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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  $\alpha$ - or  $\beta$ -P<sub>4</sub>E<sub>3</sub>X<sub>2</sub> (E = S or Se), in which a PX unit has been replaced by Se. Analysis of <sup>31</sup>P and (in part) <sup>77</sup>Se NMR spectra of the P<sub>3</sub>Se<sub>4</sub>X compounds has shown remarkable correspondence of the coupling constants and chemical shifts between the P<sub>2</sub>Se<sub>4</sub>X and  $\alpha$ -P<sub>4</sub>S<sub>3</sub>X<sub>2</sub> series of compounds. Phosphorus-31 and <sup>77</sup>Se NMR spectra of  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub> are reported for comparison. Further replacement of a PX unit by Se gives the ultimate phosphorus-poor cluster compound P<sub>2</sub>Se<sub>5</sub>, 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<sub>3</sub>Se<sub>4</sub>X halides (X = I, Br or CI), 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  $\alpha$ - and  $\beta$ -P<sub>4</sub>E<sub>3</sub>X(Y) series 1 and 2 respectively (E = S or Se; X and Y are halogen, pseudohalogen or various similar groups),<sup>1-4</sup> of which the  $\beta$  series is generally thermally unstable with respect to the  $\alpha$ . The place of bridging chalcogen atoms may be taken by other difunctional groups bonding through, e.g., silicon [in  $P_4(SiMe_2)_3$ ]<sup>5</sup> or further phosphorus [in  $P_4(PMe)_3$ ],<sup>6</sup> but except for the replacement of phosphorus by arsenic,<sup>7</sup> 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),<sup>8</sup> in which an additional selenium atom took the place of a PI unit at a vertex of the approximate P<sub>4</sub> 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  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub> or of  $\beta$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>, depending on whether Se<sub>c</sub> or Se<sub>d</sub> is thought of as replacing a PI unit. The <sup>31</sup>P NMR spectrum of P<sub>3</sub>Se<sub>4</sub>I was of immediate interest because the compound was found to exist in solution in CS<sub>2</sub> as its two optical isomers, interconverting by a skeletal rearrangement reaction on the NMR time-scale at room temperature.

We now report satisfactory preparative routes to P<sub>3</sub>Se<sub>4</sub>I, and substitution reactions to yield P<sub>3</sub>Se<sub>4</sub>Br, P<sub>3</sub>Se<sub>4</sub>Cl and solutions containing  $P_3Se_4(SR)$  (R = C<sub>6</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub> or C<sub>5</sub>H<sub>11</sub>). This has allowed not only a study of variations in NMR chemical shifts and coupling constants for the P<sub>3</sub>Se<sub>4</sub> skeleton, on substitution, comparable to analogous work on the  $\alpha$ -P<sub>4</sub>S<sub>3</sub> skeleton,<sup>4,9</sup> 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<sub>3</sub>Se<sub>4</sub>I 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,<sup>10</sup> and its formation as a decomposition product of solutions of P<sub>3</sub>Se<sub>4</sub>I.

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## **Results and Discussion**

Triphosphorus Tetraselenide Iodide.--The identification by X-ray crystallography of P<sub>3</sub>Se<sub>4</sub>I as a minor by-product in the preparation of  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub> by melting together an equimolar mixture of P<sub>4</sub>Se<sub>3</sub> and iodine<sup>8</sup> 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<sub>2</sub>, while iodine reacts with P<sub>4</sub>Se<sub>3</sub> alone to give  $\beta$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>,<sup>1</sup> it reacted with a solution containing both P<sub>4</sub>Se<sub>3</sub> and selenium, in the ratio required by equation (1), to give

$$3 P_4 Se_3 + 7 Se + 2 I_2 \longrightarrow 4 P_3 Se_4 I \tag{1}$$

P<sub>3</sub>Se<sub>4</sub>I 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



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	<sup>77</sup> Se at position	Fraction of transitions observed, for				
Compound		P <sub>A</sub>	PB	P <sub>c</sub>	<sup>77</sup> Se	(r.m.s.) deviation/Hz
$\alpha - P_4 Se_3 I_2$	_	12/12	12/12			0.69
	а	23/24	0		16/16	0.58
	b	18/32	32/48		19/26	0.19
P <sub>3</sub> Se₄I	_	4/4	4/4	4/4		0.02
5 4	а	8/8	0	5/8	0	0.69
	b	0	4/8	4/8	0	0.58
	с	0	0	6/8	0	0.41
	d	7/8	4/8	0	4/8	0.69
P <sub>3</sub> Se <sub>4</sub> Br		4/4	4/4	4/4		0.01
5 4	а	8/8	4/8	8/8	7/8	0.20
	b	8/8	8/8	8/8	7/8	0.23
	с	8/8	4/8	8/8	8/8	0.20
	d	8/8	4/8	0	4/8	0.16
P <sub>3</sub> Se <sub>4</sub> Cl		4/4	4/4	4/4		0.01
5 4	a	8/8	5/8	6/8	8/8	0.29
	b	4/8	8/8	8/8	7/8	0.25
	с	8/8	0	5/8	8/8	0.24
	d	8/8	4/8	0	5/8	0.44
$P_2Se_5$	а			4/4	4/4	0.08
_ 0	с			8/8	6/6	0.29

