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Registry No. 1, 72-33-3; **2**, 4502-08-3; *i*-PrC≡CPr-*i*, 927-99-1; *i*-Pr(d_7)C≡CPr-*i*(d_7), 88158-48-9; *sec*-BuC≡CBu-*sec*, 69393-86-8; $Et_2CHC{\equiv}CCHEt_2$, 97253-87-7; $Me_2C(OH)C{\equiv}CC(OH)Me_2$, 142-30-3; $(CD_3)_2C(OH)C{\equiv}CC(OH)(CD_3)_2$, 62875-11-0; $Co_2(CO)_8$, 10210-68-1; EtC(OH)(Me)C≡CC(OH)(Me)Et, 78-66-0; $Et_2C(OH)C{\equiv}CC(OH)Et_2$, 2044-37-3; bis(17-deoxymestranol)-β-acetylene, 97253-88-8; dicyclopentylacetylene, 97253-89-9; dicyclohexylacetylene, 62371-39-5; 1,2-dicyclopentyl-1,2-dihydroxyacetylene, 5325-62-2; 1,2-dicyclohexyl-1,2-dihydroxyacetylene, 78-54-6; bis(17-deoxymestranol)-α-acetylene, 97334-56-0.

Carbonylation of a Strained Phosphorus-Carbon Bond. Conversion of Phosphirene into 2-Keto-1,2-dihydrophosphete Complexes: An Entry into the Chemistry of the Phosphorus Analogues of Unsaturated β-Lactams

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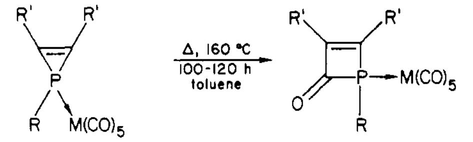
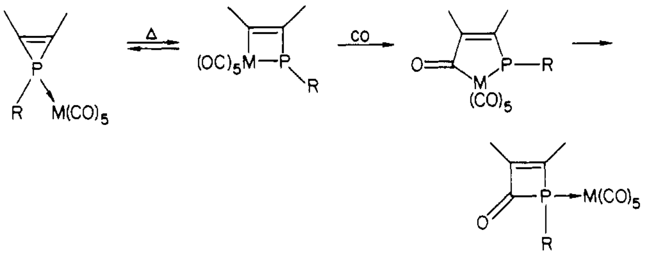
As far as we know, no clear-cut example of CO insertion in a carbon-phosphorus σ bond has ever been reported in the literature although the reverse reaction, i.e., the decarbonylation of acylphosphines by Wilkinson catalyst, has been described some time ago by Lindner.[2] While studying the chemistry of phosphirenes,[3-5] we have discovered such a carbonylation reaction through which the three-membered ring is converted into the still poorly characterized four-membered unsaturated 1,2-dihydrophosphete ring.[6] Of course, the exceptional strain of the phosphirene cycle probably weakens the intracyclic P-C σ bonds and facilitates the process. This ring enlargement has been observed during the thermolysis of phosphirene-chromium, -molybdenum, and -tungsten pentacarbonyl complexes:



1a, R=R'=Ph; M=W
b, R=Ph; R'=Et; M=W
c, R=R'=Ph; M=Cr
d, R=Ph; R'=Et; M=Cr
e, R=R'=Ph; M=Mo

2a, 34%
b, 43%
c, 8%
d, 21%
e, 24%

The reaction is performed in a sealed glass tube under autogenous pressure of carbon monoxide. The products **2a-e**[10] are sufficiently stable toward hydrolysis and can be purified by chromatography on silica gel columns. They are the complexed phosphorus analogues of the long sought and very labile azetinones.[11] We can only speculate about the precise mechanism of their formation. One possibility involves an equilibrium between phosphirene complexes and 1-phospha-2-metallacyclobutenes at high temperature:



If this mechanism is the correct one, then it may be possible to insert various other small molecules (alkenes, alkynes, SO_2, etc...) into the complexed phosphirene ring.

From a spectroscopic point of view, the most noteworthy change occurring during the carbonylation of phosphirene complexes is a dramatic deshielding of the phosphorus atom close to +247 ppm in all cases. On the ^{13}C NMR spectra, the P-CO resonance of **2** appears close to +190 ppm, suggesting a mixed amide-ketone character for the ring carbonyl of these compounds.

Of course the greatest interest of this new carbonylation reaction lies in its potential application to the synthesis of the still unknown

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(1) (a) Laboratoire CNRS-SNPE. (b) Institut Le Bel.

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(3) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484.

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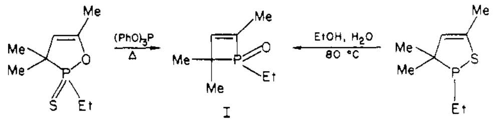
(5) Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.*, in press.

