Reaction of Phospholes with Acids; [1,5] Proton Shifts in 1*H*-λ^5-Phospholes

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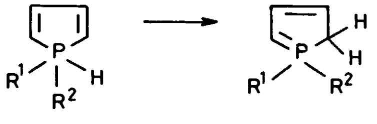
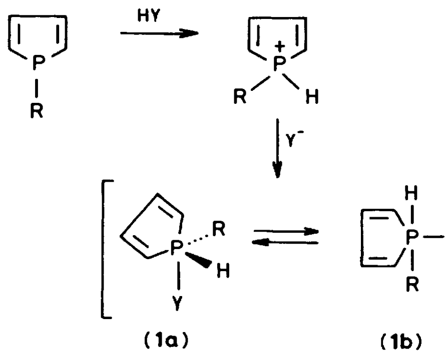
Addition to phospholes of gaseous HCl at −90 °C or of an excess of trifluoromethanesulphonic acid at −70 °C, results in *P*-protonation. The triflate solutions are stable up to room temperature, but the 1*H*-phospholium chlorides form P^V adducts at −70 °C, which rapidly rearrange by a [1,5]sigmatropic H-shift. The observed product is a 1-chloro-2,5-dihydrophospholium chloride. Addition of a chloride ion source to the triflates produces the same result. Unprotonated 3,4-dimethyl-1-phenyl phosphole was found to react at a double bond of its 1*H*-phospholium ion, forming a crystalline 1,3′-biphospholium dimer.

Considerable evidence has accumulated recently to support the concept that among phosphole derivatives [1,5] sigmatropic shifts of *P*-substituents to a ring α-carbon atom are common. Such rearrangements have been encountered when the phosphorus has co-ordination states of three (H^1 and phenyl^2 migrations), four (phenyl migration^2), and five (phenyl^3 and alkoxy^{4,5} migration). Migration appears to be faster for H than for phenyl, with alkoxy slower than either; also P^V derivatives rearrange faster than P^{IV} and P^{III}. A combination of these two effects suggests that rearrangement should be exceptionally fast when H is a substituent on phosphorus(v), as in a λ^5-phosphole (**1**).

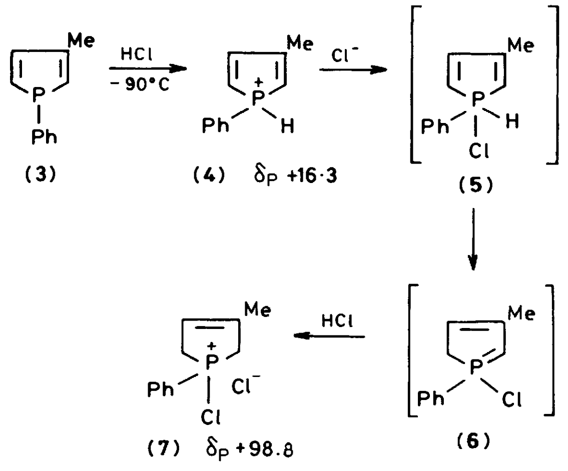
In this case the product (**2**) contains the highly reactive C=P double bond, and could react further in various ways, although some highly substituted C=P derivatives are known to be stable.^{3,4} We have considered the possibility that structure (**1**) might be generated when P^{III} phospholes are *P*-protonated with an acid whose conjugate anion has some nucleophilic character, so that a λ^5-phosphole intermediate would form (Scheme 1). Although structure (**1a**) might possess the more stable trigonal bipyramid, since the ring preference for apical-equatorial positions is observed, some contribution of (**1b**) may be expected, and the latter has the proper orientation^1 for the σ–π overlap to develop that is necessary for [1,5] H-shifts. Indeed, it is known^6 that certain phospholes react with dry HCl at room temperature to give only products where H has become attached to carbon, although 1,2,5-triphenylphosphole, which exhibits some atypical behaviour because of phenyl substitution effects, is *P*-protonated by triflic acid.^{7} Its complex with $TaCl_5$, when treated with HCl, also gives the 1*H*-phospholium ion.^{8} To account for the *C*-protonated product,^{6} the possibility was considered that *P*-protonation occurred initially and that a rearrangement followed; however, this mechanism could not be distinguished from one involving direct *C*-protonation of the P^{III} form, given preference because of the common occurrence of this attack in pyrroles. Both possibilities have been mentioned^{9,10} to explain the formation of a 2,5-dihydrophosphole oxide when anhydrous CF_3CO_2H reacted with phospholes and the product was quenched with NaOH, but again no experimental evidence was available to distinguish between the mechanisms. We have now reinvestigated the phosphole–HCl reaction at low temperature and have obtained definitive results pointing to initial *P*-protonation. The intermediacy of a P^V species that undergoes the [1,5] H-shift provides a logical explanation for the observation of a *C*-protonated product as the temperature is raised, and is supported by other data collected during this study.



