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Homo-Diels–Alder reactions of 2,4,6-tri-*tert*-butyl-1,3,5-triphospha-Dewar-benzene

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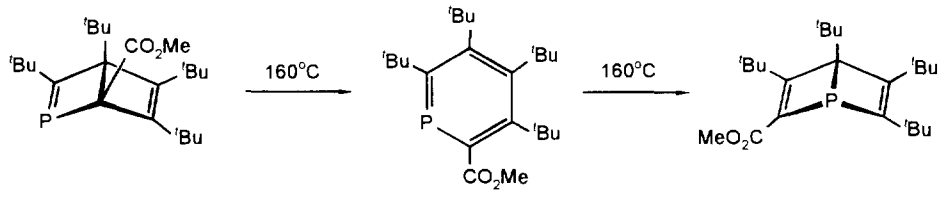
Abstract

Homo-Diels–Alder reactions take place under very mild conditions when the 1,3,5-triphospha-Dewar-benzene derivative **4** is allowed to react with electron-deficient alkynes, such as dimethyl acetylenedicarboxylate or methyl propyonate, or with *tert*-butylphosphaacetylene. The resultant [2 + 2 + 2]-cycloadducts **5**, **6**, and **8** can be isolated in excellent yields and are formed regioselectively. Moreover, the first example of a [4 + 2 + 2]-cycloaddition has been realized by the reaction of **4** with tri-*tert*-butylazacyclobutadiene **10** which yields the two exo-cycloadducts **11** and **12**. The cycloadduct **12** is unstable under the conditions of column chromatography on silica gel and undergoes rearrangement to the isomer **13**.

Keywords: Homo-Diels–Alder reaction; 1,3,5-Triphospha-Dewar-benzene; Polycyclic phosphorus–carbon compounds; *tert*-Butylphosphaacetylene; Tri-*tert*-butylazete

1. Introduction

The successful synthesis of the first 1,3,5-triphospha-Dewar-benzene **4** [1] raised the question as to the stability and reactivity of this new class of compounds. The all-carbon analogues such as, for example, hexamethyl-Dewar-benzene [2] are less stable than, for example, hexamethylbenzene [3] by around 60 kcal mol^{-1}: the thermal valency isomerization has a half-life of 105 h at 120 °C [4]. In contrast, the Dewar-benzene derivatives in the systems tetra-*tert*-butyl-Dewar-phthalate/tetra-*tert*-butyl-phthalate [5] or tetra-*tert*-butyl-Dewar-phosphabenzene [6] are the more stable forms. Accordingly, the 2-Dewar-phosphabenzene **1** [6], for example, undergoes rearrangement to the 1-Dewar-phospha-benzene **3** via the phosphabenzene **2** on being heated to 160 °C [7].



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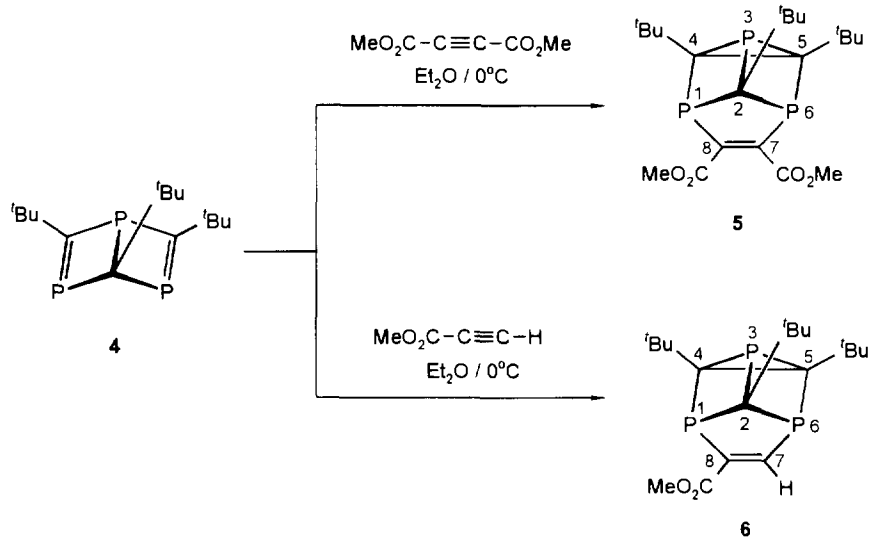
The kinetic stability of hexamethyl-Dewar-benzene renders [2 + 2 + 2]-cycloadditions (homo-Diels–Alder reactions) with electron-poor systems containing N=N or C=C double bonds possible. These reactions occur with, for example, 4-phenyl-1,2,4-triazoline-3,5-dione at room temperature [8] or with tetracyanoethene at 120 °C [9]. Homo-Diels–Alder reactions of 1- or 2-Dewar-phospha-benzenes are still unknown. The kinetic stability of the 1,3,5-triphospha-Dewar-benzene **4** should also allow the realization of homo-Diels–Alder reactions, at least with electron-poor alkynes and alkenes, since compound **4** is stable up to about 100 °C in the solid state while in solution it undergoes very slow (duration of several weeks) oligomerization and valency isomerization processes to furnish, in the latter case, the corresponding 1,3,5-triphosphabenzene which can be isolated in 20% yield [1]. At 90 °C, both reactions are complete after 5 h. According to ab initio calculations, the parent skeleton of the triphosphabenzenes is more stable than that of the Dewar derivatives by 25 kcal mol^{-1} [10].

