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Organophosphorus compounds Part 164. 2,4-Disubstituted 1,3-diphosphacyclobutadienes: generation and trapping reactions☆

Andreas Mack, Steffen Danner, Uwe Bergsträßer, Heinrich Heydt *, Manfred Regitz *

Department of Chemistry, University of Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

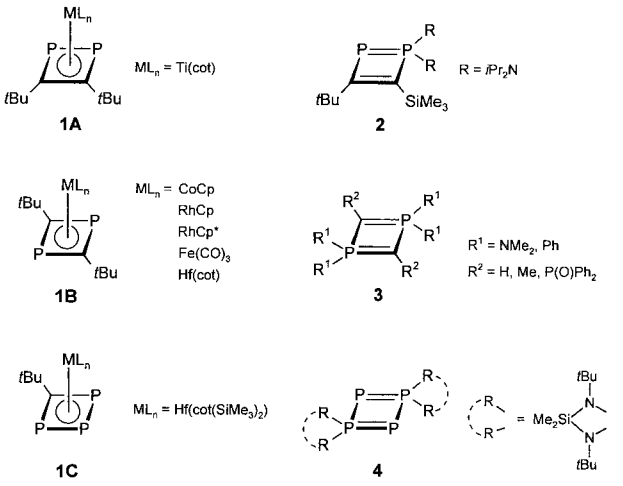
Abstract

$1\lambda^3,3\lambda^3$-Diphosphacyclobutadienes have been specifically generated for the first time through hexachloroethane-induced extrusion of the organophosphorus ligands from dimeric zirconocene–phosphaalkyne complexes. The species were chemically characterized indirectly by reactions with appropriate trapping reagents. Thus, the use of bis(acceptor)-substituted alkynes gave rise to 2,5-diphosphabenzvalenes, whereas reactions with *N*-methylmaleinimide and donor-substituted alkynes such as bis(diethylamino)acetylene resulted in the formation of 1,3-diphospha-Dewar-benzenes. Representatives of both classes of compounds were analyzed by X-ray crystallography. Kinetically stabilized phosphaalkynes reacted similarly to furnish tetraphosphabishomoprismanes through a sequence of [4 + 2] and [2 + 2 + 2] cycloaddition processes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphaalkynes; 1,3-Diphosphacyclobutadienes; 1,3-Diphospha-Dewar-benzenes; Diphosphabenzvalenes; Cycloadditions

1. Introduction

Cyclobutadienes [1] and azacyclobutadienes [2] bearing sterically demanding substituents ('corset effect') are stable and, accordingly, have attained major significance in preparative chemistry. In contrast, the free λ^3-phospha- or λ^3,λ^3-diphosphacyclobutadienes are still unknown. Up to now only η^4-complexed 1,2- and 1,3-diphosphacyclobutadienes (**1A** [3] and **1B** [4]) or 1,2,3-triphosphacyclobutadienes (**1C** [5]), together with compounds containing at least one five-coordinated phosphorus atom have been reported. Examples of the latter compounds are the 1,2-derivative **2** [6], the $1\lambda^5,3\lambda^5$-diphosphacyclobutadienes **3** [7] and the tetraphosphete **4** [8].



We now report on the targeted generation and trapping reactions of 1,3-diphosphacyclobutadienes. This has opened, for the first time, a broad access to the as yet only sparsely explored diphosphabenzene valence isomer system. 1,3-Diphosphacyclobutadienes were recently proposed as the decisive intermediates in the

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* Corresponding authors. Fax: +49-631-205-3921.
E-mail address: heydt@chemie.uni-kl.de (H. Heydt).

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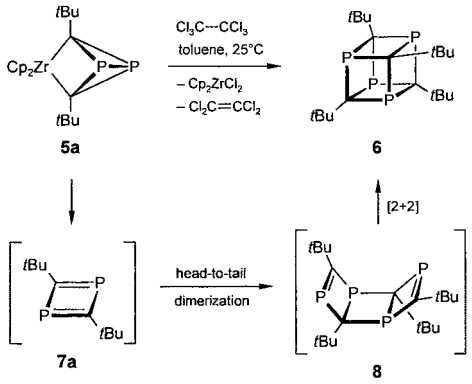
specific, metal-initiated synthesis of tetraphosphacubanes [9,10].



Thus, a plausible mechanistic explanation for the reaction of the dimeric tricyclic phosphaalkyne complex **5a** with the mild halogenating agent involves the primary generation of the 1,3-diphosphacyclobutadiene (**7a**). The subsequent dimerization of the intermediate, which cannot be detected by spectroscopy, to the similarly not detectable tricyclic species **8** is followed by an intramolecular [2 + 2] cycloaddition to afford the pentacyclic product **6**.

