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# Electronic Structure and Evolution of a Terminal Butadienylphosphinidene Complex

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The DFT study of the 1-butadienylphosphinidene complex [$CH_2{=}CHCH{=}CHP{-}Cr(CO)_5$] shows a delocalized structure with a short P−C bond at 1.789 Å and a long $C_\alpha{=}C_\beta$ double bond at 1.367 Å. The $W(CO)_5$ complex has been synthesized by copper-catalyzed decomposition of the appropriate 7-phosphanorbornadiene complex. It gives the normal reaction products with alkynes (phosphirenes) and with conjugated dienes (phospholenes and dihydrophosphepines via a phospha-Cope rearrangement), but when no trapping reagent is added to the reaction mixture, it gives a complex pentacyclic product whose structure has been established by X-ray crystal structure analysis and whose formation involves a cascade of reactions starting at the dienyl substituent of the precursor.

## Introduction

The electrophilic terminal phosphinidene complexes [$RP{-}M(CO)_5$] (M = Cr, Mo, W) are known to have an electronic structure which resembles that of singlet carbenes.[1] Their LUMO is essentially the empty $p_z$ orbital at phosphorus. Any $\pi$-system directly bonded to phosphorus will stabilize the phosphinidene by interaction with the $p_z$ orbital. From this standpoint, the high-lying $\pi$-electrons of a conjugated dienyl unit would be especially interesting as a stabilizing unit. From another standpoint, the reaction of conjugated dienes with phosphinidene complexes has been one of the most thoroughly studied reactions of phosphinidenes.[2] One can wonder through what kind of reaction a butadienylphosphinidene complex would evolve toward a stable compound. These two reasons led us to investigate the electronic structure and the trapping of these previously unreported species.

## Results and Discussion

To evaluate the effect of the introduction of a butadienyl substituent in [$RP{-}M(CO)_5$], we performed DFT calculations[3] on [(*E*)-$CH_2{=}CHCH{=}CHP{-}Cr(CO)_5$] (**1**) using the B3LYP functional[4,5] with 6-31G(d) basis sets for all atoms except Cr (lanl2dz). Our results were then compared to those obtained for [$MeP{-}Cr(CO)_5$] at the same level of formalism.[6] The computed structure of **1** is shown in Figure 1. The replacement of the methyl group by a butadienyl substituent induces some significant changes in the geometry of the complex. Both complexes adopt a staggered conformation of the P−R and $Cr(CO)_5$ units, and the R−P−Cr bond angles are identical. However, the P−C bond is short in **1** at 1.789 Å vs 1.864 Å for the P−Me complex and the $C_\alpha{=}C_\beta$ double bond is long at 1.367 Å vs 1.346 Å for the terminal double bond. As expected,

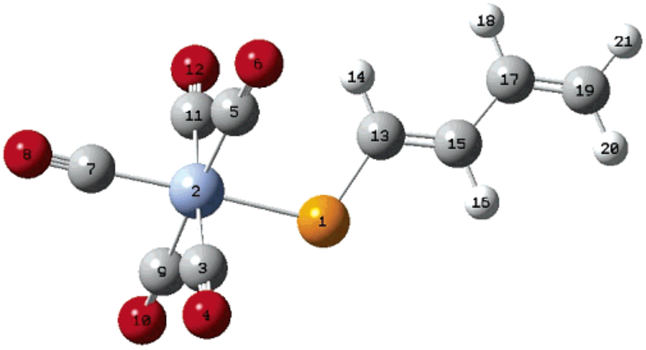

**Figure 1.** Computed structure of the (butadienylphosphinidene)pentacarbonylchromium complex **1**. Significant bond lengths (Å) and angles (deg): P1−Cr2 = 2.305, P1−C13 = 1.789, C13−C15 = 1.367, C15−C17 = 1.445, C17−C19 = 1.346; Cr2−P1−C13 = 112.0.