Table 1 Iterative fitting of NMR spectra of  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub> 1 (E = Se; X = Y = I), P<sub>3</sub>Se<sub>4</sub>X 3 (X = I, Br or Cl) and P<sub>2</sub>Se<sub>5</sub> 4

bromide P<sub>3</sub>Se<sub>4</sub>Br 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 CS2, as in the preparation of the corresponding  $\alpha$ -P<sub>4</sub>S<sub>3</sub> halides 1 (E = S; X = Y = Br or Cl),<sup>11</sup> gave the purest products, but at the lower temperature (0 °C) necessary to avoid decomposition of the P<sub>3</sub>Se<sub>4</sub> 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<sub>3</sub>Se<sub>4</sub>I, as well as by comparison of IR spectra. Use of soluble (SnEt<sub>3</sub>Br or SnMe<sub>3</sub>Cl) or slightly soluble (HgBr<sub>2</sub>) 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 <sup>31</sup>P-<sup>31</sup>P coupling constants for P<sub>3</sub>Se<sub>4</sub>Br 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<sub>3</sub>Se<sub>4</sub>Br made using HgBr<sub>2</sub> proceeded at an obviously higher rate  $(k_r = 13 \text{ s}^{-1} \text{ at } 270 \text{ K})$  than for P<sub>3</sub>Se<sub>4</sub>Br made using either AgBr or SnEt<sub>3</sub>Br  $(k_r = 1 \text{ s}^{-1}, \text{ see below})$ . 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<sub>3</sub> 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  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub> 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

$$2 P_3 Se_4 I \Longrightarrow P_2 Se_5 + \alpha P_4 Se_3 I_2$$
 (2)

postulated to explain its singlet main <sup>31</sup>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 <sup>31</sup>P and <sup>77</sup>Se NMR spectra of its <sup>77</sup>Se isotopomers, with those of the  $P_3Se_4$  halides 3 (X = Cl, Br or I), and those of  $\alpha$ - $P_4Se_3I_2$  which are also reported here.

A direct preparation of P<sub>2</sub>Se<sub>5</sub> was then achieved by hightemperature 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<sup>13</sup> 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<sup>-1</sup>, as assigned by Monteil and Vincent<sup>13</sup> to P=Se stretching, but only of medium intensity, which increased on exposure of the sample to moist air. Kudchadker et al.<sup>12</sup> used the formula P<sub>2</sub>Se<sub>5</sub>, 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,<sup>14</sup> 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

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

centres,forwhich  $K = [Se=PSe_{3/2}]/[PSe_{3/2}][Se] = 0.85 \pm 0.05$ (atom fraction)<sup>-1</sup>. 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<sub>4</sub>S<sub>10</sub>-like structure, since <sup>77</sup>Se-containing isotopomers of this molecule would constitute AB<sub>3</sub>X (exocyclic <sup>77</sup>Se) or A<sub>2</sub>B<sub>2</sub>X (endocyclic <sup>77</sup>Se) nuclear spin systems, whose NMR spectra would be quite different from those observed. Molecular P<sub>2</sub>Se<sub>5</sub> 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<sup>13</sup> is very similar to that measured by us for recrystallised P<sub>2</sub>Se<sub>5</sub>, and can reasonably be assigned to ionisation products of molecular P<sub>2</sub>Se<sub>5</sub>, together with some free selenium. Monteil and Vincent<sup>13</sup> used a maximum reaction temperature of 250 °C in preparing 'P<sub>4</sub>Se<sub>10</sub>,' and claimed that