(**1**) (**2**)



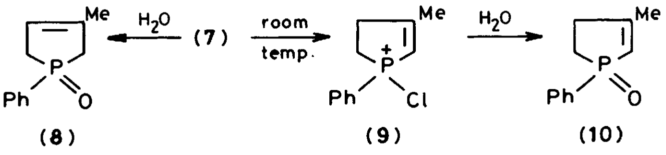
Scheme 1.



Fourier transform ^{31}P n.m.r. provides a convenient technique for following the course of phosphole–acid reactions. When the phosphole (**3**) was treated with an excess of dry HCl in CD_2Cl_2 at −90 °C, the only product was clearly the P–H form (**4**), as indicated both by its characteristic ^{31}P n.m.r. shift (δ +16.3) and by the presence of ^{1}H–^{31}P coupling (534.7 Hz) when the decoupler was shut off. No unchanged phosphole remained. When the temperature was raised to −70 °C, the P–H form disappeared, and the only ^{31}P signal was in the expected[11] region for chlorodihydrophospholium ions, δ +98.8. No P^{V} intermediate such as (5) was detected; its phosphorus shift would be at much higher field. The P^{V} form appears to undergo the [1,5] H-shift very rapidly, giving the undetected species (**6**), which reacts very rapidly with HCl to form (7).

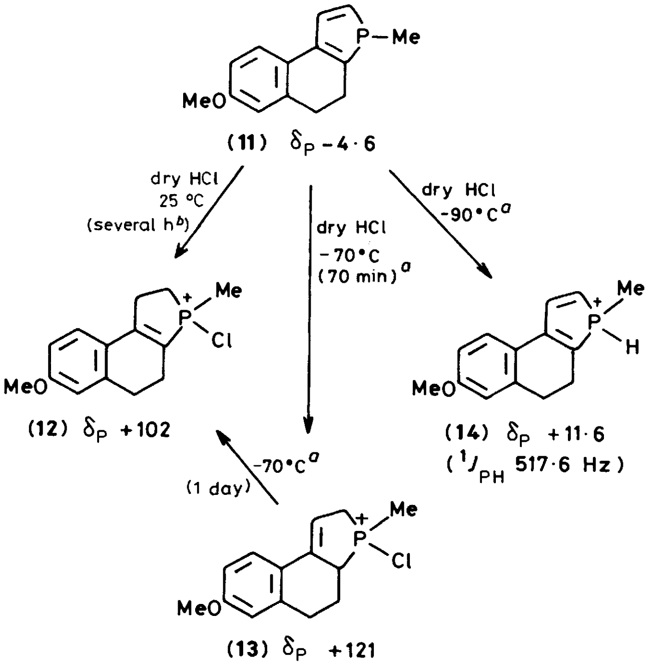
Structure (7) was proved by hydrolysis to 2,5-dihydro-3-methyl-1-phenylphosphole oxide (**8**), which showed the same ^{31}P and ^{13}C n.m.r. values as published.[12] When the phosphole–HCl reaction was conducted at 0 °C, only the dihydrophospholium ion (7) was observed, but after 2 days much rearrangement[11] to the 2,3-dihydrophospholium isomer (**9**) had occurred as indicated by a new ^{31}P signal at δ +94.2. Hydrolysis then provided the known[11] 2,3-dihydrophosphole oxide (**10**), as confirmed by its ^{13}C n.m.r. spectrum.[10] These experiments are decisive in showing that the terminus for H-migration from P is the ring α-carbon atom, as required by the [1,5] sigmatropic shift proposal.

