Novel Reactions of Phosphaalkynes in the Coordination Sphere of *tert*-Butylimido-vanadium(v) Complexes: A Simple Synthesis of 3-Aza-1,2,4,6-tetraphosphaquadricyclanes and 1,3,5-Triphosphabenzenes**

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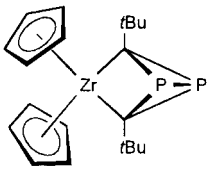
Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

Cyclooligomerization reactions of phosphaalkynes in the coordination sphere of transition metals in which the metal complex fragment is incorporated in the product have played an important role in the development of phosphaalkyne chemistry.[1] Significant examples are the cyclodimerization of *tert*-butylphosphaacetylene (**5a**) to give the tricyclic zirconium complex **1**,[2] cyclotrimerizations to give the vanadium and hafnium complexes **2**[3] and **3**,[4] and the formation of the zirconium and hafnium complexes **4**[5] by cyclotetramerization. Treatment of **1**, **3**, and **4** with hexachloroethane leads to



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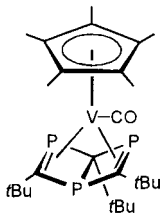

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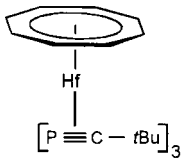

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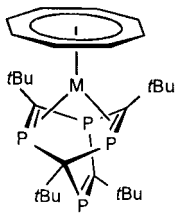
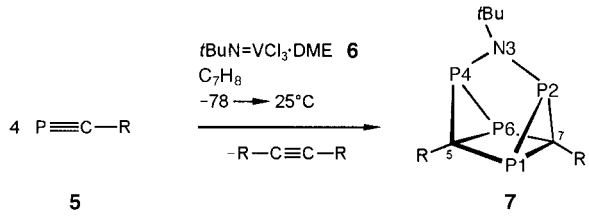


4a M = Zr
4b M = Hf

detachment of the metal complex fragments and formation of *t*Bu-substituted 1,3,5,7-tetraphosphacubane (cyclodimerization of the residual molecule),[6] 1,3,5-triphosphabenzene (**14a**),[4] and 1,3,5,7-tetraphosphabarrelene.[5] Reactions of **2** with the same reagent have not yet been investigated. We now report on the chemoselective cyclooligomerization[7] of phosphaalkynes **5a–e** with the vanadium(v) compounds *t*BuN=VCl_3 · DME (**6**)[8] (DME = 1,2-dimethoxyethane) and *t*BuN=VCl_3 (**13**)[9] to produce the title compounds in good yields.

Reaction of **5a–e** with **6** in a molar ratio of 4:1 in toluene followed by column chromatography on alumina affords the previously unknown azatetraphosphaquadricyclanes **7a–e** as yellow solids in yields of 47–76% (not optimized; Table 1).



5 **7**

Table 1. Synthesis of the azatetraphosphaquadricyclanes **7**.

5, **7**	**a**	**b**	**c**	**d**	**e**
R	*t*Bu	*t*Pent			
Yield [%]	76	53	55	57	47

The elemental analyses and mass spectra (Table 2) indicate that the heteropolycyclic compounds are formed from four molecules of the phosphaalkyne **5** with loss of one molecule of an alkyne RC≡CR (see Scheme 1) and incorporation of the imide ligand from the vanadium compound **6**.

As an example the NMR data of **7a** are discussed here (for further spectroscopic data of the compounds **7**, see Table 2).

Table 2. Selected spectroscopic data for the azatetraphosphaquadricyclanes **7**.[a]

7a: ^{1}H NMR: $\delta = 0.99$, 1.00 (2 s, each 9H, $CC(CH_3)_3$), 1.53 (pseudo-t, $^4J(P2,H) = {}^4J(P4,H) = 0.9$ Hz, 9H, $NC(CH_3)_3$); ^{13}C NMR: $\delta = 28.8-31.7$ (br m, $CC(CH_3)_3$/C5/C7), 32.1 (m, $C(CH_3)_3$), 34.0 (pseudo-t, $^3J(P,C) = 10.6$ Hz, $NC(CH_3)_3$), 56.8 (pseudo-t, $^2J(P,C) = 14.4$ Hz, $NC(CH_3)_3$); ^{31}P NMR: $\delta = -7.4$, -123.0 (AA′XX′ spin system with $J(AX) = J(A'X') = 161.1$ Hz, $J(AX') = J(A'X) = 21.0$ Hz, $J(AA') = 22.4$ Hz, $J(XX') = 5.5$ Hz); MS: *m*/*z* (%): 333 (63) [M^+], 233 (57) [$M^+ - C_5H_9P$], 177 (100) [$M^+ - C_4H_9 - C_5H_9P$], 162 (38) [$M^+ - C_4H_9N - C_5H_9P$], 57 (21) [C_4H_9]

