trifluoride. Rearrangement of the phosphorothioates $P(OR)_3S$ catalysed by Lewis acids such as tin(IV) chloride and bromide has been observed,[20] and the intermediate complexes $SnCl_4[SP(OR)_3]_2$ have been isolated from pentane–dichloromethane mixtures of the halide and the esters. Use of this solvent, instead of diethyl ether, in the reaction of $P(OMe)_3Se$ with $SnCl_4$ gave neither the complex $SnCl_4[SeP(OMe)_3]_2$ nor the rearranged ester $PO(OMe)_2(SeMe)$, but decomposition with complete loss of selenium; $P(OPh)_3Se$, in which rearrangement is very unlikely, also underwent essentially quantitative loss of selenium.

Attempts were made to alkylate the triesters, by use of triethyloxonium tetrafluoroborate to obtain $[P(OR)_3(SeEt)][BF_4]$. The compound $P(OPh)_3Se$ experienced selenium loss, while $P(OEt)_3Se$ gave an oil, in whose ^1H n.m.r. spectrum ($CDCl_3$) the chemical shifts and relative integrals [$\delta(CH_2O)$ 4.69 (6 H), $\delta(CH_2Se)$ 3.20 (2 H), and $\delta(CH_3)$ 1.57 p.p.m. (12 H)] were consistent with the presence of $[P(OEt)_3(SeEt)][BF_4]$; however the spin–spin coupling pattern could not be interpreted in terms of such a structure, and the material underwent explosive decomposition shortly after its preparation, so that no ^{31}P n.m.r. spectrum was obtained.

Mass Spectra.—The mass spectra of the triesters $P(OR)_3Se$ (R = Me, Et, Pr^i, or Ph) are in general similar to those of the phosphites[21] $P(OR)_3$. For the alkyl species the predominant decomposition path, as for the phosphites, involved alkyl or alkene loss, but there were now two parallel series of dealkylated ions, one containing selenium and the other not. The base

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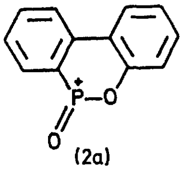
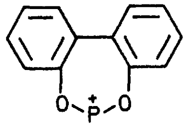
peaks of the spectra were, for R = Me, Et, and Pr^i respectively: $[P(OR)_2]^+$ [*cf.*[21] $P(OMe)_3$], $[H_3PO_3Se]^+$, and $[H_3PO_3Se]^+$. Similarly the spectrum of $P(OPh)_3Se$ resembled that of $P(OPh)_3$: ions of interest occurred at *m/e* 170 $[OPh_2]^+$, 217 $[P(OPh)_2]^+$, and 215 $[P(OPh)_2 - 2H]^+$ [structures (2a) or (2b)]. These are analogous to the ions at *m/e* 154 $[Ph_2]^+$, 185 $[PPh_2]^+$, and 183 $[PPh_2 - 2H]^+$ in the spectrum of PPh_3Se.[22] In the spectra of compounds of the type ML_n molecular ions were observed for all species having $n = 1$ and also for $[(Pr^iO)_2POSe]_2$. For M = Et, PhCO, or $PhSO_2$, the major decomposition route involved initial loss of isopropyl groups, while when M = $SiMe_3$, $SnMe_3$, $GePh_3$, or $SnPh_3$, the principal route involved initial loss of Me or Ph followed by isopropyl loss. The dimeric species exhibited only weak ions above *m/e* 245 $[PO(OPr^i)_2{}^{80}Se]$; other species with $n > 1$, *i.e.* $SnPh_2L_2$ and ML_3 (M = P, As, or SnPh), showed no molecular ions.



(2a)



(2b)

The only indications concerning the possible isomers present in any compound were the occurrence of ion clusters at *ca. m/e* 213 in the spectrum of $SnMe_3L$ and *ca. m/e* 275 in that of $SnPh_2L$: analysis of the observed isotopic patterns showed that these were due to $[SnMeSe]^+$ and $[SnPhSe]^+$ respectively.

