Phosphorus-31 and Selenium-77 Nuclear Magnetic Resonance Spectra of Phosphorus-poor Phosphorus Selenide Compounds

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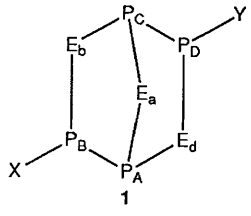
The compounds P_3Se_4X (X = I, Br, Cl, SC_2H_5, SC_5H_{11} or SC_6H_5) have been made as phosphorus-poor analogues of the corresponding compounds α- or β-$P_4E_3X_2$ (E = S or Se), in which a PX unit has been replaced by Se. Analysis of ^{31}P and (in part) ^{77}Se NMR spectra of the P_3Se_4X compounds has shown remarkable correspondence of the coupling constants and chemical shifts between the P_3Se_4X and α-$P_4S_3X_2$ series of compounds. Phosphorus-31 and ^{77}Se NMR spectra of α-$P_4Se_3I_2$ are reported for comparison. Further replacement of a PX unit by Se gives the ultimate phosphorus-poor cluster compound P_2Se_5, for which a synthesis from the elements and full NMR data are reported. This sought after higher selenide of phosphorus is thus a phosphorus-poor molecule with concatenated selenium, rather than a selenium-rich structure with exocyclic selenium. The interconversion of optical isomers of the P_3Se_4X halides (X = I, Br or Cl), by skeletal rearrangement on the NMR time-scale, has been studied at several temperatures, yielding kinetic data.

Phosphorus chalcogenides generally have molecular structures containing an approximate tetrahedron of phosphorus atoms. Edges of the tetrahedron may be bridged by chalcogen atoms, or remain as formal phosphorus–phosphorus bonds. Until recently, the only well known derivatives of these compounds containing additional, monofunctional ligands attached to the phosphorus atoms were the α- and β-$P_4E_3X(Y)$ series **1** and **2** respectively (E = S or Se; X and Y are halogen, pseudohalogen or various similar groups),[1–4] of which the β series is generally thermally unstable with respect to the α. The place of bridging chalcogen atoms may be taken by other difunctional groups bonding through, *e.g.*, silicon [in $P_4(SiMe_2)_3$][5] or further phosphorus [in $P_4(PMe)_3$],[6] but except for the replacement of phosphorus by arsenic,[7] the vertices of the tetrahedra have been occupied by phosphorus. Thus the normal minimum phosphorus content has been four atoms per molecule. The first phosphorus-poor analogue of these structures was P_3Se_4I **3** (X = I),[8] in which an additional selenium atom took the place of a PI unit at a vertex of the approximate P_4 tetrahedron of $P_4Se_3I_2$. The compound P_3Se_4I can be considered, *e.g.* for the purpose of rationalising its NMR parameters, as an analogue either of α-$P_4Se_3I_2$ or of β-$P_4Se_3I_2$, depending on whether Se_c or Se_d is thought of as replacing a PI unit. The ^{31}P NMR spectrum of P_3Se_4I was of immediate interest because the compound was found to exist in solution in CS_2 as its two optical isomers, interconverting by a skeletal rearrangement reaction on the NMR time-scale at room temperature.[8]

We now report satisfactory preparative routes to P_3Se_4I, and substitution reactions to yield P_3Se_4Br, P_3Se_4Cl and solutions containing $P_3Se_4(SR)$ (R = C_6H_5, C_2H_5 or C_5H_{11}). This has allowed not only a study of variations in NMR chemical shifts and coupling constants for the P_3Se_4 skeleton, on substitution, comparable to analogous work on the α-P_4S_3 skeleton,[4,9] but also an insight into how the rate of its isomerisation reaction depends on the exocyclic substituent.

Replacement of the remaining PI unit of P_3Se_4I by a further selenium atom would yield the molecule in this series containing the least possible number of phosphorus atoms, P_2Se_5 **4**. We report its preparation by direct reaction of the elements,[10] and its formation as a decomposition product of solutions of P_3Se_4I.



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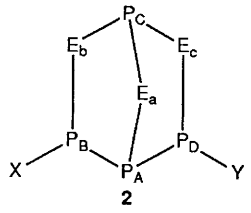

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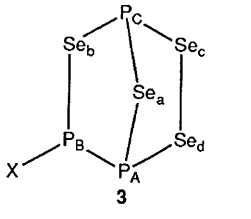

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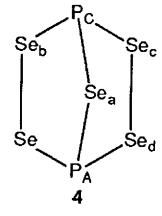

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Results and Discussion

Triphosphorus Tetraselenide Iodide.—The identification by X-ray crystallography of P_3Se_4I as a minor by-product in the preparation of α-$P_4Se_3I_2$ by melting together an equimolar mixture of P_4Se_3 and iodine[8] led us to seek a more directed preparation. Reaction of red phosphorus, grey selenium and iodine, in a melt, in the atomic ratio 3:4:1 required by the formula of P_3Se_4I, led to a much improved yield (46%). The course of the reaction is unknown, but we have also found that in solution in CS_2, while iodine reacts with P_4Se_3 alone to give β-$P_4Se_3I_2$,[1] it reacted with a solution containing both P_4Se_3 and selenium, in the ratio required by equation (1), to give

$$3\ P_4Se_3 + 7\ Se + 2\ I_2 \longrightarrow 4\ P_3Se_4I \qquad (1)$$

P_3Se_4I in 52% yield. The product, crystallising as black-red needles, could be separated from other components on account of its relatively low solubility.