Similar results were obtained with the tricyclic phosphole (**11**), which had been used in the earlier studies[6] of the HCl reaction at room temperature. The results of both studies are summarised in Scheme 2. The location of the double bond in the chlorodihydrophospholium ions (**12**) and (**13**) was established by hydrolysis to the known dihydrophosphole oxides. In the earlier work[6] on the HCl reaction of (**11**) at room temperature, the 2,5-dihydrophospholium ion (**13**) was undetected because of its rapid rearrangement to the 2,3-isomer (**12**). The earlier work also defined the sites of proton attachment as C-2 and C-3 in the phospholium ring of (**12**) by the use of DCl. This may be explained by D attachment to either α-carbon by the [1,5] shift, followed by DCl attack at the P=C bond, and an acid-promoted C=C rearrangement (Scheme 3).

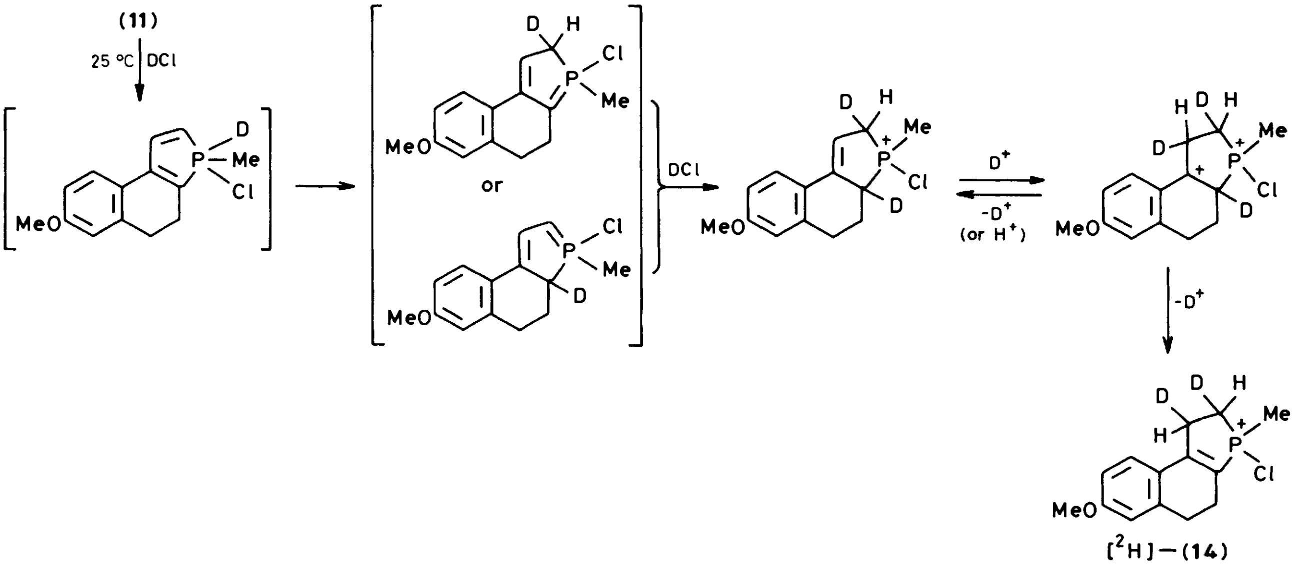


We expected that replacement of the chloride counterion with an anion (such as triflate, $CF_3SO_3^-$) devoid of nucleophilic character would prevent the formation of the P^{V} intermediate needed for the [1,5] H-shift, and lead to a more stable 1*H*-phospholium ion. This is indeed the case, as was demonstrated by treating the phospholes (3) and (**16**) with a four-fold excess of triflic acid at −70 °C; the solution of the 1*H*-phospholium ion was stable on warming to room temperature, but slow decomposition then occurred. The ions are quite stable at −30 °C, however. No product resulting from transfer of H from P to C was detected.

We reasoned next that addition of a source of Cl$^-$ to such solutions should precipitate the events leading to the *C*-protonated product, and this was tested by adding $Et_3NH^+Cl^-$

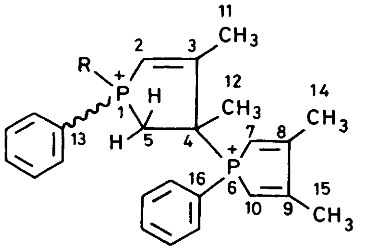


Scheme 2. *a*, This work. *b*, Ref. 6.



