Unexpected Rearrangement of 4-Chloro-2-butenylphosphinidene to 1-Chloro-2-vinylphosphirane in the Coordination Sphere of Tungsten

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The complex (4-chloro-2-butenylphosphinidene)pentacarbonyltungsten, as generated from the appropriate 7-phosphanorbornadiene complex at 58 °C in the presence of copper(I) chloride as a catalyst, readily rearranges to give the stable 1-chloro-2-vinylphosphirane complex. According to DFT calculations on similar $Cr(CO)_5$ complexes, a concerted six-electron (σ C−Cl bond, P lone pair, and π C=C double bond), five-center mechanism could be involved with a low energy barrier of 4.8 kcal mol^{-1} in the chromium series.

Introduction

Reactions driven by the halophilicity of phosphorus are among the most interesting reactions of electrophilic terminal phosphinidene complexes.[1] The first reported example of this type of reactivity was provided by the CuCl-catalyzed rearrangement of chloromethylphosphinidene to methylenechlorophosphine in the coordination sphere of tungsten.[2] Very recently, Streubel and co-workers described additional examples with tetrachloromethane[3] and benzyl bromide.[3] The initial Lewis acid−base complex [R′X→P(M)R] evolves to yield the insertion products R′−PX(M)R. In a previous work, we described the generation and reactivity of the bis-phosphinidene complex *cis*-[$(OC)_5W-PCH_2CH=CHCH_2P-W(CO)_5$].[4] As a logical extension of this initial investigation, we decided to study the generation of the corresponding mono-phosphinidene complex *cis*-[$(OC)_5W-PCH_2CH=CHCH_2Cl$]. This led us to the serendipitous discovery of an original rearrangement driven by the halophilicity of the phosphinidene phosphorus, which is the subject of this report.

Results and Discussion

The necessary phosphole precursor was synthesized as shown in Scheme 1. The condensation of the phospholide η^1 complex **1a**[5] with the dichloroalkene yielded the desired phosphole complex **2** in fair yield, together with a minor amount of the already described bis-condensation product **3**.[4] However, unexpectedly, two other minor products, **4** and **5**, were formed with ^{31}P resonances at −1.4 and −30.9 ppm, respectively ($CDCl_3$). These two isomeric products were separated by crystallization. Their mass spectrum shows the absence of chlorine (molecular peak at 488). Complex **5** was completely characterized by X-ray crystal structure analysis (Figure 1). The formula of the other isomer **4** was established by comparing its ^1H and ^{13}C NMR spectra with those of **5**. The ^{13}C spectrum is particularly informative. It displays one CH_3 resonance at 16.50 ppm (J_{C-P} = 10.5 Hz), two sp^3 CH_2 resonances at 29.69 ppm (J_{C-P} = 17 Hz) and 29.75 (J_{C-P} = 5.6 Hz), one sp^3 CH resonance at 43.18 ppm (J_{C-P} = 35.6 Hz), one sp^2 CH_2 resonance at 110.92 ppm (J_{C-P} = 7.6 Hz), three sp^2 CH resonances at 125.75 (J_{C-P} = 9.0 Hz), 128.18 (J_{C-P} = 35.1 Hz), and 130.13 ppm (J_{C-P} = 12.3 Hz), and two sp^2 C resonances at 154.08 (J_{C-P} = 3.2 Hz) and 154.32 ppm (J_{C-P} = 4.5 Hz). Since the reaction is run in basic medium, the origin of **4** is quite clear: the metalation of one methyl group of **2** produces a delocalized anion which undergoes a self-condensation with its allylic chloride subunit. This kind of reactivity has already been described with a borane complex of **1**.[6] Complex **5** is thermodynamically more stable than complex **4**, since all of its double bonds are conjugated. It is probably formed at the expense of complex **4** by rearrangement in basic medium.

