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Lewis Acid Mediated Spirocyclotrimerization of Kinetically Stabilized Phosphaalkynes – Key Step for the Selective Generation and Trapping of Triphospha Dewar Benzenes☆

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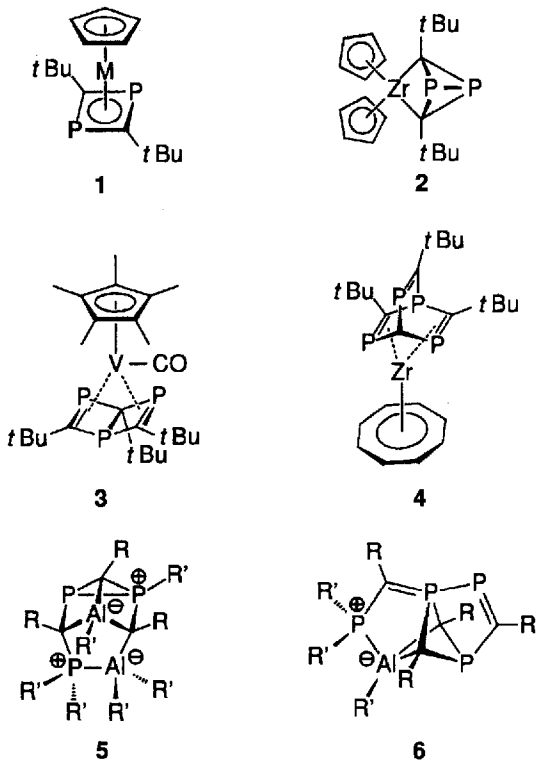
In the presence of Lewis acidic derivatives of group 13 elements, phosphaalkynes **7** undergo spirocyclotrimerization with incorporation of the corresponding Lewis acids to form **10a–f**. Scope and limitations of this novel cyclooligomerization process are examined. Starting from the spirocyclotrimer **10a** reaction with the Lewis base dimethyl sulfoxide, we have in hand for the first time a method for the selective generation of two isomeric triphospha Dewar benzene derivatives (**18**, **19**). Both can be trapped efficiently by further reaction with the phosphaalkyne to furnish the two novel phosphaalkyne cyclotetramers **20** and **21**, both still possessing a phosphorus–carbon double bond. In the case of **21**, further functionalization of the phosphaalkene unit is possible by [3 + 2] cycloaddition with a nitrile oxide (→ **23**).

Major advances in phosphaalkyne cyclooligomerization chemistry stem from transition-metal-mediated cyclooligomerization processes in which the transition-metal fragment is incorporated into the product. Along this line, phosphaalkyne cyclodimerizations, trimerizations, and tetramerizations were realized and furnished the corresponding transition-metal complexes **1**[2], **2**[3], **3**[4], and **4**[5]. For synthetic purposes, the ability to liberate the organophoshorus ligand from the metal fragment is desirable so that it can be used further as a versatile building block, especially in the synthesis of the theoretically and preparatively interesting class of phosphorus-carbon cage compounds. Although in the case of the zirconium species **2**[6] and **4**[5] this goal was reached, for the complexes **1** and **3** no such solution has yet been found.

We therefore sought a metal fragment which is capable of performing the phosphaalkyne cyclooligomerization, but still gives us the option to remove the metal fragment in a later synthetic step. In this context we developed a trialkylaluminum-mediated cyclooligomerization of phosphaalkynes[7]. Depending on the nature of the solvent, a highly selective formation of either a 2:3 (trialkylaluminum/phosphaalkyne) adduct **5** or a 1:4 (trialkylaluminum/phosphaalkyne) adduct **6** was observed, both representing the first examples of aluminum-carbon-phosphorus cage compounds.



Spirocyclotrimerization of Phosphaalkynes (7 → 10)

In this paper we report in detail on the cyclooligomerization of phosphaalkynes and phosphaalkenes involving Lewis acidic derivatives of group-13 metals and describe the

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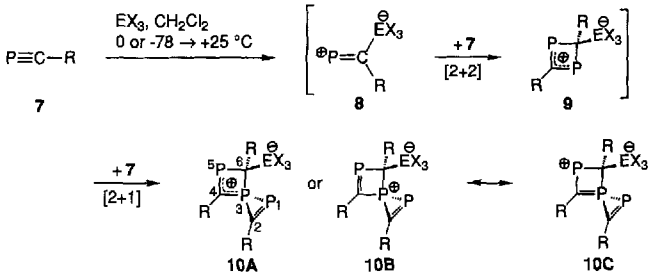
further use of the resulting products for a selective synthesis of phosphorus-carbon cage compounds[8].

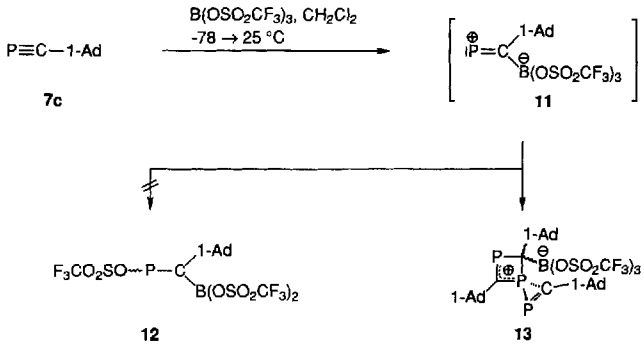
The reactions of aluminum trihalides and gallium trichloride with 3 equivalents of kinetically stabilized phosphaalkynes (**7a–c**) proceed according to an unusual spirocyclotrimerization to provide the betaines **10a–f** in a highly selective manner and in almost quantitative yields.



