

Electronic Structure and Evolution of a Terminal Butadienylphosphinidene Complex

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The DFT study of the 1-butadienylphosphinidene complex $[\text{CH}_2=\text{CHCH}=\text{CHP}-\text{Cr}(\text{CO})_5]$ shows a delocalized structure with a short P–C bond at 1.789 Å and a long $\text{C}_\alpha=\text{C}_\beta$ double bond at 1.367 Å. The $\text{W}(\text{CO})_5$ 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 dihydroposphepines via a phospho-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 $[\text{RP}-\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) 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 π -system directly bonded to phosphorus will stabilize the phosphinidene by interaction with the p_z orbital. From this standpoint, the high-lying π -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 $[\text{RP}-\text{M}(\text{CO})_5]$, we performed DFT calculations³ on $[(E)\text{-CH}_2=\text{CHCH}=\text{CHP}-\text{Cr}(\text{CO})_5]$ (**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 $[\text{MeP}-\text{Cr}(\text{CO})_5]$ 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

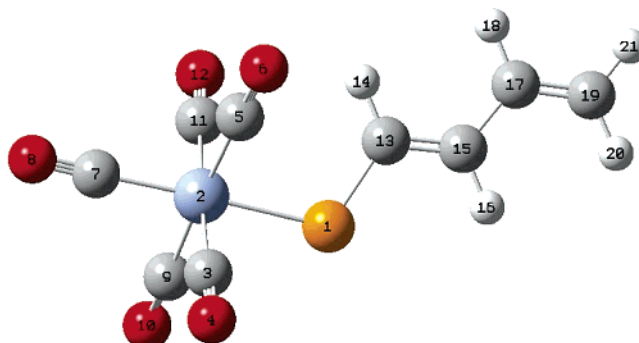


Figure 1. Computed structure of the (butadienylphosphinidene)-pentacarbonylchromium complex **1**. Significant bond lengths (Å) and angles (deg): P1–Cr2 = 2.305, P1–C13 = 1.789, C13–C15 = 1.367, C15–C17 = 1.445, C17–C19 = 1.346; Cr2–P1–C13 = 112.0.

complexes adopt a staggered conformation of the P–R and $\text{Cr}(\text{CO})_5$ 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 $\text{C}_\alpha=\text{C}_\beta$ double bond is long at 1.367 Å vs 1.346 Å for the terminal double bond. As expected,

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(1) Creve, S.; Pierloot, K.; Nguyen, M. T.; Vanquickenborne, L. G. *Eur. J. Inorg. Chem.* **1999**, 107. Grigoleit, S.; Aljiah, A.; Rozhenko, A. B.; Streubel, R.; Schoeller, W. W. *J. Organomet. Chem.* **2002**, 643–644, 223. Ehlers, A. W.; Lammertsma, K.; Baerends, E. J. *Organometallics* **1998**, 17, 2738. Frison, G.; Mathey, F.; Sevin, A. *J. Organomet. Chem.* **1998**, 570, 225.

(2) Marinetti, A.; Mathey, F. *Organometallics* **1984**, 3, 456. Lammertsma, K.; Hung, J.-T.; Chand, P.; Gray, G. M. *J. Org. Chem.* **1992**, 57, 6557. van Eis, M. J.; Nijbacker, T.; de Kanter, F. J. J.; de Wolf, W. H.; Lammertsma, K.; Bickelhaupt, F. J. *Am. Chem. Soc.* **2000**, 122, 3033. Vlaar, M. J. M.; Ehlers, A. W.; de Kanter, F. J. J.; Schakel, M.; Spek, A. L.; Lammertsma, K. *Angew. Chem., Int. Ed.* **2000**, 39, 2943.

(3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004.

(4) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.

(5) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.

(6) Compain, C.; Donnadieu, B.; Mathey, F. *Organometallics* **2006**, 25, 540.

