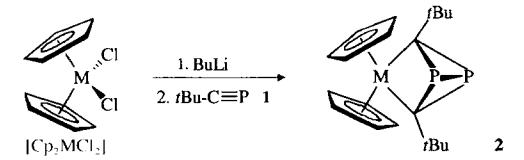
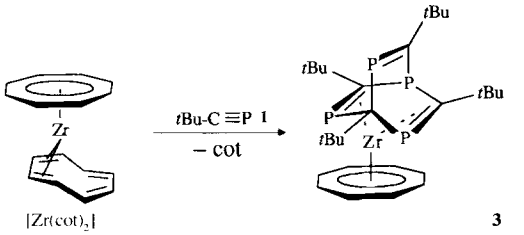
Selective Syntheses of 1,3-Diphosphacyclobutadiene, Dewar-1,3,5-triphosphabenzene, 1,3,5-Triphosphabenzene, and 1,3,5,7-Tetraphosphabarrelene by Cyclooligomerization of Phosphaalkynes**

Paul Binger,* Stefan Leininger, Jörg Stannek, Barbara Gabor, Richard Mynott, Joachim Bruckmann, and Carl Krüger

Dedicated to Professor Manfred Regitz on the occasion of his 60th birthday

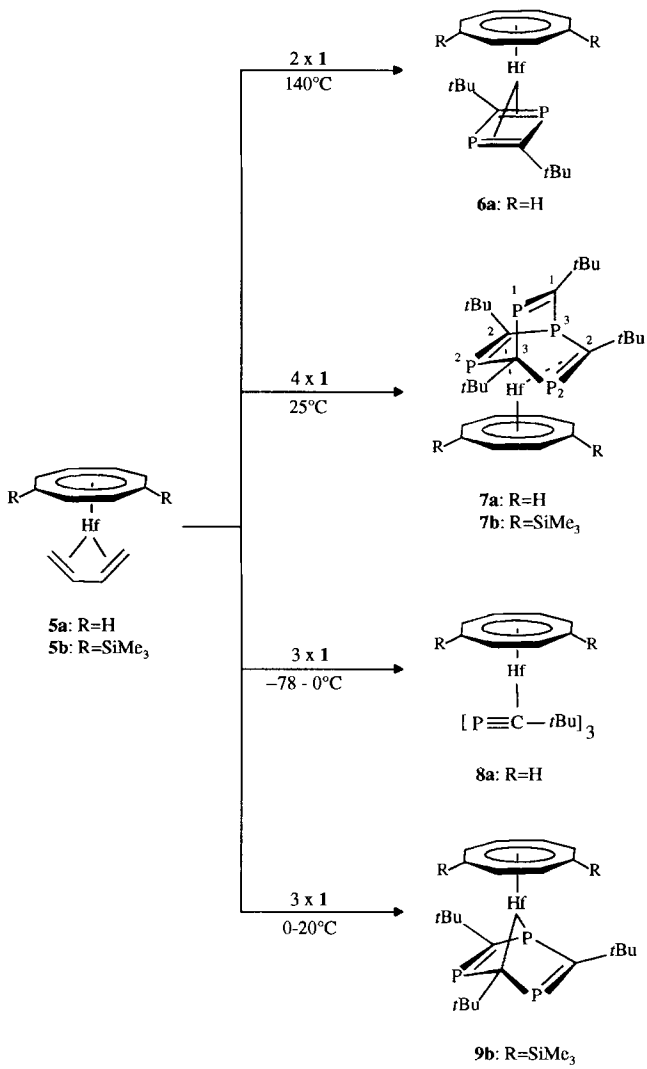
The recently described synthesis of the 1,3,5,7-tetraphosphabarrelene complex **3** from *tert*-butylphosphaacetylene **1** and bis(cyclooctatetraene)zirconium $[Zr(cot)_2]$[1] led to the assumption that the 12-valence electron fragment [cotM], formed as an intermediate by elimination of one of the two cot ligands, is an ideal template for cyclooligomerizations of phosphaalkynes. Phosphaalkynes are known to cyclodimerize on the 14-valence electron fragments $[Cp_2M']$ (M = Zr, Hf) to give the 1,3-diphosphabicyclo[1.1.0]butanediyl metallocenes such as **2**.[2]





