

Organophosphorus compounds 115.¹

Solvent-directed cooligomerization of kinetically stabilized phosphalkynes with trialkylaluminium compounds

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Abstract

The reaction of phosphalkynes **1** with trialkylaluminium reagents **4** in diethyl ether leads to a highly selective phosphalkyne cyclotetramerization with incorporation of one organometallic unit (\rightarrow **6a–c**).

When the tetracyclic compound **6a** is allowed to react with nonacarbonyldiiron (**7**), a two-fold metalation followed by a rearrangement of the cage compound occurs and the transition metal complex **8** is obtained. © 1997 Elsevier Science S.A.

Keywords: Phosphalkynes; Cooligomerization; Phosphalkyne cyclooligomers; Metallo-phosphane complex

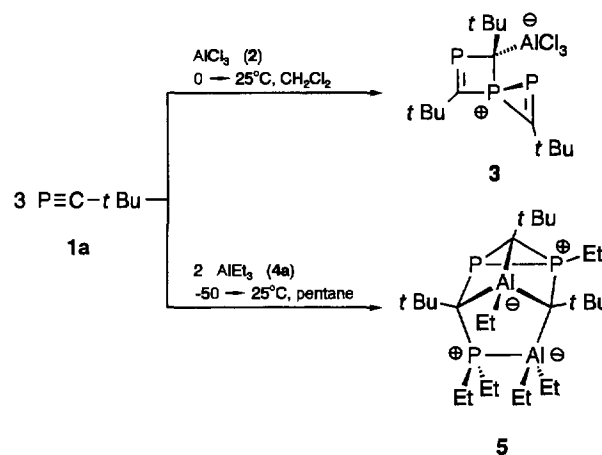
1. Introduction

Phosphorus–carbon cage compounds can be constructed specifically with the aid of various synthetic strategies (see for example Ref. [2]). A particularly versatile concept, among others, involves the Lewis-acid-induced cyclooligomerization of phosphalkynes [3,4]. Thus, for example, when the phosphalkyne **1a** is allowed to react with aluminium trichloride (**2**), the reaction stops at the stage of the spirocyclic trimer complex **3** [4] (Scheme 1). Removal of the σ -bonded metal halide by addition of dimethyl sulphoxide furnishes, in dependence on the reaction conditions, different phosphorus–carbon cage compounds [4].

Similar to the aluminium halides **2**, triorganoaluminium derivatives **4** are also able to induce an oligomerization of the phosphalkyne **1a**. In this process, the polycyclic product **5** is formed in high selectivity with incorporation of the Lewis acid **4a** [1,5] (Scheme 1).

The present paper describes a continuation of our

investigations on the generation of the polycyclic system **5** and is concerned with the solvent-dependence of the cooligomerization process occurring upon reaction of the phosphalkyne **1** with the organometallic reagent **4**. In addition, the reaction behaviour of a selected representative of the phosphorus–carbon–aluminium cage compounds towards nonacarbonyldiiron is discussed.



Scheme 1.

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¹ For part 114, see Ref. [1].

2. Results and discussion

2.1. Cooligomerization of phosphalkynes **1** with trialkylaluminium compounds **4**

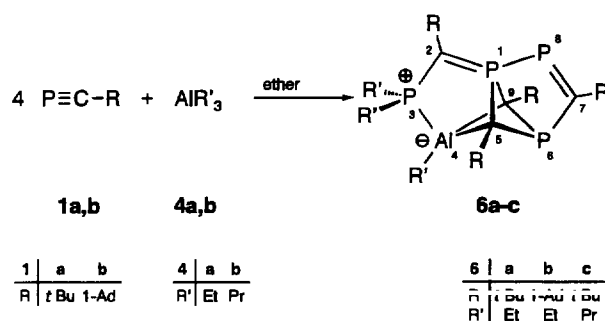
It is well known for all-carbon triple bond systems that the course of the triorganoaluminium-induced polymerization process can be influenced by the choice of the solvent [6]. A comparable dependence on the reaction medium has also been observed in the case of the kinetically stabilized phosphalkynes **1** (part of this work has been published recently as a short communication: see Ref. [5]).