(6) Recently, Russian workers[7] have reported the following reactions:



I

The four-membered ring was characterized by NMR spectroscopy but no X-ray crystal structure analysis was performed. These reactions appear somewhat surprising. On our side, we have tried to convert similarly a tervalent 1,2-oxaphospholane into a phosphetane oxide without any success even above 200 °C.[8] Moreover, the reported $^1J(Me_2C\text{-}P)$ coupling constant for I (18.3 Hz) is abnormally low for a one-bond P(O)-C coupling in a four-membered ring.[9]

(7) Nurtdinov, S. Kh.; Ismagilova, N. M.; Fakhrutdinova, R. A.; Zykova, J. V. *Zh. Obshch. Khim.* **1983**, *53*, 1045; *Chem. Abstr.* **1983**, *99*, 122548z.

(8) Mathey, F.; Mercier, F. *J. Chem. Soc., Chem. Commun.* **1980**, 191.

(9) Gray, G. A.; Cremer, S. E. *J. Org. Chem.* **1972**, *37*, 3458.

(10) **2a**: orange solid, mp 137 °C (chromatographed with hexane-toluene 80:20, $R_f \sim 0.4$); ^{31}P NMR (C_6D_6) δ +86.9, $^1J(^{31}P\text{-}^{183}W) = 231.9$ Hz; ^{13}C NMR ($CDCl_3$) δ 151.7 (d, $^1J(C\text{-}P) = 51.3$ Hz, P*C*Ph), 169.5 (d, $^2J(C\text{-}P) = 36.6$ Hz, CO*C*Ph), 190.72 (d, $^1J(C\text{-}P) = 34.2$ Hz, PCO), 195.08 (d, $^2J(C\text{-}P) = 7.3$ Hz, WCO cis), 198.17 (d, $^2J(C\text{-}P) = 24.4$ Hz, WCO trans); IR (decalin) ν(CO) 2074 w, 1955 shoulder, 1948 vs cm^{-1}; (KBr) ν(P-CO) 1710 cm^{-1}; mass spectrum (EI, ^{184}W), *m/e* 638 (M, 18%), 470 (M - 6CO, 100%), (CI, CH_4^+), *m/e* 639 (M + 1, 100%). **2b**: yellow oil (chromatographed with hexane-toluene 70:30, $R_f \sim 0.5$); ^{31}P NMR (toluene) δ +85.8, $^1J(^{31}P\text{-}^{183}W) = 227$ Hz; ^1H NMR (C_6D_6) δ 0.76 (t, CH_3), 0.86 (t, CH_3), 1.83 (q, $^4J(H\text{-}P) \sim 0$ Hz, CH_2CCO), 2.22 (dq, $^3J(H\text{-}P) \sim 10$ Hz, CH_2CP), ^{13}C NMR (C_6D_6) δ 12.48 (s, CH_3), 12.72 (s, CH_3), 19.75 (d, $^2J(C\text{-}P) = 14.6$ Hz, CH_2), 23.54 (d, $^3J(C\text{-}P) = 11$ Hz, CH_2), 163.21 (d, $^1J(C\text{-}P) = 48.8$ Hz, P*C*Et), 181.30 (d, $^2J(C\text{-}P) = 33$ Hz, CO*C*Et), 191.42 (d, $^1J(C\text{-}P) = 30.5$ Hz, PCO), 196.26 (d, $^2J(C\text{-}P) = 6.1$ Hz, WCO cis), 199.53 (d, $^2J(C\text{-}P) = 23.2$ Hz, WCO trans); IR (decalin) ν(CO) 2072 w, 1988 w, 1955 s, 1943 vs, 1910 w cm^{-1}, (KBr) ν(P-CO) 1723 cm^{-1}; mass spectrum (EI, 70 eV, ^{184}W) *m/e* 542 (M, 32%), 374 (M - 6CO, 89%), 372 (100%). **2c**: orange solid, mp 115 °C (chromatographed with hexane-ether 98:2, $R_f \sim 0.5$); ^{31}P NMR (C_6D_6) δ +133.3; IR (decalin) ν(CO) 2067 w, 1959 shoulder, 1953 vs cm^{-1}, (KBr) ν (P-CO) 1710 cm^{-1}; mass spectrum (EI, 70 eV), *m/e* 506 (M, 8.5%), 366 (M - 5CO, 100%), 338 (M - 6CO, 30%). **2d**: yellow oil (chromatographed with hexane-toluene 75:25, $R_f \sim 0.4$); ^{31}P NMR (CH_2Cl_2) δ +131.8; ^1H NMR (C_6D_6) δ 0.78 (t, CH_3), 0.85 (t, CH_3), 1.77 (q, $^4J(H\text{-}P) \sim 0$ Hz, CH_2CCO), 2.28 (dq, $^3J(H\text{-}P) \sim 10$ Hz, CH_2CP); IR (decalin) ν(CO) 2065 w, 1990 w, 1960 s, 1946 vs cm^{-1}; (KBr) ν(P-CO) 1730 cm^{-1}; mass spectrum (EI, 70 eV), *m/e* 410 (M, 18%), 270 (M - 5CO, 100%). **2e**: orange solid, mp 131 °C (chromatographed with hexane-toluene 80:20, $R_f \sim 0.4$), ^{31}P NMR (C_6D_6) δ +109.5; IR (decalin) ν(CO) 2072 w, 1960 shoulder, 1955 vs cm^{-1}; (KBr) ν(P-CO) 1725 cm^{-1}; mass spectrum (EI, 70 eV), *m/e* 552 (M, 2%), 412 (M - 5CO, 6%), 384 (M - 6CO, 19%), 178 (C_2Ph_2, 100%). The starting compound **1e** has not been described before. It is prepared according to the usual procedure[3] from the corresponding 7-phosphanorbornadiene P-$Mo(CO)_5$ complex described in ref 13 (compound **7**). Compound **7** is heated with an excess of tolan at 120 °C for 5 h in xylene. Compound **1e** thus obtained is purified by chromatography with hexane-toluene (90:10): yield 29%; mp 105 °C; ^{31}P NMR (hexane) δ -137.8.

