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The [3,3]-Phospha-Cope Rearrangement of 1,2-Divinylphosphirane Complexes

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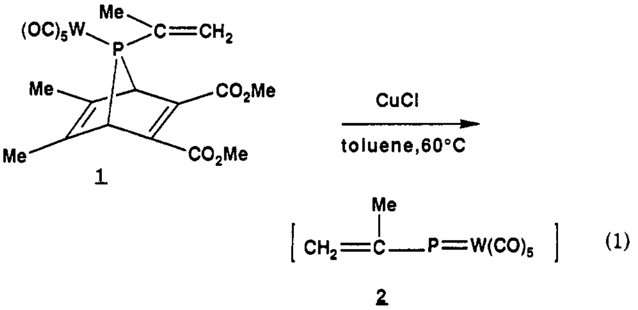
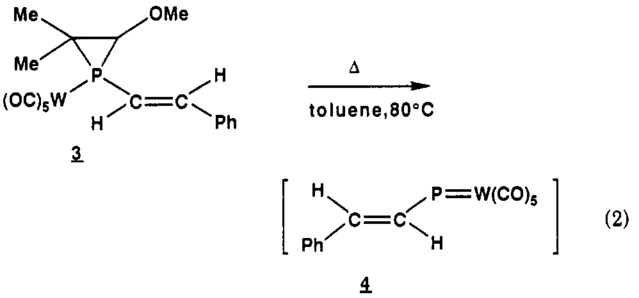
Summary: The reaction of transient terminal vinylphosphinidene complexes with conjugated dienes leads to 3,4,7-trihydrophosphepine complexes via the [3,3]-phospha-Cope rearrangement of intermediate 1,2-divinylphosphirane complexes. The P=C double bond of the seven-membered ring reacts further with another molecule of diene to give the corresponding [2 + 4] cycloadduct.

We have recently described the syntheses of two efficient precursors of transient terminal vinylphosphinidene complexes[1,2] (eqs 1 and 2) and we wish to report now on the trapping of **2** and **4** by conjugated dienes leading to seven-membered rings via an unexpected [3,3]-phospha-Cope rearrangement.

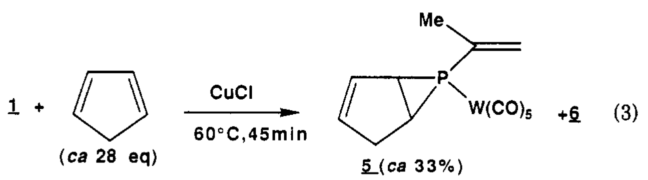


(1)



(2)

Heating **1** with a large excess of cyclopentadiene for a short time led to the expected phosphirane complex **5** (eq 3).[3,4] Complex **5** was accompanied by another product, **6**, whose presence increased with time. After 7 h, all of the phosphirane **5** was converted into **6**.[5] According to mass spectroscopic analysis, complex **6** results from the addition of one molecule of cyclopentadiene onto **5**. A [4 + 2] cycloaddition with one of the C=C double bonds of **5** was ruled out on the basis of the ^{31}P NMR data (no upfield shift corresponding to a three-membered ring). Complex **6** was subjected to an X-ray crystal structure analysis.[6] The presence of a seven-membered ring was



(3)