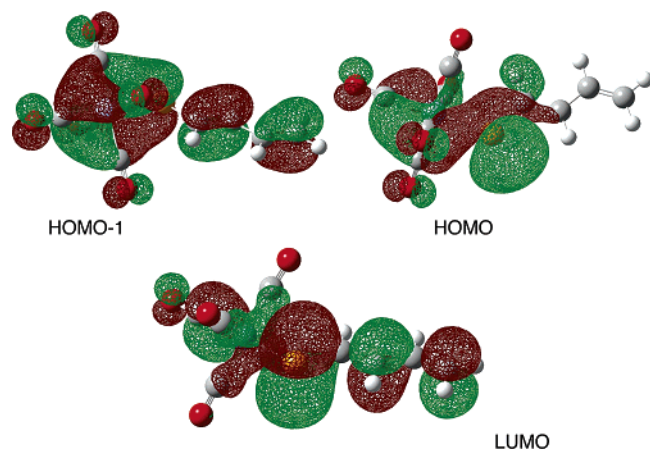
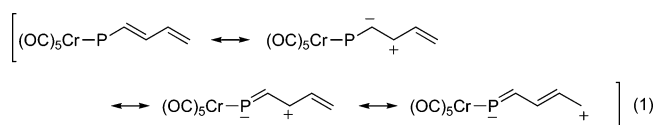


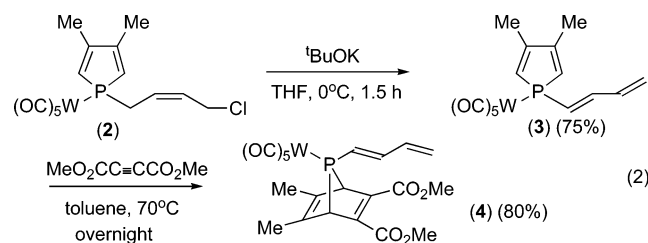
Figure 2. Frontier orbitals of **1**.

the Cr–P–C₄ 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_α, –0.606; C_β, –0.131; C_γ, –0.268; C_δ, –0.333. Thus, it appears that **1** is better represented by a mesomeric formulation as shown in eq 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 Ψ₂ 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_β, and C_δ (Figure 2).

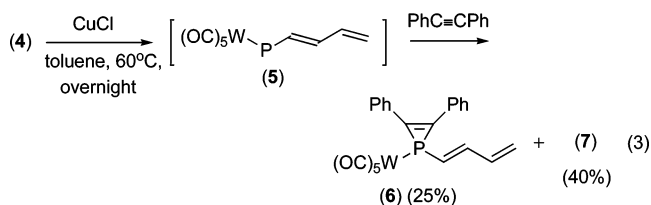
Our starting synthetic point was the 1-chlorobutenylphosphole complex **2**, whose preparation has been described in a previous work.⁷ The dehydrochlorination of the chlorobutenyl substituent by a strong base afforded the butadienylphosphole complex **3** in good yield (eq 2). The ¹³C NMR spectrum of **3** shows a



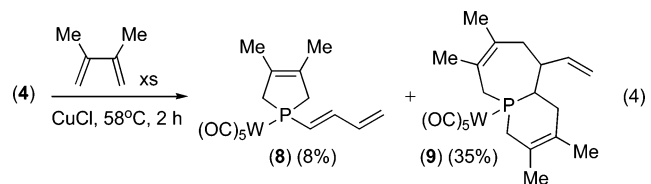
characteristic resonance for the terminal =CH₂ group as a singlet at 122.38 ppm (CDCl₃). The stereochemistry of the exocyclic PCH_α=CH_β unit was established by inspection of the ¹H NMR spectrum: H_α appears as a pseudo-triplet (J_{H-H} = J_{H-P} = 16.3 Hz) only compatible with the *E* stereochemistry.⁸ 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.

