Organophosphorus Compounds, 131[◇]

Tricyclic Phosphorus-Carbon Compounds – Synthesis by Oligomerization of Kinetically Stabilized Phosphaalkynes☆

Andreas Hoffmann[a], Andreas Mack[a], Richard Goddard[b], Paul Binger[b][+], and Manfred Regitz*[a]

Fachbereich Chemie der Universität Kaiserslautern[a],
Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany
Fax: (internat.) + 49(0)631/205-3921
E-mail: regitz@rhrk.uni-kl.de

Max-Planck-Institut für Kohlenforschung[b],
Kaiser-Wilhelm-Platz 1, D-45470 Mühlheim a. d. Ruhr, Germany
Fax: (internat.) + 49(0)208/306-2890

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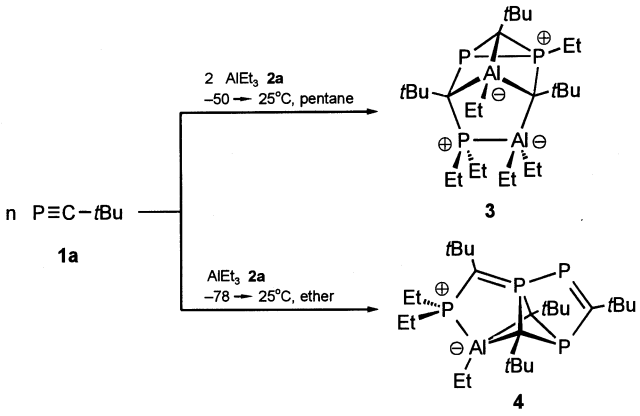
When trialkylaluminum reagents **2** bearing sterically demanding substituents are allowed to react with phosphaalkynes **1** a highly selective phosphaalkyne cyclotrimerization with incorporation of one organometal unit occurs (→ **5a–d**). The resulting triphosphaalatricycloheptenes **5** are able to function as ligands in transition metal complexes (→ **6a**,**b**), as illustrated by the reactions of **5a** with nonacarbonyldiiron or the pentacarbonyltungsten tetrahydrofuran complex. When triethylgallium (**7**) is allowed to react with phosphaalkynes **1**, tricyclic phosphorus-carbon-gallium compounds are generated (→ **8a**,**b**).

Introduction

Phosphorus-carbon cage compounds have attained increasing importance in the chemistry of low-coordinated phosphorus over the past few years. Even complicated polycyclic systems can be obtained specifically by means of various synthetic strategies[2]. One versatile concept involves the initiation of a phosphaalkyne cyclooligomerization with the help of a Lewis acid[3]. Thus, for example, the tetracyclic product **3** is obtained in high selectivity from the reaction of *tert*-butylphosphaalkyne (**1a**) with triethylaluminum (**2a**)[4][5]. A phosphaalkyne cyclooligomerization with incorporation of the Lewis acid **2a** is also observed when diethyl ether is used in place of pentane as solvent; however, in this case the cyclooligomerization process of **1a** with **2a** ends at the stage of the polycyclic betaine **4**[4][6].

The results described here represent an extension of the investigations on the preparation of the cage compounds **3** and **4** and concern the use of triorganoaluminum reagents bearing sterically demanding substituents as well as triorganogallium reagents as reaction partners for the phosphaalkynes **1**. Furthermore, the reaction behavior of a selected phosphorus-carbon-aluminum cage compound towards transition metal carbonyl complexes is discussed.

Scheme 1



Results and Discussion

Generation of the Triphosphaalatricycloheptenes (1 → 5)

Neither the cage compound **3** nor the polycyclic system **4** are formed in the reactions of the phosphaalkynes **1a–c** with the triorganoaluminum reagents **2b**,**c** bearing voluminous substituents. Instead a cyclotrimerization of the organophosphorus compounds **1** with incorporation of one trialkylaluminum unit occurs[7]. The triphosphaalatricycloheptenes **5a–d** formed in this way can be isolated by bulb-to-bulb distillation or recrystallization from non-polar

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

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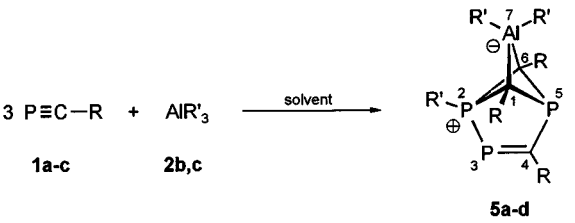
solvents and are obtained in moderate to good yields (36−82%) as yellow oils (**5a**−**c**) or a yellow solid (**5d**).

Scheme 2



2	b	c
R'	*i*Bu	$CH_2CH(Ph)CH_3$

5	a	b	c	d
R	*t*Bu	CMe_2Et	1-Ad	*t*Bu
R'	*i*Bu	*i*Bu	*i*Bu	$CH_2CH(Ph)CH_3$
solv.	ether	ether	ether	pentane

Elemental analyses and mass-spectrometric data clearly show that the polycyclic compounds **5** have the constitutions of 3:1 adducts of the respective phosphaalkyne **1** with the triorganoaluminum reagent **2**. The NMR spectra of products **5** also provide valuable diagnostic information which is discussed in detail below for the example of product **5a** (R = *t*Bu; R′ = *i*Bu).

Relevant information about the degree of oligomerization is provided by the ^{31}P-NMR spectrum which contains three signals which must result from a single molecule on account of the observed ABX spin system. The signal at low field (δ = 223.3) may unequivocally be assigned to the $\lambda^3\sigma^2$ phosphorus atom P-3[8] and its large $^1J_{P,P}$ coupling constant of 299.2 Hz confirms the adjacency to the onium phosphorus atom P-2 (δ = 53.9). The remaining signal at δ = 36.5 (P-5) is split into a double doublet by two $^2J_{P,P}$ couplings (32.2 and 19.0 Hz).

The ^{1}H-NMR spectrum of compound **5a** shows two signals for the *tert*-butyl groups (integration ratio 2:1) and a total of nine signals for the three, chemically non-equivalent isobutyl groups. A two-dimensional NMR spectrum was needed to clarify the spatial relationships between the protons (^{1}H,^{1}H-COSY-45 experiment). The signal at lowest field (δ = 2.36) is assigned to the protons of the α-methylene group at the onium phosphorus atom P-2. It is split by one H,H and two H,P couplings (7.3 and 2.0 Hz). The methyl hydrogen atoms of the isobutyl group at P-2 furnish the signal at δ = 0.96; the methine hydrogen signal occurs at δ = 2.08−2.22. The signal group at δ = 0.46, 2.08−2.22 and 1.24 as well as that at δ = 0.64, 2.22−2.32 and 1.25 can each be assigned to one of the two isobutyl groups at the aluminum atom. However, a distinction between these two alkyl groups is not possible.