7 - 10	a	b	c	d	e	f
R	*t*Bu	CMe_2Et	1-Ad	*t*Bu	*t*Bu	*t*Bu
X	Cl	Cl	Cl	Br	I	Cl
E	Al	Al	Al	Al	Al	Ga

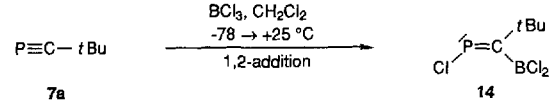
First indications of the formation of a cyclotrimerization product were obtained from the ^{1}H-NMR spectra of **10a, d, e, f** which show three magnetically different *tert*-butyl substituents. This was further confirmed by the ^{31}P-NMR spectra which reveal the signals of three completely different phosphorus environments [δ = −87.5 to −78.1 (P3), δ = 257.4 to 262.2 (P1) and δ = 412.3 to 422.4 (P5)]. The dorwn-field chemical shifts of the latter two resonances clearly show the presence of two phosphaalkene units[9], whereas the third resonance at higher field appears in the range typical of phosphirenium ions[10]. The existence of two phosphaalkene units was further confirmed in the ^{13}C-NMR spectra by two typical low-field absorptions at δ = 200.4–202.9 and δ = 241.6–245.9. The resonance of C-6 could not be detected in the case of the aluminum compounds **10a–e**, presumably because of a broadening effect on the carbon-13 signal caused by the neighborhood of the aluminum atom (I = 5/2)[11]. Fortunately, in the case of **10f** – the gallium derivative – C-6 could be detected in the range typical of sp^3 carbon atom at δ = 71.3. Final structural proof was provided by an X-ray crystal structure analysis of **10a**[8].

A plausible reaction mechanism might commence with an attack of the Lewis acid at the phosphaalkyne carbon atom, in accord with the polarization of the phosphaalkyne system[12]. The $\lambda^2\sigma^1$-phosphenium cation **8** thus derived participates in a regiospecific [2 + 2] cycloaddition with a second molecule of phosphaalkyne **7** to form the dimer complex **9**. In the case of normal alkynes, the reaction stops at this point[13], whereas with the isolobal phosphaalkynes the reaction with a third phosphorus–carbon triple-bond system occurs. In a formal [2 + 1] cycloaddition step the third phosphaalkyne adds to one of the phosphorus atoms possessing electrophilic character in **9** in a highly diastereoselective manner to furnish the final products **10a–f** in high yields.



When boron tris(triflate) in dichloromethane is used as the Lewis acid for the reaction with the phosphaalkyne **7c**, spirocyclotrimerization also occurs to furnish a mixture of diastereomers **13** (both possible substituent arrangements at C-6)[14]. A 1,2-addition of the Lewis acid to the phosphorus–carbon triple bond of **7c** which would lead to the phosphaalkene **12** (and which was observed in the reaction of boron trichloride with **7a**, see below) did not occur. The putative betaine intermediate **11** postulated for both processes cannot be detected by ^{31}P-NMR spectroscopy. The addition of boron tris(triflate) commences at −20 °C and is apparently followed by rapid further reaction to furnish **13**[14].

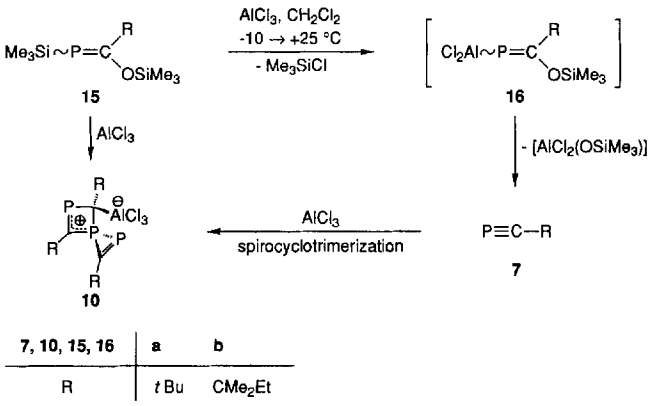
A different reaction pathway was observed in the case of boron trichloride. Addition of the phosphaalkyne **7a** to a solution of boron trichloride in dichloromethane at −78 °C followed by warming to room temperature during 6 h delivers the boron-substituted chlorophosphaalkene **14** in 87% yield as a highly moisture- and oxygen-sensitive, pale yellow oil[15].



The fact that only one singlet is seen in the ^{31}P-NMR spectrum of **14** indicates the stereospecific formation of only one phosphaalkene isomer; the ^{31}P-NMR chemical shift of δ = +269.9 is in the range typical of comparable chloro-substituted phosphaalkenes[16]. The ^{1}H NMR of **14** reveals a doublet at δ = 1.79 [J(H,P) = 3.3 Hz] for the *tert*-butyl substituent, indicating a *cis* relation between the phosphorus lone pair and the *tert*-butyl group. Further confirmation for the phosphaalkene geometry was obtained from the ^{13}C-NMR spectrum. The dependence of the ^2J(C,P) and ^3J(C,P) coupling constants in phosphaalkenes on the geometric relation to the phosphorus lone pair is well documented[9,17]. In agreement with a *cis* relation between the lone pair and the *tert*-butyl substituent, we observe ^3J(C,P) and large ^2J(C,P) coupling constants of 15.1 Hz and 19.1 Hz, respectively. The ^{11}B-NMR spectrum exhibits a singlet at δ = +59.0 in the range typical of related dichlorovinylboranes[18].

Since phosphaalkynes **7** react with a wide range of Lewis acidic compounds of group-13 elements in a clean spirocyclotrimerization process, we then went on to examine, whether phosphaalkenes **15** – the synthetic precursors of phosphaalkynes **7** – can be used as synthetic equivalents in the above-mentioned process.

Treatment of an aluminum trichloride/dichloromethane suspension at −10 °C with an equimolar solution of phosphaalkene **15a, b** in dichloromethane leads, after warming to room temperature, to the quantitative formation of the corresponding phosphaalkynes **7a, b**. Further treatment of the resulting solution with aluminum trichloride cleanly affords the spirocyclotrimerization product **10**.



