PCy_3 (0.10 mmol) were dissolved in toluene (13 mL). To the resulting solution was added TlOAc (0.12 mmol), followed by allyl acetate (1.02 mmol) and **1** ($R_1 = R_2 = CH_3$; 2.0 mmol). The reaction mixture was heated with stirring at 110 °C for 14 h to yield **9** in 86% yield.

Extension of the catalytic reaction to other allylic electrophiles is under way and will be reported later.

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Synthesis of a 2,3-Dihydro-1,2-diphosphete Ring by Electrocyclization of a 3,4-Diphosphahexatriene Unit

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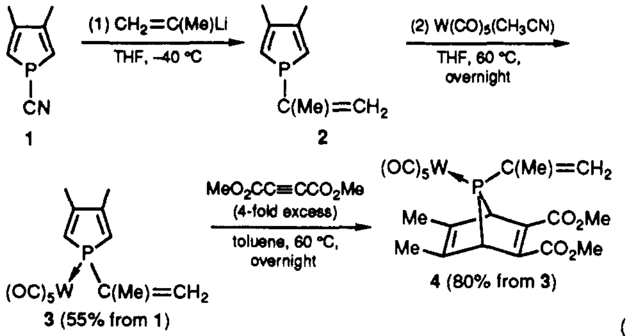
Summary: A 7-(2-propenyl)-7-phosphanorbornadiene P–W(CO)$_5$ complex has been synthesized and shown to be an efficient precursor of the transient (2-propenylphosphinidene)tungsten pentacarbonyl terminal complex. In the absence of trapping reagent, the propenylphosphinidene complex dimerizes to give a 3,4-diphosphahexatriene unit, which undergoes a spontaneous four-π-electron cyclization leading to a 2,3-dihydro-1,2-diphosphete ring. This heterocycle has been characterized by the X-ray crystal structure analysis of a [2 + 4] cycloadduct between its P=C double bond and 2,3-dimethylbutadiene.

Unsaturated four-membered rings are probably the least known carbon–phosphorus monocycles. 1,2-Dihydrophosphetes have been discovered only recently and have been the subject of several investigations.[1] 1,2-Dihydro-1,2-diphosphetes have been known since 1964[2] but only investigated in some depth during the last decade by our group.[3] Finally, the first example of the 2,3-dihydro-1,2-diphosphete ring has been briefly mentioned by Becker et al.,[4] but no characterization has been provided. In this work, we wish to describe the synthesis of this last ring via the unexpected four-π-electron cyclization of a 3,4-diphosphahexatriene unit.

Our work started as a classical investigation of the properties of the transient terminal vinylphosphinidene complexes.[5] Our hope was to observe a cyclization somewhat similar to the conversion of vinylcarbenes into cyclopropenes.[6] Accordingly, we first synthesized the appropriate 7-phosphanorbornadiene precursor **4**[7] from the readily available 1-cyano-3,4-dimethylphosphole[8] (eq 1).



(1)

Complex **4** proved to be a convenient precursor for the transient (2-propenylphosphinidene)tungsten pentacarbonyl complex **5** in the presence of catalytic amounts of copper(I) chloride at 60 °C. Contrary to our expectation, complex **5** shows no tendency to cyclize. Instead, in the absence of trapping reagent, it undergoes a classical dimerization to give the *trans*-diphosphene complex **6** as do the other terminal phosphinidene complexes.[9] Unex-

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[1] Selected references: (a) Marinetti, A.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 5001. (b) Neilson, R. H.; Boyd, B. A.; Dubois, D. A.; Hani, R.; Scheide, G. M.; Shore, J. T.; Wettermark, U. G. *Phosphorus Sulfur* **1987**, *30*, 463. (c) Boyd, B. A.; Thoma, R. J.; Neilson, R. H. *Tetrahedron Lett.* **1987**, *28*, 6121. (d) Marinetti, A.; Mathey, F. *Organometallics* **1988**, *7*, 633. (e) Tran Huy, N. H.; Ricard, L.; Mathey, F. *Organometallics* **1988**, *7*, 1791. (f) Dötz, K. H.; Tiriliomis, A.; Harms, K. *J. Chem. Soc., Chem. Commun.* **1989**, 788. (g) Doxsee, K. M.; Shen, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 9129. (h) Tran Huy, N. H.; Mathey, F. *Tetrahedron Lett.* **1988**, *29*, 3077. (i) Lukehart, C. M.; McPhail, A. T.; McPhail, D. R.; Myers, J. B., Jr.; Soni, H. K. *Organometallics* **1989**, *8*, 1007. (j) Tumas, W.; Suriano, J. A.; Harlow, R. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 75. (k) Marinetti, A.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1990**, 153. (l) Marinetti, A.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 788. (m) Doxsee, K. M.; Shen, G. S.; Knobler, C. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1649. (n) Dema, A. C.; Li, X.; Lukehart, C. M.; Owen, M. D. *Organometallics* **1991**, *10*, 1197.

