

Triphosphane-1,3-di-ium Ions

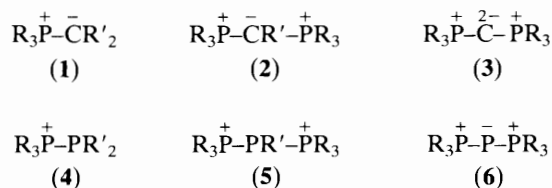
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Despite the influence of two phosphinio groups the central phosphorus in triphosphane-1,3-di-ium tetrachloro-aluminates as obtained from $R_3P + R'PCl_2 + AlCl_3$ or $[R_3P-P-PR_3]AlCl_4 + R'Cl + AlCl_3$ is still pyramidal.

Phosphonio ligands strongly reduce the stereochemical activity of a lone pair at the adjacent atom. For instance the carbon in phosphonium ylides (1) and (2) (mesomeric double bond formulae not shown) is planar in all acyclic cases¹ and the PCP angle in carbodiphosphoranes (3) is wide (116—180°).^{2,3} Substituting the first row member C⁻ for the second row member P, which has the same number of valence electrons and a comparable electronegativity, changes the situation.



Triphosphenium ions (6) isoelectronic to (3) display a small PPP angle (89—103°);⁴ their PP bond is nevertheless relatively short (213 pm as compared to 220—225 and 200—205 pm for a PP single and double bond, respectively)⁴ and indicates effective additional (π -)bonding. Although direct X-ray structural evidence is lacking, the normal pyramidal geometry of the three-co-ordinate phosphorus seems to be preserved in diphosphenium ions (4), which are isoelectronic to (1). The question remains, however, whether the influence of two phosphonio groups is great enough to lead to planarity of the central phosphorus. No triphosphanedi-ium ions (5) (nor any other phosphanedi-ium ions) were previously known to provide the answer to this question. We report here two routes for their preparation.

While phosphines and dichlorophosphines either do not react at all with each other (if R = Ph) or enter a redox reaction (if R = alkyl) yielding a cyclopentaphosphine,⁵

triphosphanedi-ium ions (5) are obtained from these reactants if aluminium chloride is added as a third component (route a). In route b triphosphenium ions (6), resulting from the reaction of R_3P with phosphorus trichloride and aluminium chloride⁴ are protonated or alkylated with the aid of more aluminium chloride. Representatives with R' = H can naturally only be prepared by route b; cyclic representatives with R' \neq H on the other hand only result from route a as the corresponding cyclic triphosphenium ions (6) resist alkylation.

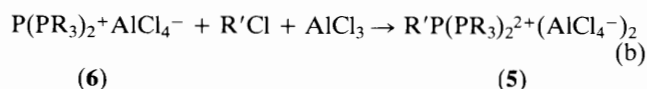
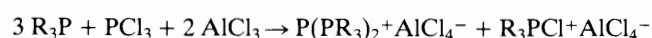
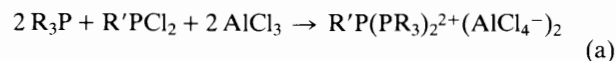
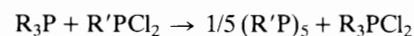
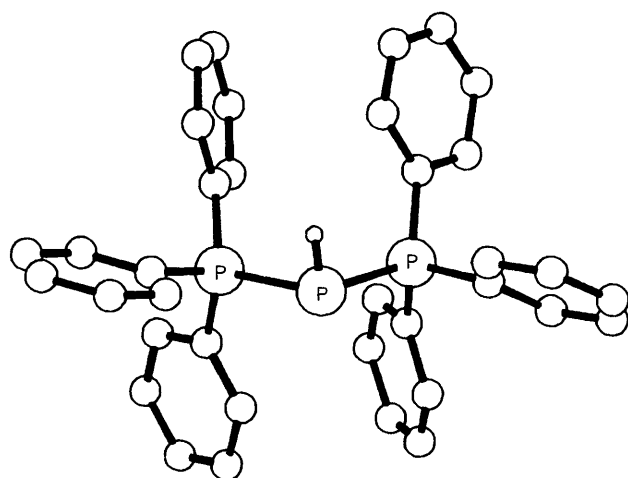


