Novel Tetraphosphabarrelene and -semibullvalene Derivatives by Reactions of 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene with Phosphaalkynes☆

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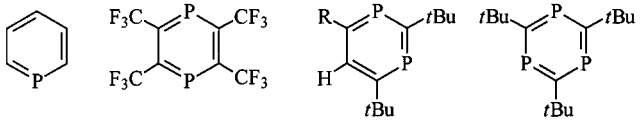
2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene **4** reacts with phosphaalkynes P≡C−R [R = *t*Bu (**5a**), *t*Pen (**5b**)] at room temperature in a formal [4 + 2] cycloaddition to yield the corresponding 1,3,5,7-tetraphosphabarrelene derivatives **8a** and **8b**, respectively. The analogous reaction of **4** with the aminophosphaethyne P≡C−N(*i*Pr)$_2$ (**9**) unexpectedly leads to the 1,3,4,7-tetraphosphasemibullvalene derivative **10** as the only product. The single-crystal X-ray analysis of **10** exhibits a diphosphirane unit with a very long PP distance of 2.274(1) Å together with a large extension of the PCP angle in the three-membered ring to 75.3(1)°.

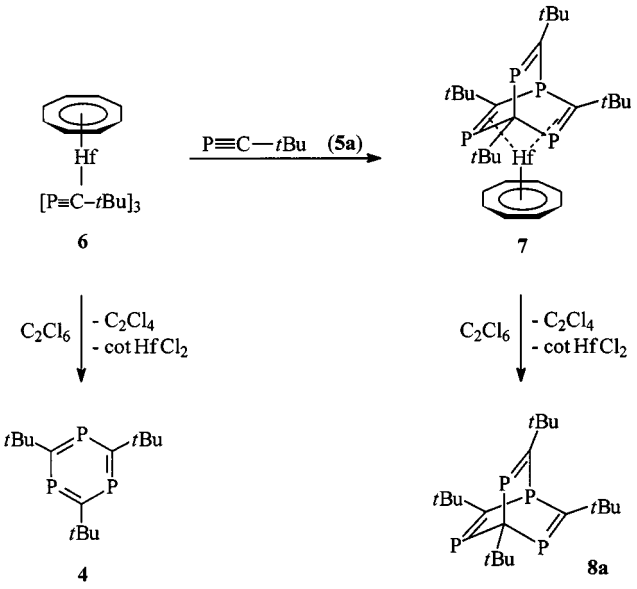
Whereas the λ^3-phosphinine (phosphabenzene) **1**[1] as well as a great number of its functional derivatives[2] have been thoroughly investigated, only little information is published on "all-λ^3" di- or triphosphinines. So far the 1,4-diphosphabenzene derivative **2** was only detected in solution, but its NMR data are not complete.[3] As first representatives of the 1λ^3,3λ^3-diphosphinines[4] and 1λ^3, 3λ^3,5λ^3-triphosphinines[5] compounds **3** and **4**, respectively, have been isolated in pure form by using transition metal complex templates for the cyclotrimerization of *tert*-butylphosphaethyne **5a**, followed by oxidative replacement, and characterized.



1 **2** **3** **4**

The preparation of **4** was accomplished by oxidative cleavage of the hafnium complex [(COT)Hf(*t*BuCP)$_3$] (**6**) with the useful reagent hexachloroethane. Template **6** was also used for the preparation of the η^4-1,3,5,7-tetraphosphabarrelene complex **7** by reaction with *t*BuC≡P (**5a**) (Scheme 1). Cleavage of **7** with C_2Cl_6 yields the 1,3,5,7-tetraphosphabarrelene derivative **8a**, which had been isolated before from the reaction of bis(cyclooctatetraene)zirconium with **5a**.[6] It is of particular interest that the valence isomers of **4**, 1,3,5- and 1,2,4-triphospha-Dewar-benzene[5][7] can be prepared selectively by the same synthetic procedure on use of modified cyclooctatetraene ligands for production of precursor analogues of **6**, and by variation of the reaction temperatures. In addition, Binger et al.[8] reported recently on homo-Diels−Alder reactions of 2,4,6-tri-*tert*-butyl-1,3,5-triphospha-Dewar-benzene.