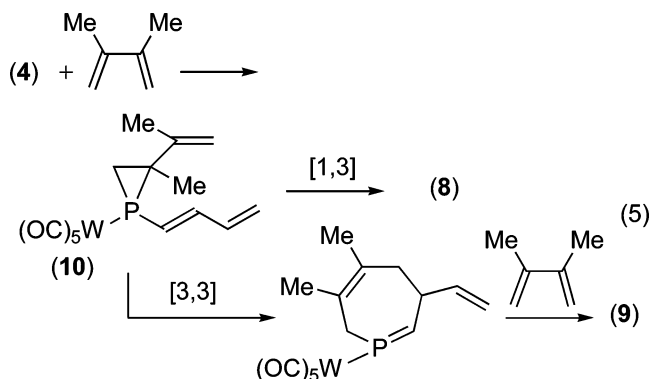
Complex **4** shows the characteristic deshielding of the ³¹P resonance at 205 ppm (CH₂Cl₂) and the characteristic ¹³C resonance for the terminal =CH₂ group at 123.19 ppm (CDCl₃). To check that **4** was a genuine precursor of the butadienylphosphinidene complex **5**, we investigated the reaction of **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 biphenyl compound (**7**), characterized by two singlet resonances at 48 and 148.6 ppm (eq 3). We shall discuss the structure of **7** later.



The phosphirene displays the characteristic shielding of its ³¹P resonance at –163.8 ppm (CDCl₃) and the terminal =CH₂ group at 122.91 ppm (CDCl₃). 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).



The ¹³C spectrum of the phospholene **8** shows the intracyclic CH₂ groups as a doublet at 44.48 ppm (¹J_{C-P} = 29.2 Hz) and the terminal CH₂ 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 scheme² or via a phospho-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).



(7) Tran Huy, N. H.; Gryaznova, T. V.; Ricard, L.; Mathey, F. *Organometallics* **2005**, *24*, 2930.

(8) Nelson, J. H. *Nuclear Magnetic Resonance Spectroscopy*; Prentice Hall: Upper Saddle River, NJ, 2003; p 161.

(9) Frison, G. Ph.D. Thesis, Paris VI University, November 13, 2000.

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

(b) Tran Huy, N. H.; Marinetti, A.; Ricard, L.; Mathey, F. *Organometallics* **1992**, *11*, 1438.

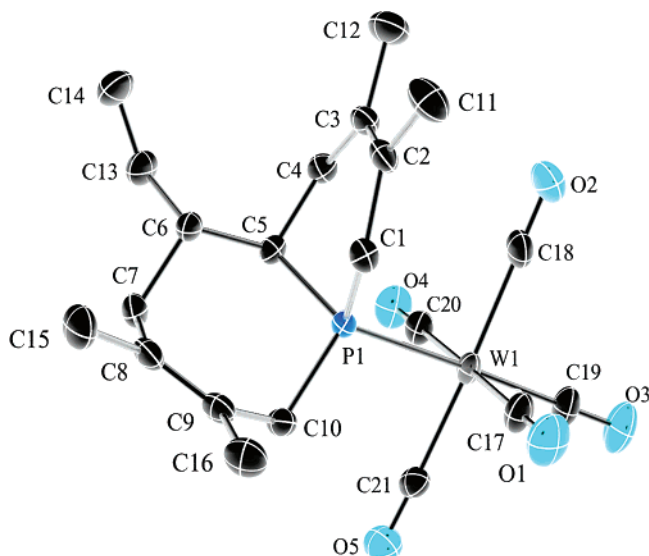
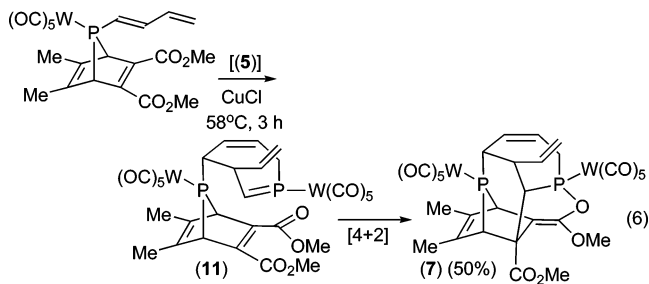


Figure 3. X-ray crystal structure of complex **9**. Thermal ellipsoids are scaled to enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg): P(1)–W(1) = 2.5187(6), P(1)–C(1) = 1.826(2), P(1)–C(5) = 1.842(2), P(1)–C(10) = 1.844(2); C(1)–P(1)–C(10) = 105.5(1), C(5)–P(1)–C(10) = 106.8(1), 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 biphenyl compound **7** as the single major product (eq 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 phosphalkene 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