[2] Mahler, W. *J. Am. Chem. Soc.* **1964**, *86*, 2306. See also: Ecker, A.; Schmidt, U. *Chem. Ber.* **1973**, *106*, 1453. Appel, R.; Barth, V. *Tetrahedron Lett.* **1980**, *21*, 1923. Binger, P.; Wettling, T.; Schneider, R.; Zurmühlen, F.; Bergsträsser, U.; Hoffmann, J.; Maas, G.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 207.

[3] (a) Charrier, C.; Guilhem, J.; Mathey, F. *J. Org. Chem.* **1981**, *46*, 3. (b) Charrier, C.; Mathey, F.; Robert, F.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 1707. (c) Charrier, C.; Maigrot, N.; Mathey, F.; Robert, F.; Jeannin, Y. *Organometallics* **1986**, *5*, 623. (d) Ricard, L.; Maigrot, N.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 548. (e) Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 950. (f) Maigrot, N.; Charrier, C.; Ricard, L.; Mathey, F. *Polyhedron* **1990**, *9*, 1363. (g) Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 534.

[4] Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Hildenbrand, U.; Westerhausen, M. *Phosphorus Sulfur* **1987**, *30*, 349.

[5] Three recent reviews have been devoted to the chemistry of terminal phosphinidene complexes: Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81. Mathey, F. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990; pp 33–47.

[6] Leading references: Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1961**, *83*, 2015. Closs, G. L.; Closs, L. E.; Böll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796. Stechl, H. H. *Chem. Ber.* **1964**, *97*, 2681.

[7] Both **3** and **4** were purified by chromatography on silica gel (70–230 mesh) with hexane–dichloromethane (4/1 and 1/1) as the eluent. ^{31}P NMR: **3**, δ +13.8, $^1J(^{31}P-^{183}W) = 210$ Hz (CH_2Cl_2); **4**, δ +213.5, $^1J(^{31}P-^{183}W) = 234$ Hz ($CDCl_3$).

[8] Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796.

[9] Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.

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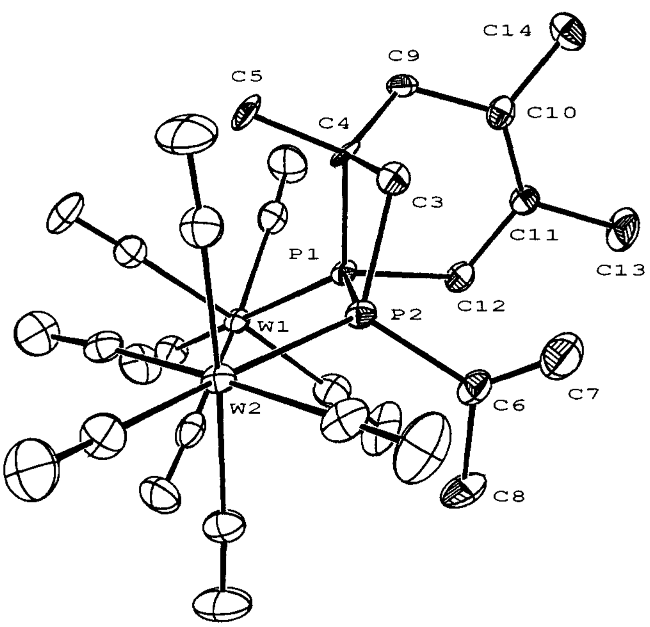
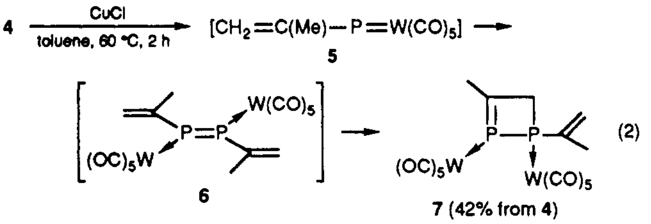


