B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**. B3LYP functional (A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–793) has been used together with standard 6-31G* basis set for H, C, N, Al, and P atoms. Effective core potential basis set of Hay and Wadt (P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310) was used for W atoms. All structures were fully optimized with subsequent vibrational analysis and correspond to the minimum on the potential energy surface; b) calculated Raman frequencies according to the B3LYP method (compare: A. Y. Timoshkin, H. F. Bettinger, H. F. Schaefer, *J. Am. Chem. Soc.* **1997**, *119*, 5668–5678): $\tilde{\nu}$(C–O): 1920, 1938, 1951, 1977, 2048; $\tilde{\nu}$(AlH): 1816, 1836; $\tilde{\nu}$(P–H): 2312, 2316 cm$^{-1}$.

[10] For $H_2$ elimination reactions which form bonds between Group 13 and Group 15 elements compare: M. Driess, S. Kuntz, K. Merz, H. Pritzkow, *Chem. Eur. J.* **1998**, *4*, 1628–1632.

[11] In toluene and $CH_2Cl_2$, $H_2$ elimination reactions occur at room temperature, whereas in donor solvents such as THF these reactions lead to rapid decomposition. The $^{31}$P NMR spectra of these solutions in THF indicate an ionic decomposition product of possible formula $[\{(CO)_5W\}_2PH_2]^-$.

[12] Crystal structure analyses of **2** and **3** were performed on a STOE IPDS diffractometer with $Ag_{K\alpha}$ radiation ($\lambda = 0.56087$ Å) for **2** and $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) for **3**. The structures were solved by direct methods with the program SHELXS-93,[23a] and full matrix least-squares refinement on $F^2$ in SHELXL-97[23b] was performed with anisotropic displacements for non-H atoms. Hydrogen atoms at carbon atoms were located in idealized positions and refined isotropically according to the riding model. The hydrogen atoms at the phosphorus, aluminum, and gallium atoms were freely refined. **2**: $C_8H_{13}AlNO_5PW$, $M_r = 444.99$, crystal dimensions $0.40 \times 0.20 \times 0.08$ mm$^3$, monoclinic, space group $P2_1/c$ (no. 14); $a = 6.562(1)$, $b = 13.495(3)$, $c = 17.295(4)$ Å, $\beta = 100.29(3)^\circ$, $T = 210(2)$ K, $Z = 4$, $V = 1506.9(5)$ Å$^3$, $\rho_{calcd} = 1.961$ Mg m$^{-3}$, $\mu(Ag_{K\alpha}) = 4.219$ mm$^{-1}$, 4058 independent reflections ($R_{int} = 0.0435$, $2\theta_{max} = 46.3^\circ$), 3637 observed with $F_o = 4\sigma(F_o)$; 173 parameters, $R_1 = 0.0246$, $wR_2 = 0.0638$. **3**: $C_8H_{13}GaNO_5PW$, $M_r = 487.73$, crystal dimensions $0.50 \times 0.30 \times 0.02$ mm$^3$, monoclinic, space group $P2_1/c$ (no. 14); $a = 6.629(1)$, $b = 11.533(2)$, $c = 20.112(4)$ Å, $\beta = 90.27(3)^\circ$, $T = 200(1)$ K, $Z = 4$, $V = 1537.4(5)$ Å$^3$, $\rho_{calcd} = 2.107$ Mg m$^{-3}$, $\mu(Mo_{K\alpha}) = 9.338$ mm$^{-1}$, 2912 independent reflections ($R_{int} = 0.1058$, $2\theta_{max} = 52^\circ$), 2623 observed with $F_o = 4\sigma(F_o)$; 161 parameters, $R_1 = 0.0437$, $wR_2 = 0.1137$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166049 (**2**) and CCDC-166050 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] J. L. Atwood, F. R. Bennett, F. M. Elms, C. Jones, C. L. Raston, K. D. Robinson, *J. Am. Chem. Soc.* **1991**, *113*, 8183–8185.

[14] C. Tessier-Youngs, C. Bueno, O. T. Beachley, Jr., M. R. Churchill, *Inorg. Chem.* **1983**, *22*, 1054–1059.

[15] U. Vogel, M. Scheer, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1593–1598.

[16] F. A. Cotton, D. J. Darensbourg, B. W. S. Kolthammer, *Inorg. Chem.* **1981**, *20*, 4440–4442.

[17] M. J. Aroney, I. E. Buys, M. S. Davies, T. W. Hambley, *J. Chem. Soc. Dalton Trans.* **1994**, 2827–2834.