In the coordination sphere of electron-rich transition metals (M = Ni, Co, Rh, Fe), phosphaalkynes prefer to cyclodimerize to give 1,3-diphosphacyclobutadiene metal complexes.[3, 4] Only two examples are known for the cyclotrimerization of phosphaalkynes on transition metal complexes: a η^6-1,3,5-triphosphabenzenemolybdenum complex is formed with tricarbonyl(η^6-cycloheptatriene)molybdenum,[5] which, however, was unsatisfactorily characterized and whose synthesis we could not follow.[6] In contrast, the structure of the dewar-1,3,5-triphosphabenzenevanadium complex, prepared from naphthalene(pentamethylcyclopentadienyl)vanadium and **1**, has been confirmed by an X-ray crystal structure analysis.[7]

A better access to coordinatively unsaturated transition metal templates [cotM] is provided by the known η^4-butadiene complexes of zirconium (**4a**) and hafnium (**5a**)[8] as well as their η^8-bis(trimethylsilyl)cyclooctatetraene derivatives **4b** and **5b**. Indeed, complexes **5a** and **5b** did react with the phosphaalkyne **1**[9] at room temperature. In these reactions **1** was cyclotetramerized in a few hours to give almost quantitative yields of the tetraphosphabarrelene complexes **7a** and **7b**, respectively (Scheme 1). The zirconium complex **4a** analogous to **5a** does



Scheme 1. Cyclooligomerization of **1** at the hafnium complexes **5a**, **b**.

[*] Prof. Dr. P. Binger, Dipl.-Chem. J. Stannek, B. Gabor, Dr. R. Mynott, Dipl.-Min. J. Bruckmann, Prof. Dr. C. Krüger
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr (Germany)
Telefax: Int. code + (208)306-2980
Dipl.-Chem. S. Leininger
Fachbereich Chemie der Universität Kaiserslautern (Germany)

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not react with **1** under these conditions, in contrast, **4b** reacts with **1** to give the zirconium complex analogous to **7b**.

An investigation of the temperature dependence of this cyclotetramerization of **1** with the hafnium complexes **5a, b** revealed that **1** reacts already at low temperatures with **5a** or **5b** to give new hafnium complexes. From this finding the postulated stepwise course of the cyclotetramerization of **1**[1] can be partly experimentally understood. Thus, even at $-78\,^{\circ}C$, the hafnium complex **8a** is the sole product of the reaction of **5a** and **1**. It is formed as a green powder in 83% yield; in **8a**, three molecules of **1** are bound to the metal atom (*m/z* 584 (M^+)).

The ^1H NMR spectrum of **8a** recorded at $-30\,^{\circ}C$ shows two sharp singlets at $\delta = 1.35$ and 0.81 (ratio of intensities 2:1) for the three *tert*-butyl groups. These signals broaden significantly at 20 °C and collapse to one singlet at 60 °C at $\delta = 1.17$. In contrast, the position and multiplicity of the signal at $\delta = 6.60$ (s) for the H atoms of the cot ring are almost independent of the temperature. In the ^{31}P NMR spectrum of **8a** at $-30\,^{\circ}C$, there are only two signals at $\delta = 17.3$ and 357.1 ($J_{P,P} = 43.7$ Hz; ratio 2:1) for the three phosphorus atoms; these signals do not separate further down to temperatures of $-80\,^{\circ}C$; at 60 °C these signals are broadened. In the ^{13}C NMR spectrum at $-30\,^{\circ}C$, the weak signals of the P-bound C atoms could only be identified clearly under INEPT conditions[10] (a doublet of triplets at $\delta = 139.3$ and a triplet at $\delta = 93.8$ (half intensity)). The signals of the C atoms of the *tert*-butyl groups show a similar splitting pattern (Table 1). Together with the result of the ligand liberation with hexachloroethane, which affords the free 1,3,5-triphosphabenzene **13** (see below), the spectroscopic findings only allow the conclusion that a cyclic trimer of **1** is bound in the complex **8a**.

