Reaction of Terminal Phosphinidene Complexes [RP−W(CO)$_5$] with (2-Oxopropylidene)triphenylphosphorane. Synthesis and X-ray Crystal Structure Analysis of 1,2,5-Oxadiphospholene Complexes

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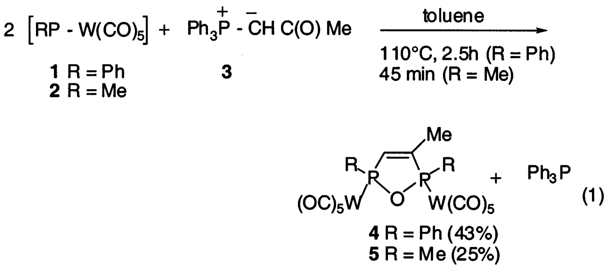
Summary: The reaction of transient terminal phosphinidene complexes [RP−W(CO)$_5$] (R = Ph, Me) with (2-oxopropylidene)triphenylphosphorane in refluxing toluene yields the corresponding five-membered cyclic 1,2,5-oxadiphospholene complexes. An initial reaction at the carbonyl group is postulated. The X-ray crystal structure analysis of the phenyl derivative shows a planar ring with trans phenyl groups.

An extensive chemistry has already been developed with the transient terminal phosphinidene complexes [RP−M(CO)$_5$] (M = Cr, Mo, W).[1] These electrophilic species are known to react, inter alia, with carbonyl derivatives[2,3] and stabilized phosphorus ylides.[4] In both cases, the initial reaction takes place at the nucleophilic center: i.e., the carbonyl oxygen in the first case and the ylidic carbon in the second. We wondered what would be the outcome of the reaction if these two types of nucleophilic centers were present in the same reagent. Thus, we decided to examine the reactivity of [RP−W(CO)$_5$] (**1**, R = Ph; **2**, R = Me) with the carbonyl-substituted ylide **3**. The transient phosphinidene complexes **1** and **2** were generated as usual from the appropriate 7-phosphanorbornadiene complexes.[5] The outcome of the reaction was completely unexpected (eq 1).



(1)

