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Thermal Transformation of Kinetically Stabilized Phosphaalkynes with Phosphinidene Precursors. Synthesis of Phosphorus-Carbon Cage Compounds by Cocyclooligomerization Processes☆

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Phosphaalkynes **2** undergo cocyclooligomerization reactions with the phosphinidene **14** or the phosphinidene-$W(CO)_5$ complex **18** to furnish the phosphorus-carbon cage compounds **16** or **23**. The phosphinidene **14** is generated by the thermal reaction of **2a–c** with the phosphole **11**, a process in which the initially formed 7-phosphanorbornadienes **12a–c** decompose to the λ^3-phosphinines **13a–c** and the desired reactive intermediate. When three further equivalents of the phosphaalkynes **2a–c** are employed, the tetraphosphahomoquadricyclanes **16a–c** can be isolated in 53–65% yields. The second approach is based on the thermal fragmentation of **17** to generate the phosphinidene-$W(CO)_5$ complex **18** which, in turn, reacts with four equivalents of the phosphaalkynes **2a** or **b** to produce the pentaphosphadeltacyclanes **23a** or **b**. The constitutions of these novel phosphorus-carbon cage compounds were confirmed by X-ray crystal structure analyses of **16a** and **23a**.

Cyclooligomerization reactions of the kinetically stabilized phosphaalkynes P≡C–R constitute a current research topic of particular interest because of its dynamic development[2–7]. In contrast to the homologous nitriles, phosphaalkynes show pronounced tendencies for the formation of oligomeric polycyclic systems and, above all, fascinating cage compounds both under thermal and under transition metal-catalyzed reaction conditions. Cyclooligomerization processes of the phosphaalkynes continue to provide surprising results in that unsymmetrical cage compounds are obtained in addition to symmetrical molecules such as, for example, the tetraphosphacubanes[8] $(PCR)_4$ and the hexaphosphaoctahedrane[4] $(PCR)_6$. The unsymmetrical cage structures can often be derived directly from the respective platonic bodies by replacement of an edge or an apex by a bridge or a surface. Thus, among others, tetraphosphabis(homo)prismanes[5,9] $(PCR)_4$, a hexaphosphahomopentaprismane[10] $P_6(CR)_4(CHR)$, and a pentamer[11] $(PCR)_5$ have been reported. Controlled syntheses are currently limited to the tetraphosphacubane system which can be obtained in good yield starting from a phosphaalkyne dimer complex[12]. In most cases, convincing mechanistic rationale for the formation of the cyclooligomers are still lacking.

In contrast, the compositions of cooligomeric phosphorus-carbon cage compounds provide clues concerning the interpretation of the mechanism of formation. This is clearly apparent when the phosphaalkynes can undergo [4 + 2] cycloadditions with the reaction partners (Scheme 1). Accordingly, reactions of the phosphaalkynes **2** with acyclic 1,3-dienes **1** selectively furnish the tricyclic diphosphaoctenes **5** as final products[13,14]. Irrespective of the employed substrate ratios, the initial Diels-Alder reaction is followed by an ene reaction with a second equivalent of the phosphaalkyne **2** to furnish the monocyclic intermediate **4** while an intramolecular Diels-Alder reaction (→ **5**) then completes the sequence. On the other hand, the poducts obtained from the reactions of **2** with carbocyclic 1,3-diene systems, such as **6**, can be plausibly explained on the assumption that the initial [4 + 2] cycloaddition (→ **7**) is followed by a homo-Diels-Alder reaction with a further equivalent of **2** to give the tetracyclic cocyclooligomers **8** as the final products[15].

We now report on the synthesis of two structurally related phosphorus-carbon cage compounds by the cocyclooligomerizations of kinetically stabilized phosphaalkynes with two phosphinidene precursors. Although an effective method has been recently devised for the generation, detection, and trapping of arylphosphinidenes[16,17], its practicability remains limited. A versatile and efficient alternative consists in using electrophilic terminal phosphinidene complexes $[RP{\rightarrow}M(CO)_5]$ (M = Cr, Mo,W)[18]. These transient

[◇]Part 102: Ref.[1].

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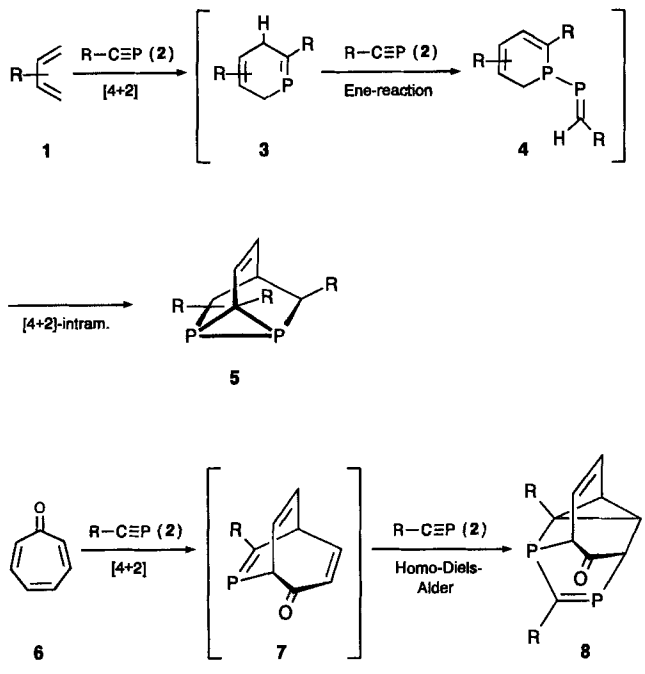
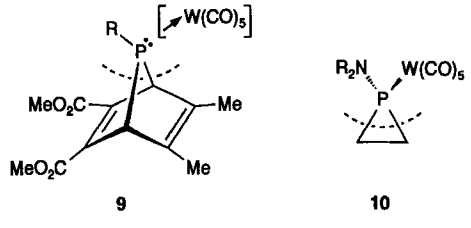
Scheme 1



species are easily generated in situ by thermally induced cycloreversion from the appropriate phosphanorbornadienes **9** and phosphiranes **10**. This approach has found numerous applications (Scheme 2)[18–23]. Besides, decomplexation techniques have demonstrated the equal value of free and terminally coordinated phosphinidenes for synthetic purposes[24]. Although the uncomplexed 7-phosphanorbornadiene system has not yet been isolated, this does not exclude its use – when formed as an intermediate – as a synthetic equivalent for the phosphinidene.