I.r. Spectra.—Chittenden and Thomas[23] recorded values of ν(P=Se) in a number of PXYZSe species of types $P(OR)_3Se$ and $PR(OR)_2Se$: they found two bands assignable to ν(P=Se) in the ranges 570—577 and 528—535 cm^{-1} respectively, and ascribed this observation to the occurrence of two conformers in these species. Two ν(P=Se) bands are similarly found[24] in $K[Se_2P(OR)_2]$ salts (580—610 and 500—530 cm^{-1}), but only one[25] in $P(NRH)_3Se$ (599 cm^{-1}) and in $[P(NRH)_2Se_2]^-$ salts (540—552 cm^{-1}). Although the observation of ν(P=Se) would be useful as a diagnostic for the *O*-bonded selenone isomers, it has been demonstrated[26] that, in species containing PSeC fragments, ν(C–Se) occurs at 569 and 530 cm^{-1} (again, there are probably two conformers), just coincident with the two ν(P=Se) ranges; similarly in the sulphur analogues[26] ν(P=S) ≃ ν(C–S). Consequently, it is felt that, even when the fragment M is not bonded to oxygen or selenium *via* carbon, the low-frequency region of the i.r. spectrum must be used with caution, and that possibly the more reliable diagnostic is ν(P=O), expected to occur in the range[27] 1 190—1 280 cm^{-1}.

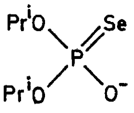
In Table 2 are recorded values of ν(P=O) and ν(P=Se): tentative inferences are that LC_2H_5, LSO_2Ph, $SiMe_3L$, $GePh_3L$, and AsL_3 contain P=O and so are *Se*-bonded isomers, while LCOPh, $SnMe_3L$, $SnPh_2L_2$, $SnPhL_3$, and PL_3 are *O*-bonded. The data for $SnPh_3L$ and $[(Pr^iO)_2POSe]_2$ (L_2) are ambiguous, while it appears that Na[L] exists predominantly as (3a) rather than as (3b).

TABLE 2

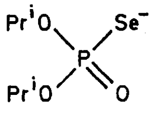
Diagnostic i.r. bands (cm^{-1})

	ν(P=O)	ν(P=Se)
$P(OMe)_3Se$		552, 498
$P(OEt)_3Se$		563, 522
$P(OPr^i)_3Se$		565, 530
Na[L]		585, 535
LC_2H_5	1 249	*a*
LCOPh		575, 538
$SiMe_3L$	1 230	
$GePh_3L$	1 243	
$SnMe_3L$		545, 538, 525
$SnPh_3L$	1 238	*b*
$SnPh_2L_2$		575, 540
$SnPhL_3$		565, 540
PL_3		582, 537
AsL_3	1 242	
LSO_2Ph	1 238	
L_2	1 250	*c*

[a] ν(C–Se) at 569 and 532 cm^{-1}. [b] Bands also at 562 and 525 cm^{-1}. [c] Bands also at 550 and 529 cm^{-1}.



(3a)



(3b)

N.m.r. Spectra.—The proton spectra all had integrals in accord with the compositions postulated: essential data are recorded in Table 3. In the spectra of some of the compounds two separate chemical shifts were observed for the methyl fragments of the isopropyl groups. In the species $PO(OPr^i)_2(SeR)$ or $P(OR)(OPr^i)_2Se$ the phosphorus atom and the methine carbons are all prochiral centres, so that there are two distinct methyl environments. The reason for the occurrence of two methyl shifts in only some species is not clear: only one methyl resonance was observed for $P(OPr^i)_3$, and $HPO(OPr^i)_2$ and for $P(OPr^i)_3X$ (X = O, S, or Se), between 35 and −60 °C.

Phosphorus spectra yielded in addition to the chemical shift δ_P the coupling constant ${}^1J({}^{31}P-{}^{77}Se)$ arising from ^{77}Se (spin, $I = \frac{1}{2}$; abundance 7.58%): the data recorded in Table 3 enable structural deductions to be made when used in collaboration with the δ_P and ${}^1J(PSe)$ data determined for a number of model compounds (Table 4): other collections of ${}^1J(PSe)$ have been published,[28,29] but only for neutral species containing alkyl or aryl substituents. For compounds of type $P(OR)_3Se$, ${}^1J(PSe)$ generally exceeds 900 Hz; for other similar species containing singly bound selenium, *e.g.* PPh_3Se, ${}^1J(PSe)$ is usually greater than 700 Hz, the lowest value