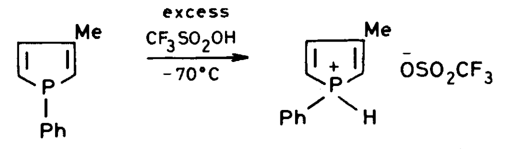
Scheme 3.

Table. ^{13}C N.m.r. data for the dimer (**18**) and its $(CD_3)_2CO$ adduct (**19**)

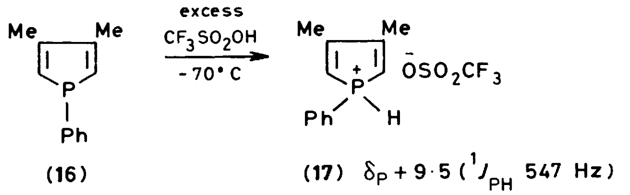


	(**18**) R = H			(**19**) R = $(CD_3)_2C(OH)$[a]		
C	δ_C	$J_{C,P\text{-}1}$[b]	$J_{C.P\text{-}6}$[b]	δ_C	$J_{C.P\text{-}1}$[b]	$J_{C.P\text{-}6}$[b]
2	114.72	77.0	7.0	110.67	72.0	9.5
3	169.86	17.0	3.0	171.44	9.6	
4[c]	52.86	7.3	44.0	51.54	6.1	46.4
5[d]	30.75	50.0	5.0	25.67	45.2	4
7 or 10	107.45		78.0	108.37		79.4
8 or 9	168.39		16.0	167.56		16
9 or 8	169.36		16.0	167.92		17
10 or 7	107.99		77.0	109.10		77.0
11	18.75	17.0		18.89	17.1	
12	20.81	5.0		21.61		
13	112.72	78.0		118.43	69.6	4.9
14, 15	18.02		17.0	17.49		17.1
16	112.72		78.0	112.73		79.3

[a] Signals for the $(CD_3)_2C(OH)$ group not observed; the adduct from $(CH_3)_2CO$ gave overlapping CH_3 doublets (diastereotopic) at δ 24.2 (J_{PC} 10.7 Hz) and 24.4 (J_{PC} 10.0), and COH at δ 72.5 (J_{PC} 52.4 Hz). [b] Assigned by selective irradiation of P-1 and P-6. [c] Signal removed by 2/(4J) pulse delay in INEPT sequence.[20] [d] Signal inverted by 3/(4J) pulse delay in INEPT sequence.[20]



(3) (15) δ_P +18·9 ($^1J_{PH}$ 530 Hz)



(16) (17) δ_P + 9·5 ($^1J_{PH}$ 547 Hz)

to the solution of (**15**) at −70 °C. Rapid rearrangement to the chlorodihydrophospholium ion (**7**) ensued. This is convincing proof of the importance of a P^V intermediate in the transfer of H from P to C.

Experiments on the triflic acid reaction with the phosphole (**16**) revealed that an excess of acid was required for the appearance of ^1H–^{31}P coupling on the ^{31}P n.m.r. spectrum. With one equivalent of acid, no coupling was observed. Apparently rapid dissociation of the proton from phosphorus occurs and coupling is not observed. With excess of acid, the dissociation is repressed. Phospholes are known to be quite weak bases from measurements[13] of pK_a, which are consistent with this behaviour.

When protonation of (**16**) was performed with 1 equiv. of triflic acid at −50 °C in toluene and the solution was warmed to room temperature, a dimeric product precipitated as a crystalline solid, m.p. 170.5 °C. The dimer had two ^{31}P n.m.r. signals (singlets) at δ +50.00 and +21.78 in CD_3CN. In CD_2Cl_2 with an excess of triflic acid, the upfield signal was split by 545 Hz when proton coupling was restored, proving the presence of directly bonded hydrogen. The downfield signal is suggestive of a quaternary phospholium ion. These facts, along with the elemental analysis, suggested structure (**18**). The dimer decomposed in a few hours in various solvents, but the structure could be stabilised in the form of the adduct* (**19**) with $(CD_3)_2CO$. ^{13}C N.m.r. spectra (see Table) are in agreement with the proposed structures (**18**) and (**19**). The greater stability of the adduct (**19**) allowed the performance of the INEPT pulse sequence, which established the presence of the CH_2 and CH groups. The large coupling to ^{31}P (45.2 Hz) leaves no doubt that the CH_2 group is attached to phosphorus. The other ring has the quaternary phospholium ion; the α-carbon atoms (non-equivalent because of the presence of chirality, presumably at C-4) have the upfield shift (δ_C 108.37 and 109.10) consistent with attachment to positive phosphorus,[14] as well as large $^1J_{PC}$ values (79.4 and 77.0 Hz, respectively). The spectrum clearly rules out the possibility that the dimerisation has followed the Diels–Alder [4 + 2] cycloaddition pathway [forming (**20**)], usually found for quaternary phospholium ions.[15] The proton n.m.r. spectra of dimer (**18**) and acetone adduct (**19**) are also consistent with the assigned structures.

