Rapid Transfer of Selenium from Tertiary Phosphine Selenides to Tertiary Phosphines

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Selenium transfer between PR_3Se and PR_3 [R_3 = $MePh_2$ or $Ph_2(CH_2PPh_2)$] in solution is rapid on the n.m.r. time scale, and a bimolecular process is indicated. Mixtures of $Ph_2P(Se)C_2H_4(Se)PPh_2$, $Ph_2P(Se)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$ display similar variable-temperature ^1H n.m.r. characteristics and their methylene-proton signals coalesce at elevated temperatures. The compound $Ph_2P(Se)CH_2(Se)PPh_2$ reacts immediately on mixing with $Ph_2PCH_2PPh_2$ to give exclusively $Ph_2P(Se)CH_2PPh_2$, whereas solutions of $Ph_2P(Se)C_2H_4(Se)PPh_2$ and $Ph_2PC_2H_4PPh_2$ equilibrate with $Ph_2P(Se)C_2H_4PPh_2$ in 1 : 1 : 2 proportions, respectively. The sulphur analogues behave similarly, but react much more slowly. Selenium reacts at ambient temperature with $Ph_2P(S)CH_2PPh_2$ to form only $Ph_2P(S)CH_2(Se)PPh_2$, but the action of sulphur on $Ph_2P(Se)CH_2PPh_2$ leads to a mixture of $Ph_2P(Se)CH_2(Se)PPh_2$, $Ph_2P(Se)CH_2(S)PPh_2$, and $Ph_2P(S)CH_2(S)PPh_2$. Controlling influences and synthetic implications of these reactions are discussed.

EVER since Gottlieb[1] observed the transfer of sulphur from PCl_3S to triaryl phosphite in 1932, the transfer process has been extensively examined and finds numerous synthetic applications.[2] The reactions usually require elevated temperatures or long reaction times, and progress only if the initial phosphorus(III) derivative is more basic than that derived from the tertiary phosphine sulphide. Yields are generally good, however, and the process can be applied either for the purpose of desulphurising phosphine sulphides [*e.g.* equation (1)][3] or for preparing phosphorus(V) sulphides [equation (2)].[4] A kinetic study[5] on such transfer processes indicated that

$$Me_2P(S)C_2H_4(S)PMe_2 + 2PBu_3 \xrightarrow{130\ ^\circ C} Me_2PC_2H_4PMe_2 + 2\ PBu_3S \quad (1)$$

$$C(CH_2PPh_2)_4 + 4\ PCl_3S \xrightarrow{125\ ^\circ C} C[CH_2(S)PPh_2]_4 + 4\ PCl_3 \quad (2)$$

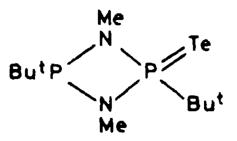
the sulphur transfer was a bimolecular process involving a transition state in which sulphur was bonded to both phosphorus atoms.

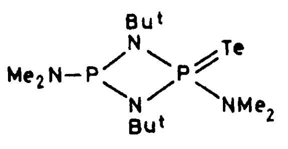
A variation on the sulphur-transfer reaction has been reported by Grim and Mitchell,[6] in which sulphur is transferred to the more basic phosphorus atom of an asymmetrical methylenediphosphine monosulphide [equation (3)]. The reaction did not follow either simple

$$Ph_2P(S)CH_2PMe_2 \xrightarrow[30\ h]{160\ ^\circ C} Ph_2PCH_2(S)PMe_2 \quad (3)$$

first-order or simple second-order kinetics, and small amounts (*ca.* 10%) of $Ph_2P(S)CH_2(S)PMe_2$ and $Ph_2PCH_2PMe_2$ were also produced. The same authors recently reported that these latter two compounds react together to form $Ph_2PCH_2(S)PMe_2$.[7]

