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Synthesis of a Stable 1λ^5,2λ^3-Diphosphete: the First Codimer of a λ^3-Phosphaalkyne with a λ^5-Phosphaalkyne

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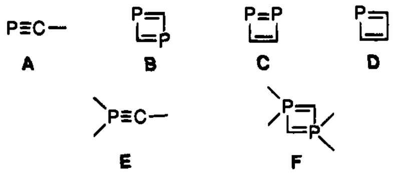
The chemistry of alkyne cyclooligomers dates back to the 18th century with the work of Berthelot[1] and Kekulé;[2] however, the first dimeric species, namely the cyclobutadienes, were only reported in 1959 as an η^4-complex[3a,b] and in 1968 as a free, not complexed molecule with a push−pull substitution pattern.[3c,4] Much more recently, the chemistry of the related λ^3-phosphaalkyne (**A**) cyclooligomers has attracted considerable attention.[5] A few dimers are stable in the coordination sphere of transition metals,[5,6] but free 1λ^3,3λ^3-diphosphetes **B** and 1λ^3,2λ^3-diphosphetes **C** behave as their antiaromatic carbon analogs and prove to be elusive.[5,7] In the same vein, only one example of transition metal-coordinated λ^3-phosphete **D**,[8] arising from the inner sphere codimerization of alkynes with λ^3-phosphaalkynes **A**, is known. In marked contrast, although a very few λ^5-phosphaalkynes **E** are stable,[9] most of them spontaneously dimerize, leading to stable 1λ^5,3λ^5-diphosphetes **F**.[10] Here we report the first example of codimerization of a λ^3-phosphaalkyne **A** with a λ^5-phosphaalkyne **E** (Chart 1).

Chart 1



In contrast to most diazo derivatives,[5b,c] bis[diisopropylamino)phosphino](trimethylsilyl)diazomethane (**1**) does not undergo a [3 + 2] cycloaddition reaction with *tert*-butylphosphaalkyne (**2**). Therefore the λ^5-phosphaalkyne **4** was generated *in-situ* by photolysis of the diazo precursor **1**[9a] in the presence of **2**. According to ^{31}P NMR data, a clean reaction occurred, leading to derivative **3**, which was isolated as a yellow oil in 90% yield.[11] Mass spectroscopy and elemental analysis are in agreement with a codimeric structure. The ^{31}P NMR spectrum consists of a doublet of quintets at +49.2 (J_{PP} = 201.2 Hz, J_{PH} = 13.6 Hz) and a doublet at +58.4 (J_{PP} = 201.2 Hz), strongly suggesting the presence of two directly bonded phosphorus atoms, one featuring two *i*-Pr$_2$N groups and the other none; moreover, the $^3J_{PH}$ coupling constant is typical of a σ^4-phosphorus atom.[12] These data rule out the 2*H*-phosphirene **5**[13] and the 1λ^5,3λ^3-diphosphete **6**, which would result from a [2 + 1] cycloaddition of **2** with the carbene form **4′**[9] and the head-to-tail codimerization of **2** with **4**, respectively. In the ^{13}C NMR spectrum, two low-field doublets of doublets are observed: the most deshielded (224.3; J_{CP} = 54.9 and 9.9 Hz) indicates the presence of an sp^2-hybridized carbon bound to a σ^2-phosphorus atom, while the chemical shift of the second (105.7; J_{CP} = 36.8 and 4.2 Hz) compares well with the values for the related 1,2λ^5-azaphosphetes.[14] These results as a whole strongly suggest that compound **3** is a 1λ^5,2λ^3-diphosphete, the first four-π-electron, four-membered ring[14,15] featuring a dicoordinated phosphorus atom (Scheme 1).

Not surprisingly, and in contrast to the 1λ^3,3λ^3-diphosphetes **B**[5,6] and the λ^3-phosphetes **D**,[8] which are coordinated to transition metals through the π-system, the 1λ^5,2λ^3-diphosphete **3** appears to be a η^1-ligand. Indeed, compound **3** reacts at room temperature with W(CO)$_5$(THF), affording complex **7**, which was isolated as orange crystals (mp 125 °C dec; 75% yield)[11] (Scheme 1). The X-ray crystal structure of **7** is shown in Figure 1, with pertinent metric parameters listed in the legend.[16] The four-membered ring is planar (mean deviation, 0.0278 Å), but the phosphorus bound to the metal is strongly pyramidalized (sum of the angles at P2, 330.79°). The carbon−carbon [1.391-

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(11) Selected spectroscopic data for compounds **3** and **7**. **3**: ^{13}C NMR (C$_6$D$_6$, 50.323 MHz) δ 4.26 (d, J_{PC} = 2.8 Hz, CH$_3$Si), 24.66, 24.71 (d, J_{PC} = 2.4 Hz, *C*H$_3$CHN), 31.10 (d, J_{PC} = 9.8 Hz, *C*H$_3$C), 41.46 (dd, J_{PC} = 52.4 and 17.6 Hz, CH$_3$*C*), 48.90 (d, J_{PC} = 5.6 Hz, CH$_3$*C*HN), 105.72 (dd, J_{PC} = 36.8 and 4.2 Hz, PCSi), 224.31 (dd, J_{PC} = 54.9 and 9.9 Hz, P*C*t-Bu). **7**: ^{13}C NMR (CDCl$_3$, 50.323 MHz) δ 3.27 (d, J_{PC} < 1 Hz, CH$_3$Si), 24.03, 24.43 (d, J_{PC} = 2.5 Hz, *C*H$_3$CHN), 30.23 (d, J_{PC} = 6.2 Hz, *C*H$_3$C), 41.04 (dd, J_{PC} = 49.2 and 15.8 Hz, CH$_3$*C*), 49.10 (d, J_{PC} = 5.2 Hz, CH$_3$*C*HN), 126.11 (dd, J_{PC} = 34.9 and 14.2 Hz, PCSi), 198.93 (dd, J_{PC} = 3.4 and 3.4 Hz, CO$_e$), 202.41 (d, J_{PC} = 17.3 Hz, CO$_a$), 209.67 (dd, J_{PC} = 39.2 and 7.1 Hz, P*C*t-Bu); ^{31}P NMR (CDCl$_3$, 81.015 MHz) δ 41.7 (d, J_{PP} = 175.4 Hz, J_{PW} = 115.3 Hz, PW), 57.37 (dq, J_{PP} = 175.4 Hz, J_{PH} = 13.4 Hz, σ^4-P); IR (CDCl$_3$) ν 1930 and 1975 cm^{-1} (CO).