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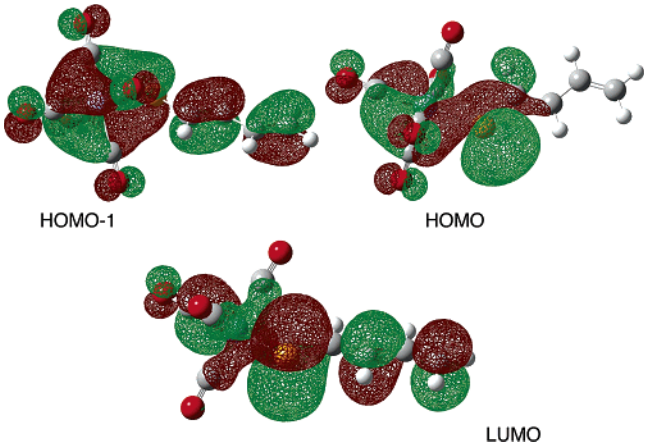
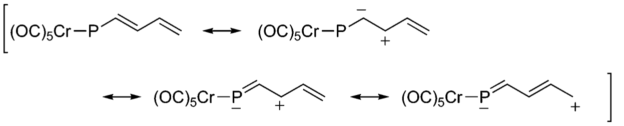


**Figure 2.** Frontier orbitals of **1**.

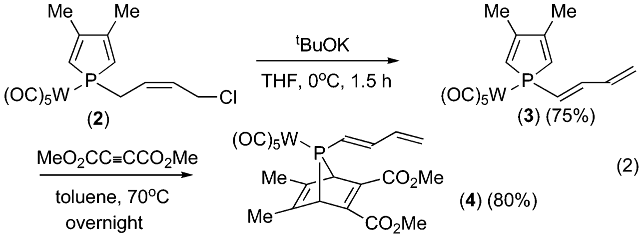
the Cr−P−$C_4$ unit of **1** is strictly planar. These data suggest a strong conjugation between phosphorus and the vicinal double bond in **1**. The NBO charges confirm this point. The charge at P is reduced at 0.534 e vs 0.60 e for P−Me. The two double bonds are highly polarized: $C_\alpha$, −0.606; $C_\beta$, −0.131; $C_\gamma$, −0.268; $C_\delta$, −0.333. Thus, it appears that **1** is better represented by a mesomeric formulation as shown in eq 1.



(1)

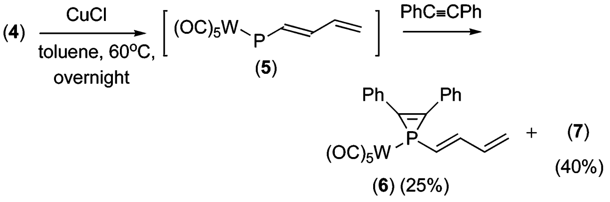
The orbital scheme confirms the strong delocalization within the phosphinidene unit. HOMO-1 is essentially the antibonding combination of the $p_z$ orbital at P and the $\Psi_2$ orbital of butadiene, the HOMO is still essentially the lone-pair orbital at P but is destabilized by 0.19 eV by comparison with the P−Me complex, and the LUMO is heavily localized at P, $C_\beta$, and $C_\delta$ (Figure 2).

Our starting synthetic point was the 1-chlorobutenylphosphole complex **2**, whose preparation has been described in a previous work.[7] The dehydrochlorination of the chlorobutenyl substituent by a strong base afforded the butadienylphosphole complex **3** in good yield (eq 2). The $^{13}$C NMR spectrum of **3** shows a characteristic resonance for the terminal $=CH_2$ group as a singlet at 122.38 ppm ($CDCl_3$). The stereochemistry of the exocyclic $PCH_\alpha=CH_\beta$ unit was established by inspection of the $^1$H NMR spectrum: $H_\alpha$ appears as a pseudo-triplet ($J_{H-H} = J_{H-P} = 16.3$ Hz) only compatible with the *E* stereochemistry.[8] Contrary to what we feared, the Diels−Alder reaction of **3** with dimethyl acetylenedicarboxylate (DMAD) exclusively took place at the cyclic diene to give the 7-phosphanorbornadiene complex **4**, once again in good yield (eq 2). Such a perfect selectivity was not observed in previous experiments with a 1-(tetramethylcyclopentadienyl)phosphole.[9] In this case, DMAD reacts with both the phosphole and cyclopentadiene rings.



