Organophosphorus Compounds, 114[◇]

Tetracyclic Phosphorus-Aluminium-Carbon Compounds – Synthesis by Cooligomerization of Kinetically Stabilized Phosphaalkynes with Trialkylaluminium Compounds[☆]

Andreas Hoffmann, Bernhard Breit, and Manfred Regitz*

Fachbereich Chemie der Universität Kaiserslautern,
Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany
Fax: (internat.) +49(0)631/205-3921

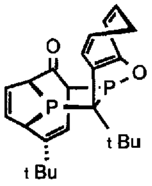
Received August 16, 1996

Keywords: Phosphaalkynes / Triorganoaluminium compounds / Cooligomerization / Cage compounds / Aluminium compounds

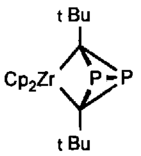
When the trialkylaluminium reagents **5** are allowed to react with phosphaalkynes **4** in *n*-pentane, a highly selective phosphaalkyne cyclotrimerization with incorporation of two organometallic units occurs (→ **6**). The tetracyclooctane derivatives **6a**–**e** represent the first examples of phosphorus-aluminium-carbon cage compounds. The polycyclic products **6** are able to function as ligands in transition-metal complexes (→ **7**), which is illustrated by the reactions of **6b**, **c** with nonacarbonyldiiron and pentacarbonyl(tetrahydrofuran)tungsten, respectively.

Kinetically stabilized phosphaalkynes occupy a unique position as building blocks for the preparation of phosphorus-carbon cage compounds[2]. Their ability to participate in cyclooligomerization processes has been successfully exploited in numerous synthetic strategies[3–5].

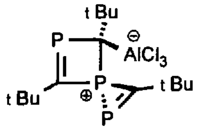
Furthermore, the enormous cycloaddition potential of the phosphorus–carbon triple bond makes itself apparent in cyclooligomerization reactions with carbocyclic π systems[6]. Thus, for example, the tropone reaction of phosphaalkynes stops at the stage of the pentacyclic compound **1** which can be formally considered as a 2:2 adduct of the starting materials[7].



1



2



3

On the other hand, the cyclooligomerization of phosphaalkynes in the coordination sphere of transition metals provides an access to a series of phosphorus-carbon cage compounds[8]. However, separation of the polycylic system from the metal center is only possible in exceptional cases. In this context, the zirconium compound **2** should be mentioned as an example since, among others, it serves as the starting material for the preparation of tetraphosphacubane[9].

The Lewis acid induced cyclooligomerization of phosphaalkynes has also proved to be a highly useful synthetic strategy[10]. Reactions of phosphaalkynes with aluminium trichloride stop at the stage of the spirocyclic trimer complex **3**[11]. Depending on the reaction conditions, compound **3** serves as the starting material for the preparation of various polycyclic systems.

As a logical continuation of the above-mentioned investigations on the reactivity of phosphaalkynes, we have now examined the question of whether triorganoaluminium derivatives are able to induce an oligomerization of the phosphaalkynes. The results of this work are described in this paper[12].

Generation of the Triphosphadialatetracyclooctanes (4 → 6)

When a mixture of the kinetically stabilized phosphaalkyne **4** and the triorganoaluminium compound **5** in pentane is allowed to warm from –50 °C to room temperature, practically quantitative cyclotrimerization of the triple-bond system of **4** with incorporation of two equivalents of the Lewis acid **5** occurs with high selectivity to furnish the polycyclic compound **6**. Cage compounds with skeletons built up of the elements phosphorus, aluminium and carbon were previously unknown[12].

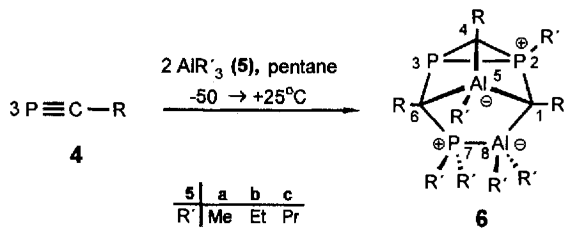
The slight excess of the phosphaalkyne **4** employed may be easily removed under vacuum. The corresponding tetracyclic products **6a**–**e** can be isolated by low-temperature recrystallization from non-polar solvents. At room temperature, the compounds **6a**, **c**, **d** exist in the form of colorless to yellow oils, whereas **6b**, **e** are obtained as colorless powders (yields 65–92%).

The construction of the polycyclic compounds **6** from three molecules of the phosphaalkyne **4** and two molecules

---

[◇] Part 113: Ref.[1].

© VCH Verlagsgesellschaft mbH, D-69451 Weinheim, 1997 0009–2940/97/0202–0255 $ 15.00+.25/0



5	a	b	c
R'	Me	Et	Pr

4	a	b	c
R	*t*Bu	*t*Pent	1-Ad

6	a	b	c	d	e
R	*t*Bu	*t*Bu	*t*Bu	*t*Pent	1-Ad
R'	Me	Et	Pr	Et	Et

of the triorganoaluminium species **5** is unambiguously demonstrated by the mass spectra. The degree of oligomerization is further reflected in the ^{31}P-NMR spectra: two signals at high field (P-3: $\delta = -136.8$ to -154.0; P-2: $\delta = -61.6$ to -75.0) can be assigned to the unsymmetrical diphosphirane structural unit[13]. The direct proximity of the two phosphorus atoms P-2 and P-3 is manifested in a ^1J(P,P) coupling constant of 152.4–163.4 Hz. The ^{31}P-NMR signal at highest field (P-3) is additionally split by a ^2J(P,P) coupling of 21.7–33.4 Hz. This latter coupling is also responsible for the doublet structure of the P-7 resonance ($\delta = -1.2$ to -27.9).