Table 1 lists preparation and ³¹P n.m.r. data of (5). The coupling in (5), R' = H is high compared to that of secondary alkyl- and aryl-phosphines.⁶ Ring strain (in decreasing the s-character of the bonding phosphorus orbital) lowers ¹J_{PH} and even more pronouncedly ¹J_{PP} in the five-membered cyclic dications (5m) and (5n) as compared to their acyclic analogues (5g) and (5h), respectively.

This sensitive response to an angle narrowing might point to a relatively wide PPP angle in the acyclic cases in accordance with the supposed effect of the two phosphonio ligands.

Table 1. Triphosphane-1,3-dium tetrachloroaluminates (**5**)(AlCl₄)₂ and their ³¹P n.m.r. data (A₂B or A₂BX spin systems); coupling constants *J* in Hz.

	R ₃ P	R'	Preparation	δ _A	δ _B	¹ J _{PP}	¹ J _{PH}
a	Ph ₃ P	H	b	+23	-120	286	236
b		Me	b	+23	-48	330	
c		CH ₂ Cl	a,b	+25	-41	330	
d		Et	b	+22	-37	334	
e		Pr ⁱ	b	+21	-23	354	
f		Ph	a	+24	-28	358	
g	MePh ₂ P	H	b	+18	-121	261	230
h		CH ₂ Cl	b	+20	-38	305	
i	Me ₂ PhP	H	b	+18	-116	255	227
j		CH ₂ Cl	b	+21	-31	300	
k	Bu ⁿ ₃ P	H	b	+38	-146	277	233
l		CH ₂ Cl	b	+39	-39	319	
m	½ C ₂ H ₄ (Ph ₂ P) ₂	H	b	+53	-157	239	218
n		CH ₂ Cl	a	+52	-78	282	
o		Bu ^t	a	+52	-79	283	

**Figure 1.** Molecular structure of the dication (**5a**). Bond lengths and bond angles; average values of (**6a**) (ref. 4) in brackets for comparison: PP 220.5(1), 222.4(1) pm [213.3(6) pm]; PH 113(2) pm; PPP 106.39(4)° [102.6(3)°]; PPH 95(1), 86(1)°.

However, the X-ray crystal structure determination of (**5a**)[†] shows little or no sign of such an effect. The central phosphorus exhibits the normal pyramidal co-ordination

[†] *Crystal data:* (**5a**), [C₃₆H₃₁P₃][AlCl₄]₂, monoclinic, space group *P*2₁/*c*, *a* = 17.883(3), *b* = 10.953(1), *c* = 21.371(2) Å, β = 90.79(1)°, *Z* = 4, *D*_c = 1.44 g cm⁻³, μ(Mo-Kα) = 7.23 cm⁻¹. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using an ω-scan. From 5432 recorded reflections (2θ_{max} = 45°, Mo-Kα), 4177 with *F*_o² > 2σ(*F*_o²) were employed in the least-squares refinement. The structure was solved by direct methods and refined to *R* = 0.063 and *R*_w = 0.057. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

(Figure 1) and PPP angles of the same size as found in polyphosphine chains.⁷ Compared to the triphosphonium ion (**6a**), the PPP angle has widened somewhat as the lone pair electron density at the central phosphorus has been reduced by the protonation, but it still remains below the tetrahedral angle. The increase in the PP bond length is in accordance with a complete loss of π-bonding between the phosphorus atoms. The bonding of the added proton is thus primarily accomplished by the use of the π-electron pair leaving the lone pair to exhibit its full stereochemical activity. The situation is paralleled by that with the phospho-allylic cations.⁸

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