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Table 2	NMR parameters for a-l	$P_4Se_3I_2 1 (E = Se; X =$	$Y = I, P_3 Se_4 X 3 (X =$	= I, Br or Cl) and $P_2Se_5$
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Compound	$\alpha$ -P <sub>4</sub> Se <sub>3</sub> I <sub>2</sub>	P <sub>3</sub> Se <sub>4</sub> I	$P_3Se_4Br$	P <sub>3</sub> Se <sub>4</sub> Cl	$P_2Se_5$
T/K	297	240	270	297	297
(a) Coupling cons	tants (Hz) <sup>a</sup>				
( <i>i</i> ) <sup>31</sup> P– <sup>31</sup> P					
${}^{1}J(\mathbf{P}_{A}\mathbf{P}_{B})$ ${}^{2}J(\mathbf{P}_{A}\mathbf{P}_{C})$ ${}^{2}J(\mathbf{P}_{B}\mathbf{P}_{C})$ ${}^{3}J(\mathbf{P}_{B}\mathbf{P}_{D})$	-239.7(3) 87.2(4) 21.4(2) 5.3(4)	-234.43(2) 120.99(2) 41.10(2)	-245.76(1) 117.85(1) 43.13(1)	-254.70(1) 115.74(1) 44.91(1)	181.0(2)
( <i>ii</i> ) ${}^{31}P - {}^{77}Se_a$					
$^{1}J(P_{A}Se_{a})$ $^{1}J(P_{C}Se_{a})$ $^{2}J(P_{B}Se_{a})$	-279.6(2) 6.0(2)	-315.4(6) -219.8(8)	-317.4(1) -215.6(1) 19.7(1)	-316.6(2) -213.2(2) 22.2(2)	-243.49(6)
$(iii)^{31}P^{-77}Se_{b}$					
${}^{1}J(P_{B}Se_{b})$ ${}^{1}J(P_{C}Se_{b})$ ${}^{2}J(P_{A}Se_{b})$	-285.41(7) -207.76(8) 13.0(1)	-299.6(10) -273.6(8)	-309.0(1) -271.5(1) 8.8(2)	-318.5(2) -271.2(2) 9.8(3)	
(iv) <sup>31</sup> P- <sup>77</sup> Se <sub>c</sub> , <sup>31</sup> H	$P - 7^7 Se_d$				
${}^{1}J(P_{A}Se_{d})$ ${}^{1}J(P_{C}Se_{c})$ ${}^{2}J(P_{A}Se_{c})$ ${}^{2}J(P_{C}Se_{d})$ ${}^{2}J(P_{B}Se_{d})$ ${}^{3}J(P_{B}Se_{c})$	48.55(7)	- 191.7(5) - 287.3(4) 4.2(9) 71.2(8)	$-192.8(1) \\ -284.0(1) \\ 16.4(1) \\ 5.0(2) \\ 74.0(2) \\ -7.7(2)$	-199.5(4) -282.3(2) 17.0(2) 5.4(8) 73.1(4) -7.9(2)	-283.6(3) 14.7(7)
(b) Chemical shifts	$(ppm)^b$				
$\delta(\mathbf{P}_{A})$ $\delta(\mathbf{P}_{B})$ $\delta(\mathbf{P}_{C})$ $\delta(\mathbf{S}e_{a})$ $\delta(\mathbf{S}e_{b})$ $\delta(\mathbf{S}e_{c})$ $\delta(\mathbf{S}e_{d})$	105.25 126.15 - 598.65 - 744.96	80.48 113.61 125.06 411.74 662.81	85.13 132.97 124.32 534.39 466.72 458.00 716.81	88.48 142.33 122.99 - 540.92 - 458.79 - 481.50 - 751.23	104.95 - 408.24 - 388.28
(c) Secondary isot	one shifts (nnh) <sup>c</sup>				
<sup>1</sup> $\Delta$ P <sub>A</sub> (Se <sub>a</sub> ) <sup>1</sup> $\Delta$ P <sub>C</sub> (Se <sub>a</sub> ) <sup>1</sup> $\Delta$ P <sub>C</sub> (Se <sub>b</sub> ) <sup>1</sup> $\Delta$ P <sub>C</sub> (Se <sub>b</sub> ) <sup>1</sup> $\Delta$ P <sub>C</sub> (Se <sub>b</sub> ) <sup>1</sup> $\Delta$ P <sub>A</sub> (Se <sub>d</sub> ) <sup>1</sup> $\Delta$ P <sub>A</sub> (Se <sub>d</sub> )	6(1) 5.8(4) 4.7(4)	7(2) 5(3) 10(3) 4(3) 2(3)	6.1(7) 6.4(7) 6.2(8) 5.3(8) 4.7(6) 5.9(7)	6(1) 3(1) 6.9(9) 4.2(9) 4(2) 6(1)	4.6(4)
$\Delta P_{\rm C}(Se_{\rm c})$		8(2)	5.9(7)	0(1)	4(2)