The ^{13}C-NMR chemical shifts of the three skeletal carbon atoms are also characteristic for the polycyclic compounds **6a–e**. The signal at highest field ($\delta = 29.3-35.1$) is assigned to the carbon atom C-4 in the three-membered ring. The distinction between C-1 ($\delta = 42.7-48.9$) and C-6 ($\delta = 65.0-70.9$) was made with the help of the carbon-phosphorus coupling constants[14]. Thus, in the case of compound **6c**, the signal at low field (C-6: $\delta = 67.7$) appears as a doublet of pseudo-triplets with two ^1J(C,P) coupling constants of 39.5 Hz and a ^2J(C,P) coupling constant of 23.9 Hz. In contrast, the signal at $\delta = 45.5$ (C-1) is split into a double doublet with just one large C,P coupling constant (43.5 Hz). This may be taken as an indication of the direct proximity of only one phosphorus atom (P-2). The migration of the three organic groups from aluminium to phosphorus is evident from a pronounced shift to low field ($\delta = 10.5-33.1$) as well as the occurrence of ^1J(C,P) couplings for the corresponding methylene carbon atoms.

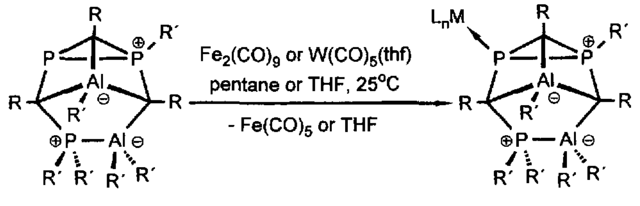
The ^{1}H-NMR and IR spectra of the compounds **6a–e** are fully consistent with the tetracyclic structures. However, their diagnostic value is very limited, such that they do not merit discussion at this point (see Experimental Section).

A crystal-structure analysis of **6b** provided final evidence for the cage structures of these products[12].

The question of the mechanism of the cooligomerization ($3 \times \mathbf{4} + 2 \times \mathbf{5} \rightarrow \mathbf{6}$) has not yet been fully resolved. However, it seems reasonable to postulate an initial attack of the Lewis acid **5** at the phosphaalkyne carbon atom with an accompanying 1,3-ethyl shift. ^{31}P-NMR spectroscopy provides an indication for the intermediate formation of a phosphaalkene (low-temperature monitoring of the reaction mixture: $\delta = 241.9$).

Metalation Reaction of the Triphosphadialacyclooctanes (6 → 7)

$\lambda^3\sigma^3$-Phosphorus atoms incorporated in polycyclic systems can serve as 2-electron donors to 16-valency-electron transition-metal fragments[15]. This property is also exhibited by the novel class of phosphorus-aluminium-carbon cage compounds described above. Accordingly, reactions of the polycyclic compounds **6b, c** with nonacarbonyldiiron[16] or in situ generated pentacarbonyl(tetrahydrofuran)tungsten[17], gave rise to the corresponding transition-metal complexes (→ **7a, b**), respectively, even at room temperature. Compound **7a** was obtained as a brown oil (yield: 73%), **7b** as a yellow powder (yield: 55%).



6b,c **7**

7	a	b
R	*t*Bu	*t*Bu
R'	Pr	Et
L_nM	Fe(CO)$_4$	W(CO)$_5$

The successful conclusion of the metalation reactions is reflected by the appearance of four or two carbonyl bands in the IR spectra (**7a**: $\tilde{\nu}$ = 2054, 1972, 1950, 1936 cm^{-1}; **7b**: $\tilde{\nu}$ = 2068, 1934 cm^{-1}). The coordination of the phosphorus atom P-3 to a metal center is evidenced by low-field shifts in the ^{31}P-NMR spectra (**7a**: $\delta = -67.9$ in comparison to **6c**: $\delta = -145.9$; **7b**: $\delta = -117.7$ in comparison to **6b**: $\delta = -147.3$). In addition, the occurrence of a ^1J(P,W) coupling constant of 216.1 Hz is observed in the case of the complex **7b**. Furthermore, complex formation is accompanied by a pronounced reduction in the ^1J(P,P) coupling constants of about 100 Hz.

The fact that all other NMR-spectroscopic data, especially the chemical shifts of the skeletal carbon atoms, do not experience any significant changes may be taken as evidence for the retention of tetracyclic structure of the cage.

We thank the *Fonds der Chemischen Industrie* for generous financial support and for postgraduate grants (to A. H. and B. B.).

Experimental Section

The reactions were carried out under Ar (purity >99.998%) in a previously oven-dried and evacuated appartus (Schlenk techniques). The solvents were dried by standard procedures (*n*-pentane and THF: Na/K alloy), redistilled, and stored under Ar. – Melting points: Mettler FP 61 (heating rate: 3°C/min). – FT IR: Perkin-Elmer Model 16 PC. – MS: Finnigan MAT 90. – NMR: Bruker AMX 400 (^{1}H: 400 MHz; ^{13}C: 101 MHz; ^{31}P: 162 MHz) and Bruker AC 200 (^{31}P: 81 MHz), solvent as internal standard (^{1}H and ^{13}C); the chemical shifts for ^{31}P are relative to external 85% orthophosphoric acid. – Compounds **4a**[18], **4b**[19], **4c**[20] were prepared by the published methods.

General Procedure for the Preparation of the Tetracyclic Compounds **6a**–**e**: To a magnetically stirred solution of the triorganoaluminium compound **5** in *n*-pentane (3 ml) at −50 °C was added dropwise a solution of phosphaalkyne **4** in *n*-pentane (3 ml). After the reaction mixture had been allowed to warm to room temperature over a period of 12 h, all volatile components were removed at 25 °C/10^{-3} mbar. The remaining crude product was taken up in a non-polar solvent and purified by recrystallization at low temperatures.

