electrons. In addition 10.3 (9.88) electrons reside in copper's outer shells: 4s (0.53 (0.49)), 3d (9.7 (9.4)), 4p (0.04 (0.02)), 4d (0.06 (0.02)). A straightforward interpretation of the data is that copper functions as a d-base through the 3d$_{x^2-y^2}$ orbital, retrieving lost electronic charge by means of backbonding to the 4s, 4p, and 3d orbitals. The analysis places 3.3 (3.1) and 7.4 (7.5) electrons at carbon and fluorine atoms, respectively. Carbon is thus depleted by + 0.7 (+ 0.9) units of charge, while fluorine gains −0.4 (− 0.5). The CF$_3$ groups carry 25.4 (25.5) electrons, precisely the average of three CF$_3^-$ groups and one CF$_3^+$ group. Charge neutralization in anion **3** by an ammonium cation to give a contact ion-pair causes no change in the electron distribution.

Attempts were made to force the SCF wavefunction to converge on the Cu^{III} state by switching filled copper d orbitals with the LUMO, the high energy counterpart of **3**'s bonding SS$_2$ MO in Figure 1. The numerical experiment led to a state with 1.99–2.00 electrons in all d orbitals except d$_{xy}$, which had 1.1 electrons. The total energy of this state is 250 kcal mol^{-1} above the fully relaxed d$_{xy}$ orbital with 1.97 electrons. This is consistent with the SCF result that the largely localized lone pair Cu d orbitals in **3** are 193–218 kcal mol^{-1} lower in energy than the HOMO. In the naked Cu^{I} monocation the same orbitals are degenerate and lie at the frontier orbital gap. An empirical argument that might be made against the interpretation of **3** as a Cu^{I} complex is the appearance of a quasi square-planar structure in the solid state, the common geometry for d^8 metal complexes. Though tetracoordinate d^{10} Cu^{I}–ligand association ordinarily produces tetrahedral structures, square-planar approximations are not unknown.[31–33]

The picture that emerges for **3** is one in which the bonding between Cu$^+$ and the average of (CF$_3^-$)$_3$ and CF$_3^+$ (i.e. (CF$_3^{-0.5}$)$_4$) is principally ionic. The covalent component derived by the full calculation is in complete accord with Figure 1. Two delocalized five-center, two-electron bonds are accompanied by two nonbonding electron pairs. The description strongly implies that oxidation of CuCF$_3$ has effectively removed electrons from a CF$_3$ ligand, and the charge depletion is then shared equally by the four trifluoromethyl substituents in product **3**. Furthermore, the electron depletion at CF$_3$ depicted in Figure 1 suggests CF$_3$–CF$_3$ to be an important thermal decomposition product, as has been observed (D. Naumann and T. Roy, private communication). Similar calculations show that analogous concepts apply to **4**.[18]

The apparent willingness of a powerful electronegative moiety such as CF$_3^-$ to undergo oxidation in preference to Cu^{I} underscores both the importance of the role of ligand in assessing oxidation pathways in metal complexes and the resistance of copper to assume the Cu^{III} state. The principles outlined herein can be expected to apply to the mechanism of cuprate addition as well as to contribute to a deeper understanding of other metals assigned high oxidation states in complexes.

Received: May 13, 1994
Revised: August 4, 1994 [Z6933IE]
German version: *Angew. Chem.* **1995**, *107*, 112

Keywords: ab initio calculations · copper compounds · cuprates · electronic structure