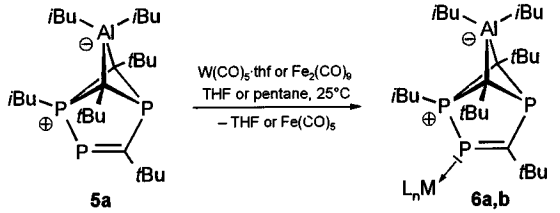
The ^{13}C-NMR-spectral data are also in harmony with the proposed structure for the polycyclic product **5a**. The signal of the phosphaalkene carbon atom C-4 is especially characteristic: it appears at relatively high field (δ = 104.4) and is split into a double doublet (50.2 and 13.4 Hz)[9]. A signal with a chemical shift of δ = 44.7 is observed for the two skeletal sp^3-carbon atoms C-1 and C-6. The signal for the methylene carbon atom at the $\lambda^4\sigma^4$-phosphorus atom (P-2) appears at relatively low field (δ = 47.2) and is split into a double doublet by two C,P couplings (24.6 and 10.5 Hz)[10].

A conclusive mechanism for the formation of the polycyclic system **5** cannot be given at present since it has not been possible to isolate or even to detect any of the occurring intermediates by NMR spectroscopy. Even so it is plausible to assume that the first step in the sequence is an attack of the Lewis acid **2** at the carbon atom of the phosphaalkyne **1**.

Metalation Reaction of the Triphosphaalatricycloheptene (5 → 6)

It has been shown elsewhere that phosphorus-carbon-aluminum cage compounds are able to act as ligands in transition metal complexes[5][6]. Complexation of the triphosphaalatricycloheptene **5a** with a carbonylmetal fragment can be realized in an analogous manner. Thus, reactions of compound **5a** with nonacarbonyldiiron[11] or the in situ generated pentacarbonyltungsten tetrahydrofuran complex[12] proceed at room temperature to furnish the transition metal complexes **6a**,**b** in practically quantitative yields (^{31}P-NMR monitoring). After recrystallization from appropriate solvents, compound **6a** is obtained as a dark-red solid (84% yield) and compound **6b** as an orange solid (76% yield).

Scheme 3



6	a	b
L_nM	$W(CO)_5$	$Fe(CO)_4$

The success of the metalation reaction is immediately apparent from the IR spectra of the reaction products **6a**,**b**. Three carbonyl bands appear in each spectrum in the expected wavenumber ranges (**6a**: $\tilde{\nu}$ = 2064, 1992, 1970 cm^{-1}; **6b**: $\tilde{\nu}$ = 2076, 1960, 1948 cm^{-1}). The mass spectra of the compounds **6a**,**b** show that in both cases only one 16-valence-electron fragment has been coordinated to the polycyclic system of **5a**. The $\lambda^3\sigma^2$-phosphorus atom of the P−C double bond functions as two-electron donor to the metal center as is confirmed by the ^{31}P-NMR spectra. Accordingly, the chemical shift of the phosphorus atom P-3 is only marginally influenced by addition of the metal fragment (**5a**: δ = 223.3; **6a**: δ = 232.2; **6b**: δ = 191.0); however, the P-2/P-3 coupling constant is markedly reduced by almost 100 Hz. Furthermore, in the case of the polycyclic compound **6b** the signal at lowest field exhibits a characteristic $^1J_{P,W}$ coupling constant of 234.1 Hz[13].

Both the ^{1}H- and the ^{13}C-NMR spectra are in accord with the proposed structures: they confirm retention of the tricyclic skeleton in the course of the transformations **5a**

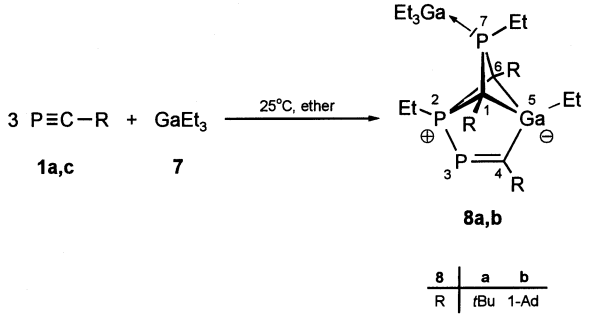
→ **6a**,**b**. In addition, the ^{13}C-NMR spectra proved relevant information about the hapticity of the polycyclic ligands. In the cases of **6a**,**b** the signals of the double-bond carbon atom C-4 experience only slight shifts to higher field in comparison to that of C-4 in the uncomplexed tricyclic compound **5a**. This finding supports the formulation of the transition metal complexes **6a**,**b** as end-on complexes and eliminates the possibility of the existence of a metallophosphacyclopropane structural unit[14].

Although the simple complexation of the tricyclic compound **5a** can easily be achieved under mild reaction conditions, it was not possible to effect complexation of a second 16-valence-electron species. Even in the presence of a large excess of the complexing reagent, the phosphorus atom P-5 remained unchanged. It is probable that the $\lambda^3\sigma^3$-phosphorus atom is sterically so strongly shielded by the three neighboring *tert*-butyl groups and by one of the isobutyl groups on the aluminum atom that an attack of the electrophilic carbonylmetal is not possible.

Generation of the Triphosphagallatricycloheptenes (1 → 8)

In many cases the chemistry of triorganogallium reagents **7** resembles that of the corresponding aluminum compounds **2**[15]. The Lewis acid **7** should thus also be able to initiate a phosphaalkyne cyclooligomerization. Indeed, when a mixture of a phosphaalkyne **1** and triethylgallium (**7**) in diethyl ether is stirred at room temperature for several days its color changes from colorless to orange-brown. Monitoring of the course of reaction by ^{31}P-NMR spectroscopy is indicative of a cyclotrimerization of the organophosphorus compound **1**. After removal of volatile materials under vacuum, recrystallization of the residue from a non-polar solvent furnishes the compounds **8a**,**b** in the

Scheme 4



8	a	b
R	*t*Bu	1-Ad

form of yellow crystals in yields of 49 and 43%, respectively.

The structural relationships between the polycyclic compounds **8** and **5** are clear: both cage compounds have a tricyclo[3.2.0.0^{2,6}]hept-3-ene skeleton. In the case of **8** however, an additional, exocyclic triethylgallium unit is coordinated at a phosphorus atom of the polycyclic system. In addition, the positions of a phosphorus atom and a gallium atom are exchanged in comparison to the polycyclic skeleton of **5**.

Elemental analytical data confirm that compound **8** is composed of three molecules of phosphaalkyne **1** and two molecules of triethylgallium (**7**). The molecular ion peak is not present in the mass spectra of **8** although the fragment ions ($M^+ - Et_3Ga$) are observed in each case.

The NMR spectra provide diagnostic information about the constitutions of compounds **8**. In the case of **8a** the degree of oligomerization is apparent from the three signals appearing in the ^{31}P-NMR spectrum as an ABX spin system. The signal with the chemical shift δ = 253.6 is assigned to the $\lambda^3\sigma^2$-phosphorus atom[8]; the onium phosphorus atom P-2 produces the signal at δ = 41.6. The direct connection between these two phosphorus atoms is reflected in the coupling constant of 336.8 Hz. The signal at δ = 38.2 (P-7) is less characteristic and is split into a double doublet by two $J_{P,P}$ couplings (40.2 Hz and 25.0 Hz).