When the phosphalkynes **1a,b** are allowed to react with triethyl- or, respectively, tripropylaluminium (**4a,b**) in diethyl ether instead of in pentane, the above-mentioned formation of a triphosphadialatetracyclooctane **5** does not occur, the cooligomerization follows a completely different course and ends at the stage of the new and unexpected tetracyclic cage compounds **6a–c** (yields: 60–74%) (Scheme 2).²

Elemental analysis and mass spectral data confirm that the reaction product **6** is indeed a cage compound constructed from four molecules of the phosphalkyne **1** and one molecule of the triorganoaluminium derivative **4**. Valuable diagnostic information is provided by the NMR spectral data which are discussed below for the example of the product **6a**.

In accord with the degree of oligomerization, four signals appear in the ³¹P NMR spectrum. The chemical shift of 208.0 ppm (P-8) is indicative of a λ³σ² phosphorus atom (for the ³¹P NMR absorptions see, for example, Ref. [7]). The phosphorus–phosphorus single bond between P-8 and the ylidic phosphorus P-1 (δ = 87.1) is reflected in a coupling constant of 320.6 Hz. The signal for the onium phosphorus atom P-3 appears as a broad doublet (²J_{P,P} = 122.0 Hz) at relatively high field (δ = –1.0); the direct proximity of the aluminate unit is responsible not only for the chemical shift but also for the signal broadening. The λ³σ³ phosphorus atom P-6 (δ = –32.8) interacts with all other phosphorus nuclei and, since the coupling constants all have comparable magnitudes, a multiplet is observed in the ³¹P NMR spectrum instead of the expected doublet of doublets.

Convincing structural evidence can also be deduced from the ¹H NMR spectrum. In addition to three sin-



Scheme 2.

glets for the four *tert*-butyl groups (integration ratio: 2:1:1), four signals for the three ethyl substituents are apparent (integration ratio: 2:1). Double resonance experiments demonstrate that two ethyl groups have migrated from aluminium to the phosphorus atom P-3. Thus, upon irradiation at the resonance frequency of the respective phosphorus atom (δ = –1.0), the H/P couplings of the methyl (δ = 1.02) and methylene protons (δ = 1.70–1.79), respectively, in the ¹H(³¹P) NMR spectrum disappear.

The ¹³C NMR spectrum of the tetracyclic compound **6a** reveals three signals for the skeletal carbon atoms. The signal at δ = 108.0 can be assigned without doubt to the phosphalkene carbon atom C-7. The ylidic carbon atom C-2 gives rise to a signal at δ = 59.3 ppm. Chemical shifts in this region are characteristic for methylenephosphoranes bearing acceptor substituents [8]. The two carbon atoms C-5 and C-9 of the bicyclo[1.1.1]pentane unit give rise to a multiplet (δ = 44.3). The transfer of two alkyl groups from aluminium to the phosphorus atom P-3 is demonstrated by a ¹J_{C,P} coupling constant of 22.0 Hz for the corresponding methylene carbon atoms (δ = 26.6).

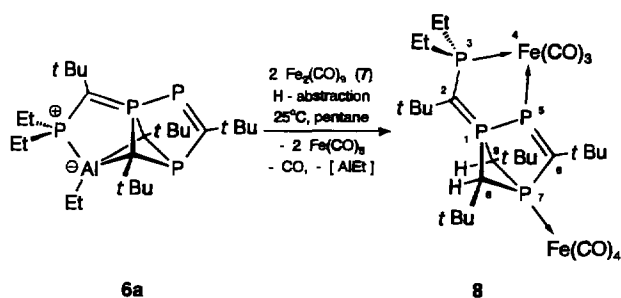
The NMR spectroscopic data provide numerous indications for the structural elucidation of the product **6a** and the proposed constitution was finally confirmed by X-ray crystallography [5].

A detailed interpretation of the mechanism of the cooligomerization process is not yet possible. However, it is fairly safe to assume that the initial step is an attack of the Lewis acid **4a** on the triply-bonded carbon atom of compound **1a**. Et–P=C(*t*Bu)(AlEt₂) is subsequently formed via a [1,3]-ethyl shift. This phosphalkene is unstable under the prevailing reaction conditions and serves as the starting point for a further sequence of reactions terminating in the formation of the tetracyclic product **6**.