1,4,6-Tri-tert-butyl-2,5,7,7,8,8-hexamethyl-3-phospha-2,7-diphosphonia-5,8-dialuminatotetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]octane (**6a**): Starting from trimethylaluminium (**5a**) (0.07 g, 1.00 mmol) and **4a** (0.18 g, 1.75 mmol), **6a** was obtained as a yellow, non-distillable oil. Yield 0.29 g (65%). – ^{1}H NMR ($\mathrm{C_6D_6}$): δ = −0.37 [d, ^3J(H,P) = 4.8 Hz, 3 H, $\mathrm{AlCH_3}$], −0.28 [d, ^3J(H,P) = 5.2 Hz, 3 H, $\mathrm{AlCH_3}$], −0.19 (s, 3 H, $\mathrm{AlCH_3}$), 1.12 [d, ^2J(H,P) = 6.0 Hz, 3 H, $\mathrm{PCH_3}$], 1.18 [s, 9 H, $\mathrm{C(CH_3)_3}$], 1.27 [s, 9 H, $\mathrm{C(CH_3)_3}$], 1.37 [d, ^2J(H,P) = 5.6 Hz, 3 H, $\mathrm{PCH_3}$], 1.48 [s, 9 H, $\mathrm{C(CH_3)_3}$], 1.57 [dd, ^2J(H,P) = 12.0 Hz, ^3J(H,P) = 5.6 Hz, $\mathrm{PCH_3}$]. – ^{13}C NMR ($\mathrm{C_6D_6}$): δ = −6.0 (s, $\mathrm{AlCH_3}$), −5.3 (s, $\mathrm{AlCH_3}$), −3.0 (s, $\mathrm{AlCH_3}$), 10.5 [pseudo-t, J(C,P) = 9.1 Hz, J(C,P) = 9.1 Hz, $\mathrm{PCH_3}$], 14.5 [pseudo-t, J(C,P) = 21.4 Hz, J(C,P) = 21.4 Hz, $\mathrm{PCH_3}$], 16.9 [dd, ^1J(C,P) = 15.3, ^2J(C,P) = 12.2 Hz, $\mathrm{PCH_3}$], 30.7 (m, C-4), 34.3 [d, ^3J(C,P) = 4.6 Hz, $\mathrm{C(}C\mathrm{H_3)_3}$], 34.4 [d, ^3J(C,P) = 4.6 Hz, $\mathrm{C(}C\mathrm{H_3)_3}$], 35.2 [d, ^2J(C,P) = 3.1 Hz, $C\mathrm{(CH_3)_3}$], 36.2 [d, ^3J(C,P) = 13.7 Hz, $\mathrm{C(}C\mathrm{H_3)_3}$], 37.1 [dd, ^2J(C,P) = 9.2 Hz, ^3J(C,P) = 4.6 Hz, $C\mathrm{(CH_3)_3}$], 39.6 [m, $C\mathrm{(CH_3)_3}$], 42.7 (m, C-1), 65.0 (m, C-6). – ^{31}P NMR ($\mathrm{C_6D_6}$): δ = −136.8 [dd, ^1J(P,P) = 152.4 Hz, ^2J(P,P) = 33.4 Hz, P-3], −75.0 [d, ^1J(P,P) = 152.4 Hz, P-2], −27.9 [d, ^2J(P,P) = 33.4 Hz, P-7].

1,4,6-Tri-tert-butyl-2,5,7,7,8,8-hexaethyl-3-phospha-2,7-diphosphonia-5,8-dialuminatotetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]octane (**6b**): Starting from triethylaluminium (**5b**) (0.23 g, 2.00 mmol) and **4a** (0.35 g, 3.50 mmol), **6b** was obtained as colorless crystals. Yield 0.48 g (91%); m.p. 175 °C. – IR (KBr): ṽ = 2960 (s), 1470 (s), 1400 (m), 1370 (s), 1160 (s, br), 1040 (s, br), 800 $\mathrm{cm^{-1}}$ (s, br). – ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 0.47–0.66 (m, 6 H, 3 $\mathrm{AlC}H_2\mathrm{CH_3}$), 1.02–2.30 (m, 24 H, 6 $\mathrm{CH_2C}H_3$ and 3 $\mathrm{PC}H_2\mathrm{CH_3}$), 1.41 [s, 9 H, $\mathrm{C(CH_3)_3}$], 1.54 [s, 9 H, $\mathrm{C(CH_3)_3}$], 1.66 [d, ^4J(H,P) = 0.6 Hz, 9 H, $\mathrm{C(CH_3)_3}$]. – ^{13}C NMR ($\mathrm{C_6D_6}$): δ = 4.2 (m, 2 $\mathrm{Al}C\mathrm{H_2CH_3}$), 8.2 (s, $\mathrm{Al}C\mathrm{H_2CH_3}$), 8.8 [dd, ^2J(C,P) = 13.2 Hz, ^3J(C,P) = 7.6 Hz, $\mathrm{PCH_2}C\mathrm{H_3}$], 10.0 (s, $\mathrm{AlCH_2}C\mathrm{H_3}$), 10.2 (s, $\mathrm{AlCH_2}C\mathrm{H_3}$), 10.9 [d, ^2J(C,P) = 5.1 Hz, $\mathrm{PCH_2}C\mathrm{H_3}$], 11.1 [d, ^2J(C,P) = 4.9 Hz, $\mathrm{PCH_2}C\mathrm{H_3}$], 11.3 (s, $\mathrm{AlCH_2}C\mathrm{H_3}$), 20.3 [d, ^1J(C,P) = 17.6 Hz, $\mathrm{P}C\mathrm{H_2CH_3}$], 20.8 [d, ^1J(C,P) = 8.3 Hz, $\mathrm{P}C\mathrm{H_2CH_3}$], 24.2 [pseudo-t, J(C,P) = 12.3, J(C,P) = 12.3, $\mathrm{P}C\mathrm{H_2CH_3}$], 32.8 [dd, ^1J(C,P) = 51.8 Hz, ^1J(C,P) = 23.4 Hz, C-4], 34.6 [dd, ^3J(C,P) = 8.3 Hz, ^3J(C,P) = 3.8 Hz, $\mathrm{C(}C\mathrm{H_3)_3}$], 34.8 [dd, ^3J(C,P) = 8.4 Hz, ^3J(C,P) = 5.0 Hz, $\mathrm{C(}C\mathrm{H_3)_3}$], 35.2 [d, ^2J(C,P) = 6.1 Hz, $C\mathrm{(CH_3)_3}$], 36.6 [d, ^3J(C,P) = 13.7 Hz, $\mathrm{C(}C\mathrm{H_3)_3}$], 37.0 [dd, ^2J(C,P) = 9.7 Hz, ^2J(C,P) = 3.3 Hz, $C\mathrm{(CH_3)_3}$], 40.3 [d, ^2J(C,P) = 7.9 Hz, $C\mathrm{(CH_3)_3}$], 45.8 (m, C-1), 68.3 (m, C-6). – ^{31}P NMR ($\mathrm{C_6D_6}$): δ = −147.3 [dd, ^1J(P,P) = 162.9 Hz, ^2J(P,P) = 21.7 Hz, P-3], −61.6 [d, ^1J(P,P) = 162.9 Hz, P-2], −1.2 [d, ^2J(P,P) = 21.7 Hz, P-7]. – MS (EI, 70 eV); *m/z* (%): 527 (100) [$\mathrm{M^+ - H}$], 500 (100) [$\mathrm{M^+ - CH_2CH_3}$], 299 (100) [$\mathrm{M^+ - H - 2\,Al(CH_2CH_3)_3}$], 57 (95) [$\mathrm{C_4H_9^+}$]. – $\mathrm{C_{27}H_{57}Al_2P_3}$ (528.6): calcd. C 61.35, H 10.87; found C 58.7, H 10.5.