Compared to their sulphur analogues, tertiary phosphine tellurides can be difficult to isolate and many tend to decompose (a glass-catalysed reaction),[8] particularly the aryl derivatives. Perhaps related to this, tellurium transfer between phosphorus atoms has been found to be fast, even on the n.m.r. time scale at room temperature. Thus, mixtures of $PMePh_2$ and $PMePh_2Te$ exhibit only one methyl-proton doublet, with a reduced coupling constant, $J(PCH)$ at ambient temperatures. (Decomposition to elemental tellurium prevented the observation of reproducible variable-temperature spectra.)[9] In a similar study, not complicated by the deposition of free tellurium, Du Mont and Kroth[10] described the rapid exchange of tellurium from PR_3Te to PR_3 ($R = Bu^t$ or NMe_2), postulating an intermediate of the type $R_3PTe \cdots PR_3$. Such a compound has been isolated and examined for R = Ph.[11] Rapid tellurium exchange between the two phosphorus atoms of the cyclodiphosphazanes (1)[12] and (2)[13] has been reported. Only one isomer was reported in each case. The ^1H n.m.r. spectrum of (2) showed a broadened doublet for the NMe_2 signals at ambient temperatures, and this collapsed to a singlet upon ^{31}P irradiation at either of two separate frequencies. Thus the tellurium exchange lifetime is less than the spin–lattice relaxation time for the ^{31}P nuclei, enabling complete ^1H-{^{31}P} decoupling to be effected by irradiating either phosphorus.[13]


(1)


(2)

Phosphorus(V) selenides resemble their analogous sulphides, rather than the tellurides, in that they are thermally stable and can be readily prepared from phosphorus(III) prescursors by the action of elemental selenium,[14] K[CNSe],[15] or organic diselenides.[16] We report here the relative rates and synthetic potential of selenium exchange between phosphorus atoms. A preliminary account has appeared.[17]

RESULTS AND DISCUSSION

Solutions of the diselenide $Ph_2P(Se)CH_2(Se)PPh_2$ and the diphosphine $Ph_2PCH_2PPh_2$ react immediately on mixing at room temperatures to produce $Ph_2P(Se)$-

CH_2PPh_2 quantitatively [equation (4)]. Mixtures of the ethylene-bridged analogues react equally quickly, but equilibrate to a 1 : 2 : 1 mixture of $Ph_2P(Se)C_2H_4(Se)PPh_2$, $Ph_2P(Se)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$ [equation (5)]. The analogous sulphur derivatives react in a similar way, but much more slowly. To reach completion (for the CH_2-bridged system) or equilibrium (for the C_2H_4-bridged compounds) requires either 24 h at 160 °C (with no solvent or in *o*-dichlorobenzene) or more than 40 d at 80 °C (in benzene).

$$Ph_2P(Se)CH_2(Se)PPh_2 + Ph_2PCH_2PPh_2 \longrightarrow 2Ph_2P(Se)CH_2PPh_2 \quad (4)$$

$$Ph_2P(Se)C_2H_4(Se)PPh_2 + Ph_2PC_2H_4PPh_2 \rightleftharpoons 2Ph_2P(Se)C_2H_4PPh_2 \quad (5)$$

These reactions can be reversed by selectively removing the more volatile diphosphine component by vacuum sublimation. Thus when $Ph_2P(S)CH_2PPh_2$ was heated *in vacuo* at 150 °C, almost pure $Ph_2PCH_2PPh_2$ sublimed out, leaving a residue rich in $Ph_2P(S)CH_2(S)PPh_2$. We conclude that even in the case of the methylene-bridged compounds, equilibration must occur in the melt, although only the monoselenide or monosulphide could be detected in solution by n.m.r. spectroscopy.

TABLE 1

Coalescence temperatures [a]

System	Components	Concentration [b]/mol dm^{-3}							
A	$PMePh_2Se$	0.33	(>447)	0.36	(438)	0.67	(428)	1.0	(418)
	$PMePh_2$	0.33		0.72		1.32		2.0	
B	$Ph_2P(Se)CH_2PPh_2$	0.53	(438)	0.67	(418)	1.0	(411)		
	$Ph_2PCH_2PPh_2$	0.27		0.67		1.0			
C	$Ph_2P(Se)C_2H_4(Se)PPh_2$	0.20	(398) [c]	0.33	(368) [c]				
	$Ph_2P(Se)C_2H_4PPh_2$	0.40		0.67					
	$Ph_2PC_2H_4PPh_2$	0.20		0.33					

[a] Measured at 60 MHz on a JEOL C60HL spectrometer with noise modulation of the ^{31}P irradiation field (P^V and P^{III} signals were generally separated by *ca.* 1 kHz). [b] In *o*-dichlorobenzene solution. Coalescence temperatures (±10 K) are given in parentheses. [c] In chlorobenzene solution. All four methylene signals from the three compounds were involved in the coalescence process.