Phosphole complex **2** was then classically transformed into the corresponding 7-phosphanorbornadiene complex **6** in 80% yield by reaction with dimethyl acetylenedicarboxylate.[7] The decomposition of **6** was carried

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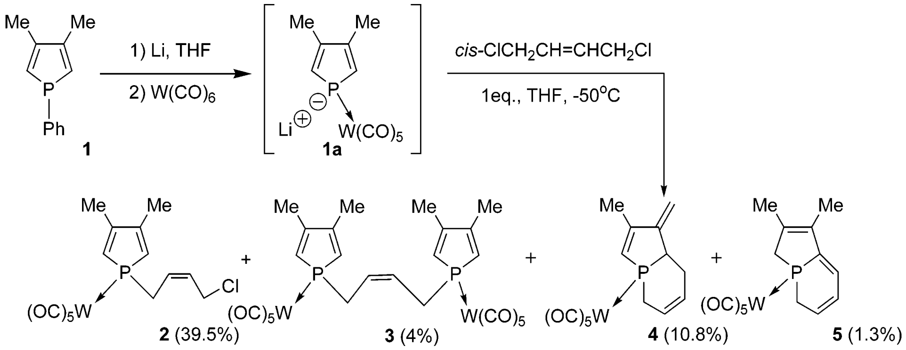
Scheme 1



out at 58 °C in the presence of copper(I) chloride as a catalyst. The two major products of the reaction were the phosphirane complex **8** and its formal dimer **9** (Scheme 2).

The identification of **8** was straightforward. The ^{31}P resonance at −80.1 ppm in CH_2Cl_2 is in the same range as that of the parent 1-chlorophosphirane tungsten complex at −98 ppm.[8] The mass spectrum shows the molecular peak at *m/z* 444, the base peak at *m/z* 305 corresponding to the loss of five CO's. The ^{13}C NMR spectrum shows the ring CH_2 at 20.49 ppm ($J_{C-P} = 22.8$ Hz), the ring CH at 31.96 ppm ($J_{C-P} = 21.2$ Hz), the vinyl CH_2 at 119.05 ppm ($J_{C-P} = 13.1$ Hz), and the vinyl CH at 132.70 ppm ($J_{C-P} = 2.7$ Hz). The mass spectrum of the dimer **9** shows the molecular peak at *m/z* 890 and the loss of 10 carbonyls at *m/z* 610. The ^{31}P NMR spectrum indicates the presence of two different P atoms: $\delta(^{31}P)$ 108.5 ($J_{P-P} = 47$ Hz, $J_{P-W} = 268$ Hz; P−Cl)) and 78.1 ($J_{P-W} = 250$ Hz; P−butenyl). The low P−P coupling constant is characteristic of 1,2-diphosphetane complexes.[9] Finally, it must be stressed that, at higher temperature in the absence of copper(I) chloride, a complex rearrangement of the 7-phosphanorbornadiene skeleton takes place in lieu of the classical generation of the phosphinidene complex.

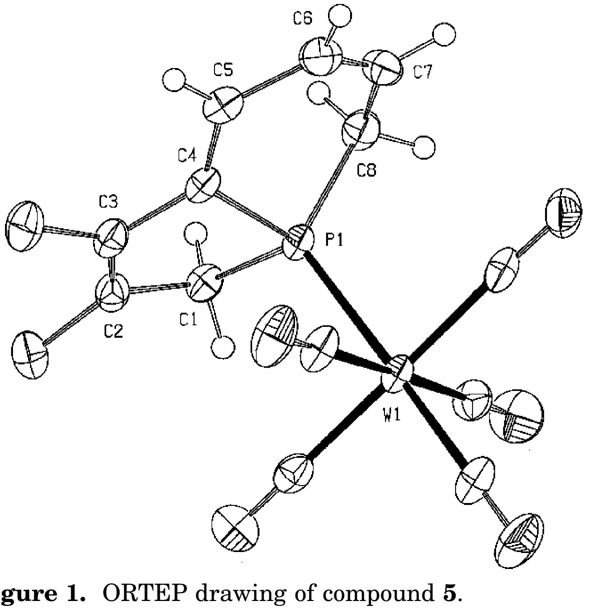
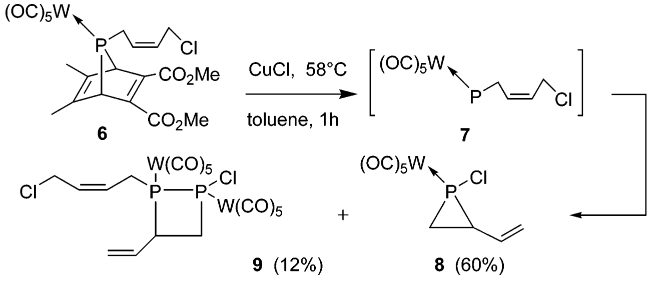


Figure 1. ORTEP drawing of compound **5**.