Scheme 1



In 1998 Regitz et al.[9] presented a new effective method for the synthesis of **4** and other alkyl-substituted analogues, based on the use of the strong Lewis acid *t*BuN=VCl$_3$ as

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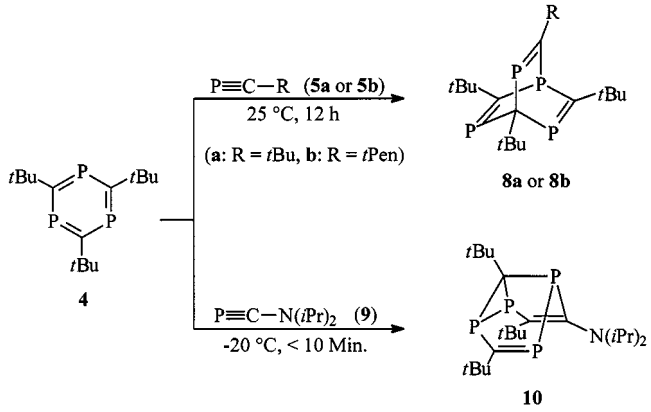
cyclotrimerization agent. The availability of **4** by the procedures mentioned above allowed reactivity studies of the 6π-heteroarene, in particular with respect to cycloaddition reactions.

For instance, the tetraphosphabarrelenes **8a** or **8b** (Scheme 2) are formed nearly quantitatively within 12 h by treating a pentane solution of **4** with the phosphaethynes **5a** and **5b**, respectively. This result demonstrates that the addition of a further phosphaalkyne molecule is possible even without coordination of a cyclotrimer of **5** to a complex fragment. Of particular interest is the possibility to prepare unsymmetrically substituted tetraphosphabarrelenes like **8b**. The reactions proceed under mild conditions indicating an astonishing reactivity of **4** against dienophiles. So far, similar reactions of phosphinines or their *P*-coordinated tungsten complexes with *t*BuC≡P (**5a**) have not been observed.[10] However, phosphinines undergo [4 + 2] cycloadditions with electron-deficient olefins under forced conditions. These reactions can be enhanced by σ-complex formation with $[(CO)_5W(THF)]$.[2b] The reactivity of phosphaarenes is also considerably increased if they contain an additional N or P atom in the 6π-system as in case of the 1,3-azaphosphinines published by Märkl et al.[11][12] or of the 1,4-diphosphinine **2**[3b], though fairly extreme conditions (100−120°C, high pressure vessel) are necessary for reactions with alkynes[3b][12] or **5a**.[11]

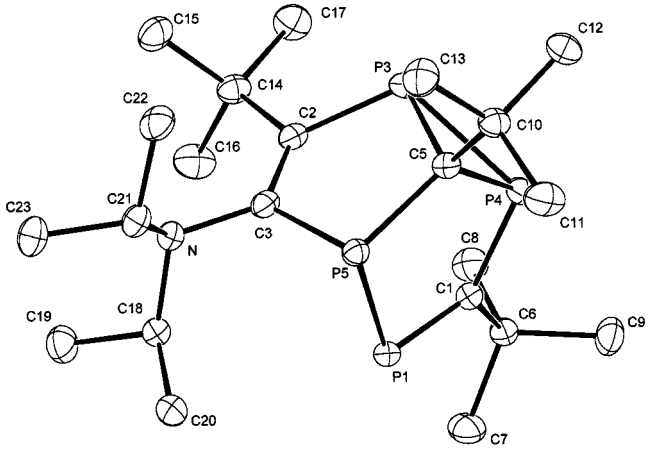
Scheme 2



The analogous reaction of **4** with di(isopropylamino)-phosphaethyne **9** leads to a really unexpected result: According to a ^{31}P-NMR control experiment the starting compounds already react at −20°C quantitatively within a few minutes to give the tetraphosphasemibullvalene derivative **10**. The unsymmetrical molecular structure of **10** is proven by three different ^{1}H-NMR signals for the *t*Bu groups as well as by four separate ^{31}P resonances of equal intensities. Only one of them is found at chemical shifts typical for phosphaalkene fragments (δ_P = 347.5). Chemical shifts and coupling constants of all ^{31}P signals are in good accordance with those of the tetra-*tert*-butyltetraphosphasemibullvalene reported by Regitz et al.[13]. The same is true for the ^{13}C-NMR data of both compounds. Fluxional behaviour as observed for the corresponding hydrocarbon derivatives (Cope rearrangement) was not detected for **10** at room temperature. Measurements at higher temperatures failed because **10** already decomposes at 20°C even in inert solvents.