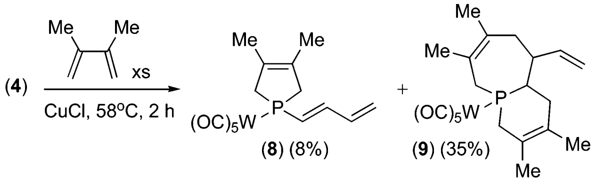
(2)

Complex **4** shows the characteristic deshielding of the $^{31}$P resonance at 205 ppm ($CH_2Cl_2$) and the characteristic $^{13}$C resonance for the terminal $=CH_2$ group at 123.19 ppm ($CDCl_3$). To check that **4** was a genuine precursor of the butadienylphosphinidene complex **5**, we investigated the reaction of **4** with diphenylacetylene at 60 °C in the presence of CuCl as a catalyst. We obtained the expected phosphirene **6**, thus demonstrating the formation of **5**, together with an unknown biphosphorus compound (**7**), characterized by two singlet resonances at 48 and 148.6 ppm (eq 3). We shall discuss the structure of **7** later.



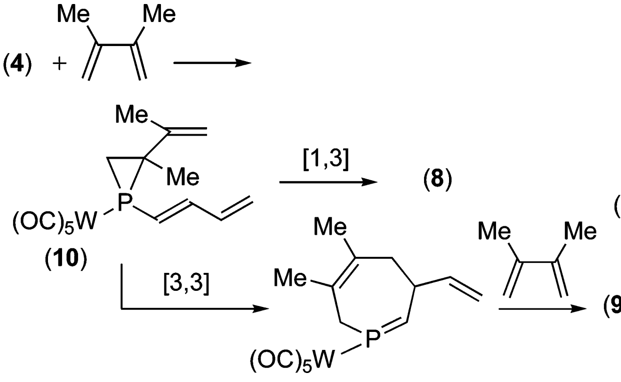
(3)

The phosphirene displays the characteristic shielding of its $^{31}$P resonance at −163.8 ppm ($CDCl_3$) and the terminal $=CH_2$ group at 122.91 ppm ($CDCl_3$). The reaction of **4** with 2,3-dimethylbutadiene was much faster and did not produce the byproduct **7**. The minor product was the phospholene **8** and the major product the bicyclic compound **9** (eq 4).



(4)

The $^{13}$C spectrum of the phospholene **8** shows the intracyclic $CH_2$ groups as a doublet at 44.48 ppm ($^1J_{C-P} = 29.2$ Hz) and the terminal $CH_2$ group as a singlet at 122.2 ppm. The formula of **9** was established by an X-ray crystal structure analysis (Figure 3). The origin of **8** and **9** is quite clear. The initial product is very likely the phosphirane **10**, which ring-expands either via a 1,3-shift to give the phospholene according to a well-known scheme[2] or via a phospha-Cope[10a] rearrangement to give a seven-membered ring with a P=C double bond that reacts with a second molecule of diene to give the bicyclic compound **9**[10b] (eq 5).



(5)

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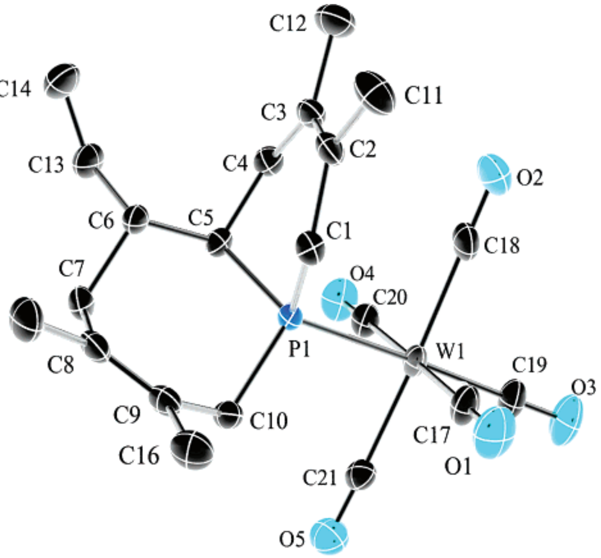
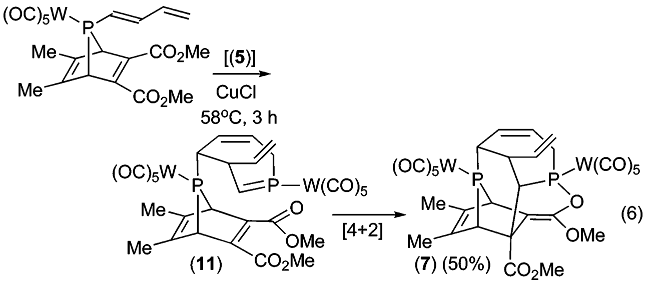