2.2. Preparation of the transition metal complex **8**

We have reported elsewhere on the ability of phosphorus–carbon–aluminium compounds to serve as ligands for transition metal complexes [1]. Metalation reac-

² In a more general investigation we have found that if a non-polar solvent such as pentane, hexane, toluene, or no solvent at all is used, the cooligomerization process of the compounds **1a** and **4a** always leads to the triphosphadialatetracyclooctane system **5**. In contrast, the tetracyclic cage compound **6a** is obtained from the same starting materials when 'coordinating' solvents such as, for example, diethyl ether, di-*n*-butyl ether, or triethylamine are employed.



Scheme 3.

tions of the triphosphadiatetracyclooctane **5** do not result in any changes in the cage structure of the starting compound [1].

In contrast, the reaction of the polycyclic compound **6a** with nonacarbonyldiiron (**7**) follows a completely unexpected course. Going beyond the expected complex formation with the cage compound **6a**, a skeletal rearrangement proceeding via cleavage of the alkylaluminum fragment to furnish the binuclear iron complex **8** is observed (Scheme 3). After work-up by column chromatography and recrystallization from diethyl ether, the complex **8** is obtained in the form of red, rectangular crystals (yield: 56%).

The elemental analysis and mass spectral data are in accord with the structure proposed for compound **8**. The incorporation of the iron carbonyl fragments is reflected in the appearance of a total of six carbonyl bands in the IR spectrum ($\bar{\nu} = 2052, 2016, 1982, 1964, 1948, 1934 \text{ cm}^{-1}$).

Diagnostic information about the constitution of **8** can be derived from the NMR spectra. Signals for four, chemically not equivalent phosphorus atoms occur in the ^{31}P NMR spectrum. The signal at $\delta = 231.1$ is indicative of a $\lambda^3\sigma^2$ phosphorus atom (P-5) [7]. A relatively small $^1J_{\text{P,P}}$ coupling constant of 91.6 Hz reveals the direct neighbourhood to P-1 ($\delta = 49.5$). Less characteristic are the chemical shifts of the two $\lambda^3\sigma^3$ phosphorus atoms complexed by the carbonyliron fragments (P-3: $\delta = 88.5$; P-7: $\delta = 50.9$). A differentiation between P-3 and P-7 is relatively easy since P-3 exhibits a $^2J_{\text{P,P}}$ coupling with P-1 of 162.9 Hz through the phosphanomethylenephosphorane structural unit [8]. In addition, the signal for the ethyl-substituted phosphorus atom (P-3) experiences a signal broadening in the proton coupled ^{31}P NMR spectrum.

The ^1H NMR spectrum furnishes a clear indication for the cleavage of the organoaluminium fragment. Signals are found for only two of the original three ethyl groups in compound **6a**. Their proximity to the phosphorus atom P-3 can be confirmed by means of double resonance experiments. Furthermore, the ^1H NMR spectrum contains a characteristic double doublet at 3.23 ppm. This chemical shift in combination with two H/P couplings (13.0 Hz and 5.2 Hz) demonstrates the

presence of two hydrogen atoms bonded directly to the polycyclic skeleton (C-8/9-H).

Accordingly, the ^{13}C NMR signal at 87.2 ppm (C-8/9) is split into a doublet in the proton-coupled spectrum ($^1J_{\text{C,H}} = 132.0 \text{ Hz}$). The two remaining skeletal carbon atoms give signals in the characteristic shift ranges for the respective structural elements. Thus, the ylidic carbon atom C-2 appears as a multiplet at $\delta = 50.5$ [8], while the phosphalkene carbon atom C-6 produces a broad doublet at $\delta = 150.9$ ($^1J_{\text{C,P}} = 15.3 \text{ Hz}$) [9,10]. In analogy to the tetracyclic compound **6a**, the signal for the methylene groups attached to the phosphorus atom P-3 ($\delta = 28.7$) is characterized by a $^1J_{\text{C,P}}$ coupling constant of 28.8 Hz.

Although these spectral data provided fairly conclusive evidence for the constitution of the polycyclic product **8**, an X-ray crystal structure analysis was deemed to be essential to clarify any residual doubts. The thus determined structure of the transition metal complex **8** is shown in Fig. 1.