Triphosphorus Tetraselenide Bromide and Chloride.—The

Table 1 Iterative fitting of NMR spectra of α-$P_4Se_3I_2$ **1** (E = Se; X = Y = I), P_3Se_4X **3** (X = I, Br or Cl) and P_2Se_5 **4**

Compound	^{77}Se at position	Fraction of transitions observed, for P_A	P_B	P_C	^{77}Se	Root mean square (r.m.s.) deviation/Hz
α-$P_4Se_3I_2$	—	12/12	12/12			0.69
	a	23/24	0		16/16	0.58
	b	18/32	32/48		19/26	0.19
P_3Se_4I	—	4/4	4/4	4/4		0.02
	a	8/8	0	5/8	0	0.69
	b	0	4/8	4/8	0	0.58
	c	0	0	6/8	0	0.41
	d	7/8	4/8	0	4/8	0.69
P_3Se_4Br	—	4/4	4/4	4/4		0.01
	a	8/8	4/8	8/8	7/8	0.20
	b	8/8	8/8	8/8	7/8	0.23
	c	8/8	4/8	8/8	8/8	0.20
	d	8/8	4/8	0	4/8	0.16
P_3Se_4Cl	—	4/4	4/4	4/4		0.01
	a	8/8	5/8	6/8	8/8	0.29
	b	4/8	8/8	8/8	7/8	0.25
	c	8/8	0	5/8	8/8	0.24
	d	8/8	4/8	0	5/8	0.44
P_2Se_5	a			4/4	4/4	0.08
	c			8/8	6/6	0.29

bromide P_3Se_4Br could be made in the same way as the iodide P_3Se_4I, by heating together stoichiometric quantities of the elements. Alternatively, the bromide or the chloride could be made from the iodide: stirring a solution of the iodide with a suspension of silver halide in CS_2, as in the preparation of the corresponding α-P_4S_3 halides **1** (E = S; X = Y = Br or Cl),[11] gave the purest products, but at the lower temperature (0 °C) necessary to avoid decomposition of the P_3Se_4 skeleton, the rate of substitution was very low. Identification of P_3Se_4X **3** (X = Br or Cl) was by detailed comparison of their NMR parameters (see below) with those of the known P_3Se_4I, as well as by comparison of IR spectra. Use of soluble ($SnEt_3Br$ or $SnMe_3Cl$) or slightly soluble ($HgBr_2$) halide-exchange reagents gave solutions containing P_3Se_4X suitable for NMR studies, in a few hours instead of many days, although the formation of poorly soluble by-products made these methods unattractive for the preparation of isolated products. The ^{31}P–^{31}P coupling constants for P_3Se_4Br were the same to within experimental error, irrespective of the method of preparation, and hence of the presence of other reaction components in the solution. Phosphorus-31 NMR chemical shifts showed only slight variations, but the skeletal rearrangement reaction of P_3Se_4Br made using $HgBr_2$ proceeded at an obviously higher rate (k_r = 13 s^{-1} at 270 K) than for P_3Se_4Br made using either AgBr or $SnEt_3Br$ (k_r = 1 s^{-1}, see below). It is interesting that this rate of rearrangement could be affected, probably by weak complexation of the bromine atom by dissolved mercury compounds, without a pronounced effect on coupling constants or chemical shifts. An attempt to force complex formation by P_3Se_4Cl, by addition of excess $HgCl_2$, led to complete decomposition to PCl_3 and insoluble, unidentified products.

Diphosphorus Pentaselenide.—The decomposition of solutions of P_3Se_4I in CS_2 over several weeks at room temperature, led to the formation of α-$P_4Se_3I_2$ and the new binary selenide P_2Se_5 **4**, in a reaction which can probably be represented by the equilibrium in equation (2). The compound P_2Se_5, initially

$$2\ P_3Se_4I \rightleftharpoons P_2Se_5 + \alpha\text{-}P_4Se_3I_2 \qquad (2)$$

postulated to explain its singlet main ^{31}P NMR spectrum and the appearance of its molecular ion in the electron impact (EI) mass spectrum of the mixture, was positively identified (see below) by comparison of its NMR parameters, obtained from the ^{31}P and ^{77}Se NMR spectra of its ^{77}Se isotopomers, with those of the P_3Se_4 halides **3** (X = Cl, Br or I), and those of α-$P_4Se_3I_2$ which are also reported here.

A direct preparation of P_2Se_5 was then achieved by high-temperature combination of the elements. Procedures have been described previously for making P_2Se_5[12] or P_4Se_{10},[13] but while these materials were amorphous solids of unknown structure, which could not be dissolved without reaction, extra annealing and extraction stages have now produced a molecular compound that can be recrystallised. It formed black-red crystals which were sparingly soluble in CS_2 to give straw-coloured solutions. Monteil and Vincent[13] preferred the formula P_4Se_{10} for their product, and gave some IR evidence that it contained one-co-ordinate, exocyclic selenium atoms, corresponding to a structure analogous to that of P_4S_{10}. Our product showed an IR absorption at 500 cm^{-1}, as assigned by Monteil and Vincent[13] to P=Se stretching, but only of medium intensity, which increased on exposure of the sample to moist air. Kudchadker *et al.*[12] used the formula P_2Se_5, but found that their product would react with alcohols to give oxygen diesters of diselenophosphoric acid, in which phosphorus(v) carried a one-co-ordinate selenium atom. More recently,[14] magic angle spinning solid-state NMR has shown that phosphorus-poor P–Se glasses can best be described in terms of an equilibrium [equation (3)] between three- and four-co-ordinate phosphorus