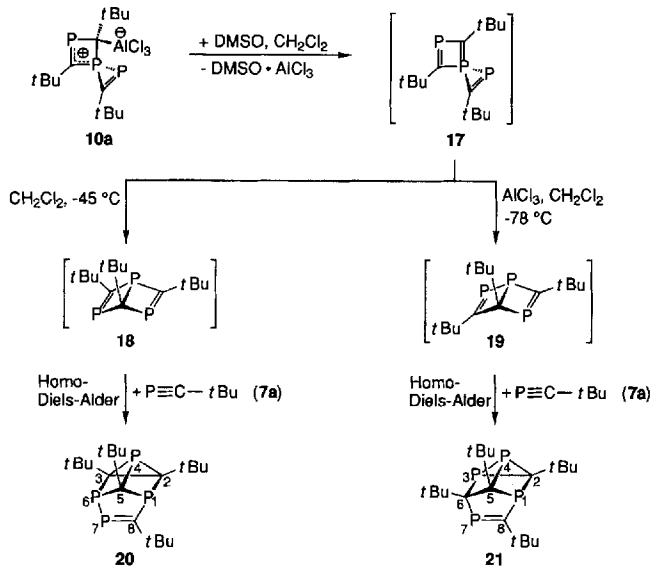
The initial step of this novel phosphaalkyne synthesis is most likely the formation of **16a, b** with elimination of chlorotrimethylsilane. A subsequent β-elimination of [$AlCl_2(OSiMe_3)$] then furnishes the phosphaalkynes **7a, b**[19].

Generation and Trapping of the Triphospha Dewar Benzenes (17 → 18, 19 → 20, 21)

Following the successful preparation of the spirocyclotrimer betaine complexes **10**, we returned to our initial question of whether it would be possible to remove the metal template and use the liberated phosphaalkyne trimer as a building block. Fortunately, even the weak Lewis base dimethyl sulfoxide is sufficiently reactive to remove the aluminum trichloride in **10a** completely.

Treatment of **10a** at −45 °C with dimethyl sulfoxide presumably generates the highly reactive spirocyclic diphosphete **17**, which undergoes spontaneous P–P bond cleavage in the diphosphirene unit and ring enlargement to the 1,3,5-triphospha Dewar benzene **18**, which could not be isolated. Addition of a further equivalent of phosphaalkyne **7a** prior to the liberation of **17** allows the efficient trapping of **18** in a homo Diels-Alder addition which furnishes the tetraphosphatetracyclic compound **20**, a previously unknown phosphaalkyne tetramer, isolated in about 37% yield.

The mass spectrum of **20** proves its tetrameric structure and shows a successive fragmentation of the tetramer down to the monomer, the phosphaalkyne **7a** (M^+ = 100) itself. The constitution of **20** can be determined by NMR-spectroscopic methods. The unsymmetrical structure is immediately indicated by four different signals of the *tert*-butyl



substituents, partly split by ^4J(H,P) coupling constants of 0.9–1.5 Hz. In agreement with this, four different phosphorus resonances are observed in the ^{31}P-NMR spectrum. The chemical shift and splitting values unambiguously prove the constitution. Characteristic of **20** is the expected high-field absorption at δ = −160 of P4 in the phosphirane system[20] and the low-field absorption at δ = +417.1 (P7), a value still typical of a phosphaalkene unit[9]. The latter resonance is split into a doublet with a ^1J(P,P) coupling constant of 264.8 Hz. As expected the same coupling constant was found for the resonance of P6 (δ = +134.3), indicating their direct neighborhood. The resonance of P1 at δ = 111.5 is in a range typical of $\lambda^3\sigma^3$-phosphorus in comparable polycyclic systems[3b] and split into a doublet of pseudotriplets with small ^2J(P,P) coupling constants of 32.1, 32.9, and 16.6 Hz. Noteworthy in the ^{13}C-NMR spectrum is the resonance of the phosphaalkene C-8 at δ = 211.6[21].

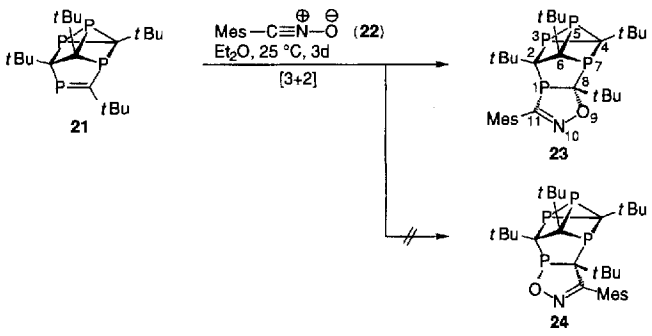
In a second experiment, the suspension of **10a** with an excess of aluminum trichloride in dichloromethane was treated at −78 °C with dimethyl sulfoxide. Although the exact role of the additional aluminum trichloride is not clear yet, its presence leads to a reversal of the chemoselectivity. Instead of P–P bond cleavage, we now observe only P–C bond cleavage in the diphosphirane system of **17**, leading to the unsymmetrical 1,2,5-triphospha-Dewar benzene **19**. Again, addition of further phosphaalkyne results in the efficient trapping of **19** in a homo Diels-Alder reaction, leading exclusively to the tetraphosphatetracyclic compound **21**, an isomer of **20**.

Mass spectrometry confirmed the tetrameric nature of **21**, and the C_1 symmetry is obvious from the ^{1}H-NMR spectrum which shows four different *tert*-butyl substituents. Here again, the ^{31}P-NMR spectrum furnishes conclusive evidence of the constitution. Typical high-field signals of a diphosphirane ring system are observed at δ = −174.4 and −147.3 [^1J(P,P) = 83.0 Hz][20]. The phosphaalkene phosphorus atom P7 appears at δ = +399.0 as a singlet, indicat-

ing that no other phosphorus atom is in the direct neighborhood. The signal of P1 (δ = 64.6) shows only a small ^2J(P,P) splitting of 31.2 Hz, again indicating the absence of a direct phosphorus neighbor.