If the hafnium complex **5b** is allowed to react with **1** at 0 °C, the reaction likewise does not proceed further than the stage of a cyclotrimeric complex of **1**. The bonding between the metal atom and the phosphaalkyne trimer in the new hafnium complex **9b** evidently differs from that in complex **8a**, since two broad signals at $\delta = 263$ and 140 appear in the ^{31}P NMR spectrum of **9b** in the temperature range $-40\,^{\circ}C$ to 30 °C; the coupling constants, however, could not be determined. In the ^1H NMR spectrum of **9b**, the signals for the *tert*-butyl groups are resolved only at $-40\,^{\circ}C$; two singlets are observed at $\delta = 1.32$ and 1.34 in the ratio 2:1 (Table 1). A meaningful ^{13}C NMR spectrum of **9b** has not been obtained yet. According to the analytical results gathered to date, **9b** has the structure given in Scheme 1; the metal atom possibly interacts in a rapid exchange with one of the two P=C bonds. This proposed structure is supported by the liberation reaction with hexachloroethane, which affords the dewar-1,3,5-triphosphabenzene **14** (see below).

The course of the reaction between **5a** and **1** at higher temperatures is surprising. An approximate 1:1 mixture of the tetraphosphabarrelene complex **7a** and the 1,3-diphosphete complex **6a** is formed at about 80 °C, whereas at about 140 °C only **6a** is formed in 68% yield. The spectroscopic data of **6a** indicate that the π electrons are not completely delocalized in the η^4-bound 1,3-diphosphete ligand, as in the corresponding 1,3-diphosphete complexes of Co, Rh, or Fe.[4] In the ^{31}P and ^{13}C NMR spectra of **6a**, the signals of the phosphorus and carbon atoms of the four-membered ring are considerably shifted downfield in comparison to those in the spectra of the 1,3-diphosphacyclobutadienecobalt and -rhodium complexes (^{31}P: $\delta = 38-50 \rightarrow 201.7$; ^{13}C: $\delta = 108-113 \rightarrow 149.7$). Similar shifts were determined in the recently synthesized η^8-cyclooctatetraene(η^4-di-*tert*-butyl-1,3-diphosphete)titanium complex.[11] Our assumptions were confirmed by a crystal structure analysis of this compound: in the complex-bound 1,3-diphosphete, the P–C bond lengths alternate (1.748 and 1.828 Å).[11] A localization of the π electrons in the 1,3-diphosphete ligand of **6a** should result in a weaker interaction with the metal atom.

An experimental test of the reactivity of **6a** towards hexachloroethane revealed that the 1,3-diphosphete **10** can be liberated from **6a** even at room temperature by a redox reaction. To date this has not been achieved with any of the other known η^4-1,3-diphosphete complexes.[3, 4, 11] However, as expected, **10** is so unstable that it cannot be isolated or detected by spectroscopy. The only isolable reaction product is the tetraphosphacubane **11**, [12] which is formed from **10** in 34% yield through a sequence of [4 + 2]- and [2 + 2]cycloadditions[2b] (Scheme 2).

Thus, **6a** shows the same reactivity towards hexachloroethane as the recently described cyclooctatetraene(tetraphosphabarrelene)zirconium complex **3**[1] and the two tetraphosphabarrelenehafnium complexes **7a** and **7b** described here for the first time. In all three cases two of the double bonds π-bound to the metal atom were liberated under oxidation of the metal to [(cot)MCl_2] and reduction of the hexachloroethane to give the tetrachloroethylene. In this way, as described recently for the

Table 1. Selected physical data of **6a**, **7a**, **8a**, **9b**, **13**, and **14** [a, b].

