Additional experiments are now in progress in an effort to distinguish between the possible spontaneous reaction mechanism for **5b**.

Acknowledgment. This investigation was supported by Public Health Service Grants No. CA-17278 and CA-26086 from the National Cancer Institute.

Registry No. 5a, 2461-34-9; **5b**, 82167-70-2; **8b**, 2472-22-2; deuterium, 16873-17-9.

Generation and Trapping of Terminal Phosphinidene Complexes. Synthesis and X-ray Crystal Structure of Stable Phosphirene Complexes

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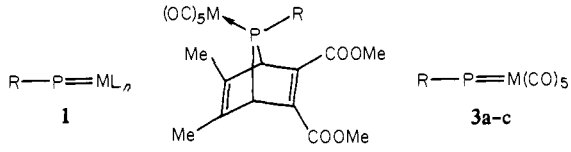
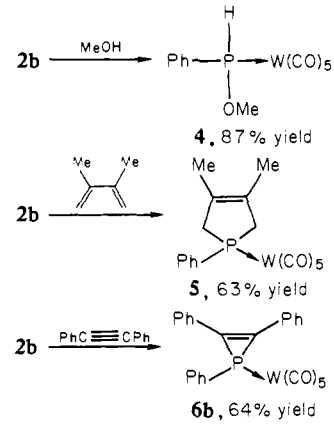
Phosphinidenes (RP) are known to act as μ^2-, μ^3-, and μ^4-bridging ligands in their transition-metal complexes.[1] No complex such as **1** including a terminal phosphinidene unit with a dic-



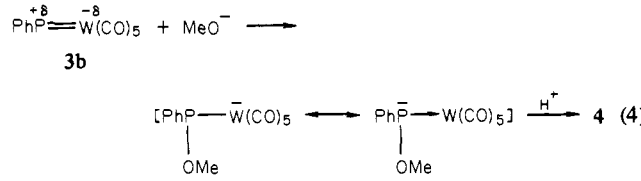
2a, M = Cr; R = Ph
b, M = W; R = Ph
c, M = W; R = Me

oordinated phosphorus atom and a formal phosphorus–metal double bond has ever been described in the literature up to now. We report here on the generation and trapping of such species.

In a previous communication,[2] we described the synthesis of stable 7-phosphanorbornadiene complexes **2**. We also found that **2b** was able to generate the terminal phosphinidene complex **3b** upon pyrolysis in a mass spectrometer. Besides, the X-ray crystal structure of **2a** showed long (1.877 (2) Å) and weak intracyclic P–C bonds. These data strongly suggested that complexes such as **2** were ideal candidates for the generation of terminal phosphinidene complexes under standard experimental conditions. Thus we decided to study the thermolysis of complexes **2a–c** in the presence of trapping reagents. The preliminary experiments were carried out with **2b**. When heated in toluene at 150 °C for 16–17 h with an excess of methanol, 2,3-dimethylbutadiene, or tolane, **2b** yielded respectively **4**,[3] **5**,[4] or **6b** in good yield (eq 1–3).

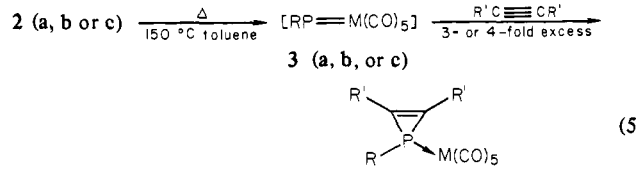


The intermediacy of the terminal phosphinidene complex **3b** is thus firmly established. In the first case, the logical mechanism implies a nucleophilic attack of MeO^- on the positively charged phosphorus[5] (eq 4).



The second reaction is just the reverse of the reaction generating **3b** itself and probably involves **3b** in its singlet state. The last reaction can be either a cheletropic reaction involving only phosphorus or a [2 + 2] cycloaddition giving transiently a four-membered carbon–phosphorus–tungsten ring.