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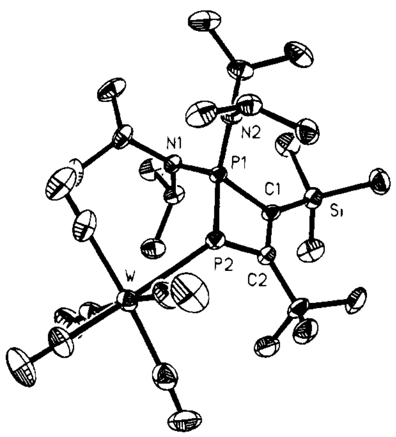
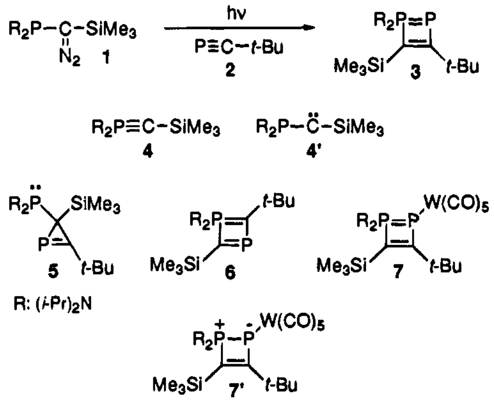


Figure 1. Thermal ellipsoid plot (30% probability) of derivative **7** showing the numbering scheme used. For clarity, hydrogen atoms have been omitted. Selected distances (Å) and angles (deg): P(1)–N(1), 1.664(6); P(1)–N(2), 1.651(6); P(1)–C(1), 1.804(7); C(1)–C(2), 1.391(10); C(2)–P(2), 1.842(7); P(2)–P(1), 2.176(3); P(2)–W, 2.623(2); C(1)–Si, 1.892(7); P(1)–C(1)–C(2), 95.1(5); C(1)–C(2)–P(2), 109.6(5); C(2)–P(2)–P(1), 71.9(3); P(2)–P(1)–C(1), 83.1(2).

Scheme 1



(10) Å] and both phosphorus–carbon [1.804(7) and 1.842(7) Å] bond lengths are in the range expected for prolonged CC double bonds and PC single bonds, respectively. Lastly, the value of the phosphorus–phosphorus bond distance [2.176(3 Å)] is comparable to that observed in free or coordinated phosphinylidene phosphoranes (RP=PR'$_3$).[17] These geometric parameters as a whole strongly suggest that the four-π-electron, four-membered ring **7** features a localized carbon–carbon double bond and a strongly polarized phosphorus–phosphorus ylide bond, as shown in **7'**.[18]

Formally, **3** results from the head-to-head codimerization (governed by steric factors) of the λ^3-phosphaalkyne **2** with the λ^5-phosphaalkyne **4**. However, it is known that **4** undergoes [1 + 2] cycloaddition reactions with nitriles, affording isolable 2-phosphino-2*H*-azirines, which rearrange in the presence of a suitable catalyst into 1,2λ^5-azaphosphetes.[14c] Therefore, it is quite likely that the codimerization first produces the 2-phosphino-2*H*-phosphirene **5**. The spontaneous ring expansion reaction can easily be explained by the known instability of 2*H*-phosphirenes[13,19] compared to the remarkable stability observed for **3** and for related non-antiaromatic four-π-electron, four-membered heterocycles.[14,15]

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Supporting Information Available: Tables of crystal and intensity collection data, positional and thermal parameters, interatomic distances and angles, and least-squares plane equations and two ORTEP diagrams (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(16) Crystal data for **7**: $C_{26}H_{46}N_2O_5P_2SiW$, mol wt = 740.53, monoclinic, space group $P2_1/n$, a = 10.143(1) Å, b = 17.734(1) Å, c = 18.721(2) Å, β = 97.39(1)°, V = 3339.5(5) Å^3, Z = 4, D_{calcd} = 1.473 g cm^{-3}, λ(Mo Kα) = 0.710 73 Å (graphite monochromated), μ = 3.624 mm^{-1}. A Siemens P4 diffractometer was used to collect 8800 independent reflections (1.59 < θ < 29.00°) on a crystal of 0.35 × 0.20 × 0.15 mm dimension. Data were corrected for absorption by semiempirical Ψ-scans [T_{min} = 0.424; T_{max} = 0.938]; 4764 reflections were observed [$F_o^2 > 2\sigma(F_o^2)$]. The direct methods program SHELXS-86 was used for the initial structure solution, and final model was obtained by least-squares refinement (based on F^2) in combination with difference Fourier synthesis with the program SHELXL-93. All hydrogen atoms were placed in calculated positions with B_{iso} equivalent to 1.2B_{iso} of the bonded non-hydrogen atom. R = 0.0693, R_w = 0.1264, 334 variables, S = 1.12. The largest positive peak in the final difference Fourier map had an electron density of +2.228 eÅ^{-3} and was located in the region near W.

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