The absence of three-bond ^{31}P–^{31}P coupling in the dimer (**18**) can be explained by the adoption of a conformation where a torsion angle of about 90° relates these nuclei,[16] or by rapid dissociation–recombination of the species. The proton could be removed from dimer (**18**) with sodium carbonate, forming the

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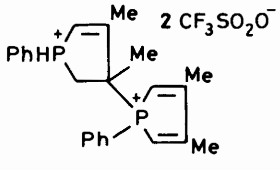
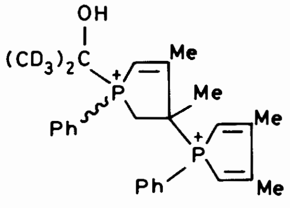
* This appears to be a new observation for a phosphine salt. Other examples have been encountered in related work and will be reported elsewhere (L. D. Quin and S. E. Belmont).



(18)



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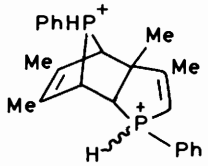

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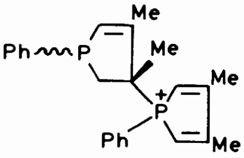
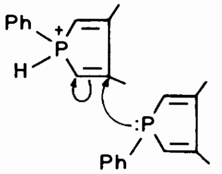


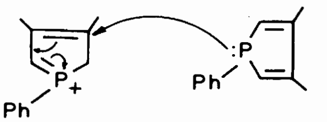
(21)

phosphine derivative (21) (δ_P −7.2 and +46.4, $^3J_{PP}$ 13.4 Hz). Compound (21), a non-crystallising oil, was unstable in solution and a ^{13}C n.m.r. spectrum could not be obtained.

The mechanism of dimerisation is partially revealed by the observation that the dimer fails to form when more than 1 equiv. of acid is added to the phosphole. Under these conditions, no free phosphole is present. This suggests the participation of the phosphole itself as a nucleophile in an addition to the *P*-protonated form (A). A proton shift, or proton transfer from the medium, would complete the process forming (18). It is also possible that the product (22) of a [1,5] H-shift of the protonated phospholium ion acts as the acceptor.

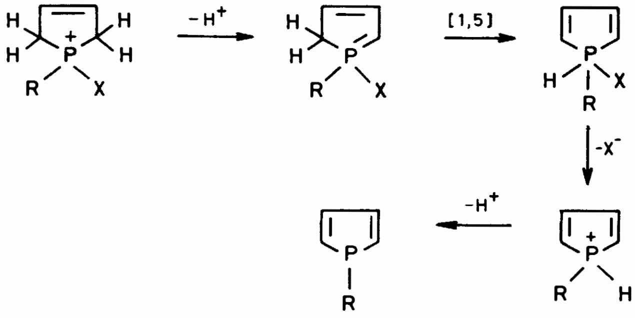
(A)





(22)

Finally, we note that the formation of the 1-chloro-2,5-dihydrophospholium ion by action of HCl on a phosphole is formally the reverse of the synthetically useful process[17] for forming phospholes by dehydrohalogenation of such ions. The mechanism of the dehydrohalogenation has not been studied, but it now requires consideration that the reaction may proceed through a [1,5] H-shift in the opposite direction, from C to P (Scheme 4).



Scheme 4.

Experimental

^{31}P N.m.r. spectra (Fourier transform, proton-decoupled) were taken with a JEOL FX-90Q instrument at 36.2 MHz; chemical shifts are given in p.p.m. relative to 85% H_3PO_4 as reference, with downfield signals positive signs. Carbon-13 n.m.r. spectra (Fourier transform, proton-decoupled) were obtained with the FX-90Q instrument at 22.5 MHz, by using an internal deuterium lock.