Whatever the mechanism through which they are formed, the obtention of stable complexes such as **4** or **6b** is very exciting. Indeed, the corresponding free ligands are unknown. In the case of **4**, the free ligand probably loses spontaneously methanol to give the cyclopolyphosphine $(PhP)_n$. In the case of **6b**, the only literature report on a phosphirene oxide[6] was later shown to be wrong.[7] This type of ring is so extraordinary that we decided to perform a more systematic study of its synthesis. It appeared immediately that this synthesis was quite general (eq 5).



6a, M = Cr; R = R' = Ph; 15 h, 72%
b, M = W; R = R' = Ph; 17 h, 64%
c, M = W; R = Ph; R' = Et; 16 h, 50%
d, M = W; R = Me; R' = Ph; 17 h, 60%
e, M = W; R = Me; R' = Et; 5 h, 71%

(1) For the only well-characterized μ^2-phosphinidene complex, see: Huttner, G.; Muller, H. D.; Frank, A.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 705. For various recently described μ^3- and μ^4-phosphinidene complexes, see: Richter, F.; Beurich, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1979**, *166*, C5. Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Sartorelli, U. *Ibid.* **1981**, *204*, C10. Natarajan, K.; Zsolnai, L.; Huttner, G. *Ibid.* **1981**, *220*, 365. Natarajan, K.; Scheidsteger, O.; Huttner, G. *Ibid.* **1981**, *221*, 301. Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904. Natarajan, K.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1981**, *209*, 85.

(2) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 667.

(3) Complex **4** was purified by chromatography on a silica gel column under argon with hexane–toluene (90:10); mp 80 °C; ^{1}H NMR (C_6D_6) δ 2.76 (d, ^3J(H–P) = 12.5 Hz, 3 H, OMe), 7.15 (m, 5 H, Ph), 7.24 (d, ^1J(H–P) = 346 Hz, 1 H, P–H); ^{31}P NMR (toluene–methanol) δ +105.1 ppm; IR (Decalin) ν(CO) 2076 m, 1989 w, 1959 sh, 1950 vs cm^{-1}; IR (KBr) ν (PH) 2335, (POC) 1020 cm^{-1}; mass spectrum (70 eV, 100 °C, ^{184}W), *m/e* 464 (M, 30%), 436 (M–CO, 10%), 408 (M – 2CO, 14%), 380 (M – 3CO, 13%), 324 (M – 5CO, 100%) [*m/e* 28 (CO peak) excluded].

(4) Complex **5** was purified by chromatography on silica gel with hexane–toluene (90:10); mp 74 °C; ^{1}H NMR (C_6D_6) δ 1.25 (s, 6 H, Me), 2.67 (m, 4 H, CH_2P), 7.15 (m, 5 H, Ph); ^{31}P NMR (toluene) δ –3.2; IR (Decalin) ν(CO) 2070 m, 1976 w, 1945 sh, 1940 vs cm^{-1}; mass spectrum (70 eV, 100 °C, ^{184}W), *m/e* 514 (M, 40%), 486 (M – CO, 19%), 430 (M – 3CO, 75%), 402 (M – 4CO, 46%), 374 (M – 5CO, 100%) [CO peak excluded]; correct C, H, P elemental analysis.

(5) On the basis of the relative electronegativities of phosphorus and carbon and in view of the properties of methylenephosphines (see, for example: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731), it appears that the phosphinidene group is slightly more electropositive than the carbene group. Since in carbene–W(CO)$_5$ complexes the carbenic carbon bears a positive charge (see, for example: Casey, C. P.; Burkhardt, T. J.; Bunnel, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127), the same is very probably true for phosphorus in **3b** and in other similar complexes.

(6) Koos, E. W.; Vander Kooi, J. P.; Green, E. E.; Stille, J. K. *J. Chem. Soc., Chem. Commun.* **1972**, 1085.

(7) Quast, H.; Heuschmann, M. *J. Chem. Soc., Chem. Commun.* **1979**, 390.

