The First $1\lambda^5,3\lambda^5,5\lambda^5$-Triphosphabenzene Derivative

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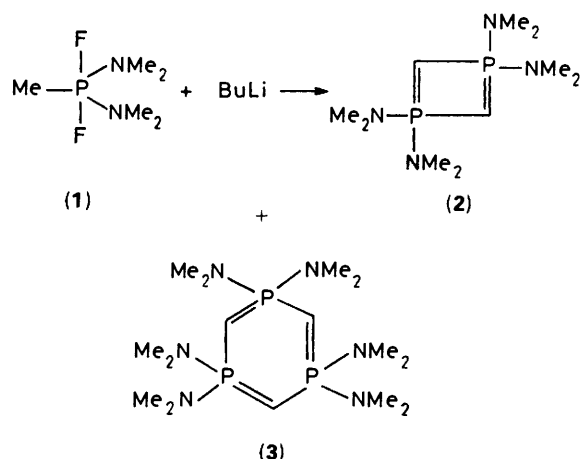[b] Institut für Anorganische Chemie der Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80

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The synthesis, NMR data and an X-ray structural analysis of 1,1,3,3,5,5-hexakis(dimethylamino)-$1\lambda^5,3\lambda^5,5\lambda^5$-triphosphabenzene (**3**) are described.

We report briefly on the first $1\lambda^5,3\lambda^5$-diphosphabenzene derivatives,[1,2] In 1986 we described the synthesis of a $1\lambda^5,3\lambda^5,5\lambda^3$-triphosphabenzene derivative from the reaction of 1,1,3,3-tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphete (**2**), with 2,2-dimethylpropylidynephosphane.[3,4] Compound (**2**) is the principal product of the reaction between methylbis(dimethyl-amino)difluorophosphorane, (**1**), and two equivalents of butyl-lithium in hexane at -70 °C.[5] One of the by-products produced (ca. 8–10%) has now been identified as 1,1,3,3,5,5-hexakis-(dimethylamino)-$1\lambda^5,3\lambda^5,5\lambda^5$-triphosphabenzene (**3**).

Compound (**3**), in contrast to the $1\lambda^5,3\lambda^5,5\lambda^3$-triphos-phabenzene derivative described in,[3,4] is resistant to hydrolysis.

Figure. Molecular structure of (3). Only one of the two crystallographically independent, but very similar molecules, is shown; the H atoms have been omitted for clarity. The ring atoms are approximately planar: the average and the maximum deviations of the 'best' plane in each molecule are 1.1 and 2.8 pm or 1.5 and 4.7 pm respectively. The corresponding distances (pm) and angles (°) are also almost identical: P–C 168.7(2)–169.7(3); P–C–P 126.6(1)–127.0(1); C–P–C 113.0(1)–113.4(1).

The reaction first produces the metallated ylide LiCH=P(F)(NMe$_2$)$_2$ (4). The formation of (2) and (3) from (4) probably results, as numerous observations suggest, from an intermolecular abstraction of LiF, and not from the intramolecular elimination to the $\sigma^3\lambda^5$-species, HC≡P(NMe$_2$)$_2$, followed by its dimerisation to (2) or its trimerisation to (3). A 1λ^5,3λ^5,5λ^5-triphosphabenzene derivative was postulated earlier on the basis of NMR data,[6] which should now be assigned to a different product as indicated by our measurements.

Compound (3) forms colourless crystals, which are air-stable and only slightly sensitive to moisture. It melts at 88.5–89 °C and is soluble in benzene and chloroform. In the ^{31}P{^{1}H} NMR spectrum (C$_6$D$_6$, 85% H$_3$PO$_4$ reference) the chemical shift of (3) is 65.4 ppm. The ^{31}C{^{1}H,^{31}P} NMR spectrum (C$_6$D$_6$, TMS reference) shows a singlet at −3.2 ppm; while in the ^{13}C{^{1}H} NMR spectrum the 12-line X portion of the A$_2$BX system of the ring atoms in (3) is observed with ^1J(PC) 142.5 Hz. The H atoms bonded to C-1, C-2, and C-3 produce a singlet at 0.32 ppm in the ^{1}H{^{31}P} NMR spectrum (C$_6$D$_6$, TMS reference). The NMR data confirm, in agreement with the results of the X-ray structure determination (see Figure),* the ring structure of (3) and indicate a highly ylidic character for the endocyclic PCP triad (*cf.* ref. 4).