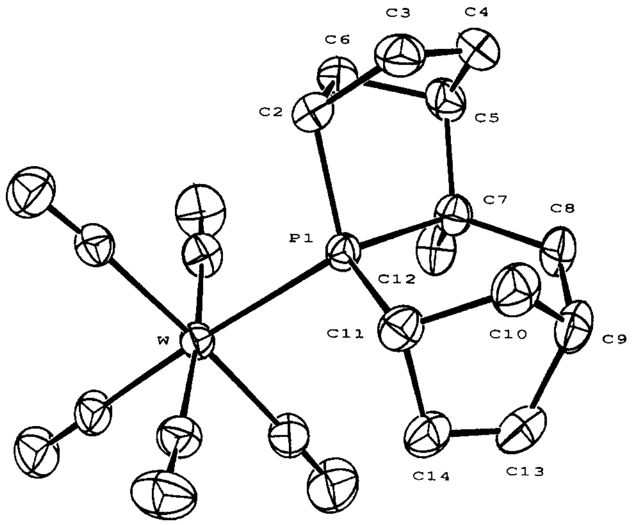


Figure 1. ORTEP drawing of one molecule of **6**. Thermal ellipsoids are grown at the 50% probability level. Hydrogen atoms are omitted for clarity. Principal bond distances (Å): W-P_1, 2.562 (1); P_1-C_2, 1.875 (4); P_1-C_7, 1.919 (5); P_1-C_{11}, 1.859 (4); C_2-C_3, 1.510 (7); C_2-C_6, 1.538 (7); C_3-C_4, 1.328 (8); C_4-C_5, 1.522 (7); C_5-C_6, 1.529 (6); C_5-C_7, 1.567 (5); C_7-C_8, 1.562 (6); C_7-C_{12}, 1.531 (6); C_8-C_9, 1.539 (7); C_9-C_{10}, 1.521 (7); C_9-C_{13}, 1.501 (7); C_{10}-C_{11}, 1.524 (7); C_{11}-C_{14}, 1.515 (6); C_{13}-C_{14}, 1.322 (7). Selected bond angles (deg): W-P_1-C_2, 111.6 (1); W-P_1-C_7, 123.4 (1); W-P_1-C_{11}, 111.7 (1); C_2-P_1-C_7, 91.3 (2); C_2-P_1-C_{11}, 113.2 (2); C_7-P_1-C_{11}, 104.0 (2).

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[1] Tran Huy, N. H.; Ricard, L.; Mathey, F. *Organometallics* **1991**, *10*, 3958.

[2] Marinetti, A.; Ricard, L.; Mathey, F. *Synthesis*, in press.

[3] Complex **5** was purified by chromatography on silica gel (70–230 mesh) with pentane as the eluent. ^{31}P NMR ($CDCl_3$): δ −139.3, $^1J(^{31}P-^{183}W)$ = 262 Hz. ^{13}C NMR ($CDCl_3$): δ 21.63 (d, ^2J(C–P) = 12.7 Hz, Me), 25.87 (d, ^1J(C–P) = 13.5 Hz, CH–P), 35.96 (s, CH_2), 36.51 (d, ^1J(C–P) = 13.7 Hz, CH–P), 126.14 (d, ^2J(C-P) = 11.2 Hz, $=CH_2$), 129.68 (s, =CH), 134.67 (d, J(C–P) = 10.1 Hz, =CH), 142.24 (d, ^1J(C–P) = 18.2 Hz, Me*C*=), 195.71 (d, ^2J(C–P) = 7.8 Hz, cis CO), 197.30 (d, ^2J(C–P) = 30.5 Hz, trans CO). Mass spectrum (^{184}W): *m/z* 462 (M^+), 396 ($M^+ - C_5H_6$), 368 (396 − CO), 340 (396 − 2CO), 322 (M^+ − 5CO).

[4] Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

[5] The reaction of **1** (600 mg) with cyclopentadiene (3 mL) in the presence of CuCl (40 mg) at 60 °C for 7 h in a sealed tube yielded 400 mg of **6** (78%) after purification by chromatography on silica gel with pentane/CH_2Cl_2 (9/1) as the eluent. **6**: ^{31}P NMR (CH_2Cl_2) δ +9.1, $^1J(^{31}P-^{183}W)$ = 236.4 Hz; ^{13}C NMR ($CDCl_3$) δ 31.58 (d, J(C–P) = 4.1 Hz, CH_2), 37.14 (d, ^1J(C–P) = 10.7 Hz, CH–P), 38.07 (s, CH_3), 39.15 (d, ^1J(C–P) = 23.4 Hz, *C*–P), 40.24 (s, CH_2), 42.65 (d, ^1J(C–P) = 9.7 Hz, CH–P), 44.48 (d, J(C–P) = 17.4 Hz, CH_2), 51.53 (d, J(C–P) = 4.3 Hz, CH), 57.95 (s, CH), 135.69 (d, J(C–P) = 10.1 Hz, =CH), 137.91 (s, =CH), 139.08 (d, J(C–P) = 15 Hz, =CH), 139.16 (s, =CH), 198.33 (d, ^2J(C–P) = 6.5 Hz, cis CO); mass spectrum (^{184}W) *m/z* 528 (M^+, 40%), 388 (M^+ – 5CO, 60%), 320 (100%). Anal. Calcd for $C_{18}H_{17}O_5PW$: C, 40.93; H, 3.24. Found: C, 40.91; H, 3.16.