2. Results and discussion

The above mentioned results prompted the present work. In order to enable the chemical detection of the title compounds, we ensured that suitable trapping agents were present during the extrusion reaction of **5** with hexachloroethane [11]. At room temperature *N*-methylmaleinimide (**9**) undergoes regioselective addition to the liberated 1,3-diphosphacyclobutadiene (**7a**) to afford the *endo*-tricyclic species **10** that can be isolated in the pure state by column chromatography and crystallization, albeit with a significant loss in yield. Elemental analyses and mass spectral data (Table 1) indicate that the adduct **10** is formed from one equivalent each of 1,3-diphosphacyclobutadiene (**7a**) and the *Z*-alkene **9**. The constitution of **10** was deduced from its NMR data. The ^{31}P-NMR spectrum alone, showing two signals at $\delta = 66.9$ (P1) and $\delta = 425.0$ (P3) unequiv-

Table 1
Selected spectroscopic data for the heterocyclic compounds **10**, **12**–**14** and **16** [a]

10: M.p.: 108 °C; ^{1}H-NMR: $\delta = 1.00$ (d, ^4J(P,H) = 0.7 Hz, 9H, *t*-Bu), 1.10 (s, 9H, *t*-Bu), 2.60 (s, 3H, NCH_3), 2.62 (dd, ^2J(P,H) = 21.0 Hz, ^3J(H,H) = 8.0 Hz, 1H, H6), 3.14 (ddd, ^3J(H,H) = 8.0 Hz, ^3J(P,H) = 3.1 and 1.3 Hz, 1H, H5); ^{13}C-NMR: $\delta = 31.6$ (dd, ^1J(P,C) = 16.5 and 10.6 Hz, C5), 40.2 (dd, J(P,C) = 8.1 and 5.6 Hz, C1 or C6), 43.7 (d, J(P,C) = 1.7, C6 or C1), 174.2 (d, J(P,C) = 3.4 Hz, C=O), 176.0 (d, J(P,C) = 3.4 Hz, C=O), 232.1 (dd, ^1J(P,C) = 58.5 and 40.3 Hz, C3); ^{31}P-NMR: $\delta = 66.9$ (d, ^2J(P,P) = 26.2 Hz, P2), 425.0 (d, ^2J(P,P) = 26.2 Hz, P4); MS; *m*/*z* (%): 311 (41) [M^+], 57 (100) [*t*-Bu^+].

12: B.p.: 100–110 °C/10^{-3} mbar; ^{1}H-NMR: $\delta = 0.96$ (t, ^3J(H,H) = 7.5 Hz, 6H, $CH_2C\underline{H}_3$), 1.04 (t, ^3J(H,H) = 7.4 Hz, 6H, $CH_2C\underline{H}_3$), 1.32 (s, 9H, *t*-Bu), 1.33 (d, ^4J(P,H) = 0.5 Hz, 9H, *t*-Bu), 2.50–3.55 (m, 8H, $C\underline{H}_2CH_3$); ^{13}C-NMR: $\delta = 43.1$ (dd, ^1J(P,C) = 28.8 and 17.8 Hz, C4), 136.2 (dd, J(P,C) = 26.3 and 21.5 Hz, C5 or C6), 143.3 (dd, J(P,C) = 17.0 and 4.2 Hz, C6 or C5), 247.6 (dd, ^1J(P,C) = 50.0 and 49.3 Hz, C2); ^{31}P-NMR: $\delta = 31.9$ (d, ^2J(P,P) = 16.0 Hz, P1), 329.9 (d, ^2J(P,P) = 16.0 Hz, P3); MS; *m*/*z* (%): 368 (37) [M^+], 153 (100) [$(CNEt_2)_2-CH_3^+$].

13: ^{31}P-NMR: $\delta = 26.3$ (d, ^2J(P,P) = 34.9 Hz, P1), 233.3 (d, ^2J(P,P) = 34.9 Hz, ^1J(P,W) = 226.7 Hz, P3); MS; *m*/*z* (%): 692 (7) [M^+], 73 (100) [$HNEt_2^+$].

14: M.p.: 142 °C (dec.); ^{31}P-NMR: $\delta = 53.2$ (d, ^2J(P,P) = 17.4 Hz, ^1J(P,W) = 235.4 Hz, P1), 266.6 (d, ^2J(P,P) = 17.4 Hz, ^1J(P,W) = 226.9 Hz, P3); MS; *m*/*z* (%): 1015 (9) [M^+], 215 (100) [$C_{10}H_{19}NP_2^+$].

16a: B.p.: 110 °C/10^{-3} mbar; ^{1}H-NMR: $\delta = 1.14$ (s, 18H, *t*-Bu), 3.34 (s, 6H, OCH_3); ^{13}C-NMR: $\delta = 30.6$ (t, ^3J(P,C) = 3.8 Hz, $C(\underline{C}H_3)_3$), 34.8 (t, ^2J(P,C) = 9.2 Hz, $\underline{C}(CH_3)_3$), 51.9 (s, OCH_3), 109.6 (t, ^1J(P,C) = 45.8 Hz, C1/C6), 163.5 (AXX′, ^1J(P,C) = 68.0 Hz, ^2J(P,C) = 4.0 Hz, C3/C4), 164.1 (AXX′, ^2J(P,C) = 23.0 Hz, ^3J(P,C) = 4.0 Hz, ^2J(P,P) = 12.0 Hz, C=O); ^{31}P-NMR: $\delta = -19.3$ (s); MS; *m*/*z* (%): 342 (5) [M^+], 327 (6) [M^+-CH_3], 311 (19) [M^+-OCH_3], 285 (90) [M^+-t-Bu], 230 (100) [$M^+-2C_4H_8$], 169 (17) [$P(Ct\text{-Bu})_2^+$], 131 (5) [$P_2(Ct\text{-Bu})^+$], 57 (29) [*t*-Bu^+].