Information on the constitution of **8a** is also provided by the ^{1}H-NMR spectrum. The signals were assigned with the help of a two-dimensional NMR spectrum (^{1}H,^{1}H-COSY-45 experiment). In addition to two signals for the *tert*-butyl groups (integration ratio 2:1) there is a total of eight signals resulting from the six ethyl substituents. The two multiplets at low field (δ = 2.30−2.37 and δ = 2.05−2.10) are assigned to the α-methylene groups at the phosphorus atoms P-2 and P-7. Furthermore, the ethyl groups of the exocyclic triethylgallium unit give rise to a triplet at δ = 1.52 and a quadruplet at δ = 0.80 in the ^{1}H-NMR spectrum.

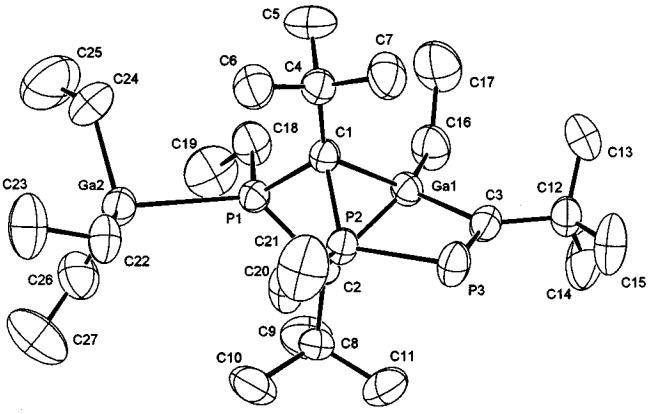
The ^{13}C-NMR spectrum is also in accord with the proposed structure for the polycyclic compound **8a**. The signal for the phosphaalkene carbon atom C-4 appears at relatively high field (δ = 79.0) while the two sp^3-skeletal carbon atoms C-1 and C-6 give rise to a double doublet (J = 23.2 and 16.7 Hz) at δ = 46.5.

The constitutions of the cyclooligomerization products were finally confirmed by an X-ray crystallographic analysis of **8a**. Crystals of the tricyclic compound **8a** are monoclinic, space group $P2_1/n$ (no. 14). A plot of the crystal structure is shown in Figure 1.

The central structural element of compound **8a** is a tricyclo[3.2.0.0^{2,6}]hept-3-ene system bearing an exocyclic triethylgallium unit. The double-bond carbon atom, all phosphorus atoms as well as the gallium atoms lie in the same plane. The sp^3-carbon atoms C-1 and C-2 are arranged in mirror symmetry around this plane.

The bond lengths and angles for compound **8a** are all of the expected magnitude; this holds especially for the P-2−P-3 linkage [2.203(2) Å; ref.[16]: 2.249 Å] and the P−C double bond [1.682(5) Å; ref.[17]: 1.670 Å]. A further characteristic feature, already observed in the structures of the polycyclic compounds **3** and **4**, is the shortening of the P−C single bonds to a $\lambda^4\sigma^4$-phosphorus atom [P-2−C-1: 1.818(4) Å; P-2−C-2: 1.811(5) Å; ref.[16]: 1.80 Å]. In contrast, the distances between the neighboring carbon atoms and the phosphorus atom P-1 are in the typical range for $\lambda^3\sigma^3$-P−C bonds [P-1−C-1: 1.869(4) Å; P-1−C-2: 1.879(4) Å; ref.[16]: 1.86 Å]. These observations, together with the P-1−Ga-2-separation of 2.581(1) Å [ref.[18]: 2.553(2)], support

Figure 1. Molecular structure of **8a**[a]



[a] Selected bond lengths [Å] and angles [°]: P1−C1 1.869(4), P1−C2 1.879(4), P2−C1 1.818(4), P2−C2 1.811(5), C2−Ga1 2.145(4), C1−Ga1 2.180(4), P2−P3 2.203(2), P3−C3 1.682(5), C3−Ga1 2.037(5), P1−P2 2.544(2), P1−Ga1 2.872(1), P2−Ga1 2.584(1), P1−Ga2 2.581(1); C3−Ga1−C1 101.6(2), C2−P1−C1 78.6(2), C3−Ga1−C2 102.6(2), C2−Ga1−C1 66.6(2), C2−P2−C1 81.7(2), C2−P2−P3 113.7(2), C1−P2−P3 113.9(2), C3−P3−P2 92.1(2), P2−C1−P1 87.3(2), P3−C3−Ga1 113.1(3), P1−C2−Ga1 90.8(2), P2−C2−Ga1 81.1(2), P2−C2−P1 87.2(2).

the existence of a donor-acceptor bond between the exocyclic triethylgallium unit and the polycyclic skeleton.

Again in this case of a cyclooligomerization of a kinetically stabilized phosphaalkyne **1** with triethylgallium (**7**), the question of the mechanism of formation of the polycyclic system **8** cannot be answered unambiguously. However, it is still reasonable to assume that the first step also involves an attack of the Lewis acid **7** at the carbon atom of the phosphaalkyne **1**.

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Experimental Section

General Remarks: The reactions were carried out under argon (purity > 99.998%) in a previously oven-dried and evacuated apparatus (Schlenk techniques). The solvents were dried by standard procedures (*n*-pentane, diethyl ether and THF: Na/K alloy), distilled and stored under argon. Melting points: Mettler FP 61 (heating rate: 3°C/min). − FT-IR spectra: Perkin-Elmer infrared spectrometer 16PC. − Mass spectra: Finnigan MAT 90 spectrometer. − NMR spectra: Bruker AMX 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz) and Bruker AC 200 (^{31}P: 81 MHz) spectrometers, solvent as internal standard (^{1}H and ^{13}C); the chemical shifts for ^{31}P are relative to external 85% orthophosphoric acid. Compounds **1a**[19], **1b**[20], **1c**[19], **2c**[15] were prepared by published methods. Compounds **2b**, **7** were purchased from Aldrich and used without further purification.