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[1] B. E. Rossiter, N. M. Swingle, *Chem. Rev.* **1992**, *92*, 771.
[2] B. H. Lipshutz, S. Sengupta, *Org. React.* **1992**, *41*, 135.
[3] "CuCl": S. H. Bertz, E. H. Fairchild in *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. Paquette), Wiley, Chichester, in press.
[4] G. Hallnemo, T. Olsson, C. Ullenius, *J. Organomet. Chem.* **1985**, *282*, 133–144.
[5] B. Christenson, T. Olsson, C. Ullenius, *Tetrahedron* **1989**, *45*, 523–534.
[6] S. H. Bertz, R. A. J. Smith, *J. Am. Chem. Soc.* **1989**, *111*, 8276–8277.
[7] E. J. Corey, N. W. Boaz, *Tetrahedron Lett.* **1984**, *25*, (29), 3063–3066.
[8] E. J. Corey, N. W. Boaz, *Tetrahedron Lett.* **1985**, *26*, (49), 6015–6018.
[9] S. Sharma, A. C. Oehlschlager, *Tetrahedron* **1991**, *47*, 1177–1184.
[10] N. Krause, R. Wagner, A. Gerold, *J. Am. Chem. Soc.* **1994**, *116*, 381–382.
[11] S. R. Krauss, S. G. Smith, *J. Am. Chem. Soc.* **1981**, *103*, 141–148.
[12] C. R. Johnson, G. A. Dutra, *J. Am. Chem. Soc.* **1973**, *95*, 7783.
[13] J. P. Collman, L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, **1980**.
[14] A. E. Dorigo, K. Morokuma, *J. Am. Chem. Soc.* **1989**, *111*, 4635–4643.
[15] A. E. Dorigo, K. Morokuma, *J. Am. Chem. Soc.* **1989**, *111*, 6524–6536.
[16] H. O. House, W. L. Respess, G. M. Whitesides, *J. Org. Chem.* **1966**, *31*, 3128.
[17] D. Naumann, T. Roy, K.-F. Tebbe, W. Crump, *Angew. Chem.* **1993**, *105*, 1555–1556; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1482–1483. Meanwhile, a superconducting salt with [Cu(CF$_3$)$_4$]$^-$ as anion has been reported: J. A. Schleuter, U. Geiser, J. M. Williams, H. H. Wang, W.-K. Kwok, J. A. Fendrich, K. D. Carlson, C. A. Achenbach, J. D. Dudek, D. Naumann, T. Roy, J. E. Schirber, W. R. Bayless, *J. Chem. Soc. Chem. Commun.* **1994**, 1599–1600.
[18] M. A. Willert-Porada, D. J. Burton, N. C. Baenziger, *J. Chem. Soc., Chem. Commun.* **1989**, 1633.
[19] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
[20] V. Jonas, G. Frenking, M. T. Reetz, *J. Comput. Chem.* **1992**, *13*, (8), 919–934.
[21] M. Böhme, G. Frenking, M. T. Reetz, *Organometallics*, submitted.
[22] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres; K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, *Gaussian 92*, Revision A ed., Gaussian, Inc., Pittsburg, PA, **1992**.
[23] The ECP-2/MP2 combination used here provides results comparable with all-electron calculations. For Cu–F we find r(Cu–F) = 1.747 Å and μ = 5.21 D. A recent near-Hartree–Fock limit plus MP2 calculation gave 1.786 Å and 6.12 D [24] (vs. experimental values of 1.745 Å and 5.77 D [25]). For Cu–CH$_3$ we obtain r(Cu–C) = 1.913 Å and μ = 2.29 D. An all-electron triple-ζ optimization with correlation yielded 1.936 Å and 2.41 D, respectively [26].
[24] P. Schwerdtfeger, P. D. W. Boyd, G. A. Bowmaker, L. P. Aldridge, *Struct. Chem.* **1990**, *1*, 405–415.
[25] K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure. Constants of Diatomic Molecules*, Van Nostrand, New York, **1979**.
[26] C. W. Bauschlicher Jr., S. R. Langhoff, H. Partidge, L. A. Barnes, *J. Chem. Phys.* **1989**, *91*, 2399–2411.
[27] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735.
[28] A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 1736.
[29] A. E. Reed, F. Weinhold, *J. Am. Chem. Soc.* **1986**, *108*, 3586–3593 and references therein.
[30] A. E. Reed, L. A. Curtis, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.
[31] B. Chiari, U. Piovesana, T. Tarantelli, P. F. Zanazzi, *Inorg. Chem.* **1984**, *23*, 2542–2547.
[32] J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, A. H. White, *J. Chem. Soc. Dalton Trans.* **1985**, *4*, 839–844.
[33] M. Hakansson, S. Jagner, M. Nilsson, *J. Organomet. Chem.* **1987**, *336*, 279–285.