16b: M.p.: 176 °C; ^{31}P-NMR: $\delta = -26.0$ (s); MS; *m*/*z* (%): 498 (22) [M^+], 135 (100) [Ad^+].

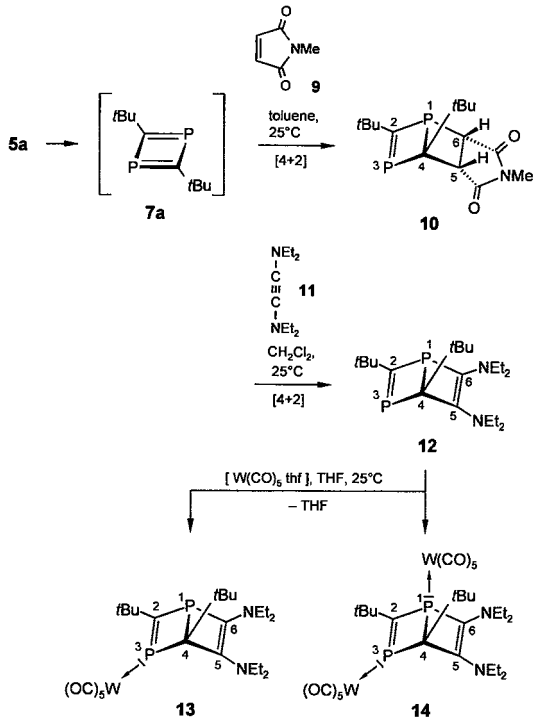
16c: ^{1}H-NMR: $\delta = 0.91$ (t, ^3J(H,H) = 7.1 Hz, 6H, $CH_2C\underline{H}_3$), 1.12 (s, 18H, *t*-Bu), 3.95 (q, ^3J(H,H) = 7.1 Hz, 4H, $C\underline{H}_2CH_3$); ^{13}C-NMR: $\delta = 14.0$ (s, $CH_2\underline{C}H_3$), 30.7 (t, ^3J(P,C) = 4.4 Hz, $C(\underline{C}H_3)_3$), 34.8 (t, ^2J(P,C) = 9.1 Hz, $C(\underline{C}H_3)_3$), 61.4 (s, $\underline{C}H_2CH_3$), 109.3 (t, ^1J(P,C) = 45.0 Hz, C1/C6), 163.4 (AXX′, ^1J(P,C) = 64.1 Hz, ^2J(P,C) = 4.0 Hz, C3/C4), 163.7 (AXX′, ^2J(P,C) = 23.6 Hz, ^3J(P,C) = 6.0 Hz, ^2J(P,P) = 12.0 Hz, C=O); ^{31}P-NMR: $\delta = -18.3$ (s).

16d: M.p.: 61 °C; ^{31}P-NMR: $\delta = -7.7$ (s); MS; *m*/*z* (%): 362 (100) [M^+].

16e: M.p.: 61 °C; ^{31}P-NMR: $\delta = -3.8$ (s); MS; *m*/*z* (%): 378 (19) [M^+], 105 (100) [$COPh^+$].

[a] NMR: Bruker AMX-400, ^{1}H-NMR (400.1 MHz) and ^{13}C-NMR (100.6 MHz) in C_6D_6, ^{31}P-NMR (162.0 MHz) in C_6D_6 (85% H_3PO_4 external standard), all at $T = 25$ °C; MS (EI, 70 eV): Finnigan MAT 90.

ocally demonstrates the structure of a 1,3-diphosphacyclobutene unit [12]. The *endo*-addition is clearly visible from the ^{1}H-NMR data; the *cis*-position of proton H6 ($\delta = 2.62$) to the free electron pair at P1 is evident from the large ^2J(P,H) coupling of 21.0 Hz [13]. The second skeletal proton H5 gives a signal at $\delta = 3.14$ with a characteristic splitting pattern. The skeletal carbon atoms C4, C5 and C6 gave signals with chemical shifts typical for a four-membered ring containing phosphorus ($\delta = 31.6$–43.7) [4e,12]. The signal for the phosphaalkene carbon atom C2 occurs at characteristic low field ($\delta = 232.1$) [14]. The two ^1J(P,C) coupling constants of 58.5 and 40.3 Hz confirm the proximity to P1 and P3.



The reaction with the ynediamine **11** as a trapping reagent for the liberated 1,3-diphosphacyclobutadiene (**7a**) proceeds selectively to afford the first member of the new class of 1,3-diphospha-Dewar-benzenes. The bicyclic compound **12** was isolated by bulb-to-bulb distillation in 47% yield. Surprisingly, a valence isomerization to furnish the corresponding 1,3-diphosphabenzene does not occur, even at 100–110 °C. The constitution of **12** is demonstrated by its NMR data. The presence of a 1,3-diphosphacyclobutene increment is shown by the ^{31}P-NMR [$\delta = 31.9$ (P1) and $\delta = 329.9$ (P3)] and the ^{13}C-NMR signals [$\delta = 43.1$ (C4) and $\delta = 247.6$ (C2)]. The C=C double bond in **12** is recognized from the ^{13}C-NMR signals of C5 and C6 at $\delta = 136.2$ and 143.3. The oily consistency of the 1,3-diphospha-Dewar-benzene **12** does not allow an X-ray crystallographic analysis. Thus, in order to obtain a