6a: ^1H NMR: $\delta = 1.20$ (s, 18H, *t*Bu), 6.89 (s, 8H, cot); ^{13}C NMR: $\delta = 149.7$ (t, J(C,P) = 55.4 Hz, ring-C), 37.7 (t, J(C,P) = 8.2, *t*Bu), 34.5 (q, t, J(C,H) = 125, J(C,P) = 5.0 Hz, *t*Bu), 91.6 (d, ^1J(C,H) = 171, cot); ^{31}P NMR: $\delta = 201.7$ (s); MS (70 eV): *m/z* [%]: 484 (M^+) [80], 469 ($M^+ - CH_3$) [100], 346 ($M^+ - C_2tBu_2$) [51], 284 ($M^+ - 2P{\equiv}CtBu$) [17]

7a [1]: ^1H NMR: $\delta = 1.13$ (s, 18H, *t*Bu), 1.35 (s, 9H, *t*Bu), 1.50 (s, 9H, *t*Bu), 6.39 (s, 8H, cot); ^{13}C NMR: $\delta = 216.6$ (J(C,P1) = 99.8, J(C,P2) = 6.9, J(C,P3) = 59.8 Hz, C1), 43.6 (J(C,P1) = 25.2, J(C,P3) = 22.7 Hz, *t*Bu at C1), 35.4 (^1J(C,H) = 126, J(C,P1) = 14.8, J(C,P3) = 8.7 Hz, *t*Bu at C1), 74.1 (J(C,P2A) + J(C,P2B) = 101.9, J(C,P3) = 46.1 Hz, C2), 37.3 (J(C,P2A) + J(C,P2B) = 20.9, J(C,P3) = 12.6 Hz, *t*Bu at C2), 35.7 (^1J(C,H) = 125, J(C,P2A) + J(C,P2B) = J(C,P3) = 10.0 Hz, *t*Bu at C2), 34.9 (J(C,P1) = 84.9, J(C,P2) = 71.4, J(C,P3) = 3.8 Hz, C3), 37.2 (J(C,P1) = 21.2, J(C,P2) = 12.0, J(C,P3) = 3.1 Hz, *t*Bu at C3), 31.2 (^1J(C,H) = 126, J(C,P1) = 12.0, J(C,P2) = 4.8 Hz, *t*Bu at C3); ^{31}P NMR: $\delta = 283.2$ (J(P1,P2) = 8.1, J(P1,P3) = 7.3 Hz, P1), −134.2 (J(P2,P3) = 23.4, J(P2,P1) = 8.1, J(P2,P3) = 23.4 Hz, P2), −140.7 (J(P3,P1) = 7.3, J(P3,P2) = 23.4 Hz, P3); MS (70 eV): *m/z* [%]: 684 (M^+) [15], 627 ($M^+ - tBu$) [14], 402 ($(P{\equiv}CtBu)_4^+ + H_2$) [70], 262 [46], 231 [86], 169 [87], 131 [58], 41 [100]