Scheme 2

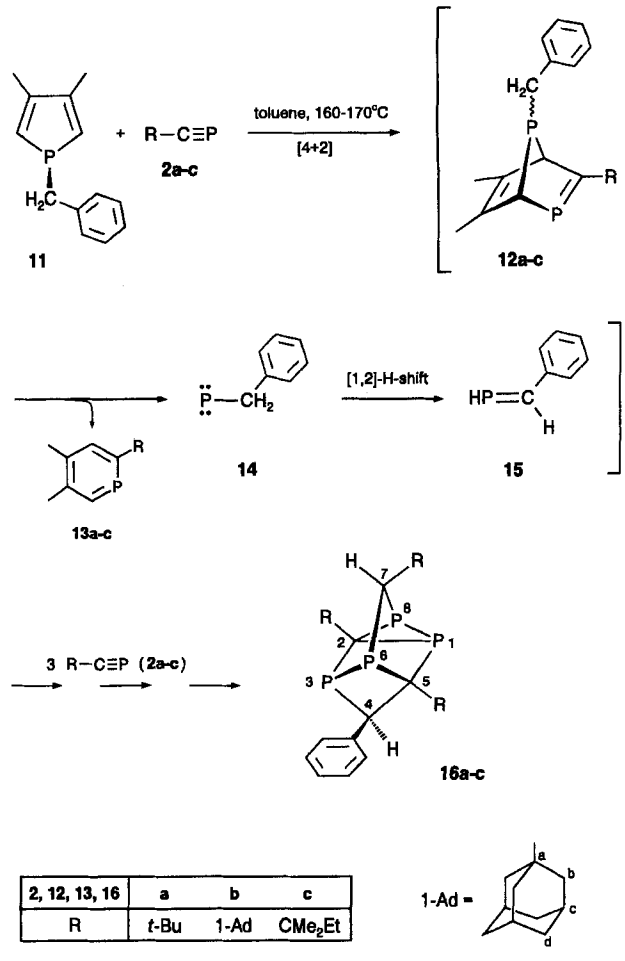


In the first phase of our investigations, the phosphinidene was generated from a bicyclic precursor of the type **9** (uncomplexed) while, in the second phase, the phosphinidene complex was liberated by thermal cycloelimination from a complexed phosphirane of the type **10**.

Synthesis of the Tetraphosphahomoquadricyclanes 16a–c

When a solution of the phosphole **11** was allowed to react with a fourfold excess of a phosphaalkyne **2a–c** in toluene at a temperature between 160 and 170°C in a Schlenk pressure tube, both the λ^3-phosphinines **13a–c**[25,26] and the phosphorus-carbon cage compounds **16a–c** could be isolated from the dark red to brown reaction solutions by column chromatography on silica gel (Scheme 3).

Scheme 3

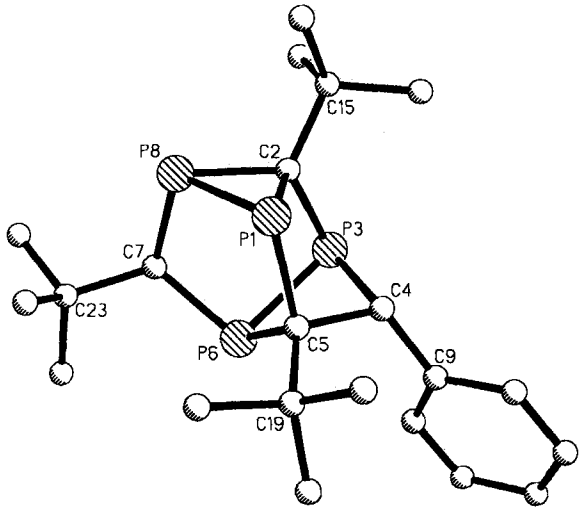


The $^{31}P\{^1H\}$-NMR spectra of the solutions from the reactions of **11** with **2a** or **c** indicate almost quantitative conversions (crude yields: >95%). The lower yields of isolated products (**16a**: 65%, **16c**: 63%) result either from the drastic conditions needed to separate the λ^3-phosphinine **13a** (bulb-to-bulb distillation) or from the only slight difference in the R_f values of the λ^3-phosphinine **13c** and the tetracyclic product **16c** (on adsorption chromatography). The even lower yield (53%) of the adamantyl-substituted product **16b** is the consequence of the formation of an oligomeric byproduct (<10%) which has not yet been identified. An essential prerequisite for the successful preparation of the tetraphosphahomoquadricyclanes **16a–c** is the performance of the reactions under the conditions mentioned above. When the reaction was carried out at room temperature, the concentrations of the starting materials in fact decreased steadily with formation of the λ^3-phosphinine **13** but, surprisingly, no trace of the tetracyclic system could be detected by $^{31}P\{^1H\}$-NMR spectroscopy. Similar observations were made when the phosphole **11** was allowed to react with an excess of the phosphaalkyne **2a** at room temperature in the absence of a solvent or alternatively at 130°C under argon

pressure. Numerous oligomeric phosphorus-carbon compounds of unknown structures [$^{31}P\{^1H\}$-NMR spectroscopy] were formed but could not be separated even after repeated chromatography on various stationary phases and recrystallization. The tetracyclic product **16a** was, however, not formed under these conditions.

The tetracyclic products **16a–c** produced by the thermolysis reactions in toluene were obtained as colorless, crystalline powders and could be recrystallized from suitable solvents. Their cooligomeric compositions were confirmed both by elemental analysis and mass spectrometry. Thus, **16** is formally composed of three units of the phosphaalkyne **2** and one unit of benzylphosphinidene (**14**). The formation of stereoisomeric mixtures is excluded on the basis of the NMR spectral data. Final confirmation of the structures was provided by a crystal structure analysis of the *tert*-butyl-substituted product **16a** (Figure 1).

Figure 1. Structure of **16a** in the crystal[a]



[a] Selected bond lengths [Å] and angles [°]: P1–C2 1.870(2), P1–P8 2.1886(9), P1–C5 1.898(2), C2–P3 1.875(2), C2–P8 1.852(2), P3–C4 1.893(2), P3–P6 2.2066(9), C4–C5 1.589(3), C5–P6 1.906(2), P6–C7 1.856(2), C7–P8 1.859(2); P1–C2–P8 72.03(8), C2–P1–C5 92.89(9), C2–P1–P8 53.60(7), C5–P1–P8 103.57(7), C2–P3–C4 93.48(9), C2–P3–P6 93.55(7), C4–P3–P6 77.30(7), P3–P6–C5 75.80(7), P3–P6–C7 95.16(7), C5–P6–C7 108.63(9), P1–P8–C2 54.38(6), P1–P8–C7 102.63(7), C2–P8–C7 99.58(9), P8–C2–P1 72.03(8), C15–C2–P3 114.71(14), P8–C2–P3 116.68(10), P1–C2–P3 107.20(10), C5–C4–P3 93.16(12), P6–C7–P8 109.98(10), C4–C5–P1 100.75(12), C4–C5–P6 94.36(12), P1–C5–P6 108.56(9)

Formally, the basic skeleton can be described as an edge-bridged quadricyclane system. The atom groups P-1/C-2/P-8 and C-5/P-3/P-6 represent the triangular surfaces; the imaginary edge P-3/C-5 is bridged by a phenylmethylene group (C-4). The original phosphinidene unit (P-3, C-4) can be localized; however, only one hydrogen atom remains bound to C-4, the second hydrogen atom is now at C-7. The configurations at C-4 and C-7 are unequivocally characterized by the structure analysis. The P–P bond lengths of 2.1886 Å (P-1–P-8) and 2.2066 Å (P-3–P-6) are within the expected range (average literature value: 2.214 Å[27]).