1,4,6-Tri-tert-butyl-2,7,7-triisobutyl-3,5-diphospha-2-phosphonia-7-aluminatotricyclo[3.2.0.0^{2,6}]hept-3-ene (**5a**): To a magnetically stirred solution of 0.94 g (4.75 mmol) of triisobutylaluminum (**2b**) in diethyl ether (10 ml) was added 1.67 g (16.68 mmol) of phosphaalkyne **1a**. After the reaction mixture had been heated to 100°C for 10 h in a Schlenk pressure tube, all volatile components were removed at 25°C/10^{-3} mbar. The remaining crude product was purified by bulb-to-bulb distillation (150°C/10^{-3} mbar): 1.56 g, 66% yield, yellow oil. − IR (pentane, cm^{-1}): $\tilde{\nu}$ = 1210 (s), 1200 (s), 1090 (s), 810 (s), 790 (s), 680 (s). − ^{31}P NMR (C_6D_6): δ = 36.5 (dd, $^2J_{P,P}$ = 32.2 Hz, $^2J_{P,P}$ = 19.0 Hz, P-5), 53.9 (dd, $^1J_{P,P}$ = 299.2 Hz, $^2J_{P,P}$ = 32.2 Hz, P-2), 223.3 (dd, $^1J_{P,P}$ = 299.2 Hz, $^2J_{P,P}$ = 19.0 Hz, P-3). − ^{1}H NMR (C_6D_6): δ = 0.46 [d, $^3J_{H,H}$ = 7.2 Hz, 2 H, AlCH_2CH(CH$_3$)$_2$], 0.64 [dd, $^4J_{H,P}$ = 2.3 Hz, $^3J_{H,H}$ = 7.1 Hz, 2 H, AlCH_2CH(CH$_3$)$_2$], 0.96 [d, $^3J_{H,H}$ = 6.7 Hz, 6 H, P-2-CH$_2$CH(CH_3)$_2$], 1.05 [s, 18 H, 2 C(CH_3)$_3$], 1.24 [d, $^3J_{H,H}$ = 6.5 Hz, 6 H, AlCH$_2$CH(CH_3)$_2$], 1.25 [d, $^3J_{H,H}$ = 6.5 Hz, 6 H, AlCH$_2$CH(CH_3)$_2$], 1.37 [s, 9 H, C(CH_3)$_3$], 2.08−2.22 [m, 2 H, AlCH$_2$CH(CH$_3$)$_2$ and P-2-CH$_2$CH(CH$_3$)$_2$], 2.22−2.32 [m, 1 H, AlCH$_2$CH(CH$_3$)$_2$], 2.36 [d-pseudo-t, $^2J_{H,P}$ = 7.3 Hz, $J_{H,P}$ = 2.0 Hz, $^3J_{H,H}$ = 7.3 Hz, 2 H, P-2-CH_2CH(CH$_3$)$_2$]. − ^{13}C NMR (C_6D_6): δ = 24.7 [pseudo-t, $J_{C,P}$ = 4.9 Hz, $J_{C,P}$ = 4.9 Hz, P-2-CH$_2$CH(CH_3)$_2$], 26.3 [s, broad, 2 AlCH_2CH(CH$_3$)$_2$], 26.8 [s, broad, CH$_2$CH(CH$_3$)$_2$], 27.8 [d, $J_{C,P}$ = 3.1 Hz, CH$_2$CH(CH$_3$)$_2$], 27.9 [s, CH$_2$CH(CH_3)$_2$], 29.1 [s, AlCH$_2$CH(CH_3)$_2$], 29.3 [s, AlCH$_2$CH(CH_3)$_2$], 32.1 [pseudo-t, $J_{C,P}$ = 9.0 Hz, $J_{C,P}$ = 9.0 Hz, C-4-C(CH_3)$_3$], 34.6 [dd, $J_{C,P}$ = 7.5 Hz, $J_{C,P}$ = 5.5 Hz, C-1/6-C(CH_3)$_3$], 35.8 [s, broad, 3C(CH$_3$)$_3$], 44.7 (d-pseudo-t, $^1J_{C,P}$ = 20.8 Hz, $J_{C,P}$ = 10.4 Hz, $J_{C,P}$ = 10.4 Hz, C-1/6), 47.2 [dd, $^1J_{C,P}$ = 24.6 Hz, $J_{C,P}$ = 10.5 Hz, P-2-CH_2CH(CH$_3$)$_2$], 104.4 (dd, $^1J_{C,P}$ = 50.2 Hz, $^1J_{C,P}$ = 13.4 Hz, C-4). − MS (CI, 120 eV); *m/z* (%): 500 (5) [M$^+$ + 2 H], 499 (17) [M$^+$ + H], 442 (24) [M$^+$ − C$_4$H$_8$], 441 (100) [M$^+$ − C$_4$H$_9$], 341 (4) [M$^+$ − C$_4$H$_9$ − PC$_5$H$_9$]. − $C_{27}H_{54}AlP_3$ (498.63): calcd. C 65.04, H 10.92; found C 63.5, H 11.2.

1,4,6-Tris(1,1-dimethylpropyl)-2,7,7-triisobutyl-3,5-diphospha-2-phosphonia-7-aluminatotricyclo[3.2.0.0^{2,6}]hept-3-ene (**5b**): To a magnetically stirred solution of 0.20 g (1.00 mmol) of triisobutylaluminum (**2b**) in diethyl ether (10 ml) was added 0.40 g (3.50 mmol) of phosphaalkyne **1b** (32 mol-% solution in hexamethyldisiloxane). After the reaction mixture had been heated to 100°C for 6 h in a Schlenk pressure tube, all volatile components were removed at 25°C/10^{-3} mbar. The remaining crude product was purified by bulb-to-bulb distillation (200°C/10^{-3} mbar): 0.25 g, 46% yield, yellow oil. − IR (pentane, cm^{-1}): $\tilde{\nu}$ = 1380 (s), 1362 (m), 1166 (m), 1100 (m), 1060 (m), 1014 (m), 796 (m), 670 (s). − ^{31}P NMR (C_6D_6): δ = 36.7 (dd, $^2J_{P,P}$ = 32.8 Hz, $^2J_{P,P}$ = 18.7 Hz, P-5), 52.7 (dd, $^1J_{P,P}$ = 299.1 Hz, $^2J_{P,P}$ = 32.8 Hz, P-2), 228.7 (dd, $^1J_{P,P}$ = 299.1 Hz, $^2J_{P,P}$ = 18.7 Hz, P-3). − ^{1}H NMR (C_6D_6): δ = 0.56 [d, $^3J_{H,H}$ = 7.2 Hz, 2 H, AlCH_2CH(CH$_3$)$_2$], 0.76 [dd, $J_{H,P}$ = 2.3 Hz, $^3J_{H,H}$ = 7.1 Hz, 2 H, AlCH_2CH(CH$_3$)$_2$], 0.82 [t, $^3J_{H,H}$ = 7.5 Hz, 6 H, 2 C(CH$_3$)$_2$CH$_2$CH_3], 0.87 [t, $^3J_{H,H}$ = 7.5 Hz, 3 H, C(CH$_3$)$_2$CH$_2$CH_3], 0.96 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH$_2$CH(CH_3)$_2$], 1.01 [s, broad, 6 H, C(CH_3)$_2$CH$_2$CH$_3$], 1.04 [s, broad, 6 H, C(CH_3)$_2$CH$_2$CH$_3$], 1.31 [d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH$_2$CH(CH_3)$_2$], 1.33 [d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH$_2$CH(CH_3)$_2$], 1.33 [s, broad, 6 H, C(CH_3)$_2$CH$_2$CH$_3$], 1.45−1.55 [m, 4 H, 2 C(CH$_3$)$_2$CH_2CH$_3$], 1.79 [q, 2 H, $^3J_{H,H}$ = 7.5 Hz, C(CH$_3$)$_2$CH_2CH$_3$], 2.12−2.23 [m, 1 H, CH$_2$CH(CH$_3$)$_2$], 2.22−2.31 [m, 1 H, CH$_2$CH(CH$_3$)$_2$], 2.30−2.41 [m, 1 H, CH$_2$CH(CH$_3$)$_2$], 2.45 [pseudo-t, broad, $^2J_{H,P}$ = 6.2 Hz, $^3J_{H,H}$ = 6.2 Hz, 2 H, P-2-CH_2CH(CH$_3$)$_2$]. − ^{13}C NMR (C_6D_6): δ = 9.2 [s, C(CH$_3$)$_2$CH$_2$CH_3], 9.3 [s, 2 C(CH$_3$)$_2$CH$_2$CH$_3$], 24.7 [pseudo-t, $J_{C,P}$ = 5.0 Hz, $J_{C,P}$ = 5.0 Hz, P-2-CH$_2$CH(CH_3)$_2$], 27.0 [s, broad, CH$_2$CH(CH$_3$)$_2$], 27.8 [d, $J_{C,P}$ = 3.0 Hz, CH$_2$CH(CH$_3$)$_2$], 27.9 [s, CH$_2$CH(CH_3)$_2$], 29.1 [s, AlCH$_2$CH(CH_3)$_2$], 29.3 [s, AlCH$_2$CH(CH_3)$_2$], 30.1 [pseudo-t, broad, $J_{C,P}$ = 6.3 Hz, $J_{C,P}$ = 6.3 Hz, 2 C(CH_3)$_2$CH$_2$CH$_3$], 30.9 [pseudo-t, $J_{C,P}$ = 6.1 Hz, $J_{C,P}$ = 6.1 Hz, C(CH_3)$_2$CH$_2$CH$_3$], 38.5 [pseudo-t, $J_{C,P}$ = 2.2 Hz, $J_{C,P}$ = 2.2 Hz, 2 C(CH$_3$)$_2$CH_2CH$_3$], 39.1 [dd, $J_{C,P}$ = 8.5 Hz, $J_{C,P}$ = 5.8 Hz, C-4-C(CH$_3$)$_2$CH$_2$CH$_3$], 40.1 [m, C(CH$_3$)$_2$CH$_2$CH$_3$], 47.3 [m, C1/6 and P-2-CH_2CH(CH$_3$)$_2$], 105.3 (dd, $^1J_{C,P}$ = 51.5 Hz, $^1J_{C,P}$ = 14.0 Hz, C-4)[21]. − MS (EI, 70 eV); *m/z* (%): 540 (1) [M$^+$], 484 (14)