1,4,6-Tri-tert-butyl-2,5,7,7,8,8-hexapropyl-3-phospha-2,7-diphosphonia-5,8-dialuminatotetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]octane (**6c**): Starting from tripropylaluminium (**5c**) (0.31 g, 2.00 mmol) and **4a** (0.35 g, 3.50 mmol), **6c** was obtained as a nearly colorless, non-distillable oil. Yield 0.50 g (82%). – IR (pentane): ṽ = 1192 (w), 1080 (m), 1043 (m), 812 (m), 670 $\mathrm{cm^{-1}}$ (w). – ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 0.30–0.58 (m, 6 H, 3 $\mathrm{AlC}H_2\mathrm{CH_2CH_3}$), 0.73–2.21 (m, 36 H, 3 $\mathrm{PC}H_2\mathrm{CH_2CH_3}$, 6 $\mathrm{CH_2C}H_2\mathrm{CH_3}$, and 6 $\mathrm{CH_2CH_2C}H_3$), 1.22 [s, 9 H, $\mathrm{C(CH_3)_3}$], 1.37 [s, 9 H, $\mathrm{C(CH_3)_3}$], 1.50 [s, 9 H, $\mathrm{C(CH_3)_3}$]. – ^{13}C NMR ($\mathrm{C_6D_6}$): δ = 15.7 [d, J(C,P) = 14.5 Hz], 16.1 [d, J(C,P) = 13.6 Hz], 16.6 (s), 16.6 [d, J(C,P) = 13.5 Hz], 17.3 (s, $\mathrm{Al}C\mathrm{H_2CH_2CH_3}$), 17.5 (s, $\mathrm{Al}C\mathrm{H_2CH_2CH_3}$), 18.7 (m), 19.2 (s), 20.3 (s, 2 $\mathrm{CH_2}C\mathrm{H_2CH_3}$), 20.8 (s, $\mathrm{Al}C\mathrm{H_2CH_2CH_3}$), 21.5 [d, J(C,P) = 5.3 Hz], 21.7 (s), 21.8 (s), 22.3 [d, J(C,P) = 12.0 Hz], 30.3 [d, ^1J(C,P) = 17.0 Hz, $\mathrm{P}C\mathrm{H_2CH_2CH_3}$], 30.5 [d, ^1J(C,P) = 7.2 Hz, $\mathrm{P}C\mathrm{H_2CH_2CH_3}$], 32.7 [dd, ^1J(C,P) = 51.5 Hz, ^1J(C,P) = 22.6 Hz, C-4], 33.1 (m, $\mathrm{P}C\mathrm{H_2CH_2CH_3}$), 34.5 [s, $\mathrm{C(}C\mathrm{H_3)_3}$], 34.7 [s, $\mathrm{C(}C\mathrm{H_3)_3}$], 35.1 [m, $C\mathrm{(CH_3)_3}$], 36.5 [d, ^3J(C,P) = 13.7 Hz, $\mathrm{C(}C\mathrm{H_3)_3}$], 37.0 [d, ^2J(C,P) = 9.7 Hz, $C\mathrm{(CH_3)_3}$], 40.4 [m, $C\mathrm{(CH_3)_3}$], 45.5 [dd, ^1J(C,P) = 43.5 Hz, ^2J(C,P) = 24.8 Hz, C-1], 67.7 [d-pseudo-t, ^1J(C,P) = 39.5 Hz, ^1J(C,P) = 39.5 Hz, ^2J(C,P) = 23.9 Hz, C-6]. – ^{31}P NMR ($\mathrm{C_6D_6}$): δ = −145.9 [dd, ^1J(P,P) = 162.7 Hz, ^2J(P,P) = 24.0 Hz, P-3], −64.7 [d, ^1J(P,P) = 162.7 Hz, P-2], −7.5 [d, ^2J(P,P) = 24.0 Hz, P-7]. – MS (EI, 70 eV); *m/z* (%): 612 (1) [$\mathrm{M^+}$], 611 (3) [$\mathrm{M^+ - H}$], 570 (27) [$\mathrm{M^+ - C_3H_6}$], 569 (100) [$\mathrm{M^+ - C_3H_7}$]. – $\mathrm{C_{33}H_{69}Al_2P_3}$: calcd. 612.4243, found 612.4251 (MS).