The central structural element of the polycyclic compound **8** is a triphosphabicyclo[2.1.1]hexene system bearing an exocyclic, phosphano-substituted phosphorus ylid. All phosphorus atoms as well as the carbon atoms C-1 and C-4 lie in a plane. The methylene carbon atoms C-2 and C-3 are arranged in mirror symmetry about this plane. These carbon atoms each bear one *tert*-butyl group and one hydrogen atom as substituents. Coordination of the iron carbonyl fragments on the one hand is by way of the two $\lambda^3\sigma^3$ phosphorus atoms P-3 and P-4. From the bond lengths (P-4/Fe-1: 2.286(3) Å; P-3/Fe-

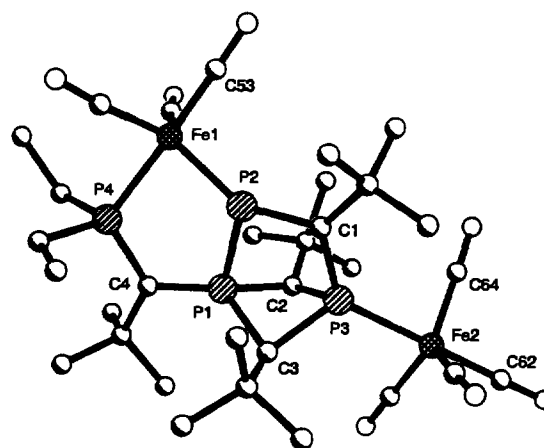


Fig. 1. XP-plot of compound **8** in the crystal state. Hydrogen atoms are omitted for the sake of clarity (see footnote 5 in text). Selected bond lengths (Å) and bond angles (deg), standard deviations in parentheses: Fe-1/P-2 2.083(3), P-2/C-1 1.692(9), C-1/P-3 1.801(10), P-3/Fe-2 2.250(3), P-3/C-3 1.850(8), P-3/C-2 1.877(9), C-2/P-1 1.840(9), C-3/P-1 1.851(9), P-1/P-2 2.118(4), P-1/C-4 1.667(9), C-4/P-4 1.766(10), P-4/Fe-1 2.286(3), P-2/Fe-1/P-4 87.16(11), P-4/Fe-1/C-53 177.7(4), P-4/C-4/P-1 112.5(5), C-4/P-1/P-2 107.8(4), P-1/P-2/C-1 94.7(4), Fe-1/P-2/C-1 151.2(4), P-2/C-1/P-3 109.6(5), C-1/P-3/Fe-2 128.3(3), P-3/Fe-2/C-62 174.4(4), P-3/Fe-2/C-64 88.0(3).

2: 2.250(3) Å) [11] and the respective bond angles (P-4/Fe-1/C-53: 177.7(4)°; P-3/Fe-2/C-62: 174.4(4)°) it is apparent that P-4 and P-3 each are coordinated towards an iron atom, Fe-1 and Fe-2 respectively, in an axial position of their slightly distorted, trigonal bipyramidal environments. In contrast, the $\lambda^3\sigma^2$ phosphorus atom P-2 functions as a two electron donor to an equatorial ligand position (Fe-1/P-2: 2.083(3) Å; P-2/Fe-1/P-4: 87.16(11)°) [12]. The end-on complexation of the P-2/C-1-double bond results in merely a slight lengthening of the phosphorus–carbon separation (P-2/C-1: 1.692(9) Å) in comparison with the standard value for a phosphalkene (1.670 Å) [13].

When the transformation **6a** → **8** is monitored by ^{31}P NMR spectroscopy, various intermediates can be detected. However, a sure assignment of potential intermediates from the point of view of an interpretation of the reaction mechanism is still very difficult. Even so, the metalation of **6a** not only at the $\lambda^3\sigma^3$ - but also at the $\lambda^3\sigma^2$ -phosphorus atom can be considered as a plausible initial reaction. A reaction sequence comprising cleavage of the phosphorus–aluminium bond, nucleophilic expulsion of a carbonyl ligand, cleavage of an organo-aluminium fragment, and abstraction of two hydrogen atoms from the solvent would rationalize the formation of the polycyclic system **8** as final product of the metalation reaction.

2.3. Conclusions

The cooligomerization of the phosphalkynes **1** with the triorganoaluminium derivatives **4** can be specifically controlled by an appropriate choice of the reaction solvent. The use of a non-polar solvent (e.g. pentane) always results in the formation of the triphosphadialate-tracyclooctane system **5** [1], whereas the cyclooligomerization in a 'coordinating' solvent (e.g. diethyl ether) ends at the stage of the tetracyclic cage system **6**.