[18] J. L. Atwood, K. W. Butz, M. G. Gardiner, C. Jones, G. A. Koutsantonis, C. L. Raston, K. D. Robinson, *Inorg. Chem.* **1993**, *32*, 3482–3487.

[19] M. A. Petrie, K. Ruhlandt-Senge, P. P. Power, *Inorg. Chem.* **1992**, *31*, 4038–4039.

[20] G. Linti, R. Frey, K. Polborn, *Chem. Ber.* **1997**, *130*, 663–668.

[21] K. Ruff, *Inorg. Synth.* **1967**, *9*, 30–37.

[22] D. F. Shriver, A. E. Shirk, *Inorg. Synth.* **1977**, *17*, 42–45.

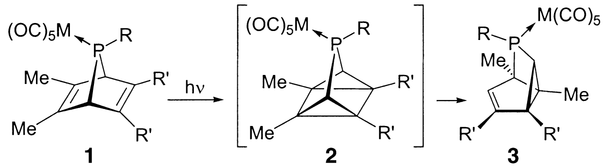
[23] a) G. M. Sheldrick, SHELXS-93, Universität Göttingen, **1993**; b) G. M. Sheldrick, SHELXL-97, Universität Göttingen, **1997**.

---

# Norbornadiene–Quadricyclane Valence Isomerism for a Tetraphosphorus Derivative**

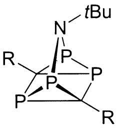
Mark J. M. Vlaar, Andreas W. Ehlers, Marius Schakel, Scott B. Clendenning, John F. Nixon, Martin Lutz, Anthony L. Spek, and Koop Lammertsma*

The photochemically induced valence isomerization of norbornadiene to the higher energy quadricyclane is well established[1] and this is also the case for the 7-oxa- and 7-azanorbornadienes.[2] The related 7-phospha analogue **1** on the other hand undergoes a UV-induced rearrangement to the tricyclic compound **3** [Eq. (1), R = Ph, Me; R′ = $CO_2Me$; M = W, Cr] presumably via an intermediate quadricyclane **2**, however, this has not been established definitely.[3]



(1)

Recently, we found that tetraphosphaquadricyclane **8** is formed with surprising ease, together with the polycyclic compound **7** (Scheme 1), from the reaction of 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**4**) with the transient phosphinidene complex $[PhPW(CO)_5]$,[4, 5] which is generated in situ by thermal degradation of **1** (R = Ph, M = W). The mechanism for the unexpected formation of **8** was not elucidated, but an intramolecular [2+2] cycloaddition of the two P=C units of an intermediate tetraphosphanorbornadiene complex, the 1,4-adduct **6**,[6] was assumed. A similar process has been proposed for the formation of quadricyclane **9**, R = alkyl, but intermediate norbornadiene derivatives were not detected in this case either.[7]



**9**

Norbornadienes containing two or more P atoms have been proposed as intermediates, mostly in the cyclooligomerization of phosphaalkynes,[7, 8] but to date only one triphospha-7-

---

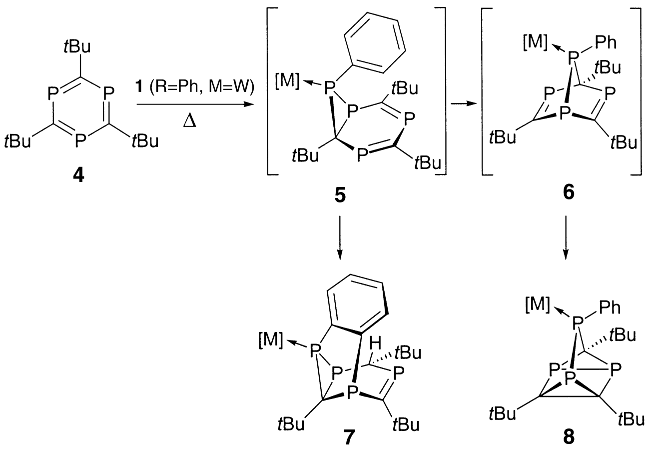
[*] Prof. Dr. K. Lammertsma, M. J. M. Vlaar, Dr. A. W. Ehlers, Dr. M. Schakel
Department of Organic and Inorganic Chemistry
Faculty of Sciences, Vrije Universiteit
De Boelelaan 1083, NL-1081 HV, Amsterdam (The Netherlands)
Fax: (+31) 20-444-7488
E-mail: lammert@chem.vu.nl

S. B. Clendenning, Prof. Dr. J. F. Nixon
The School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 9QJ (UK)

Dr. M. Lutz, Dr. A. L. Spek
Bijvoet Center for Biomolecular Research
Utrecht University, Padualaan 8, NL-3584 CH, Utrecht (The Netherlands)

[**] The Netherlands Organization for Scientific Research (NOW/CW) is acknowledged for partial support (A.L.S., M.L., K.L.), as are the NSERC of Canada for a scholarship (S.B.C.), and EPSRC for funding phosphaorganometallic chemistry at Sussex University (J.F.N.). Dr. H. Zappey is thanked for the HR-MS spectra and J. C. Slootweg for his initiative.