Reaction of Phospholes with HCl *at Low Temperatures.*—The phosphole (3) or (11) (*ca.* 100 mg) was dissolved in CD_2Cl_2 in a 5 mm n.m.r. tube, and the solution was then cooled to −94 °C in liquid nitrogen–hexane. Anhydrous gaseous HCl was then introduced through a capillary tube for about 3 s, and the tube was closed for ^{31}P n.m.r. spectral measurements as follows: (3) −90 °C, single peak, δ_P +16.3 with $^1J_{PH}$ 534.7 Hz for (4); warming to −50 °C gave a single peak, δ_P +98.8 for (7); warming to 25 °C gave δ_P +98.8 [major, (7)] and +85 (minor, unidentified); (11) −90 °C, major peak δ_P +11.6 with $^1J_{PH}$ 517.6 Hz for (14); warming to −70 °C and measurement after 70 min gave the major peaks at δ_P +119 for (13) (minor peaks, δ_P +39.9 and +31.7, unidentified) and +11.6 for (14); warming to room temperature gave the major peak at +102 (12).

Reaction of Phospholes with HCl *at or above* 0 °C.—The solutions as prepared from (3) and (11) in the preceding experiment were treated with gaseous HCl at room temperature [phosphole (11)] or 0 °C [phosphole (3)]. ^{31}P N.m.r. spectra were immediately taken, and the predominant species were found to be the 2,5-dihydrophospholium ions (7) (δ_P +99) from (3), and (13) (δ_P +121) from (11).

Hydrolysis of 2,5-*Dihydrophospholium Ions* (7) and (13).—The contents of the n.m.r. tubes used in the preceding phosphole–HCl reactions were added to water and the solutions were stirred for 30 min, then extracted with $CHCl_3$. The extract was dried ($MgSO_4$), and concentrated for n.m.r. measurements in $CDCl_3$. The product from the 2,5-dihydrophospholium ion (7) [2,5-dihydro-3-methyl-1-phenylphosphole 1-oxide (8)] had δ_P +57.2 (lit.,[12] +55.4) and a ^{13}C n.m.r. spectrum matching a published spectrum.[12] The product from the 2,5-dihydrophospholium ion (13) gave the two ^{31}P n.m.r. signals (δ_P +70.7 and +62.3) for the *cis*- and *trans*-isomers of 2,3a,4,5-tetrahydro-7-methoxy-3-methyl-1*H*-benzo[*e*]phosphindole 3-oxide (lit.,[18] +70.5 and +62.5); a small amount of the 1,2,4,5-tetrahydro isomer (δ_P +65.4; lit.,[19] +66.4) was also formed.

Formation and Hydrolysis of the 2,3-*Dihydrophospholium Ion* (**9**).—The phosphole (**3**) was treated with HCl at 0 °C as before, and the solution was set aside for 2 days. ^{31}P N.m.r. signals for the 2,5-dihydrophospholium ion (**7**) (δ_P +97.5) and the 2,3-dihydrophospholium ion (**9**) (δ_P +94.2) were present. Hydrolysis as before gave a mixture of phosphole oxides (**8**) and (**10**), identified by their ^{31}P n.m.r. shifts (δ_P +62.4 and 58.2, respectively) and by their ^{13}C n.m.r. spectra, which matched reported spectra.[12]

Reaction of the Phospholes (**3**) *and* (**16**) *with Trifluoromethanesulphonic Acid.*—A solution of the phosphole (0.1 g) in CD_2Cl_2 (0.5 ml) was treated at −70 °C with neat trifluoromethanesulphonic (triflic) acid (*ca.* 0.1 g; two-fold excess). The ^{31}P n.m.r. spectrum was taken immediately, and had only the signal for the protonated phosphole (**15**) (δ_P +18.9, ${}^{1}J_{PH}$ 530 Hz) or (**17**) (δ_P +9.5, ${}^{1}J_{PH}$ 547 Hz). The signals persisted on warming the solutions to room temperature.

Reaction of the Phospholium Triflate (**15**) *with Chloride.*—A CD_2Cl_2 solution of the phospholium triflate (**15**) [from 0.1 g of the phosphole (**3**)] at −70 °C was treated with a suspension of triethylamine hydrochloride in CH_2Cl_2. After 30 min at −70 °C, the ^{31}P n.m.r. spectrum was taken. The major component had δ_P +100 [for (**7**)]; three minor signals were also present.