**Figure 3.** X-ray crystal structure of complex **9**. Thermal ellipsoids are scaled to enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg): P(1)−W(1) = 2.5187(6), P(1)−C(1) = 1.826(2), P(1)−C(5) = 1.842(2), P(1)−C(10) = 1.844(2); C(1)−P(1)−C(10) = 105.5(1), C(5)−P(1)−C(10) = 106.8(1), C(1)−P(1)−C(5) = 98.1(1), C(4)−C(5)−C(6) = 111.6(2).

The formation of **8** and **9** demonstrated that the reaction of the butadienylphosphinidene **5** toward a conjugated diene was similar to that of a vinylphosphinidene complex.[10b] We were ready then to study the generation and evolution of **5** in the absence of additional reagent. Upon heating in the presence of CuCl as a catalyst, the phosphanorbornadiene **4** gave the already observed biphosphorus compound **7** as the single major product (eq 6).



(6)

The structure of **7** was established by an X-ray analysis (Figure 4). On the basis of what we had observed in the reaction of **5** with dimethylbutadiene, the origin of **7** is very likely the following. The phosphinidene **5** first reacts with the butadienyl substituent of a second molecule of precursor **4** to give a seven-membered ring (**11**) via a phospha-Cope rearrangement. In **11**, the reactive P═C double bond is close to a C═CC═O unit of the phosphanorbornadiene. An intramolecular [4 + 2] cycloaddition takes place between the phosphaalkene and the α,β-unsaturated ester to give the pentacyclic product **7** in fair yield.

This complex and subtle chemistry once again demonstrates the extraordinary versatility of the phosphole−phosphanorbornadiene route to electrophilic terminal phosphinidene complexes.[11]

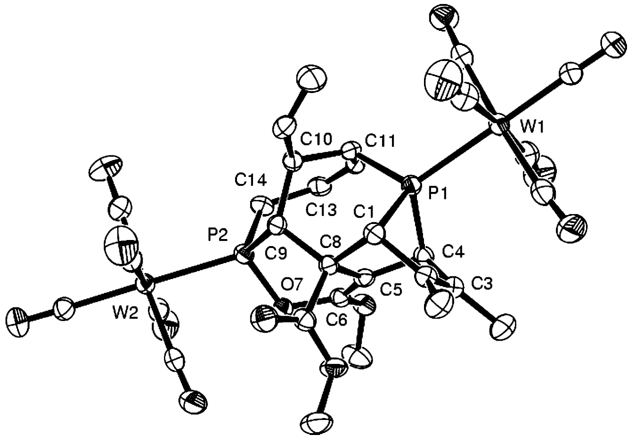


**Figure 4.** X-ray crystal structure of complex **7**. Thermal ellipsoids are scaled to enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg): W(1)−P(1) = 2.4957(8), W(2)−P(2) = 2.467(1), P(1)−C(1) = 1.849(3), P(1)−C(4) = 1.874(3), P(1)−C(11) = 1.886(3), P(2)−O(7) = 1.653(2), P(2)−C(9) = 1.856(3), P(2)−C(14) = 1.833(4); C(1)−P(1)−C(4) = 80.8(1), C(1)−P(1)−C(11) = 103.9(1), C(4)−P(1)−C(11) = 107.4(1), O(7)−P(2)−C(9) = 103.1(1), O(7)−P(2)−C(14) = 102.6(1), C(9)−P(2)−C(14) = 105.3(2).