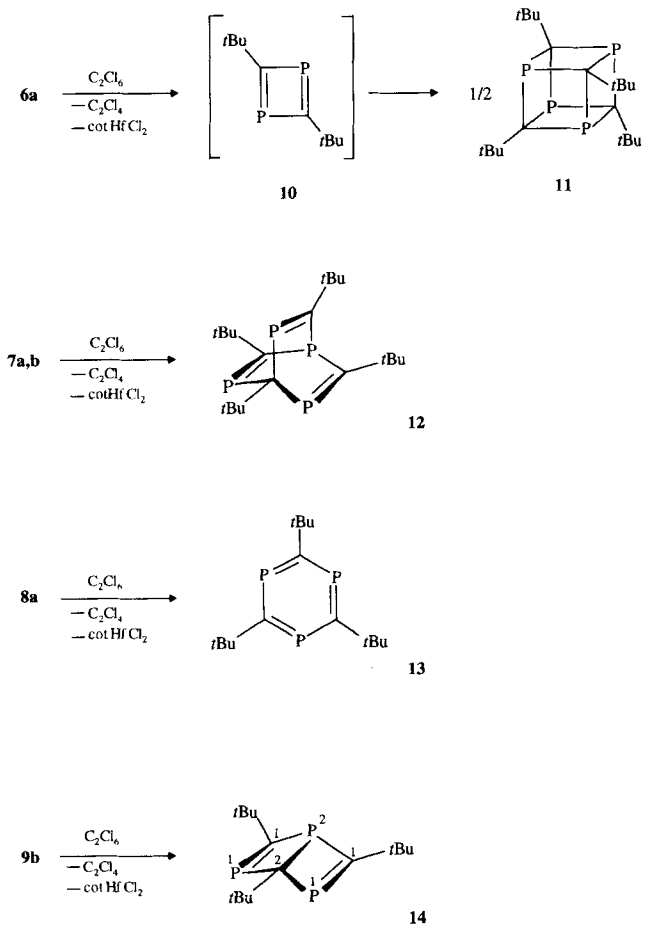
8a: ^1H NMR (−30 °C): $\delta = 0.81$ (s, 9H, *t*Bu), 1.35 (s, 18H, *t*Bu), 6.60 (s, 8H, cot); ^1H NMR (+60 °C): $\delta = 1.17$ (s, 27H, *t*Bu), 6.5 (s, 8H, cot); ^{13}C NMR (−30 °C): $\delta = 139.3$ (dt, J(C,P) = 74, J(C,P) + J(C,P′) = 69.4 Hz, ring-C), 93.8 (t, J(C,P) = 59.4 Hz, ring-C), 40.1 (J(C,P) = 18.9, J(C,P) + J(C,P′) = 22.0 Hz, *t*Bu), 35.1 (^1J(C,H) = 125 Hz, *t*Bu), 38.7 (J(C,P) = 9.5 Hz, *t*Bu), 30.8 (^1J(C,H) = 125, J(C,P) = 7.4 Hz, *t*Bu), 95.5 (^1J(C,H) = 171 Hz, cot); ^{31}P NMR (−30 °C): $\delta = 357.1$ (t, J(P,P) = 43.8, 2P), 17.3 (d, 1P); MS (70 eV): *m/z* [%]: 584 (M^+) [38], 515 ($M^+ - CtBu$) [19], 469 ($M^+ - P{\equiv}CtBu - Me$) [19], 446 ($M^+ - C_2tBu_2$) [100], 346 [68], 299 [26]

9b: ^1H NMR (−40 °C): $\delta = 0.49$ (s, 18H, $SiMe_3$), 1.32 (s, 18H, *t*Bu), 1.34 (s, 9H, *t*Bu), 6.46 and 6.72 (m, 4H, AA′BB′ spin system, ^3J(H,H) = 11.3, 11.1, ^4J(H,H) = 1.2 Hz, cot), 6.84 (s, 2H, cot); ^{31}P NMR: $\delta = 263$ (br., 2P), 140 (br., 1P); MS (70 eV): *m/z* [%]: 728 (M^+) [1], 590 ($M^+ - tBu_2C_2$) [6], 300 ($P_3C_3tBu_3^+$) [84], 175 (cotSiMe$_3$) [89], 73 ($SiMe_3^+$) [100]

13: ^1H NMR: $\delta = 1.71$ (s, *t*Bu); ^{13}C NMR{^1H}: $\delta = 211.8$ (X component of an A_2BX spin system, $|J(P,P)| = 8.0$, ^1J(P,C) = ±77.0, ^3J(P,C) = ±15.2, $(\nu_A - \nu_B) =$ ±10.2 Hz (from iteration), ring-C), 44.5 (A_2BX spin system, $|J(P,P)| = 8.1$, ^2J(P,C) = ±24.5, ^4J(P,C) = ±1.6, $(\nu_A - \nu_B) =$ ±0.7 Hz (from iteration), *t*Bu), 36.1 (^1J(P,P) = 8.0, ^3J(P,C) = ±14.5, ^5J(P,C) = ±1.1, $(\nu_A - \nu_B) =$ ±0.1 Hz (from iteration), *t*Bu); ^{31}P NMR: $\delta = 232.6$ (s); MS (70 eV): *m/z* [%]: 300 (M^+) [39], 169 ($PC_2tBu_2^+$) [100], 100 ($P{\equiv}CtBu^+$) [32]