$$PSe_{3/2} + Se \rightleftharpoons Se{=}PSe_{3/2} \qquad (3)$$

centres, for which $K = [Se{=}PSe_{3/2}]/[PSe_{3/2}][Se] = 0.85 \pm 0.05$ (atom fraction)$^{-1}$. The Se atom in equation (3) represents 'selenium atoms in excess of a $PSe_{3/2}$ stoichiometry, assumed to engage in Se–Se bonding.' Clearly, our extracted product could not have a P_4S_{10}-like structure, since ^{77}Se-containing isotopomers of this molecule would constitute AB_3X (exocyclic ^{77}Se) or A_2B_2X (endocyclic ^{77}Se) nuclear spin systems, whose NMR spectra would be quite different from those observed. Molecular P_2Se_5 may have been formed in previous work, but remained undiscovered because of lack of foreknowledge of how to extract, handle and identify it: the mass spectrum listed by Monteil and Vincent[13] is very similar to that measured by us for recrystallised P_2Se_5, and can reasonably be assigned to ionisation products of molecular P_2Se_5, together with some free selenium. Monteil and Vincent[13] used a maximum reaction temperature of 250 °C in preparing 'P_4Se_{10},' and claimed that

Table 2 NMR parameters for α-$P_4Se_3I_2$ **1** (E = Se; X = Y = I), P_3Se_4X **3** (X = I, Br or Cl) and P_2Se_5 **4**

Compound	α-$P_4Se_3I_2$	P_3Se_4I	P_3Se_4Br	P_3Se_4Cl	P_2Se_5
T/K	297	240	270	297	297
(*a*) Coupling constants (Hz)[a]					
(*i*) ^{31}P–^{31}P					
$^1J(P_AP_B)$	−239.7(3)	−234.43(2)	−245.76(1)	−254.70(1)	
$^2J(P_AP_C)$	87.2(4)	120.99(2)	117.85(1)	115.74(1)	181.0(2)
$^2J(P_BP_C)$	21.4(2)	41.10(2)	43.13(1)	44.91(1)	
$^3J(P_BP_D)$	5.3(4)				
(*ii*) ^{31}P–$^{77}Se_a$					
$^1J(P_ASe_a)$	−279.6(2)	−315.4(6)	−317.4(1)	−316.6(2)	
$^1J(P_CSe_a)$		−219.8(8)	−215.6(1)	−213.2(2)	−243.49(6)
$^2J(P_BSe_a)$	6.0(2)		19.7(1)	22.2(2)	
(*iii*) ^{31}P–$^{77}Se_b$					
$^1J(P_BSe_b)$	−285.41(7)	−299.6(10)	−309.0(1)	−318.5(2)	
$^1J(P_CSe_b)$	−207.76(8)	−273.6(8)	−271.5(1)	−271.2(2)	
$^2J(P_ASe_b)$	13.0(1)		8.8(2)	9.8(3)	
(*iv*) ^{31}P–$^{77}Se_c$, ^{31}P–$^{77}Se_d$					
$^1J(P_ASe_d)$		−191.7(5)	−192.8(1)	−199.5(4)	
$^1J(P_CSe_c)$		−287.3(4)	−284.0(1)	−282.3(2)	−283.6(3)
$^2J(P_ASe_c)$			16.4(1)	17.0(2)	14.7(7)
$^2J(P_CSe_d)$		4.2(9)	5.0(2)	5.4(8)	
$^2J(P_BSe_d)$	48.55(7)	71.2(8)	74.0(2)	73.1(4)	
$^3J(P_BSe_c)$			−7.7(2)	−7.9(2)	
(*b*) Chemical shifts (ppm)[b]					
$\delta(P_A)$	105.25	80.48	85.13	88.48	
$\delta(P_B)$	126.15	113.61	132.97	142.33	
$\delta(P_C)$		125.06	124.32	122.99	104.95
$\delta(Se_a)$	−598.65		−534.39	−540.92	−408.24
$\delta(Se_b)$	−744.96		−466.72	−458.79	
$\delta(Se_c)$		−411.74	−458.00	−481.50	−388.28
$\delta(Se_d)$		−662.81	−716.81	−751.23	
(*c*) Secondary isotope shifts (ppb)[c]					
$^1\Delta\ P_A(Se_a)$	6(1)	7(2)	6.1(7)	6(1)	
$^1\Delta\ P_C(Se_a)$		5(3)	6.4(7)	3(1)	4.6(4)
$^1\Delta\ P_B(Se_b)$	5.8(4)	10(3)	6.2(8)	6.9(9)	
$^1\Delta\ P_C(Se_b)$	4.7(4)	4(3)	5.3(8)	4.2(9)	
$^1\Delta\ P_A(Se_d)$		2(3)	4.7(6)	4(2)	
$^1\Delta\ P_C(Se_c)$		8(2)	5.9(7)	6(1)	4(2)

[a] Standard deviations (σ) in parentheses. [b] ^{31}P NMR shifts relative to 85% H_3PO_4–H_2O; ^{77}Se NMR shifts relative to saturated H_2SeO_3–H_2O; all ^{77}Se shifts measured at 297 K. [c] Relative to main ^{31}P NMR spectrum shifts, *i.e.* to average shifts for all Se isotopomers, but excluding those containing any ^{77}Se.

at higher temperatures irreversible polymerisation took place. Kudchadker *et al.*[12] and ourselves used temperatures of 450 and 400 °C respectively, but in our method this was followed by very long annealing (four months) at 100 °C, just above the glass-transition temperature of the mixture.