1,3,5,7-Tetraphosphabarrelene: A New Cyclic Phosphaalkyne Tetramer**

Paul Binger,* Gerald Glaser, Barbara Gabor, and Richard Mynott

The chemistry of phosphaalkynes (RC≡P) has gained considerable momentum through the use of transition-metal templates in cyclooligomerizations.[1] The cyclodimerization of *tert*-butylphosphaacetylene **5** to give the cobalt[2] and rhodium[3] η^4-1,3-diphosphacyclobutadiene complexes **1**, the unexpected formation of the tricyclic zirconium and hafnium complexes **2**

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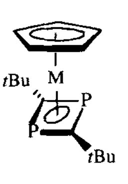
[**] This work was supported by the Volkswagen-Stiftung and the Deutsche Forschungsgemeinschaft (Graduiertenkolleg: phosphorus as a connecting link between different chemical disciplines).

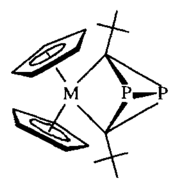
0570-0833/95/0101-0081 $ 10.00+.25/0

from **5**,[4] and the cyclotrimerization of **5** to yield the 1,3,5-triphosphadewarbenzene complex **3** with vanadium as the central atom[5] are important milestones in an area that is still rapidly developing.



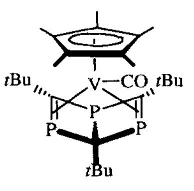
1

M = Co, Rh



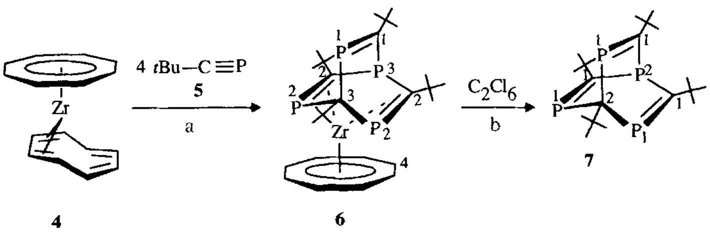
2

M = Zr, Hf



3

Of these metal complexes with heterocyclic ligands, only the zirconium and hafnium compounds **2** have thus far emerged as viable starting materials for the synthesis of novel phosphaheterocycles.[4b, 6] In this context, the remarkable synthesis of a symmetrical tetraphosphacubane from **2** deserves a special mention.[7] We report here the first successful cyclotetramerization of the phosphaalkyne **5** with the bis(cyclooctatetraene)–zirconium complex **4** to yield the η^4-1,3,5,7-tetraphosphabarrelene–zirconium complex **6** and the reaction of **6** with hexachloroethane to liberate the 1,3,5,7-tetraphosphabarrelene derivative **7**, a novel, cyclic tetramer of phosphaalkyne **5** (Scheme 1).



Scheme 1. a: toluene, 2 d, 70 °C, −cot; b: pentane, 12 h, −78–20 °C, $-C_2Cl_4$, $-[(cot)ZrCl_2]$

The zirconium complex **6** was obtained as a dark green, microcrystalline solid in 81 % yield after prolonged heating of **4**[8] with excess *tert*-butylphosphaacetylene **5** at 70 °C. Although we have not yet been able to grow crystals suitable for a crystal structure analysis, the structure of **6** could nevertheless be established unambiguously through spectroscopic methods (mass spectrometry; ^1H, ^{13}C, and ^{31}P NMR spectroscopy).

The mass spectrum of **6** exhibits a molecular ion peak at *m/z* 594 and a base peak at *m/z* 400 corresponding to a tetramer of **5** (Table 1). This was the first significant clue that complex **6** contained a tetramer of **5** that could be cleaved from **6** as a stable compound. In the ^{31}P NMR spectrum of **6**, three signals are observed for the four phosphorus atoms, in a ratio of 1:2:1 at $\delta = 285.3$, -113.4, and -137.6; these are assigned to the phosphorus atoms 1, 2, and 3, respectively (for the atomic numbering, see the structure formula for **6**). As a result of the very similar coupling constants ($J(P1,P2) = 8.8$, $J(P1,P3) = 7.8$ Hz), the signal for the P 1 atom appears as a pseudoquartet, whereas a doublet of doublets ($J(P2,P3) = 16$ Hz) is observed for the P 2 center, and a triplet of doublets for P 3.