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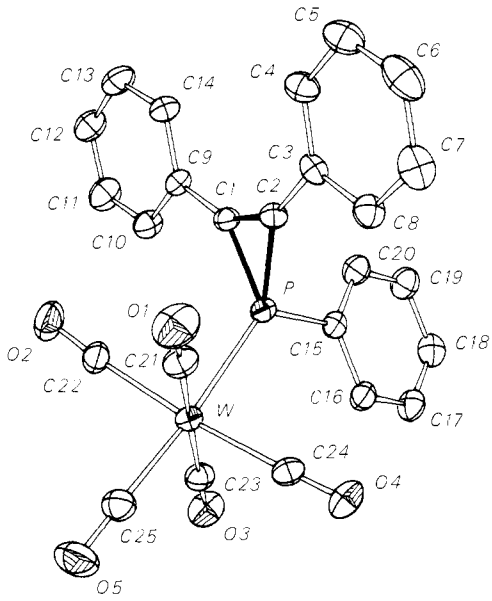
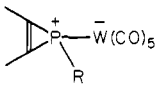


Figure 1. Structure of complex **1**. Ellipsoids are scaled to enclose 30% of the electronic density; hydrogen atoms are omitted. Principal bond distances (Å): C1–C2, 1.307 (6); P–C1, 1.790 (4); P–C2, 1.787 (4); P–C15, 1.831 (4); P–W, 2.496 (1); C1–C9, 1.453 (6); C2–C3, 1.474 (6). Selected bond angles (deg): C1–P–C2, 42.8 (2); C1–P–C15, 106.6 (2); C2–P–C15, 108.6 (2); P–C1–C2, 68.4 (3); P–C2–C1, 68.7 (3); C1–P–W, 124.5 (1); C2–P–W, 124.6 (1); W–P–C15, 123.4 (1); C1–C2–C3, 150.0 (4); C2–C1–C9, 149.5 (4).

Even though the reaction conditions have not been fully optimized, it is very interesting to note that the reaction works better and faster with electron-rich (**6e**) than with electron-poor (**6d**) alkynes, confirming that terminal phosphinidene complexes are electrophilic. The various phosphirenes thus obtained[8] are characterized by a strong upfield shift of their ^{31}P resonances, which has been observed previously on numerous three-membered phosphorus rings including phosphiranes.[9] Otherwise, the ^{1}H NMR, ^{13}C NMR, and IR spectral data are surprisingly normal (see, for example, ref 10 for ^{13}C NMR data on classical $LM(CO)_5$ complexes).

This observation seemed to rule out a stabilization of the phosphirene ring by delocalization within a zwitterionic structure such as **7**.



7

To check this point and to find out, if possible, the origin of the extraordinary stability of these complexes (no decomposition at 150 °C in toluene for 15 h), we decided to perform an X-ray crystal structure analysis of **6b**, which gave the following crystal data: $WPO_5C_{25}H_{15}$, mol wt 610.2; triclinic;[11] a = 12.276 (4) Å, b = 12.347 (4) Å, c = 7.911 (3) Å, α = 95.38 (2)°, β = 95.96 (2)°, γ = 88.51 (2)° U = 1187 Å^3, d_{obsd} = 1.68 ± 0.02 g cm^{-3}, d_{calcd} = 1.70 g cm^{-3}, Z = 2, space group $P\bar{1}$ (No. 2); Cu Kα (1.5418 Å) radiation for cell dimensions and intensity measurements; μ = 100.4 cm^{-1}, F_{000} = 588.

Diffraction data were collected in the $\theta/2\theta$ flying step-scan mode by using a Philips PW1100/16 automatic diffractometer, graphite-monochromated Cu K$\bar{\alpha}$ radiation and a spherical crystal of mean diameter 0.021 cm. The structure was solved by the heavy-atom method using the Enraf-Nonius SDP/V18[12] package on a PDP 11/60 computer. Full-matrix refinement using 3011 reflexions having $I > 3\sigma(I)$ converged to conventional agreement factors R_1 and R_2 of 0.025 and 0.044. Hydrogen atoms were introduced by their computed coordinates but not refined.