The expected ABCD spin system for the ^{31}P nuclei of **16** is seen in both the 1D- (**16a, b**) and the 2D-$^{31}P\{^1H\}$-NMR spectra (**16c**; $^{31}P,^{31}P$-COSY-45). The ^{31}P nuclei each give rise to threefold doublet signals or, respectively, to three crosspeaks of different intensities. The atoms P-1 (δ = −65.6 to −55.4) and P-8 (δ = −113.0 to −104.0) give rise to signals in the high-field region typical of diphosphiranes[28]. In the ^1H-NMR spectra, the signals for the two skeletal protons 4-H (δ = 2.64–2.99) and 7-H (δ = 4.02–4.33) with the expected splitting patterns are observed in addition to those for the phenyl and *tert*-butyl, adamantyl, or *tert*-pentyl groups. As a result of the double heteroatom substitution at C-7, the signal for 7-H appears at lower field and is split into a double doublet by the two ^2J(H,P) couplings to P-6 and P-8. Selective irradiation experiments [$^1H\{^{31}P\}$-NMR spectroscopy] confirmed the assignments made for the ^{31}P nuclei. The $^{13}C\{^1H\}$-NMR spectrum of the homoquadricyclane **16a** is in full accord with the postulated structure. Thus, C-2 gives rise to a signal at relatively high field (δ = 55.8) as expected for a diphosphirane system in spite of its threefold heteroatom substitution. The signal is split into a fourfold doublet by three ^1J(C,P) and one ^2J(C,P) couplings. The remaining skeletal carbon atoms C-4, C-5, and C-7 give rise to signals in the region typical of sp^3-hybridized carbon atoms in organophosphorus cage compounds[9,10,29–31]. In the cases of C-5 and C-7, the presence of directly adjacent phosphorus atoms is revealed by the C,P coupling constants. No C,P coupling constants could be determined for C-4 on account of the multiplet structure of the signal (see also Experimental).

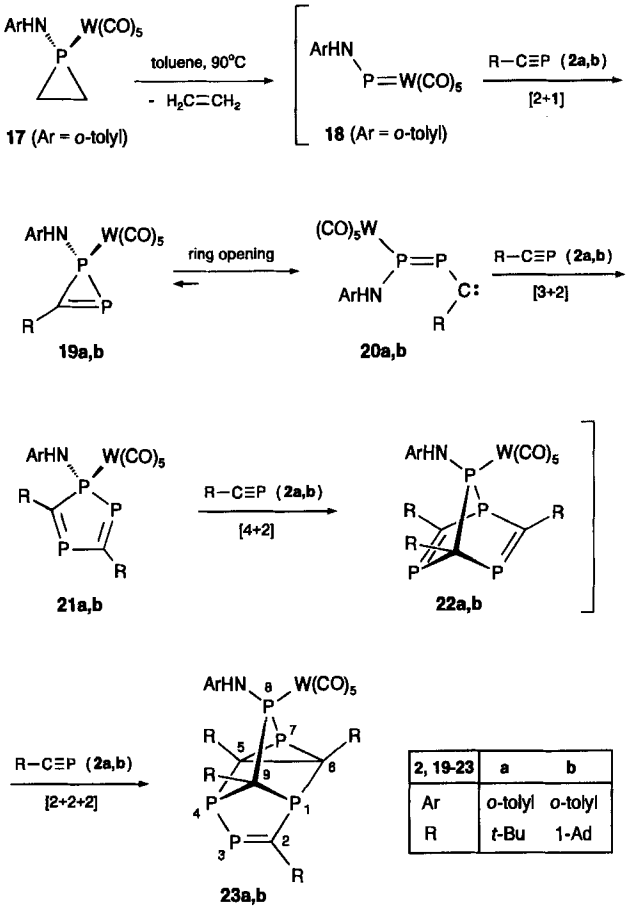
The carbocyclic parent compound C_8H_{10} corresponding to **16** was prepared independently by Freeman[32] and Kirmse[33] by intramolecular carbene insertion reactions. Wipff[34] also demonstrated that the tetracyclic parent skeleton of **16** is accessible by way of a homo-1,4-chelotropic addition of difluorocarbene to 7,7-difluoronorbornadiene. These mechanisms, however, fail in the case of the tetraphosphahomoquadricyclane **16**. Questions concerning the mechanism of formation of **16** cannot yet be answered conclusively since no intermediates were isolated or even detected by NMR spectroscopy. Even so, the initial steps are plausible: a Diels-Alder reaction of the phosphole **11** with the phosphaalkynes **2a–c** leads to the formation of the diphosphanorbornadienes **12a–c** which decompose with aromatization immediately on account of their instabilities to the λ^3-phosphinines **13a–c**. The free benzylphosphinidene (**14**) is generated concomitantly. When the benzyl group in the phosphole **11** is replaced by a phenyl group, formation of the respective λ^3-phosphinine is observed [$^{31}P\{^1H\}$-NMR spectroscopy] but not the cooligomerization. Accordingly, the methylene group in the phosphinidene **14** is a prerequisite for the formation of the tetracyclic products **16a–c**. This observation is suggestive of an isomerization of **14** by a [1,2]-H shift to a phosphaalkene structure. Ab initio calculations for this rearrangement have been reported[35].

In the following section, we report on the construction of a phosphorus-carbon cage compound by way of an in situ generated phosphinidene complex.

Synthesis of the Pentaphosphadeltacyclanes 23a and b

The syntheses of the complexed pentaphosphadeltacyclanes **23a** and **b** were achieved by the thermal decomposition of the phosphinidene complex precursor **17** at 90°C in toluene in the presence of a 7- to 10-fold excess of the phosphaalkynes **2a** or **b** (Scheme 4). The tetracyclic products **23a** and **b** could be isolated as red crystals by crystallization from toluene.