7b: ^{13}C NMR: $\delta = 28.7-31.3$ (br m, C5/C7), 56.9 (pseudo-t, $^2J(P,C) = 13.6$ Hz, $NC(CH_3)_3$); ^{31}P NMR: $\delta = -9.2$, -123.2; MS: *m*/*z* (%): 361 (66) [M^+]

7c: ^{13}C NMR: $\delta = 30.1-32.9$ (br m, C5/C7), 56.7 (pseudo-t, $^2J(P,C) = 14.4$ Hz, $NC(CH_3)_3$); ^{31}P NMR: $\delta = -14.7$, -130.8, MS: *m*/*z* (%): 489 (19) [M^+]

7d: ^{13}C NMR: $\delta = 28.8-31.4$ (br m, C5/C7), 56.8 (pseudo-t, $^2J(P,C) = 13.6$ Hz, $NC(CH_3)_3$); ^{31}P NMR: $\delta = -5.8$, -123.8; MS: *m*/*z* (%): 385 (69) [M^+]

7e: ^{13}C NMR: $\delta = 28.6-30.6$ (br m, C5/C7), 56.4 (pseudo-t, $^2J(P,C) = 13.6$ Hz, $NC(CH_3)_3$); ^{31}P NMR: $\delta = -11.9$, -125.3; MS: *m*/*z* (%): 413 (34) [M^+]

[a] NMR: Bruker AC-200; ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) in C_6D_6; ^{31}P NMR (81 MHz) in C_6D_6 with 85% H_3PO_4 as external standard; MS: Finnigan MAT90, 70 eV.

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The ^{31}P NMR spectrum of the tetracyclic product **7a** contains two signals at $\delta = -7.4$ (P2, P4) and -123.0 (P1, P6); the four P atoms form an AA′XX′ spin system. While the A part of the spectrum gives rise to very broad signals on account of the vicinity of P2 and P4 to the nitrogen atom, the coupling constants (Table 2) can be derived from the X part of the spectrum.[10] The ^{1}H NMR spectrum confirms this proposal by way of two different signals for the *t*Bu groups at C5 and C7; the signal of the *t*Bu group bound to N3 is split by small ^{4}J coupling. The skeletal carbon atoms C5 and C7 appear as a multiplet in the ^{13}C NMR spectrum and cannot be distinguished (Table 2).

The NMR data are in harmony with structure **7a** which has been confirmed by a single crystal X-ray structure analysis (Figure 1).[11] The compound has a C_1-symmetric quadricyclane structure, which is distorted owing to the pyramidal geometry at nitrogen.

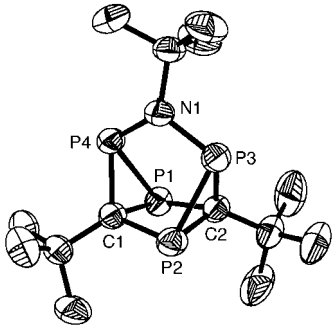
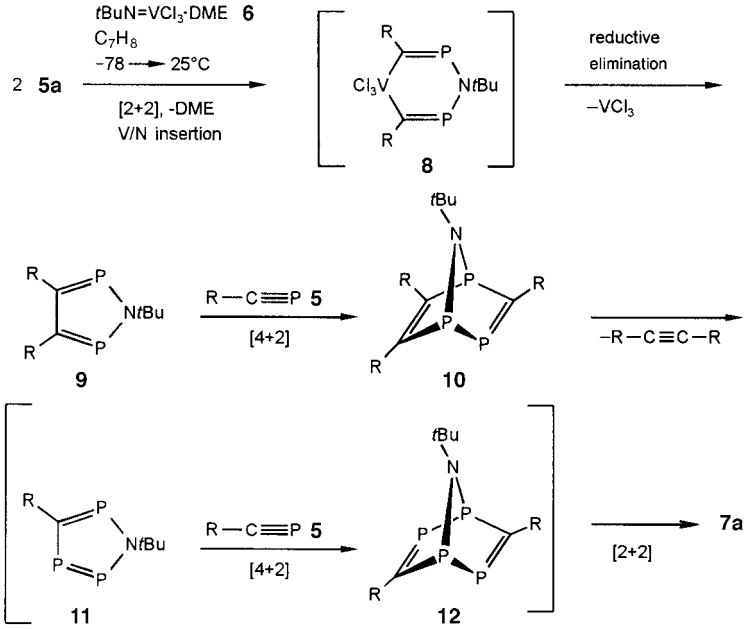