[$M^+ - C_4H_8$], 483 (48) [$M^+ - C_4H_9$], 427 (41) [$M^+ - C_4H_9 - C_4H_8$], 369 (100) [$M^+ - 3\ C_4H_9$]. – MS (CI, 120 eV); *m/z* (%): 541 (17) [$M^+ + H$], 483 (37) [$M^+ - C_4H_9$], 345 (100) [$M^+ - 3\ C_4H_8 - Al$]. – HR MS (EI): calcd. 540.3723; found 540.3755. – $C_{30}H_{60}AlP_3$ (540.70).

1,4,6-Triadamant-1-yl-2,7,7-triisobutyl-3,5-diphospha-2-phosphonia-7-aluminatotricyclo[3.2.0.0^{2,6}]hept-3-ene (**5c**): To a magnetically stirred solution of 0.15 g (0.76 mmol) of triisobutylaluminum (**2b**) in diethyl ether (10 ml) was added 0.47 g (2.66 mmol) of phosphaalkyne **1c**. After the reaction mixture had been stirred at room temperature for 3 weeks, all volatile components were removed at 120°C/10^{-3} mbar. The remaining crude product was taken up in pentane and purified by recrystallization at low temperatures: 0.20 g, 36% yield, yellow oil. – ^{31}P NMR (C_6D_6): δ = 26.5 (dd, $^2J_{P,P}$ = 33.2 Hz, $^2J_{P,P}$ = 16.3 Hz, P-5), 51.7 (dd, $^1J_{P,P}$ = 299.4 Hz, $^2J_{P,P}$ = 33.2 Hz, P-2), 227.3 (dd, $^1J_{P,P}$ = 299.4 Hz, $^2J_{P,P}$ = 16.3 Hz, P-3). – ^{1}H NMR (C_6D_6): δ = 0.54 [d, $^3J_{H,H}$ = 7.3 Hz, 2 H, AlC*H*$_2$CH(CH$_3$)$_2$], 0.72 [d, broad, $^3J_{H,H}$ = 7.3, 2 H, AlC*H*$_2$CH(CH$_3$)$_2$], 1.05 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.30 [d, $^3J_{H,H}$ = 6.4 Hz, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.30 [d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.58–2.16 (m, 45 H, Ad-H), 2.19–2.33 [m, 3 H, 3 CH$_2$C*H*(CH$_3$)$_2$], 2.50 [pseudo-t, broad, $^2J_{H,P}$ = 6.8 Hz, $^3J_{H,H}$ = 6.8 Hz, 2 H, P-2-C*H*$_2$CH(CH$_3$)$_2$]. – ^{13}C NMR (C_6D_6): δ = 24.8 [s, broad, P-2-CH$_2$CH(*C*H$_3$)$_2$], 26.7 [s, broad, 2 AlCH$_2$CH(*C*H$_3$)$_2$], 27.3 [s, broad, CH$_2$*C*H(CH$_3$)$_2$], 28.0 [s, CH$_2$*C*H(CH$_3$)$_2$], 28.1 [s, CH$_2$*C*H(CH$_3$)$_2$], 29.1 (s), 29.3 (s), 29.4 (s), 29.5 (s, 6 Ad-C), 36.8 (s, 3 Ad-C), 37.1 (s, 6 Ad-C), 38.3 (s, 2 Ad-C), 44.1 (s, Ad-C), 45.1 (s, broad, 3 Ad-C), 47.3 [m, C-1/6 and P-2-*C*H$_2$CH(CH$_3$)$_2$], 48.1 [pseudo-t, $J_{C,P}$ = 6.0 Hz, $J_{C,P}$ = 6.0 Hz, 6 Ad-C], 105.7 (dd, $^1J_{C,P}$ = 50.8 Hz, $^1J_{C,P}$ = 13.4 Hz, C-4). – MS (EI, 70 eV); *m/z* (%): 732 (1) [M^+], 675 (2) [$M^+ - C_4H_9$], 591 (5) [$M^+ - Al(C_4H_9)_2$], 325 (34) [$M^+ - 2\ H - 3\ C_{10}H_{15}$], 135 (100) [$C_{10}H_{15}^+$]. – $C_{45}H_{72}AlP_3$ (732.97).