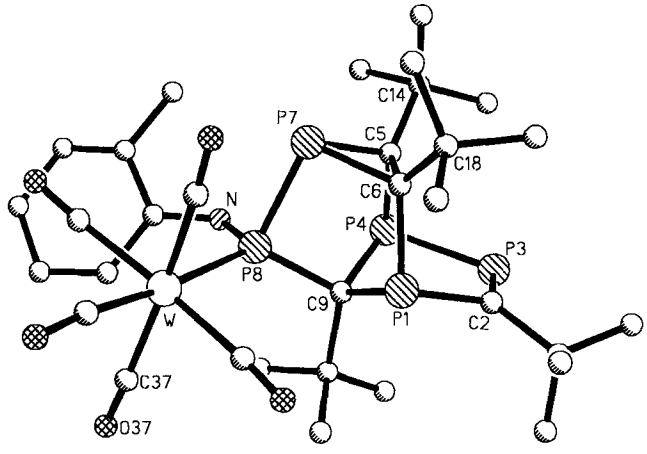
Scheme 4



Mass spectral and microanalytical data for the complex **23a** support its cooligomeric construction from four phosphaalkyne units and one phosphinidene complex fragment. The ^{31}P-NMR data have a high diagnostic value with regard to the constitutions of the novel cage compounds **23a** and **b**. Characteristic are the $^{31}P\{^1H\}$-NMR signals of the $\lambda^3\sigma^2$-phosphorus atom P-3 at low field and of the phosphirane phosphorus atom P-7 at high field. The signals for P-3 appear at δ = 407.2 and 408.2, respectively, and are split into double doublets by coupling to P-4 [^1J(P,P) = 289.4 and 291.3 Hz] and to P-1 [^2J(P,P) = 15.3 and 16.4 Hz, respectively]. The signals for P-7 appear as doublets due to ^1J couplings to P-8 (228.9 and 221.5 Hz, respectively) at δ = −135.8 and −139.8. The ^{183}W satellites [^1J(P,W) = 230.5 and 232.7 Hz, respectively] of the ^{31}P signals at δ = 50.1 and 41.5, respectively, confirm the coordination of the $W(CO)_5$ fragment at P-8. The remaining ^{31}P signals occur in the expected regions. In the absence of protons directly bound to skeletal atoms, the ^{1}H-NMR spectra merely provide less diagnostically helpful signals for the *o*-tolylamino and *tert*-butyl or adamantyl groups. The signal for the carbon atom of the phosphorus-carbon double bond appears in the $^{13}C\{^1H\}$-NMR spectrum of **23a** as a multiplet at low field (δ = 207.9) as is typical of this compound class[9]. The remaining skeletal carbon atom signals also exhibit complicated splitting patterns (see also Experimental).

Last doubts concerning the structure were resolved by a crystal structure analysis. Figure 2 shows the structure of product **23a** and also includes selected bond lengths and bond angles. The assumption of η^1-coordination is based on the length of the W–P-8 bond (2.540 Å). The two P–P bond lengths of 2.189 (P-7–P-8) and 2.208 Å (P-4–P-3) are in the expected range, as is also the P=C bond length of 1.67 Å (P-3–C-2).

Figure 2. Structure of **23a** in the crystal[a]



[a] Selected bond lengths [Å] and angles [°]: W–P8 2.540(2), P7–P8 2.189(7), P7–C5 1.84(2), P7–C6 1.83(2), P8–C9 1.87(2), P4–P3 2.208(8), P4–C9 1.89(2), P4–C5 1.85(2), P1–C9 1.85(2), P1–C2 1.85(2), P1–C6 1.85(2), P3–C2 1.67(2), C5–C6 1.56(2); P8–P7–C5 98.3(6), P8–P7–C6 96.0(6), C5–P7–C6 50.5(7), P7–P8–C9 95.3(6), P3–P4–C9 96.8(6), P3–P4–C5 97.3(6), C9–P4–C5 93.8(8), C9–P1–C2 99.1(7), C9–P1–C6 93.6(7), C2–P1–C6 99.5(7), P4–P3–C2 98.2(7), P8–C9–P4 105.2(8), P8–C9–P1 103.2(7), P4–C9–P1 101.1(8), P7–C5–P4 114.8(9), P4–C5–C14 108.2(13), P7–C5–C6 64.5(9), P4–C5–C6 110.2(12), P1–C2–P3 117.4(10), P7–C6–P1 115.9(9), P7–C6–C5 65.1(9), P1–C6–C5 111.9(11), P1–C6–C18 113.0(12)

Considerations on the reaction mechanism led to the reasonable conclusion that, after in situ generation of the phosphinidene complex **18** by thermally induced elimination of ethylene from the phosphirane complex **17**, the first equivalent of the phosphaalkyne **2** undergoes a [2 + 1] cycloaddition with **18** to form the diphosphirene complex **19** (see also ref.[23]). Subsequent steps comprise ring opening to furnish the carbene **20** and [3 + 2] cycloaddition of the second equivalent of **2** to **20** to give the triphosphole complex **21**. A Diels-Alder reaction of the complex **21** with

another equivalent of **2** leads to the tetraphosphanorbornadiene **22** which possesses the structural requirements for a [2 + 2 + 2] cycloaddition (homo Diels-Alder reaction)[9,15,36,37] with the fourth equivalent of the phosphaalkyne **2** ultimately responsible for the formation of the product.

Conclusions

In combination with the previously available investigations[23], the present results demonstrate that phosphorus-carbon cage compounds are accessible from thermolysis reactions of kinetically stabilized phosphaalkynes in the presence of phosphinidene precursors and that, in addition to the reaction conditions, the substituents at the phosphinidene phosphorus atom are of decisive importance for the success of the reaction and the constitutions of the polycyclic products finally isolated. Our future investigations will be focused on the primary adducts of the reactions of phosphaalkynes with in situ generated phosphinidenes and phosphinidene complexes.

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Experimental

The reactions were carried out under argon (purity >99.998%) in thick-walled (2 mm) Schlenk pressure tubes fitted with a teflon typ and a screw cap. **Caution:** if reactions are performed at elevated temperatures and argon pressure, additional safety shields should be used. Solvents were dried by standard procedures (toluene: Na; ether and petroleum ether 30–75°C: Na/K alloy), redistilled, and stored under argon. Bulb-to-bulb distillations were carried out in a Büchi GKR 50 apparatus, the temperatures stated are oven temperatures. 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). – Microanalyses: Perkin-Elmer Model 2400 elemental analyzer. – Melting points: Mettler FP 61 (heating rate: 3°C/min), uncorrected. – FT IR: Perkin-Elmer Model 16 PC. – MS: Finnigan MAT 90. – NMR: Bruker AMX 400 (^{1}H: 400 MHz; ^{13}C: 101 MHz; ^{31}P: 162 MHz), solvent as internal standard (^{1}H and ^{13}C). The chemical shifts for ^{31}P are relative to external 85% orthophosphoric acid. – Compounds **11**[38], **2a**[39], **2b**[40], **2c**[41], and **17**[42] were prepared by the published methods.