The marked difference in the equilibrium positions of equations (4) and (5) is presumably because the more electron-deficient P^V atom in $Ph_2P(Se)CH_2PPh_2$ deactivates the P^{III} atom of that moleule, whereas in $Ph_2P(Se)C_2H_4PPh_2$, where the P atoms are separated by two CH_2 groups, this effect is small or absent. A similar effect is transmitted through (NR) bridges and has led to the quantitative production of the cyclodiphosphazane monoselenide $Me_2NP(\mu\text{-}NBu^t)_2P(Se)NMe_2$ from $Me_2NP(\mu\text{-}NBu^t)_2PNMe_2$ and $Me_2N(Se)P(\mu\text{-}NBu^t)_2P(Se)NMe_2$.[13] Interestingly, however, Mann [18] proposed an inductive deactivation effect operating across two CH_2 bridge groups to account for the weakness of the attachment of one S atom to arsenic in $PhBuAs(S)C_2H_4(S)AsBuPh$, resulting in a change of configuration at one As centre on mild heating.

The slow redistribution of sulphur, and the fast redistribution of selenium or tellurium,[9] between the phosphorus atoms of diphosphine systems thus appears to be a general process. Equation (3) and the processes related to that system [6,7] are simply specific examples of this, complicated by the differing substituent groups on phosphorus.

The exchange of selenium between phosphorus atoms is fast on the n.m.r. time scale at elevated temperatures (Table 1). Thus the two methyl singlets produced after ^{31}P decoupling of a mixture of $PMePh_2$ and $PMePh_2Se$ broaden and coalesce as the temperature is raised. The process covers a wide temperature range and the coalescence temperature (the lowest temperature at which no valley could be discerned between the individual signals) is difficult to measure accurately. Nevertheless the phenomenon is concentration dependent, and the transfer process presumably proceeds *via* a bimolecular route analogous to those proposed for sulphur [5] and tellurium.[10]

Mixtures of $Ph_2P(Se)CH_2PPh_2$ and $Ph_2PCH_2PPh_2$, and of $Ph_2P(Se)C_2H_4(Se)PPh_2$, $Ph_2P(Se)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$, displayed similar variable-temperature n.m.r. characteristics. No separate coalescence phenomena for the components $Ph_2P(Se)CH_2PPh_2$ or $Ph_2P(Se)C_2H_4PPh_2$ in these mixtures could be discerned, the two methylene signals of the former system and the four methylenes of the latter coalescing respectively to single broad resonances. Thus the transfer process appears to be at least predominantly intermolecular in these cases also. A similar concentration dependence, and hence intermolecular process, has been found for tellurium transfer in $Me_2NP(\mu\text{-}NBu^t)_2P(Te)NMe_2$.[13]

The coalescence temperatures for 1,2-bis(diphenylphosphino)ethane with its selenides were substantially lower than those involving $Ph_2PCH_2PPh_2$ or $PMePh_2$ (Table 1). On the other hand, solutions of $Ph_2P(Se)CH_2PPh_2$, alone or with $Ph_2P(Se)CH_2(Se)PPh_2$, failed to reach coalescence in the temperature range examined (up to *ca.* 450 K). Obviously the nature of the substituents on phosphorus affects the rate of selenium transfer. The failure to reach coalescence with $Ph_2P(Se)CH_2PPh_2$ presumably once more reflects the deactivating effect of the nearby $Ph_2P(Se)$ group, and suggests in this case that it is the nature of the P^{III} atom which is most critical to the process.

It thus appears that although phosphine selenides resemble their analogous sulphides in their ease of preparation and general stability, the rate of selenium transfer between phosphorus atoms is rapid, and more like that for tellurium than sulphur. This combination of properties suggests that selenium would be better suited than sulphur as a protecting group for phosphorus(III) when this is required. The facility for subsequent rapid removal of the selenium under mild conditions could offer distinct advantages.