As anticipated, the ^1H NMR spectrum of **6** features three singlets for the *tert*-butyl groups in the expected region and in a ratio of 2:1:1; the protons of the η^8-bound cyclooctatetraene ligand (cot) are assigned to a singlet at $\delta = 6.89$. The ^{13}C NMR spectrum completes the structure determination for the η^4-bound 1,3,5,7-tetraphosphabarrelene in complex **6**: The four carbon atoms of the bicyclic system (C 1–C 3) give rise to three groups of signals. The sp^3 C atom (C 3) resonates at highest field ($\delta = 37.7$). The coupling constants to the four P atoms are $J(C3,P1) = 84$ Hz (d), $J(C3,P2) = 69.6$ Hz (t), and $J(C3,P3) = 2.6$ Hz (d). As expected, the largest downfield shift to $\delta = 219.8$ is observed for the signal arising from the uncomplexed P=C bond (C 1), which is split into a doublet of doublets of triplets (see Table 1). The C atoms of the π-coordinated P=C bonds (C 2) give rise to a multiplet at $\delta = 76.7$, which corresponds to the X component of an ABMX system (A, B, M = ^{31}P; X = ^{13}C; $J(P1,C2)$ not detectable). A simulation of the multiplet generates a value of 56.8 Hz for $J(P2_A,P2_B)$ (for $J(C,P)$, see Table 1). The large upfield shift relative to the P=C signal in free tetraphosphabarrelene supports the presence of a strong interaction with the zirconium atom.

Table 1. Selected physical data for **6** and **7** [a,b].