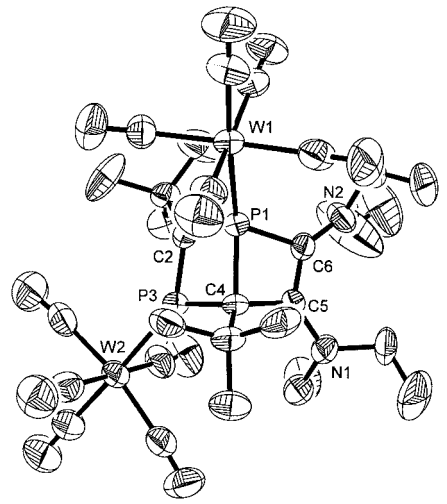
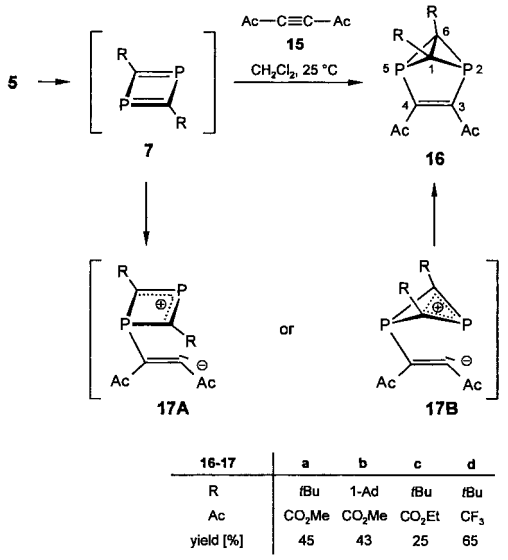


Fig. 1. Structure of **14** in the crystal state (XP plot [26], thermal ellipsoids with 50% occupancy probability). Selected bond lengths (Å) and bond angles (°): W1–P1 2.578(2), W2–P3 2.516(2), P3–C2 1.680(9), C5–C6 1.354(12), P1–C2 1.840(9), P1–C4 1.874(8), P1–C6 1.830(9), P3–C4 1.895(9), C4–C5 1.531(12); W2–P3–C2 135.9(3), W2–P3–C4 135.5(3), C2–P3–C4 88.5(3), C4–P1–C2 84.6(4), C4–P1–C6 75.7(4), P3–C2–P1 97.1(5), P1–C4–P3 89.0(4), C5–C4–P1 86.6(5), C5–C6–P1 93.8(7), C6–C5–C4 103.8(8).

crystalline derivative of **12**, we allowed it to react with $[W(CO)_5THF]$. Irrespective of the stoichiometry, we always obtained a mixture of the two complexes **13** and **14**. Both metal complexes are less sensitive to hydrolysis than the uncomplexed molecule **12** and can, thus, be separated by column chromatography. The coordination of the pentacarbonyltungsten fragments at P3 (**13**) or at P1 and P3 (**14**) is demonstrated by the respective ^{183}W satellite signals in the ^{31}P-NMR spectra (Table 1). An X-ray crystallographic analysis of the bis$[W(CO)_5]$ complex **14** obtained as the minor product impressively confirmed the 1,3-diphospha-Dewar-benzene structure (Fig. 1) [15]. At the same time it unambiguously proved the constitution of the new diphosphabenzene valence isomer **12**. The bicyclic skeleton exhibits a pronounced folding along the P1–C4 axis; the two idealized planes defined by the atoms P1–C2–P3–C4 and P1–C4–C5–C6, respectively, intersect at an angle of 109.6°. The P–C and C–C single bond lengths are in the range 1.830(9)–1.895(9) Å and around 1.531(12) Å, respectively, in good agreement with those of other polycyclic systems [16]. The P3–C2 bond length of 1.680(9) Å shows that the phosphaalkene function is still intact after the η^1-complexation [14].

The presence of various bis(acceptor) substituted acetylenes **15** during the extrusion reaction of **5** with C_2Cl_6 does not result in diphospha-Dewar-benzenes. Instead, these reactions lead to the unexpected but selective formation of the new diphosphabenzvalenes **16** that can be isolated in yields of up to 65% by column chromatography.



16-17	a	b	c	d
R	*t*Bu	1-Ad	*t*Bu	*t*Bu
Ac	CO_2Me	CO_2Me	CO_2Et	CF_3
yield [%]	45	43	25	65

The constitutions of the highly stable, colorless tricyclic compounds **16** were unequivocally demonstrated from their elemental analyses and their mass and NMR spectroscopic data (Table 1). This is illustrated below by the discussion of the NMR data for the product **16a**. The two isochronous phosphorus nuclei P2 and P5 give a ^{31}P-NMR signal at $\delta = -19.3$, an unusually low field for phosphiranes [17]. However, this value is in good harmony with that for the up to date only previously known diphosphabenzvalene [18]. In the ^{13}C-NMR spectrum, the two chemically equivalent skeletal carbon atoms C1 and C6 give a signal at $\delta = 109.6$, an unusual and dramatic shift to low field for a phosphacyclopropane [17]. The direct adjacency to the two P atoms results in a triplet structure (^1J(P,C) = 45.8 Hz). The signals of the two double-bonded carbon atoms (C=C; $\delta = 163.5$ and C=O; $\delta = 164.1$) appear as an AXX′ spin system that can be resolved by simulations (Table 1). It is then also possible to deduce a value of 12.0 Hz for the not directly measurable ^2J(P,P) coupling constants.