1,4,6-Tri-tert-butyl-2,7,7-tris(2-phenylpropyl)-3,5-diphospha-2-phosphonia-7-aluminatotricyclo[3.2.0.0^{2,6}]hept-3-ene (**5d**): To a magnetically stirred solution of 0.31 g (0.80 mmol) of triorganoaluminum **2c** in pentane (8 ml) was added 0.28 g (2.80 mmol) of phosphaalkyne **1a** at −78°C. After the reaction mixture had been allowed to warm to room temperature and stirred for 3 d, all volatile components were removed at 25°C/10^{-3} mbar. Recrystallization from pentane at +4°C gave pure **5d** as a mixture of four diastereomers (**A**–**D**): 0.45 g, 82% yield, yellow crystals, m.p. 128–130°C. – IR (KBr, cm^{-1}): ṽ = 3024 (w, C=CH), 2956 (s, CH), 2862 (s, CH), 1600 (w), 1492 (m), 1452 (m), 1386 (w), 1360 (m), 1028 (m), 806 (m), 760 (s), 700 (s). – ^{31}P NMR (C_7D_8, 105°C): **5dA**: δ = 43.8 (dd, $^2J_{P,P}$ = 34.9 Hz, $^2J_{P,P}$ = 17.6 Hz, P-5), 60.0 (dd, $^1J_{P,P}$ = 299.9 Hz, $^2J_{P,P}$ = 34.9 Hz, P-2), 230.0 (dd, $^1J_{P,P}$ = 299.9 Hz, $^2J_{P,P}$ = 17.6 Hz, P-3). – **5dB**: δ = 43.8 (dd, $^2J_{P,P}$ = 34.9 Hz, $^2J_{P,P}$ = 15.6 Hz, P-5), 60.0 (dd, $^1J_{P,P}$ = 299.9 Hz, $^2J_{P,P}$ = 34.9 Hz, P-2), 229.9 (dd, $^1J_{P,P}$ = 299.9 Hz, $^2J_{P,P}$ = 15.6 Hz, P-3). – **5dC**: δ = 42.0 (dd, $^2J_{P,P}$ = 35.2 Hz, $^2J_{P,P}$ = 18.8 Hz, P-5), 57.7 (dd, $^1J_{P,P}$ = 306.7 Hz, $^2J_{P,P}$ = 35.2 Hz, P-2), 229.0 (dd, $^1J_{P,P}$ = 306.7 Hz, $^2J_{P,P}$ = 18.8 Hz, P-3). – **5dD**: δ = 42.0 (dd, $^2J_{P,P}$ = 35.2 Hz, $^2J_{P,P}$ = 18.8 Hz, P-5), 57.6 (dd, $^1J_{P,P}$ = 306.4 Hz, $^2J_{P,P}$ = 35.2 Hz, P-2), 228.8 (dd, $^1J_{P,P}$ = 306.4 Hz, $^2J_{P,P}$ = 18.8 Hz, P-3). – ^{1}H NMR (C_6D_6): δ = 0.86 (s, broad, 24 H), 0.91 (s, broad, 12 H), 0.96 (s, broad, 24 H), 1.01 (s, broad, 12 H), 1.19-1.24 (m, 16 H), 1.30 (s, broad, 36 H), 1.59–1.69 (m, 36 H), 2.67–2.87 (m, 4 H), 2.89–3.00 (m, 4 H), 3.22–3.38 (m, 8 H), 3.43–3.50 (m, 4 H), 6.99–7.19 (m, 28 H), 7.22–7.28 (m, 16 H), 7.33–7.42 (m, 8 H), 7.48–7.52 (m, 8 H). – ^{13}C NMR (C_6D_6): δ = 24.1 (s), 25.6 (m), 26.8 (s, broad), 27.9 (s), 28.0 (s), 28.1 (s), 28.3 (s), 28.8 (s), 29.1 (s), 32.0 (m), 34.5 (m), 35.4 (m), 35.6 (m), 38.2 (s, broad), 39.2 (s, broad), 39.3 (s, broad), 44.3–44.8 (m, 4 C-1/6), 46.2–46.9 [m, 4 P-2-*C*H$_2$CH(Ph)CH$_3$], 104.4 (d, broad, $^1J_{C,P}$ = 50.3 Hz, 4 C-4), 125.5 (s, broad), 125.6 (s, broad), 126.8 (m), 127.2 (s, broad), 127.3 (s, broad), 127.4 (s, broad), 128.6 (s, broad), 128.7 (m), 129.3 (m), 145.1 (s, broad), 153.4 (d, $J_{C,P}$ = 14.4 Hz), 153.5 (s). – MS (EI, 70 eV); *m/z* (%): 684 (1) [M^+], 683 (2) [$M^+ - H$], 564 (100) [$M^+ - H - C_9H_{11}$], 465 (60) [$M^+ - C_9H_{11} - PC_5H_9$], 365 (59) [$M^+ - C_9H_{11} - 2\ PC_5H_9$], 265 (74) [$M^+ - C_9H_{11} - 3\ PC_5H_9$], 119 (31) [$C_9H_{11}^+$]. – $C_{42}H_{60}AlP_3$ (684.85).

Tetracarbonyl{(3-η)-1,4,6-tri-tert-butyl-2,7,7-triisobutyl-3,5-diphospha-2-phosphonia-7-aluminatotricyclo[3.2.0.0^{2,6}]hept-3-ene}iron (**6a**): Nonacarbonyldiiron (0.54 g, 1.50 mmol) was added to a solution of triphosphaalatricycloheptene **5a** (0.25 g, 0.50 mmol) in pentane (15 ml) at 25°C. The reaction mixture was allowed to stir for 2 d, followed by a filtration to remove all insoluble components. Recrystallization of the crude product from the remaining solution at −78°C provided 0.28 g of **6a** (84%), red crystals, m.p. 108 – 110°C. – IR (pentane, cm^{-1}): ṽ = 2064 (s, CO), 1992 (s, CO), 1970 (s, CO), 1260 (w), 1100 (w), 1020 (w), 812 (w), 670 (m), 634 (m). – ^{31}P NMR (C_6D_6): δ = 39.4 (dd, $^2J_{P,P}$ = 50.1 Hz, $^2J_{P,P}$ = 19.0 Hz, P-5), 48.2 (dd, $^1J_{P,P}$ = 206.0 Hz, $^2J_{P,P}$ = 50.1 Hz, P-2), 232.2 (dd, $^1J_{P,P}$ = 206.0 Hz, $^2J_{P,P}$ = 19.0 Hz, P-3). – ^{1}H NMR (C_6D_6): δ = 0.43 [d, $^3J_{H,H}$ = 7.2 Hz, 2 H, AlC*H*$_2$CH(CH$_3$)$_2$], 0.69 [d, broad, $^3J_{H,H}$ = 5.7 Hz, 2 H, AlC*H*$_2$CH(CH$_3$)$_2$], 1.02 [s, broad, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.10 [s, 18 H, 2 C(C*H*$_3$)$_3$], 1.25 [d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.28 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.35 [s, 9 H, C(C*H*$_3$)$_3$], 2.14–2.25 [m, 1 H, CH$_2$C*H*(CH$_3$)$_2$], 2.26–2.32 [m, 1 H, CH$_2$C*H*(CH$_3$)$_2$], 2.35–2.46 [m, 3 H, CH$_2$C*H*(CH$_3$)$_2$ and P-2-C*H*$_2$CH(CH$_3$)$_2$]. – ^{13}C NMR (C_6D_6): δ = 24.8 [d, $^3J_{C,P}$ = 7.0 Hz, P-2-CH$_2$CH(*C*H$_3$)$_2$], 25.3 [d, $J_{C,P}$ = 4.8 Hz, CH$_2$*C*H(CH$_3$)$_2$], 25.7 [s, broad, 2 AlCH$_2$CH(*C*H$_3$)$_2$], 27.8 [s, broad, 2 CH$_2$*C*H(CH$_3$)$_2$], 29.0 [s, AlCH$_2$CH(*C*H$_3$)$_2$], 29.1 [s, AlCH$_2$CH(*C*H$_3$)$_2$], 31.7 [pseudo-t, $J_{C,P}$ = 10.1 Hz, $J_{C,P}$ = 10.1 Hz, C-4-C(*C*H$_3$)$_3$], 34.2 [pseudo-t, $J_{C,P}$ = 6.5 Hz, $J_{C,P}$ = 6.5 Hz, C-1/6-C(*C*H$_3$)$_3$], 35.4 [s, broad, C-1/6-*C*(CH$_3$)$_3$ and C-4-*C*(CH$_3$)$_3$], 44.3 [m, P-2-*C*H$_2$CH(CH$_3$)$_2$ and C-1/6], 101.3 (dd, $^1J_{C,P}$ = 51.0 Hz, $^1J_{C,P}$ = 15.9 Hz, C-4), 215.1 (d, $^2J_{C,P}$ = 12.0 Hz, 4 CO). – MS (CI, 120 eV); *m/z* (%): 667 (14) [$M^+ + H$], 609 (19) [$M^+ - 2\ CO - H$], 499 (49) [$M^+ + H - Fe(CO)_4$], 442 (24) [$M^+ - Fe(CO)_4 - C_4H_8$], 441 (100) [$M^+ - Fe(CO)_4 - C_4H_9$]. – $C_{31}H_{54}AlFeO_4P_3$ (666.51).