Assignment of NMR Spectra.—The main ^{31}P NMR spectra of selenium isotopomers not containing ^{77}Se, of the compounds P_3Se_4X **3** (X = I, Br, Cl, SC_2H_5, SC_5H_{11} or SC_6H_5) were readily observed and analysed, initially as first-order spin systems, the hand analysis being followed in each case by iterative fitting using computer programs NUMARIT[15] or PANIC.[16] Fitting data are shown in Table 1 and results in Tables 2 and 3. The main ^{31}P NMR spectrum parameters for α-$P_4Se_3I_2$, initially analysed as an AA′MM′ spin system, were confirmed similarly (Tables 1 and 2).[3]

The rate of isomerisation of the P_3Se_4 skeleton increased in the order P_3Se_4Cl < P_3Se_4Br < P_3Se_4I (see below), and while ^{77}Se satellites in the ^{31}P NMR spectrum of P_3Se_4Cl could be observed at 297 K, it was necessary to study those of P_3Se_4Br and P_3Se_4I at 270 and 240 K respectively, when their isomerisation reactions were just sufficiently slowed down. Marginal solubility of the compounds at low temperatures made these satellite spectra extremely difficult to distinguish from noise (after accumulation over 16 h), while useful ^{77}Se NMR spectra could be obtained only at ambient temperature (during 64 h accumulations), limiting observable ^{77}Se transitions to those invariant in the exchange. Insolubility was not a major problem in the case of α-$P_4Se_3I_2$, but many of the ^{77}Se satellite peaks were overlaid by the non-first-order ^{31}P main NMR spectrum. These limitations are shown in Table 1 in terms of the fractions of transitions observed with sufficient certainty for inclusion in the iterative fitting, and were responsible for the omission of some of the smaller ^{31}P–^{77}Se couplings and secondary isotope shifts from Table 2.

The main ^{31}P NMR spectrum of P_2Se_5 was a readily observed singlet at δ 104.95, surrounded by the four strong lines of the satellite spectrum due to isotopomers **4c** (^{77}Se present as Se_c) (ABX spin system) and the two lines of the satellite spectrum due to isotopomers **4a** (A_2X spin system). Only after

Table 3 NMR parameters for $P_3Se_4(SR)$ **3** (X = SR) where R = C_2H_5, C_5H_{11} or C_6H_5

Compound	$P_3Se_4(SC_2H_5)$	$P_3Se_4(SC_5H_{11})$	$P_3Se_4(SC_6H_5)$
(*a*) ^{31}P–^{31}P Coupling constants (Hz)[a]			
$^1J(P_AP_B)$	−286.6	−288.6	−280.3
$^2J(P_AP_C)$	115.4	114.4	115.9
$^2J(P_BP_C)$	39.5	37.2	39.7
(*b*) ^{31}P Chemical shifts (ppm)[b]			
$\delta(P_A)$	79.5	77.5	81.2
$\delta(P_B)$	125.4	125.0	125.0
$\delta(P_C)$	116.5	114.0	116.7

[a] Standard deviations (σ) in parentheses. [b] Relative to 85% H_3PO_4–H_2O.

long accumulations (as above) using saturated solutions, could all the ^{31}P and ^{77}Se transitions due to isotopomers **4c** be found, allowing all three coupling constants to be determined (Table 2). The ^{77}Se triplet of isotopomers **4a** was barely distinguishable from noise, but the correct assignment of the selected peaks was borne out by the excellent r.m.s. deviation obtained in fitting it (Table 1). The measured ratio of integrals in the ^{31}P NMR spectrum for isotopomers **4c** and **4a** was 4.02:1 (expected ratio 4:1). Of the four sets of isotopomers of P_2Se_5 containing two ^{77}Se nuclei, isotopomers **4cd** (^{77}Se present as Se_c and Se_d) and isotopomers **4bd** constituted AA′XX′ spin systems, differing practically only in the values of their ^{77}Se–^{77}Se coupling constants. The two strongest peaks in the ^{31}P NMR spectra of these isotopomers were therefore coincident, and had enough combined intensity to be clearly visible in the best experimental spectra.

^{31}P–^{31}P *Coupling Constants.*—Within the P_3Se_4 halide series, only $^1J(P_AP_B)$ changed markedly, becoming more negative with increasing electronegativity of the halogen (Table 2), and still more negative on substitution of alkylthio- or arylthio-groups (Table 3). The changes closely paralleled those for the α-P_4S_3 halides **1** (E = S; X = Y = I, Br or Cl)[4] and thioalkylates and thioarylates **1** (E = S; X = Y = SC_2H_5 or SC_6H_5),[17] constant differences of 9.3–8.5 or 2.2–2.1 Hz being observed between corresponding members of the respective series.