The molecular structure of **10** was deduced from a single-crystal X-ray analysis and supports the conclusions drawn from the NMR spectroscopic investigations. Figure 1 shows one of the enantiomers observed in the crystal lattice.

Figure 1. Molecular structure of **10** in the crystal; the hydrogen atoms are omitted for clarity[a]



[a] Selected bond lengths [Å] and angles [°]: P1−P5 2.207(1), P3−P4 2.274(1), P3−C5 1.858(2), P4−C5 1.865(2), P5−C5 1.856(2), P1−C1 1.693(2), P3−C2 1.809(2), P4−C1 1.796(2), P5−C3 1.874(2), C2−C3 1.366(2), N−C3 1.450(2), N−C18 1.506(2), N−C21 1.494(2); C1−P1−C5 100.4(1), C5−P3−P4 52.5(1), C2−P3−P4 111.8(1), C5−P3−C2 99.4(1), C5−P4−C1 101.5(1), C1−P4−P3 107.1(1), C5−P4−P3 52.2(1), C5−P5−P1 99.7(1), C5−P5−C3 97.3(1), C3−P5−P1 87.7(1), C3−C2−P3 116.6(1), C2−C3−P5 116.2(1), P4−C5−P3 75.3(1), P5−C5−P3 109.2(1), P5−C5−P4 115.1(1).

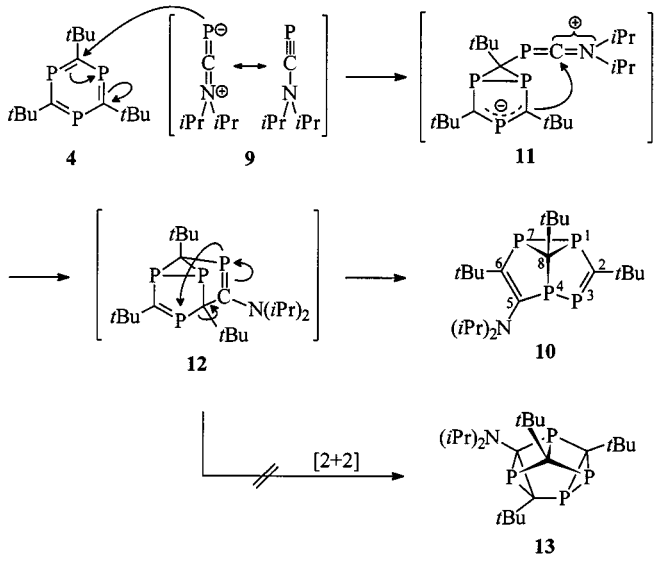
As to be expected, the P−(sp^2)C single bonds in the tricyclic phosphorus/carbon skeleton of **10** are significantly shorter (P3−C2: 1.809, P4−C1: 1.796 Å) than P−(sp^3)C distances (1.856 to 1.874 Å). The P1−C1 bond length of 1.693 Å is very close to the average value (1.67 Å) of localized P=C double bonds.[14] The distance P3−P4 amounts to 2.274 Å and, so far, represents the longest PP bond in diphosphirane derivatives.[9][13][15][16] Consequently the angle P3−C5−P4 within the three-membered ring is opened to 75.3°.

The formation of **10** from **4** and **9** is not directly evident, although **9**, due to its electronic structure[17], often shows a different behaviour to alkyl-substituted phosphaalkynes, especially in cycloaddition reactions.[18] Assuming that the π-donor interaction of the R_2N substituent enhances the nucleophilicity of the *P*-atom, an attack of **9** at one of the ring carbon atoms seems reasonable as the first reaction step followed by a ring closure to the tricyclic intermediate **12**. The stable end product is reached by a further nucleophilic attack of the aminophosphaalkene *P*-atom and by valence isomerization. The competitive intramolecular [2 + 2] cycloaddition with formation of the pentacyclic compound **13** is less probable for two reasons:

(i) Aminophosphaalkenes are not suited for cycloaddition reactions due to the loss of olefinic character,

(ii) high-level ab initio calculations[19] on different $(HCP)_4$ isomers favour the semibullvalene system over the cuneane structure.

Scheme 3



In conclusion, the work presented in this paper has led to a selective synthesis of the tetraphosphabarrelene derivatives **8a** and **8b** from the 1,3,5-triphosphabenzene **4** and to a surprising reaction of **4** with **9** affording the novel tetraphosphasemibullvalene derivative **10**, thus enlarging our knowledge about cyclotetramers of phosphaalkynes[20] and clearly demonstrating the important influence of *C*-amino groups on the reactivity of P≡C systems.