The formation of the transition metal complex **8** demonstrates that unexpected subsequent reactions may accompany the metalation of phosphorus–carbon–aluminium cage compounds by nonacarbonyldiiron (**7**).

3. Experimental section

3.1. General methods

All reactions were carried out under an atmosphere of argon (purity > 99.998%) in a previously baked-out and evacuated apparatus (Schlenk techniques). The solvents were dried by standard procedures (pentane, hexane, and diethyl ether, Na–K alloy; toluene and di-*n*-butyl ether, Na; triethylamine, KOH), distilled, and stored under argon. Column chromatography was performed in water-cooled glass tubes. Alumina was heated

for 8 h in vacuum (160 °C) and then deactivated with 4% water (Brockmann activity II). Melting points were obtained on a Mettler FP 61 (heating rate: 3 °C min⁻¹) and are uncorrected. IR spectra were recorded on Perkin–Elmer infrared spectrometer 16PC FT-IR. Mass spectra were measured on a Finnigan MAT 90 spectrometer. ^1H NMR-spectra and ^{13}C NMR-spectra were recorded on a Bruker AMX 400 instrument (solvent as internal standard). ^{31}P NMR spectra were also recorded on a Bruker AMX 400 instrument (85% H_3PO_4 as external standard). The starting materials **1a** [14], **3** **1b** [17] (see also Ref. [18]) were prepared by published methods. Compounds **4a,b** were purchased from Aldrich and used without further purification.

3.2. 2,5,7,9-Tetra-*tert*-butyl-3,3,4-triethyl-1- λ^5 -6,8-triphospha-3-phosphonia-4-aluminatetracyclo-[4.2.1.0^{1,5}.0^{4,9}]nona-1,7-diene (**6a**)

To a magnetically stirred solution of triethylaluminium **4a** (0.34 g, 3.00 mmol) in diethyl ether (8 ml) at –78 °C was added dropwise a solution of phosphalkyne **1a** (1.20 g, 12.00 mmol) in diethyl ether (2 ml). After the reaction mixture had been allowed to warm to room temperature during 12 h, the solution was stirred for 3 days and all volatile components were removed at 25 °C/10⁻³ mbar. The remaining brown oil was taken up in pentane or diethyl ether and purified by recrystallization at +4 °C to yield compound **6a** as red-brown crystals (1.14 g, 74%); m.p. 168–169 °C. MS (EI): *m/z* (%) 514 (4) [M^+], 431 (29) [$\text{M} - 3\text{C}_2\text{H}_4 + \text{H}^+$], 414 (5) [$\text{M} - \text{C}_5\text{H}_9\text{P}^+$], 325 (100) [$\text{M} - \text{C}_5\text{H}_9\text{P} - 3\text{C}_2\text{H}_6 + \text{H}^+$], 314 (90) [$\text{M} - 2\text{C}_5\text{H}_9\text{P}^+$], 57 (8) [C_4H_9^+]. Anal. Found: C, 59.9; H, 9.7. $\text{C}_{26}\text{H}_{51}\text{AlP}_4$ calc.: C, 60.69; H, 9.99%. IR (KBr): $\bar{\nu}$ 2956 (s), 2902 (m), 2860 (m), 1472 (m), 1460 (m), 1390 (w), 1360 (m), 1232 (w), 1210 (w), 1072 (w), 922 (w), 810 (w), 708 (m), 668 (m) cm⁻¹. ^{31}P (^1H) NMR (162 MHz, C_6D_6): δ –32.8 (m, P-6), –1.0 (d, br, $^2J_{\text{P,P}} = 122.0$ Hz, P-3), 87.1 (ddd, $^1J_{\text{P,P}} = 320.6$ Hz, $^2J_{\text{P,P}} = 122.0$ Hz, $^2J_{\text{P,P}} = 14.4$ Hz, P-1), 208.0 (dd, $^1J_{\text{P,P}} = 320.6$ Hz, $^2J_{\text{P,P}} = 10.8$ Hz, P-8). ^1H NMR (400 MHz, C_6D_6): δ 0.55 (q, $^3J_{\text{H,H}} = 8.1$ Hz, 2H, AlCH_2CH_3), 1.02 (dt, $^3J_{\text{H,P}} = 19.2$ Hz, $^3J_{\text{H,H}} = 7.8$ Hz, 6H, 2 P-3- CH_2CH_3), 1.22 (s, 18H, 2 $\text{C}(\text{CH}_3)_3$), 1.40 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.43 (t, $^3J_{\text{H,H}} = 8.1$ Hz, 3H, AlCH_2CH_3), 1.47 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.70–1.79 (m, 4H, 2 P-3- CH_2CH_3). ^{13}C (^1H) NMR (101 MHz, C_6D_6): δ 0.8 (m, br, AlCH_2CH_3), 10.3 (d, $J_{\text{C,P}} = 2.6$ Hz, AlCH_2CH_3), 12.8 (d, $^2J_{\text{C,P}} = 4.1$ Hz, 2 P-3- CH_2CH_3), 26.6 (dd, $^1J_{\text{C,P}} = 22.0$ Hz, $J_{\text{C,P}} = 2.2$ Hz, 2 P-3- CH_2CH_3), 32.4 (dd, $J_{\text{C,P}} = 11.4$ Hz, $J_{\text{C,P}} = 7.2$ Hz, $\text{C}(\text{CH}_3)_3$), 33.4 (d,