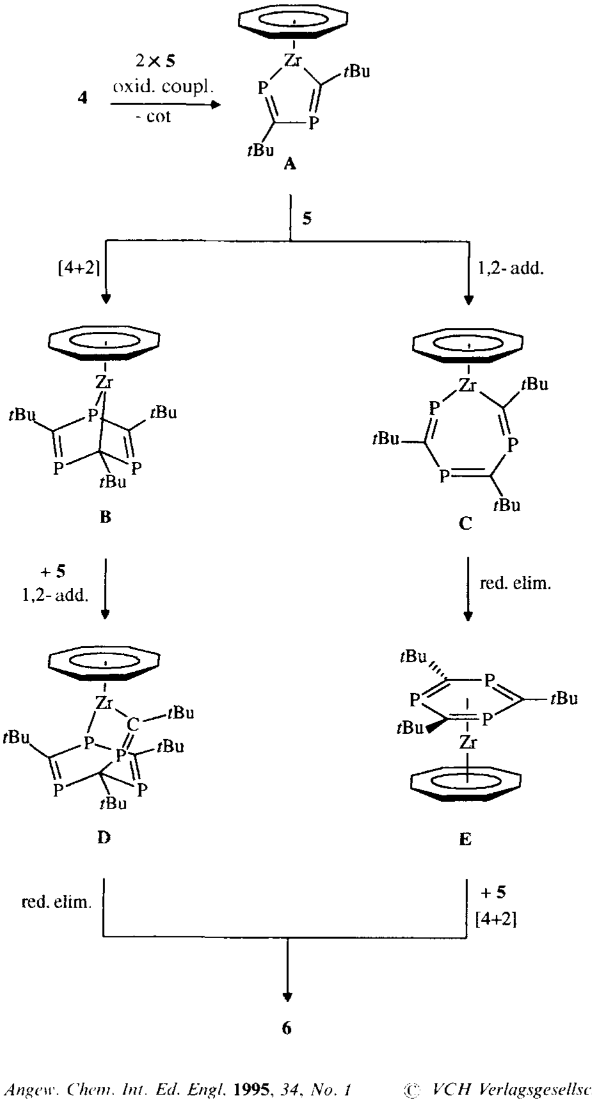
6: ^1H NMR [c]: $\delta = 1.08$ (s, 18 H, *t*Bu at C-2), 1.23 (s, 9 H, *t*Bu at C-3) 1.29 (s, 9 H, *t*Bu at C-1), 6.89 (s, 8 H, cot); ^{13}C NMR: $\delta = 37.72$ ($J_{(C,P1)} = 84.0$, $J_{(C,P2)} = 69.6$, $J_{(C,P3)} = 2.6$ Hz, C-3), 37.70 ($J_{(C,P1)} = 21.0$, $J_{(C,P2)} = 12.4$, $J_{(C,P3)} = 2.8$ Hz, $C(CH_3)_3$ at C-3), 31.3 ($^1J_{(C,H)} = 125$, $J_{(C,P1)} = 12.0$, $J_{(C,P2)} = 6.9$ Hz, $C(CH_3)_3$ at C-3), 76.7 (X component of a ABMX spin system [d]; $^1J_{(P2_A,C)} = 97.0$, $^3J(P2_B,C) = 3.7$, $J_{(C,P3)} = 42.8$ Hz, C-2), 38.0 ($J_{(C,P2_A)} + J_{(C,P2_B)} = 22.4$, $J_{(C,P3)} = 14.3$ Hz, $C(CH_3)_3$ at C-2), 35.9 ($^1J_{(C,H)} = 125$, $J_{(C,P2_A)} + J_{(C,P2_B)} = 10.0$, $J_{(C,P3)} = 10.1$ Hz, $C(CH_3)$ at C-2), 219.8 ($J_{(C,P1)} = 97.6$, $J_{(C,P2)} = 5.6$, $J_{(C,P3)} = 58.6$ Hz, C-1), 43.6 ($J_{(C,P1)}$, $J_{(C,P3)} = 22.7$, 25.2 Hz, $C(CH_3)_3$ at C-1), 35.7 ($^1J_{(C,H)} = 125$, $J_{(C,P1)}$, $J_{(C,P3)} = 14.8$, 9.1 Hz, $C(CH_3)_3$ at C-1), 97.2 ($^1J_{(C,H)} = 168$ Hz, C-4); ^{31}P NMR: $\delta = 285.3$ ($J_{(P1,P2)} = 8.8$, $J_{(P1,P3)} = 7.8$ Hz, P-1), -113.4 ($J_{(P1,P2)} = 8.8$, $J_{(P2,P3)} = 16.0$ Hz, P-2), -137.6 ($J_{(P1,P3)} = 7.8$, $J_{(P2,P3)} = 16.0$ Hz, P-3); MS (70 eV): *m/z* [%]: 594 (M^+) [16], 537 ($M^+ - t$Bu) [19], 463 ($M^+ - t$BuC≡P − P) [16], 425 ($M^+ - t$BuC≡P − *t*BuC) [21], 400 (M^+ − cotZr) [100], 300 ($(tBuP{\equiv}C)_3^+$) [10], 262 ($(tBuC{\equiv}P)_4^+ - tBu_2C_2$) [92], 169 [83]

7: ^1H NMR: $\delta = 2.01$ (s, 9 H, *t*Bu),1.52 (s, 27 H, *t*Bu); ^{13}C NMR: $\delta = 229.6$ (X component of a AB_2MX spin system [d]; $^1J(C,P1_A) = \pm 55.8$, $^3J(C,P1_B) = \pm 4.9$, $^1J(C,P2) = 45.8$ Hz, C-1), 43.7 (m, $C(CH_3)_3$ at C-1), 32.7 (m, $C(CH_3)_3$ at C-1), 102.7 (dq, $J_{(C,P1)} = 70.8$, $J_{(C,P2)} = 7.5$ Hz, C-2), 38.0 (q, $J_{(C,P1)} = 16.1$ Hz, $C(CH_3)_3$ at C-2), 32.7 (m, $C(CH_3)_3$ at C-2); ^{31}P NMR: $\delta = 324.1$ (d, $J_{(P,P)} = 13.0$ Hz), -87.0 (q, $J_{(P,P)} = 13.0$ Hz); MS (70 eV): *m/z* (%): 400 $(M)^+$ [41], 300 $(M - P{\equiv}CtBu)^+$ [6], 262 $(M - C_2tBu_2)^+$ [100], 200 $(P_2C_2(tBu)_2)^+$ [14], 169 [73]