The above-described reaction sequence allows for the first time the selective construction of phosphaalkyne tetramers by starting with metal template-stabilized phosphaalkyne trimer systems. The phosphaalkyne tetramers **20** and **21** thus derived still possess phosphorus–carbon double bonds which, in the case of **21**, can be used for further functionalization.

Thus, the reaction of **21** with the stable 1,3-dipole mesitylnitrile oxide **22** leads in a clean, regio- and stereospecific [3 + 2] cycloaddition step to the pentacyclic system **23**. Neither the formation of the regioisomer **24** nor that of the corresponding *exo*-stereoisomer were observed.



The ^{1}H-NMR spectrum reveals, in addition to the four *tert*-butyl resonances, signals of a rotationally hindered mesityl substituent. In the ^{31}P-NMR spectrum the disappearance of the phosphorus–carbon double bond in **21** is reflected in a dramatic high-field shift of about $\Delta\delta$ = 300 of the signal of P1 (δ = +75.6). All other phosphorus resonances show almost no change in chemical shift and splitting in comparison with the starting material **21**. A previously reported X-ray crystal structure of **23** irrevocably confirmed constitution and stereochemistry of the polycyclic system[8].

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Experimental

All reactions were carried out under argon (purity >99.998%) by using Schlenk techniques. The solvents were dried by standard procedures, distilled and stored under argon. – Column chromatography was performed in water-cooled glass tubes with a positive pressure of argon on the column. The eluate was monitored with a UV absorbance detector (λ = 254 nm). Silica gel was heated for 3 h in vacuo and then deactivated with 4% water (Brockmann activity II). – MPLC: Büchi MPLC-681 system (column size 46 · 2.6 cm), silica gel (Merck: 15–20 µm). – Melting points: Mettler FP 61 (heating rate: 3°C/min) uncorrected values. – IR: Perkin-Elmer infrared spectrometer 710B and 310. – MS: Finnigan MAT 90 spectrometer. – ^{1}H NMR: Varian EM 390 (90 MHz) and Bruker AMX 400 (400 MHz). – ^{13}C NMR: Bruker AMX 400 (100.64 MHz) referred to the solvent as internal standard. – ^{31}P NMR: Bruker AC 200 (80.82 MHz) and AMX 400 (161.98 MHz) with 85% H_3PO_4 as external standard. – Compounds **7a**[22], **7b**[23], **7c**[24], **15a**[22], **15b**[23], **22**[25] were prepared by published methods.

General Procedure for the Preparation of Spirocyclotrimers **10a–f**: To a magnetically stirred suspension of 5 mmol of element halide in dichloromethane (5 ml) at 0°C was added dropwise a solution of 15 mmol of phosphaalkyne **7** in dichloromethane (5 ml). After stirring for 1 h at 0°C the solution was allowed to warm to room temperature and stirred for further 2 h. Evaporation of the solvent at 25°C/10^{-3} mbar provided the spectroscopically pure spirocyclotrimers **10a–f**.

2,4,6-Tri-tert-butyl-1,5-diphospha-3-phosphoniaspiro[3.4]hexa-1,4-diene-6-yl Trichloroaluminate (**10a**): Starting from aluminum trichloride (0.67 g) and **7a** (1.5 g), we obtained 2.06 g (95%) of **10a** as yellow crystals; m.p. 134°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2950 (s), 2907 (sh), 1455 (m), 1360 (s), 1260 (s), 1100 (m, br), 730 cm^{-1} (s). – ^{1}H NMR (CD_2Cl_2): δ = 1.34 [dd, ^4J(H,P) = 0.7 Hz, ^4J(H,P) = 0.8 Hz, 9H, $C(CH_3)_3$], 1.43 [d, ^4J(H,P) = 1.2 Hz, 9H, $C(CH_3)_3$], 1.59 [pseudo-t, ^4J(H,P) = 0.9 Hz, $C(CH_3)_3$]. – ^{13}C NMR (CD_2Cl_2): δ = 31.9 [s, $C(CH_3)_3$], 33.8 [pseudo-t, ^3J(C,P) = 9.2 Hz, $C(CH_3)_3$], 34.9 [dd, ^3J(C,P) = 12.2 Hz, ^4J(C,P) = 12.5 Hz bzw. 4.5 Hz, $C(CH_3)_3$], 41.1 [d, ^2J(C,P) = 8.4 Hz, $C(CH_3)_3$], 43.6 [pseudo-t, ^2J(C,P) = 2.0 Hz, $C(CH_3)_3$], 48.1 [d, ^2J(C,P) = 3.0 Hz, $C(CH_3)_3$], 202.9 [d, ^1J(C,P) = 65.4 Hz, P=C-1], 245.9 [dd, ^1J(C,P) = 81.7 Hz, ^1J(C,P) = 68.2 Hz, P=C-4]. – ^{31}P NMR (CD_2Cl_2): δ = –80.1 [d, ^1J(P,P) = 214.5 Hz, P-3], 261.4 [dd, ^1J(P,P) = 214.5 Hz, ^3J(P,P) = 18.0 Hz, P-1], 417.9 [d, ^3J(P,P) = 18.0 Hz, P-5]. – $C_{15}H_{27}AlCl_3P_3$ (433.6): calcd. C 41.55, H 6.28; found C 40.3, H 6.1. – Note: Rapid addition of the phosphaalkyne solution led to the formation of the diastereomer of **10a** as a byproduct (≤5%). – ^{31}P NMR (CD_2Cl_2): δ = –82.6 [d, ^1J(P,P) = 223.6 Hz, P-3], 283.0 [dd, ^1J(P,P) = 223.6 Hz, ^3J(P,P) = 35.3 Hz, P-1], 439.8 [d, ^3J(P,P) = 35.3 Hz, P-5].