<sup>a</sup> Standard deviations ( $\sigma$ ) in parentheses. <sup>b 31</sup>P NMR shifts relative to 85% H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O; <sup>77</sup>Se NMR shifts relative to saturated H<sub>2</sub>SeO<sub>3</sub>-H<sub>2</sub>O; all <sup>77</sup>Se shifts measured at 297 K. <sup>c</sup> Relative to main <sup>31</sup>P NMR spectrum shifts, *i.e.* to average shifts for all Se isotopomers, but excluding those containing any <sup>77</sup>Se.

at higher temperatures irreversible polymerisation took place. Kudchadker *et al.*<sup>12</sup> 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 <sup>31</sup>P NMR spectra of selenium isotopomers not containing <sup>77</sup>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<sup>15</sup> or PANIC.<sup>16</sup> Fitting data are shown in Table 1 and results in Tables 2 and 3. The main <sup>31</sup>P NMR spectrum parameters for  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>, initially analysed as an AA'MM' spin system, were confirmed similarly (Tables 1 and 2).<sup>3</sup>

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 <sup>77</sup>Se satellites in the <sup>31</sup>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 <sup>77</sup>Se NMR spectra could be obtained only at ambient temperature (during 64 h accumulations), limiting observable <sup>77</sup>Se transitions to those invariant in the exchange. Insolubility was not a major problem in the case of  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>, but many of the <sup>77</sup>Se satellite peaks were overlaid by the non-first-order <sup>31</sup>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 <sup>31</sup>P-<sup>77</sup>Se couplings and secondary isotope shifts from Table 2.

The main <sup>31</sup>P NMR spectrum of  $P_2Se_5$  was a readily observed singlet at  $\delta$  104.95, surrounded by the four strong lines of the satellite spectrum due to isotopomers **4c** (<sup>77</sup>Se present as Se<sub>c</sub>) (ABX spin system) and the two lines of the satellite spectrum due to isotopomers **4a** (A<sub>2</sub>X spin system). Only after

Compound	$P_3Se_4(SC_2H_5)$	$P_3Se_4(SC_5H_{11})$	$P_3Se_4(SC_6H_5)$
(a) ${}^{31}P - {}^{31}P C$	oupling constants (Hz)	a	
${}^{1}J(\mathbf{P}_{A}\mathbf{P}_{B})$	-286.6	-288.6	-280.3
$^{2}J(\mathbf{P}_{A}\mathbf{P}_{C})$	115.4	114.4	115.9
$^{2}J(\mathbf{P}_{B}\mathbf{P}_{C})$	39.5	37.2	39.7
(b) <sup>31</sup> P Chemi	cal shifts (ppm) <sup>b</sup>		
$\delta(\mathbf{P}_{\star})$	79.5	77.5	81.2
$\delta(\mathbf{P_n})$	125.4	125.0	125.0
$\delta(\mathbf{P}_{c})$	116.5	114.0	116.7

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

long accumulations (as above) using saturated solutions, could all the <sup>31</sup>P and <sup>77</sup>Se transitions due to isotopomers **4c** be found, allowing all three coupling constants to be determined (Table 2). The <sup>77</sup>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 <sup>31</sup>P NMR spectrum for isotopomers **4c** and **4a** was 4.02:1 (expected ratio 4:1). Of the four sets of isotopomers of P<sub>2</sub>Se<sub>5</sub> containing two <sup>77</sup>Se nuclei, isotopomers **4cd** (<sup>77</sup>Se present as Se<sub>c</sub> and Se<sub>d</sub>) and isotopomers **4bd** constituted AA'XX' spin systems, differing practically only in the values of their <sup>77</sup>Se-<sup>77</sup>Se coupling constants. The two strongest peaks in the <sup>31</sup>P NMR spectra of these isotopomers were therefore coincident, and had enough combined intensity to be clearly visible in the best experimental spectra.