14: ^1H NMR: $\delta = 1.34$ (s, 18H, *t*Bu), 1.40 (s, 9H, *t*Bu); ^{13}C NMR: $\delta = 236.7$ (ddd, ^1J(C,P) = 55.9, 47.5, ^3J(C,P) = 20.0 Hz, C1), 39.5 (dt, ^2J(C,P) = 6.8, ^4J(C,P) = 3.4 Hz, *t*Bu at C1), 32.1 (dt, ^3J(C,P) = 5.4, ^5J(C,P) = 4.4 Hz, *t*Bu at C1), 46.6 (dt, ^1J(C,P) = 39.8, 28.0, C2), 35.3 (dt, ^2J(C,P) = 6.7, 1.8 Hz, *t*Bu at C2), 28.5 (pseudo-q, ^3J(P,C) = 7.2 Hz, *t*Bu at C2); ^{31}P NMR: $\delta = 336.8$ (d, ^2J(P,P) = 23.5 Hz, P1), 93.6 (t, ^2J(C,P) = 23.5 Hz, P2); MS (70 eV): *m/z* [%]: 300 (M^+) [42], 200 ($M^+ - P{\equiv}CtBu$) [30], 169 ($PC_2tBu_2^+$) [100], 100 ($P{\equiv}CtBu^+$) [30]

[a] ^1H NMR (TMS): 300 MHz (**6a**–**8a**), 400 MHz (**9b**, **13**, **14**); ^{13}C NMR (TMS): 100.6 MHz; ^{31}P NMR (85% H_3PO_4): 162.0 MHz; solvent: [D_8]THF (**6a**, **8a**, **13**), [D_8]toluene (**7a**, **14**), CD_2Cl_2 (**9b**); MS: Varian-CH5. [b] For the numbering of the C and P atoms see Scheme 1 and 2.



Scheme 2. Liberation of the phosphorus heterocycles **10**–**14**.

tetraphosphabarrelenezirconium complex **3**,[11] the 1,3,5,7-tetraphosphabarrelene **12** was obtained in over 80% yield from **7a** and **7b** (Scheme 2).

The structure of **12**, which had already been identified unambiguously on the basis of its spectroscopic data,[11] was confirmed by an X-ray structure analysis (Fig. 1).[13]

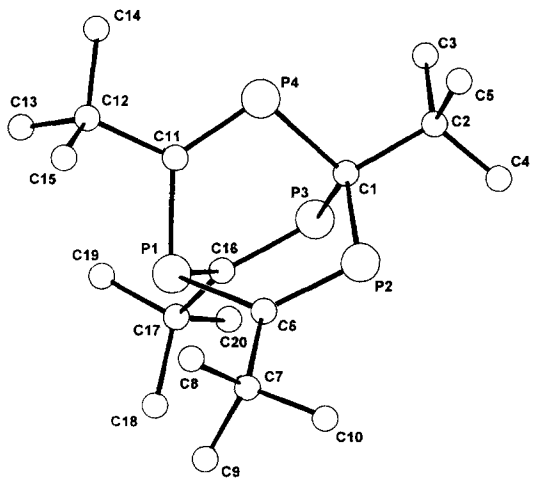


Fig. 1. Crystal structure of **12**. Selected bond lengths [Å] and angles [°]: P1-C6 1.862(1), P1-C11 1.851(1), P1-C16 1.858(1), P2-C1 1.877(1), P2-C6 1.671(1), P3-C1 1.871(1), P3-C16 1.667(1), P4-C1 1.869(1), P4-C11 1.668(1); C16-P1-C11 100.1(1), C16-P1-C6 98.8(1), C11-P1-C6 99.9(1), C6-P2-C1 104.7(1), C16-P3-C1 104.4(1), C11-P4-C1 104.5(1), P4-C1-P3 110.6(1), P4-C1-P2 110.0(1), P3-C1-P2 109.1(1), P2-C6-P1 122.3(1), P4-C11-P1 122.8(1), P3-C16-P1 122.8(1).