³ For the optimized procedure see Ref. [15]; see also Ref. [16].

$J_{C,P} = 4.8$ Hz, $C(CH_3)_3$), 35.2–35.4 (m, 3 $C(CH_3)_3$), 35.6 (d, $J_{C,P} = 12.1$ Hz, $C(CH_3)_3$), 36.4 (dd, $J_{C,P} = 8.8$ Hz, $J_{C,P} = 3.8$ Hz, 2 $C(CH_3)_3$), 44.3 (m, br, 2 C-5/9), 59.3 (dpt, $^1J_{C,P} = 39.8$ Hz, $J_{C,P} = 12.6$ Hz, $J_{C,P} = 12.6$ Hz, C-2), 108.0 (dpt, $^1J_{C,P} = 40.9$ Hz, $J_{C,P} = 8.7$ Hz, $J_{C,P} = 8.7$ Hz, C-7).

3.3. 2,5,7,9-Tetraadamant-1-yl-3,3,4-triethyl-1- λ^5 -6,8-triphospha-3-phosphonia-4-aluminatotetracyclo-[4.2.1.0^{1,5}.0^{4,9}]nona-1,7-diene (**6b**)

To a magnetically stirred solution of triethylaluminum **4a** (0.11 g, 1.00 mmol) in diethyl ether (8 ml) at 0 °C was added phosphalkyne **1b** (0.72 g, 4.00 mmol). After the reaction mixture had been allowed to warm to room temperature, it was stirred for 2 weeks and the solvent evaporated (25 °C/10⁻³ mbar). The remaining brown oil was taken up in pentane and purified by recrystallization. The slightly brown solid was washed two times with pentane (2 ml) yielding the cage compound **6b** (0.55 g, 67%); m.p. 235–237 °C. MS (EI): m/z (%) 826 (0.1) $[M]^+$, 648 (18) $[M - C_{11}H_{15}P]^+$, 470 (7) $[M - 2C_{11}H_{15}P]^+$, 386 (17) $[M - 2C_{11}H_{15}P - 3C_2H_4]^+$, 135 (100) $[C_{10}H_{15}]^+$. ^{31}P NMR (162 MHz, C_6D_6): δ -44.7 (m, P-6), -0.7 (d, br, $^2J_{P,P} = 122.8$ Hz, P-3), 81.1 (ddd, $^1J_{P,P} = 323.3$ Hz, $^2J_{P,P} = 122.8$ Hz, $^2J_{P,P} = 17.5$ Hz, P-1), 213.4 (d, br, $^1J_{P,P} = 323.3$ Hz, P-8). 1H NMR (400 MHz, C_6D_6): δ 0.69 (q, $^3J_{H,H} = 8.0$ Hz, 2H, $AlCH_2CH_3$), 1.14 (dt, $^3J_{H,P} = 19.0$ Hz, $^3J_{H,H} = 8.0$ Hz, 6H, 2 P-3- CH_2CH_3), 1.51–2.33 (m, 67H, $AlCH_2CH_3$, 2 P-3- CH_2CH_3 , and 60 Ad-H). ^{13}C NMR (101 MHz, C_6D_6): δ 10.7 (s, br, $AlCH_2CH_3$), 13.0 (d, $^2J_{C,P} = 3.9$ Hz, 2 P-3- CH_2CH_3), 27.5 (d, br, $^1J_{C,P} = 19.7$ Hz, 2 P-3- CH_2CH_3), 29.4 (s, 3 Ad-C), 30.0 (s, 6 Ad-C), 30.3 (s, 3 Ad-C), 37.0 (s, 3 Ad-C), 37.2 (s, 3 Ad-C), 37.4 (s, 6 Ad-C), 43.4 (d, $J_{C,P} = 6.1$ Hz, 3 Ad-C), 47.4 (s, br, 3 Ad-C), 49.1 (pt, $J_{C,P} = 6.1$ Hz, $J_{C,P} = 6.1$ Hz, 6 Ad-C), 109.1 (d, br, $^1J_{C,P} = 32.6$ Hz, C-7).⁴