[6] X-ray structure determination for **6**: Crystals of **6** ($C_{18}H_{17}O_5PW$) were grown at −18 °C from a dichloromethane solution of the compound. Data were collected at −100 ± 0.5 °C on an Enraf-Nonius CAD4 diffractometer. The crystal structure was solved and refined using the supplied Enraf-Nonius SDP package. The compound crystallizes in space group $P2_1/c$, with a = 14.653 (1) Å, b = 9.174 (1) Å, c = 13.675 (1) Å, β = 107.50 (1)°, V = 1753.12 (53) Å^3, Z = 4, d_{calc} = 2.001 g/cm^3, Mo Kα radiation (λ = 0.71073 Å), graphite monochromator), μ = 68.4 cm^{-1}, and $F(000)$ = 1016. A total of 5086 unique reflections were recorded in the range $2° \le 2\theta \le 60.0°$, of which 1087 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 3999 for solution and refinement. The structure was solved by Patterson methods, yielding a solution for the tungsten atom. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement, while anisotropic temperature factors were used for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.07. The final agreement factors were R = 0.031, R_w = 0.042, and GOF = 1.05.

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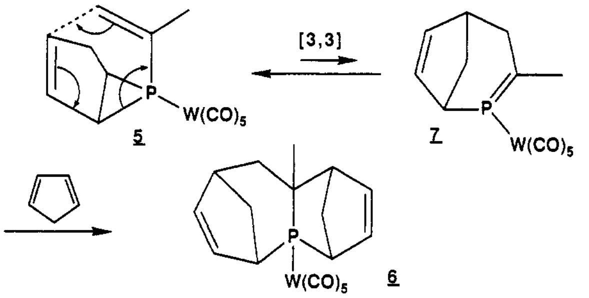
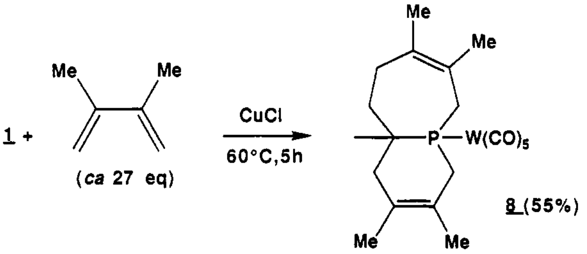
thus established (Figure 1). The only logical explanation includes a [3,3]-phospha-Cope equilibrium[7] partly driven to the right by the release of the strain of the three-membered ring of **5** (eq 4).

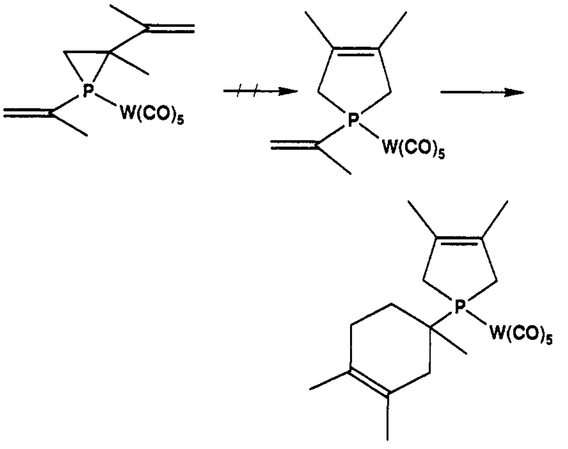


(4)