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recorded [28] being 656 Hz for PBu^t(Ph)HSe. Other compounds of this type are [30] $PPh_2(OMe)Se$ (J 837 Hz) and $P(CN)(O_2C_5H_{11})Se$ (J 1 040 Hz). The lowest value recorded for a compound of type $P(OR)_3Se$ is 894 Hz for $P(OEt)_2(OH)Se$.[29] McFarlane and Rycroft [28] showed that, for compounds of type PXYZSe, ^1J(PSe) is usually negative, and is an additive function of the groups X, Y, and Z, which reflects the effective electronegativity of the group X,Y,Z. Their parameters (in Hz) are: Me, −230; Ph, −245; NMe_2, −270; and OMe, −320. The data in Table 4 indicate the values: OMe, −318; OEt, −316; OPr^i, −308; OPh, −342; $PhCO_2$, −369; and O$^-$, −138; to which may be added [29] CN, −408. For species containing two-co-ordinate selenium directly bound to phosphorus, ^1J(PSe) is usually less than 500 Hz; examples other than those in Table 4 are 205 Hz for $PMe_2(SeMe)$ and 341 Hz for $PMe_2S(SeMe)$,[31] 536 and 263 Hz for P_4Se_3,[32] and 466 and 488 Hz for the two isomers of $PO(O_2C_6H_{13})(SeMe)$.[33] Anions [PO-$(OR)_2Se]^-$ have ^1J(PSe) *ca.* 770 Hz. On the basis of these data, it may be postulated that *any* species ML_n $^1J(PSe) > 850$ Hz has the *O*-bonded selenone structure (1b), that species with $^1J(PSe) < 550$ Hz are *Se*-bonded (1a), while for those having $850 > {}^1J(PSe) > 550$ Hz the form of L is best described as essentially ionic and possibly bidentate (1c).

TABLE 3

N.m.r. data for derivatives of L (in $CDCl_3$ solution)

Compound	$\delta[(C\mathit{H}_3)_2CH]$ [a]	$\delta[(CH_3)_2C\mathit{H}]$ [a]	δ_P [b]	^1J(PSe)/Hz	Other resonances
Na[L]	1.30, 1.34	4.63	48.08	754.6	
LC_2H_5	1.35, 1.38	4.77	17.47	479.6	$\delta(C\mathit{H}_2Se)$ 2.90, $\delta(C\mathit{H}_3CH_2)$ 1.51, ^1J(CSe), 52.0
LCOPh	1.33, 1.41	5.01	58.97	985.0	δ(aryl) 7.3—7.7, 7.9—8.1
$SiMe_3L$	1.40	4.50	18.06	466.8	$\delta(C\mathit{H}_3Si)$ 0.33
$GePh_3L$	1.37	4.42	19.71	507.9	δ(aryl) 7.3—7.9
$SnMe_3L$	1.28	4.55	30.41	644.1	$\delta(C\mathit{H}_3Sn)$ 0.71, $^2J(\mathit{H}C^{119}\mathit{Sn})$ 67, $^2J(\mathit{H}C^{117}\mathit{Sn})$ 64
$SnPh_3L$	1.15	4.33	16.45	479.7	δ(aryl) 7.2—7.8, $^2J(\mathit{P}SSe\mathit{Sn})$, 49.5
$SnPh_2L_2$	1.13, 1.25	4.40	24.35	545.9	δ(aryl) 7.2—7.6, 7.9—8.2
$SnPhL_3$	1.34	4.78	33.09	*c*	δ(aryl) 7.2—7.6, 7.9—8.2
PL_3	1.37	4.92	58.25	874.2	
AsL_3	1.43	4.87	12.44	473.3	
LSO_2Ph	1.22, 1.34	4.90	8.90	495.0	δ(aryl) 7.3—7.9
L_2	1.42	4.90	11.70	515.9	

[a] Proton shifts in p.p.m. from $SiMe_4$. [b] Phosphorus shifts in p.p.m. from 85% H_3PO_4. [c] Unstable (see text).