3.4. 2,5,7,9-Tetra-tert-butyl-3,3,4-tri-*n*-propyl-1- λ^5 -6,8-triphospha-3-phosphonia-4-aluminatotetracyclo-[4.2.1.0^{1,5}.0^{4,9}]nona-1,7-diene (**6c**)

To a solution of tripropylaluminum **4b** in diethyl ether (8 ml) at -78 °C was added dropwise a solution of phosphalkyne **1a** in diethyl ether (2 ml) and the reaction mixture was allowed to warm to room temperature during 12 h. After the solution had been stirred for 3 days, all volatile components were removed (25 °C/10⁻³ mbar). The remaining brown oil could not be purified by vacuum distillation (200 °C/10⁻³ mbar),

by column chromatography, or by recrystallization (hexane or diethyl ether) (yield, 60% by ^{31}P NMR spectroscopy). ^{31}P NMR (162 MHz, C_6D_6): δ -32.1 (m, P-6), -8.1 (d, br, $^2J_{P,P} = 122.1$ Hz, P-3), 87.6 (ddd, $^1J_{P,P} = 320.3$ Hz, $^2J_{P,P} = 122.1$ Hz, $^2J_{P,P} = 14.4$ Hz, P-1), 210.4 (dd, $^1J_{P,P} = 320.3$ Hz, $^2J_{P,P} = 11.7$ Hz, P-8).

3.5. [(7- η)-2,6,8,9-Tetra-tert-butyl-4,4,4-tricarbonyl-3,3-diethyl-1- λ^5 -3,5,7-tetraphospha-4-ferratricyclo-[5.1.1.0^{1,5}]nona-1,5-diene]tetracarbonyliron (**8**)