[a] ^1H (300 MHz, TMS), ^{13}C (75.5 MHz, TMS), ^{31}P NMR spectra (121.5 MHz, 85% H_3PO_4); **6** in $[D_8]$THF; **7** in C_6D_6; MS: Varian-CH5. [b] For numbering of the C and P atoms, see structural formulae of **6** and **7**. [c] Assignments by $^{31}P-^1H$ and $^{13}C-^1H$ correlation. [d] From simulation of the multiplets. The chemical shifts of **A** and **B** are different owing to ^{13}C isotope effects.

The η^4-bound tetraphosphabarrelene could be removed from complex **6** with the help of hexachloroethane. After the reaction mixture had been stirred for 12 h at 20 °C, **7** was obtained as a yellow microcrystalline solid in 88% yield. Compound **7** was found to be sensitive to oxidation, but surprisingly thermally stable: for example, it sublimes unchanged in vacuo above approximately 250 °C. In the absence of crystals suitable for a crystal structure analysis, the structure of **7** was determined spectroscopically. Both a correct elemental analysis and the molecular mass of 400 obtained by mass spectrometry confirm that **7** is a tetramer of **5**. Because of the symmetry of the molecule, the ^{31}P NMR spectrum shows only two sets of signals for the four P atoms in an intensity ratio of 3:1. The doublet at $\delta = 324.1$ ($J(P,P) = 13.0$ Hz) is assigned to the three equivalent phosphorus atoms of the P=C bonds, whilst the quartet at $\delta = -87.0$ corresponds to the triply coordinated P 2 atom (see Table 1). Both signals lie in the expected region. The ^1H NMR spectrum of **7** contains equally few signals: two singlets are found at $\delta = 1.52$ and 2.01 in a ratio of 3:1, corresponding to the two distinct *tert*-butyl groups bound to C1 and C2 (see structural formula of **7** for atomic numbering). In agreement with our proposed structure, only two sets of signals are observed in the ^{13}C NMR spectrum of **7** for the four carbon atoms of the bicyclic structure: a multiplet at $\delta = 229.6$ for the three sp^2 carbon atoms (C1) and a quartet of doublets at $\delta = 102.7$ (J(C,P1) = 70.8, J(C,P2) = 7.5 Hz) for the sp^3 carbon atom (C2). The multiplet assigned to C1 is the X component of an AB_2MX spin system (A, B, M = ^{31}P; X = ^{13}C), which was likewise simulated. The chemical shifts of the *tert*-butyl signals (see Table 1) require no further explanation. Thus, the structure of **7** corresponds to that of 1,3,5,7-tetraphosphabarrelene (1,3,5,7-tetraphosphabicyclo[2.2.2]octatriene).

With the synthesis of tetraphosphabarrelene complex **6**, it has for the first time been possible to cyclotetramerize four phosphaalkyne units at a metal center. The previously known phosphaalkyne tetramers, such as, tetraphosphacubane[7] or tetraphosphatricyclooctadiene,[9] were accessed through the cycloaddition reactions of 1,3- or 1,2-diphosphets, which were in turn liberated from the corresponding metal–phosphaalkyne dimer complex (e.g., **2**). The uniformity with which the cyclotetramerization of **5** proceeds is remarkable. Comparable cyclotetramerizations of alkynes at transition-metal centers to yield barrelenes are not known, although certain metal complexes do catalyze the cyclotetramerization of alkynes to cyclooctatetraene.[10]



The question as to the pathway of this unusual tetramerization of **5** cannot be answered conclusively. A stepwise process seems plausible, with an oxidative coupling of two phosphaalkyne molecules to give the 2-zircona-1,4-diphosphacyclopentadiene **A** as the initial step. This might be followed either by a 1,2-addition of **5** to give **C** or by a [4 + 2] cycloaddition of **5** to **A** to yield **B**. Complex **6** would then be formed by a 1,2-addition of a fourth molecule of **5** to intermediate **B** and reductive elimination from **D**, or alternatively by a [4 + 2] cycloaddition of **5** to the 1,3,5-triphosphabenzene complex **E**.