Pentacarbonyl{(3-η)-1,4,6-tri-tert-butyl-2,7,7-triisobutyl-3,5-diphospha-2-phosphonia-7-aluminatotricyclo[3.2.0.0^{2,6}]hept-3-ene}tungsten (**6b**): A solution of hexacarbonyltungsten (0.35 g, 1.00 mmol) in THF (50 ml) was irradiated at 0°C. After 0.5 h triphosphaalatricycloheptene **5a** (0.20 g, 0.40 mmol) in THF (5 ml) was added at 25°C and the reaction mixture was allowed to stir for 14 h, followed by evaporation of all volatile components (25°C/10^{-3} mbar). The residue was extracted with pentane (10 ml) and filtered. Recrystallization at −78°C from the same solvent provided 0.25 g of **6b** (76%), orange crystals. – IR (pentane, cm^{-1}): ṽ = 2076 (m, CO), 1960 (s, CO), 1948 (s, CO), 1260 (m), 1100 (m), 1018 (m), 806 (m). – ^{31}P NMR (C_6D_6): δ = 40.0 (dd, $^2J_{P,P}$ = 52.7 Hz, $^2J_{P,P}$ = 15.6 Hz, P-5), 59.6 (dd, $^2J_{P,W}$ = 24.4 Hz, $^1J_{P,P}$ = 199.0 Hz, $^2J_{P,P}$ = 52.7 Hz, P-2), 191.0 (dd, $^1J_{P,W}$ = 234.1 Hz, $^1J_{P,P}$ = 199.0 Hz, $^2J_{P,P}$ = 15.6 Hz, P-3). – ^{1}H NMR (C_6D_6): δ = 0.47 [d, $^3J_{H,H}$ = 7.3 Hz, 2 H, AlC*H*$_2$CH(CH$_3$)$_2$], 0.72 [dd, $J_{P,H}$ = 2.6 Hz, $^3J_{H,H}$ = 7.3 Hz, 2 H, AlC*H*$_2$CH(CH$_3$)$_2$], 1.05 [d, $^3J_{H,H}$ = 6.4 Hz, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.10 [s, 18 H, 2 C(C*H*$_3$)$_3$], 1.26 [d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.29 [d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.41 [s, 9 H, C(C*H*$_3$)$_3$], 2.14–2.25 [m, 1 H, CH$_2$C*H*(CH$_3$)$_2$], 2.25–2.33 [m, 1 H, CH$_2$C*H*(CH$_3$)$_2$], 2.46–2.59 [m, 3 H, CH$_2$C*H*(CH$_3$)$_2$ and P-2-C*H*$_2$CH(CH$_3$)$_2$]. – ^{13}C NMR (C_6D_6): δ =

25.2 [d, $J_{C,P}$ = 7.0 Hz, P-2-$CH_2CH(CH_3)_2$], 25.4 [d, $J_{C,P}$ = 4.9 Hz, $CH_2CH(CH_3)_2$], 26.5 [s, broad, 2 $AlCH_2CH(CH_3)_2$], 27.7 [s, $CH_2CH(CH_3)_2$], 27.8 [s, $CH_2CH(CH_3)_2$], 29.0 [s, $AlCH_2CH(CH_3)_2$], 29.1 [s, $AlCH_2CH(CH_3)_2$], 32.4 [pseudo-t, $J_{C,P}$ = 10.3 Hz, $J_{C,P}$ = 10.3 Hz, C-4-$C(CH_3)_3$], 34.2 [pseudo-t, $J_{C,P}$ = 6.8 Hz, $J_{C,P}$ = 6.8 Hz, C-1/6-$C(CH_3)_3$], 35.5 [s, broad, C-1/6-$C(CH_3)_3$ and C-4-$C(CH_3)_3$], 44.4 [dd, $^1J_{C,P}$ = 23.2 Hz, $J_{C,P}$ = 8.6 Hz, P-2-$CH_2CH(CH_3)_2$], 45.9 (m, C-1/6), 101.3 (dd, $^1J_{C,P}$ = 50.5 Hz, $^1J_{C,P}$ = 15.0 Hz, C-4), 195.9 (d, $^2J_{C,P}$ = 8.1 Hz, $^1J_{C,W}$ = 130.4 Hz, 4 *cis*-CO), 198.4 (d, $^2J_{C,P}$ = 31.8 Hz, *trans*-CO). – MS (CI, 120 eV); *m/z* (%): 823 (1) [M^+ + H], 767 (3) [M^+ + H – 2 CO], 683 (2) [M^+ + H – 5 CO], 499 (21) [M^+ + H – $W(CO)_5$], 441 (100) [M^+ + H – $W(CO)_5$ – C_4H_{10}]. – $C_{32}H_{54}AlO_5P_3W$ (822.53).