2,5,7-Tri-tert-butyl-4-phenyl-1,3,6,8-tetraphosphatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane (**16a**): To a solution of **11** (0.88 g, 4.35 mmol) in toluene (5 ml) was added **2a** (1.92 g, 19.18 mmol), and the mixture was stirred at 160–170°C and 8 bar argon pressure for 4 h. The resultant brown solution was then allowed to cool to room temp., and the solvent and excess **2a** were subsequently removed in vacuo (10^{-3} mbar). The λ^3-phosphinine **13a** was separated by bulb-to-bulb distillation at 150°C/0.013 mbar [^{31}P NMR: δ = 187.5 (C_6D_6); ref.[25]: δ = 186.6 ($CDCl_3$)]. The residue was purified by column chromatography on silica gel (column: 2 × 30 cm). Using petroleum ether/ether (5:1) as eluent, we obtained **16a** as a yellow powder. Crystallization from petroleum ether at −20°C gave pure **16a** as colorless prisms. Yield 1.19 g (65%), m.p. 156–157°C. – IR (KBr): $\tilde{\nu}$ = 3078, 3056, 3022 (CH-aryl), 2950, 2894, 2858 (CH), 1598, 1492, 1466, 1450, 1394, 1358, 1220, 766, 700 cm^{-1}. – ^{1}H NMR (C_6D_6): δ = 1.07, 1.15, 1.24 [each s, 9H, C(CH_3)$_3$], 2.88 [d, ^2J(H,P-3) = 4.0 Hz, 1H, 4-H], 4.30 [dd, ^2J(H,P-6) = 27.1, ^2J(H,P-8) = 8.3 Hz, 1H, 7-H], 6.99 [t, ^3J(H,H) = 7.2 Hz, 1H, *p*-H], 7.08 [dd, ^3J(H,H) = 7.2 Hz each, 2H, *m*-H], 7.68 [d, ^3J(H,H) = 7.2 Hz, 2H, *o*-H]. – ^{13}C{^{1}H} NMR (C_6D_6): δ = 31.1 [dd, ^3J(C,P) = 10.1 and 6.0 Hz, C(CH_3)$_3$], 32.1 [ddd, ^3J(C,P) = 10.1 and 3.6, J(C,P) = 3.6 Hz, C(CH_3)$_3$], 32.9 [dd, ^3J(C,P) = 8.1 Hz each, C(CH_3)$_3$], 34.6–35.1 [m, *C*(CH$_3$)$_3$], 38.7 [ddd, ^2J(C,P) = 19.0 and 9.5, J(C,P) = 2.0 Hz, *C*(CH$_3$)$_3$], 55.8 [dddd, ^1J(C,P) = 63.3, 49.0, and 43.4, ^2J(C,P) = 3.8 Hz, C-2], 62.6 (m, C-4), 81.7 [dd, ^1J(C,P) = 53.4 and 45.2 Hz, C-7], 97.8 [dddd, ^1J(C,P) = 60.1 and 29.9, ^2J(C,P) = 9.0 and 2.3 Hz, C-5], 127.0 (m, C-*p*), 128.5 (s, C-*m*), 130.6 [dd, ^3J(C,P) = 10.8, ^4J(C,P) = 4.7 Hz, C-*o*], 140.1 (m, C-*i*). – ^{31}P{^{1}H} NMR (C_6D_6): δ = −104.0 [ddd, ^1J(P-8,P-1) = 202.2, ^2J(P,P) = 11.5 and 5.7 Hz, P-8], −55.4 [ddd, ^1J(P-1,P-8) = 202.2, ^2J(P,P) = 11.4 and 9.5 Hz, P-1], 36.4 [ddd, ^1J(P-6,P-3) = 103.0, ^2J(P,P) = 11.5 and 11.4 Hz, P-6], 43.4 [ddd, ^1J(P-3,P-6) = 103.0, ^2J(P,P) = 9.5 and 5.7 Hz, P-3]. – MS (CI, 200 eV), *m/z* (%): 422 (100) [M$^+$]. – $C_{22}H_{34}P_4$ (422.4): calcd. C 62.56, H 8.11; found C 62.60, H 8.16.

Crystal Data and Summary of Data Collection Parameters for **16a**[43]: Diffractometer Siemens P4; radiation Mo-K_α; $C_{22}H_{34}P_4$; M = 422.37 g/mol; crystal size 0.35 × 0.30 × 0.20 mm; triclinic $P\bar{1}$; a = 10.55.0(2), b = 1097.7(29, c = 1173.2(2) pm, α = 65.90(3), β = 76.00(3), γ = 87.48(3)°; V = 1.2011(4) nm^3; Z = 2; $d_{calcd.}$ = 1.168 Mg/m^3; Θ range 1.96–30.00°; no. of reflections measured 7729; no of independent reflections 6703; $R1$ = 0.0494, $wR2$ = 0.0866.