2. Results and discussion

Experiments have shown that electron-poor alkynes such as, for example, dimethyl acetylenedicarboxylate or methyl propynoate, participate in [2 + 2 + 2]-cycloadditions with the triphospha-Dewar-benzene **4** under surprisingly mild conditions. Thus, the reaction between **4** and dimethyl acetylenedicarboxylate in diethyl ether at 0 °C is complete after only 0.5 h. The sole product of this reaction is the cycloadduct **5** which, after a single recrystallization from diethyl ether, is obtained in 82% yield in the form of yellow crystals with m.p. 98 °C. The tetracyclic compound **6** results in the form of a yellow solid in 71% yield from the reaction of **4** with methyl propynoate under identical conditions. In relation to the ^{31}P NMR time scale both reactions occur regiospecifically; in each case only that cycloadduct is formed in which two phosphorus atoms are linked to the alkene unit arising from the original C≡C triple bond.



4 **5** **6**

The structures of the two cycloadducts **5** and **6** can be readily deduced from their spectroscopic data. In the ^{31}P NMR spectra of compounds **5** and **6**, the signals for P3 are found as triplets ($\delta = -158.3$ and -152.0 ppm respectively) in the region typical for phosphirane units. The other two phosphorus atoms P1 and P6 are found as a doublet at $\delta = 104.2$ ppm for **5** and as a double doublet at $\delta = 87$ and 89 ppm for **6**. The ^{13}C NMR data of **5** reflect the C_S-symmetry of the molecule, as also do the ^{1}H NMR data of **5** (see Section 3). In contrast, the unsymmetrical structure of **6** is readily apparent from its ^{13}C and ^{1}H NMR spectra, the signals all appear in the expected regions (see Section 3).

The structure of compound **5** was additionally confirmed by a crystal structure analysis (see below; Fig. 1) which revealed that practically all P–C and C–C bond lengths were in the expected ranges. The strain in the molecule can first of all be recognized by the markedly lengthened P3–C5 bond length of 1.940(4) Å. The two 1,3-diphosphethane rings are practically planar; because of the three-membered ring structure the dihedral angles are different, with 48.1(2)° for C1–P3–C2 and 102.1(2)° for P1–C5–P2.

X-ray crystal structure analysis of **5**: single crystal from diethyl ether; 0.21 × 0.39 × 0.49 mm, Enraf–Nonius CAD4 diffractometer; Mo Kα (graphite monochro-