Triethyl{(7-η)-1,4,6-tri-tert-butyl-2,5,7-triethyl-3,7-diphospha-2-phosphonia-5-gallatotricyclo-[3.2.0.0^{2,6}]hept-3-ene}gallium (**8a**): To a magnetically stirred solution of 0.25 g (1.60 mmol) of triethylgallium (**7**) in diethyl ether (10 ml) was added 0.48 g (4.80 mmol) of phosphaalkyne **1a**. After the reaction mixture had been stirred at room temperature for 48 h, all volatile components were removed at 25°C/10^{-3} mbar. The remaining crude product was taken up in pentane and purified by recrystallization at +4°C: 0.48 g, 49% yield, yellow crystals, m.p. 45–48°C. – IR (pentane, cm^{-1}): $\tilde{\nu}$ = 1360 (s), 1260 (s), 1238 (m), 1100 (s), 1020 (s), 806 (s), 692 (m), 656 (m). – ^{31}P NMR (C_6D_6): δ = 38.2 (dd, $^2J_{P,P}$ = 40.2 Hz, $^2J_{P,P}$ = 25.0 Hz, P-7), 41.6 (dd, $^1J_{P,P}$ = 336.8 Hz, $^2J_{P,P}$ = 40.2 Hz, P-2), 253.6 (dd, $^1J_{P,P}$ = 336.8 Hz, $^2J_{P,P}$ = 25.0 Hz, P-3). – ^{1}H NMR (C_6D_6): δ = 0.80 [q, $^3J_{H,H}$ = 8.1 Hz, 6 H, $Ga(CH_2CH_3)_3$], 0.94 (q, $^3J_{H,H}$ = 8.0 Hz, 2 H, $GaCH_2CH_3$), 1.03 [s, 18 H, 2 C-1/6-$C(CH_3)_3$], 1.30–1.35 (m, 6 H, 2 PCH_2CH_3), 1.31 [d, $J_{P,H}$ = 1.5 Hz, 9 H, C-4-$C(CH_3)_3$], 1.36 (t, $^3J_{H,H}$ = 8.0 Hz, 3 H, $GaCH_2CH_3$), 1.52 (t, $^3J_{H,H}$ = 8.1 Hz, 9 H, 3 $GaCH_2CH_3$), 2.05–2.10 (m, 2 H, PCH_2CH_3), 2.30–2.37 (m, 2 H, PCH_2CH_3). – ^{13}C NMR (C_6D_6): δ = 7.1 (s, broad, CH_2CH_3), 10.8 (s, CH_2CH_3), 10.9 (d, $J_{C,P}$ = 4.9 Hz, CH_2CH_3), 11.0 (d, $J_{C,P}$ = 4.8 Hz, CH_2CH_3), 11.8 (d, $J_{C,P}$ = 13.2 Hz, CH_2CH_3), 12.0 (s, CH_2CH_3), 14.1 (d, $J_{C,P}$ = 14.6 Hz, CH_2CH_3), 18.8 (s, broad, CH_2CH_3), 29.2 [pseudo-t, $J_{C,P}$ = 26.8 Hz, $J_{C,P}$ = 26.8 Hz, C-4-$C(CH_3)_3$], 31.6 [d, $J_{C,P}$ = 13.6 Hz, C-4-$C(CH_3)_3$], 34.4 [dd, $J_{C,P}$ = 7.5 Hz, $J_{C,P}$ = 4.9 Hz, C-1/6-$C(CH_3)_3$], 35.1 [dd, $J_{C,P}$ = 4.9 Hz, $J_{C,P}$ = 1.6 Hz, C-1/6-$C(CH_3)_3$], 46.5 (dd, $^1J_{C,P}$ = 23.2 Hz, $^1J_{C,P}$ = 16.7 Hz, C-1/6), 79.0 (d, broad, $^1J_{C,P}$ = 15.0 Hz, C-4). – MS (EI, 70 eV); *m/z* (%): 457 (34) [M^+ + H – $Ga(C_2H_5)_3$], 428 (100) [M^+ – $Ga(C_2H_5)_3$ – C_2H_4], 328 (76) [M^+ – $Ga(C_2H_5)_3$ – C_2H_4 – PC_5H_9], 227 (93) [M^+ – $Ga(C_2H_5)_3$ – C_2H_5 – 2 PC_5H_9]. – HR MS (EI, 70 eV); [M^+ – $Ga(C_2H_5)_3$]: calcd. 456.1755; found 456.1761. – $C_{27}H_{57}Ga_2P_3$ (614.10): calcd. C 52.81, H 9.36; found C 50.28, H 9.00.

Triethyl{(7-η)-1,4,6-triadamant-1-yl-2,5,7-triethyl-3,7-diphospha-2-phosphonia-5-gallatotricyclo[3.2.0.0^{2,6}]hept-3-ene}gallium (**8b**): To a magnetically stirred solution of 0.13 g (0.83 mmol) of triethylgallium (**7**) in diethyl ether (10 ml) was added 0.44 g (2.50 mmol) of phosphaalkyne **1c**. After the reaction mixture had been stirred at room temperature for 72 h, all volatile components were removed at 25°C/10^{-3} mbar. The remaining crude product was taken up in pentane and purified by recrystallization at +4°C: 0.30 g, 43% yield, yellow crystals. – IR (pentane, cm^{-1}): $\tilde{\nu}$ = 1260 (s), 1100 (s), 1020 (s), 806 (s). – ^{31}P NMR (C_6D_6): δ = 36.1 (dd, $^1J_{P,P}$ = 333.8 Hz, $^2J_{P,P}$ = 58.6 Hz, P-2), 40.3 (dd, $^2J_{P,P}$ = 58.6 Hz, $^2J_{P,P}$ = 27.2 Hz, P-7), 257.0 (dd, $^1J_{P,P}$ = 333.8 Hz, $^2J_{P,P}$ = 27.2 Hz, P-3). – ^{1}H NMR (C_6D_6): δ = 1.22 (q, $^3J_{H,H}$ = 7.9 Hz, 2 H, CH_2CH_3), 1.35–2.20 (m, 71 H, CH_2CH_3 and Ad-H), 2.35–2.45 (m, 2 H, PCH_2CH_3). – MS (CI, 120 eV); *m/z* (%): 661 (1) [M^+ – $Ga(C_2H_5)_3$ – C_2H_5], 495 (25) [M^+ – $Ga(C_2H_5)_3$ – 2 C_2H_6 – $C_{10}H_{15}$], 255 (100) [M^+ – $Ga(C_2H_5)_3$ – C_2H_6 – 3 $C_{10}H_{15}$]. – $C_{45}H_{75}Ga_2P_3$ (848.44).

Crystal Structure Analysis of **8a**[22]: Enraf-Nonius CAD4 diffractometer, graphite monochromator, Mo-K_α radiation, structure solution by heavy-atom method (SHELXS-97[23]) and structure refinement by SHELXL-97[24]; monoclinic, space group $P2_1/n$; lattice constants a = 11.191(2), b = 20.303(3); c = 15.156(2) Å, β = 107.95(1)°, V = 3276.0(7) Å^3, Z = 4, μ(Mo-K_α) = 1.804 mm^{-1}, crystal size 0.25 × 0.35 × 0.39 mm; θ_{max} = 27.4°; 7470 independent reflections (R_{int} = 0.0453) measured of which 3670 were considered observed with $I > 2\sigma(I)$; analytical absorption correction: max./min. transmission 0.5061/0.6588; max./min. residual electronic density 0.351 and −0.475 e/Å^3. 289 parameters [C, Ga and P anisotropic, the positions of the H atoms were calculated for idealized positions (d_{C-H} = 0.980 Å)]; R_1 = 0.0462; wR^2 = 0.1009.

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[22] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101440. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].
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