Figure 1. Structure of **7a** in the crystalline state (50% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: P1–C2 1.880(2), P1–C1 1.894(2), P1–P4 2.2185(11), P2–C1 1.881(2), P2–C2 1.896(2), P2–P3 2.1782(10), P3–N1 1.716(2), P3–C2 1.865(2), P4–N1 1.716(2), P4–C1 1.842(2); C2-P1-C1 83.44(9), C1-P1-P4 52.50(6), C1-P2-C2 83.39(9), C2-P2-P3 53.94(6), C2-P3-P2 55.27(7), C1-P4-P1 54.67(7), P4-N1-P3 116.67(9), P4-C1-P1 72.83(8), P2-C1-P1 95.06(9), P3-C2-P2 70.79(8), P1-C2-P2 95.05(9).

In the 1,3-diphosphacyclobutane ring, the two carbon atoms protrude upwards out of the plane of the ring, as reflected in the dihedral angle at the P atoms of 19.6°. The P–C bond lengths in the 1,3-diphosphacyclobutane unit[6] and the two diphosphirane rings[12] of 1.842–1.896 Å are in the expected range. While one of the three-membered rings contains a relatively long P–P bond of 2.219 Å and a short P–C single bond length of 1.842 Å, the other three-membered ring has typical bond lengths.[12] Both diphosphirane rings exhibit the typically widened internal P-C-P angles of 70.8 and 72.8°, respectively.[12]

A firm proposal for the mechanism of formation of the azatetraphosphaquadricyclanes **7** can be made, since two intermediates were identified by NMR spectroscopic monitoring of the reaction of **5a** with **6** (Scheme 1). When the reaction is performed with a molar ratio of 2:1 under otherwise identical conditions and the solvent and unchanged **5a** are removed at 25°C and 10^{-2} mbar, a residue consisting of **7a** and the azadiphosphole **9** (R = *t*Bu) is obtained. The latter is the first representative of this previously unknown class of



Scheme 1. Mechanism for the formation of **7a**.

heterocyclic compounds; its NMR data[13] are consistent with the proposed structure. Formation of **9** presumably involves a [2+2] cycloaddition of **5a** to **6** and incorporation of a second phosphaalkyne molecule into the V–N bond of the adduct to furnish **8**. Reductive elimination of VCl_3 (isolated as $VCl_3 \cdot 1.5$ DME) then gives **9**. On addition of an excess of **5a** to the reaction mixture at room temperature, **9** is converted into **7a**. Firstly, an addition reaction gives the azatriphosphanorbornadiene **10** (R = *t*Bu).[14] The retro-Diels–Alder reaction of **10** to give **11** readily explains the above-mentioned liberation of the acetylene RC≡CR. After reaction of **5c** with **6**, bis(adamant-1-yl)acetylene was isolated and identified on the basis of literature data.[15] The conversion of **11** into **12** and the final intramolecular head-to-tail cycloaddition of the phosphaalkene units[16] to afford **7a** are equally plausible to **12** and the final intramolecular head-to-tail cycloaddition of the phosphaalkene units[16] to give **7a** are also plausible.

Cyclooligomerization reactions of the phosphaalkynes **5a–e** with the strong Lewis acid **13** follow a completely different course; under comparable reaction conditions they selectively furnish the yellow 1,3,5-triphosphabenzenes **14a–e** (Table 3). The easy accessibility of the cyclotrimeriza-

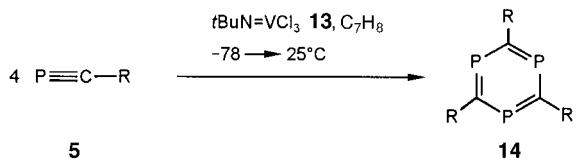


Table 3. Synthesis of the 1,3,5-triphosphabenzenes **14**.

5, 14	a	b	c	d	e
R	*t*Bu	*t*Pent			
Yield [%]	68	59	36	37	44

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tion reagent **13**[9] and the satisfactory yields (36–68%, not optimized) are major advantages compared to the previously described synthesis of **14a** via the hafnium complex **3**[4] and thus make comprehensive studies on the reactivity of this novel heteroaromatic system possible. Cyclotrimerizations of phosphaalkynes **5** with Lewis acids to give metal-free products have not been reported previously. Their spirocyclotrimerization with aluminum trichloride is noteworthy; however, in this case the metal fragment is incorporated into the product.[17] The heteroarene **14b** is obtained as an oil, whereas **14a**, **c**–**e** are crystalline. The elemental analyses and comparison of the ^{31}P ($\delta = 238.1 - 242.8$) and ^{13}C NMR spectra ($\delta = 208.8 - 212.2$) for the skeletal atoms of **14b**–**e** with those of **14a**[4] ($\delta(P) = 232.6$; $\delta(C) = 211.8$) unambiguously confirm the constitutions of the heteroarenes.