2,4,6-Tris-(2,2-dimethylpropyl)-1,5-diphospha-3-phosphoniaspiro[3.4]hexa-1,4-diene-6-yl Trichloroaluminate (**10b**): Starting from aluminum trichloride (0.22 g, 1.67 mmol) and **7b** (0.57 g, 5 mmol), we obtained 2.25 g (95%) of **10b** as a red-brown, non-distillable oil. – IR (film): $\tilde{\nu}$ = 2975 (w), 1413 (vs), 1319 (m), 1254 cm^{-1} (vs). – ^{1}H NMR (CD_2Cl_2): δ = 0.9–2.2 (m, all H). – ^{31}P NMR (CD_2Cl_2): δ = –82.8 [d, ^1J(P,P) = 223.8 Hz, P-3), 257.4 [dd, ^1J(P,P) = 223.8 Hz, ^3J(P,P) = 21.4 Hz, P-1], 417.6 [d, ^3J(P,P) = 21.4 Hz, P-5].

2,4,6-Tris-(1-adamantyl)-1,5-diphospha-3-phosphoniaspiro[3.4]hexa-1,4-diene-6-yl Trichloroaluminate (**10c**): Starting from aluminum trichloride (0.67 g) and **7c** (2.67 g), we obtained 4.02 g (95%) of **10c** as a red-brown, non-distillable oil; yellow crystals from dichloromethane, m.p. 140°C (dec.). – IR (film): $\tilde{\nu}$ = 2880 (vs, br), 1445 (s), 1340 (s), 1305 (m), 1255 (m), 1100 (s), 1025 (m), 950 (s), 905 cm^{-1} (w). – ^{1}H NMR (CD_2Cl_2): δ = 1.6–2.3 (m, all H). – ^{31}P NMR (CD_2Cl_2): δ = –87.5 [d, ^1J(P,P) = 215.2 Hz, P-3], 262.2 [dd, ^1J(P,P) = 215.2 Hz, ^3J(P,P) = 18.5 Hz, P-1], 422.4 [d, ^3J(P,P) = 18.5 Hz, P-5].

2,4,6-Tri-tert-butyl-1,5-diphospha-3-phosphoniaspiro[3.4]hexa-1,4-diene-6-yl Tribromoaluminate (**10d**): The reaction was carried out by starting from –78°C to minimize halogen transfer between aluminum tribromide and the solvent dichloromethane. Starting from aluminum tribromide (1.33 g) and **7a** (1.5 g), we obtained 2.4 g (85%) of **10d** as a yellow-brown, non-distillable oil. – IR (film): $\tilde{\nu}$ = 2950 (vs), 1490 (w), 1460 (s), 1395 (m), 1365 (s), 1210 (m, br), 810 cm^{-1} (m, br). – ^{1}H NMR (CD_2Cl_2): δ = 1.30, 1.42, 1.53 [each s, each 9H, $C(CH_3)_3$]. – ^{13}C NMR (CD_2Cl_2): δ = 29.0, 30.9, 32.0 [each s (br), each $C(CH_3)_3$], 38.2 [d-pseudo-t, ^2J(C,P) = 7.1 Hz, ^3J(C,P) = 21.9 Hz, $C(CH_3)_3$], 40.7, 44.9 [each pseudo-t, ^2J(C,P) = 7.1 and 5.1 Hz, respectively, $C(CH_3)_3$], 200.4 [d, ^1J(C,P) = 51.9 Hz,

P=C-2], 242.0 [dd, ^1J(C,P) = 63.0 Hz, ^1J(C,P) = 52.4 Hz, P=C-4]. – ^{31}P NMR (CD_2Cl_2): δ = −80.3 [d, ^1J(P,P) = 215.8 Hz, P-3], 259.5 [dd, ^1J(P,P) = 215.8 Hz, ^3J(P,P) = 16.9 Hz, P-1], 413.8 [d, ^3J(P,P) = 16.9 Hz, P-5].

2,4,6-Tri-tert-butyl-1,5-diphospha-3-phosphoniaspiro[3.4]hexa-1,4-diene-6-yl Triiodoaluminate (**10e**): The reaction was carried out by starting from −78°C to minimize halogen transfer between aluminum triiodide and the solvent dichloromethane. Starting from aluminum triiodide (2.04 g) and **7a** (1.5 g), we obtained 3.36 g (95%) of **10e** as a brown, non-distillable oil. – IR (film): ṽ = 2940 (vs), 1455 (s), 1390 (m), 1360 (vs), 1255 (s), 1195 cm^{-1} (m, br). – ^{1}H NMR (CD_2Cl_2): δ = 1.31, 1.40, 1.57 [each s, each 9H, $C(CH_3)_3$]. – ^{13}C NMR (CD_2Cl_2): δ = 29.1 [s, $C(CH_3)_3$], 30.9 [pseudo-t, ^3J(C,P) = 9.3 Hz, $C(CH_3)_3$], 32.0 [dd, ^3J(C,P) = 14.2 Hz, ^2J(C,P) = 2.2 Hz, $C(CH_3)_3$], 38.3 [d, ^2J(C,P) = 8.7 Hz, $C(CH_3)_3$], 40.9, 45.1 [each s, $C(CH_3)_3$], 201.2 [d, ^1J(C,P) = 65.4 Hz, P=C-1], 242.5 [dd, ^1J(C,P) = 83.4 Hz, ^1J(C,P) = 68.1 Hz, P=C-4]. – ^{31}P NMR (CD_2Cl_2): δ = −82.2 [d, ^1J(P,P) = 214.2 Hz, P-3], 259.0 [dd, ^1J(P,P) = 214.2 Hz, ^3J(P,P) = 17.4 Hz, P-1], 416.1 [d, ^3J(P,P) = 17.4 Hz, P-5]. – Note: Rapid addition of the phosphaalkyne solution led to the formation of the diastereomer of **10e** as a byproduct (≤5%). – ^{31}P NMR (CD_2Cl_2): δ = −82.5 [d, ^1J(P,P) = 222.3 Hz, P-3], 284.1 [dd, ^1J(P,P) = 222.3 Hz, ^3J(P,P) = 33.0 Hz, P-1], 439.3 [d, ^3J(P,P) = 33.0 Hz, P-5].

