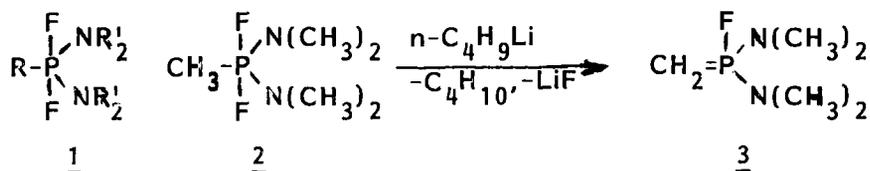


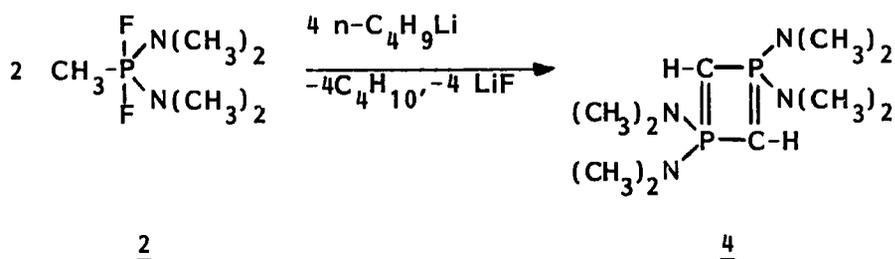
FROM 1,3-DIPHOSPHACYCLOBUTADIENE TO 1,3,5-TRIPHOSPHABENZENE

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Alkyl- and aryldiaminodifluorophosphoranes 1 can easily be obtained by fluorination of alkyl- and aryldiaminophosphoranes with sulfur tetrafluoride, SF₄¹. Peralkylated alkyldiaminodifluorophosphoranes react with one mole of n-butyllithium to form P-fluoro-ylides, a class of compounds which had not been described previously². Methylbis(dimethylamino)difluorophosphorane 2, e.g., reacts with butyllithium to give methylenebis(dimethylamino)fluorophosphorane 3, a colorless liquid, b.p. 42 °C (10 Torr)²:

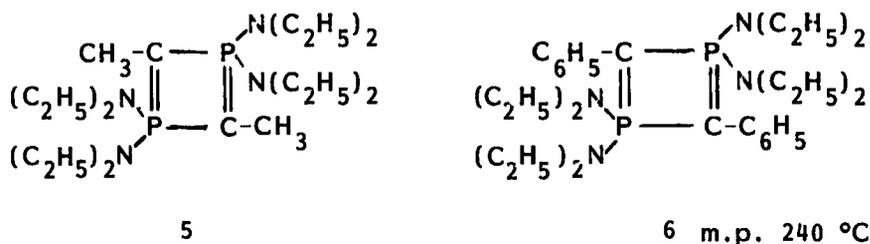


For P-chloro-ylides such as (t-C₄H₉)₂PCl=CHSi(CH₃)₃³, the chloro ligand is substituted by the alkyl group upon reaction with methyl- or n-butyllithium^{3,4}; however, P-fluoro-ylides behave in a different way. If 2 is reacted with two moles of butyllithium, the main product is the crystalline, colorless 1,1,3,3-tetrakis(dimethylamino)-1λ⁵,3λ⁵-diphosphete or 1,1,3,3-tetrakis(dimethylamino)-1λ⁵,3λ⁵-diphosphacyclobutadiene 4 (chemical shift δ(P) = 48.9 ppm)⁵.

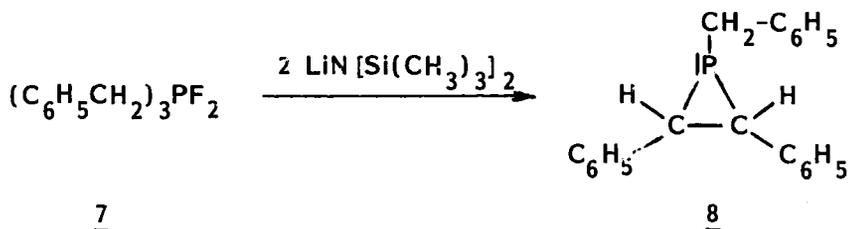


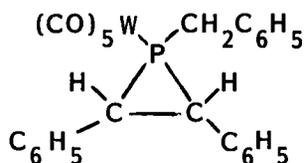
The four-membered ring of 4 is completely planar with equal C-P distances of 172.5 pm⁵.

In an analogous way, the C-substituted diphosphetes 5 and 6 can be obtained ⁶.

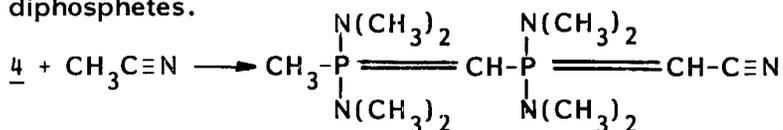


The cleavage of HF by strong nucleophilic reagents is also observed with trialkyldifluorophosphoranes. Tribenzoyldifluorophosphorane 7 reacts with lithium bis(trimethylsilyl)amide in tetrahydrofuran to give 1-benzyl-2,3-diphenylphosphirane 8 (m.p. 77-79 °C; chemical shift $\delta(\text{P}) = -181$ ppm) which can be separated from the reaction mixture by chromatography. Only one of the possible stereoisomers is formed. With $\text{W}(\text{CO})_5 \cdot \text{THF}$, the stable complex 9 is formed (m.p. 121-122 °C; chemical shift $\delta(\text{P}) = -126.8$ ppm, $^1\text{J}(\text{PW}) = 263.2$ Hz) ⁷.

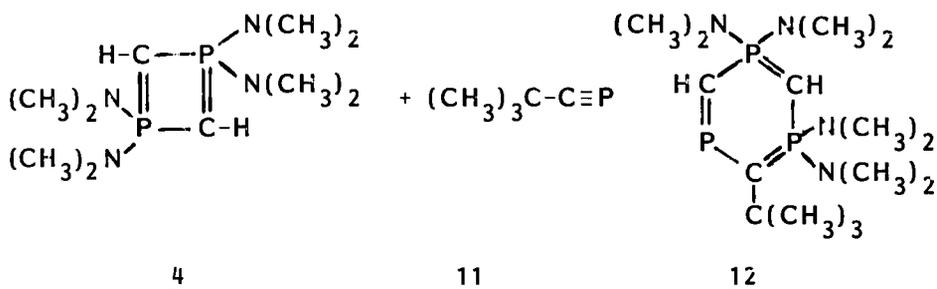


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Diphosphetes are extremely sensitive towards oxygen and water; with acetonitrile, the ring is opened. Reaction between 4 and acetonitrile yields compound 10, a colorless solid, m.p. 34 - 36 °C⁸. Other nitriles such as benzonitrile or $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{N}$ do not react with diphosphetes.

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If the phosphorus analogue $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{P}$ 11⁹ is used instead of $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{N}$, the carbanionic C atoms in 4 attack the phosphorus atom. As a result the propylidyne phosphane 11 is inserted to give the first 1,3,5-triphosphabenzene 12, a pale yellow crystalline substance, m.p. 50 - 55 °C¹⁰.

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The six-membered ring is nearly planar; all bond distances P-C are nearly equally long ($170.2^{\pm 1.2}$ pm) with the exception of $\text{P}^{\text{V}}\text{C}-\text{C}(\text{CH}_3)_3$ (175.8 pm). The chemical shifts of 12 are $\delta(\text{P}) = 295.5$ ppm (P^{III}) and 57.5, 59.0 ppm (P^{V}).

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