A suitable single crystal of the 1-adamantyl derivative **16b** has also enabled the first ever crystallographic analysis of a diphosphabenzvalene to be made (Fig. 2) [19]. The standard criteria for characterizing a bicyclobutane system [20] are the folding angle between the planes of the two three-membered rings and the length of the bridging bond; in the case of **16b** these were found to be 114° and 1.499(4) Å, respectively. In spite of their incorporation in a tricyclic framework, the phosphirane units still show their typical geometric parameters [17], although the bond lengths P2–C1 (1.859(2) Å) and P2–C6 (1.848(2) Å) do differ slightly. Also typical is the C3=C4 double bond length of 1.328(5) Å.

The kinetically stabilized phosphaalkyne **18** also undergoes a highly selective addition to the liberated 1,3-diphosphacyclobutadiene (**7a**). The primarily formed 1,3,5-triphospha-Dewar-benzene **19**, however, cannot be detected but rather participates in a spontaneous, regioselective homo-Diels–Alder reaction with a further molecule of *tert*-butylphosphaacetylene (**18**) [21b]. This results in the construction of the tetraphosphabishomoprismane **21** as the final product isolated in 82% yield.

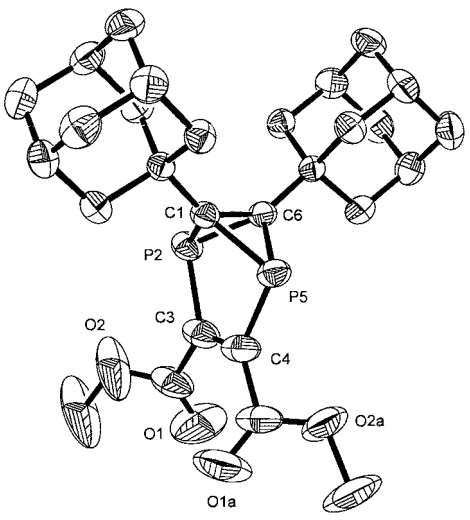
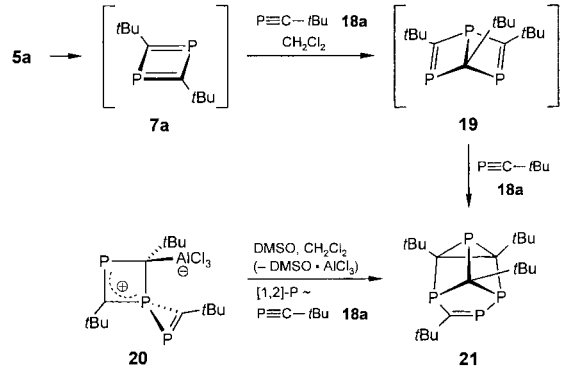


Fig. 2. Structure of **16b** in the crystal state (XP plot [26], thermal ellipsoids with 50% occupancy probability). Selected bond lengths (Å) and bond angles (°): C1–P5 1.842(2), C6–P2 1.842(2), P2–C1 1.859(2), P2–C3 1.848(2), C1–C6 1.499(4), C3–C4 1.328(5); C6–P2–C1 47.78(10), C6–C1–P2 65.53(11), C3–P2–C1 98.04(9), P5–C1–P2 100.12(9), C4–C3–P2 114.11(7).



The cage compound **21** is also accessible by another route [21]. Elimination of the Lewis acid from the spirocyclic betaine **20** by dimethyl sulfoxide in the presence of the phosphaalkyne **18** also leads to the formation of **21** [21a]. The intermediate existence of the 1,3,5-triphospha-Dewar-benzene **19** is, thus, also plausible in the present reaction and can be rationalized by a [1,2]-P shift subsequent to extrusion of $AlCl_3$. The NMR data of the tetramer **21**, prepared from **5a**, are in excellent agreement with those reported in the literature [21a].

3. Experimental

General procedure for the preparation of **10**, **12**, **16**, and **21**: in a Schlenk pressure tube **5a** or the analogous 1-adamantyl-zirconium complex **5b** [9b] is dissolved in an appropriate solvent [22]. At 25 °C the trapping reagent and C_2Cl_6 are added consecutively. After completion of the reaction (^{31}P-NMR monitoring) volatile materials are evaporated at 25 °C/10^{-3} mbar, the residue is treated with *n*-pentane (4 × 15 ml) and filtered through Celite™ (D3 glass sinter). The final product is isolated either by column chromatography on silica gel (63–200 μm, heated for 16 h at 175 °C and 10^{-3} mbar, then deactivated with 4% Ar-saturated water) or by bulb-to-bulb distillation.