TABLE 4

Phosphorus n.m.r. parameters of model compounds

Compound	δ_P [a]	^1J(PSe)/Hz
$P(OMe)_3Se$	78.01	955.6
$P(OEt)_3Se$	72.47	949.3
$P(OEt)_3Se$ [b]	68.08	904.2
P(OPr^i)$_3$Se	66.56	923.9
$P(OPh)_3Se$	58.61	1 027.1
$Na[SeOP(OMe)_2]$	53.07	774.7
$Na[SeOP(OEt)_2]$	50.24	769.6
Na[SeOP(OPr^i)$_2$]	48.08	754.6
$PO(OMe)_2(SeMe)$	23.41	473.2
$PO(OEt)_2(SeEt)$	19.63	467.7
PPh_3Se	35.19	736.2
PPh_3Se [b]	34.11	606.9
PPh_3Se [c]	37.21	418.0
$[PPh_3(SeEt)][BF_4]$ [d]	35.79	465.4
$[CdCl_2(SePPh_3)_2]$ [e]	35.40	729.5
$SnCl_4(SePPh_3)_2$	35.34	719.3
$I_2\cdot PPh_3Se$	43.52	*f*
$Br_2\cdot PPh_3Se$	51.96	*f*

[a] Phosphorus shifts in p.p.m. from 85% H_3PO_4, in $CDCl_3$ except as noted. [b] In CF_3CO_2H. [c] In H_2SO_4. [d] ^1J(CSe) 54.8 Hz. [e] $^2J(\mathit{P}Se\mathit{Cd})$ 10.5 Hz. [f] See text.

The compound LC_2H_5 is therefore regarded, on the basis of both i.r. and ^{31}P n.m.r. spectra, as PO(OPr^i)$_2$(SeEt) while LCOPh is regarded as P(O_2CPh)(OPr^i)$_2$Se: these structures are analogous to those found in the corresponding phosphorothioates.[5,6] Also regarded as *Se*-bonded (1a) are AsL_3, LSO_2Ph, $SiMe_3L$, $GePh_3L$, $SnPh_3L$, and L_2, in which the two phosphorus atoms are identical, while PL_3 is *O*-bonded (1b) and $SnMe_3L$ and $SnPh_3L_2$ probably contain bidentate L, structure (1c). For $SnPhL_3$, ^1J(PSe) was not observed because of the low thermal stability of the compound (the ^{31}P spectrum was very noisy), and no deduction can therefore be made. These assignments suggest that ν(P=O) is a more reliable i.r. diagnostic than ν(P=Se). On the basis of the similarity of the i.r. spectra of $SnPh_2L_2$ and $SnPhL_3$, the latter is assigned structure (1c) with bidentate L. Attempts to determine ^{77}Se chemical shifts by ^{31}P-{^{77}Se} decoupling were not successful.

Some of the data in Table 4 are worthy of comment. *Se*-Alkylation of PPh_3Se to give $[PPh_3(SeEt)]^+$ occasioned essentially no change in δ_P (35.2—35.8 p.p.m.), but caused a reduction of ^1J(PSe) from 736.2, typical of PXYZSe, to 465.4 Hz, typical of two-co-ordinate selenium. Similarly, no change in δ_P was found on alkylation of PPh_3S (δ_P 42.6 p.p.m.) to $[PPh_3(SEt)]^+$ (δ_P 44.5 p.p.m.). Triphenylphosphine oxide, on the other hand, is subject to a large downfield shift from 24.9 p.p.m. in PPh_3O to 62 p.p.m. in [34] $[PPh_3(OEt)]^+$. The corresponding shifts in the methylated derivatives are reported [35] as: $[PPh_3(OMe)]^+$, 65; $[PPh_3(SMe)]^+$, 46.6; and $[PPh_3(SeMe)]^+$, 35.8 p.p.m. [^1J(PSe) not

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reported]. None of $P(OMe)_3Se$, $P(OPh)_3Se$, and PPh_3Se formed adducts with methyl iodide.