The importance of the rate of chalcogen transfer is illustrated by the preparation of the mixed dichalcogenide derivative $Ph_2P(S)CH_2(Se)PPh_2$. In principle, this can be prepared either by the action of sulphur on $Ph_2P(Se)CH_2PPh_2$, or by the action of selenium on $Ph_2P(S)CH_2PPh_2$. Both these reactions were followed in $CDCl_3$ solution at ambient temperature by ^1H n.m.r. spectroscopy. The reaction between $Ph_2P(S)CH_2PPh_2$ and black selenium powder proceeded slowly over *ca.* 4 d to produce exclusively $Ph_2P(S)CH_2(Se)PPh_2$ [equation (6)]. The reaction between $Ph_2P(Se)CH_2PPh_2$ and sulphur, on the other hand, was more complex. After 4 h,

$$Ph_2P(S)CH_2PPh_2 + \tfrac{1}{8}Se_8 \longrightarrow Ph_2P(S)CH_2(Se)PPh_2 \quad (6)$$

n.m.r. signals due to $Ph_2P(Se)CH_2PPh_2$, $Ph_2P(Se)CH_2(Se)PPh_2$, $Ph_2P(S)CH_2(Se)PPh_2$, $Ph_2P(S)CH_2PPh_2$, and $Ph_2P(S)CH_2(S)PPh_2$ were all observed, and the final product was a 1 : 2 : 1 mixture of $Ph_2P(S)CH_2(S)PPh_2$, $Ph_2P(S)CH_2(Se)PPh_2$, and $Ph_2P(Se)CH_2(Se)PPh_2$

$$4Ph_2P(Se)CH_2PPh_2 + \tfrac{1}{2}S_8 \longrightarrow Ph_2P(Se)CH_2(Se)PPh_2 + 2Ph_2P(Se)CH_2(S)PPh_2 + Ph_2P(S)CH_2(S)PPh_2 \quad (7)$$

[equation (7)]. The mixed products presumably arise *via* selenium exchange between $Ph_2P(Se)CH_2PPh_2$ and $Ph_2P(Se)CH_2(S)PPh_2$. Although this would not be expected to be fast on the n.m.r. time scale (see above) an independent experiment established that the equilibrium (8) was established within 20 min at room temperature. Thus the relative ease of selenium transfer

$$Ph_2P(Se)CH_2(Se)PPh_2 + Ph_2P(S)CH_2PPh_2 \rightleftharpoons Ph_2P(Se)CH_2(S)PPh_2 + Ph_2P(Se)CH_2PPh_2 \quad (8)$$

establishes reaction (6) as the preferred route to the mixed dichalcogenide.

EXPERIMENTAL

Nuclear magnetic resonance spectra were recorded on Varian T60, Varian HA-100, and JEOL C-60HL instruments. Phosphorus chemical shifts measured by ^1H-{^{31}P} double resonance are relative to external H_3PO_4 with positive as downfield. Table 2 lists some relevant data. Coalescence temperatures were measured for the collapse of singlet methyl or methylene proton signals (produced by complete ^{31}P decoupling) in the systems A and B (see Table 1). Differences in coalescence temperatures give an approximate measure of the relative rates of exchange since they are dependent on the chemical shift between the two signals in the absence of exchange.[19] This shift was in the range 35—50 Hz for systems A—C (Table 1) so that only substantial differences in coalescence temperatures (30 °C) reflect real changes in rate. Concentration effects on the coalescence temperature for a given solute do give a good relative measure of exchange rates.

The compounds $Ph_2P(Se)CH_2(Se)PPh_2$, $Ph_2P(Se)C_2H_4(Se)PPh_2$, $Ph_2P(S)CH_2(S)PPh_2$, and $Ph_2P(S)C_2H_4(S)PPh_2$ were prepared [20] by the action of selenium or sulphur on the respective diphosphine in refluxing benzene; $Ph_2P(S)CH_2PPh_2$[21] was prepared from the addition of 1 mol equivalent of sulphur to $Ph_2PCH_2PPh_2$ in benzene.

Preparation of $Ph_2P(Se)CH_2PPh_2$.—The diphosphine diselenide $Ph_2P(Se)CH_2(Se)PPh_2$ (0.6 g, 1.1 mmol) was stirred in ethanol (25 cm³) and $Ph_2PCH_2PPh_2$ (0.425 g, 1.1 mmol) was added. The resulting solution was refluxed for a few minutes and filtered while hot. Lustrous white crystals of $Ph_2P(Se)CH_2PPh_2$ (0.81 g, 79%) deposited when the solution cooled (Found: C, 64.7; H, 4.95. Calc. for $C_{25}H_{22}P_2Se$: C, 64.8; H, 4.80%). Its i.r. spectrum revealed ν(PSe) at 531 cm^{-3}.