The structure (Figure 1)[13] consists of discrete molecules linked only by van der Waals contacts and hydrogen bonds. Selected geometrical details are given in the caption of Figure 1.

The most interesting features of this structure are related to the geometry of the P–C1–C2 triangle. The C1–P–C2 bond angle of 42.8 (2)° is the smallest C–P–C angle yet known.[14] The P–C intracyclic bond lengths of 1.788 (3) Å in mean compared to the P–C15 bond of 1.831 (6) Å are surprisingly long. This observation together with a very localized C1–C2 bond (1.307 (6) Å) indicates that electron density over the ring is indeed poorly delocalized. The structural features of the P → $W(CO)_5$ subunit being quite normal, we are tempted to admit that the stabilization of the phosphirene ring is merely due to the classical electron-withdrawing ability and bulkiness of the $W(CO)_5$ group.

Registry No. 2a, 82265-63-2; **2b**, 82265-64-3; **2c**, 82265-65-4; **4**, 82265-66-5; **5**, 82281-49-0; **6a**, 82265-67-6; **6b**, 82265-68-7; **6c**, 82265-69-8; **6d**, 82265-70-1; **6e**, 82281-50-3; PhC≡CPh, 501-65-5; EtC≡CEt, 928-49-4; MeOH, 67-56-1; 2,3-dimethyl-1,3-butadiene, 513-81-5.

Supplementary Material Available: Table I listing the atomic coordinates and $\beta(i,j)$ and Table II listing the observed and calculated structure factors (times 10) for all observed reflexions (15 pages). Ordering information is given on any current masthead page.

(8) The phosphirene complexes were purified by chromatography on silica gel with hexane (**6b** and **6e**) or hexane–toluene (90:10) (**6a**, **6c** and **6d**). **6a**: mp 115 °C; ^{31}P NMR (toluene) −111.5; IR (Decalin) ν(CO) 2065 w, 1950 vs. cm^{-1}. **6b**: mp 115 °C; ^{31}P NMR (toluene) δ −161.4; IR (Decalin) ν(CO) 2072 w, 1945 vs cm^{-1}; ^{13}C NMR (C_6D_6) δ 196.87 (dd, ^{2}J(C-P) = 8.5 Hz, $^{1}J(^{13}C-^{183}W)$ = 125.7 Hz, *cis*-CO), 198.32 (d, ^{2}J(C–P) = 30.5 Hz, *trans*-CO); mass spectrum (70 eV, 170 °C, ^{184}W), m/e 610 (M, 33%), 554 (M − 2CO, 13%), 526 (M − 3CO, 9%), 498 (M − 4CO, 33%), 470 (M − 5CO, 100%), 178 (C_2Ph_2, 95%); correct C, H, P elemental analysis. **6c**: ^{31}P NMR (toluene) δ −162.1 ($^{1}J(^{31}P-^{183}W)$ = 266 Hz); IR (Decalin) ν(CO) 2070 w, 1942 vs. cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.96 (t, ^{3}J(H–H) = 7.1 Hz, 6 H, Me), 2.34 (dq, ^{3}J(H–P) = 8 Hz, 4 H, CH_2), 7.0–7.5 (m, 5 H, Ph); ^{13}C NMR (C_6D_6) δ 12.23 (d, ^{3}J(C–P) = 5 Hz, Me), 19.66 (d, ^{2}J(C–P) = 6.1 Hz, CH_2), 197.0 (dd, ^{2}J(C–P) 8.5 Hz, $^{1}J(^{13}C-^{183}W)$ = 124.5 Hz, *cis*-CO), 198.6 (d, ^{2}J(C–P) = 29.3 Hz, *trans*-CO); mass spectrum (70 eV, 100 °C, ^{184}W), m/e 514 (M, 76%), 458 (M = 2CO, 15%), 430 (M − 3CO, 30%), 402 (M − 4CO, 93%), 374 (M − 5CO, 87%), 372 (100%), 348 ($PhPW(CO)_2$, 63%), 320 (PhPW(CO), 50%), 292 (PhPW, 80%) [$m/e \geq 250$]. **6d**: mp 121 °C; ^{31}P NMR (toluene) δ −169.5 ($^{1}J(^{31}P-^{183}W)$ = 259 Hz); IR (Decalin) ν(CO) 2070 w, 1948 s, 1942 vs cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.20 (d, ^{2}J(H–P) = 5.6 Hz, 3 H, Me), 7.16 (m, 6 H, *m*-, *p*-Ph), 7.66 (m, 4 H, *o*-Ph); ^{13}C NMR (C_6D_6) δ 23.62 (d, ^{1}J(C–P) = 2.4 Hz, MeP), 196.62 (d, ^{2}J(C–P) = 8.5 Hz, *cis*-CO), 198.47 (d, ^{2}J(C–P) = 29.3 Hz, *trans*-CO). **6e**: ^{31}P NMR (hexane) δ −168 ($^{1}J(^{31}P-^{183}W)$ = 264 Hz; IR (Decalin) ν(CO) 2069 w, 1940 vs cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.94 (t, ^{3}J(H–H) = 7.5 Hz, 6 H, CH_3CH_2), 1.01 (d, ^{2}J(H–P) = 5.8 Hz, 3 H, Me–P), 2.25 (dq, ^{3}J(H–P) = 8.5 Hz, 4 H, CH_3CH_2); ^{13}C NMR (C_6D_6) δ 12.66 (d, ^{3}J(C–P) = 4.9 Hz, CH_3CH_2), 20.32 (d, ^{2}J(C–P) = 6.1 Hz, CH_3CH_2), 25.38 (d, ^{1}J(C–P) 4.9 Hz, Me–P), 135.25 (d, ^{1}J(C–P) 13.4 Hz, C_2P ring), 197.62(dd, ^{2}J(C–P) = 9.8 Hz, $^{1}J(^{13}C-^{183}W)$ = 125.7 Hz, *cis*-CO), 199.78 (d, ^{2}J(C–P) = 28 Hz, *trans*-CO).