The changes in $^2J(P_AP_C)$ between P_3Se_4X compounds were about half of those between the corresponding α-P_4S_3 halides **1** (E = S; X = Y = I, Br or Cl), but in the same sense. In the unsymmetric compounds α-$P_4S_3X(Y)$ **1** (E = S; X ≠ Y), $^2J(P_AP_C)$ has been shown to depend approximately equally on the two substituents X and Y.[4,9] The changes within the P_3Se_4 halide series, where there was only one substituent, were very similar to those within the P_4S_3 cyanide halides **1** (E = S; X = I, Br or Cl; Y = CN),[4] where only one substituent was changed. Despite this similarity of differences, the actual values of $^2J(P_AP_C)$ [and of $^2J(P_BP_C)$] were much more positive for the P_3Se_4 skeleton than for α-P_4E_3 skeletons (E = S or Se). The presence of the larger Se_c in P_3Se_4I, instead of P_DI in α-$P_4Se_3I_2$, caused increased bond angles at Se_a and Se_b,[3,8] which transmitted the couplings $^2J(P_AP_C)$ and $^2J(P_BP_C)$; an increased bond angle has been shown to be associated with more positive transmitted $^2J(^{31}P$–$^{31}P)$ couplings.[18] Replacement of the remaining P_BI unit in P_3Se_4I by Se to give P_2Se_5 was found to cause an even larger increase in $^2J(P_AP_C)$ (Table 2).

Signs of ^{31}P–^{77}Se *Coupling Constants.*—All the ^1J coupling constants were assumed to be negative, in accord with previous results.[19] Positive signs could be established for $^2J(P_BSe_d)$ and $^2J(P_ASe_b)$ in the necessarily non-first-order spin system of α-$P_4Se_3I_2$. The non-bonded distance $P_B \cdots Se_d$ is known to be less than the sum of the van der Waals radii,[3] and the coupling $^2J(P_BSe_d)$ was probably dominated by a through-space mechanism, which generally leads to positive $^2J(^{31}P$–$^{31}P)$ couplings,[20] and presumably also to positive $^2J(^{31}P$–$^{77}Se)$ couplings. The magnitude of $^2J(P_BSe_d)$ in α-$P_4Se_3I_2$ was greater than might have been expected for through-bond coupling.

For the P_3Se_4 halides, each set of isotopomers containing ^{77}Se at a particular skeletal position constituted an ABCX spin system, but in contrast to the P_4E_3 compounds, the phosphorus part of the spin system was sufficiently first order that it was practically impossible to find the sign of the ^{31}P–^{77}Se coupling constants from the relative success of iterative fitting. However, some other information was available. The coupling $^2J(P_BSe_d)$ had an even larger value in P_3Se_4I than in α-$P_4Se_3I_2$, while the measured $P_B \cdots Se_d$ distance was practically the same in both compounds.[8] This implies a positive sign for $^2J(P_BSe_d)$ in P_3Se_4I too. That $^2J(P_BSe_d)$ and $^1J(P_ASe_d)$ were of opposite sign in both P_3Se_4I and P_3Se_4Br, could be proved because ^{77}Se NMR spectra, at temperatures at which the sketetal exchange was taking place on the NMR time-scale, showed sharp $^{77}Se_d$ peaks only for those transitions which were separated by $^2J(P_BSe_d) + {}^1J(P_ASe_d)$ and were hence invariant to the exchange of roles of P_A and P_B (see below). Since the magnitudes of the couplings could be measured at low temperatures in the P_B or P_A regions respectively, the relationship between their signs could be obtained.

The sign of $^2J(P_ASe_c)$ was opposite to that of $^1J(P_CSe_c)$, and therefore positive, for the necessarily non-first-order ABX spin system of P_2Se_5, so the very similar $^2J(P_ASe_c)$ couplings in P_3Se_4Br and P_3Se_4Cl were also positive. The smaller, though geometrically similar, couplings $^2J(P_CSe_d)$ in the P_3Se_4 halides were assumed positive by analogy, as were $^2J(P_ASe_b)$, where the signs were confirmed by analogy with α-$P_4Se_3I_2$. The coupling $^3J(P_BSe_c)$ in P_3Se_4Br was of opposite sign to $^2J(P_ASe_c)$, and therefore negative, again shown by the extra sharpness of peaks separated by $^3J(P_BSe_c) + {}^2J(P_ASe_c)$ in the Se_c multiplet at 297 K (estimated k_r for the exchange = 15 s^{-1}). The analogous ^{31}P–^{31}P coupling $^3J(P_BP_D)$ is positive in the α-P_4S_3 halides **1** (E = S; X = Y = I, Br or Cl) but is negative in all other symmetric α-P_4S_3 compounds **1** (E = S; X = Y) for which it has been reported.[4,9]

Most doubt remains about the sign of $^2J(P_BSe_a)$. This was unobtainable for α-$P_4Se_3I_2$, where the satellite spectrum due to isotopomers **1a** (E = Se, X = Y = I) was not resolved from the main spectrum in the P_B region. If the atoms P_C, Se_b and Se_c in the P_3Se_4 halides **3**, or P_C, Se_b and P_D in α-$P_4Se_3I_2$, though not constituting a formally bonded three-membered ring, are considered analogous to the basal P_3 ring in $[P_7H]^{2-}$,[20] then if $^2J(P_BSe_d)$ is positive because of through-space lone-pair overlap (see above), $^2J(P_BSe_a)$ should be negative.