*3.1. 3,5-Ditert-butyl-8-methyl-8-aza-2,4-diphosphatricyclo[4.3.0.0^{2,5}]non-3-ene-7,9-dione (**10**)*

Amounts: **5a** (250 mg, 0.59 mmol), **9** (264 mg, 2.37 mmol), C_2Cl_6 (168 mg, 0.71 mmol) in 3 ml toluene; reaction time: 7 days; column chromatography: eluent *n*-pentane–Et_2O (2:1), after removal of the solvent mixture at 25 °C/10^{-3} mbar and recrystallization from *n*-pentane at −30 °C, lemon-yellow crystals of **10** are obtained. Yield: 11 mg (6%).

*3.2. 2,4-Ditert-butyl-N,N,N′,N′,-tetraethyl-1,3-diphosphabicyclo[2.2.0]hexa-2,5-diene-5,6-diamine (**12**)*

Amounts: **5a** (469 mg, 1.11 mmol), **11** [23] (560 mg, 3.33 mmol), C_2Cl_6 (394 mg, 1.67 mmol) in 4 ml CH_2Cl_2; reaction time: 36 h; bulb-to-bulb distillation (100–110 °C/10^{-3} mbar) furnishes **12** as a yellow oil. Yield: 192 mg (47%).

*3.3. Complexation of **12**: (2,4-ditert-butyl-N,N,N′,N′-tetraethyl-1,3-diphosphabicyclo[2.2.0]hexa-2,5-diene-5,6-diamino-3-yl)pentacarbonyltungsten (**13**) and (2,4-ditert-butyl-N,N,N′,N′-tetraethyl-1,3-diphosphabicyclo[2.2.0]hexa-2,5-diene-5,6-diamino-1,3-diyl)bi(pentacarbonyltungsten) (**14**)*

To a solution of [$W(CO)_5$THF] [24], prepared by irradiation of $W(CO)_6$ (153 mg, 0.43 mmol) in THF (50 ml), **12** (80 mg, 0.22 mmol) is added in THF (3 ml). After 4 h the solvent is removed at 25 °C/10^{-3} mbar and the residue is chromatographed on silica gel with *n*-pentane. The first zone contains the bis[$W(CO)_5$] complex **14** (yield: 13 mg (6%), red needles) and the second zone the mono-complex **13** (yield: 25 mg (17%), orange–red solid).

*3.4. Dimethyl 1,6-ditert-butyl-2,5-diphospha[3.1.0.0^{2,6}]-hex-3-ene-3,4-dicarboxylate (**16a**)*

Amounts: **5a** (490 mg, 1.16 mmol), **15a** (827 mg, 5.82 mmol), C_2Cl_6 (414 mg, 1.75 mmol) in 4 ml CH_2Cl_2; reaction time: 5 days; column chromatography: eluent *n*-pentane–Et_2O (8:1), after removal of the solvent mixture (25 °C/10^{-3} mbar) **16a** is obtained as a colorless oil. Yield: 179 mg (45%).

*3.5. Dimethyl 1,6-di(1-adamantyl)-2,5-diphospha-[3.1.0.0^{2,6}]hex-3-ene-3,4-dicarboxylate (**16b**)*

Amounts: **5b** (527 mg, 0.91 mmol), **15b** (648 mg, 4.56 mmol), C_2Cl_6 (323 mg, 1.37 mmol) in 4 ml CH_2Cl_2; reaction time: 6 days; column chromatography: eluent *n*-pentane–Et_2O (10:1), after removal of the solvent mixture (25 °C/10^{-3} mbar) **16b** is obtained as a colorless solid. Yield: 172 mg (38%).

*3.6. Diethyl 1,6-ditert-butyl-2,5-diphospha-[3.1.0.0^{2,6}]hex-3-ene-3,4-dicarboxylate (**16c**)*

Amounts: **5a** (250 mg, 0.59 mmol), **15c** (404 mg, 2.37 mmol), C_2Cl_6 (163 mg, 0.69 mmol) in 5 ml CH_2Cl_2; reaction time: 6 days; column chromatography: eluent *n*-pentane–Et_2O (first 150 ml 20:1, then 100 ml 5:1), after removal of the solvent mixture (25 °C/10^{-3} mbar) **16c** is obtained as a colorless oil. Yield: 55 mg (25%).

*3.7. 1,6-Ditert-butyl-3,4-bis(trifluoromethyl)-2,5-diphospha[3.1.0.0^{2,6}]hex-3-ene (**16d**)*

Amounts: **5a** (243 mg, 0.58 mmol), **15d** (470 mg, 2.90 mmol), C_2Cl_6 (206 mg, 0.87 mmol) in 4 ml CH_2Cl_2; reaction time: 6 days; column chromatography: eluent *n*-pentane–Et_2O (20:1), after removal of the solvent mixture (25 °C/10^{-3} mbar) **16d** is obtained as a colorless solid. Yield: 163 mg (65%).