Experimental Section

7a: **5a**[18] (0.19 g, 1.90 mmol) was added to a stirred suspension of **6**[8] (0.15 g, 0.47 mmol) in toluene (5 mL) at −78°C, and the mixture was allowed to warm to room temperature. After 12 h all volatile materials were removed at 25°C and 10^{-2} mbar. The residue was worked up by column chromatography on neutral aluminum oxide (deactivated with 4% water; column: 20 × 1.5 cm) with *n*-pentane as eluent. The yellow fraction was collected, the solvent evaporated, and the residue recrystallized from *n*-pentane at −78°C to give pale yellow crystals. Yield: 0.12 g (76%); m.p. 76°C.

14a: **5a**[18] (0.18 g, 1.76 mmol) was added to a stirred solution of **13**[9] (0.10 g, 0.44 mmol) in toluene (2 mL) at −78°C, and the mixture was allowed to warm to room temperature. The solvent was evaporated at 25°C and 10^{-2} mbar and the residue purified by column chromatography on silica gel (deactivated with 4% water; column: 15 × 1.0 cm) with *n*-pentane as eluent. The yellow fraction was collected, and evaporation of the solvent gave pure **14a**. Yield: 0.12 g (68%); m.p. 88°C. Identification by comparison of the NMR data with those of an authentic sample.[4]

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[11] Single crystals of **7a** were obtained from *n*-pentane at −78°C. $C_{17}H_{27}NP_4$, $M_r = 369.28$, yellow rhomboids, crystal dimensions 0.3 × 0.3 × 0.2 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.728(2)$, $b = 10.292(2)$, $c = 10.601(2)$ Å, $\alpha = 82.59(3)$, $\beta = 83.07(3)$, $\gamma = 63.41(3)°$, $V = 938.7(3) \times 10^6$ pm^3, $Z = 2$, $\rho_{calcd} = 1.306$ g cm^{-3}, $F(000) = 392$, $\mu = 3.9$ cm^{-1}. Imaging Plate Diffraction System (IPDS-STOE), 289 exposures, ψ increment 0.9°, 4 min per exposure, 9652 measured reflections ($2.22° \le \theta \le 26.0°$), of which 3412 independent reflections ($R_{int} = 0.0285$) and 3407 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods and refined on F^2 with SHELXTL (Version 5, Siemens). All heavy atoms were refined anisotropically; the H atoms were isotropically refined in calculated positions (173 parameters). $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.0349$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.0878$ (all data: $R1 = 0.0448$, $wR2 = 0.1054$), GOF = 1.041, max./min. residual electron density 0.27/−0.21 e Å^{-3}). Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-407858.

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[13] Determined on the mixture of **9** (R = *t*Bu) and **7a** (the signals of pure **7a** are known). ^1H NMR (200 MHz, C_6D_6): $\delta = 1.59$ (t, $^4J(H,P) = 0.9$ Hz, 9H, $NC(CH_3)_3$), 1.66 (d, $^4J(P,H) = 3$ Hz, 18H, $CC(CH_3)_3$); ^{13}C NMR (50 MHz, C_6D_6): $\delta = 34.9$ (t, $^3J(C,P) = 9.3$ Hz, $NC(CH_3)_3$), 35.3 (d, $^3J(C,P) = 19.5$ Hz, $CC(CH_3)_3$), 37.6 (dd, $^2J(C,P) = 27.2$ Hz, $^3J(C,P) = 1.7$ Hz, $CC(CH_3)_3$), 59.4 (t, $^2J(C,P) = 12.7$ Hz, $NC(CH_3)_3$), 180.7 (dd, $^1J(C,P) = 47.5$ Hz, $^2J(C,P) = 11.4$ Hz); ^{31}P NMR (81 MHz, C_6D_6): $\delta = 285.75$ (s).

[14] The typical signals of **10** are observed by NMR spectroscopic monitoring directly after thawing of the mixture; they then disappear rapidly, and the signals of **7a** appear. ^{31}P NMR (81 MHz, C_6D_6): $\delta = 106.1$ (d, $^2J(P,P) = 34.9$ Hz), 135.7 (dd, $^1J(P,P) = 226.7$ Hz, $^2J(P,P) = 34.9$ Hz), 314.7 (d, $^1J(P,P) = 226.7$ Hz).

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  1433-7851/98/3709-1235 $ 17.50+.50/0