(9) Chan, S.; Goldwhite, H.; Keyzer, H.; Rowsell, D. G.; Tang, R. *Tetrahedron* **1969**, *25*, 1097.

(10) Braterman, P. S.; Milne, D. W.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* **1973**, 1027.

(11) The lattice of $WPO_5C_{25}H_{15}$ is effectively pseudosymmetric. Before the data were collected, the following checks were performed: (a) a photographic search for symmetry elements using a precession camera; (b) comparison of pseudoequivalent intensities on the diffractometer with the sphere used later in data collection (to avoid the influence of different absorption factors); (c) refinement of the unit cell parameters using 25 carefully selected reflections, three in each octant plus the 6$\bar{6}$4; the θ values range from 36.14 to 42.03° for these 25 reflections; (d) using program TRACER II and the refined unit cell parameters, we searched for the value of Δ needed to change from triclinic to monoclinic. This change occurs for $\Delta > 5$. Usually, with the same method, a higher symmetry is detected if $\Delta \simeq 0.4$. The results of all tests show unambiguously that the unit cell is pseudosymmetric but remains triclinic. Furthermore, no special problem arose during refinement, and no correlations greater than 0.4 were observed in the inverted least-squares matrix. Hence, the crystal system is undeniably triclinic.

(12) Frenz, B. A. "The Enraf-Nonius CAD4-SDP. Computing in Crystallography"; Schenk, H., Othof-Hazekamp, R., Van Koningsved, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; p 64.

(13) Drawing performed by using program ORTEP: Johnson, C. K., Report ORNL 3794, Oak Ridge, TN, 1965.

(14) An intracyclic CPC angle of 47.4° has been measured by microwaves on a phosphirane: Bowers, M. T.; Beaudet, R. A.; Goldwhite, H.; Tang, R. *J. Am. Chem. Soc.* **1969**, *91*, 17.