When **5** is heated alone, it is impossible to detect this equilibrium. In the presence of an excess of cyclopentadiene, however, the intermediate phosphaalkene complex **7** is instantaneously trapped as a [2 + 4] cycloadduct via its P=C double bond and the equilibrium is completely shifted to the right. This reaction is quite general. Thus, **1** reacts with 2,3-dimethylbutadiene to yield a similar product, **8**[8] (eq 5). In that case, an alternative formulation was possible on the basis of a 2-vinylphosphirane → 2,5-dihydrophosphole rearrangement[4,9] (eq 6). However, this formulation was ruled out since the ^{13}C NMR spectrum of **8** shows 5 CH_3, 5 CH_2, and 4 sp^2 C as inequivalent groups. Besides, the 1-propenyl C=C double bond is very probably unreactive toward dimethylbutadiene at 60 °C.

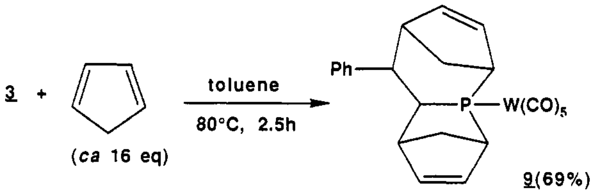


(5)



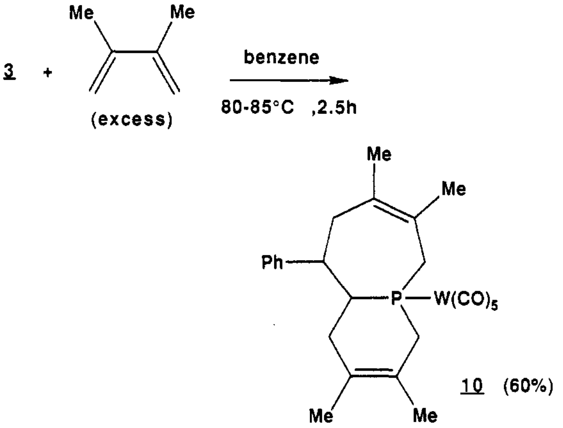
(6)

A similar chemistry was observed with **4**. Thus, the reaction of the precursor **3** with cyclopentadiene leads to the phospha-Cope product **9**[10] (eq 7).



(7)

The precursor **3** also reacts with 2,3-dimethylbutadiene to give complex **10**,[11] analogous to **8** (eq 8).



(8)

This easy route to seven-membered rings containing phosphorus is an interesting addition to the few methods allowing the synthesis of such compounds.[12]

Registry No. 1, 137202-53-0; 2, 139524-28-0; 3, 139524-29-1; 4, 139524-30-4; 5, 139524-30-4; 6, 139524-32-6; 7, 139524-33-7; 8, 139524-34-8; 9, 139524-35-9; 10, 139524-36-0; 1,3-cyclopentadiene, 542-92-7; 2,3-dimethyl-1,3-butadiene, 513-81-5.

Supplementary Material Available: Listings of experimental details for the X-ray study, positional parameters, thermal parameters, and bond distances and angles for 6 (5 pages); a table of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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(7) Appel, R.; Kochta, J.; Winkhaus, V. *Chem. Ber.* **1988**, *121*, 631.

(8) The reaction of 1 (400 mg) with dimethylbutadiene (2 mL) in the presence of CuCl (40 mg) at 60 °C for 5 h in a sealed tube yielded 200 mg of 8 (55%) after purification by chromatography with hexane/CH_2Cl_2 (4/1) as the eluent. 8: ^{31}P NMR ($CDCl_3$) δ -14.4, $^1J(^{31}P-^{183}W)$ = 234.4 Hz; ^{13}C NMR ($CDCl_3$) δ 20.40 (s, CH_3), 21.13 (s, CH_3), 21.54 (d, J(C-P) = 9.0 Hz, CH_3), 22.29 (s, CH_3), 24.66 (d, J(C-P) = 8.7 Hz, CH_3), 30.37 (s, CH_2), 30.39 (d, ^1J(C-P) = 25.5 Hz, CH_2), 32.77 (s, CH_2), 34.10 (d, ^1J(C-P) = 20.2 Hz, CH_2), 35.88 (d, ^1J(C-P) = 17.8 Hz, sp^3 C), 48.18 (s, CH_2), 119.63 (s, sp^2 C), 125.36 (d, J(C-P) = 10.5 Hz, sp^2 C), 125.94 (d, J(C-P) = 9.9 Hz, sp^2 C), 134.84 (d, J(C-P) = 6.1 Hz, sp^2 C), 197.70 (d, ^2J(C-P) = 6.8 Hz, cis CO); mass spectrum (^{184}W) m/z 560 (M^+), 476 (M^+ - 3CO), 420 (M^+ - 5CO), 338 (M^+ - 5CO - C_6H_{10}, base peak).