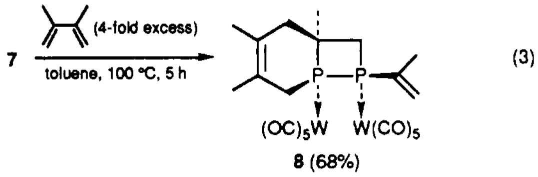
Figure 1. ORTEP drawing of one molecule of 8. Vibrational ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Principal bond distances (Å): W_1–P_1 = 2.490 (1); W_2–P_2 = 2.510 (1); P_1–P_2 = 2.245 (2); P_1–C_4 = 1.873 (4); P_1–C_{12} = 1.848 (4); P_2–C_3 = 1.855 (4); P_2–C_6 = 1.812 (4); C_3–C_4 = 1.556 (6); C_4–C_5 = 1.516 (6); C_4–C_9 = 1.528 (6); C_6–C_7 = 1.300 (7); C_6–C_8 = 1.503 (7); C_9–C_{10} = 1.514 (6); C_{10}–C_{11} = 1.329 (6); C_{11}–C_{12} = 1.500 (6). Selected bond angles (deg): W_1–P_1–P_2 = 130.04 (5); W_1–P_1–C_4 = 125.5 (1); W_1–P_1–C_{12} = 113.0 (1); P_2–P_1–C_4 = 77.8 (1); P_2–P_1–C_{12} = 103.1 (2); C_4–P_1–C_{12} = 100.0 (2); W_2–P_2–P_1 = 127.70 (5); W_2–P_2–C_3 = 117.8 (1); W_2–P_2–C_6 = 113.7 (2); P_1–P_2–C_3 = 78.1 (1); P_1–P_2–C_6 = 105.3 (2); C_3–P_2–C_6 = 108.6 (2); P_2–C_3–C_4 = 99.1 (3); P_1–C_4–C_3 = 98.2 (3); P_1–C_4–C_5 = 111.7 (3); P_1–C_4–C_9 = 111.4 (3); C_3–C_4–C_5 = 110.7 (3); C_3–C_4–C_9 = 113.8 (4); C_4–C_9–C_{10} = 114.4 (4); C_9–C_{10}–C_{11} = 121.4 (4); C_{10}–C_{11}–C_{12} = 124.3 (4); P_1–C_{12}–C_{11} = 120.2 (3).

pectedly, however, this dimeric complex **6** spontaneously electrocyclizes to yield the 2,3-dihydro-1,2-diphosphete ring **7**[10] (eq 2).



That the cyclization has indeed taken place was immediately obvious on inspection of the ^{31}P NMR spectrum of **7** ($CDCl_3$): AX system, δ_A +231.2 ppm (*P*=C), δ_X +26.6 ppm (*P*C_2), *J*(A–X) = 83 Hz. Relatively weak P–P couplings have also been found in the related 1,2-dihydro-1,2-diphosphetes.[3c,d] The ^1H and ^{13}C NMR spectra were also very informative. Both indicated the disappearance of one 2-propenyl unit. In the ^{13}C spectrum ($CDCl_3$), the cyclic CH_2 appears as a doublet at 49.91 ppm (^1J(C–P) = 29.4 Hz) and P=*C* as a doublet at 209.21 ppm (^1J(C–P) = 25.9 Hz). The protons of the ring methyl show a characteristic high coupling with phosphorus (^3J(H–P) = 26.3 Hz).