2,4,6-Tri-tert-butyl-1,5-diphospha-3-phosphoniaspiro[3.4]hexa-1,4-diene-6-yl Trichlorogallate (**10f**): Starting from gallium trichloride (0.88 g) and **7a** (1.5 g), we obtained 2.26 g (95%) of **10f** as a yellow, non-distillable oil; colorless crystals from benzene, m.p. 132°C (dec.). – IR (film): ṽ = 2985 (s), 1465 (s), 1400 (m), 1370 (s), 1260 (m), 1130 (s, br), 810 cm^{-1} (m). – ^{1}H NMR (CD_2Cl_2): δ = 1.38, 1.47, 1.60 [each s, each 9H, $C(CH_3)_3$]. – ^{13}C NMR (CD_2Cl_2): δ = 28.5 [s, $C(CH_3)_3$], 30.4 [pseudo-t, ^3J(C,P) = 8.6 Hz, $C(CH_3)_3$], 31.1 [pseudo-t, ^3J(C,P) = 5.7 Hz, $C(CH_3)_3$], 38.0 [d, ^2J(C,P) = 7.6 Hz, $C(CH_3)_3$], 40.3, 44.7 [each s, each $C(CH_3)_3$], 71.3 [d, ^1J(C,P) = 61.0 Hz, C6], 199.8 [d, ^1J(C,P) = 62.9 Hz, P=C-1], 241.6 [dd, ^1J(C,P) = 83.9 Hz, ^1J(C,P) = 66.8 Hz, P=C-4]. – ^{31}P NMR (CD_2Cl_2): δ = −78.1 [d, ^1J(P,P) = 218.2 Hz, P-3], 259.0 [dd, ^1J(P,P) = 218.2 Hz, ^3J(P,P) = 19.3 Hz, P-1], 411.3 [d, ^3J(P,P) = 19.3 Hz, P-5].

(E)-Chloro-(3-dichloroboryl-2,2-dimethylpropylidene)phosphane (**14**): To a magnetically stirred solution of boron trichloride (1.17 g, 10 mmol) in dichloromethane (5 ml), a solution of **7a** (1.0 g, 10 mmol) in dichloromethane (2 ml) was added dropwise at −78°C. The reaction solution was allowed to warm during 6 h to room temperature and then stirred for further 12 h. Evaporation of all volatile components yielded 1.9 g (87%) of **14** as a pale yellow, highly air- and moisture-sensitive, non-distillable oil. – IR (film): ṽ = 2950 (s), 1390 (m, br), 1255 (s), 1055 (m, br), 800 cm^{-1} (s). – ^{1}H NMR (CH_2Cl_2): δ = 1.39 [d, ^4J(H,P) = 3.3 Hz, $C(CH_3)_3$]. – ^{13}C NMR (CD_2Cl_2): δ = 32.0 [d, ^3J(C,P) = 15.1 Hz, $C(CH_3)_3$], 43.4 [d, ^2J(C,P) = 19.1 Hz, $C(CH_3)_3$], 215–217 (s, br, P=C). – ^{11}B NMR (CD_2Cl_2): δ = 59.0 (s). – ^{31}P NMR (CD_2Cl_2): δ = 269.9 (s). – MS (70 eV); *m/z* (%): 135.3 (23.2) [M^+ − BCl_2], 100.2 (66.0) [M^+ − BCl_3], 81.1 (18.7) [BCl_2], 57.2 (100) [$C(CH_3)_3$].

Reaction of Phosphaalkenes **15a, b** *with Aluminum Trichloride. – General Procedure for the Preparation of Phosphaalkynes* **7a, b**: To a magnetically stirred suspension of aluminum trichloride (0.45 g, 3.37 mmol) in dichloromethane (8 ml) a solution of phosphaalkene **15a, b** (3.37 mmol) in dichloromethane (8 ml) was added dropwise at −10°C. The reaction mixture was stirred for further 5 h at −10°C followed by condensation of all volatile components at −10°C/10^{-3} mbar into a Schlenk flask cooled to −196°C.

2,2-Dimethylpropylidinephosphane (**7a**): Starting from aluminum trichloride and **15a** (0.89 g), we obtained 0.32 g (95%) of **7a** (determined by NMR) as a solution in dichloromethane and chlorotrimethylsilane. Spectroscopic data are identical with those described in ref.[22].

2,2-Dimethylbutylidinephosphane (**7b**): Starting from aluminum trichloride (0.73 g, 5.48 mmol) and **15b** (0.89 g, 5.48 mmol), we obtained 0.56 g (90%) of **7b** (determined by NMR) as a solution in dichloromethane and chlorotrimethylsilane. Spectroscopic data are identical with those described in ref.[23].