Magnitude of ^{31}P–^{77}Se *Coupling Constants.*—Just as $^2J(P_AP_C)$ became more positive with increasing bond angle at Se_a (see above), the average of the two ^1J couplings to Se_a became less negative (−279.6, −267.6 and −243.49 Hz for α-$P_4Se_3I_2$, P_3Se_4I and P_2Se_5 respectively) (Table 2), again supporting previous conclusions for P_4E_3 compounds.[18] About this average for the P_3Se_4 halides, there was a balancing of the

two couplings: $^1J(P_ASe_a)$ became more negative than in α-$P_4Se_3I_2$, as $^1J(P_CSe_a)$ became much less negative. For couplings to the diselenide bridge nuclei, the situation was reversed: $^1J(P_CSe_c)$ was much more negative than $^1J(P_ASe_d)$ in the P_3Se_4 halides, attaining approximately the value found for $^1J(P_CSe_c)$ in P_2Se_5, while $^1J(P_ASe_d)$ was similar in value to $^1J(P_ASe_d)$ in α-$P_4Se_3I_2$ [tabulated as $^1J(P_CSe_b)$]. These variations seem connected mostly with changes in environment of the P_C nucleus in going from α-$P_4Se_3I_2$ to the P_3Se_4 halides: $^1J(P_BSe_b)$ altered relatively little, while $^1J(P_CSe_b)$ became, surprisingly, much more negative [resulting in the reversal of the order $^1J(P_CSe_b) > {}^1J(P_CSe_a)$]. As might be expected, $^1J(P_BSe_b)$ was noticeably dependent on the exocyclic ligand attached to P_B, becoming more negative with more electronegative halogen to an extent, coincidently, very similar to that for the ^{31}P–^{31}P couplings $^1J(P_AP_B)$ (see above). It was surprising that $^2J(P_BSe_d)$ in the P_3Se_4 halides was insensitive to the substituent.

Chemical Shifts.—The shift of P_B, carrying the exocyclic substituent, moved to higher frequency for the P_3Se_4 halides, with more electronegative halogen, the intervals being quite similar to those observed for corresponding α-$P_4S_3X(CN)$.[4] The average shifts of the bridgehead nuclei P_A and P_C (δ 102.77, 104.72 and 105.74 for P_3Se_4I, P_3Se_4Br and P_3Se_4Cl respectively) were close to the values for α-$P_4Se_3I_2$ (δ 105.25) and for P_2Se_5 (δ 104.95). The variation in these averages was about two-thirds of that within the α-P_4S_3 dihalide series, presumably for reasons similar to those discussed above for the coupling $^2J(P_AP_C)$. Clearly there was a balancing of these bridgehead shifts somewhat similar to the balancing of the couplings $^1J(P_ASe_a)$ and $^1J(P_CSe_a)$ described above: as $\delta(P_A)$ moved to more positive frequency with more electronegative substituents, this was partly balanced by a decrease in $\delta(P_C)$. Compared with α-$P_4Se_3I_2$, the increased value of $\delta(P_C)$ in the P_3Se_4 halides may be attributed to the deshielding effect of the extra, electronegative adjacent selenium atom; the decrease in the value of $\delta(P_A)$ then followed.

Shifts of Se_a and particularly Se_b reflected the increase in bond angles at these atoms, on going from α-$P_4Se_3I_2$ to the P_3Se_4 halides, in accord with previous findings for P_4E_3 molecules.[18] The shifts of the diselenide bridge nuclei Se_c and Se_d in the P_3Se_4 halides were unexpectedly more sensitive to the exocyclic substituent than were those of the monoselenide bridge nuclei.

Secondary Isotope Shifts.—Fitting of ^{77}Se satellite spectra in the ^{31}P region yielded ^{31}P NMR chemical shifts which differed slightly from those found for the main ^{31}P NMR spectra. The secondary isotope shifts thus found (Table 2) were generally positive, because the atomic mass of ^{77}Se is slightly less than the weighted average of the masses of the remaining isotopes. Values of $^1\Delta$ were typically in the range 4–7 ppb, while $^2\Delta$ was rarely significantly non-zero. Results in these ranges were useful confirmations of the correct assignment of satellite spectra, but were rarely sufficiently precise for further chemical conclusions.

The Skeletal Exchange of P_3Se_4 Compounds.—Changes in main and satellite ^{31}P NMR spectra of P_3Se_4I and P_3Se_4Br with temperature, and the appearance of their ^{77}Se spectra, were consistent with intramolecular skeletal rearrangement in which P_A and P_B exchanged roles. Atom Se_d of the diselenide bridge was connected alternatively to P_A or P_B, while the halogen ligand alternated between connection to P_B or P_A respectively. The result of the rearrangement was interconversion of the two optical isomers of the compound. Atoms P_C, Se_c and Se_d did not change their roles, so some transitions of their NMR multiplets were visible at all temperatures: even though Se_d changed its connectivity in the rearrangement, in either optical isomer it was connected to a bridgehead phosphorus atom. In contrast, although Se_a and Se_b remained connected between P_C and P_A or P_B respectively, their roles changed along with the change in roles of P_A or P_B. Lineshape simulation using the program DNMR3[21] of parts of the NMR spectra which showed maximum change at each temperature, yielded rate constants for the exchange.