2,5,7,7,8,8-Hexaethyl-1,4,6-tris(1,1-dimethylpropyl)-3-phospha-2,7-diphosphonia-5,8-dialuminatotetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]octane (**6d**): Starting from triethylaluminium (**5b**) (0.23 g, 2.00 mmol) and **4b** (0.40 g, 3.50 mmol), **6d** was obtained as a nearly colorless, non-distillable oil. Yield 0.45 g (79%). – ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 0.30–0.52 (m, 6 H, 3 $\mathrm{AlC}H_2\mathrm{CH_3}$), 0.83–1.65 [m, 51 H, 6 $\mathrm{CH_2C}H_3$, 3 $\mathrm{C(C}H_3\mathrm{)_2CH_2CH_3}$, 3 $\mathrm{C(CH_3)_2C}H_2\mathrm{CH_3}$, and 3 $\mathrm{C(CH_3)_2CH_2C}H_3$], 1.74–2.11 (m, 6 H, 3 $\mathrm{PC}H_2\mathrm{CH_3}$). – ^{13}C NMR ($\mathrm{C_6D_6}$): δ = 4.3 (s, 2 $\mathrm{Al}C\mathrm{H_2CH_3}$), 8.7 (s, $\mathrm{Al}C\mathrm{H_2CH_3}$), 8.9 [dd, ^2J(C,P) = 13.5 Hz, ^3J(C,P) = 7.5 Hz, $\mathrm{PCH_2}C\mathrm{H_3}$], 9.2 (s), 9.8 (s), 10.0 (s), 10.1 (s), 10.3 (s), 10.9 [d, ^2J(C,P) = 5.8 Hz, $\mathrm{PCH_2}C\mathrm{H_3}$], 11.2 [d, ^2J(C,P) = 4.7 Hz, $\mathrm{PCH_2}C\mathrm{H_3}$], 11.4 (s, $\mathrm{AlCH_2}C\mathrm{H_3}$), 20.4 [d, ^1J(C,P) = 17.3 Hz, $\mathrm{P}C\mathrm{H_2CH_3}$], 21.1 [d, ^1J(C,P) = 7.9 Hz, $\mathrm{P}C\mathrm{H_2CH_3}$], 24.9 [dd, ^1J(C,P) = 14.2 Hz, ^2J(C,P) = 10.5 Hz, $\mathrm{P}C\mathrm{H_2CH_3}$], 29.3 [d, ^3J(C,P) = 5.4 Hz, $\mathrm{C(}C\mathrm{H_3)_2CH_2CH_3}$], 29.7 [m, $\mathrm{C(}C\mathrm{H_3)_2CH_2CH_3}$], 30.0 [dd, ^3J(C,P) = 9.8 Hz, ^3J(C,P) = 4.4 Hz, $\mathrm{C(}C\mathrm{H_3)_2CH_2CH_3}$], 30.4 [pseudo-t, J(C,P) = 6.5 Hz, J(C,P) = 6.5 Hz, $\mathrm{C(}C\mathrm{H_3)_2CH_2CH_3}$], 31.0 [d, ^3J(C,P) = 14.9 Hz, $\mathrm{C(}C\mathrm{H_3)_2CH_2CH_3}$], 31.3 [d, ^3J(C,P) = 13.5 Hz, $\mathrm{C(}C\mathrm{H_3)_2CH_2CH_3}$], 35.1 [dd, ^1J(C,P) = 51.2 Hz, ^1J(C,P) = 21.6 Hz, C-4), 37.8 [s, $\mathrm{C(CH_3)_2}C\mathrm{H_2CH_3}$], 39.2 [pseudo-t, J(C,P) = 5.8 Hz, J(C,P) = 5.8 Hz, $\mathrm{C(CH_3)_2}C\mathrm{H_2CH_3}$], 39.6 [dd, ^3J(C,P) = 9.3 Hz, ^3J(C,P) = 3.4 Hz, $\mathrm{C(CH_3)_2}C\mathrm{H_2CH_3}$], 41.1 [d, ^2J(C,P) = 13.2 Hz, $C\mathrm{(CH_3)_2CH_2CH_3}$], 43.2 [m, 2 $C\mathrm{(CH_3)_2CH_2CH_3}$], 48.9 (m, C-1), 70.9 (m, C-6). – ^{31}P NMR ($\mathrm{C_6D_6}$): δ = −149.6 [dd, ^1J(P,P) = 162.3 Hz, ^2J(P,P) = 24.4 Hz, P-3], −61.9 [d, ^1J(P,P) = 162.3 Hz, P-2], −2.5 [d, ^2J(P,P) = 24.4 Hz, P-7]. – MS (EI, 70 eV); *m/z* (%): 570 (28) [$\mathrm{M^+}$], 542 (31) [$\mathrm{M^+ - C_2H_4}$], 541 (100) [$\mathrm{M^+ - C_2H_5}$], 327 (21) [$\mathrm{M^+ - C_2H_6 - 3\,C_5H_{11}}$], 71 (50) [$\mathrm{C_5H_{11}^+}$]. – $\mathrm{C_{30}H_{63}Al_2P_3}$: calcd. 570.3774, found 570.3801 (MS).