Scheme 2



To understand the mechanism of this curious rearrangement, we decided to perform DFT calculations[10] on the phosphinidene and phosphirane complexes in the pentacarbonylchromium series. Geometry optimizations were carried out using the B3LYP functional[11,12] in combination with 6-31G(d) basis sets for all atoms except for Cr and Cu (lanl2dz). The optimized geometry of the phosphinidene complex **7Cr** is shown in Figure 2. It appears to be closely similar to that of the ground state of [MeP−Cr(CO)$_5$], as computed by Nguyen and co-workers.[13] In both cases, the complex adopts a staggered conformation. At 2.270 Å, the P−Cr bond length of **7Cr** is almost identical with that of the methyl complex, but the P−C bond appears to be longer—1.89 vs 1.86 Å—probably for steric reasons. At 113°, the Cr−P−C angle is in the normal range for such complexes. The most interesting observation in connection with our study is the almost eclipsed disposition of the P−C and Cl−C bonds, which leads to a P⋯Cl distance of 4.64 Å. Of course, this conformation might not be the only stable one.

Following the theoretical work of Lammertsma on the CuCl-catalyzed decomposition of 7-phosphanorborna-

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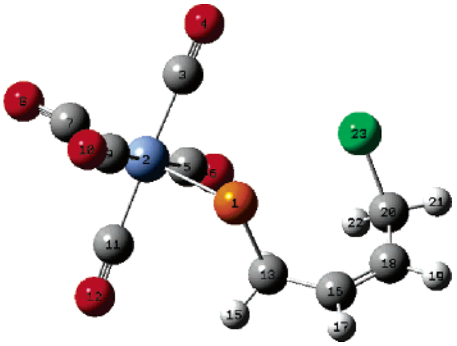

Figure 2. Computed structure of the η^1-phosphinidene complex **7Cr**. Significant distances (Å) and angles (deg): P(1)−Cr(2) = 2.270, P(1)−C(13) = 1.893, P(1)···C(16) = 2.741, C(20)−Cl(23) = 1.842, P(1)···Cl(23) = 4.640; Cr(2)−P(1)−C(13) = 113.32, P(1)−C(13)···C(20)−Cl(23) = 2.97.

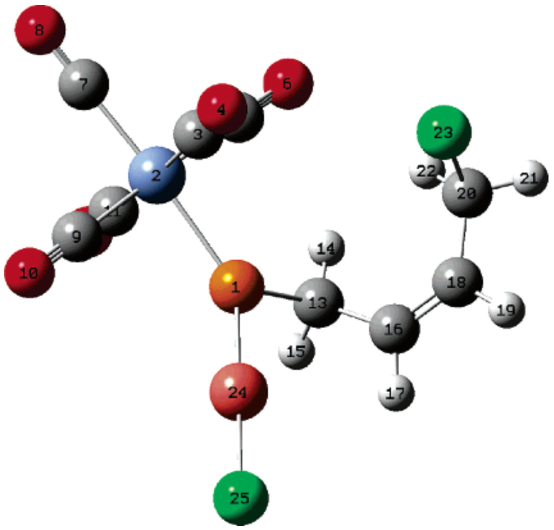

Figure 3. Computed structure of the μ_2-phosphinidene complex **7CrCu**. Significant distances (Å) and angles (deg): P(1)−Cr(2) = 2.252, P(1)−Cu(24) = 2.200, P(1)−C(13) = 1.880, C(20)−Cl(23) = 1.840, P(1)···C(16) = 2.740, P(1)···Cl(23) = 4.357; Cr(2)−P(1)−Cu(24) = 132.84, Cr(2)−P(1)−C(13) = 119.36, P(1)−C(13)···C(20)−Cl(23) = 3.11.