Lewis Acid Displacement Reactions with Dimethyl Sulfoxide. – Synthesis of 2,3,5,8-Tetra-tert-butyl-1,4,6,7-tetraphosphatetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene (**20**): To a magnetically stirred solution of **10a** (1.47 g, 3.4 mmol) in dichloromethane (10 ml), **7** (0.34 g, 3.4 mmol) and a solution of dimethyl sulfoxide (0.8 ml, 11.3 mmol) in dichloromethane (5 ml) were added successively at −45°C. The reaction mixture was allowed to warm during 6 h to room temp., stirred for further 18 h at 25°C followed by evaporation of all volatile components at 25°C/10^{-3} mbar. The residue was extracted with *n*-pentane (5 × 10 ml) to give, after evaporation of the solvent, from the combined extracts 0.5 g (37%) of **20** as a red oil. Further purification was achieved by MPLC on silica gel with *n*-pentane as the eluant. – IR (film): ṽ = 2950 (s), 2850 (sh), 1450 (s), 1380 (s), 1355 (s), 1207 (s), 1015 (w), 780 cm^{-1} (s). – ^{1}H NMR (C_6D_6): δ = 0.96 [s, 9H, $C(CH_3)_3$], 1.40 [d, ^4J(H,P) = 0.9 Hz, $C(CH_3)_3$], 1.43 [d, ^4J(H,P) = 1.5 Hz, 9H, $C(CH_3)_3$], 1.58 [pseudo-t, ^4J(H,P) = 1.4 Hz, 9H, $C(CH_3)_3$]. – ^{13}C NMR (C_6D_6): δ = 31.9 [dd, ^3J(C,P) = 15.1 Hz, ^4J(C,P) = 6.0 Hz, $C(CH_3)_3$], 32.6 [pseudo-t, ^3J(C,P) = 10.1 Hz, $C(CH_3)_3$], 33.1 [pseudo-t, ^3J(C,P) = 14.6 Hz, $C(CH_3)_3$], 34.7 [s, $C(CH_3)_3$], 36.7 [d, ^2J(C,P) = 12.1 Hz, $C(CH_3)_3$], 36.9 [m, $C(CH_3)_3$], 38.2 [m, $C(CH_3)_3$], 40.8 [m, $C(CH_3)_3$], 42.1, 58.2 (each m, C-2, C-3, respectively), 96.7 (m, C-5), 211.6 (m, C-8). – ^{31}P NMR (C_6D_6): δ = −160.0 [pseudo-p, ^2J(P,P) = 32.9 and 16.6 Hz, respectively, ^3J(P,P) = 13.2 Hz, P-4], 111.5 [d-pseudo-t, ^2J(P,P) = 33.1 and 32.9 Hz, respectively, ^2J(P,P) = 16.6 Hz, P-1], 134.3 [ddd, ^1J(P,P) = 264.8 Hz, ^2J(P,P) = 33.1 and 19.8 Hz, respectively, P-6)], 417.1 [d-pseudo-t, ^1J(P,P) = 264.8 Hz, ^3J(P,P) = 13.2 Hz, P-7]. – MS (70 eV); *m/z* (%): 401 (20) [M^+ + H], 355 (5) [M^+ − 3 Me], 300 (10) [M^+ − PC*t*Bu], 262 (25) [M^+ − (C*t*Bu)$_2$], 231 (8) [M^+ − P(C*t*Bu)$_2$], 216 (15) [M^+ − P(C*t*Bu)$_2$ − Me], 200 (8) [M^+/2], 169 (100) [M^+/2 − P], 131 (19) [P_2C*t*Bu], 100 (8) PC*t*Bu], 81 (15) [C_2*t*Bu], 69 (17) [C*t*Bu], 57 (22) [*t*Bu].

Synthesis of 2,5,6,8-Tetra-tert-butyl-1,3,4,7-tetraphosphatetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene (**21**): According to the general procedure described above, a suspension of **10a** and aluminum trichloride in dichloromethane (12 ml) was prepared by starting from aluminum trichloride (0.95 g, 7.1 mmol) and **7a** (0.8 g, 8 mmol). The suspension was concentrated and the residue again suspended in dichloromethane (10 ml). The resultant suspension was cooled to −78°C and successively treated with **7a** (0.26 g, 2.6 mmol) and a solution of dimethyl sulfoxide (0.62 ml, 8.7 mmol) in dichloromethane (4 ml). After 15 min the cold bath was removed and the reaction mixture allowed to warm to room temp. After stirring for further 20 h at room temp., all volatile components were removed at 25°C/10^{-3} mbar and the remaining solid was extracted with *n*-pentane (5 × 10 ml) to give, after evaporation of the solvent, from the combined extracts 0.39 g (37%) of **21**. Further purification was achieved by column chromatography on silica gel with *n*-pentane as eluant to give 0.17 g (16%) of **21** as a bright yellow oil. – IR (film): ṽ = 2995 (w), 2940 (s), 2850 (m), 1450 (s), 1380 (s), 1355 (s), 1205 (m), 1090 (w), 1020 (w), 970 (w), 925 (w), 860 (w), 835 (w), 790 (w), 740 (w), 720 (w), 685 cm^{-1} (w). – ^{1}H NMR (C_6D_6):