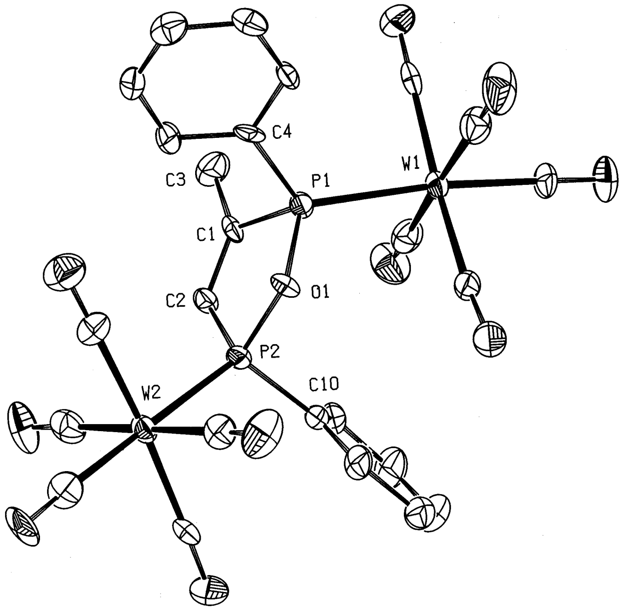


Figure 1. Crystal structure of **4**. Significant bond distances (Å) and angles (deg): P(1)−O(1) = 1.660(8), P(1)−C(1) = 1.83(1), P(1)−C(4) = 1.82(1), P(1)−W(1) = 2.489(3), P(2)−O(1) = 1.650(8), P(2)−C(2) = 1.78(1), P(2)−C(10) = 1.82(1), P(2)−W(2) = 2.464(3), C(1)−C(2) = 1.32(1), C(1)−C(3) = 1.54(2); O(1)−P(1)−C(1) = 94.2(5), O(1)−P(1)−C(4) = 101.8(5), C(4)−P(1)−C(1) = 102.8(5), O(1)−P(1)−W(1) = 115.9(3), C(4)−P(1)−W(1) = 122.5(4), C(1)−P(1)−W(1) = 115.1(3), O(1)−P(2)−C(2) = 95.4(5), O(1)−P(2)−C(10) = 102.7(5), C(2)−P(2)−C(10) = 104.8(5), O(1)−P(2)−W(2) = 117.3(3), C(2)−P(2)−W(2) = 119.0(4), C(10)−P(2)−W(2) = 114.8(4), C(2)−C(1)−P(1) = 114(1), C(1)−C(2)−P(2) = 116(1), C(2)−C(1)−C(3) = 126(1), P(2)−O(1)−P(1) = 118.7(5).

In both cases, the only isolated products were the presently unknown[6] 1,2,5-oxadiphospholene complexes **4** and **5**.[7] The triphenylphosphine byproduct was identified by its ^{31}P resonance in the crude reaction mixture. The structure of **4** was unambiguously established by X-ray analysis[8] (Figure 1). The two phenyl groups and the two tungsten atoms adopt a trans disposition. The five-membered ring is practically planar (sum of extracyclic supplementary angles 361.7°).

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[1] Recent reviews: Mathey, F.; Tran Huy, N. H.; Marinetti, A. *Helv. Chim. Acta* **2000**, *84*, 2938. Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, 1127.

[2] Inubushi, Y.; Tran Huy, N. H.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1996**, 1903. Inubushi, Y.; Tran Huy, N. H.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **1997**, *533*, 83.

[3] Streubel, R.; Ostrowski, A.; Wilkens, H.; Ruthe, F.; Jeske, J.; Jones, P. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 378.

[4] Hoffmann, N.; Wismach, C.; Jones, P. G.; Streubel, R.; Tran Huy, N. H.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **2002**, 454. Tran Huy, N. H.; Compain, C.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **2002**, *650*, 57.

[5] Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982,** 667.

[6] For a very recent review on heterophospholes: Schmidpeter, A. In *Phosphorus−Carbon Heterocyclic Chemistry*: *The Rise of a New Domain*; Mathey, F., Ed.; Elsevier: Amsterdam, 2001; p 363.

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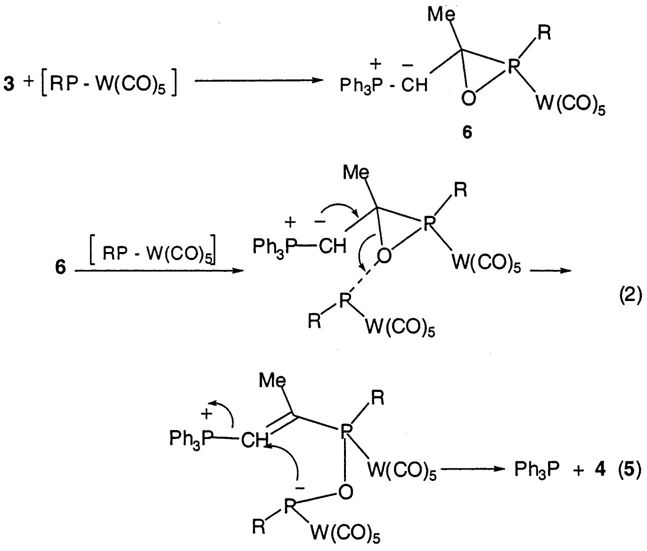
The most logical mechanism for the formation of **4** and **5** is as follows. The first step involves the formation of the oxaphosphirane **6** by reaction of a phosphinidene complex with the carbonyl group of **3** in a reaction which has analogies in the work of Streubel et al.[3] The second step then involves the nucleophilic attack of the oxaphosphirane oxygen on a second molecule of phosphinidene, followed by cyclization with elimination of Ph_3P (eq 2).