<sup>31</sup>P-<sup>31</sup>P Coupling Constants.—Within the P<sub>3</sub>Se<sub>4</sub> halide series, only <sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) 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  $\alpha$ -P<sub>4</sub>S<sub>3</sub> halides 1 (E = S; X = Y = I, Br or Cl)<sup>4</sup> and thioalkylates and thioarylates 1 (E = S; X = Y = SC<sub>2</sub>H<sub>5</sub> or SC<sub>6</sub>H<sub>5</sub>),<sup>17</sup> 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  ${}^{2}J(P_{A}P_{C})$  between  $P_{3}Se_{4}X$  compounds were about half of those between the corresponding  $\alpha$ -P<sub>4</sub>S<sub>3</sub> halides 1 (E = S; X = Y = I, Br or Cl), but in the same sense. In the unsymmetric compounds  $\alpha$ -P<sub>4</sub>S<sub>3</sub>X(Y) 1 (E = S; X  $\neq$  Y),  $^{2}J(P_{A}P_{C})$  has been shown to depend approximately equally on the two substituents X and Y.<sup>4,9</sup> The changes within the P<sub>3</sub>Se<sub>4</sub> 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),<sup>4</sup> where only one substituent was changed. Despite this similarity of differences, the actual values of  ${}^{2}J(\dot{P}_{A}P_{C})$  [and of  ${}^{2}J(\dot{P}_{B}P_{C})$ ] were much more positive for the  $P_3Se_4$  skeleton than for  $\alpha$ - $P_4E_3$  skeletons (E = S or Se). The presence of the larger Se<sub>c</sub> in  $P_3Se_4I$ , instead of  $P_DI$  in  $\alpha$ - $P_4Se_3I_2$ , caused increased bond angles at Se<sub>a</sub> and Se<sub>b</sub>,<sup>3,8</sup> 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  ${}^{2}J({}^{31}P{}^{-31}P)$  couplings.<sup>18</sup> 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  ${}^{2}J(P_{A}P_{C})$  (Table 2).

Signs of <sup>31</sup>P<sup>-77</sup>Se Coupling Constants.—All the <sup>1</sup>J coupling constants were assumed to be negative, in accord with previous results.<sup>19</sup> Positive signs could be established for <sup>2</sup>J(P<sub>B</sub>Se<sub>d</sub>) and <sup>2</sup>J(P<sub>A</sub>Se<sub>b</sub>) in the necessarily non-first-order spin system of  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>. The non-bonded distance P<sub>B</sub> · · · Se<sub>d</sub> is known to be less than the sum of the van der Waals radii,<sup>3</sup> and the coupling <sup>2</sup>J(P<sub>B</sub>Se<sub>d</sub>) was probably dominated by a through-space mechanism, which generally leads to positive <sup>2</sup>J(<sup>31</sup>P<sup>-31</sup>P) couplings,<sup>20</sup> and presumably also to positive  ${}^{2}J({}^{31}P-{}^{77}Se)$  couplings. The magnitude of  ${}^{2}J(P_{B}Se_{d})$  in  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub> was greater than might have been expected for through-bond coupling.

For the P<sub>3</sub>Se<sub>4</sub> halides, each set of isotopomers containing <sup>77</sup>Se at a particular skeletal position constituted an ABCX spin system, but in contrast to the P<sub>4</sub>E<sub>3</sub> compounds, the phosphorus part of the spin system was sufficiently first order that it was practically impossible to find the sign of the <sup>31</sup>P-<sup>77</sup>Se coupling constants from the relative success of iterative fitting. However, some other information was available. The coupling  ${}^{2}J(P_{B}Se_{d})$ had an even larger value in  $P_3Se_4I$  than in  $\alpha$ - $P_4Se_3I_2$ , while the measured  $P_B \cdots Se_d$  distance was practically the same in both compounds.<sup>8</sup> 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 <sup>77</sup>Se NMR spectra, at temperatures at which the sketetal exchange was taking place on the NMR time-scale, showed sharp <sup>77</sup>Se<sub>d</sub> peaks only for those transitions which were separated by  $J(P_BSe_d) + {}^{1}J(P_ASe_d)$  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  ${}^{2}J(P_{A}Se_{c})$  was opposite to that of  ${}^{1}J(P_{C}Se_{c})$ , and therefore positive, for the necessarily non-first-order ABX spin system of  $P_{2}Se_{5}$ , so the very similar  ${}^{2}J(P_{A}Se_{c})$  couplings in  $P_{3}Se_{4}Br$  and  $P_{3}Se_{4}Cl$  were also positive. The smaller, though geometrically similar, couplings  ${}^{2}J(P_{C}Se_{d})$  in the  $P_{3}Se_{4}$  halides were assumed positive by analogy, as were  ${}^{2}J(P_{A}Se_{b})$ , where the signs were confirmed by analogy with  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>. The coupling  ${}^{3}J(P_{B}Se_{c})$  in  $P_{3}Se_{4}Br$  was of opposite sign to  ${}^{2}J(P_{A}Se_{c})$ , and therefore negative, again shown by the extra sharpness of peaks separated by  ${}^{3}J(P_{B}Se_{c}) + {}^{2}J(P_{A}Se_{c})$  in the Se<sub>c</sub> multiplet at 297 K (estimated  $k_{r}$  for the exchange = 15 s<sup>-1</sup>). The analogous  ${}^{31}P_{-}{}^{31}P$  coupling  ${}^{3}J(P_{B}P_{D})$  is positive in the  $\alpha$ -P<sub>4</sub>S<sub>3</sub> halides 1 (E = S; X = Y = I, Br or Cl) but is negative in all other symmetric  $\alpha$ -P<sub>4</sub>S<sub>3</sub> compounds 1 (E = S; X = Y) for which it has been reported. <sup>4,9</sup>