In 98% sulphuric acid, δ_P for PPh_3Se (*ca.* 0.1 mol dm^{-3}) was again essentially unchanged (37.2 p.p.m.) (as was that for PPh_3S at 42.4 p.p.m.), but the value of $^1J(PSe)$, 418.0 Hz, indicates complete protonation to $[PPh_3(SeH)]^+$: in 100% trifluoroacetic acid (tfa), $^1J(PSe)$ was 606.9 Hz. If it is assumed that the relation between $^1J(PSe)$ and the degree of protonation is linear, then if a fraction x of PPh_3Se is protonated, we obtain equation (1) ($\pm$ according to whether the two J values have the same or different signs).

$$(1 - x)J(PPh_3Se) \pm xJ[PPh_3(SeH)^+] = J_{obs.} \quad (1)$$

$^1J(PSe)$ is usually negative for PXYZSe,[28] but for compounds containing two-coordinate selenium it may be negative as in $PMe_2(SeMe)$ [31] or positive as for $^1J(P'Se)$ in $P(SeP')_3$.[32] Irrespective of the sign of J in $[PPh_3(SeH)]^+$, $J_{obs.}$ of 606.9 Hz *must* have the same sign as J in PPh_3Se. No mixture of H_2SO_4 and tfa was found in which $[PPh_3Se]$ exceeded $[H_2SO_4]$, nor is PPh_3Se soluble in 70% H_2SO_4, 60% $HClO_4$, 55% HI, or BF_3–$MeCO_2H$; consequently the relative signs of J in PPh_3Se and $[PPh_3(SeH)]^+$ could not be found. For the same signs, $x \simeq 0.40_6$, or $[PPh_3(SeH)^+]/[PPh_3Se] = x/(1 - x) \simeq 0.68$; for different signs, $x \simeq 0.11_2$, with $[PPh_3(SeH)^+]/[PPh_3Se] \simeq 0.13$. Chemical-shift data for PPh_3O in solvents of different basicity [36] indicate that, in tfa, $[PPh_3(OH)^+]/[PPh_3O]$ is *ca.* 2.0, showing the much higher basicity of the phosphine oxide. *OO'O''*-Triethyl phosphoroselenoate, $P(OEt)_3Se$, is unstable in H_2SO_4 solution, rapidly losing selenium and being converted into $PO(OEt)_3$; in tfa its $^1J(PSe)$ is reduced to 904.2 Hz from the value of 949.3 Hz in $CDCl_3$. Taking 500 Hz as a very crude estimate for J in the fully protonated species, $[P(OEt)_3(SeH)^+]/[P(OEt)_3Se]$ in tfa is 0.11 or 0.03 for the two cases of the J values having the same or different signs respectively, indicating that $P(OEt)_3Se$ is a much weaker base than PPh_3Se. The ester $P(OPh)_3Se$ is insoluble in tfa, and rapidly loses selenium in H_2SO_4, being converted into $PO(OPh)_3$.

Apparently anomalous are the values of $^1J(PSe)$ for the complexes $SnCl_4(SePPh_3)_2$ and $[CdCl_2(SePPh_3)_2]$, 719.3 and 729.5 Hz respectively: that these data are for the complexed, as opposed to the dissociated, ligands is demonstrated, at least for the cadmium complex, by the observation of cadmium satellites in the ^{31}P n.m.r. spectrum having $^2J(PCd)$ 10.5 Hz: resolution of the satellites due to ^{111}Cd ($I = \frac{1}{2}$; 12.75% abundant) and ^{113}Cd ($I = \frac{1}{2}$; 12.26% abundant) was not achieved. These data suggest that essentially *no* perturbation of the electron density in the PSe fragment of the ligand occurs on complex formation. If it is assumed that the SeC and SeH interactions in $[PPh_3(SeEt)]^+$ and $[PPh_3(SeH)]^+$ respectively are essentially covalent, then in these metal complexes the bonding between selenium and the metal appears to be largely electrostatic; this conclusion is rather surprising, in view of the softness of selenium-containing ligands. (It is perhaps noteworthy in this context that complexes of PPh_3Se with metal ions such as Co^{2+} and Cu^{2+} could not be prepared.[14]) Unfortunately the further complexes $[HgI_2(SePPh_3)]$ and $[PdCl_2(SePPh_3)_2]$ were insoluble in all the solvents investigated. Even more surprising is the observation of *no* ^{77}Se satellites in the ^{31}P spectra of $SeI_2(PPh_3)$ and $SeBr_2(PPh_3)$, although the presence of selenium bonded to phosphorus was demonstrated by mass spectrometry, the spectra containing only peaks assignable to $[PPh_3Se]^+$, $[X_2]^+$, and their decomposition products. The values of $^1J(PSe)$ in complexes of PPh_3Se clearly warrant further investigation.

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