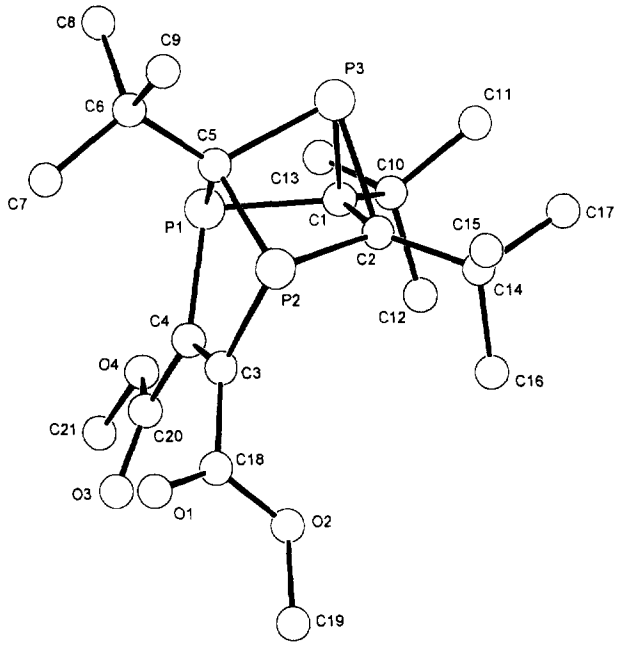
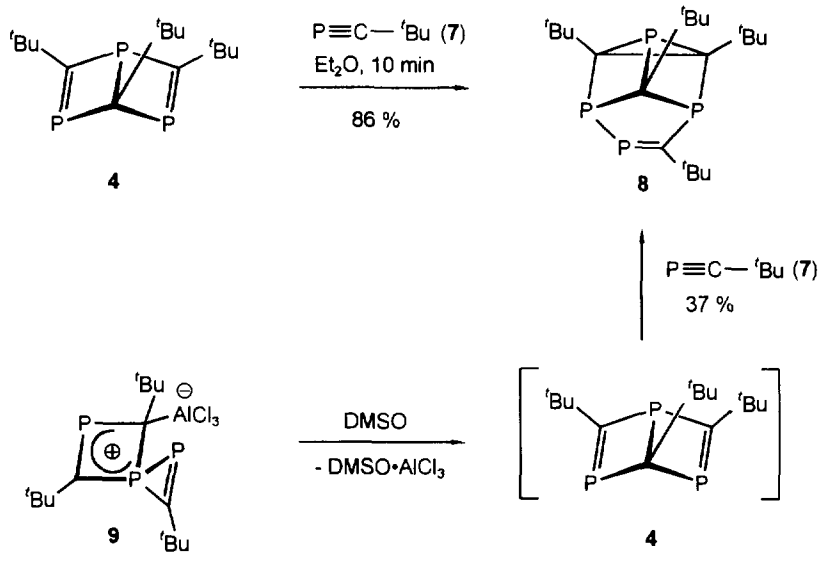


Fig. 1. Crystal structure of **5**; selected bond lengths (Å) and angles (°): C1–C2 = 1.536(5), C1–P1 = 1.877(4); C2–P2 = 1.879(4); C1–P3 = 1.880(4); P3–C5 = 1.940(4), P2–C3 = 1.846(4); C3–C4 = 1.336(5); P1–C5–P2 = 102.1(2); P2–C5–P3 = 91.8(2); C1–P3–C2 = 48.1(2); C2–P3–C5 = 80.0(2); P3–C1–C2 = 66.2(2).

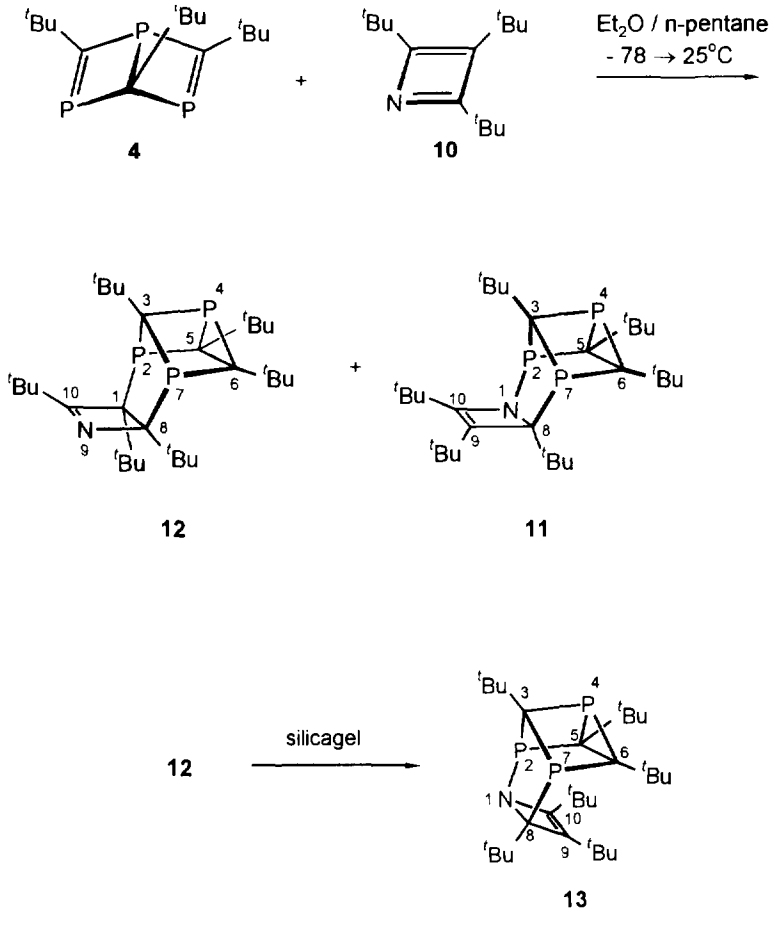
mator, $\lambda = 0.71069$), empirical formula $C_{21}H_{33}P_3O_4$, space group $P\bar{1}$; unit cell dimensions: $a = 8.853(1)$, $b = 9.116(1)$, $c = 17.220(2)$ Å, $\alpha = 78.83$, $\beta = 77.60$, $\gamma = 62.47°$; $d_{calc.} = 1.23\,g\,cm^{-3}$, $V = 1196.4(2)$ Å^3, $Z = 2$; $\mu(Mo\,K\alpha) = 2.64\,cm^{-1}$, range for data collection $2\theta_{max} = 45.3°$; ω scan; index ranges: $-10 \le h \le 11$, $-11 \le k \le 11$, $0 \le l \le 21$; reflections collected 5153; independent reflections 4836; parameters 264; no absorption correction. Structure solution: direct methods, structure refinement: full matrix least squares on F^2, $R_{obs} = 0.058$, $R_w = 0.181$ based on 3854 reflections with $I > 2\sigma(I)$.