(9) Richter, W. J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 292; *Chem. Ber.* **1983**, *116*, 3293; **1985**, *118*, 1575.

(10) The reaction of 3 (400 mg) with cyclopentadiene (1 mL) in toluene (2 mL) at 80 °C for 2.5 h yielded 300 mg of 9 (69%) after purification by chromatography on silica gel with hexane as the eluent. 9: ^{31}P NMR (hexane) δ -19.6, $^1J(^{31}P-^{183}W)$ = 238.2 Hz; ^{13}C NMR (C_6D_6) δ 33.32 (d, J(C-P) = 4.0 Hz, CH_2), 39.69 (d, ^1J(C-P) = 10.6 Hz, CH-P), 44.50 (d, ^1J(C-P) = 23.7 Hz, CH-P), 44.60 (s, CH), 45.76 (d, J(C-P) = 16.6 Hz, CH_2), 49.12 (s, CH), 49.38 (s, CH), 49.82 (d, J(C-P) = 4.5 Hz, CH), 135.91 (d, J(C-P) = 10.6 Hz, =CH), 137.08 (d, J(C-P) = 7.5 Hz, =CH), 137.64 (d, J(C-P) = 12.6 Hz, =CH), 140.82 (s, =CH), 198.61 (d, ^2J(C-P) = 7 Hz, cis CO), 199.42 (d, ^2J(C-P) = 22.6 Hz, trans CO); mass spectrum (^{184}W) m/z 590 (M^+, 42%), 450 (M^+ - 5CO, 38%), 440 (M^+ - 3CO - Cp, 68%), 384 (M^+ - 5CO - Cp, 89%), 382 (100%). Anal. Calcd for $C_{23}H_{19}O_5PW$: C, 46.80; H, 3.24. Found: C, 46.61; H, 3.28.

(11) The reaction of 3 (300 mg) with dimethylbutadiene (0.5 mL) in benzene (2 mL) at 80 °C for 2.5 h yielded 200 mg of 10 (60%) after chromatography with hexane. 10: ^{31}P NMR (hexane) δ -22.7, $^1J(^{31}P-^{183}W)$ = 239.2 Hz; ^{13}C NMR (C_6D_6): δ 19.95 (s, CH_3), 20.46 (s, CH_3), 21.66 (d, J(C-P) = 7.4 Hz, CH_3), 22.14 (s, CH_3), 28.37-44.23 (CH_2 + CH), 120.89 (s, sp^2 C), 124.78 (d, J(C-P) = 10.6 Hz, sp^2 C), 126.16 (d, J(C-P) = 11.1 Hz, sp^2 C), 133.72 (d, J(C-P) = 6 Hz, sp^2 C), 147.03 (d, ^3J(C-P) = 7 Hz, (Ph)C), 197.87 (d, ^2J(C-P) = 7 Hz, cis CO) (these data are very similar to those of 8); mass spectrum (^{184}W) m/z 622 (M^+, 25%), 541-539 (M^+ - C_6H_{10}, 100%), 400 (M^+ - 5CO - C_6H_{10}, 83%). Anal. Calcd for $C_{25}H_{27}O_5PW$: C, 48.25; H, 4.37. Found: C, 48.91; H, 4.33.

(12) Quin, L. D. *The Heterocyclic Chemistry of Phosphorus*; Wiley: New York, 1981; pp 181-195. Quin, L. D.; Hughes, A. N. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Chichester, U.K., 1990; pp 295-384.