diene complexes,[14] we investigated the stability of various structures incorporating CuCl and **7Cr**. Complexation at P via Cl or at the allyl chloride unit do not correspond to local minima of energy. Conversely, the μ_2-bridging complex **7CrCu** resulting from the complexation of the P lone pair of **7Cr** by copper(I) chloride must be considered as a possible intermediate in the rearrangement. Its computed structure is shown in Figure 3. The structures of the phosphinidene unit appear to be similar in **7Cr** and **7CrCu**, and the P···Cl distance appears to be only slightly shorter (4.36 Å) in the latter complex. Coordination of a second molecule of CuCl onto the allyl chloride unit of **7CrCu** does not correspond to a local minimum of energy. This seems to rule out the intermediacy of **7CrCu** in the observed rearrangement.

The computed geometry of the phosphirane complex **8Cr** is shown in Figure 4. The parameters of the ring are close to those experimentally determined for the (1-chlorophosphirane)pentacarbonyltungsten complex.[8] The most striking feature of this structure is the significant lengthening of the P−CH(vinyl) bond by comparison with the unsubstituted P−C ring bond: 1.877 vs 1.840 Å. This explains why this P−CH(vinyl) bond tends to insert a phosphinidene unit to give the 1,2-diphosphetane complex **9**. This insertion is reminiscent of a similar reaction taking place between terminal phosphinidene complexes and 2-alkynyl-substituted phosphirene complexes.[15]

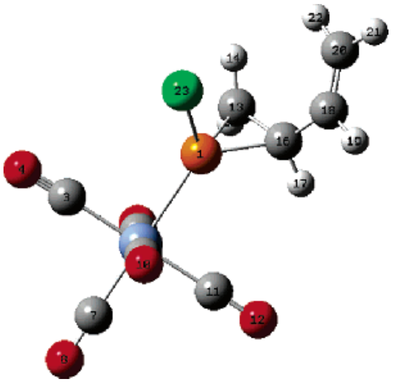

Figure 4. Computed structure of the 1-chlorophosphirane complex **8Cr**. Significant distances (Å) and angles (deg): P(1)−Cr(2) = 2.384, P(1)−Cl(23) = 2.086, P(1)−C(13) = 1.840, P(1)−C(16) = 1.877, C(13)−C(16) = 1.519, C(16)−C(18) = 1.482, C(18)−C(20) = 1.335; Cl(23)−P(1)−C(13) = 103.55, Cl(23)−P(1)−C(16) = 105.58, C(13)−P(1)−C(16) = 48.23, Cl(23)−P(1)−Cr(2) = 120.05.

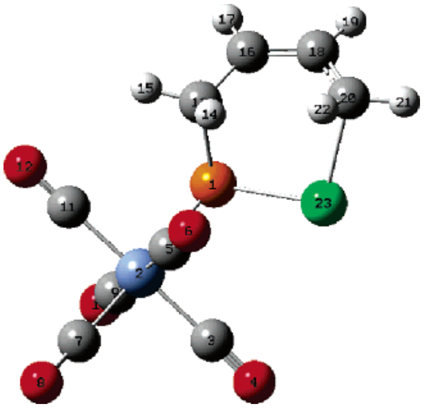

Figure 5. Structure of the computed transition state between **7Cr** and **8Cr**. Significant distances (Å) and angles (deg): P(1)−Cr(2) = 2.416, P(1)−Cl(23) = 2.355, P(1)−C(13) = 1.959, Cl(23)−C(20) = 2.214, P(1)−C(16) = 2.705, C(13)−C(16) = 1.468, C(16)−C(18) = 1.369, C(18)−C(20) = 1.421; P(1)−Cl(23)−C(20) = 100.4.

The computed transition state (STQN method (QST2) followed by IRC calculation) is shown in Figure 5 (one imaginary frequency). The chlorine atom occupies a bridging position between the phosphorus and the terminal carbon atom. We have checked that there is no local minimum of energy on the reaction pathway between **7Cr** and the TS and between the TS and **8Cr**. In addition, a bicyclic structure such as **10** does not correspond to a local minimum of energy. Thus, we propose the mechanism given in Scheme 3 for the rearrangement of phosphinidene **7** to phosphirane **8**.