1,4,6-Triadamant-1-yl-2,5,7,7,8,8-hexaethyl-3-phospha-2,7-diphosphonia-5,8-dialuminatotetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]octane (**6e**): Starting from triethylaluminium (**5b**) (0.12 g, 1.00 mmol) and **4c** (0.31 g, 1.75 mmol) and with stirring of the reaction mixture for 5 d at 25 °C, **6e** was obtained as colorless crystals. Yield 0.35 g (92%); m.p. 300 °C (dec.). – ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 0.30–0.64 (m, 6 H, 3 $\mathrm{AlC}H_2\mathrm{CH_3}$), 0.96–2.20 (m, 69 H, 3 $\mathrm{PC}H_2\mathrm{CH_3}$, 6 $\mathrm{CH_2C}H_3$, and 45 Ad-*H*). – ^{13}C NMR ($\mathrm{C_6D_6}$): δ = 4.4 (s, 2 $\mathrm{Al}C\mathrm{H_2CH_3}$), 9.3 (m, $\mathrm{PCH_2}C\mathrm{H_3}$), 9.9 (s, $\mathrm{Al}C\mathrm{H_2CH_3}$), 10.3 (s, $\mathrm{CH_2}C\mathrm{H_3}$), 11.1 (s, 2 $\mathrm{CH_2}C\mathrm{H_3}$), 11.3 [d, ^2J(C,P) = 4.9 Hz, $\mathrm{PCH_2}C\mathrm{H_3}$], 11.6 (s, $\mathrm{CH_2}C\mathrm{H_3}$), 21.1 [d, ^1J(C,P) = 17.7 Hz, $\mathrm{P}C\mathrm{H_2CH_3}$], 21.9 [d, ^1J(C,P) = 8.3 Hz, $\mathrm{P}C\mathrm{H_2CH_3}$], 26.3 (m, $\mathrm{P}C\mathrm{H_2CH_3}$), 29.3 (m, C-4), 29.8 (s, Ad-*C*), 30.1 (s, Ad-*C*), 30.4 (s, Ad-*C*), 37.1 (s, 5 Ad-*C*), 39.6

(m, Ad-*C*), 43.8 (m, C-1), 46.0 (s, Ad-*C*), 47.3 (s, Ad-*C*), 48.9 [d, ^3J(C,P) = 13.7 Hz, Ad-*C*], 70.2 (m, C-6). – ^{31}P NMR (C_6D_6): δ = −154.0 [dd, ^1J(P,P) = 163.4 Hz, ^2J(P,P) = 23.6 Hz, P-3], −63.5 [d, ^1J(P,P) = 163.4 Hz, P-2], −2.9 [d, ^2J(P,P) = 23.6 Hz, P-7]. – MS (CI, 120 eV); *m/z* (%): 762 (7) [M^+], 734 (54) [$M^+ - C_2H_4$], 733 (100) [$M^+ - C_2H_5$], 584 (6) [$M^+ - 2\ C_2H_5 - 4\ C_2H_6$], 135 (86) [$C_{10}H_{15}^+$]. – $C_{45}H_{75}Al_2P_3$: calcd. 762.4713, found 762.4661 (MS).

Tetracarbonyl[(3-η)-1,4,6-tri-tert-butyl-2,5,7,7,8,8-hexapropyl-3-phospha-2,7-diphosphonia-5,8-dialuminatotetracyclo[3.3.0.0^{2,4}.0^{3,6}]-octane]iron (**7a**): To a solution of triphosphadialatetracyclooctane **6c** (0.30 g, 0.49 mmol) in pentane (10 ml) was added nonacarbonyldiiron (0.53 g, 1.46 mmol) at 25 °C. After stirring for 24 h, the solution was concentrated and the precipitate removed at 4 °C. Evaporation of the remaining solvent (25 °C/10^{-3} mbar) afforded **7a** as a brown, non-distillable oil. Yield 0.28 g (73%). – IR (pentane): $\tilde{\nu}$ = 2054 (m, CO), 1972 (s, CO), 1950 (s, CO), 1936 (m, CO), 1260 (m), 1098 (m), 1018 (m), 808 cm^{-1} (m). – ^{1}H NMR (C_6D_6): δ = 0.30–0.65 (m, 6 H, 3 $\mathrm{AlC}\mathit{H}_2\mathrm{CH_2CH_3}$), 0.80–2.05 (m, 32 H, 6 $\mathrm{CH_2CH_2C}\mathit{H}_3$, 6 $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_3}$, and $\mathrm{PC}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.29 [s, 9 H, $C(CH_3)_3$], 1.41 [s, 9 H, $C(CH_3)_3$], 1.48 [s, 9 H, $C(CH_3)_3$], 2.48–2.57 (m, 2 H, $\mathrm{PC}\mathit{H}_2\mathrm{CH_2CH_3}$), 2.85–2.98 (m, 2 H, $\mathrm{PC}\mathit{H}_2\mathrm{CH_2CH_3}$). – ^{13}C NMR ($C_6D_6$): δ = 15.8 [d, *J*(C,P) = 13.7 Hz], 16.2 (s), 16.5 [d, *J*(C,P) = 15.3 Hz], 16.8 (s, $\mathrm{Al}\mathit{C}\mathrm{H_2CH_2CH_3}$), 18.3 (s, $\mathrm{Al}\mathit{C}\mathrm{H_2CH_2CH_3}$), 18.4 (s), 18.6 (s, $\mathrm{Al}\mathit{C}\mathrm{H_2CH_2CH_3}$), 20.1 [d, *J*(C,P) = 4.4 Hz], 20.3 (s), 21.0 [d, *J*(C,P) = 3.3 Hz], 21.6 (s), 21.7 [d, *J*(C,P) = 12.9 Hz], 21.9 (s), 22.1 (s), 26.7 [d, *J*(C,P) = 6.5 Hz], 29.1 [dd, ^1J(C,P) = 14.5 Hz, *J*(C,P) = 7.2 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2CH_3}$], 30.3 [d, ^1J(C,P) = 16.9 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2CH_3}$], 30.6 [d, ^1J(C,P) = 7.2 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2CH_3}$], 33.1 (m, C-4), 33.8 [s, $\mathrm{C}(\mathit{C}\mathrm{H_3})_3$], 34.4 [s, $\mathrm{C}(\mathit{C}\mathrm{H_3})_3$], 35.8 [m, $\mathit{C}(\mathrm{CH_3})_3$], 37.0 [d, ^3J(C,P) = 13.7 Hz, $\mathrm{C}(\mathit{C}\mathrm{H_3})_3$], 40.8 [m, $\mathit{C}(\mathrm{CH_3})_3$], 45.1 (m, C-1), 75.2 (m, C-6), 219.3 (s, 4 CO). – ^{31}P NMR (C_6D_6): δ = −72.9 [d, ^1J(P,P) = 58.7 Hz, P-2], −67.9 [dd, ^1J(P,P) = 58.7 Hz, ^2J(P,P) = 10.9 Hz, P-3], −1.6 [d, ^2J(P,P) = 10.9 Hz, P-7]. – MS (EI, 70 eV); *m/z* (%): 752 (10) [$M^+ - CO$], 724 (14) [$M^+ - 2\ CO$], 668 (29) [$M^+ - 4\ CO$], 611 (11) [$M^+ - Fe(CO)_4 - H$], 569 (100) [$M^+ - Fe(CO)_4 - C_3H_7$].