Whereas there was little doubt that the cyclization had occurred, we were unable to grow satisfactory crystals for X-ray analysis. We thus performed the reaction of **7** with 2,3-dimethylbutadiene (eq 3). The resulting [2 + 4] cycloadduct **8**[11] gave satisfactory crystals that were analyzed (Figure 1). The cycloaddition selectively takes place on the less hindered 2-propenyl side of **7**. The four-membered ring of **8** only slightly deviates from planarity. The torsion angle P_2–P_1–C_4–C_3 is 19.3°. The P_1–P_2 bond is normal for a single bond at 2.245 (2) Å. The strain associated with the four-membered ring apparently has no significant influence on the intracyclic bond lengths.



The synthesis of four-membered rings incorporating a P=C double bond has proven to be rather difficult.[12] The ready cyclization of **6** into **7** is all the more surprising since complexes such as [(*E*)-PhP=PPh][Cr(O)$_5$]$_2$ are stable.[13] Obviously, a powerful driving force is associated with the increase of the coordination number of P_2 from 3 to 4 during the cyclization.

Supplementary Material Available: Text describing the preparation and spectroscopic and analytical data for 3, 4, 7, and 8 and details of the X-ray structure determination of 8, including tables of positional and thermal parameters, bond distances and angles, and crystal data (8 pages); a table of observed and calculated structure factors for 8 (31 pages). Ordering information is given on any current masthead page.

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[10] Complex 7 was obtained as yellow crystals by chromatography with hexane/dichloromethane (4/1) as the eluent. ^1H NMR ($CDCl_3$): δ 2.18 (d, ^3J(H–P) = 11.2 Hz, 3 H, *Me*C=CH_2), 2.37 (d, ^3J(H–P) = 26.3 Hz, 3 H, *Me*C=P), 3.68 (pseudo d, 2 H, CH_2P), 5.66 (d, ^3J(H–P) = 19.5 Hz, 1 H, =CH_2), 5.78 (d, ^3J(H–P) = 40 Hz, 1 H, =CH_2). ^{13}C NMR ($CDCl_3$): δ 20.2 (d, ^2J(C–P) = 11.1 Hz, Me), 25.7 (d, ^2J(C–P) = 13.9 Hz, Me), 49.91 (d, ^1J(C–P) = 29.4 Hz, CH_2P), 127.34 (dd, ^2J(C–P) = 13.9 Hz, ^3J(C–P) = 3.4 Hz, =CH_2), 142.26 (d, ^1J(C–P) = 12.4 Hz, Me*C*=CH_2), 193.32 (d, ^2J(C–P) = 8.1 Hz, cis CO), 195.6 (d, ^2J(C–P) = 5.7 Hz, cis CO), 197.32 (d, ^2J(C–P) = 31.7 Hz, trans CO), 198.17 (d, ^2J(C–P) = 24.6 Hz, trans CO), 209.21 (d, ^1J(C–P) = 25.9 Hz, *C*=P). Mass spectrum (^{184}W): *m/z* 793 (M^+ + 1, 25%), 510 (100%). Anal. Calcd for $C_{16}H_{10}O_{10}P_2W_2$: C, 24.2; H, 1.3. Found: C, 24.7; H, 1.3.

[11] Purification as for 7. 8: white crystals; ^{31}P NMR ($CDCl_3$) AX system, δ_A +36.4, δ_X +1.0, ^1J(A–X) = 63 Hz; ^{13}C NMR ($CDCl_3$) δ 20.81–21.73 (3 Me), 31.0 (d, *J*(C–P) = 9 Hz, Me), 39.26 (s, CH_2), 39.74 (d, ^1J(C–P) ≈ 30 Hz, C–P), 42.65 (d, *J*(C–P) = 25.8 Hz, CH_2), 46.89 (d, *J*(C–P) = 6.6 Hz, CH_2), 122.60 (d, ^2J(C–P) = 4.1 Hz, =CH_2), 124.67 (d, *J*(C–P) = 7.9 Hz, Me*C*=), 130.87 (d, *J*(C–P) = 8.6 Hz, Me*C*=), 142.60 (d, ^1J(C–P) = 11 Hz, =C—P). Anal. Calcd for $C_{22}H_{20}O_{10}P_2W_2$: C, 30.2; H, 2.3. Found: C, 30.7; H, 2.3.

[12] Marinetti, A.; Le Floch, P.; Mathey, F. *Organometallics* **1991**, *10*, 1190.

[13] Borm, J.; Zsolnai, L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 977.