1433-7851/01/4023-4412 $ 17.50+.50/0



Scheme 1. Synthesis of **7** and **8**; [M] = W(CO)$_5$.

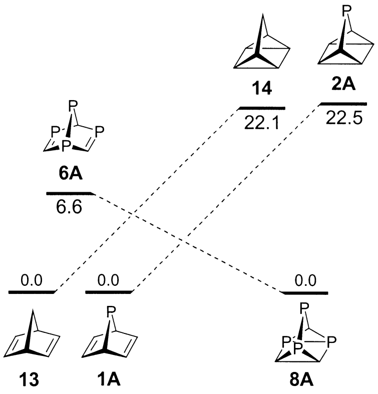
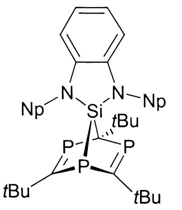
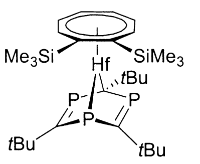


Figure 2. G3(MP2) computed energy difference between **6A** and **8A**, compared to the energy difference between **13** and **14** (experimental)[14] and **1A** and **2A** (MP2/6-31G).[3b]

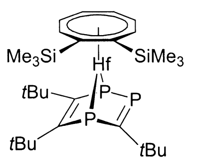
silanorbornadiene (**10**; Np = CH$_2$*t*Bu)[9] and two triphospha-7-hafnanorbornadiene complexes (**11** and **12**)[10] have been isolated. While **10** is stable up to 80 °C and does not isomerize to the corresponding quadricyclane, such a quadricyclane intermediate was proposed for the thermal rearrangement of **11** to **12**.[10a]



**10**



**11**



**12**

We evaluated the proposed conversion of **6** into **8** by ab initio MO theory.[11] The MP2/6-31G* optimized geometries for the parent systems (**6A** and **8A**) are depicted in Figure 1. The geometry of quadricyclane **8A** is in good agreement with the experimentally determined molecular structure of **8**.[4] The reduced steric congestion, because of the absence of the bulky W(CO)$_5$ and *t*-butyl groups, is expressed in a shortening of the C1–C2 bond and all the P–C bonds.

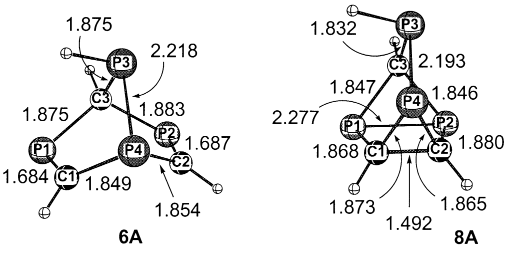
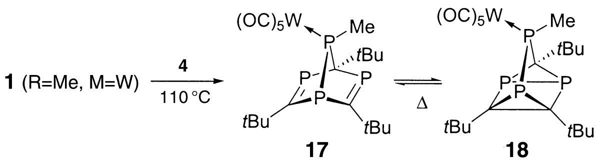


Figure 1. MP2/6-31G* optimized geometries for structures **6A** and **8A**, with selected bond lengths [Å.]

In line with the experimental data, quadricyclane structure **8A** is more stable than its norbornadiene isomer **6A**, by 6.6 kcal mol$^{-1}$ at the G3(MP2) level (Figure 2).[12, 13] This sharply contrasts with the hydrocarbon analogues, since norbornadiene (**14**) is energetically favored over quadricyclane (**13**) by as much as 22.1 kcal mol$^{-1}$ experimentally[14] and by 24.4 and 23.8 kcal mol$^{-1}$ at the G3(MP2)[15] and CCSD(T)//MP2/6-31G* levels,[16] respectively. Likewise, the parent 7-phosphanorbornadiene **1A** is energetically preferred over its quadricyclane isomer **2A** by 22.5 kcal mol$^{-1}$ at the MP2/6-31G* level (Figure 2).[3b]