Phosphaalkynes such as *tert*-butylphosphaacetylene (**7**) also readily undergo a [2 + 2 + 2]-cycloaddition with **4**. This type of reaction of phosphaalkynes with 2-phosphabicyclo[2.2.*n*]alka-2,5-dienes has been know for several years [11]; for a general review on the cycloaddition behavior of phosphaalkynes, see Ref. [12]. Even at 0 °C the reaction of **7** with **4** is complete within 10 min and furnishes the tetracyclic compound **8** in 96% yield as a red oil. The regiochemistry of the reaction is the same as that of the reaction of **4** with electron-poor acetylenes. Attack at the $\lambda^3\sigma^2$-phosphorus atoms has a considerably more favorable transition state than that at the sp^2-carbon atoms of the 1,4-diene system, as has been deduced from ab initio calculations on the parent system [13].

Compound **8** has previously been prepared by the reaction of the spirocyclotrimer **9** with *tert*-butylphosphaacetylene (**7**) in the presence of DMSO [14]. The reaction most probably proceeds by way of the 1,3,5-triphospha-Dewar-benzene **4** which cannot be isolated as such but can be trapped by a homo-Diels–Alder reaction. The successful synthesis of **8** from **4** presented here demonstrates that homo-Diels–Alder reactions between **4** and a phosphaalkyne are possible under the previously employed conditions. The spectroscopic data of **8** are in complete agreement with the data published previously [14].



As the first example of a [4 + 2 + 2]-cycloaddition, we have investigated the reaction between **4** and tris(*tert*-butyl)azacyclobutadiene [tri-*tert*-butylazete] (**10**) [15] which is well-known to possess an enormous potential for cycloaddition reactions [16]. This reaction also occurs smoothly at temperatures between −30 °C and room temperature. After completion of the process, two isomers in a ratio of 1:2 can be detected in the reaction solution by ^{31}P NMR spectrometry. The minor product was unambiguously identified as the homo-Diels–Alder adduct **11** by crystal structure analysis (Fig. 2) after column chromatographic separation. However, isolation of the main product **12** was not possible, since it underwent quantitative rearrangement to a third product **13** during attempted chromatographic separation. NMR spectroscopic analysis of the reaction mixture supports the assumption that the major primary product is the isomer **12**. The structure **13** was assigned to the rearrangement product on the basis of its NMR spectroscopic data. The [4 + 2 + 2]-cycloaddition of the tri-*tert*-butylazete **10** to **4** is obviously not regiospecific. The (presumably acid-catalyzed) rearrangement of the major product **12** with an exo orientation of the azete ring accordingly gives rise to the endo isomer **13**. No conclusions can as yet be drawn about the course of the isomerization process.



4 **10** **12** **11** **12** **13**

From the crystal structure analysis of **11** (see below; Fig. 2) it is clear that the azete undergoes addition to the triphospha-Dewar-benzene **4** by way of its C≡N bond and that, similar to **5**, new bonds are formed at the two low-coordinated phosphorus atoms. The structure of the pentacyclic skeleton (bond lengths and angles) is certainly comparable with that of **5**, except that in **11** it is not the σ-bond between the bridgehead atoms P3–C3 (1.888(2) Å) but rather the four-membered ring edge P3–C2 (1.916(8) Å) that is lengthened. Bond stretching in **11** is also observed between P1 and C4 (1.923(7) Å) while the distance between P2 and C3 is somewhat shortened. This gives rise to a slight distortion of the cage skeleton on the side of the nitrogen-substituted phosphorus atom P2. The values for the C–N single and C=C double bonds of the azete ring are in the expected range.