δ = 1.00 [s, 9H, $C(CH_3)_3$], 1.17 [s, 9H, $C(CH_3)_3$], 1.43 [d, ^4J(H,P) = 2.0 Hz, 9H, $C(CH_3)_3$], 1.80 [s, 9H, $C(CH_3)_3$]. – ^{13}C NMR (C_6D_6): δ = 29.9 [d, ^3J(C,P) = 8.4 Hz, $C(CH_3)_3$)] 31.3 [s, $C(CH_3)_3$], 31.6 [d, ^3J(C,P) = 11.5 Hz, $C(CH_3)_3$], 33.9 [d, ^3J(C,P) = 6.1 Hz, $C(CH_3)_3$], 36.5 [pseudo-t, ^2J(C,P) = 20.6 Hz, $C(CH_3)_3$], 37.0 [d, ^2J(C,P) = 9.2 Hz, $C(CH_3)_3$], 39.1 [pseudo-t, ^2J(C,P) = 12.2 Hz, $C(CH_3)_3$], 41.0 [pseudo-t, ^2J(C,P) = 16.0 Hz, $C(CH_3)_3$], 60.1 [pseudo-t, ^1J(C,P) = 34.3 Hz, C-2], 64.2 (m, C-5 or C-6, respectively), 89.3 (m, C-5 or C-6, respectively), 224.3 [pseudo-t, ^1J(C,P) = 54.2 Hz, C-8]. – ^{31}P NMR (C_6D_6): δ = –174.4 [d, ^1J(P,P) = 83.0 Hz, P-3 or P-4, respectively], –147.3 [ddd, ^1J(P,P) = 83.0 Hz, ^2J(P,P) = 31.2 and 16.6 Hz, respectively, P-3 or P-4, respectively], 64.6 [d, ^2J(P,P) = 31.2 Hz, P-1], 399.0 (s, P-7). – MS (70 eV); *m/z* (%): 401 (45) [M^+ + H], 300 (10) [M^+ – PC*t*Bu], 262 (62) [M^+ –(C_tBu)$_2$], 200 (22) [M^+/2], 169 (100) [M^+/2 – P], 131 (46) [M^+/2 – C*t*Bu], 100 (16) [PC*t*Bu], 99 (50) [PC*t*Bu – H], 69 (47) [C*t*Bu], 57 (36) [*t*Bu].

9-Oxa-10-aza-2,4,6,8-tetra-tert-butyl-11-(2,4,6-trimethylphenyl)-1,3,5,7-tetraphosphapentacyclo[6.3.0.0^{2,6}.0^{3,5}.0^{4,7}]dodec-10-ene (**23**): To a magnetically stirred solution of **21** (0.11 g, 0.28 mmol) in diethyl ether (5 ml) a solution of **22** (0.04 g, 0.28 mmol) in diethyl ether (3 ml) was added dropwise at –78 °C. After 15 min the cold bath was removed and the reaction solution was allowed to warm to room temp. After stirring for further 3 d, the solvent was removed in vacuo. MPLC on silica gel with *n*-pentane/ether (10:1) followed by recrystallization from *n*-pentane provided 0.06 g (71%) of **23** as colorless crystals; m.p. 184 °C. – IR (KBr): $\tilde{\nu}$ = 2940 (s), 1440 (w, br), 1380 (w), 1350 (m), 1250 (s), 1075 (s), 1010 (s), 910 (m), 790 cm^{-1} (s). – ^{1}H NMR (C_6D_6): δ = 1.27 [s, 9H, $C(CH_3)_3$], 1.31 [d, ^4J(H,P) = 0.5 Hz, 9H, $C(CH_3)_3$], 1.36 [s, 18H, 2 × $C(CH_3)_3$], 2.12 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 3.17 (s, 3H, CH_3), 6.76 (s, 1H, aryl-H), 6.93 (s, 1H, aryl-H). – ^{13}C NMR (C_6D_6): δ = 20.9 (s, *p*-CH_3), 22.8 (d, ^4J(C,P) = 12.9 Hz, *o*-CH_3), 23.0 (d, ^4J(C,P) = 10.7 Hz, *o*-CH_3), 27.8 [pseudo-t, ^3J(C,P) = 8.4 Hz, $C(CH_3)_3$], 30.1 [m, br, $C(CH_3)_3$], 30.9 [m, $C(CH_3)_3$], 31.8 [m, $C(CH_3)_3$], 33.0 [m, $C(CH_3)_3$], 36.6 [pseudo-t, ^2J(C,P) = 11.1 Hz, $C(CH_3)_3$], 38.9 [dd, ^2J(C,P) = 21.0 and 20.9 Hz, respectively, $C(CH_3)_3$], 40.1 [pseudo-t, ^2J(C,P) = 22.9 Hz, $C(CH_3)_3$], 60.8 (m, C-4), 65.9 (s, C-6), 80.9 (m, C-2), 108.6 [dd, ^1J(C,P) = 53.4 and 37.4 Hz, respectively, C-8], 129.5 [d, ^2J(C,P) = 13.7, ipso-aryl-C], 130.1, 130.7, 136.2, 137.8, 139.1 (each s, each aryl-C), 156.5 [dd, ^1J(C,P) = 56.8 Hz, ^3J(C,P) = 5.0 Hz, C-11]. – ^{31}P NMR (C_6D_6): δ = –148.9 [ddd, ^1J(P,P) = 83.3 Hz, ^2J(P,P) = 26.9 and 10.7 Hz, respectively, P-3], –142.4 [dd, ^1J(P,P) = 83.3 Hz, ^2J(P,P) = 10.7 Hz, P-5], 75.6 (s, P-1), 93.6 [d, ^2J(P,P) = 26.9 Hz, P-7]. – MS (70 eV); *m/z* (%): 504 (0.08) [M^+ – *t*Bu], 448 (0.44) [M^+ – *t*Bu, – C_4H_8], 417 (30) [M^+ + H, – MesCN], 401 (6) [M^+ + H, – MesCNO], 384 (8) [M^+ + H, – MesCNO, – Me], 262 (6) [M^+ – MesCNO, – (C_tBu)$_2$], 200 (5) [M^+ – MesCNO, – 2 PC*t*Bu], 169 (22) [M^+ – MesCNO, – 2 PC*t*Bu, – P], 161 (100) [MesCNO], 146 (62) [MesCNH], 145 (72) [MesCN], 130 (96) [MesCN – Me], 119 (13) [Mes], 103 (11) [Mes – CH_4], 69 (10) [C*t*Bu], 57 (33) [*t*Bu]. – $C_{30}H_{47}NOP_4$ (561.6): calcd. C 64.16, H 8.44, N 2.49; found C 64.1, H 8.3, N 2.5.

☆ Dedicated to Professor *H. W. Roesky* on the occasion of his 60th birthday.

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