## Experimental Section

NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at 300.13 for $^1$H, 75.47 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 1-Butadienylphosphole Complex 3.** To a solution of complex **2** (10.5 g, 20 × $10^{-3}$ mol) in THF (100 mL) at 0 °C was added $^t$BuOK (3 g, 26 × $10^{-3}$ mol). The solution was stirred for 1.5 h. After evaporation of the solvent, the residue was chromatographed on silica gel with hexane/$CH_2Cl_2$ (9/1) as the eluent. **3** was obtained as a yellow powder, yield 7.3 g (75%).

$^{31}$P NMR ($CDCl_3$): δ 0.9. $^1$H NMR ($CDCl_3$): δ 2.42 (s, 6H, Me), 5.55 (d, 1H, $J_{H-H}$ = 10 Hz, ═$CH_2$), 5.66 (d, 1H, $J_{H-H}$ = 16.9 Hz, ═$CH_2$), 5.98 (pseudo t, 1H, $J_{H-H}$ = $J_{H-P}$ = 16.3 Hz, PCH═), 6.58 (d, 2H, $^2J_{H-P}$ = 36.7 Hz, ring ═CH−P), 6.66 (m, 1H, ═CH), 6.95 (m, 1H, ═CH). $^{13}$C NMR ($CDCl_3$): δ 17.67 (d, $J_{C-P}$ = 11.5 Hz, Me), 122.38 (s, ═$CH_2$), 123.25 (d, $J_{C-P}$ = 40.5 Hz, ═CHP), 129.45 (d, $J_{C-P}$ = 44.8 Hz, ring ═CHP), 136.36 (d, $J_{C-P}$ = 18.8 Hz, ═CH), 145.98 (d, $J_{C-P}$ = 8.6 Hz, ═CH),151.42 (d, $J_{C-P}$ = 9.0 Hz, ═*C*Me), 196.49 (d, $J_{C-P}$ = 6.7 Hz, *cis*-CO), 199.45 (d, $J_{C-P}$ = 27.8 Hz, *trans*-CO). Anal. Calcd for $C_{15}H_{13}O_5PW$: C, 36.91; H, 2.68. Found: C, 37.02; H, 2.64.

**Synthesis of 7-Butadienyl-7-phosphanorbornadiene Complex 4.** Complex **3** (5 g, 10 × $10^{-3}$ mol) and DMAD (3 mL) were heated overnight at 70 °C in toluene (2 mL). The product was chromatographed on silica gel with hexane/$CH_2Cl_2$ (1/1) as the eluent. **4** was obtained as a yellow powder, yield 5 g (80%).

$^{31}$P NMR ($CH_2Cl_2$): δ 205.4. $^1$H NMR ($CDCl_3$): δ 1.99 (s, 6H, Me), 3.72 (d, 2H, $J_{H-P}$ = 1.9 Hz, CH−P), 3.80 (s, 6H, OMe), 5.33 (d, 1H, $J_{H-H}$ = 9.1 Hz, $CH_2$), 5.42 (d, 1H, $J_{H-H}$ = 16.1 Hz, $CH_2$), 6.14 (pseudo t, 1H, $J_{H-H}$ = $J_{H-P}$ = 16.2 Hz, PCH═), 6.35−6.46 (m, 2H, ═CH). $^{13}$C NMR ($CDCl_3$): δ 16.24 (d, $J_{C-P}$ = 2.3 Hz, Me), 52.82 (s, OMe), 60.47 (d, $J_{C-P}$ = 21.5 Hz, CHP), 123.19 (s, ═$CH_2$), 131.47 (d, $J_{C-P}$ = 10.1 Hz, ═CH), 136.33 (d, $J_{C-P}$ = 13.4 Hz, ═CH), 138.45 (d, $J_{C-P}$ = 17.0 Hz, ═C(Me)), 144.71 (d, $J_{C-P}$ = 5.4 Hz, ═CH), 146.27 (d, $J_{C-P}$ = 4.6 Hz, ═C($CO_2$Me)), 165.39 (d, $J_{C-P}$ = 2.8 Hz, $CO_2$), 196.20 (d, $J_{C-P}$ = 6.8 Hz, *cis*-CO), 198.43 (d, $J_{C-P}$ = 25.4 Hz, *trans*-CO).