2,5,7-Triadamant-1-yl-4-phenyl-1,3,6,8-tetraphosphatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane (**16b**): To a solution of **11** (0.80 g, 4.00 mmol) in toluene (10 ml) was added **2b** (3.80 g, 21.30 mmol), and the mixture was stirred at 160–170°C and 8 bar argon pressure for 3 h. Upon cooling to room temp. a white solid precipitated. After the suspension had been concentrated in vacuo (10^{-3} mbar), the residue was purified by chromatography on silica gel using petroleum ether as eluent (column: 2 × 30 cm). The first fraction contained the λ^3-phosphinine **13b** [^{31}P NMR: δ = 192.8 ($CDCl_3$); ref.[26]: δ = 188.0 (C_6D_6)] and small amounts of an oligomeric organophosphorus compound of unknown structure. Compound **16b** was obtained analytically pure as a colorless powder by using petroleum ether/ether (25:1) as eluent. The cage compound **16b** differs from **16a** and **16c** in its low solubility in common solvents. Yield 1.39 g (53%), dec. ≥110°C. – IR (KBr): $\tilde{\nu}$ = 3078, 3056, 3022 (CH-aryl), 2900, 2846 (CH), 1598, 1492, 1448, 1342, 1308, 1102, 696 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.27–1.89 (m, 45H, adamantyl), 2.64 [d, ^2J(H,P-3) = 5.0 Hz, 1H, 4-H], 4.02 [dd, ^2J(H,P-6) = 27.6, ^2J(H,P-8) = 8.2 Hz, 1H, 7-H], 7.05 [t, ^3J(H,H) = 7.1 Hz, 1H, *p*-H], 7.13 [dd, ^3J(H,H) = 7.1 and 6.5 Hz, 2H, *m*-H], 7.52 [d, ^3J(H,H) = 6.5 Hz, 2H, *o*-H]. – ^{13}C{^{1}H} NMR (C_6D_6): δ = 28.7, 29.0, 29.1 (each s, C-c), 35.7 [ddd, ^2J(C,P) = 22.1 and 9.9, J(C,P) = 9.9 Hz, C-a], 36.5 (m, C-a), 36.6, 36.7, 36.8 (each s, C-d), 40.5 [dd, ^2J(C,P) = 16.8 and 8.5 Hz, C-a], 42.4 [dd, ^3J(C,P) = 9.9 and 5.4 Hz, C-b], 45.1 (m, C-b), 45.7 [dd, ^3J(C,P) = 8.4 and 8.3 Hz, C-b], 54.4 (m, C-2), 60.8 (m, C-4), 82.0 [dd, ^1J(C,P) = 53.4 and 45.8 Hz, C-7], 97.5 [ddd, ^1J(C,P) = 58.0 and 29.0, ^2J(C,P) = 7.6 Hz, C-5], 126.7 (s, C-*p*), 128.1 (s, C-*m*), 130.2 [dd, ^3J(C,P) = 10.7, J(C,P) = 4.6 Hz, C-*o*], 140.1 [dd, ^2J(C,P) = 9.2, J(C,P) = 4.6 Hz, C-*i*]. – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −113.0 [ddd, ^1J(P-8,P-1) = 200.8, ^2J(P,P) = 9.5 and 5.7 Hz, P-8], −65.6 [ddd, ^1J(P-1,P-8) = 200.8, ^2J(P,P) = 9.5 Hz each, P-1], 19.1 [ddd, ^1J(P-6,P-3) = 99.5, ^2J(P,P) = 9.5 Hz each, P-6], 42.3 [ddd, ^1J(P-3,P-6) = 99.5, ^2J(P,P) = 9.5 and 5.7 Hz, P-3]. – MS (EI, 70 eV), *m/z* (%): 656

(100) [M^+], 565 (4) [$M^+ - CH_2Ph$], 521 (6) [M^+ − adamantyl], 386 (34) [M^+ − 2 adamantyl]. − $C_{40}H_{52}P_4$ (656.8): calcd. C 73.15, H 7.98; found C 73.03, H 8.01.

2,5,7-Tri-tert-pentyl-4-phenyl-1,3,6,8-tetraphosphatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane (**16c**): To a solution of **11** (0.40 g, 1.98 mmol) in toluene (5 ml) was added a solution of **2c** (1.18 g, 10.40 mmol) in hexamethyldisiloxane (32 mol %), and the mixture was stirred at 160−170°C and 8 bar argon pressure for 3 h. The resultant ruby-red solution was then allowed to cool to room temp., and the solvents and excess **2c** were subsequently removed in vacuo (10^{-3} mbar). The residue mainly consisting of **16c** and the λ^3-phosphinine **13c** was separated by column chromatography on silica gel (column: 2 × 30 cm). The first fraction resulting from elution with petroleum ether gave **13c** as a viscous, yellow oil [^{31}P NMR: δ = 192.8 ($CDCl_3$); ref.[26]: δ = 191.0 (C_6D_6)]. A second fraction from petroleum ether furnished **16c** as colorless prisms upon cooling (−20°C) and concentration *in vacuo* (10^{-3} mbar). Yield 0.58 g (63%), m.p. 126−127°C. − IR (KBr): $\tilde{\nu}$ = 3078, 3056, 3020 (CH-aryl), 2958, 2894, 2876, 2848 (CH), 1598, 1540, 1522, 1506, 1388, 1358, 1178, 768, 698 cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 0.67, 0.84, 0.89 [each t, ^3J(H,H) = 7.4 Hz, 3H, CH_2CH_3], 0.98, 1.00, 1.10, 1.12, 1.13, 1.18 (each s, 3H, CH_3), 1.52−1.77 (m, 6H, CH_2), 2.99 [d, ^2J(H,P-3) = 5.4 Hz, 1H, 4-H], 4.33 [dd, ^2J(H,P-6) = 27.6, ^2J(H,P-8) = 8.0 Hz, 1H, 7-H], 6.98 [t, ^3J(H,H) = 7.3 Hz, 1H, *p*-H], 7.08 [dd, ^3J(H,H) = 7.4 and 7.3 Hz, 2H, *m*-H], 7.67 [d, ^3J(H,H) = 7.4 Hz, 2H, *o*-H]. − ^{13}C{^{1}H} NMR (C_6D_6): δ = 8.8, 9.0, 9.5 (each s, CH_2CH_3), 26.6 [dd, ^3J(C,P) = 9.0 Hz each, CH_3], 26.9 [dd, ^3J(C,P) = 10.2 and 5.8 Hz,CH_3], 27.2−28.6 (m, CH_3), 27.3−28.7 (m, CH_3), 29.2 [dd, ^3J(C,P) = 8.0 and 7.8 Hz, CH_3], 29.6 [dd, ^3J(C,P) = 10.0 and 5.2 Hz, CH_3], 34.3 [dd, ^3J(C,P) = 10.8 and 5.9 Hz, CH_2], 37.1 [dd, ^3J(C,P) = 9.0 and 2.1 Hz, CH_2], 37.6, 37.7 [each m, $C(CH_3)_2CH_2CH_3$], 38.4 [dd, ^3J(C,P) = 8.0 and 7.9 Hz, CH_2], 41.5 [ddd, ^2J(C,P) = 17.1 and 9.6, *J*(C,P) = 2.0 Hz, $C(CH_3)_2CH_2CH_3$], 55.8 [dddd, ^1J(C,P) = 63.8, 50.1, and 43.3, ^2J(C,P) = 3.9 Hz, C-2], 62.4 (m, C-4), 79.7 [dd, ^1J(C,P) = 54.2 and 46.0 Hz, C-7], 99.3 [dddd, ^1J(C,P) = 60.2 and 30.3, ^2J(C,P) = 7.9 and 1.9 Hz, C-5], 127.0 (s, C-*p*), 128.5 (s, C-*m*), 130.6 [dd, ^3J(C,P) = 11.0, *J*(C,P) = 5.1 Hz, C-*o*], 140.3 (m, C-*i*). − ^{31}P{^{1}H} NMR (C_6D_6): δ = −106.8 [ddd, ^1J(P-8,P-1) = 205.6, ^2J(P,P) = 8.6 and 4.5 Hz, P-8], −56.9 [ddd, ^1J(P-1,P-8) = 205.6, ^2J(P,P) = 11.5 and 9.9 Hz, P-1], 31.6 [ddd, ^1J(P-6,P-3) = 101.0, ^2J(P,P) = 11.5 and 8.6 Hz, P-6], 41.2 [ddd, ^1J(P-3,P-6) = 101.0, ^2J(P,P) = 9.9 and 4.5 Hz, P-3]. − MS (EI, 70 eV), *m/z* (%): 464 (100) [M^+], 449 (9) [$M^+ - CH_3$], 435 (35) [$M^+ - C_2H_5$], 393 (30) [$M^+ - C_5H_{11}$], 350 (11) [$M^+ - PCC_5H_{11}$], 259 (40) [$M^+ - PCC_5H_{11}$, $- CH_2Ph$]. − $C_{25}H_{40}P_4$ (464.5): calcd. C 64.65, H 8.68; found C 64.86, H 8.63.