Most doubt remains about the sign of  ${}^{2}J(P_{B}Se_{a})$ . This was unobtainable for  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>, where the satellite spectrum due to isotopomers **1a** (E = Se, X = Y = I) was not resolved from the main spectrum in the P<sub>B</sub> region. If the atoms P<sub>C</sub>, Se<sub>b</sub> and Se<sub>c</sub> in the P<sub>3</sub>Se<sub>4</sub> halides **3**, or P<sub>C</sub>, Se<sub>b</sub> and P<sub>D</sub> in  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>, though not constituting a formally bonded three-membered ring, are considered analogous to the basal P<sub>3</sub> ring in [P<sub>7</sub>H]<sup>2-,20</sup> then if  ${}^{2}J(P_{B}Se_{d})$  is positive because of through-space lone-pair overlap (see above),  ${}^{2}J(P_{B}Se_{a})$  should be negative.

Magnitude of <sup>31</sup>P-<sup>77</sup>Se Coupling Constants.—Just as <sup>2</sup> $J(P_AP_C)$  became more positive with increasing bond angle at Se<sub>a</sub> (see above), the average of the two <sup>1</sup>J couplings to Se<sub>a</sub> became less negative (-279.6, -267.6 and -243.49 Hz for  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>, P<sub>3</sub>Se<sub>4</sub>I and P<sub>2</sub>Se<sub>5</sub> respectively) (Table 2), again supporting previous conclusions for P<sub>4</sub>E<sub>3</sub> compounds.<sup>18</sup> About this average for the P<sub>3</sub>Se<sub>4</sub> halides, there was a balancing of the

two couplings:  ${}^{1}J(P_{A}Se_{a})$  became more negative than in  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>, as  ${}^{1}J(P_{C}Se_{a})$  became much less negative. For couplings to the diselenide bridge nuclei, the situation was reversed:  ${}^{1}J(P_{C}Se_{c})$  was much more negative than  ${}^{1}J(P_{A}Se_{d})$  in the P<sub>3</sub>Se<sub>4</sub> halides, attaining approximately the value found for  ${}^{1}J(P_{C}Se_{c})$  in P<sub>2</sub>Se<sub>5</sub>, while  ${}^{1}J(P_{A}Se_{d})$  was similar in value to  ${}^{1}J(P_{A}Se_{d})$  in  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub> [tabulated as  ${}^{1}J(P_{C}Se_{b})$ ]. These variations seem connected mostly with changes in environment of the P<sub>C</sub> nucleus in going from  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub> to the P<sub>3</sub>Se<sub>4</sub> halides:  ${}^{1}J(P_{B}Se_{b})$  altered relatively little, while  ${}^{1}J(P_{C}Se_{b})$  became, surprisingly, much more negative [resulting in the reversal of the order  ${}^{1}J(P_{C}Se_{b}) > {}^{1}J(P_{C}Se_{a})$ ]. As might be expected,  ${}^{1}J(P_{B}Se_{b})$  was noticeably dependent on the exocyclic ligand attached to P<sub>B</sub>, becoming more negative with more electronegative halogen to an extent, coincidently, very similar to that for the  ${}^{31}P_{-}{}^{31}P$  couplings  ${}^{1}J(P_{A}P_{B})$  (see above). It was surprising that  ${}^{2}J(P_{B}Se_{d})$  in the P<sub>3</sub>Se<sub>4</sub> halides was insensitive to the substituent.

Chemical Shifts.--The shift of P<sub>B</sub>, carrying the exocyclic substituent, moved to higher frequency for the P<sub>3</sub>Se<sub>4</sub> halides, with more electronegative halogen, the intervals being quite similar to those observed for corresponding  $\alpha$ -P<sub>4</sub>S<sub>3</sub>X(CN).<sup>4</sup> The average shifts of the bridgehead nuclei  $P_A$  and  $P_C$  ( $\delta$  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  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub> ( $\delta$  105.25) and for  $P_2Se_5$  ( $\delta$  104.95). The variation in these averages was about two-thirds of that within the  $\alpha$ -P<sub>4</sub>S<sub>3</sub> dihalide series, presumably for reasons similar to those discussed above for the coupling  ${}^{2}J(P_{A}P_{C})$ . Clearly there was a balancing of these bridgehead shifts somewhat similar to the balancing of the couplings  ${}^{1}J(P_{A}Se_{a})$  and  ${}^{1}J(P_{C}Se_{a})$  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  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>, 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  $\delta(\mathbf{P}_{\mathbf{A}})$  then followed.