TABLE 2

Selected n.m.r. data

Compound	N.m.r. data [a]
$PMePh_2Se$	CH_3, 2.25 (d); $^2J(PH)$ 13.2 Hz; ^{31}P, 23.3
$PMePh_2$	CH_3, 1.47 (d); $^2J(PH)$ 4.0 Hz; ^{31}P, −26.9
$Ph_2P(Se)CH_2(Se)PPh_2$	CH_2, 4.30 (t); $^2J(PH)$ 13.2 Hz; ^{31}P, 22.4
$Ph_2P(Se)CH_2PPh_2$ [b]	CH_2, 3.42 (dd); $^2J(P^{III}H)$ 0.9 Hz, $^2J(P^{V}H)$ 13.4 Hz; $^{31}P^{III}$, −26.6, $^{31}P^{V}$, 30.5; $^2J(PP)$ 83 ± 2 Hz [c]
$Ph_2PCH_2PPh_2$ [b]	CH_2, 2.80 (t); $^2J(PH)$ 1.9 Hz; ^{31}P, −22.0
$Ph_2P(Se)C_2H_4(Se)PPh_2$	CH_2, 3.03 (d);[d] $^2J(PH) + {}^3J(PH)$ 2.0 Hz [e]
$Ph_2P(Se)C_2H_4PPh_2$	CH_2, 2.55 (d);[d] $^2J(PH) + {}^3J(PH)$ 3.8 Hz [e]
$Ph_2PC_2H_4PPh_2$	CH_2, 2.18 (t);[f] $^2J(PH) + {}^3J(PH)$ 8.4 Hz [e]
$Ph_2P(S)CH_2(S)PPh_2$	CH_2, 3.95 (t); $^2J(PH)$ 13.4 Hz
$Ph_2P(S)CH_2PPh_2$ [b]	CH_2, 3.25 (dd); $^2J(P^{III}H)$ 0.9 Hz, $^2J(P^{V}H)$ 13.4 Hz; $^{31}P^{III}$, − 27.3, $^{31}P^{V}$, 39.2; $^2J(PP)$ 73 ± 3 Hz [c]
$Ph_2P(S)C_2H_4(S)PPh_2$	CH_2, 2.85 (d);[d] $^2J(PH) + {}^3J(PH)$ 2.0 Hz [e]
$Ph_2P(S)C_2H_4PPh_2$	CH_2, 2.47 (d);[d] $^2J(PH) + {}^3J(PH)$ 3.0 Hz [e]
$Ph_2P(S)CH_2(Se)PPh_2$	CH_2, 4.13 (t); $^2J(PH)$ 13.4 Hz; $^{31}P(S)$, 35.2; $^{31}P(Se)$, 24.9; $^2J(PP)$ +16.3 Hz; $^1J(PSe)$ 739.6 Hz

[a] In *o*-dichlorobenzene unless otherwise stated. Proton chemical shifts (δ/p.p.m.) relative to internal $SiMe_4$. d = doublet, dd = doublet of doublets, and t = triplet. Phosphorus chemical shifts are relative to external H_3PO_4, positive shifts being downfield of this reference. [b] In C_6D_6. [c] The sign of $^2J(PP)$ was found to be opposite to the signs of $^2J(P^{III}H)$ and $^2J(P^{V}H)$, which, for the latter, are known to be negative (W. McFarlane and D. S. Rycroft, *J.C.S. Dalton*, 1973, 2162), the former being usually small and positive, but can be negative (W. McFarlane, *Proc. Roy. Soc.*, 1968, **306**, 185). [d] Broadened doublet. [e] See for example A. J. Carty and R. K. Harris, *Chem. Comm.*, 1967, 234. [f] Deceptively simple methylene proton spectrum, which resembles a 1 : 2 : 1 triplet (ref. of footnote *e*).

Preparation of $Ph_2P(S)CH_2(Se)PPh_2$.—The monosulphide $Ph_2P(S)CH_2PPh_2$ (0.5 g) was dissolved in toluene (25 cm³) at room temperature and black selenium powder (0.2 g) was added. The mixture was stirred at room temperature for 5 d, after which the excess of selenium was filtered off and the toluene evaporated *in vacuo*. Recrystallisation from methanol yielded $Ph_2P(S)CH_2(Se)PPh_2$ (0.3 g, 50%) as fine colourless needles (Found: C, 60.6; H, 4.55. Calc. for $C_{25}H_{22}PSSe$: C, 60.6; H, 4.50%). Its i.r. spectrum (KBr disc) clearly showed ν(PS) at 608 cm^{-1} and ν(PSe) at 533 cm^{-1}.

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