Pentacarbonyl {2,5,6,9-tetra-tert-butyl-8-(o-tolylamino)-1,3,4,7,8-pentaphosphatetracyclo[4.3.0.0^{4,9}.0^{5,7}]non-2-ene-P-8}tungsten (**23a**): A solution of **2a** (1.00 g, 10.00 mmol) and **17** (0.49 g, 1.00 mmol) in toluene (2 ml) was heated at 90°C for 1 h with magnetic stirring and then allowed to cool. After removal of the solvent and excess **2a** in vacuo (10^{-3} mbar) the residue was taken up in toluene and purified by recrystallization at −20°C to furnish **23a** as red crystals. Yield 0.26 g (30%), dec. ≥110°C. − IR (pentane): $\tilde{\nu}$ = 2072, 2010, 1954 cm^{-1} (CO). − ^{1}H NMR (C_6D_6): δ = 1.13, 1.29, 1.40, 1.52 [each s, 9H, $C(CH_3)_3$], 2.12 (s, 3H, aryl-CH_3), 6.90−7.00 (m, 1H, aryl-H), 7.20 (br. s, 3H, aryl-H), 7.79 [d, ^2J(H,P) = 8.2 Hz, NH]. − ^{13}C{^{1}H} NMR (C_6D_6): δ = 17.5 (s, CH_3), 31.2, 31.7 [each s, $C(CH_3)_3$], 32.2 [d, ^3J(C,P) = 8.4 Hz, $C(CH_3)_3$], 36.4 [dd, ^2J(C,P) = 10.4 and 6.9 Hz, $C(CH_3)_3$], 39.2 [dd, ^2J(C,P) = 8.2 Hz each, $C(CH_3)_3$], 40.1 [dd, ^2J(C,P) = 10.6 Hz each, $C(CH_3)_3$], 41.8 [dd, ^2J(C,P) = 15.8 and 9.2 Hz, $C(CH_3)_3$], 44.5, 52.4, and 74.5 (m each, C-5,6,9), 128.4−131.9 (C-aryl), 196.1 [d, ^2J(C,P) = 7.9, ^1J(C,W) = 124.8 Hz (satellites), CO-eq], 197.8 [dd, ^2J(C,P) = 20.1, ^3J(C,P) = 8.3 Hz, CO-ax], 207.9 (m, P=C). − ^{31}P{^{1}H} NMR (C_6D_6): δ = −135.8 [d, ^1J(P-7,P-8) = 228.9 Hz, P-7], 50.1 [ddd, ^1J(P-8,P-7) = 228.9, ^2J(P,P) = 145.0 and 22.9, ^1J(P,W) = 230.5 Hz (satellites), P-8], 119.4 [ddd, ^2J(P,P) = 145.0, 15.3, and 15.3 Hz, P-1], 137.1 [ddd, ^1J(P-4,P-3) = 289.4, ^2J(P,P) = 22.9 and 15.3 Hz, P-4], 407.2 [dd, ^1J(P-3,P-4) = 289.4, ^2J(P,P) = 15.3 Hz, P-3]. − MS (EI, 70 eV); *m/z* (%): 861 (3) [M^+], 833 (4) [M^+ − CO], 805 (2) [M^+ − 2 CO], 537 (20) [$M^+ - W(CO)_5$], 437 (100) [$M^+ - W(CO)_5$, $- PCC(CH_3)_3$], 336 (30) [$M^+ - W(CO)_5$, $- 2\ PCC(CH_3)_3$]. − $C_{32}H_{44}NO_5P_5W$ (861.4): calcd. C 44.62, H 5.15, N 1.63; found C 43.90, H 5.04, N 1.60.

Crystal Data and Summary of Data Collection Parameters for **23a**[43]: Diffractometer Enraf Nonius CAD4; radiation Mo-K_α; $C_{32}H_{44}NO_5P_5W$; M = 861.37 g/mol; crystal size 0.25 × 0.28 × 0.30 mm; monoclinic $P2_{(1)}/c$; a = 1094.8(2), b = 1988.9(4), c = 1656.3(5) pm, β = 96.85(2)°; V = 3.581(2) nm^3; Z = 4; $d_{calcd.}$ = 1.598 Mg/m^3; Θ range 2.02−22.68°; no of reflections measured 5147; no. of independent reflections 4951; $R1$ = 0.0911, $wR2$ = 0.1095.

Pentacarbonyl{2,5,6,9-tetraadamant-1-yl-8-(o-tolylamino)-1,3,4,7,8-pentaphosphatetracyclo[4.3.0.0^{4,9}.0^{5,7}]non-2-ene-P-8}tungsten (**23b**): A solution of **2b** (1.25 g, 7.00 mmol) and **17** (0.49 g, 1.00 mmol) in toluene (5 ml) was heated at 90°C for 1 h with magnetic stirring and then allowed to cool. After removal of the solvent in vacuo (10^{-3} mbar) excess **2b** was sublimed off at 50°C (10^{-3} mbar). The residue was taken up in toluene and **23b** induced to crystallize as red crystals by cooling to −20°C. Yield 0.18 g (15%), dec. ≥120°C. − IR (pentane): $\tilde{\nu}$ = 2076, 1950 cm^{-1} (CO). − ^{1}H NMR (C_6D_6): δ = 1.60−2.00 (m, 60H, adamantyl), 2.13 (s, 3H, aryl-CH_3) 7.00−7.10 (m, 1H, aryl-H), 7.30 (br. s, 3H, aryl-H), 7.70 [d, ^2J(H,P) = 8.6 Hz, NH]. − ^{31}P{^{1}H} NMR (C_6D_6): δ = −139.8 [d, ^1J(P-7,P-8) = 221.5 Hz, P-7], 41.5 [ddd, ^1J(P-8,P-7) = 221.5, ^2J(P,P) = 138.2 and 24.8, ^1J(P,W) = 232.7 Hz (satellites), P-8], 111.6 [dd, ^2J(P,P) = 138.2 and 16.4 Hz, P-1], 125.1 [dd, ^1J(P-4,P-3) = 291.3, ^2J(P,P) = 24.8 Hz, P-4], 408.2 [dd, ^1J(P-3,P-4) = 291.3, ^2J(P,P) = 16.4 Hz, P-3].