Shifts of Se<sub>a</sub> and particularly Se<sub>b</sub> reflected the increase in bond angles at these atoms, on going from  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub> to the P<sub>3</sub>Se<sub>4</sub> halides, in accord with previous findings for P<sub>4</sub>E<sub>3</sub> molecules.<sup>18</sup> The shifts of the diselenide bridge nuclei Se<sub>c</sub> and Se<sub>d</sub> in the P<sub>3</sub>Se<sub>4</sub> halides were unexpectedly more sensitive to the exocyclic substituent than were those of the monoselenide bridge nuclei.

Secondary Isotope Shifts.—Fitting of <sup>77</sup>Se satellite spectra in the <sup>31</sup>P region yielded <sup>31</sup>P NMR chemical shifts which differed slightly from those found for the main <sup>31</sup>P NMR spectra. The secondary isotope shifts thus found (Table 2) were generally positive, because the atomic mass of <sup>77</sup>Se is slightly less than the weighted average of the masses of the remaining isotopes. Values of <sup>1</sup> $\Delta$  were typically in the range 4–7 ppb, while <sup>2</sup> $\Delta$  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 <sup>31</sup>P NMR spectra of  $P_3Se_4I$  and  $P_3Se_4Br$ with temperature, and the appearance of their <sup>77</sup>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<sup>21</sup> 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 <sup>31</sup>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 ( $k_r = 11 \text{ s}^{-1}$ ) 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<sub>A</sub> and P<sub>B</sub> multiplets showed slight broadening, but this was sufficient for most of their satellite peaks to become invisible. At 260 K  $(k_r = 35 \text{ s}^{-1})$  and 270 K  $(k_r = 90 \text{ s}^{-1})$  the satellites of P<sub>C</sub> had disappeared, except for those due to <sup>77</sup>Se<sub>c</sub>. [Since both P<sub>C</sub> and Se<sub>c</sub> retained their roles in the exchange, these peaks were visible at all temperatures: fitting at 297 K gave  ${}^{1}J(P_{c}Se_{c})$  of -286.1(1) Hz; the change of coupling constant with temperature (cf. Table 2) was similar to that found for endocyclic  ${}^{1}J({}^{31}P-{}^{31}P)$  in  $\alpha$ -P<sub>4</sub>S<sub>3</sub> compounds.<sup>22</sup> The satellites of P<sub>C</sub> 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<sub>c</sub> 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<sub>C</sub> appeared at a splitting corresponding to the average of  ${}^{1}J(P_{C}Se_{a})$  and  ${}^{1}J(P_{C}Se_{b})$ . While at high temperatures the main spectrum of  $P_{C}$  appeared as a triplet, because both positions  $P_{A}$ and P<sub>B</sub>, 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 <sup>77</sup>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 <sup>77</sup>Se<sub>e</sub>. At 297 K ( $k_r = 800 \text{ s}^{-1}$ ) the P<sub>A</sub> multiplet had lost all structure, while the  $J(P_A P_B)$  splitting of the P<sub>B</sub> multiplet was barely discernible. In the <sup>77</sup>Se NMR spectrum (57.3 MHz), the Se<sub>a</sub> and Se<sub>b</sub> absorptions had collapsed so as to be insufficiently visible for chemical shift measurement. The Se multiplet appeared as an intense doublet  $[{}^{1}J(P_{c}Se_{c})]$ , further split by  $|{}^{2}J(P_{A}Se_{c}) + {}^{3}J(P_{B}Se_{c})|$  [2.7(2) Hz], and the Se<sub>d</sub> multiplet as a doublet  $[{}^{1}J(P_{A}Se_{d}) + {}^{2}J(P_{B}Se_{d})]$  further split by  $^{2}J(P_{C}Se_{d})$ . At 315 K  $(k_{r} = 2600 \text{ s}^{-1})$  all structure of the  $P_{B}$ multiplet had been lost, but coalescence to a single peak for  $\boldsymbol{P}_{\boldsymbol{A}}$ and  $P_B$  had not yet been reached.