This inversion of relative stabilities for the tetraphospha compounds, compared with their hydrocarbon analogues, originates from differences in strain energies. Because of their larger number of small hydrocarbon rings quadricyclanes **14** and **2A** are both much more strained than the corresponding norbornadienes **13** and **1A**. However, **8A** is much less strained than hydrocarbon **14** because of the presence of four P atoms in **8A**, phosphorus can accommodate smaller bond angles[17] than carbon and this is reflected in the 6.7 kcal mol$^{-1}$ smaller G2(MP2) strain energy of the three-membered phosphirane ring than that of cyclopropane.[18] A more dramatic illustration is the difference in strain energies for tetraphosphacubane (74.8 kcal mol$^{-1}$)[17, 19] and the all-hydrocarbon cubane (165.1 kcal mol$^{-1}$).[20] Note that the higher strain energy of **8A** (compared to **6A**), however, is compensated for by the conversion of two of its two highly energetic P=C π bonds (49.4 kcal mol$^{-1}$) into four P–C σ bonds (66.1 kcal mol$^{-1}$).[21]

To test the accessibility of valence isomerism for the tetraphospha derivatives experimentally, we treated triphosphabenzene **4** at 110 °C with [MePW(CO)$_5$] [Eq. (2)], generated in situ from **1** (R = Me, M = W).[22] The advantage of



(2)

using the methyl substituted synthon is that no side-products such as **7** can be obtained.[4] Gratifyingly, we indeed obtained a mixture of the expected products **17** and **18** in a 1:8 ratio, as determined from integration of the $^{31}$P NMR resonance signals.

The $^1$H, $^{13}$C, and $^{31}$P NMR spectra of **18** are very similar to those of **8**.[4] The $^{31}$P NMR resonance signals are at $\delta = -112.2$ and $-138.1$ (CPP ring), $\delta = -122.3$ (CCP ring), and $\delta = 24.2$ (P bridge) and all show multiple P–P couplings. The structure of **17**, the first tetraphosphanorbornadiene compound, is readily deduced from NMR spectroscopy. The phosphaalkene bonds have characteristic downfield $^{31}$P NMR resonances ($\delta = 335.3$ and 322.0) and $^{13}$C NMR resonances ($\delta = 229.8$ and 226.8),[23] all of which are similar to those reported for **10**.[9] However, the $^{31}$P NMR resonance for the bridgehead phosphorus (P4 in Figure 3) at $\delta = 27.3$ is much further downfield than that of **10** ($\delta = -63.8$) and has a typical $^1J$(P,P) coupling constant of 174.6 Hz to the neighboring bridging phosphorus (P3, $\delta = 138.8$, $^1J$(W,P) = 220.5 Hz), which is shielded by 60.8 ppm relative to the corresponding atom in the 7-phosphanorbornadiene complex **1** (R = Me, M = W).[24]

A single-crystal X-ray diffraction study confirmed the structure of **17** (Figure 3). The two P=C bonds P1–C1 and P2–C2 (1.678(2), 1.676(2) Å), as well as the P3–P4 bond (2.2078(8) Å), and the P–C single bonds (1.846(3)–1.900(2) Å) are all of the expected lengths. The W1-P3-C16 angle (109.15(9)°) is about 6° smaller than the corresponding angle of tetraphosphaquadricyclane **8**, and reflects an increased steric congestion between the substituents at the bridgehead phosphorus and the *tert*-butyl groups in **17**. The P4-P3-C3 angle for **17** of 89.68(8)° is correspondingly smaller. The MP2/6-31G* optimized geometry of **6A** compares well with the X-ray structure of **17**, when the absence of the W(CO)$_5$, *tert*-butyl, and methyl groups in **6A** is taken into account; most of the P–C single bonds of **6A** are slightly shorter, whereas its P=C bonds are slightly elongated.