X-ray crystal structure analysis of **11**: single crystal from pentane; 0.3 × 0.3 × 0.15 mm, Enraf–Nonius CAD4 diffractometer; Mo Kα (graphite monochro-

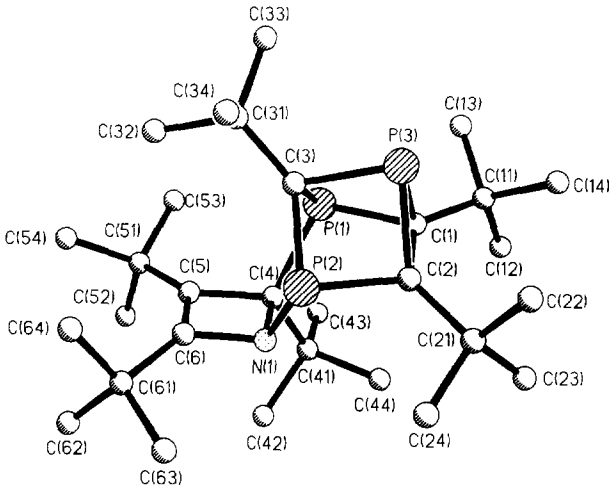


Fig. 2. Crystal structure of **11**; selected bond lengths (Å) and angles (°): P1–C1 = 1.889(8), P2–C2 = 1.881(8); P3–C3 = 1.888(8); P3–C2 = 1.916(8); P3–C1 = 1.870(8), N1–C4 = 1.533(9); C5–C6 = 1.336(10); P1–C3–P2 = 98.9(3); C1–P3–C2 = 48.5(3); C1–C2–P3 = 64.2(4); P2–C2–P3 = 87.7(3).

mator, $\lambda = 0.71073$), empirical formula $C_{30}H_{54}NP_3$, space group $P\bar{1}$; unit cell dimensions: $a = 12.661(3)$, $b = 15.693(3)$, $c = 15.968$ Å, $\alpha = 89.94(3)$, $\beta = 89.21(3)$, $\gamma = 77.40(3)°$; $d_{calc.} = 1.119\ g\ cm^{-3}$, $V = 3096.0(1)$ Å^3, $Z = 4$; μ(Mo Kα) = 2.64 cm^{-1}, range for data collection: 1.28–21.00°, ϖ scan, index ranges: $-1 \leq h \leq 12$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$; reflections collected 7721; independent reflections 6578; parameters 613; no absorption correction. Structure solution: direct methods, structure refinement: full matrix least squares on F^2, $R_{obs} = 0.0783$, $R_w = 0.2181$ based on 6570 reflections with $I > 2\sigma(I)$.

Further details of the crystal structure investigations of **5** and **11** may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository numbers CSD-58878 and 405196, the names of the authors, and the journal citation.

There are only a few significant differences in the NMR spectroscopic data of the three pentacyclic compounds **11**, **12**, and **13**. Characteristic above all are the positions of the signals for the sp^2-C atoms in their ^{13}C NMR spectra. For compounds **11** and **13**, two sp^2-C atoms are observed in the range $\delta = 138$–154 ppm, while compound **12** exhibits only one sp^2-C atom with a pronounced lowfield shift to $\delta = 196.6$ ppm which is characteristic for C=N double bonds. In the ^{31}P NMR spectra of the three compounds, signals for the phosphorus atoms of the newly formed three-membered rings are observed between $\delta = -169$ and -194 ppm in the highfield region typical for phosphiranes. In the case of compound **12**, two different signals are seen at $\delta = 164$ and 107 ppm for the further two bridgehead phosphorus atoms, whereas for the exo/endo isomers **11** and **13** two signal groups at almost identical chemical shifts of $\delta \approx 100$ or $\delta \approx 120$ ppm respectively, are found in each case.

In the present work we have achieved the first examples of a homo-Diels–Alder reaction of the triphospha-Dewar-benzene **4** with electron-poor alkynes, the phosphaalkyne **7**, and the tri-*tert*-butylazete (**10**) which all proceed under extremely mild conditions, Comparable cycloadditions of Dewar-benzene derivatives require temperatures in excess of 100 °C [8,9]. It may be assumed that the polarity of the two P=C double bonds in **4** facilitate these cycloadditions. Preliminary experiments have also shown that electron-poor olefins such as, for example, diethyl fumarate can undergo [2 + 2 + 2]-cycloadditions with **4**. The results of these investigations will be reported elsewhere.