The following observations for P_3Se_4I were for a ^{31}P operating frequency of 121.5 MHz. At 240 K (estimated $k_r = 4$ s^{-1}) all ^{31}P intensities were almost those predicted for a static system, using NUMARIT. At 250 K ($k_r = 11$ s^{-1}) the centre peaks of the P_C main multiplet had broadened, while the outer peaks [separated by the sum of $J(P_AP_C)$ and $J(P_BP_C)$, which were thus shown to have the same sign] remained sharp. The P_A and P_B multiplets showed slight broadening, but this was sufficient for most of their satellite peaks to become invisible. At 260 K ($k_r = 35$ s^{-1}) and 270 K ($k_r = 90$ s^{-1}) the satellites of P_C had disappeared, except for those due to $^{77}Se_c$. [Since both P_C and Se_c retained their roles in the exchange, these peaks were visible at all temperatures: fitting at 297 K gave $^1J(P_CSe_c)$ of $-286.1(1)$ Hz; the change of coupling constant with temperature (*cf.* Table 2) was similar to that found for endocyclic $^1J(^{31}P$–$^{31}P)$ in α-P_4S_3 compounds.[22] The satellites of P_C due to $^{77}Se_d$ were obscured by the main spectrum at all temperatures.] By 285 K ($k_r = 300$ s^{-1}) the centre peaks of the P_C multiplet had collapsed, being replaced by a central peak, as P_A and P_B started to appear equivalent; the $J(P_BP_C)$ splitting of the P_B multiplet had disappeared, but all four peaks of the P_A multiplet were still just visible. At 285 K and higher temperatures, satellites of P_C appeared at a splitting corresponding to the average of $^1J(P_CSe_a)$ and $^1J(P_CSe_b)$. While at high temperatures the main spectrum of P_C appeared as a triplet, because both positions P_A and P_B, rendered equivalent by the exchange, were occupied by spin $\frac{1}{2}$ nuclei, this spectrum was further split only into a doublet in the satellite spectrum due to Se_a and Se_b, since only one of those positions was occupied at a time by ^{77}Se, although the positions were rendered equivalent and showed an averaged coupling to P_C. This satellite spectrum had twice the intensity of that due to $^{77}Se_c$. At 297 K ($k_r = 800$ s^{-1}) the P_A multiplet had lost all structure, while the $J(P_AP_B)$ splitting of the P_B multiplet was barely discernible. In the ^{77}Se NMR spectrum (57.3 MHz), the Se_a and Se_b absorptions had collapsed so as to be insufficiently visible for chemical shift measurement. The Se_c multiplet appeared as an intense doublet [$^1J(P_CSe_c)$], further split by $|^2J(P_ASe_c) + {}^3J(P_BSe_c)|$ [2.7(2) Hz], and the Se_d multiplet as a doublet [$^1J(P_ASe_d) + {}^2J(P_BSe_d)$] further split by $^2J(P_CSe_d)$. At 315 K ($k_r = 2600$ s^{-1}) all structure of the P_B multiplet had been lost, but coalescence to a single peak for P_A and P_B had not yet been reached.

The compound P_3Se_4Br exchanged more slowly than P_3Se_4I ($k_r = 1$ s^{-1} at 270 K; 30 s^{-1} at 305 K), so measurement of rates could be made only by simulating the P_C multiplet. At 297 K, the Se_a and Se_b multiplets, and Se_d peaks not separated by $^1J(P_ASe_d) + {}^2J(P_BSe_d)$, were visible, besides the peaks seen for P_3Se_4I. Evidence for exchange of P_3Se_4Cl could be seen only at high temperatures ($k_r = 5$ s^{-1} at 360 K), while P_3Se_4 thioalkylates and thioarylates showed no evidence for exchange at temperatures up to 370 K.

Fitting of rates gave $\Delta H^\ddagger = 52.4(6)$ kJ mol^{-1} and $\Delta S^\ddagger = -13(2)$ J K^{-1} mol^{-1} for P_3Se_4I, and $\Delta H^\ddagger = 66(4)$ kJ mol^{-1} and $\Delta S^\ddagger = 0(12)$ J K^{-1} mol^{-1} for P_3Se_4Br. The single rate constant obtained for P_3Se_4Cl corresponded to $\Delta G^\ddagger = 84$ kJ mol^{-1}. It was interesting that exchange was observed for P_3Se_4I but not for α-$P_4Se_3I_2$, despite the similar distance $P_B \cdots Se_d$ (see above) corresponding to the bond made in the exchange mechanism. Analogous fluxionality for the α-$P_4E_3X(Y)$ compounds **1** would probably result in inversion at the phosphorus, P_D, taking the place of Se in P_3Se_4I, relative to the new bridging selenium, so the product would be the asymmetric invertomer of the starting material, rather than its optical isomer, and ΔG would not be identically zero for the rearrangement. While NMR spectra have been assigned to such asymmetric invertomers in the β-$P_4S_3X(Y)$ series,[17,23] no fluxionality, analogous to that in P_3Se_4I, has yet been reported for any $P_4E_3X(Y)$ compound.

The distance $P_B \cdots Se_d$ was probably similar throughout the P_3Se_4 halide series, since the mainly non-bonded coupling $^2J(P_BSe_d)$ had similar values (Table 2). Similar orbital availability at P_A and Se_d was evidenced by similarity of most static NMR parameters associated with each respectively. It is probable, therefore, that the contribution of phosphorus–halogen bond strengths to the activation enthalpy is the chief factor which differentiates the rates of rearrangement of these compounds.