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Experimental Section

All experiments were carried out under argon (or by using a standard vacuum line) in anhydrous solvents. Reaction vessels were either Schlenk flasks or ampoules with several break seals and an NMR tube. $-^1$H and ^{13}C NMR: Bruker AC 200, AC 300, and AMX 400; chemical shifts relative to the solvent signals, calibrated to TMS. $-^{31}$P NMR: Bruker AC 200, AC 300, external standard H_3PO_4. 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene **4**[5][9] and the Phosphaalkynes *t*BuC≡P (**5a**)[21a], *t*PenC≡P (**5b**)[21b], $(i\text{Pr})_2$NC≡P (**9**)[22] were prepared according to the literature.

Standard Procedure for the Preparation of the Tetraphosphabarrelenes **8a**, **8b**: A pentane solution (2 ml) of the phosphaalkyne **5a** (80 mg, 0.8 mmol) or **5b** (100 mg, 0.9 mmol) was added at room temperature to a pentane solution (3 ml) of the triphosphabenzene derivative **4** (200 mg, 0.67 mmol). The mixture was stirred for 12 h, and volatile components were removed in vacuo. The residue was taken up in pentane and filtered through a layer of silica gel. After evaporation of the solvent in vacuo the tetraphosphabarrelene **8a** and **8b**, respectively, was obtained as a yellow powder (**8a**: 260 mg, 0.65 mmol, 98% yield; **8b**: 265 mg, 0.64 mmol, 96% yield).

2,4,6,7-Tetra-tert-butyl-1,3,5,8-tetraphosphabicyclo[2.2.2]octa-2,5,7-triene (**8a**) was characterized by comparison of the NMR data with those of an authentic sample.[6]

[4,6,7-Tri-tert-butyl-2-tert-pentyl]-1,3,5,8-tetraphosphabicyclo-[2.2.2]octa-2,5,7-triene (**8b**): $-^1$H NMR (C_6D_6, 200.1 MHz, 25°C): δ = 0.70 (q, *J* = 7.4 Hz, 2 H, CH_2CH_3), 1.39 (3 H, CH_2CH_3), 1.43 [s, br., 15 H, $C(CH_3)_3$ and $C(CH_3)_2CH_2$], 1.77 [s, br., 18 H, $C(CH_3)_3$]. $-^{13}$C {^{1}H} NMR (C_6D_6, 50.3 MHz, 25°C): δ = 28.3 [m, CH_3CH_2 and $(CH_3)_2C$], 30.5 [m, $(CH_3)_3C$], 30.7 [m, ^3J(P,C) = 0.3 and 14.9 Hz, $(CH_3)_3C$], 33.4 [t, ^3J(P,C) = 9.5 Hz, CH_3CH_2], 35.8 [q, ^2J(P,C) = 16.1 Hz, $C(CH_3)_3$], 41.6 [m, $C(CH_3)_3$], 44.8 [dd, ^2J(P,C) = 19.1 and 25.4 Hz, $C-CH_2CH_3$], 101.1 [m, C-4], 225.4 [m, C-2], 227.3 [m, C-6, C-7]. $-^{31}$P{^{1}H} NMR (C_6D_6, 81.0. MHz, 25°C): δ = -92.0 [q, ^2J(P,P) = 12.6 Hz, *P*−C=P], 320.7 [t, ^2J(P,P) = 12.6 Hz, P=C−$C(CH_3)_3$], 324.8 [q, ^2J(P,P) = 12.6 Hz, P=C−$C(CH_3)_2C_2H_5$]. −MS (EI, 70 eV); *m/z* (%): 414 (68) [M^+], 314 (9) [$M^+ - PC_5H_9$], 300 (3) [$M^+ - PC_6H_{11}$], 276 (74) [$M^+ - 2\,C_5H_9$], 262 (100) [$M^+ - C_5H_9 - C_6H_{11}$], 200 (22) [$M^+ - PC_5H_9 - PC_6H_{11}$].