According to the calculations, the rearrangement is extremely facile, the TS being only 4.8 kcal mol^{-1} higher

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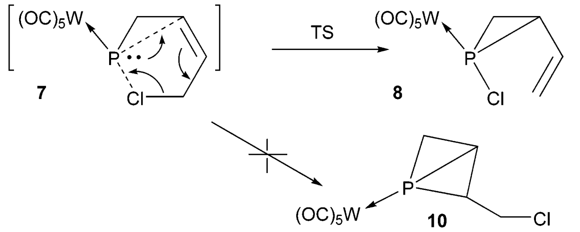
Scheme 3



in energy (ZPE included) than the phosphinidene complex in the chromium series. Since B3LYP is not very accurate for pericyclic reactions,[16] this computed barrier only gives an order of magnitude. As expected, the phosphirane Cr complex is substantially more stable than the phosphinidene Cr complex by 29.6 kcal mol^{-1}. This original six-electron (C−Cl σ bond, P lone pair, and C═C π bond) rearrangement has no equivalent in carbon chemistry. 1-Chloro-2-vinylcyclopropane is known[17] but has never been prepared from the 4-chlorobut-2-enylcarbene.

Experimental Section

NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at 300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, and 121.50 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (^{1}H and ^{13}C) and external 85% aqueous H_3PO_4 (^{31}P). Elemental analyses were performed by the *Service de microanalyse du CNRS,* Gif-sur-Yvette, France.

Synthesis of Complexes 2−5. A THF solution of lithium [3,4-dimethylphospholide]pentacarbonyltungsten (**1a**) was prepared from phosphole **1** (20 g, 10.6 × 10^{-2} mol) as described in ref 5. *cis*-1,4-Dichlorobut-2-ene (15 mL, 14.2 × 10^{-2} mol) in THF (50 mL) was added to this solution at −50 °C. After the usual treatment, the organic residue was chromatographed twice on silica gel with hexane/dichloromethane (10/1) as the eluent. Complex **2** was eluted first (22 g, 39.5%), then a mixture of complexes **4** and **5** (7 g), and finally complex **3** (4 g, 4%). Complexes **4** (5.6 g, 10.8%) and **5** (0.7 g, 1.3%) were separated by recrystallization in hexane/dichloromethane (10/1).

Complex **2**: ^{31}P NMR ($CDCl_3$) δ 3.7; ^{1}H NMR ($CDCl_3$) δ 2.08 (s, Me), 2.76 (dd, $J_{H-H} \approx J_{H-P} \approx 8$ Hz, P−CH_2), 3.91 (d, J_{H-H} = 7.8 Hz, $ClCH_2$), 5.36 (m, ═CH), 5.63 (m, ═CH), 6.19 (d, $^2J_{H-P}$ = 35.7 Hz, ═CH−P); ^{13}C NMR ($CDCl_3$) δ 17.63 (d, J_{C-P} = 11.2 Hz, Me), 29.63 (d, J_{C-P} = 22.0 Hz, PCH_2), 39.00 (d, J_{C-P} = 2 Hz, $ClCH_2$), 126.40 (d, J_{C-P} = 7.9 Hz, ═CH), 128.37 (d, J_{C-P} = 41.3 Hz, ═CH−P), 128.61 (d, J_{C-P} = 9.9 Hz, ═CH),152.29 (d, J_{C-P} = 8.0 Hz, ═*C*−Me), 196.30 (d, J_{C-P} = 6.8 Hz, *cis*-CO), 199.24 (d, J_{C-P} = 18.7 Hz, *trans*-CO); mass spectrum *m/z* 524 (M$^+$). Anal. Calcd for $C_{15}H_{14}ClO_5PW$: C, 34.35; H, 2.69. Found: C, 34.51; H, 2.79.