Experimental

All operations were carried out under dry argon by Schlenk methods. Carbon disulphide was dried by distillation from P_4O_{10}. NMR spectra were measured using a Bruker AC250 spectrometer operating at 101.27 MHz for ^{31}P, or using a Bruker WM300WB spectrometer operating at 121.5 MHz for ^{31}P and 57.3 MHz for ^{77}Se. [$^2H_6$]Benzene was used as the internal lock and temperature-dependent measurements were carried out in evacuated and sealed glass tubes, or a $(CD_3)_2CO$ capillary was used as the external lock and normal capped (and wax-sealed) 10 mm diameter tubes were used. Mass spectra were measured using a Kratos MS80 spectrometer in the EI mode at 50–70 eV ($0.80–1.12 \times 10^{-17}$ J), samples being introduced as solutions in CS_2 into the ionisation chamber at *ca.* 220 °C.

Preparation of P_3Se_4I **3** (X = I).—*High temperature method.* Red phosphorus (4.59 g, 148 mmol), grey selenium (15.6 g, 198 mmol) and I_2 (6.27 g, 24.7 mmol) were sealed under vacuum in a glass ampoule, then heated to 250 °C until a homogeneous melt was obtained. The ampoule was cooled slowly to room temperature, then the product was stirred with CS_2 (200 cm^3) for 3 d. The solution, after filtration and cooling to −30 °C for 8 h, yielded dark red crystals of P_3Se_4I. The extraction procedure was repeated ten times, using the mother-liquor as solvent, to give a total yield of 12.2 g (22.8 mmol, 46.1%).

Solution method. The compound P_4Se_3 (4.3 g, 11.9 mmol) and Se (2.2 g, 27.9 mmol) were dissolved in CS_2 (250 cm^3) at room temperature and I_2 (2.0 g, 7.9 mmol) in CS_2 (60 cm^3) was added at a rate of one drop per second. Precipitates appearing while the solution was stirred for a further 12 h, were removed by filtration. On cooling the dark red filtrate to −30 °C, P_3Se_4I precipitated as black-red needles. The crystals were filtered off, washed with CS_2 and dried in vacuum. The yield was 4.4 g (8.2 mmol, 52% based on P_4Se_3 taken). IR: ν_{max} at 390s, 364m, 354w, 342w, 333m, 313vs (PI), 289s and 225m cm^{-1}.

Halide Exchange Using Silver Halides.—Preparation of P_3Se_4Cl **3** (X = Cl). Silver chloride (3.2 g, 22 mmol) and P_3Se_4I (1.5 g, 2.8 mmol) were stirred in CS_2 (200 cm^3) at 0 °C for 10 d, with intermittent monitoring of compounds in solution by ^{31}P NMR spectroscopy. After filtration to remove AgI and unreacted starting materials, and evaporation of most of the CS_2 under vacuum, the resulting red solution gave dark-orange needles of P_3Se_4Cl after 1 h at −30 °C (yield < 5%). IR: ν_{max} at 452s, 430vs (PCl), 400m, 370m, 360w, 335s, 318m and 302vs cm^{-1}. Brown P_3Se_4Br **3** (X = Br) was made similarly. IR: ν_{max} at 404s, 400w, 375w, 370w, 350vs (PBr), 330vs, 320m and 292w cm^{-1}.

Alkylthio and Arylthio Derivatives $P_3Se_4(SR)$ **3** (X = SR; R = C_2H_5, C_5H_{11} *or* C_6H_5).—These were prepared from P_3Se_4I by a low-temperature modification of the method used previously,[17] for the thioalkylation of α-$P_4S_3I_2$. Triethylamine in CS_2 was added dropwise to a rapidly stirred solution of P_3Se_4I and the appropriate thiol in CS_2 at −50 °C, the three reagents being taken in equimolar quantities with careful avoidance of excess base. The mixture was allowed to warm, with stirring, to room temperature over 10 h to give a yellow solution suitable for NMR studies. Removal of CS_2 gave a yellow, oily solid which turned red in 1 h at room temperature, indicating decomposition.

Preparation of P_2Se_5 **4**.—Red phosphorus (0.762 g, 24.6 mmol) and grey selenium (4.858 g, 61.5 mmol) were sealed under vacuum in a quartz ampoule, then heated to 400 °C until a homogeneous melt was obtained (10 d). The ampoule was quenched in ice–water, then the product was powdered, resealed in glass, and annealed at 100 °C, *i.e.* above the glass-transition temperature, for 4 months. Stirring of the resulting powder with CS_2 (200 cm^3) at room temperature for several days gave, after filtration, a straw-coloured solution, which on cooling slowly to −50 °C yielded black crystals of P_2Se_5 **4**. Repeating the extraction five times, using the same mother-liquor, gave a combined yield of 0.32 g (5.62%) of P_2Se_5; EI MS (with relative intensities of specified peaks in isotope patterns given in parentheses): *m/z* 458 (13, $P_2Se_5^+$), 300 (24, $P_2Se_3^+$), 222 (5, $P_2Se_2^+$), 191 (9, PSe_2^+), 160 (20, Se_2^+), 142 (13, P_2Se^+) and 111 (100, PSe^+); IR (CsI disc): ν_{max} at 500m, 389s, 358vs, 322(sh), 310s, 245w and 220w cm^{-1}.

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