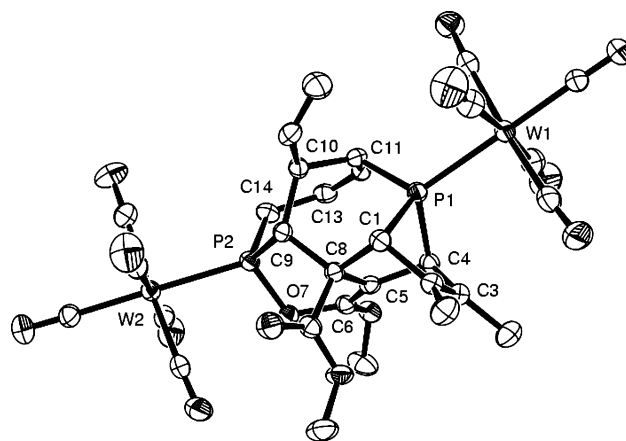


Figure 4. X-ray crystal structure of complex **7**. Thermal ellipsoids are scaled to enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg): W(1)–P(1) = 2.4957(8), W(2)–P(2) = 2.467(1), P(1)–C(1) = 1.849(3), P(1)–C(4) = 1.874(3), P(1)–C(11) = 1.886(3), P(2)–O(7) = 1.653(2), P(2)–C(9) = 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 ¹H, 75.47 for ¹³C, and 121.50 MHz for ³¹P. Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (¹H and ¹³C) and external 85% aqueous H₃PO₄ (³¹P). 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 ^tBuOK (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/CH₂Cl₂ (9/1) as the eluent. **3** was obtained as a yellow powder, yield 7.3 g (75%).

³¹P NMR (CDCl₃): δ 0.9. ¹H NMR (CDCl₃): δ 2.42 (s, 6H, Me), 5.55 (d, 1H, *J*_{H–H} = 10 Hz, =CH₂), 5.66 (d, 1H, *J*_{H–H} = 16.9 Hz, =CH₂), 5.98 (pseudo t, 1H, *J*_{H–H} = *J*_{H–P} = 16.3 Hz, PCH=), 6.58 (d, 2H, ²*J*_{H–P} = 36.7 Hz, ring =CH–P), 6.66 (m, 1H, =CH), 6.95 (m, 1H, =CH). ¹³C NMR (CDCl₃): δ 17.67 (d, *J*_{C–P} = 11.5 Hz, Me), 122.38 (s, =CH₂), 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, =CMe), 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 C₁₅H₁₃O₅–PW: 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/CH₂Cl₂ (1/1) as the eluent. **4** was obtained as a yellow powder, yield 5 g (80%).

³¹P NMR (CH₂Cl₂): δ 205.4. ¹H NMR (CDCl₃): 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, CH₂), 5.42 (d, 1H, *J*_{H–H} = 16.1 Hz, CH₂), 6.14 (pseudo t, 1H, *J*_{H–H} = *J*_{H–P} = 16.2 Hz, PCH=), 6.35–6.46 (m, 2H, =CH). ¹³C NMR (CDCl₃): 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, =CH₂), 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(CO₂Me)), 165.39 (d, *J*_{C–P} = 2.8 Hz, CO₂), 196.20 (d, *J*_{C–P} = 6.8 Hz, *cis*-CO), 198.43 (d, *J*_{C–P} = 25.4 Hz, *trans*-CO).

(11) Reviews: (a) Mathey, F.; Tran Huy, N. H.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938. (b) Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, *4*, 1127.

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/CH₂Cl₂ (9/1) as the eluent. The phosphirene complex **6** was thus obtained (0.06 g, 25%). Complex **7** was then eluted with hexane/CH₂Cl₂ (2/3), yield 0.15 g, 40%.