*3.8. 2,3,5,8-Tetratert-butyl-1,4,6,7-tetraphosphatetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene (**21**)*

Amounts: **5a** (220 mg, 0.52 mmol), **18** (104 mg, 1.04 mmol), C_2Cl_6 (184 mg, 0.78 mmol) in 3 ml CH_2Cl_2; reaction time: 2 days; after filtration through Celite™ and removal of the volatile materials at 25 °C/10^{-3} mbar **21** is obtained as a red oil; identification by comparison of its NMR data with those of an authentic sample [21a]. Yield: 171 mg (82%).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC nos. 174178 and 174179 for compounds **14** and **16b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) S. Masamune, N. Nakamura, M. Suda, H.J. Ona, J. Am. Chem. Soc. 95 (1973) 8481;
(b) G. Maier, S. Pfriem, U. Schäfer, R. Matusch, Angew. Chem. 90 (1978) 552; Angew. Chem. Int. Ed. Engl. 12 (1978) 520;
(c) H. Wingert, M. Regitz, Chem. Ber. 119 (1986) 224.

[2] U.-J. Vogelbacher, M. Regitz, R. Mynott, Angew. Chem. 98 (1986) 835; Angew. Chem. Int. Ed. Engl. 25 (1986) 842.

[3] (a) Review: M. Regitz, U. Bergsträßer, Science of Synthesis, vol. 9, Thieme, Stuttgart, 2001, p. 157ff;
(b) P. Binger, G. Glaser, S. Albus, Chem. Ber. 128 (1995) 1261.

[4] (a) Review: M. Regitz, U. Bergsträßer, Science of Synthesis, vol. 9, Thieme, Stuttgart, 2001, p. 159ff;
(b) P. Binger, R. Milczarek, R. Mynott, E. Raabe, C. Krüger, M. Regitz, Angew. Chem. 98 (1986) 645; Angew. Chem. Int. Ed. Engl. 25 (1986) 644;
(c) P.B. Hitchcock, M.J. Maah, J.F. Nixon, J. Chem. Soc. Chem. Commun. (1986) 737;
(d) P. Binger, B. Biedenbach, R. Schneider, M. Regitz, Synthesis (1989) 960;
(e) P. Binger, S. Leininger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann, C. Krüger, Angew. Chem. 107 (1995) 2411; Angew. Chem. Int. Ed. Engl. 34 (1995) 2227.

[5] (a) Review: M. Regitz, U. Bergsträßer, Science of Synthesis, vol. 9, Thieme, Stuttgart, 2001, p. 169f;
(b) P. Binger, S. Leininger, K. Günther, U. Bergsträßer, Chem. Ber./Recl. 130 (1997) 1491.

[6] (a) Review: M. Regitz, U. Bergsträßer, Science of Synthesis, vol. 9, Thieme, Stuttgart, 2001, p. 156f;
(b) R. Armbrust, M. Sanchez, R. Réau, U. Bergsträßer, M. Regitz, G. Bertrand, J. Am. Chem. Soc. 117 (1995) 10785.

[7] (a) Review: M. Regitz, U. Bergsträßer, Science of Synthesis, vol. 9, Thieme, Stuttgart, 2001, p. 149ff;
(b) J. Svara, E. Fluck, H. Riffel, Z. Naturforsch. B 40 (1985) 1258;
(c) B. Neumüller, E. Fluck, Phosphorus Sulfur Relat. Elem. 29 (1987) 23;
(d) H. Keller, G. Maas, M. Regitz, Tetrahedron Lett. 27 (1986) 1903;
(e) G. Bertrand, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme, Stuttgart, 1990, p. 443ff;
(f) E. Fluck, G. Heckmann, K. Lange, Z. Anorg. Allg. Chem. 619 (1993) 1551.

[8] (a) Review: M. Regitz, U. Bergsträßer, Science of Synthesis, vol. 9, Thieme, Stuttgart, 2001, p. 172ff;
(b) W. Frank, V. Petry, E. Gerwalin, G.J. Reiß, Angew. Chem. 108 (1996) 1616; Angew. Chem. Int. Ed. Engl. 35 (1996) 1512;
(c) T. Hofmann, PhD Thesis, University of Kaiserslautern, 2000.

[9] (a) T. Wettling, B. Geißler, R. Schneider, S. Barth, P. Binger, Angew. Chem. 104 (1992) 761; Angew. Chem. Int. Ed. Engl. 31 (1992) 758;
(b) B. Geißler, T. Wettling, S. Barth, P. Binger, M. Regitz, Synthesis (1994) 1337;
(c) B. Geißler, S. Barth, U. Bergsträßer, M. Slany, J. Durkin, P.B. Hitchcock, M. Hofmann, P. Binger, J.F. Nixon, P. von Ragué Schleyer, M. Regitz, Angew. Chem. 107 (1995) 485; Angew. Chem. Int. Ed. Engl. 34 (1995) 484.

[10] Review: A. Mack, M. Regitz, Chem. Ber./Recl. 130 (1997) 823.

[11] See also: (a) A. Mack, PhD Thesis, University of Kaiserslautern, 1998;
(b) A. Mack, M. Regitz, Adv. Str. Int. Org. Mol. (1999) 199 (Suppl. 1);
(c) M. Regitz, U. Bergsträßer, Pol. J. Chem. 73 (1999) 135;
(d) A. Mack, U. Bergsträßer, M. Regitz, Synthesis (1999) 639.

[12] (a) J. Grobe, D. Le Van, B. Broschk, M. Hegemann, B. Lüth, G. Becker, M. Böhringer, E.-U. Würthwein, J. Organomet. Chem. 529 (1997) 177;
(b) M. Schmitz, R. Göller, U. Bergsträßer, S. Leininger, M. Regitz, Eur. J. Inorg. Chem. (1998) 227.

