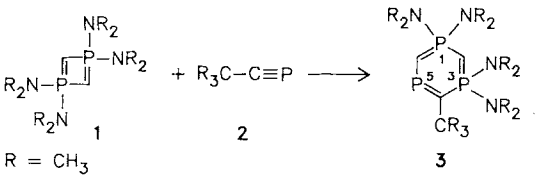
A $1\lambda^5,3\lambda^5,5\lambda^3$-Triphosphabenzene Derivative

By *Ekkehard Fluck,* Gerd Becker, Bernhard Neumüller, Robert Knebl, Gernot Heckmann,* and *Heinz Riffel*

Monophosphabenzene and a series of its derivatives were first described in the 1960s; later, diphosphabenzenes were also reported.[1] We report here the synthesis of the first 1,3,5-triphosphabenzene derivative. 1,1,3,3-Tetrakis(dimethylamino)-4-*tert*-butyl-$1\lambda^5,3\lambda^5,5\lambda^3$-triphosphabenzene **3** is the sole product formed upon reaction of 1,1,3,3-tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphete **1**[2] with 2,2-dimethylpropylidynephosphane **2**.[3] The reaction can be regarded formally as an insertion. Mechanistically, it probably involves a cycloaddition, followed by spontaneous valence isomerization.[4]



Compound **3** forms air- and moisture-sensitive, pale yellow crystals, m.p. = 50–55 °C, which are soluble in benzene and *n*-pentane. In the $^{31}P\{^1H\}$-NMR spectrum (C_6D_6, standard 85% H_3PO_4) of **3**, the chemical shifts of the phosphorus atoms 1, 3, and 5 are $\delta = 57.5$, 59.0, and 295.5, respectively. In the $^{13}C\{^1H\}$-NMR spectrum (C_6D_6, standard TMS), the C atoms 6 and 4 exhibit the smallest chemical shifts ($\delta = 62.8$ and 100.8) so far recorded for phosphaalkenes. This is an indication of the significant ylide character of the C4–P5–C6 structural fragment. The ring structure of **3**, established by NMR triple resonance experiments, is in agreement with the results of an X-ray structure analysis (Fig. 1).[5]

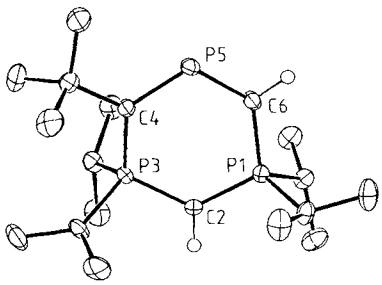


Fig. 1. ORTEP plot of the crystal structure of **3** (thermal ellipsoids at 50% probability). Bond lengths [pm] and angles [°]: P1-C2 168.8(2), C2-P3 169.7(2), P3-C4 175.8(2), C4-P5 170.9(2), P5-C6 170.0(2), C6-P1 171.5(2); P1C2P3 128.1(1), C2P3C4 111.9(1), P3C4P5 121.9(1), C4P5C6 113.7(1), P5C6P1 128.2(1), C6P1C2 109.4(1). The numbering of the atoms corresponds to the systematic name of **3**.

The six-membered ring is nearly planar and the distances between the ring atoms are nearly identical (170.2 ± 1.2 pm). An exception is the P3–C4 distance (175.8 pm). In the mass spectrum of **3**, the molecular-ion peak is very intense.

[*] Prof. Dr. E. Fluck
Gmelin-Institut für Anorganische Chemie der Max-Planck-Gesellschaft
Varrentrappstrasse 40/42, D-6000 Frankfurt am Main 90 (FRG)
Prof. Dr. G. Becker, Dipl.-Chem. B. Neumüller, Dipl.-Chem. R. Knebl, Dr. G. Heckmann, Dr. H. Riffel
Institut für Anorganische Chemie der Universität
Pfaffenwaldring 55, D-7000 Stuttgart 80 (FRG)

Experimental Procedure

All operations were carried out under argon. A solution of **1** [2] (2.07 g, 7.83 mmol) in 5 mL of dimethoxyethane was added dropwise over 20 min to a stirred solution of **2** [3] (1.06 g, 10.6 mmol) in 3 mL of dimethoxyethane at 0°C. The brown reaction mixture was allowed to warm slowly to room temperature and then stirred for 48 h. The solvent and excess **2** were removed under vacuum. The residual oil crystallized at −20°C and the solid was recrystallized three times from *n*-pentane. Yield of **3**: 1 g (35%).

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[1] Cf., for example, G. Märkl, *Phosphorus Sulfur 3* (1977) 77; G. Märkl in *Houben-Weyl-Müller: Methoden der Organischen Chemie, 4. Aufl., Bd. E1*, Thieme, Stuttgart 1982, p. 72ff.

[2] J. Svara, E. Fluck, H. Riffel, *Z. Naturforsch. B40* (1985) 1258.

[3] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch. B36* (1981) 16.

[4] Cf. J. Fink, W. Rösch, U.-J. Vogelbacher, M. Regitz, *Angew. Chem. 98* (1986) 265; *Angew. Chem. Int. Ed. Engl. 25* (1986) 280.

[5] **3**: triclinic, space group $P\bar{1}$, $a=878.0(5)$, $b=971.2(5)$, $c=1279.2(6)$ pm; $\alpha=99.91(4)$, $\beta=91.33(4)$, $\gamma=104.68(4)°$; $Z=2$, $\rho_{calcd}=1.167$ g/cm^3. All atoms occupy the general positions of the space group. The structure was derived from 4754 unique reflections (of which 4071 were observed) by statistical methods and Fourier syntheses and refined to $R=0.038$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-52046, the names of the authors, and the journal citation.