Experimental Procedure

6: A solution of **4** (0.92 g, 3.1 mmol) and **5** (1.3 g, 13 mmol) in toluene (60 mL) was heated for 2 d at 70 °C. A change in color from dark violet to dark green was observed. After removal of solvent, the residue was taken up in ether (40 mL). Small amounts of insoluble material were removed by filtration through a D3 frit, and the clear solution was kept at −78 °C. After 2 d, **6** was filtered off as a dark green microcrystalline solid. Yield: 1.50 g (81 %); m.p. 175 °C (decomp.).

7 from **6**: Hexachloroethane (0.47 g, 2 mmol) was added to a suspension of **6** (1.0 g, 1.68 mmol) in pentane (50 mL) at −78 °C. The mixture was allowed to warm to room temperature and was then stirred for 12 h. Insoluble [(cot)$ZrCl_2$] and excess C_2Cl_6 were filtered off, and solvent was removed from the filtrate at 0.5 mbar. The yellow-red solid residue was dissolved in ether (5 mL) and cooled to −78 °C. After 3 d, a microcrystalline yellow precipitate was filtered off and dried at 10^{-3} mbar. Yield: 538 mg (88 %); m.p. 93 °C.

Received: 25 August, 1994 [Z 7265 IE]
German version: *Angew. Chem.* **1995**, *107*, 114

Keywords: cyclizations oligomerizations · phosphaalkynes · tetraphosphabarrelene · zirconium compounds

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[1] Reviews: a) J. F. Nixon, *Chem. Rev.* **1988**, *88*, 1327–1362; b) M. Regitz, P. Binger, *Angew. Chem.* **1988**, *100*, 1541–1565; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1484–1508; c) P. Binger in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), 1st ed., Thieme, Stuttgart, **1990**, pp. 90–111; d) M. Regitz in *Organic Synthesis via Organometallics* (OSM 4, Aachen) (Eds.: D. Enders, H.-J. Gais, W. Keim), Vieweg, Wiesbaden, **1993**, pp. 93–113; e) latest publication: 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.

[2] a) P. Binger, R. Milczarek, R. Mynott, M. Regitz, W. Rösch, *Angew. Chem.* **1986**, *98*, 645–646; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 644–645; b) P. Binger, R. Milczarek, R. Mynott, C. Krüger, Y.-H. Tsay, E. Raabe, M. Regitz, *Chem. Ber.* **1988**, *121*, 637–645.

[3] a) P. B. Hitchcock, M. J. Maah, J. F. Nixon, *J. Chem. Soc. Chem. Commun.* **1986**, 737–738; b) P. Binger, B. Biedenbach, R. Mynott, C. Krüger, P. Betz, M. Regitz, *Angew. Chem.* **1988**, *100*, 1219–1221; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1158–1160.

[4] a) P. Binger, B. Biedenbach, C. Krüger, M. Regitz, *Angew. Chem.* **1987**, *99*, 798–799; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 764–765; b) S. Barth, Dissertation, Universität Kaiserslauten, **1993**.

[5] R. Milczarek, W. Rüsseler, P. Binger, K. Jonas, K. Angermund, C. Krüger, M. Regitz, *Angew. Chem.* **1987**, *99*, 957–958; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 908–909.

[6] P. Binger, T. Wettling, R. Schneider, F. Zurmühlen, U. Bergsträsser, J. Hoffmann, G. Maas, M. Regitz, *Angew. Chem.* **1991**, *103*, 208–211; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 207–210.

[7] 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.

[8] H.-J. Kablitz, G. Wilke, *J. Organomet. Chem.* **1973**, *51*, 241–271.

[9] 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.* in press.

[10] a) W. Reppe, O. Schlichting, K. Klager, T. Toepel, *Justus Liebigs Ann. Chem.* **1948**, *560*, 1–92; b) review: N. E. Schore, *Chem. Rev.* **1988**, *88*, 1081–1119.