(11) Kretschmer, G.; Warrener, R. N. *Tetrahedron Lett.* **1975**, 1335.

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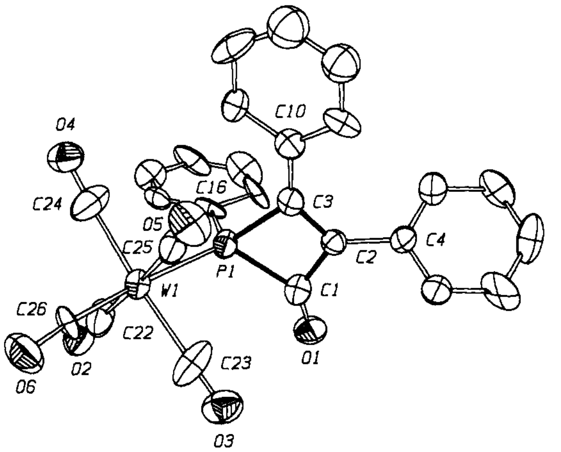
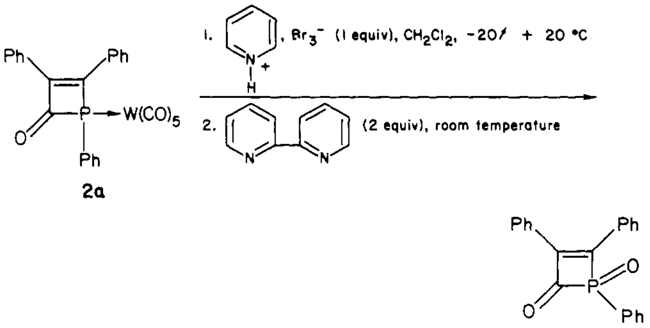


Figure 1. Structure of one molecule of complex **2a**. Thermal ellipsoids are scaled to enclose 50% of the electron density; hydrogen atoms are omitted. Principal bond distances (Å, means between the two units): W-P1, 2.470 (3); P1-C1, 1.93 (1); P1-C3, 1.83 (1); P1-C16, 1.85 (1); C1-O1, 1.16 (1); C1-C2, 1.48 (1); C2-C3, 1.36 (1); C2-C4, 1.52 (1); C3-C10, 1.46 (1); Cphe-Cphe, 1.371 (4); W-C, 2.02-2.06 (1); C-O, 1.134 (6). Selected bond angles (deg, means between the two units): W1-P1-C1, 121.8 (3); W1-P1-C3, 120.5 (3); W1-P1-C16, 121.2 (4); C1-P1-C3, 71.9 (5); P1-C1-C2, 88.8 (7); P1-C3-C2, 97.0 (7); C1-C2-C3, 102.2 (9); Cphe-Cphe-Cphe, 119.9 (2).

phosphorus analogues of unsaturated β-lactams. Thus we have also studied the decomplexation of complex **2a**. We have followed the same general scheme as for the synthesis of 1,2,3-triphenylphosphirene from its P-W(CO)$_5$ complex.[4] In a first step, the P-W bond of **2a** is weakened through oxidation of tungsten by 1 mol of pyridinium tribromide, then the phosphorus ligand is displaced from the brominated complex by 2 mol of 2,2′-bipyridyl. P-Oxidation takes place spontaneously.



