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

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Alkyl- and arylidaminodifluorophosphoranes 1 can easily be obtained by fluorination of alkyl- and arylidaminophosphanes with sulfur tetrafluoride, SF$_4$ 1. Peralkylated alkylidaminodifluorophosphoranes 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:

\[
\begin{align*}
\text{R-P-}\underset{1}{\text{N}(\text{CH}_3)_2} & \quad \text{F} \quad \underset{2}{\text{N}(\text{CH}_3)_2} \\
\text{CH}_3 & \quad \text{F} \\
\text{F} & \quad \text{F}
\end{align*}
\]

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)-1\(^5\),3\(^5\)-diphosphete or 1,1,3,3-tetrakis(dimethylamino)-1\(^5\),3\(^5\)-diphosphacyclobutadiene 4 (chemical shift $\delta(P) = 48.9$ ppm) 5.
The four-membered ring of 4 is completely planar with equal C-P distances of 172.5 pm.

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

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 $\delta(P) = -181$ ppm) which can be separated from the reaction mixture by chromatography. Only one of the possible stereoisomers is formed. With W(CO)$_5$·THF, the stable complex 9 is formed (m.p. 121-122 °C; chemical shift $\delta(P) = -126.8$ ppm, $^1$J(PW) = 263.2 Hz).
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. Other nitriles such as benzonitrile or (CH₃)₃C-C≡N do not react with diphosphetes.

\[
\text{4 + CH₃C≡N} \rightarrow \text{CH₃-P-CH-P-CH-C≡N}
\]

If the phosphorus analogue (CH₃)₃C-C≡P 11 is used instead of (CH₃)₃C-C≡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.

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 Ves-C(CH₃)₃ (175.8 pm). The chemical shifts of 12 are δ(P) = 295.5 ppm (P III) and 57.5, 59.0 ppm (P V).
REFERENCES

8. B. Neumüller and E. Fluck, unpublished results.