Pentacarbonyl[(3-η)-1,4,6-tri-tert-butyl-2,5,7,7,8,8-hexaethyl-3-phospha-2,7-diphosphonia-5,8-dialuminatotetracyclo[3.3.0.0^{2,4}.0^{3,6}-octane]tungsten (**7b**): A solution of hexacarbonyltungsten (0.35 g, 1.00 mmol) in THF (50 ml) was irradiated at 0 °C[17]. After 0.5 h, triphosphadialatetracyclooctane **6b** (0.34 g, 0.64 mmol) in THF (5 ml) was added at 25 °C and the reaction mixture was allowed to stir for 24 h. The volatile components were then evaporated (25 °C/10^{-3} mbar), the residue was extracted with pentane (10 ml) and filtered. Recrystallization from the same solvent afforded **7b** as yellow crystals. Yield 0.30 g (55%); m.p. 200 °C (dec.). – IR (pentane): $\tilde{\nu}$ = 2068 (m, CO), 1934 (s, br, CO), 1380 (m), 1260 (s), 1098 (s), 1018 (s), 806 cm^{-1} (s). – ^{1}H NMR (C_6D_6): δ = 0.30–0.65 (m, 6 H, 3 $\mathrm{AlC}\mathit{H}_2\mathrm{CH_3}$), 0.95–1.06 (m, 6 H, 2 $\mathrm{CH_2C}\mathit{H}_3$), 1.18–1.50 (m, 12 H, 4 $\mathrm{CH_2C}\mathit{H}_3$), 1.26 [s, 9 H, $C(CH_3)_3$], 1.29 [s, 9 H, $C(CH_3)_3$], 1.38 [d, ^4J(H,P) = 0.9 Hz, 9 H, $C(CH_3)_3$], 1.95–2.13 (m, 2 H, $\mathrm{PC}\mathit{H}_2\mathrm{CH_3}$), 2.42–2.51 (m, 2 H, $\mathrm{PC}\mathit{H}_2\mathrm{CH_3}$), 2.76–2.88 (m, 2 H, $\mathrm{PC}\mathit{H}_2\mathrm{CH_3}$). – ^{13}C NMR ($C_6D_6$): δ = 4.0 (s, $\mathrm{Al}\mathit{CH}_2\mathrm{CH_3}$), 5.0 (s, $\mathrm{Al}\mathit{CH}_2\mathrm{CH_3}$), 7.5 (s, $\mathrm{Al}\mathit{CH}_2\mathrm{CH_3}$), 9.3 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 9.8 (s, 2 $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 10.5 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 11.1 [d, ^2J(C,P) = 5.9 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$], 11.3 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 16.6 (m, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$), 17.0 [dd, ^1J(C,P) = 15.2 Hz, *J*(C,P) = 6.8 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$], 28.4 [dd, ^1J(C,P) = 17.2 Hz, *J*(C,P) = 5.5 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$], 34.7 [pseudo-t, *J*(C,P) = 3.3 Hz, *J*(C,P) = 3.3 Hz, $\mathrm{C}(\mathit{C}\mathrm{H_3})_3$], 35.1 [pseudo-t, *J*(C,P) = 6.4 Hz, *J*(C,P) = 6.4 Hz, $\mathrm{C}(\mathit{C}\mathrm{H_3})_3$], 36.0 [dd, *J*(C,P) = 7.7 Hz, *J*(C,P) = 3.3 Hz, $\mathit{C}(\mathrm{CH_3})$], 36.2 [m, $\mathit{C}(\mathrm{CH_3})_3$], 36.7 [d, *J*(C,P) = 13.6 Hz, $\mathrm{C}(\mathit{C}\mathrm{H_3})_3$], 40.0 [m, $\mathit{C}(\mathrm{CH_3})_3$], 44.7 (m, C-1), 77.6 (m, C-6), 196.3 [d, ^2J(C,P) = 27.8 Hz, *trans*-CO], 198.7 [d, ^2J(C,P) = 5.4 Hz, ^1J(W,C) = 128.4 Hz, 4 *cis*-CO][21]. – ^{31}P NMR (C_6D_6): δ = −117.7 [dd, ^1J(P,W) = 216.1 Hz, ^1J(P,P) = 56.3 Hz, ^2J(P,P) = 10.3 Hz, P-3], −61.2 [d, ^1J(P,P) = 56.3 Hz, P-2], 2.5 [d, ^2J(P,P) = 10.3 Hz, P-7]. – MS (EI, 70 eV); *m/z* (%): 852 (0.1) [M^+], 768 (0.4) [$M^+ - 3\ CO$], 712 (0.3) [$M^+ - 5\ CO$], 528 (12) [$M^+ - W(CO)_5$], 500 (21) [$M^+ - W(CO)_5 - C_2H_4$], 442 (47) [$M^+ - W(CO)_5 - C_2H_4 - 2\ C_2H_5$], 299 (100) [$M^+ - W(CO)_5 - C_2H_6 - 2\ C_2H_5 - Al(C_2H_5) - Al(C_2H_5)_2$].