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**Synthesis of 1-Butadienylphosphirene Complex 6.** Complex **4** (0.64 g, 1 × $10^{-3}$ mol), diphenylacetylene (0.2 g, 1.2 × $10^{-3}$ mol), and CuCl (0.03 g) were heated overnight at 60 °C in toluene (8 mL). The crude product was chromatographed on silica gel with hexane/$CH_2Cl_2$ (9/1) as the eluent. The phosphirene complex **6** was thus obtained (0.06 g, 25%). Complex **7** was then eluted with hexane/$CH_2Cl_2$ (2/3), yield 0.15 g, 40%.

Data for **6** are as follows. $^{31}$P NMR ($CDCl_3$): $\delta$ −163.8. $^{1}$H NMR ($CDCl_3$): $\delta$ 5.32 (d, 1H, $J_{\mathrm{H-H}} = 9.8$ Hz, =$CH_2$), 5.43 (d, 1H, $J_{\mathrm{H-H}} = 16.9$ Hz, =$CH_2$), 5.69 (pseudo t, 1H, $J_{\mathrm{H-H}} = J_{\mathrm{H-P}} = 16.6$ Hz, PCH=), 6.38 (m, 1H, =CH), 6.79 (m, 1H, =CH). $^{13}$C NMR ($CDCl_3$): 122.91 (s, =$CH_2$), 127.90 (d, $J_{\mathrm{C-P}} = 6.7$ Hz, =C−), 129.19 (d, $J_{\mathrm{C-P}} = 8.5$ Hz, =C−), 129.67 (s, =CH(Ph)), 130.63 (d, $J_{\mathrm{C-P}} = 5.5$ Hz, =CH(Ph)), 130.95 (s, =CH(Ph)), 134.65 (d, $J_{\mathrm{C-P}} = 6.3$ Hz, =CH), 135.65 (d, $J_{\mathrm{C-P}} = 19.8$ Hz, =CH), 147.68 (d, $J_{\mathrm{C-P}} = 13.7$ Hz, =CH), 196.22 (d, $J_{\mathrm{C-P}} = 8.6$ Hz, CO), 198.22 (d, $J_{\mathrm{C-P}} = 30.5$ Hz, CO). Mass spectrum ($^{184}$W): *m*/*z* 586 (M, 14%), 446 (M − 5CO, 100%).

**Synthesis of 1-Butadienylphospholene Complex 8 and Bicyclic Complex 9.** Complex **4** (0.32 g, 0.5 × $10^{-3}$ mol), 2,3-dimethylbutadiene (0.5 mL), and CuCl (0.02 g) were heated for 2 h at 58 °C in toluene (5 mL). The crude product was chromatographed on silica gel with hexane/$CH_2Cl_2$ (9.5/0.5) as the eluent. The phospholene complex **8** was first recovered (0.02 g, 8%) and then the bicyclic complex **9** (0.1 g, 35%).

Data for **8** are as follows. $^{31}$P NMR ($CDCl_3$): $\delta$ −12.1. $^{1}$H NMR ($CDCl_3$): $\delta$ 1.75 (s, 6H, Me), 2.74−2.98 (m, 4H, $CH_2$P), 5.31 (d, 1H, $J_{\mathrm{H-H}} = 9.8$ Hz, =$CH_2$), 5.40 (d, 1H, $J_{\mathrm{H-H}} = 16.8$ Hz, =$CH_2$), 6.03 (pseudo t, 1H, $J_{\mathrm{H-H}} = J_{\mathrm{H-P}} = 15.8$ Hz, =CHP), 6.43 (m, 1H, =CH), 6.58 (m, 1H, =CH). $^{13}$C NMR ($CDCl_3$): 16.53 (d, $J_{\mathrm{C-P}} = 7.9$ Hz, Me), 44.48 (d, $J_{\mathrm{C-P}} = 29.2$ Hz, $CH_2$P), 122.21 (s, =$CH_2$), 130.15 (s, =C(Me)), 130.61 (d, $J_{\mathrm{C-P}} = 35.4$ Hz, =CHP), 136.28 (d, $J_{\mathrm{C-P}} = 17.0$ Hz, =CH), 143.46 (d, $J_{\mathrm{C-P}} = 7.5$ Hz, =CH), 197.06 (d, $J_{\mathrm{C-P}} = 7{,}2$ Hz, CO). Mass spectrum (CI, $NH_3$; $^{184}$W): *m*/*z* 491 (M + H, 76%), 436 (100%).