The chemistry of this new ring is currently under investigation.

Supporting Information Available: Tables giving X-ray crystallographic data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) **4**: purified by chromatography on silica gel with 5:1 hexane$-CH_2Cl_2$; ^{31}P NMR ($CDCl_3$) δ 147.7 and 156.8, $\sum J_{PP} = 44.6$ Hz; ^1H NMR ($CDCl_3$) δ 2.20 (d, $^3J_{HP} = 11.8$ Hz, Me), 6.8 (dd, $J_{HP} = 32.5$ and 43.6 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 16.51 (dd, $J_{CP} = 13.9$ and 19.2 Hz, Me), 134.32 (dd, $J_{CP} = 12.5$ and 35.0 Hz, HC=), 155.88 (dd, $J_{CP} = 5.8$ and 25.0 Hz, Me *C*−P), 195.45 and 195.67 (2d, $J_{CP} = 7.7$ and 7.5 Hz, cis-CO), 198.24 and 199.01 (2d, $J_{CP} = 27.8$ and 27.3 Hz, trans-CO); EIMS (^{184}W) *m/z* 922 ($M^+ + 2H$, 47%), 698 (922 − 8CO, 100%), 642 (922 − 10CO, 78%). Anal. Calcd for $C_{25}H_{14}O_{11}P_2W_2$: C, 32.64; H, 1.53. Found: C, 32.71; H, 1.51. **5**: ^{31}P NMR ($CDCl_3$) δ 148.5 and 151.5, $\sum J_{PP} = 43.7$ Hz; ^1H NMR ($CDCl_3$) δ 2.04 and 2.06 (2d, $^3J_{HP} = 7.3$ and 7.4 Hz, Me−P), 2.16 (dm, $J_{HP} = 12.0$ Hz, Me−C), 6.57 (dd, $J_{HP} = 32.6$ and 45.1 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 15.55 (dd, $J_{CP} = 14.0$ and 20.1 Hz, *Me*−C), 28.07 (d, $J_{CP} = 19.4$ Hz, MeP), 29.80 (d, $J_{CP} = 20.4$ Hz, Me−P), 136.60 (dd, $J_{CP} = 12.5$ and 32.7 Hz, HC=), 154.58 (dd, $J_{CP} = 5.7$ and 24.8 Hz, Me *C*−P), 195.69 and 195.72 (2d, $J_{CP} = 7.6$ and 7.7 Hz, cis-CO), 198.76 and 199.19 (2d, $J_{CP} = 26.4$ and 26.3 Hz, trans-CO); EIMS (^{184}W) *m/z* 798 ($M^+ + 2H$, 70%), 600 (798 − 7CO, 100%).

(8) Crystallographic data for **4**, $C_{25}H_{14}O_{11}P_2W_2$: $M_r = 920.00$; monoclinic; space group $P2_1$; $a = 10.119(5)$ Å, $b = 27.659(5)$ Å, $c = 10.430(5)$ Å, $\beta = 105.960(5)^\circ$, $V = 2807(2)$ Å^3; $Z = 4$; $D = 2.177$ g cm^{-3} ; $\mu = 8.362$ cm^{-1}; $F(000) = 1720$; crystal dimensions 0.20 × 0.20 × 0.14 mm; 12 861 total reflections collected; 12 033 reflections with $I > 2\sigma(I)$; goodness of fit on F^2 0.990; $R(I > 2\sigma(I)) = 0.0478$, wR2 = 0.1284 (all data); maximum/minimum residual density 0.926(0.140)/−0.888(0.140) e Å^{-3}, refined as racemic twin; BASF = 0.298. Data were collected on a KappaCCD diffractometer at 150.0(10) K with Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Full details of the crystallographic analysis are described in the Supporting Information.