☆ Dedicated to Professor *H.-J. Bestmann* on the occasion of his 70th birthday.

[1] Part 102: T. W. Mackewitz, U. Bergsträßer, S. Leininger, M. Regitz, *Heteroatom Chemistry* **1995**, *6*, in press.

[2] R. Streubel, *Angew. Chem.* **1995**, *107*, 478−480; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 436−438.

[3] B. Geißler, S. Barth, U. Bergsträßer, M. Slany, J. Durkin, P. B. Hitchcock, M. Hofmann, P. Binger, J. F. Nixon, P. von R. Schleyer, M. Regitz, *Angew. Chem.* **1995**, *107*, 485−488; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 484−487.

[4] V. Caliman, P. B. Hitchcock, J. F. Nixon, M. Hofmann, P. von R. Schleyer, *Angew. Chem.* **1994**, *106*, 2284−2286; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2202−2204.

[5] B. Geißler, T. Wettling, S. Barth, P. Binger, M. Regitz, *Synthesis* **1994**, 1337−1343.

[6] P. Binger, G. Glaser, B. Gabor, R. Mynott, *Angew. Chem.* **1995**, *107*, 114−116; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 81−83.

[7] M. Regitz, U. Bergsträßer, A. Hoffmann, *Chem. Rev.* **1995**, *95*, in press.

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

[9] B. Breit, U. Bergsträßer, G. Maas, M. Regitz, *Angew. Chem.* **1992**, *104*, 1043−1046; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1055−1058.

[10] D. Hu, H. Schäufele, H. Pritzkow, U. Zenneck, *Angew. Chem.* **1989**, *101*, 929−931; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 900−902.

[11] R. Bartsch, P. B. Hitchcook, J. F. Nixon, *J. Organomet. Chem.* **1989**, *375*, C31−34.

[12] T. Wettling, B. Geißler, R. Schneider, S. Barth, P. Binger, M. Regitz, *Angew. Chem.* **1992**, *104*, 761–762; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 758–759.
[13] E. P. O. Fuchs, W. Rösch, M. Regitz, *Angew. Chem.* **1987**, *99*, 1058–1059; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1011–1012.
[14] H. Heydt, U. Bergsträßer, R. Fäßler, E. Fuchs, N. Kamel, T. Mackewitz, G. Michels, W. Rösch, M. Regitz, P. Mazerolles, C. Laurent, A. Faucher, *Bull. Soc. Chim. Fr.* **1995**, in press.
[15] M. Julino, U. Bergsträßer, M. Regitz, *J. Org. Chem.* **1995**, *60*, in press.
[16] X. Li, D. Lei, M. Y. Chiang, P. P. Gaspar, *J. Am. Chem. Soc.* **1992**, *114*, 8526–8531.
[17] X. Li, S. I. Weissman, T.-S. Lin, P. P. Gaspar, A. H. Cowley, A. I. Smirnov, *J. Am. Chem. Soc.* **1994**, *116*, 7899–7900.
[18] F. Mathey in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 34–47.
[19] A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Am. Chem. Soc.* **1982**, *104*, 4484–4485.
[20] A. Marinetti, C. Charrier, F. Mathey, J. Fischer, *Organometallics* **1985**, *4*, 2134–2138.
[21] C. Charrier, N. Maigrot, F. Mathey, *Organometallics* **1987**, *6*, 586–591.
[22] F. Mercier, B. Deschamps, F. Mathey, *J. Am. Chem. Soc.* **1989**, *111*, 9098.
[23] F. Mercier, L. Ricard, F. Mathey, M. Regitz, *J. Chem. Soc., Chem. Commun.* **1991**, 1305–1307; E. Niecke, R. Streubel, M. Nieger, D. Stahlke, *Angew. Chem.* **1989**, *101*, 1708–1710; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1673–1674; E. Niecke, D. Barion, *Tetrahedron Lett.* **1989**, *30*, 459–460.
[24] F. Mathey, A. Marinetti, F. Mercier, *Synlett* **1992**, 363–370.
[25] W. Rösch, M. Regitz, *Z. Naturforsch., Teil B*, **1986**, *41*, 931–933.
[26] M. Hafner, Diploma Thesis, University of Kaiserslautern, **1989**.
[27] *CRC Handbook of Chemistry and Physics*, 73th ed. (Ed.: D. R. Lide), CRC Press, Boca Raton, **1992**, p. 9–1.
[28] F. Mathey, *Chem. Rev.* **1990**, *90*, 997–1025.
[29] U. Zenneck, *Angew. Chem.* **1990**, *102*, 171–182; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 126–137.
[30] D. Böhm, D. Hu, U. Zenneck, *Phosphorus Sulfur* **1993**, *77*, 5–8.
[31] S. S. Al-Juaid, P. B. Hitchcock, R. M. Matos, J. F. Nixon, *J. Chem. Soc., Chem. Commun.* **1993**, 267–269.
[32] P. K. Freeman, V. N. Mallikarjuna Rao, *J. Chem. Soc., Chem. Commun.* **1965**, *21*, 511–512.
[33] T. W. Bentley, B. Goer, W. Kirmse, *J. Org. Chem.* **1988**, *53*, 3066–3073.
[34] C. W. Jefford, V. de los Heros, J.-C. E. Gehret, G. Wipff, *Tetrahedron Lett.* **1980**, *21*, 1629–1632.
[35] S.-J. Kim, T. P. Hamilton, H. F. Schaefer III, *J. Phys. Chem.* **1993**, *97*, 1872–1877.
[36] U. Annen, M. Regitz, *Tetrahedron Lett.* **1988**, *29*, 1681–1684.
[37] R. Yamaguchi, M. Ban, M. Kawanisi, *Bull. Soc. Chem. Jpn.* **1988**, *61*, 2909–2912.
[38] A. Breque, F. Mathey, P. Savignac, *Synthesis* **1981**, 983–985.
[39] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch., Teil B*, **1981**, *36*, 16–19. Optimized procedure cf. W. Rösch, U. Hees, M. Regitz, *Chem. Ber.* **1987**, *120*, 1645–1652, and G. Becker, H. Schmidt, G. Uhl, *Inorg. Synth.* **1990**, *27*, 249–253.
[40] T. Allspach, M. Regitz, G. Becker, W. Becker, *Synthesis* **1986**, 31–36.
[41] T. Allspach, Ph. D. Thesis, University of Kaiserslautern, **1986**.
[42] In analogy to B. Deschamps, L. Ricard, F. Mathey, *Polyhedron* **1989**, *8*, 2671–2676; *o*-tolyl instead of phenyl.
[43] Further details of the crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-401857, -401858, the authors, and the journal citation.

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