[13] W.G. Bentrude, W.N. Setzer, in: J.G. Verkade, L.D. Quin (Eds.), Phosphorus 31 NMR Spectroscopy in Stereochemical Analysis, VCH, Weinheim, 1987, p. 365ff.

[14] R. Appel, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme, Stuttgart, 1990, p. 157ff.

[15] Single crystals (red needles) of **14** were obtained from an *n*-pentane solution at −30 °C. Data collection with a Siemens P4 diffractometer, Mo–K_α radiation, $\lambda = 0.71073$ Å with graphite monochromator; $C_{30}H_{38}N_2O_{10}P_2W_2$, $M = 1016.26$ g mol^{-1}, triclinic, space group $P1$, $a = 10.157(2)$ Å, $b = 10.8142(15)$ Å, $c = 17.935(3)$ Å, $\alpha = 99.187(13)°$, $\beta = 103.22(2)°$, $\gamma = 91.86(2)°$, $Z = 2$; $V = 1888.3(5)$ Å^3, $\rho_{calc} = 1.787$ g cm^{-3}, $\mu = 6.223$ mm^{-1}, $F(000) = 980$; absorption correction: semi-empirical from Ψ-scans, max and min transmission 1.0000 and 0.6733; 9052 collected reflections with 7412 independent reflections [$R_{int} = 0.0303$] and 4616 reflections with $I = 2\sigma(I)$ were refined by full-matrix least-squares method on F^2 (SHELXL-93 [25]); goodness-of-fit = 1.073. The structure model converged with $R_1 = 0.0519$, $wR_2 = 0.0806$ ($R_1 = 0.1068$, $wR_2 = 0.1185$ for all data). The final Fourier difference analysis showed a maximum of 0.927 e Å^{-3} and a minimum of −0.637 e Å^{-3}.

[16] D. Hu, H. Schäufele, H. Pritzkow, U. Zenneck, Angew. Chem. 101 (1989) 929; Angew. Chem. Int. Ed. Engl. 28 (1989) 900.

[17] F. Mathey, Chem. Rev. 90 (1990) 997.

[18] Y. Kobayashi, S. Fujino, H. Hamana, I. Kumadaki, Y. Hanzawa, J. Am. Chem. Soc. 99 (1977) 8511.

[19] Single crystals (colorless rhomboid crystals) of **16b** were obtained from an *n*-pentane–diethyl ether (10:1) solution at −30 °C. Data collection with an Imaging Plate Diffraction System (IPDS-STOE), Mo–K_α radiation, $\lambda = 0.71073$ Å with a graphite monochromator; $C_{28}H_{36}O_4P_2$, $M = 498.51$ g mol^{-1}, orthorhombic, space group $Ccca$, $a = 10.342(2)$ Å, $b = 31.861(6)$ Å, $c = 15.734(3)$ Å, $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 90.00°$, $Z = 8$; $V = 5185(2)$ Å^3, $\rho_{calc} = 1.277$ g cm^{-3}, $\mu = 0.200$ mm^{-1}, $F(000) = 2128$; 19 318 collected reflections with 2543 independent reflections [$R_{int} = 0.0464$] and 1899 reflections with $I \geq 2\sigma(I)$ were refined by full-matrix least-squares method on F^2 (SHELXL-93 [25]); goodness-of-fit = 1.204. The structure model converged with $R_1 = 0.0436$, $wR_2 = 0.0935$ ($R_1 = 0.0592$, $wR_2 = 0.0977$ for all data). The final Fourier difference analysis showed a maximum of 0.307 e Å^{-3} and a minimum of −0.261 e Å^{-3}.

[20] H. Irngartinger, K.L. Lukas, Angew. Chem. 91 (1979) 959; Angew. Chem. Int. Ed. Engl. 18 (1979) 694.
[21] (a) B. Breit, U. Bergsträßer, G. Maas, M. Regitz, Angew. Chem. 104 (1992) 1043; Angew. Chem. Int. Ed. Engl. 31 (1992) 1055;
(b) P. Binger, S. Leininger, M. Regitz, U. Bergsträßer, J. Bruckmann, C. Krüger, J. Organomet. Chem. 529 (1997) 215.
[22] The extrusion reaction of **5** with C_2Cl_6 occurs in CH_2Cl_2 about eight times more rapidly than in toluene. In order to avoid competing reactions (formation of **6**) with less reactive trapping reagents, a longer reaction time must be selected. This can be achieved by using toluene.
[23] G. Himbert, H. Naßhan, S. Kosack, Synlett (1991) 117.
[24] W. Strohmeier, F.-J. Müller, Chem. Ber. 102 (1969) 3608.
[25] G.M. Sheldrick, SHELXL-93, Fortran Program for Crystal Structure Refinement, Department of Organic Chemistry, University of Göttingen, Göttingen, Germany, 1993.
[26] XP-Graphics Program of the SHELXTLPC™ Program Packet, version 5.03, 1990.
[27] S.M.F. Asmus, M. Regitz, Tetrahedron Lett. 42 (2001) 7543.