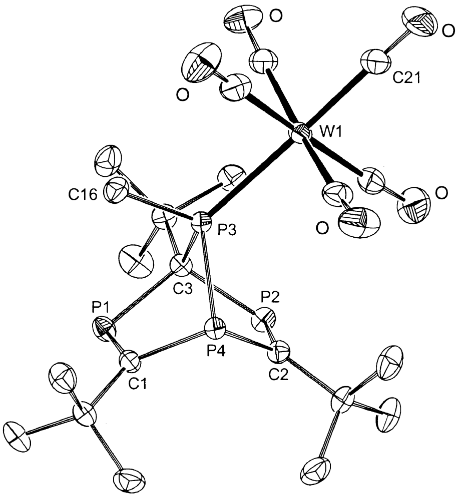


Figure 3. ORTEP plot of **17** with ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles and torsion angles [°]: W1-P3 2.5450(6), P3-C3 1.900(2), P3-P4 2.2078(8), P4-C1 1.861(2), P4-C2 1.861(2), P1-C1 1.678(2), P2-C2 1.676(2), P1-C3 1.892(2), P2-C3 1.878(2), P3-C16 1.846(3); P3-W1-C21 177.79(11), P4-P3-C3 89.68(8), P1-C3-P2 107.86(12), C1-P4-C2 99.67(10), C1-P1-C3 100.08(10), C2-P2-C3 100.24(11), P1-C1-P4 118.46(12), P2-C2-P4 118.46(13), W1-P3-P4 115.14(3), W1-P3-C3 127.48(7), W1-P3-C16 109.15(9), P4-P3-C16 103.77(9), C3-P3-C16 108.28(11), P3-P4-C1 92.27(8), P3-P4-C2 89.67(8); P1-C3-P3 105.16(10), P2-C3-P3 102.87(11), C3-P1-C1-P4 0.39(16), C3-P2-C2-P4 1.31(16).

Heating a toluene solution of isolated **17** or **18** at 110 °C resulted in both cases in the formation of the same 1:8 mixture of **17** and **18**, as determined by $^{31}$P NMR, which suggests these compounds are in thermal equilibrium. Despite some degradation during the isomerization, a Gibbs free energy difference of 2 kcal mol$^{-1}$ could be estimated. This value is 5 kcal mol$^{-1}$ smaller than the G3(MP2) computed energy difference between **6A** and **8A** and is a result of the presence of the stabilizing W(CO)$_5$ fragment[24, 25] and the bulky *tert*-butyl groups.

Whereas concerted [2+2] cycloadditions are Woodward–Hoffman forbidden processes, both head-to-head and head-to-tail thermally induced dimerizations of phosphaalkenes are well known and possibly follow a stepwise reaction path involving ionic or biradical intermediates.[23, 26] However, the photochemically induced [$\pi^2_s + \pi^2_s$] cyclization, which is Woodward–Hoffman allowed, is also feasible for **17**. Thus, full conversion into **18** is observed when a toluene solution of **17** is exposed to daylight for several hours, although extended exposure resulted in complete decomposition.

In conclusion, tetraphospha structures **17** and **18** undergo both thermally and photochemically a norbornadiene–quadricyclane valence isomerism similar to their hydrocarbon analogues, except that the tetraphosphaquadricyclane is the more stable isomer.

## *Experimental Section*

NMR spectra were recorded on a Bruker Avance 250 ($^{31}$P; 85% H$_3$PO$_4$) and an MSL 400 ($^1$H, $^{13}$C; TMS) spectrometer, high-resolution mass spectra (HR-MS) on a Finnigan Mat 90, and infrared (IR) spectra on a Mattson 630 Galaxy spectrometer.

Reaction of **4** with [MePW(CO)$_5$]: Complex **1** (R = Me, 0.37 g, 0.66 mmol) and **4** (0.20 g, 0.66 mmol) were heated in refluxing toluene (5 mL) for 18 h. Evaporation to dryness and chromatography over silica with pentane as eluent gave a mixture of **17** and **18** in a 1:8 ratio. Fractional crystallization from a hexane/dichloromethane mixture afforded 0.22 g (49%) of **18** as yellow crystals and 24 mg (6%) of **17** as orange crystals.