The compound  $P_3Se_4Br$  exchanged more slowly than  $P_3Se_4I$ ( $k_r = 1 \text{ s}^{-1}$  at 270 K; 30 s<sup>-1</sup> at 305 K), so measurement of rates could be made only by simulating the  $P_C$  multiplet. At 297 K, the Se<sub>a</sub> and Se<sub>b</sub> multiplets, and Se<sub>d</sub> peaks not separated by <sup>1</sup>J( $P_ASe_d$ ) + <sup>2</sup>J( $P_BSe_d$ ), were visible, besides the peaks seen for  $P_3Se_4I$ . Evidence for exchange of  $P_3Se_4Cl$  could be seen only at high temperatures ( $k_r = 5 \text{ s}^{-1}$  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<sup>-1</sup> and  $\Delta S^{\ddagger} =$ -13(2) J K<sup>-1</sup> mol<sup>-1</sup> for P<sub>3</sub>Se<sub>4</sub>I, and  $\Delta H^{\ddagger} = 66(4)$  kJ mol<sup>-1</sup> and  $\Delta S^{\ddagger} = 0(12) \text{ J } \text{K}^{-1} \text{ mol}^{-1} \text{ for } P_3\text{Se}_4\text{Br}$ . The single rate constant obtained for P<sub>3</sub>Se<sub>4</sub>Cl corresponded to  $\Delta G^{\ddagger} = 84 \text{ kJ mol}^{-1}$ . It was interesting that exchange was observed for P<sub>3</sub>Se<sub>4</sub>I but not for  $\alpha$ -P<sub>4</sub>Se<sub>3</sub>I<sub>2</sub>, despite the similar distance P<sub>B</sub> · · · Se<sub>d</sub> (see above) corresponding to the bond made in the exchange mechanism. Analogous fluxionality for the  $\alpha$ -P<sub>4</sub>E<sub>3</sub>X(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  $\Delta G$  would not be identically zero for the rearrangement. While NMR spectra have been assigned to such asymmetric invertomers in the  $\beta$ -P<sub>4</sub>S<sub>3</sub>X(Y) series,<sup>17,23</sup> 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

### Experimental

compounds.

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 <sup>31</sup>P, or using a Bruker WM300WB spectrometer operating at 121.5 MHz for <sup>31</sup>P and 57.3 MHz for <sup>77</sup>Se. [<sup>2</sup>H<sub>6</sub>]Benzene was used as the internal lock and temperature-dependent measurements were carried out in evacuated and sealed glass tubes, or a (CD<sub>3</sub>)<sub>2</sub>CO 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 × 10<sup>-17</sup> J), samples being introduced as solutions in CS<sub>2</sub> 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<sub>2</sub> (200 cm<sup>3</sup>) 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<sup>3</sup>) at room temperature and  $I_2$  (2.0 g, 7.9 mmol) in  $CS_2$  (60 cm<sup>3</sup>) 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:  $v_{max}$  at 390s, 364m, 354w, 342w, 333m, 313vs (PI), 289s and 225m cm<sup>-1</sup>.

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<sup>3</sup>) at 0 °C for 10 d, with intermittent monitoring of compounds in solution by <sup>31</sup>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:  $v_{max}$  at 452s, 430vs (PCl), 400m, 370m, 360w, 335s, 318m and 302vs cm<sup>-1</sup>. Brown  $P_3Se_4Br 3 (X = Br)$  was made similarly. IR:  $v_{max}$  at 404s, 400w, 375w, 370w, 350vs (PBr), 330vs, 320m and 292w cm<sup>-1</sup>.

Alkylthio and Arylthio Derivatives  $P_3Se_4(SR)$  3 (X = SR; R = C<sub>2</sub>H<sub>5</sub>, C<sub>5</sub>H<sub>11</sub> or C<sub>6</sub>H<sub>5</sub>).—These were prepared from P<sub>3</sub>Se<sub>4</sub>I by a low-temperature modification of the method used previously,<sup>17</sup> for the thioalkylation of  $\alpha$ -P<sub>4</sub>S<sub>3</sub>I<sub>2</sub>. Triethylamine in CS<sub>2</sub> was added dropwise to a rapidly stirred solution of P<sub>3</sub>Se<sub>4</sub>I and the appropriate thiol in CS<sub>2</sub> at -50 °C, the three reagents being taken in equimolar quantities with careful avoidance of excess base. The mixture was allowed to warm,

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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<sub>2</sub>Se<sub>5</sub> 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<sup>3</sup>) 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<sub>2</sub>Se<sub>5</sub> 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<sub>2</sub>Se<sub>5</sub><sup>+</sup>), 300 (24, P<sub>2</sub>Se<sub>3</sub><sup>+</sup>), 222 (5,  $P_2Se_2^+$ ), 191 (9,  $PSe_2^+$ ), 160 (20,  $Se_2^+$ ), 142 (13,  $P_2Se^+$ ) and 111 (100, PSe<sup>+</sup>); IR (CsI disc): v<sub>max</sub> at 500m, 389s, 358vs, 322(sh), 310s, 245w and 220w cm<sup>-1</sup>.

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