3. Experimental

The reactions were performed under argon (purity: greater than 99.9, 98%) in previously evacuated and baked-out Schlenk vessels. The solvents used (Et_2O, pentane) were dried with Na-K alloy prior to distillation and stored under argon. Melting points were determined on a Mettler FP61 apparatus (heating rate 3 °C min^{-1}). Microanalyses were performed with a Perkin–Elmer analyzer 240. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC 200 and Bruker AMX 400 spectrometers with TMS as internal standard. ^{31}P NMR spectra were measured on a Bruker AC 200 (80.8 MHz) spectrometer with 85% H_3PO_4 as external standard. Mass spectra were recorded with a Finnigan MAT 90 spectrometer. Chemicals: dimethyl acetylenedicarboxylate and methyl propynoate (Fluka) were used without further purification; 1,3,5-triphospha-Dewar-benzene (**4**) [1], *tert*-butylphosphaacetylene (**7**) [17] (for optimized procedure see Ref. [18]) and tri-*tert*-butylazete (**10**) [15] were prepared by published procedures.

3.1. Dimethyl 2,4,5-tris(tert-butyl)-1,3,6-triphosphatricyclo[4.2.0.0^{2,6}.0^{3,5}]oct-7-ene-7,8-dicarboxylate (5)

Dimethyl acetylenedicarboxylate (250 mg, 1.7 mmol) is added dropwise to a solution of **4** (510 mg, 1.7 mmol) in diethyl ether (20 ml) at 0 °C. After stirring for 2 h the color of the solution changes from orange to yellow. Cooling to −30 °C results in the deposition of **5** as yellow crystals: yield 520 mg (82%), m.p. 98 °C.

^{1}H NMR (C_6D_6, 400.1 MHz): $\delta = 0.89$ (s, 9H, ^{t}Bu), 1.43 (s, 18H, ^{t}Bu), 3.45 (s, 6H, CO_2CH_3). ^{13}C {H} NMR (C_6D_6, 100.6 MHz): $\delta = 32.3$ (m, 4-$\underline{C}(CH_3)_3$),

34.2 (dt, ^3J(C,P) = 6.4, ^4J(C,P) = 3.2 Hz, 4-C($\overline{CH_3}$)$_3$), 33.9 (pseudo q, ^2J(C,P) = 6.2 Hz, 2-C($\overline{CH_3}$)$_3$), 27.4 (dt, ^3J(C,P) = 7.2 and 4.0 Hz, 2-C($\overline{CH_3}$)$_3$), 51.5 (td, ^1J(C,P) = 31.0, ^2J(C,P) = 10.4 Hz, C4, C5), 51.9 (d, ^4J(C,P) = 3.2 Hz, CO_2CH_3), 165.2 (pseudo t, J(C,P) = 10.5 Hz, CO_2CH_3), 166.6 (ddd, ^1J(C,P) = 37.0, ^2J(C,P) = 30.5, ^3J(C,P) = 15.0 Hz, C7, C8), C-2 could not be detected.

^{31}P NMR (C_6D_6, 80.8 MHz): δ = 104.2 (d, ^2J(P,P) = 24 Hz, P1, P6), −158.3 (t, J(P,P) = 24 Hz, P3).

MS (70 eV): m/z (%) = 442 (74) [M^+], 242 (45) [M^+ − 2PC^{t}Bu], 169 (100) [$PC_2(^tBu)_2^+$].

Anal. Found: C, 56.35; H, 7.58. $C_{21}H_{33}P_3O_4$ (443.41). Calc.: C, 57.01; H, 7.52%.

3.2. *Methyl 2,4,5-tris(tert-butyl)-1,3,6-triphosphatetracyclo[4.2.1.0^{2,6}.0^{3,5}]oct-7-ene-8-carboxylate (6)*

At 0 °C methyl propynoate (0.7 ml, 0.4 mmol) is added to a solution of **4** (120 mg, 0.4 mmol) in diethyl ether. The solvent is removed in vacuo (10^{-3} mbar), the solid residue is dissolved in diethyl ether (8 ml), filtered over Celite to remove some insoluble particles, and the volume of the solution is reduced to half. After cooling to −30 °C yellow crystals of **6** are obtained; yield: 110 mg (71%), m.p. 84 °C.

^{1}H NMR (C_6D_6, 400.1 MHz): δ = 0.8 (s, 9H, ^{t}Bu), 1.25 (dd, 9H, J(H,P) = 1.5 and 0.5 Hz, ^{t}Bu), 1.38 (dd, 9H, J(H,P) = 2.0 and 0.7 Hz, ^{t}Bu), 3.44 (s, 3H, CO_2CH_3), 8.21 (dd, 1H, ^2J(H,P) = 44.5 Hz, ^3J(H,P) = 5.1 Hz, CH-olefin).