The two trimer complexes **8a** and **9b** also react readily with hexachloroethane at room temperature. Thus, in this way one example from the class of 1,3,5-triphosphabenzenes (**13**) and one from the class of dewar-1,3,5-triphosphabenzenes (**14**) could be synthesized and characterized for the first time. The triphosphabenzene **13** was obtained in 53% yield from **8a** in the form of a pale yellow, microcrystalline powder by stirring with hexachloroethane at room temperature for 12 h. Under similar conditions, the dewar-triphosphabenzene derivative **14** is formed in 70% yield from **9b** in the form of orange microcrystals. Both compounds are stable at room temperature under exclusion of air and moisture. An isomerization of **14** to **13** can be achieved by heating to 90 °C; after 5 h 20% of **14** had rearranged into **13**. For the parent compounds, the triphosphabenzene is 25 kcal mol^{-1} more stable than the dewar-triphosphabenzene.[14]

The structures of the two new compounds **13** and **14** were established unambiguously by mass spectrometry and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The mass spectra of the two compounds exhibit a molecular ion peak at m/z 300; the spectra of **13** and **14** differ only slightly in the intensities of the fragment ion signals (Table 1). The different structures of **13** and **14** are clearly evident in their ^{31}P NMR spectra; in the spectrum of **13** a singlet appears at $\delta = 232.6$ for all three phosphorus atoms, whereas in the spectrum of **14** a doublet appears at $\delta = 336.8$ ($J_{P,P} = 23.5$ Hz) for the two unsaturated phosphorus atoms P1 and a triplet appears at $\delta = 93.6$ for the bridgehead phosphorus atom P2 (for atom numbering see Scheme 2). All the NMR signals lie in the expected range.[1, 6, 15] The structure determinations of **13** and **14** were completed by their ^{13}C NMR spectra: the ring carbon atoms of **13** give rise to one signal at $\delta = 211.8$, whose coupling pattern corresponds to the X component of an A_2BX spin system (Table 1). A multiplet for the two sp^2 carbon atoms C1 at $\delta = 236.7$ ($^1J_{C,P} = 55.9, 47.5$ Hz, $^3J_{C,P} = 20$ Hz), which can be roughly analyzed as a first order signal (ddd), and a triplet of doublets at $\delta = 46.6$ ($^1J_{C,P} = 39.8, 28.0$ Hz) for the bridgehead carbon atom C2 appear in the spectrum for the differently bound carbon atoms of the bicycle **14**. The chemical shifts of the C atoms of the *tert*-butyl groups do not require an explanation. Neither do their signals in the ^1H NMR spectra (one signal for **13** and two singlets in the ratio 2:1 for **14**; Table 1).

According to its NMR spectra (^1H, ^{13}C, ^{31}P), the free 1,3,5-triphosphinine **13** is a π^6-heteroarene. Its relationship to the many known phosphinines[16] and the two recently synthesized 1,3-diphosphinines[15] is unmistakable. A 1,4-diphosphinine, 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphinine has so far only been detected in solution; NMR spectroscopic data of this compound are not known.[17] The spectroscopic data of a well-known $1\lambda^5,3\lambda^5,5\lambda^3$-triphosphinine differ considerably from those of the compound **13**.[18]

The NMR spectra of the dewar-1,3,5-triphosphabenzene (dewar-1,3,5-triphosphinine) **14** resemble those of dewar-1-phosphinine[19] and of dewar-2-phosphinine.[20] The only notable difference between the spectra is the position of the signal of the bridgehead phosphorus atom P2, which is considerably shifted downfield in **14**. However, the corresponding phosphorus atom in a dewar-1,3,5-triphosphabenzenevanadium complex adopts a similar position ($\delta = 84.4$).[6]

With the successful synthesis of the 1,3,5-triphosphabenzene **13** and its dewar benzene valence isomer **14**, we are now in the position to investigate the reactivity of these new phosphorus heterocycles. Our priorities in this respect are the study of the cycloaddition behavior and the properties of these compounds as complex ligands in transition metal chemistry.

Experimental Procedure

6a: **1** (1.12 g, 11.2 mmol) in xylene (10 mL) was added dropwise over 0.5 h to a boiling solution of **5a** (2.0 g, 5.6 mmol) in xylene (40 mL). The mixture was stirred for a further 0.5 h at about 140 °C and then the solvent was removed at 0.5 mbar. The resulting brown solid was suspended in pentane (20 mL), filtered with a D3 frit, washed with pentane, and dried at 10^{-3} mbar. Recrystallization from toluene afforded **6a** (1.83 g, 68%) as brown microcrystals; m.p. 163 °C (decomp.).