2,6,8-Tri-tert-butyl-5-diisopropylamino-1,3,4,7-tetraphosphatricyclo[5.1.0.0 ^{4,8}]octa-2,5-diene (**10**): 80 mg (0.27 mmol) of the triphosphabenzene derivative **4** were placed in an ampoule with break seals and an NMR tube together with 0.5 ml [D_8]toluene. 45 mg (0.31 mmol) of di(isopropyl)aminophosphaethyne **9** were then introduced by vacuum condensation at −196°C. During warm−up to −20°C the mixture was continuously stirred and afterwards tranfused in the NMR tube. Measurements at −30°C indicated a complete reaction of the triphosphabenzene **4** and the quantitative formation of the tetraphosphasemibullvalene derivative **10**. Orange crystals of **10** were obtained on cooling the [D_8]toluene solution at −78°C. Their quality was sufficient for a single-crystal X-ray structure analysis. $-^1$H NMR (C_7D_8, 400.1 MHz, −30°C): δ = 0.90 [s, 9 H, $C(CH_3)_3$)], 1.21 [d, *J* = 6.5 Hz, 6 H, $CH(CH_3)_2$], 1.28 [d, *J* = 6.5 Hz, 6 H, $CH(CH_3)_2$], 1.38 [s, 9 H, $C(CH_3)_3$], 1.48 [s, 9 H, $C(CH_3)_3$], 3.38 [sept, *J* = 6.5 Hz, 2 H, $CH(CH_3)_2$]. $-^{13}$C {^{1}H} NMR (C_7D_8, 75.5 MHz, −35°C): δ = 24.8 [s, $CH(CH_3)_2$], 29.6 [s, br., $C(CH_3)_3$ at C-8], 32.3 [d, ^3J(P-6,C) = 11.3 Hz, $C(CH_3)_3$ at C-6], 34.3 [dd, ^3J(P-3,C) = ^3J(P-1,C) = 7.6 Hz, $C(CH_3)_3$ at C-2], 34.9 [q, ^2J(P-1,C) = ^2J(P-4,C) = ^2J(P-7,C) = 11.7 Hz, $C(CH_3)_3$ at C-8], 37.3 [d, ^2J(P-7,C) = 25.2 Hz, $C(CH_3)_3$ at C-6], 42.2 [dd, ^2J(P-3,C) = 22.6, ^2J(P-1,C) = 13.6 Hz, $C(CH_3)_3$ at C-2], 55.6 [s, br., $CH(CH_3)_2$], 63.0 (m, C-8), 156.1 [dm, ^1J(P-7,C) = 65.5 Hz, C-6], 177.7 [d, ^1J(P-4,C) = 39.9 Hz, C-5], 211.8 [t, ^1J(P-3,C) = ^1J(P-1,C) = 83.0 Hz, C-2] (for numbering see Scheme 3). $-^{31}$P{^{1}H} NMR (C_7D_8, 121.5. MHz, −35°C): δ = −92.1 [dd, ^1J(P-1,P-7) = 174.6, ^2J(P-4,P-7) = 16.4 Hz, P-7], −19.6 [ddd, ^1J(P-1,P-7) = 174.6, ^2J(P-1,P-3) = ^3J(P-1,P-4) = 23.5 Hz, P-1], 88.7 [ddd, ^1J(P-3,P-4) = 270.0, ^2J(P-1,P-4) = 23.5, ^2J(P-4,P-7) = 16.4 Hz, P-4], 347.5 [dd, ^1J(P-3,P-4) = 270.0, ^2J(P-1,P-3) = 23.5 Hz, P-3] (for numbering see Scheme 3).

Crystal Structure Analysis of **10**[23]: Enraf-Nonius-CAD4 Diffractometer (Mo-K_α radiation), *T* = 100 K; structure solution by heavy-atom method (SHELXS-86[24]) and structure refinement by SHELXL-93[25]; monoclinic, space group $P2_1/c$; lattice constants *a* = 10.0494(10), *b* = 20.4954(10), *c* = 12.3895(10) Å, β = 99.983(10)°; *V* = 2513.2(3) Å^3; *Z* = 4; μ(Mo-K_α) = 0.308 mm^{-1}, crystal size 0.42 × 0.39 × 0.35 mm; 9113 independent reflections (R_{int} = 0.0648) 28745 measured of which 6630 were considered observed with $I > 2\sigma(I)$; residual electronic density 0.481 and −0.357 e/Å^3. 408 parameters (C, N, and P anisotropic, the positions of the H-Atoms were found and refined isotropically); R_1 = 0.0441; wR^2 = 0.1180.

☆ Dedicated to Professor *Bernt Krebs* on the occasion of his 60th birthday.

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[23] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102329. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44-1223/ 336-033, E-mail: deposit@chemcrys.cam.ac.uk].

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