^{13}C {H} NMR (C_6D_6, 100.1 MHz): δ = 27.5 (td, ^3J(C,P) = 6.7 and 3.3 Hz, 2-C($\overline{CH_3}$)$_3$), 32.1 (dt, ^2J(C,P) = 13.6 and 6.8 Hz, 2-C($\overline{CH_3}$)$_3$); 33.7 (pseudo-t, ^2J(C,P) = 14.8 Hz, 4-C($\overline{CH_3}$)$_3$), 34.1 (pseudo-t, ^3J(C,P) = 3.8 Hz, 4-C($\overline{CH_3}$)$_3$), 33.8 (pseudo-t, ^2J(C,P) = 14.5 Hz, 5-C($\overline{CH_3}$)$_3$), 34.2 (pseudo t, ^3J(C,P) = 4.2 Hz, 5-C($\overline{CH_3}$)$_3$), 51.1 (m, C4), 51.2 (m, C5), 51.6 (s, CO_2CH_3), 164.4 (dd, ^2J(C,P) = 21.6 Hz, ^3J(C,P) = 1.6 Hz, C=O), 166.4 (d, ^1J(C,P) = 45.6 Hz, C7), 167.3 (dd, ^1J(C,P) = 49.0 Hz, ^2J(C,P) = 1.7 Hz, C8) C3 could not be detected.

^{31}P NMR (C_6D_6, 80.8 MHz): δ = −152 (pseudo t, ^2J(P,P) = 24.3 and 24.5 Hz, P3), 87 and 89 (d,d, ^2J(P,P) = 30.4 and 24.5 Hz) P1, P6).

MS (70 eV): m/z (%) = 384 (3) [M^+], 216 (7) 169 (100).

3.3. *2,4,5,8-Tetrakis(tert-butyl)-1,3,6,7-tetraphosphatetracyclo[4.2.0.0^{2,6}.0^{3,5}]oct-7-ene (8)*

tert-Butylphosphaacetylene **7** (140 mg, 1.4 mmol) is added to a solution of **4** (330 mg, 1.1 mmol) in diethyl ether (10 ml). After 10 min stirring at 0 °C the color of the reaction solution has changed to dark red. Removal of the solvent in vacuo (10^{-3} mbar) provides **8** as a red oil; yield 400 mg (96%). The ^{1}H, ^{13}C, and ^{31}P NMR values are identical with those of an authentic sample [14].

3.4. *exo / endo-3,5,6,8,9,10-Hexakis(tert-butyl)-1-aza-2,4,7-triphosphapentacyclo-[6.2.0.0^{2,5}.0^{3,7}.0^{4,8}]dec-9-ene (11 / 13), exo-3,5,6,8,9,10-hexakis(tert-butyl)-9-aza-2,4,7-triphosphapentacyclo[6.2.0.0^{2,5}.0^{3,7}.0^{4,8}]-dec-9-ene (12)*

At −78 °C a solution of **4** (390 mg, 1.3 mmol) in diethyl ether (10 ml) is added dropwise to a solution of tri-*tert*-butylazete (**10**) (290 mg, 1.3 mmol) in pentane (5 ml). The mixture is allowed to warm to room temperature and the solvent is removed in vacuo (10^{-3} mbar). ^{31}P NMR spectroscopy of the oily residue reveals that the two isomers **11** and **12** are present in the ratio 1:2. Since compound **12** rearranges during the attempted separation of **11** from **12** by column chromatography on silica gel, **12** could only be characterized in the mixture with **11**.

12: ^{31}P NMR (C_6D_6, 80.8 MHz): δ = 164.2 (d,d, ^2J(P,P) = 16.1 and 11.8 Hz, P3), 107.1 (d,d, ^2J(P,C) = 19.1 and 16.1 Hz, P8), −169.2 (d,d, ^2J(P,P) = 19.1 and 11.8 Hz, P5).

Column chromatography of the mixture of **11** and **12** on silica gel with pentane as eluent gives **11**, whereas with a 1:1 mixture of pentane–diethyl ether as eluent compound **13** is obtained as product of the rearrangement of **12**.

11: yield 170 mg (25%), colorless crystals, m.p. 68 °C.

^{1}H NMR (C_6D_6, 200 MHz): δ = 1.20 (s, 9H, ^{t}Bu), 1.26 (s, 9H, ^{t}Bu), 1.35 (s, 9H, ^{t}Bu), 1.41 (s, 9H, ^{t}Bu), 1.46 (s, 9H, ^{t}Bu), 1.53 (s, 9H, ^{t}Bu).