Data for **9** are as follows. $^{31}$P NMR ($CDCl_3$): $\delta$ −23.2. $^{1}$H NMR ($CDCl_3$): $\delta$ 1.60 (s, 3H, Me), 1.73 (s, 3H, Me), 1.75 (s, 6H, Me), 4.95 (d, 1H, $J_{\mathrm{H-H}} = 16.9$ Hz, =$CH_2$), 5.03 (d, 1H, $J_{\mathrm{H-H}} = 10.0$ Hz, =$CH_2$), 5.59 (m, 1H, =CH). $^{13}$C NMR ($CDCl_3$): 20.49 (s, Me), 21.10 (d, $J_{\mathrm{C-P}} = 2.1$ Hz, Me), 22.20 (d, $J_{\mathrm{C-P}} = 8.0$ Hz, Me), 22.66 (d, $J_{\mathrm{C-P}} = 2.9$ Hz, Me), 28.69 (d, $J_{\mathrm{C-P}} = 26.0$ Hz, $CH_2$), 36.32 (s, $CH_2$), 39.52 (d, $J_{\mathrm{C-P}} = 19.8$ Hz, $CH_2$), 41.38 (d, $J_{\mathrm{C-P}} = 3.6$ Hz, CH), 41.93 (s, $CH_2$), 42.10 (d, $J_{\mathrm{C-P}} = 19.5$ Hz, CH−P), 115.01 (s, =$CH_2$), 120.84 (d, $J_{\mathrm{C-P}} = 3.5$ Hz, =C−), 125.30 (d, $J_{\mathrm{C-P}} = 10.2$ Hz, =C−), 126.05 (d, $J_{\mathrm{C-P}} = 11.5$ Hz, =C−), 133.39 (d, $J_{\mathrm{C-P}} = 6.5$ Hz, =C−), 143.33 (d, $J_{\mathrm{C-P}} = 8.6$ Hz, =CH). Mass spectrum (CI, $NH_3$; $^{184}$W): *m*/*z* 572 (M, 100%). Anal. Calcd for $C_{21}H_{25}O_5PW$: C, 44.08; H, 4.39. Found: C, 43.91; H, 4.39.

**Synthesis of the Polycyclic Complex 7 by Thermolysis of the 7-Butadienyl-7-phosphanorbornadiene Complex 4.** Complex **4** (1 g, 1.58 × $10^{-3}$ mol) and CuCl (0.03 g) were heated for 3 h at 58 °C in toluene (8 mL). The crude product was chromatographed on silica gel with hexane/$CH_2Cl_2$ (1/1) as the eluent. Complex **7** was recovered as yellow crystals (0.4 g, 50%).