**17**: mp 127–129 °C; $^{31}$P NMR (CDCl$_3$, 101.3 MHz): $\delta = 335.3$ (ddd, $^2J$(P,P) ≈ $^2J$(P,P) ≈ 18 Hz, $^2J$(P,P) = 9.1 Hz; C=P), 322.0 (ddd, $^2J$(P,P) ≈ $^2J$(P,P) ≈ 18 Hz, $^2J$(P,P) = 6.5 Hz; C=P), 138.8 (ddd, $^1J$(P,P) = 174.6 Hz, $^2J$(P,P) = 9.1 Hz, $^2J$(P,P) = 6.5 Hz, $^1J$(W,P) = 220.5 Hz; W-*P*-P), 27.3 (ddd, $^1J$(P,P) = 174.6 Hz, $^2J$(P,P) ≈ $^2J$(P,P) ≈ 18 Hz; W-P-*P*); $^1$H NMR (CDCl$_3$ 400.1 MHz): $\delta = 2.16$ (dd, $^2J$(H,P) = 6.9 Hz, $^3J$(H,P) = 4.2 Hz, 3H; P-CH$_3$), 1.67 (s, 9H; C(CH$_3$)$_3$), 1.49 (d, $^4J$(H,P) = 1.7 Hz, 9H; C(CH$_3$)$_3$), 1.46 (d, $^4J$(H,P) = 1.8 Hz, 9H; C(CH$_3$)$_3$); $^{13}$C NMR (CDCl$_3$ 100.6 MHz): $\delta = 229.8$ (dddd, $^1J$(P,C) ≈ $^1J$(P,C) ≈ 56 Hz, $^2J$(P,C) ≈ 12 Hz, $^3J$(P,C) ≈ 3 Hz; C=P), 226.8 (m; C=P), 197.8 (d, $^2J$(P,C) = 24.1 Hz; *trans*-CO), 197.4 (dd, $^2J$(P,C) = 5.7 Hz, $^3J$(P,C) = 2.6 Hz, $^1J$(W,C) = 117.7 Hz; *cis*-CO), 95.8 (dddd, $^1J$(P,C) = 67.6 Hz, $^1J$(P,C) = 61.1 Hz, $^1J$(P,C) = 23.0 Hz, $^2J$(P,C) = 6.3 Hz; P$_3$*C*C(CH$_3$)$_3$), 43.2 (ddd, $^2J$(P,C) = 56.7 Hz, $^2J$(P,C) = 20.2 Hz, $^3J$(P,C) = 3.2 Hz; *C*(CH$_3$)$_3$), 43.0 (ddd, $^2J$(P,C) = 56.0 Hz, $^2J$(P,C) = 19.8 Hz, $^3J$(P,C) = 2.6 Hz; *C*(CH$_3$)$_3$), 38.7 (pst, $^2J$(P,C) = 15.9 Hz; *C*(CH$_3$)$_3$), 33.1 (m, 2 C(*C*H$_3$)$_3$), 32.6 (dd, $^3J$(P,C) = 14.1 Hz, $^3J$(P,C) = 7.7 Hz; C(*C*H$_3$)$_3$), 27.8 (dd, $^1J$(P,C) = 12.1 Hz, $^2J$(P,C) = 6.1 Hz; P-*C*H$_3$); $^1$H NMR (CDCl$_3$): $\delta = 2.16$ (dd, $^2J$(H,P) = 6.9 Hz, $^3J$(H,P) = 4.1 Hz, 3H; P-CH$_3$), 1.67 (s, 9H; C(CH$_3$)$_3$), 1.49 (d, $^4J$(H,P) = 1.9 Hz, 9H; C(CH$_3$)$_3$), 1.46 (d, $^4J$(H,P) = 2.0 Hz, 9H; C(CH$_3$)$_3$); HR-MS: calcd for C21H30P4O5W: 670.05536; found: 670.05339; IR (CH$_2$Cl$_2$): $\tilde{\nu} = \nu$(CO) 1937 cm$^{-1}$ (s), 2069 cm$^{-1}$ (w).

**18**: mp 187–188 °C; $^{31}$P NMR (CDCl$_3$, 101.3 MHz): $\delta = 24.2$ (dd, $^1J$(P,P) = 257.4 Hz, $^2J$(P,P) = 15.4 Hz, $^1J$(W,P) = 222.6 Hz; W-*P*-P), $-112.2$ (d, $^2J$(P,P) = 47.6 Hz), $-122.3$ (d, $^1J$(P,P) = 257.4 Hz; W-P-*P*), $-138.1$ (dd, $^2J$(P,P) = 47.6 Hz, $^2J$(P,P) = 15.4 Hz; P); $^{13}$C NMR (CDCl$_3$, 100.6 MHz): $\delta = 198.9$ (d, $^2J$(P,C) = 22.8 Hz; *trans*-CO), 197.5 (dd, $^2J$(P,C) = 5.8 Hz, $^3J$(P,C) = 4.8 Hz, $^1J$(W,C) = 126.0 Hz; *cis*-CO), 69.6 (dddd, $^1J$(P,C) =