The six-membered ring is almost planar with equal distances between the ring atoms. In the EI mass spectrum of (3) the
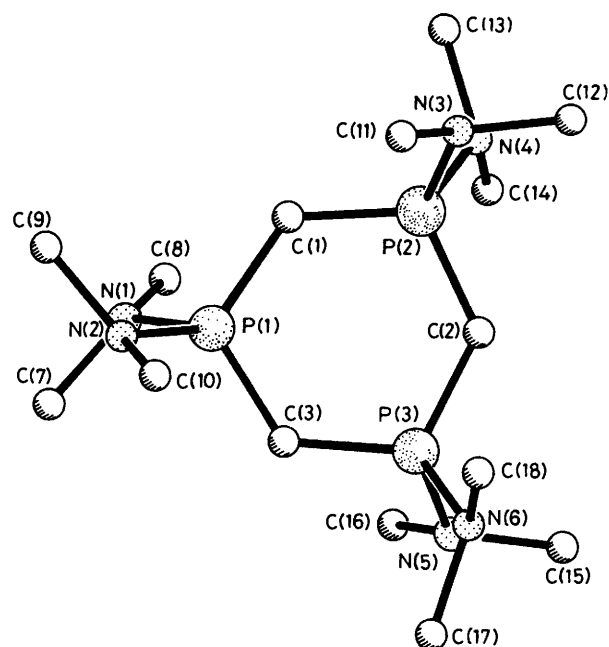
molecular peak appears with a relative intensity of 86% (20 eV, 320 K).

Experimental

All the work was conducted under anhydrous argon of the highest purity. To a solution of (1) (101.3 g, 0.59 mol) in pentane (200 ml) at −70 °C was added, dropwise over 4 h and with stirring, 2.5M butyl-lithium (471 ml, 1.18 mol) in hexane. The yellow solution was then warmed to room temperature over 12 h. The LiF was filtered off, extracted 4 times with pentane (50 ml), and the extracts combined with the filtrate. After concentration at −20 °C compound (2) (40.7 g, 0.15 mol, 52%) crystallised out. The oil that separated from the mother liquor on evaporation of solvent under reduced pressure was mixed with acetonitrile (40 ml) at 0 °C. At room temperature compound (3) (2.7 g, 3.5%) crystallized out.

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* Triclinic, P$\bar{1}$ (No. 2); Z = 4; a = 1 143.5(1), b = 1 385.3(2), c = 1 567.6(1) pm; α = 101.456(9); β = 104.225(7); γ = 95.22(1)°; ρ$_{calc}$ = 1.13 g/cm^3 at 22 °C; Enraf-Nonius CAD4 four circle diffractometer (graphite monochromator, scintillation counter, Mo-K_α); ω-scans in the region 4.0° < 2θ < 56°; 11 246 symmetry independent reflections, 8 162 with F > 3σ(F); empirical absorption correction with ψ-scans; structure solution with direct methods in P1; refinements with full matrix least squares (455 parameter), R = 0.047 (R' = 0.067 considering the 'unobserved' reflections); wR = 0.047, goodness of fit 1.299; after anisotropic refinement of the P, N, and C atoms, the H atoms were localised by differential Fourier synthesis. Finally, the H atoms on the ring C atoms and those in the methyl groups were refined with a common distance and a common temperature factor, respectively; in the final structure-factor calculation those in the methyl groups were 'riding' on the C atoms and were considered with a common temperature factor; all calculations with SHELXTL-PLUS from G. M. Sheldrick, Göttingen 1987. Atomic co-ordinates, bond lengths, bond angles, and thermal parameters are available on request from the Cambridge Crystallographic Data Centre. [See 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 1*, 1990, Issue 1.]

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