Complex **4**: ^{1}H NMR ($CDCl_3$) δ 2.10 (s, Me), 2.52−2.74 (m, CH_2), 3.46 (s br, CH−P), 5.32 (d, J_{H-P} = 34.6 Hz, ═CH−P), 5.89−6.08 (m, ═CH_2); ^{13}C NMR ($CDCl_3$) δ 16.50 (d, $^3J_{C-P}$ = 10.5 Hz, Me), 29.70 (d, $^1J_{C-P}$ = 17.0 Hz, CH_2P), 29.75 (d, $^2J_{C-P}$ = 5.6 Hz, CH_2CHP), 43.7 (d, $^1J_{C-P}$ = 35.6 Hz, CHP), 110.92 (d, $^3J_{C-P}$ = 7.6 Hz, ═CH_2), 125.75 (d, J_{C-P} = 9.0 Hz, ═CH), 128.18 (d, $^1J_{C-P}$ = 35.1 Hz, ═CHP), 130.13 (d, J_{C-P} = 12.3 Hz, ═CH), 154.08 (d, $^2J_{C-P}$ = 3.2 Hz, C═CH_2), 154.32 (d, $^2J_{C-P}$ = 4.5 Hz, ═CMe), 196.90 (d, J_{C-P} = 7.4 Hz, cis CO), 200.27 (d, J_{C-P} = 20.6 Hz, trans CO); mass spectrum (CI, NH_3) *m/z* 489 (M + 1, 60%), 344 (100%). Anal. Calcd for $C_{15}H_{13}O_5PW$: C, 36.91; H, 2.68. Found: C, 36.46; H, 2.69.

Complex **5**: ^{1}H NMR ($CDCl_3$) δ 1.95 (s, Me), 2.05 (s, Me), 2.79−3.00 (m, CH_2), 6.02, 6.28, 6.47 (3 × m, ═CH); ^{13}C NMR ($CDCl_3$) δ 11.56 (d, J_{C-P} = 5.7 Hz, Me), 18.19 (d, J_{C-P} = 5.7 Hz, Me), 28.57 (d, J_{C-P} = 23.8 Hz, CH_2P), 42.65 (d, J_{C-P} = 24.7 Hz, CH_2P), 118.72 (d, J_{C-P} = 2.5 Hz, ═CH), 121.02 (d, J_{C-P} = 8.5 Hz, ═CH), 130.41 (d, J_{C-P} = 18.8 Hz, ═CH), 133.38 (d, J_{C-P} = 17.4 Hz, C═), 142.32 (d, J_{C-P} = 3.7 Hz, C═), 144.15 (d, J_{C-P} = 46.4 Hz, C═), 197.00 (d, J_{C-P} = 7.0 Hz, CO), 199.82 (d, J_{C-P} = 20.7 Hz, CO). Anal. Calcd for $C_{15}H_{13}O_5PW$: C, 36.91; H, 2.68. Found: C, 37.04; H, 2.59.

Synthesis of the 7-Phosphanorbornadiene Complex 6. A solution of phosphole complex **2** (16 g, 3 × 10^{-2} mol) and dimethyl acetylenedicarboxylate (10 mL, 8.1 × 10^{-2} mol) in toluene (15 mL) was heated at 70 °C overnight. After evaporation, the organic residue was chromatographed on silica gel with hexane/dichloromethane (2/1) as the eluent. Yield of **6**: 16 g (78.7%). ^{31}P NMR ($CDCl_3$): δ 205.0, J_{p-w} = 242 Hz. ^{1}H NMR ($CDCl_3$): δ 1.99 (s, Me), 3.22 (m, P−CH_2), 3.65 (d, J_{H-P} = 2.4 Hz. P−CH), 3.85 (s, OMe), 4.08 (d, J_{H-H} = 7.7 Hz, CH_2-Cl), 5.55 (m, ═CH), 5.85 (m, ═CH). ^{13}C NMR ($CDCl_3$): δ 16.40 (s, Me), 35.42 (s, CH_2P), 39.48 (s, CH_2Cl), 53.12 (s, OMe), 59.53 (d, J_{C-P} = 18.8 Hz, CH−P), 124.89 (s, ═CH), 130.28 (d, J_{C-P} = 9.6 Hz, ═CH), 139.24 (d, J_{C-P} = 16.4 Hz, ═C(Me)), 145.70 (d, J_{C-P} = 4.6 Hz, ═C(CO_2Me)), 165.38 (d, J_{C-P} = 2.9 Hz, CO_2), 196.25 (d, J_{C-P} = 6.6 Hz, *cis*-CO), 197.62 (d, J_{C-P} = 26.7 Hz, *trans*-CO). Mass spectrum: *m/z* 668 (M + 2). Anal. Calcd for $C_{21}H_{20}ClO_9PW$: C, 37.84; H, 3.02. Found: C, 37.91; H, 3.02.