☆ Dedicated to Professor *Michael Hanack* on the occasion of his 65th birthday.

[1] Part 113: M. Regitz, S. Krill, *Phosphorus, Sulfur and Silicon*, in press.

[2] T. Wettling, J. Schneider, O. Wagner, C. G. Kreiter, M. Regitz, *Angew. Chem.* **1989**, *101*, 1035–1037; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1013–1014.

[3] M. Regitz, T. Wettling, B. Breit, M. Birkel, B. Geißler, U. Bergsträßer, S. Barth, P. Binger, *Phosphorus, Sulfur and Silicon* **1993**, *76*, 1–4; M. Regitz, T. Wettling, R. Fäßler, B. Breit, B. Geißler, M. Julino, A. Hoffmann, U. Bergsträßer, *Phosphorus, Sulfur and Silicon* **1996**, *109–110*, 425–428.

[4] M. Regitz, A. Hoffmann, U. Bergsträßer in *Modern Acetylene Chemistry* (Eds.: F. Diederich, P. Stang), VCH, New York, **1995**, p. 173.

[5] Short review: R. Streubel, *Angew. Chem.* **1995**, *107*, 478–480; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 436–438.

[6] See, for example: U. Annen, M. Regitz, *Tetrahedron Lett.* **1988**, *29*, 1681–1684; H. Heydt, U. Bergsträßer, R. Fäßler, E. Fuchs, N. Kamel, T. Mackewitz, G. Michels, W. Rösch, M. Regitz, P. Mazerolles, C. Laurent, A. Faucher, *Bull. Soc. Chim. Fr.* **1995**, *132*, 652–668.

[7] M. Julino, U. Bergsträßer, M. Regitz, *J. Org. Chem.* **1995**, *60*, 5884–5890.

[8] See, for example: M. Regitz, P. Binger in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 58; M. Regitz in *Organic Synthesis via Organometallics* (Eds.: D. Enders, H.-J. Gais, W. Keim), Vieweg, Wiesbaden, **1993**, p. 93; D. Böhm, D. Hu, U. Zenneck, *Phosphorus, Sulfur and Silicon* **1993**, *77*, 5–8.

[9] T. Wettling, B. Geißler, R. Schneider, S. Barth, P. Binger, M. Regitz, *Angew. Chem.* **1992**, *104*, 761–762; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 758–759; B. Geißler, T. Wettling, S. Barth, P. Binger, M. Regitz, *Synthesis* **1994**, 1337–1343.

[10] G. Becker, W. Becker, R. Knebl, H. Schmidt, U. Hildenbrand, M. Westerhausen, *Phosphorus, Sulfur and Silicon* **1987**, *30*, 349–352.

[11] B. Breit, U. Bergsträßer, G. Maas, M. Regitz, *Angew. Chem.* **1992**, *104*, 1043–1046; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1055–1058; B. Breit, M. Regitz, *Chem. Ber.* **1996**, *129*, 489–494.

[12] Part of this work has been published recently as a short communication: B. Breit, A. Hoffmann, U. Bergsträßer, L. Ricard, F. Mathey, M. Regitz, *Angew. Chem.* **1994**, *106*, 1541–1543; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1491–1493.

[13] For the ^{31}P-NMR absorptions see, for example: J. C. Tebby, *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*, CRC Press, Boca Raton, **1991**, p. 121; F. Mathey, *Chem. Rev.* **1990**, *90*, 997–1025.

[14] See, for example: J. G. Verkade, L. D. Quin, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH, Deerfield Beach, **1987**, p. 391.

[15] See, for example: A. Nachbauer, *Diplomarbeit*, Universität Kaiserslautern, **1995**; M. Birkel, J. Schulz, U. Bergsträßer, M. Regitz, *Angew. Chem.* **1992**, *104*, 870–873; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 879–882.

[16] P. S. Braterman, W. J. Wallace, *J. Organomet. Chem.* **1971**, *30*, C17–C18.

[17] W. Strohmeier, F.-J. Müller, *Chem. Ber.* **1969**, *102*, 3608–3612.

[18] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1981**, *36B*, 16–19; optimized procedure: W. Rösch, U. Hees, M. Regitz, *Chem. Ber.* **1987**, *120*, 1645–1652; see also: W. Rösch, T. Allspach, U. Bergsträßer, M. Regitz in *Synthetic Methods of Organometallic and Inorganic Chemistry, vol. 3* (Eds.: W. A. Herrmann, H. H. Karsch), Thieme, Stuttgart, **1996**, p. 11.

[19] W. Rösch, U. Vogelbacher, T. Allspach, M. Regitz, *J. Organomet. Chem.* **1986**, *306*, 39–53.

[20] T. Allspach, M. Regitz, G. Becker, W. Becker, *Synthesis* **1986**, 31–36; see also: W. Rösch, T. Allspach, U. Bergsträßer, M. Regitz in *Synthetic Methods of Organometallic and Inorganic Chemistry, vol. 3* (Eds.: W. A. Herrmann, H. H. Karsch), Thieme, Stuttgart, **1996**, p. 14.

[21] Note: The resonance of C-4 cannot be reported since it is obscured by another signal.

[96179]