^{13}C {H} NMR (C_6D_6, 50.3 MHz): δ = 31.0 (d, ^3J(C,P) = 3.4 Hz, C($\overline{CH_3}$)$_3$), 31.8 (q, ^3J(C,P) = 5.1 Hz, C($\overline{CH_3}$)$_3$), 32.7 (pseudo t, ^3J(C,P) = 3.4 Hz, C($\overline{CH_3}$)$_3$), 34.9 (d, ^3J(C,P) = 5.1 Hz, C($\overline{CH_3}$)$_3$), 35.1 (s, C($\overline{CH_3}$)$_3$), 35.4 (d, ^3J(C,P) = 4.8 Hz, C($\overline{CH_3}$)$_3$), 31.9 (d, ^2J(C,P) = 5.1 Hz, C($\overline{CH_3}$)$_3$), 32.4 (pseudo t, ^2J(C,P) = 3.4 Hz, C($\overline{CH_3}$)$_3$), 34.2 (d, ^2J(C,P) = 4.8 Hz, C($\overline{CH_3}$)$_3$), 34.5 (s, C($\overline{CH_3}$)$_3$), 38.8 (d, ^2J(C,P) = 6.7 Hz, C($\overline{CH_3}$)$_3$), 47.0 (dt, ^1J(C,P) = 27.2, ^2J(C,P) = 3.6, C6), 49.1 (dt, ^1J(C,P) = 52.2, ^2J(C,P) = 3.4, C5), 85.1 (dd, ^1J(C,P) = 81 Hz, ^3J(C,P) = 6.2 Hz, C8) 138.7 (d, ^2J(C,P) = 20.1 Hz, C9), 155.6 (s, C10); C3 could not be detected.

^{31}P NMR (C_6D_6, 80.8 MHz): δ = 99 (dd, ^2J(P,P) = 13 and 6.6 Hz), 100 (dd, ^2J(P,P) = 30.1 and 13.0 Hz), P1/P7), −183 (dd, ^2J(P,P) = 30.1 and 6.6 Hz, P4).

MS (70 eV): m/z (%) = 521 (38) [M^+], 506 (32) [$M^+ - CH_3$], 464 (17) [$M^+ - C_4H_9$], 383 (4) [$M^+ - C_2^tBu_2$], 300 (4) [$(P_3C_3^tBu_3)^+$], 220 (9), 206(43), 169 (100).

Anal. Found: C, 68.84; H, 10.33. $C_{30}H_{54}NP_3$ (521.7). Calc.: C, 69.10; H, 10.36%.

13: yield 200 mg (38%), colorless crystals from diethyl ether, m.p. 77 °C.

^{1}H NMR (C_6D_6, 200 MHz): δ = 1.23 (s, 9H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu), 1.44 (m, 9H, ^{t}Bu), 1.47 (s, 9H, ^{t}Bu), 1.49 (s, 18H, ^{t}Bu).

^{13}C{H} NMR (C_6D_6, 50.3 MHz): δ = 30.9 (td, ^3J(C,P) = 11.9 and 3.4 Hz, $C(CH_3)_3$), 31.2 (s, $C(CH_3)_3$), 31.8 (d, ^3J(C,P) = 5.1 Hz, $C(CH_3)_3$), 33.0 (s, $C(CH_3)_3$), 34.6 (dd, ^3J(C,P) = 11.8 and 3.4 Hz, $C(CH_3)_3$), 36.0 (dd, $^3J(C,P)$ = 15.2 and 8.5 Hz, $C(CH_3)_3$), 27.2 (s, $C(CH_3)_3$), 29.4 (s, $C(CH_3)_3$), 33.5 (m, $C(CH_3)_3$), 33.9 (dd, ^2J(C,P) = 13.6 and 6.8 Hz, $C(CH_3)_3$), 34.9 (t, ^2J(C,P) = 5.1 Hz, $C(CH_3)_3$), 40.4 (d, ^2J(C,P) = 18.7 Hz, $C(CH_3)_3$), 55.2 (dd, ^1J(C,P) = 39.8 and 18.0 Hz, C5), 60.7 (ddd, ^1J(C,P) = 45.7 and 32.2 Hz, ^2J(C,P) = 5.1 Hz, C6), 105.7 (dd, ^1J(C,P) = 63.1 Hz, ^2J(C,P) = 4.7 Hz, C8), 145.6 (d, ^2J(C,P) = 8.5 Hz, C9), 154.9 (pseudo t, ^2J(C,P) = 3.4 Hz, C10), C3 could not be detected.

^{31}P NMR (C_6D_6, 80.8 MHz): δ = 123.5 (dd, ^2J(P,P) = 21.7 and 15.8 Hz), 118.1 (dd, ^2J(P,P) = 21.7 and 19.1 Hz) P2/P7), −194 (dd, $^2J(P,P)$ = 19.1 and 15.8 Hz, P4).

MS (70 eV): m/z(%) = 521 (52) [M^+], 506 (27) [$M^+ - CH_3$], 464 (8) [$M^+ - C_4H_9$], 383 (8), 300 (25) [$P_3C_3^tBu_3^+$], 220 (24), 206 (100), 169(85).

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