Dimer Formation from the Phospholium Ion (**17**).—A solution of the phosphole (**16**) (0.53 g, 2.82 mmol) and triflic acid (0.42 g, 2.82 mmol) in toluene was prepared at −50 °C and then allowed to warm to room temperature. The *dimer* (**18**) (52%) crystallised from the mixture; m.p. 170.5 °C; δ_P +20.1 and +49.9 (both s); δ_H (CD_3CN, numbering in Table) 1.79 (3 H, d, ${}^{3}J_{H,P-6}$ 18.5 Hz, H_3-12), 2.15 (3 H, dd, ${}^{4}J_{H,P-1} \simeq 1.7$, ${}^{4}J_{H,P-6}$ 1.6 Hz, H_3-11), 2.33 (6 H, d, ${}^{4}J_{H,P-6}$ 2.5 Hz, H_3-15 and H-14), 2.82 (1 H, ddd, ${}^{2}J_{H,H-5}$ 17.3, ${}^{3}J_{H,P-6}$ 19, ${}^{2}J_{H,P-1}$ 15.1 Hz, H′-5), 3.65 (1 H, ddd, ${}^{2}J_{H,H'-5}$ 17.3, ${}^{3}J_{H,P-6}$ 16.5, ${}^{2}J_{H,P-1}$ 6.5 Hz, H-5), 6.36 (1 H, ddq, ${}^{2}J_{H.P}$ 27.8, ${}^{4}J_{H,P-6}$ 4, ${}^{4}J_{H,H_3-11}$, H-2), and 6.99 (2 H, dq, ${}^{2}J_{H,P-6}$ 32.2, ${}^{4}J_{H,CH_3}$ 1.5 Hz, H-7 and H-10); for δ_C see Table (Found: C, 46.5; H, 4.2; P, 8.7. $C_{26}H_{28}F_6O_6P_2S_2$ requires C, 46.2; H, 4.2; P, 9.15%).

When the phosphole was treated with a four-fold excess of triflic acid under the same conditions, the protonated phosphole that formed was stable; no dimer precipitated, nor was any detected in solution by ^{31}P n.m.r.

Reaction of the Dimer (**18**) *with Base.*—The dimer was suspended in CH_2Cl_2 and stirred with saturated aqueous Na_2CO_3. After 5 min, the dimer had dissolved completely. The organic layer was separated, dried ($MgSO_4$), and evaporated *in vacuo*. The residual oil (**21**) was taken up in $CDCl_3$ and had δ_P +46.4 and −7.2 (d, J_{PP} 13.4 Hz). The compound decomposed during attempts to obtain the ^{13}C n.m.r. spectrum in various solvents.

Reprotonation of the phosphine with CF_3SO_3H in CD_2Cl_2 gave back the ^{31}P signals for the fully protonated dimer, as obtained when the dimer (**18**) is suspended in CD_2Cl_2 and treated with an excess of CF_3SO_3H.

Acetone Adduct of the Dimer (**18**).—The adduct (**19**) formed on dissolving the dimer (**18**) in acetone; after 1 min the solvent was evaporated off to leave a yellow oil. When prepared in $(CD_3)_2CO$, the adduct had ^{31}P δ +58.1 and +48.3 (both d, ${}^{3}J_{PP}$ 30 Hz); the ^{13}C n.m.r. spectrum is given in the Table; δ_H [$(CD_3)_2CO$] 1.91 (3 H, d, ${}^{3}J_{H,P-6}$ 17.6 Hz, H_3-12), 2.7 (9 H, m, other CH_3), 3.87 (2 H, ABMX m, H_2-5), 7.43 (1 H, dq, ${}^{2}J_{H.P-6}$ 36, ${}^{4}J_{H,CH_3}$ 1.5 Hz, H-2), 7.62 (1 H, m, ${}^{2}J_{H,P-6}$ 36, ${}^{4}J_{H,CH_3}$ 1.5, ${}^{4}J_{H,H-10}$ 2.2 Hz, H-7), 7.69 (dq, ${}^{2}J_{H,P-6}$ 36, ${}^{4}J_{H,CH_3}$ 1.5 Hz, H-10), and 7.9—8.7 (10 H, m, 2 Ph).

Acknowledgement

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