The 2,2′-bipyridyl complexes which are present in the crude reaction mixture together with **3** are precipitated by adding ether to the medium. After filtration and evaporation, **3** is recrystallized in a mixture of dichloromethane and hexane.[12] Finally, since the 1,2-dihydrophosphete ring was never structurally characterized before, we decided to perform the X-ray crystal structure analysis of **2a**, which gave the following crystal data: $C_{26}H_{15}O_6PW$, M_w 638.23; triclinic; $a = 9.954$ (3) Å, $b = 24.817$ (6) Å, $c = 9.824$ (3) Å, $\alpha = 99.00$ (2)°, $\beta = 90.37$ (2)°, $\gamma = 97.94$ (2)°, $U = 2373$ Å^3, $d_{\text{obsd}} = 1.77 \pm 0.03$ g cm^{-3}, $Z = 4$, $d_{\text{calcd}} = 1.786$ g cm^{-3}, space group $P\bar{1}$ (No. 2). Mo Kα (0.71073 Å) radiation was used for cell dimension determination and intensity measurement at −100 °C (cold nitrogen flow); $\mu = 50.762$ cm^{-1}, $F_0 = 1232$.

Diffraction data were collected in the $\theta/2\theta$ flying step-scan mode with a Philips PW 1100/16 automatic diffractometer at −100 °C, graphite monochromated Mo Kα radiation, and a crystal of dimensions 0.018 × 0.016 × 0.024 cm. Absorption corrections were applied by the numerical integration method (transmission factor 0.89 → 1.10). The structure was solved by the heavy atom method with the Enraf-Nonius SDP/V+1 package on a PDP 11/60 computer. Full-matrix refinement using 4537 reflections having $I > 3\sigma(I)$ converged to conventional agreement factors R_1 and R_2 of 0.047 and 0.079 with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were introduced by their computed coordinates but not refined.

The asymmetric unit contains two independent W(CO)$_5$(P-C$_3$O(C$_6$H$_5$)$_3$) moieties which are not significantly different from each other. The structure (Figure 1 shows one moiety) consists of discrete molecules with no nonusual intramolecular bonds. Selected geometrical averages between the two molecules are given in the caption of Figure 1.

The insertion of CO in the P-C-C triangle leads to an opening of the intracyclic C-P-C angle from 42.8 (2)° to 71.9 (5)°. The P-C intracyclic bonds are significantly different, the longest being on the carbonyl side, whereas the shortest has a normal value for a P-C single bond. The C=C intracyclic double bond remains well localized between C2 and C3 (molecule 1).

Supplementary Material Available: Listings of atomic positional and thermal parameters and of observed and calculated structure factors (×10) (25 pages). Ordering information is given on any current masthead page.

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(12) **3**: yellow solid, mp 130 °C; ^{31}P NMR (CH$_2$Cl$_2$) δ +63; ^{13}C NMR (CD$_2$Cl$_2$) δ 141.36 (d, ^1J(C-P) = 44.5 Hz, P*C*(Ph)), 160.46 (d, ^1J(C-P) = 84.3 Hz, P*C*Ph), 180.35 (d, ^2J(C-P) = 70.5 Hz, CO*C*Ph), 202.13 (d, ^1J(C-P) = 65.7 Hz, PCO); IR (KBr) ν(P-CO) 1722 cm^{-1}, ν(P=O) 1217 cm^{-1}; mass spectrum (CI, CH$_4$, ^{184}W), *m/e* 331 (M + 1, 100%).

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Long-Distance Electron Transfer in Pentaammineruthenium (Histidine-48)-Myoglobin. Reorganizational Energetics of a High-Spin Heme

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Both the kinetics and thermodynamics of long-distance electron transfer[1,2] have been successfully determined in two ruthenium-modified metalloproteins, a$_5$Ru(His-33)-cytochrome *c* (a = NH$_3$)[1a,b] and a$_5$Ru(His-83)-azurin.[1c,d] In both proteins the electron-acceptor site is buried in the protein interior, and it is inferred from the weak temperature dependence of the electron-transfer rate constant that the reorganizational enthalpy of the low-spin ferriheme[3] or blue copper is very small. An obvious test of the postulated origin of the weak (or lack of) temperature dependence is to examine a system with an acceptor where the inner-sphere reorganizational energy is relatively large, namely, a ruthenium-modified protein containing a high-spin ferriheme. We report here our results on one such semisynthetic system, a$_5$Ru(His-48)-myoglobin (Figure 1).[4,5]

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(3) Analysis of the oxidized and reduced cytochrome *c* X-ray structures suggests a low theoretical value as well (Churg, A. K.; Weiss, R. M.; Warshel, A.; Takano, T. *J. Phys. Chem.* **1983**, *87*, 1683-1694).

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