To a solution of 0.30 g (0.58 mmol) of the tetracyclo[4.2.1.0^{1,5}.0^{4,9}]nona-1,7-diene **6a** in pentane (10 ml) were added 0.95 g (2.61 mmol) nonacarbonyliron (**7**) at 25 °C. After stirring for 10 days, the precipitate was removed and the solution evaporated to dryness (25 °C/10⁻³ mbar). The resultant red-brown oily residue was purified by column chromatography over alumina. Using pentane-ether (10:1) as eluent, a red fraction was collected and the solvent removed. Recrystallization of the crude product from diethyl ether at +4 °C afforded red crystals of compound **8** (0.25 g, 56%); m.p. 222–223 °C. HR-MS (EI): Found: $[M]^+$ 768.1042. Calc.: $[M]^+$ 768.1049. MS (EI): m/z (%) 768 (1) $[M]^+$, 600 (21) $[M - Fe(CO)_4]^+$, 572 (14) $[M - Fe(CO)_4 - CO]^+$, 516 (100) $[M - Fe(CO)_4 - 3CO]^+$, 416 (61) $[M - Fe(CO)_4 - 3CO - PC_5H_9]^+$, 57 (45) $[C_4H_9]^+$. Anal. Found: C, 44.7; H, 6.6. $C_{31}H_{48}Fe_2O_7P_4$ calc.: C, 48.46; H, 6.30%. IR (pentane): $\bar{\nu}$ (CO) 2052 (m), 2016 (s), 1982 (w), 1964 (m), 1948 (s), 1934 (m) cm^{-1} . ^{31}P NMR (162 MHz, C_6D_6): δ 49.5 (ddd, $^2J_{P,P} = 162.9$ Hz, $^1J_{P,P} = 91.6$ Hz, $^2J_{P,P} = 13.5$ Hz, P-1), 50.9 (dd, $^2J_{P,P} = 42.3$ Hz, $^2J_{P,P} = 13.5$ Hz, P-7), 88.5 (dd, $^2J_{P,P} = 162.9$ Hz, $^2J_{P,P} = 60.0$ Hz, P-3), 231.1 (ddd, $^1J_{P,P} = 91.6$ Hz, $^2J_{P,P} = 60.0$ Hz, $^2J_{P,P} = 42.3$ Hz, P-5). 1H NMR (400 MHz, C_6D_6): δ 1.09 (dt, $^3J_{H,P} = 18.2$ Hz, $^3J_{H,H} = 7.6$ Hz, 6H, 2 P-3- CH_2CH_3), 1.15 (s, 9H, $C(CH_3)_3$), 1.27 (s, 18H, 2 $C(CH_3)_3$), 1.67 (s, 9H, $C(CH_3)_3$), 1.72–1.82 (m, 2H, P-3- CH_2CH_3), 1.89–2.00 (m, 2H, P-3- CH_2CH_3), 3.23 (dd, $J_{H,P} = 13.0$ Hz, $J_{H,P} = 5.2$ Hz, 2H, 2C-8/9-H). ^{13}C NMR (101 MHz, C_6D_6): δ 10.5 (s, 2 P-3- CH_2CH_3), 28.7 (d, $^1J_{C,P} = 28.8$ Hz, 2 P-3- CH_2CH_3), 32.2 (pt, $J_{C,P} = 5.1$ Hz, $J_{C,P} = 5.1$ Hz, 2 $C(CH_3)_3$), 33.5 (dd, $J_{C,P} = 10.8$ Hz, $J_{C,P} = 5.0$ Hz, $C(CH_3)_3$), 34.8 (d, $J_{C,P} = 3.6$ Hz, $C(CH_3)_3$), 36.6 (s, 2 $C(CH_3)_3$), 37.0 (dd, $J_{C,P} = 9.6$ Hz, $J_{C,P} = 5.4$ Hz, $C(CH_3)_3$), 40.4 (m, $C(CH_3)_3$), 50.5 (m, C-2), 87.2 (pt, $^1J_{C,P} = 10.6$ Hz, $^1J_{C,P} = 10.6$ Hz, $^1J_{C,H} = 132.0$ Hz, 2 C-8/9), 150.9 (d, br, $^1J_{C,P} = 15.3$ Hz, C-6), 214.3 (d, $^2J_{C,P} = 17.5$ Hz, 4 CO), 214.5 (d, br, $^2J_{C,P} = 11.3$ Hz, 3 CO).

3.6. X-ray structure determination of **8**

Crystallographic data for **8**: $C_{31}H_{48}Fe_2O_7P_4$, $M = 768.31$, monoclinic, space group $C2/c$, $a = 21.388(4)$,

⁴The ^{13}C NMR absorptions of $AlCH_2CH_3$, 4 Ad-C, 2 C-5/9, and C-2 could not be detected because they were obscured by other signals or had low signal intensity, respectively.

$b = 10.021(2)$, $c = 33.752(7)$ Å; $\beta = 101.25(3)^\circ$; $V = 7095(3)$ Å³; $Z = 8$; $\rho_{\text{calcd}} = 1.438$ g cm⁻³, $F(000) = 3104$, $\mu = 10.39$ cm⁻¹; 6899 reflections measured, 5592 independent ($1.23 \leq \theta \leq 24.05^\circ$), $T = 293$ K, Mo K α radiation, Siemens P4 diffractometer. The structure was solved by direct methods (SHELXS86). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL93). The final indices were $R_1 = 0.0764$, $wR_2 = 0.1377$ for 5564 reflections with $I \geq 2\sigma(I)$ and for 397 parameters. Maximum residual density 0.463 e Å⁻³ and minimum residual density -0.466 e Å⁻³. The positions of the hydrogen atoms were calculated geometrically and taken into consideration in the final refinement cycles.⁵

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⁵ Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405790, the authors, and the journal citation.