8a: **1** (3.4 g, 34 mmol) was added dropwise to a solution of **5a** (4.0 g, 11.2 mmol) in toluene (10 mL) and pentane (10 mL) at −78 °C and stirred for 18 h at −78 °C. The green-brown suspension was filtered at −78 °C and the residue washed twice with pentane (2 × 20 mL). Recrystallization from THF (10 mL) afforded **8a** (5.39 g, 83%) as green microcrystals; m.p. ca. 138 °C (decomp.).

9b: **1** (1.3 g, 13 mmol) was added dropwise to a solution of **5b** (2.08 g, 4.32 mmol) in Et_2O (30 mL) at 0 °C. After 1 h the reaction solution was cooled to −30 °C, the green crystals of **9b** which precipitated were filtered off and dried at 10^{-3} mbar; **9b** (2.8 g, 89%); m.p. 107 °C (decomp.).

13: Hexachloroethane (0.2 g, 0.86 mmol) was added to a suspension of **8a** (0.5 g, 0.86 mmol) in toluene (30 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature over the course of 12 h, filtered, and the filtrate was evaporated to dryness at 0.5 mbar. The residue was dissolved in pentane (20 mL) and small amounts of insoluble material were removed by filtration. The yellow filtrate was concentrated to 5 mL and cooled to −78 °C. After 8 h, 0.14 g of **13** (53%) had precipitated in the form of a yellow solid; m.p. 88 °C (decomp.).

14: Hexachloroethane (425 mg, 1.8 mmol) was added to a solution of **9b** (1.3 g, 1.8 mmol) in toluene (10 mL) at room temperature and the mixture was stirred for 2 h. The solvent was removed at 0.5 mbar, the residue was taken up in pentane (40 mL) and filtered over Celite to remove insoluble material. On cooling to −30 °C small amounts of [bis(trimethylsilyl)cyclooctatetraene]hafnium dichloride precipitated, which was likewise filtered off. The clear filtrate was concentrated to 20 mL, and subsequent cooling to −30 °C led to the precipitation of **14** (380 mg, 70%) in the form of orange microcrystals; m.p. about 128 °C (decomp.).

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meso-Tetrakis[4-(diphenylphosphino)-phenyl]porphyrin and a Water-Soluble Octakis-(phosphonium salt) Porphyrin Double-Decker with a Cage Structure

Gottfried Märkl,* Martin Reiss, Peter Kreitmeier, and Heinrich Nöth

Dedicated to Professor Rolf Huisgen on the occasion of his 75th birthday

Water-soluble porphyrins are important because of their potential interactions with biological systems (e.g. double-stranded cleavage of DNA, photochemical oxidations, photodynamic tumor therapy, photoinduced intramolecular electron- and energy transfer).[1–3] As a result, a series of ammonio-substituted porphyrins,[4–6] porphyrinyl uridines,[7] and sugar-substituted porphyrins[8] have been reported. So far there are no reports of phosphinoporphyrins; we are only aware of complexes of octaethylporphyrin (OEP) and tri- or pentavalent phosphorus as the "metallic" central atom, $([P(OEP)]^+X^-$ and $([P[OEP)-(OH)_2]^+ClO_4^-)$.[9] Here, we describe a phosphino-substituted porphyrin for the first time, the tetrakis[4-diphenylphosphino)phenyl]porphyrin **2a**, whose cationic form represents a new type of water-soluble porphyrin.

[*] Prof. Dr. G. Märkl, Dipl.-Chem. M. Reiss, Dr. P. Kreitmeier
Institut für Organische Chemie der Universität
Universitätsstrasse 31, D-93040 Regensburg (Germany)
Telefax: Int. code + (941)943-4504
Prof. Dr. H. Nöth
Institut für Anorganische Chemie der Universität
Meiserstrasse 1, D-80333 München (Germany)
Telefax: Int. code + (89)590-2451