63.1 Hz, $^{1}J$(P,C) = 58.4 Hz, $^{1}J$(P,C) = 20.6 Hz, $^{2}J$(P,C) = 3.4 Hz; $P_3C$C($CH_3$)$_3$), 55.9 (dddd, $^{1}J$(P,C) = 51.2 Hz, $^{1}J$(P,C) = 30.6 Hz, $^{2}J$(P,C) ≈ $^{2}J$(P,C) ≈ 4.5 Hz; $CP_2$), 51.1 (ddd, $^{1}J$(P,C) = 49.4 Hz, $^{1}J$(P,C) = 28.5 Hz, $^{2}J$(P,C) = 4.5 Hz; $CP_2$), 37.3 (ddd, $^{2}J$(P,C) = 16.2 Hz, $^{2}J$(P,C) = 12.4 Hz, $^{2}J$(P,C) = 3.8 Hz; *C*($CH_3$)$_3$), 35.1 (dddd, $^{2}J$(P,C) = 18.2 Hz, $^{2}J$(P,C) = 9.2 Hz, $^{3}J$(P,C) = 3.2 Hz, $^{3}J$(P,C) ≈ 1 Hz; *C*($CH_3$)$_3$), 34.7 (dd, $^{2}J$(P,C) = 18.6 Hz, $^{2}J$(P,C) = 8.2 Hz; *C*($CH_3$)$_3$), 33.4 (ddd, $^{3}J$(P,C) = 8.7 Hz, $^{3}J$(P,C) = 6.6 Hz, $^{3}J$(P,C) = 3.1 Hz; C(*C*$H_3$)$_3$), 31.4 (dd, $^{3}J$(P,C) = 11.4 Hz, $^{3}J$(P,C) = 6.1 Hz; C(*C*$H_3$)$_3$), 30.9 (dd, $^{3}J$(P,C) = 11.7 Hz, $^{3}J$(P,C) = 6.9 Hz; C(*C*$H_3$)$_3$), 23.6 (dddd, $^{1}J$(P,C) = 17.2 Hz, $^{2}J$(P,C) = 7.7 Hz, $^{3}J$(P,C) = 3.1 Hz, $^{3}J$(P,C) = 2.3 Hz; P-*C*$H_3$); $^{1}$H NMR ($CDCl_3$, 400.1 MHz): $\delta = 2.08$ (dd, $^{2}J$(H,P) = 8.3 Hz, $^{3}J$(H,P) = 5.3 Hz, 3H; P-$CH_3$), 1.30 (s, 9H; C($CH_3$)$_3$), 1.26 (s, 9H; C($CH_3$)$_3$), 1.25 (s, 9H; C($CH_3$)$_3$); HR-MS: calcd for C21H30P4O5W: 670.05536; found: 670.054938; IR ($CH_2Cl_2$): $\tilde{\nu} = \nu$(CO) 1935 $cm^{-1}$ (s), 2070 $cm^{-1}$ (w).

Crystal structure determination of **17**: $C_{21}H_{30}O_5P_4W$, $Fw = 670.18$, yellow block, $0.30 \times 0.30 \times 0.24$ $mm^3$, triclinic, $P\bar{1}$ (No. 2), $a = 10.9447(1)$, $b = 11.1640(1)$, $c = 11.3277(1)$ Å, $\alpha = 81.9368(5)$, $\beta = 88.5556(5)$, $\gamma = 76.8724(3)^\circ$, $V = 1334.57(2)$ Å$^3$, $Z = 2$, $\rho = 1.668$ g$cm^{-3}$, 28416 measured reflections, 6069 unique reflections ($R_{int} = 0.072$). Intensities were measured on a Nonius KappaCCD diffractometer with rotating anode ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å) at a temperature of 150 K. Absorption correction based on multiple measured reflections using the program PLATON[27] (routine MULABS, $\mu = 4.60$ $mm^{-1}$, 0.17–0.29 transmission). The structure was solved with automated Patterson methods with the program DIRDIF97[28] and refined with the program SHELXL97[29] against $F^2$ of all reflections up to a resolution of $(\sin \vartheta/\lambda)_{max} = 0.65$ Å$^{-1}$. Non-hydrogen atoms were refined freely with anisotropic displacement parameters, hydrogen atoms were refined freely with isotropic displacement parameters. $R$ ($I > 2\sigma(I)$): $R1 = 0.0214$, $wR2 = 0.0497$. $R$ (all data): $R1 = 0.0231$, $wR2 = 0.0505$, $S = 1.041$. Residual electron density between $-1.28$ and 1.33 eÅ$^3$. The drawings, structure calculations, and checking for higher symmetry was performed with the program PLATON.[27] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164106 (**17**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: June 8, 2001 [Z17255]

---

[1] V. A. Bren, A. D. Dubonsov, V. I. Minkin, V. A. Chenoivanov, *Russ. Chem. Rev.* **1991**, *60*, 451–469.