Synthesis of the 1-Chloro-2-vinylphosphirane Complex 8 and Dimer Complex 9. A solution of 7-phosphanorbornadiene complex **6** (2.5 g, 3.7 × 10^{-3} mol) in toluene (15 mL) was heated for 1 h at 58 °C with CuCl (100 mg). After evaporation, the organic residue was chromatographed on silica gel with hexane/dichloromethane (10/1) as the eluent.

Yield of **8**: 1 g (60%). For the characterization, see the discussion. ^{1}H NMR ($CDCl_3$): δ 1.60 (m, 1H, ring CH_2), 2.18 (m, 1H, ring CH_2), 2.87 (m, 1H, ring CH), 5.08 (m, 1H, vinyl CH_2), 5.24 (m, 1H, vinyl CH_2), 5.88 (m, 1H, vinyl CH). Anal. Calcd for $C_9H_6ClO_5PW$: C, 24.32; H, 1.36. Found: C, 24.43; H, 1.29.

Yield of **9**: 200 mg (12%). ^{1}H NMR ($CDCl_3$): δ 3.04 (m, 1H, CH_2), 3.48 (m, 2H, CH_2), 3.58 (m, 1H, CH_2), 4.14 (m, 2H, $ClCH_2$), 4.54 (m, 1H, PCH), 5.31 (m, 2H, ═CH_2), 5.78−6.05 (m, 3H, ═CH). ^{13}C NMR ($CDCl_3$): δ 27.28 (pseudo t, CH_2), 38.76 (s, $ClCH_2$), 45.13 (dd, J_{C-P} = 3.0 and 17.4 Hz, PCH_2), 48.68 (dd, J_{C-P} = 4.6 and 23.9 Hz, PCH), 118.75 (d, J_{C-P} = 8.6 Hz, ═CH_2), 125.63 (d, J_{C-P} = 9.1 Hz, ═CH), 131.10 (d, J_{C-P} = 11.3 Hz, ═CH), 132.71 (dd, J_{C-P} = 6.5 and 13.6 Hz, ═CH), 194.33 (d, J_{C-P} = 6.5 Hz, cis-CO), 194.90 (dd, J_{C-P} = 1.3 and 6.9 Hz, cis-CO), 197.07 (d, J_{C-P} = 35.5 Hz, trans-CO), 197.61 (d, J_{C-P} = 28.8 Hz, trans-CO). Anal. Calcd for $C_{18}H_{12}Cl_2O_{10}P_2W_2$: C, 24.32; H, 1.36. Found: C, 24.87; H, 1.25.

X-ray Structure Data: Nonius KappaCCD diffractometer, ϕ and ω scans, Mo Kα radiation (λ = 0.710 73 Å), graphite monochromator, T = 150 K, structure solution with SIR97,[18] refinement against F^2 in SHELXL97[19] with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters.

Data Collection for 5: colorless block, 0.20 × 0.20 × 0.16 mm, monoclinic, $P2_1/n$, a = 10.7390(10) Å, b = 12.1620(10) Å, c = 13.5770(10) Å, b = 113.0300(10)°, V = 1631.9(2) Å^3, Z = 4, ρ_{calcd} = 1.987 g cm^{-3}, μ = 7.195 cm^{-1}, F(000) = 928, θ_{max} = 30.01°, *hkl* ranges −15 to +15, −17 to +15, and −19 to +18, 7964 data collected, 4737 unique (R_{int} = 0.0171), 4163 data with $I > 2\sigma(I)$, 201 parameters refined, GOF (F^2) = 1.055, final R indices (R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/$

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$\sum w(F_o^2)^2]^{1/2}$) R1 = 0.0265 and wR2 = 0.0722, maximum/minimum residual electron density 1.615(0.136)/−1.916(0.136) e Å^{-3}.

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Supporting Information Available: X-ray crystal structure analysis of complex **5** and tables giving Cartesian coordinates and energies of the theoretical structures **7Cr,** **8Cr**, and **TS**. This material is available free of charge via the Internet at http://pubs.acs.org.

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