Data for **7** are as follows. $^{31}$P NMR ($CDCl_3$): $\delta$ 48.0, 148.6. $^{13}$C NMR ($CDCl_3$): $\delta$ 14.83 (d, $J_{\mathrm{C-P}} = 3.7$ Hz, Me), 15.28 (d, $J_{\mathrm{C-P}} = 2.7$ Hz, Me), 38.61 (s, OMe), 41.05 (d, $J_{\mathrm{C-P}} = 10.3$ Hz, P−$CH_2$), 51.71 (d, $J_{\mathrm{C-P}} = 21.2$ Hz, P−CH), 53.76 (d, $J_{\mathrm{C-P}} = 7.7$ Hz, OMe), 54.12 (dd, $J_{\mathrm{C-P}} = 21.3$ and 5.8 Hz, P−CH), 55.18 (s, P−CH), 56.28 (s, P−CH), 56.50 (d, $J_{\mathrm{C-P}} = 18.6$ Hz, P−CH), 74.96 (s, C), 98.32 (d, $J_{\mathrm{C-P}} = 8.7$ Hz, =C), 118.37 (s, =$CH_2$), 122.94 (dd, =CH), 123.62 (s, =CH), 133.40 (d, $J_{\mathrm{C-P}} = 10.5$ Hz, =CMe), 138.75 (d, $J_{\mathrm{C-P}} = 14.6$ Hz, =CMe), 141.13 (d, $J_{\mathrm{C-P}} = 14.7$ Hz, vinyl =CH), 152.52 (s, =COO), 172.76 (s, $CO_2Me$), 195.75 (d, $J_{\mathrm{C-P}} = 7.6$ Hz, *cis*-CO), 196.26 (d, $J_{\mathrm{C-P}} = 6.8$ Hz, *cis*-CO), 197.89 (d, $J_{\mathrm{C-P}} = 27.0$ Hz, *trans*-CO), 198.91 (d, $J_{\mathrm{C-P}} = 28.6$ Hz, *trans*-CO), 197.89 (d, $J_{\mathrm{C-P}} = 27.0$ Hz, *trans*-CO). Anal. Calcd for $C_{30}H_{24}O_{14}P_2W_2$: C, 34.71; H, 2.33. Found: C, 34.53; H, 2.36.

**X-ray Structure Data.** General details are as follows: Nonius Kappa CCD diffractometer, $\phi$ and $\omega$ scans, Mo K$\alpha$ radiation ($\lambda = 0.710\,73$ Å), graphite monochromator, $T = 150$ K, structure solution with SIR97,[12] refinement against $F^2$ in SHELXL97[13] with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters.

Data collection for **7**: colorless plate, 0.20 × 0.14 × 0.12 mm; monoclinic, $P2_1/c$, $a = 17.0670(10)$ Å, $b = 13.4710(10)$ Å, $c = 16.3210(10)$ Å, $\beta = 115.1700(10)°$; $V = 3396.1(4)$ Å$^3$, $Z = 4$, $\rho_{\mathrm{calcd}} = 2.030$ g cm$^{-3}$, $\mu = 6.930$ cm$^{-1}$, $F(000) = 1976$, $\theta_{\max} = 30.03°$, *hkl* ranges −24 to +24, −18 to +16, −22 to +22, 16 351 data collected, 9903 unique data ($R_{\mathrm{int}} = 0.0256$), 7814 data with $I > 2\sigma(I)$, 437 parameters refined, GOF($F^2$) = 1.008, final *R* indices (R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$), R1 = 0.0290, wR2 = 0.0693, maximum/minimum residual electron density +1.300(0.142)/−1.512(0.142) e Å$^{-3}$.

Data collection for **9**: colorless plate, 0.20 × 0.20 × 0.14 mm; triclinic, $P\bar{1}$, $a = 8.3200(10)$ Å, $b = 10.2930(10)$ Å, $c = 14.1890(10)$ Å, $\alpha = 91.3990(10)°$, $\beta = 95.9020(10)°$, $\gamma = 112.7390(10)°$, $V = 1112.00(19)$ Å$^3$, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.709$ g cm$^{-3}$, $\mu = 5.293$ cm$^{-1}$, $F(000) = 560$, $\theta_{\max} = 29.99°$, *hkl* ranges −11 to +11, −14 to +14, −19 to +19, 9450 data collected, 6434 unique data ($R_{\mathrm{int}} = 0.0190$), 6049 data with $I > 2\sigma(I)$, 257 parameters refined, GOF($F^2$) = 1.058, final *R* indices (R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$), R1 = 0.0241, wR2 = 0.0629, maximum/minimum residual electron density +1.113(0.113)/−1.575(0.113) e Å$^{-3}$.

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**Supporting Information Available:** CIF files giving data for the X-ray crystal structure analyses of complexes **7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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