[2] W. Tochtermann, G. Olsson, *Chem. Rev.* **1989**, *89*, 1203–1214.

[3] a) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *Nouv. J. Chim.* **1984**, *8*, 453–457; b) B. Wang, C. H. Lake, K. Lammertsma, *Organometallics* **1997**, *16*, 4145–4149.

[4] M. J. M. Vlaar, A. W. Ehlers, M. Schakel, S. B. Clendenning, J. F. Nixon, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Eur. J.* **2001**, *7*, 3545–3550.

[5] For reviews on electrophilic phosphinidene complexes see: a) F. Mathey, *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 38; b) F. Mathey, *Angew. Chem.* **1987**, *99*, 285–296; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 275–286; c) K. D. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, **1998**, p. 19.

[6] A related 1,4-adduct has been reported previously for the reaction of [PhPW(CO)$_5$] with [5]metacyclophane. M. J. van Eis, C. M. D. Komen, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt, *Angew. Chem.* **1998**, *110*, 1656–1659; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1547–1550.

[7] F. Tabellion, A. Nachbauer, S. Leininger, C. Peters, M. Regitz, F. Preuss, *Angew. Chem.* **1998**, *110*, 1318–1321; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1233–1235.

[8] a) A. Elvers, F. W. Heinemann, B. Wrackmeyer, U. Zenneck, *Chem. Eur. J.* **1999**, *5*, 3143–3153; b) M. Julino, M. Slany, U. Bergsträßer, F. Mercier, F. Mathey, M. Regitz, *Chem. Ber.* **1995**, *128*, 991–997.

[9] S. B. Clendenning, B. Gehrhus, P. B. Hitchcock, J. F. Nixon, *Chem. Commun.* **1999**, 2451–2452.

[10] a) P. Binger, S. Leininger, K. Günther, U. Bergsträßer, *Chem. Ber.* **1997**, *130*, 1491–1494; b) P. Binger, S. Leininger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann, C. Krüger, *Angew. Chem.* **1995**, *107*, 2411–2412; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2227–2230.

[11] Gaussian98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**..

[12] G3(MP2): L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, J. A. Pople, *J. Chem. Phys.* **1999**, *110*, 4703–4709.

[13] The G3(MP2) absolute energies (Hartree) are $-1480.175672$ for **6A** and $-1480.186172$ for **8A**.

[14] a) D. W. Rogers, L. S. Choi, R. S. Girellini, T. J. Holmes, N. L. Allinger, *J. Phys. Chem.* **1980**, *84*, 1810–1814; b) W. V. Steele, *J. Chem. Thermodyn.* **1978**, *10*, 919–927.

[15] D. W. Rogers, F. J. McLafferty, *J. Phys. Chem. A* **1999**, *103*, 8733–8737.

[16] R. D. Bach, I. L. Schilke, H. B. Schlegel, *J. Org. Chem.* **1996**, *61*, 4845–4847.

[17] S. M. Bachrach, L. M. Perriott, *Tetrahedron Lett.* **1993**, *34*, 6365–6368.

[18] K. Lammertsma, B. Wang, J.-T. Hung, A. W. Ehlers, G. M. Gray, *J. Am. Chem. Soc.* **1999**, *121*, 11650–11651.

[19] S. M. Bachrach, B. D. Gailbraeth, *Tetrahedron Lett.* **1998**, *39*, 4211–4214.

[20] J. D. Cox, G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, **1970**.

[21] P. von R. Schleyer, D. Kost, *J. Am. Chem. Soc.* **1988**, *110*, 2105–2109.

[22] A. Marinetti, F. Mathey, *J. Am. Chem. Soc.* **1982**, *104*, 4484–4485.

[23] R. Appel in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, New York, **1990**, pp. 157–219.

[24] A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Chem. Soc. Chem. Commun.* **1982**, 667–668.

[25] M. J. van Eis, H. Zappey, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt, *J. Am. Chem. Soc.* **2000**, *122*, 3386–3390.

[26] a) L. N. Markovski, V. D. Romanenko, *Tetrahedron* **1989**, *45*, 6019–6090; b) R. Appel, F. Knoll, *Adv. Inorg. Chem.* **1989**, *33*, 259–361.

[27] A. L. Spek, PLATON. A multipurpose crystallographic tool, Utrecht University, The Netherlands, **2001**.

[28] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, The DIRDIF97 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1997**.

[29] G. M. Sheldrick, SHELXL-97, Program for crystal structure refinement, University of Göttingen, Germany, **1997**.