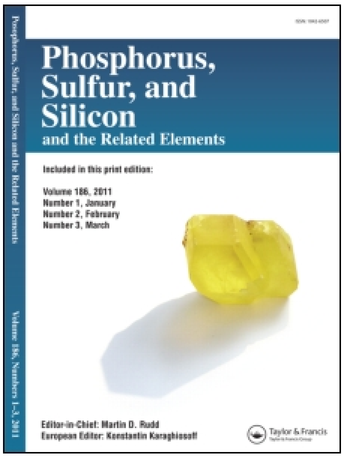

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From 1,3-Diphosphacyclobutadiene to 1,3,5-Triphosphabenzene

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

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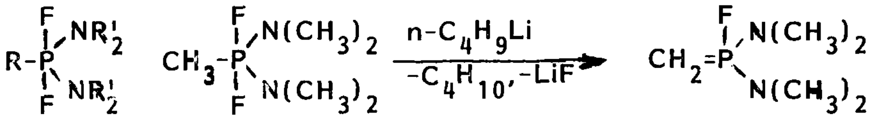
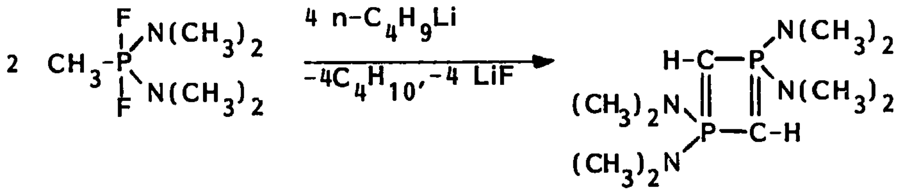
Alkyl- and aryldiaminodifluorophosphoranes 1 can easily be obtained by fluorination of alkyl- and aryldiaminophosphanes with sulfur tetrafluoride, SF$_4$ [1]. Peralkylated alkyldiaminodifluorophosphoranes react with one mole of n-butyllithium to form P-fluoro-ylides, a class of compounds which had not been described previously [2]. 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]:



1 2 3

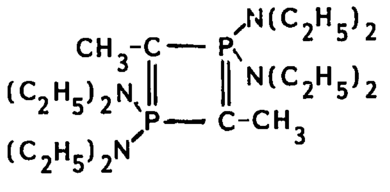
For P-chloro-ylides such as (t-C$_4$H$_9$)$_2$PCl=CHSi(CH$_3$)$_3$, the chloro ligand is substituted by the alkyl group upon reaction with methyl- or n-butyllithium [3,4]; however, P-fluoro-ylides behave in a different way. If 2 is reacted with two moles of butyllithium, the main product is the crystalline, colorless 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete or 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphacyclobutadiene 4 (chemical shift δ(P) = 48.9 ppm) [5].



2 4

The four-membered ring of 4 is completely planar with equal C-P distances of 172.5 pm [5].

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



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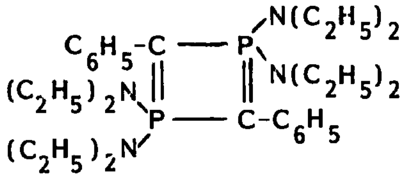
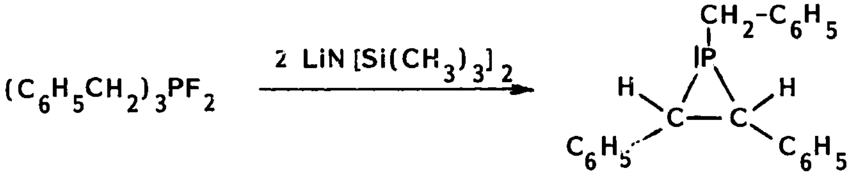
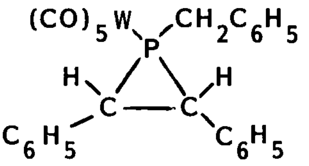


6 m.p. 240 °C

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

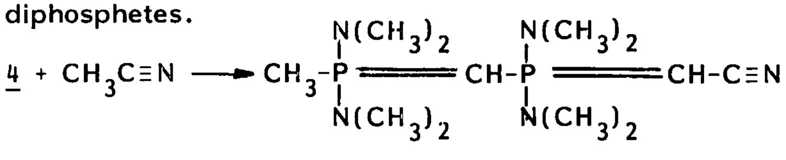


7 8



9

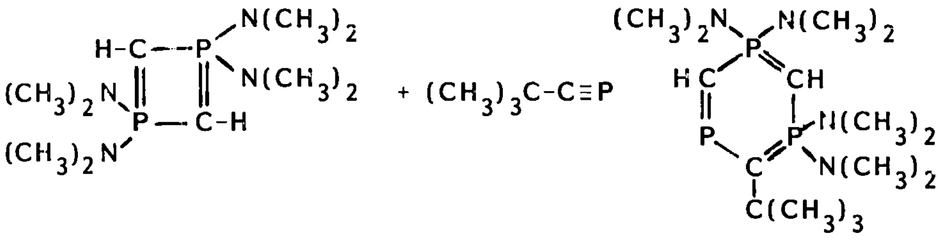
Diphosphetes are extremely sensitive towards oxygen and water; with acetonitrile, the ring is opened. Reaction between 4 and acetonitrile yields compound 10, a colorless solid, m.p. 34 - 36 °C [8]. Other nitriles such as benzonitrile or $(CH_3)_3C\text{-}C\equiv N$ do not react with diphosphetes.



$$4 + CH_3C\equiv N \longrightarrow CH_3\text{-}\overset{N(CH_3)_2}{\underset{N(CH_3)_2}{P}}=CH\text{-}\overset{N(CH_3)_2}{\underset{N(CH_3)_2}{P}}=CH\text{-}C\equiv N$$

10

If the phosphorus analogue $(CH_3)_3C\text{-}C\equiv P$ 11 [9] is used instead of $(CH_3)_3C\text{-}C\equiv N$, 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 °C [10].



4 11 12

The six-membered ring is nearly planar; all bond distances P-C are nearly equally long (170.2 ± 1.2 pm) with the exception of $P^V C\text{-}C(CH_3)_3$ (175.8 pm). The chemical shifts of 12 are $\delta(P)$ = 295.5 ppm (P^{III}) and 57.5, 59.0 ppm (P^V).

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