Data for **6** are as follows. ³¹P NMR (CDCl₃): δ -163.8. ¹H NMR (CDCl₃): δ 5.32 (d, 1H, $J_{H-H} = 9.8$ Hz, =CH₂), 5.43 (d, 1H, $J_{H-H} = 16.9$ Hz, =CH₂), 5.69 (pseudo t, 1H, $J_{H-H} = J_{H-P} = 16.6$ Hz, PCH=), 6.38 (m, 1H, =CH), 6.79 (m, 1H, =CH). ¹³C NMR (CDCl₃): 122.91 (s, =CH₂), 127.90 (d, $J_{C-P} = 6.7$ Hz, =C-), 129.19 (d, $J_{C-P} = 8.5$ Hz, =C-), 129.67 (s, =CH(Ph)), 130.63 (d, $J_{C-P} = 5.5$ Hz, =CH(Ph)), 130.95 (s, =CH(Ph)), 134.65 (d, $J_{C-P} = 6.3$ Hz, =CH), 135.65 (d, $J_{C-P} = 19.8$ Hz, =CH), 147.68 (d, $J_{C-P} = 13.7$ Hz, =CH), 196.22 (d, $J_{C-P} = 8.6$ Hz, CO), 198.22 (d, $J_{C-P} = 30.5$ Hz, CO). Mass spectrum (¹⁸⁴W): 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/CH₂Cl₂ (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. ³¹P NMR (CDCl₃): δ -12.1. ¹H NMR (CDCl₃): δ 1.75 (s, 6H, Me), 2.74–2.98 (m, 4H, CH₂P), 5.31 (d, 1H, $J_{H-H} = 9.8$ Hz, =CH₂), 5.40 (d, 1H, $J_{H-H} = 16.8$ Hz, =CH₂), 6.03 (pseudo t, 1H, $J_{H-H} = J_{H-P} = 15.8$ Hz, =CHP), 6.43 (m, 1H, =CH), 6.58 (m, 1H, =CH). ¹³C NMR (CDCl₃): 16.53 (d, $J_{C-P} = 7.9$ Hz, Me), 44.48 (d, $J_{C-P} = 29.2$ Hz, CH₂P), 122.21 (s, =CH₂), 130.15 (s, =C(Me)), 130.61 (d, $J_{C-P} = 35.4$ Hz, =CHP), 136.28 (d, $J_{C-P} = 17.0$ Hz, =CH), 143.46 (d, $J_{C-P} = 7.5$ Hz, =CH), 197.06 (d, $J_{C-P} = 7.2$ Hz, CO). Mass spectrum (CI, NH₃; ¹⁸⁴W): m/z 491 (M + H, 76%), 436 (100%).

Data for **9** are as follows. ³¹P NMR (CDCl₃): δ -23.2. ¹H NMR (CDCl₃): δ 1.60 (s, 3H, Me), 1.73 (s, 3H, Me), 1.75 (s, 6H, Me), 4.95 (d, 1H, $J_{H-H} = 16.9$ Hz, =CH₂), 5.03 (d, 1H, $J_{H-H} = 10.0$ Hz, =CH₂), 5.59 (m, 1H, =CH). ¹³C NMR (CDCl₃): 20.49 (s, Me), 21.10 (d, $J_{C-P} = 2.1$ Hz, Me), 22.20 (d, $J_{C-P} = 8.0$ Hz, Me), 22.66 (d, $J_{C-P} = 2.9$ Hz, Me), 28.69 (d, $J_{C-P} = 26.0$ Hz, CH₂), 36.32 (s, CH₂), 39.52 (d, $J_{C-P} = 19.8$ Hz, CH₂), 41.38 (d, $J_{C-P} = 3.6$ Hz, CH), 41.93 (s, CH₂), 42.10 (d, $J_{C-P} = 19.5$ Hz, CH-P), 115.01 (s, =CH₂), 120.84 (d, $J_{C-P} = 3.5$ Hz, =C-), 125.30 (d, $J_{C-P} = 10.2$ Hz, =C-), 126.05 (d, $J_{C-P} = 11.5$ Hz, =C-), 133.39 (d, $J_{C-P} = 6.5$ Hz, =C-), 143.33 (d, $J_{C-P} = 8.6$ Hz, =CH). Mass spectrum (CI, NH₃; ¹⁸⁴W): m/z 572 (M, 100%). Anal. Calcd for C₂₁H₂₅O₅PW: 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/CH₂Cl₂ (1/1) as the eluent. Complex **7** was recovered as yellow crystals (0.4 g, 50%).

Data for **7** are as follows. ³¹P NMR (CDCl₃): δ 48.0, 148.6. ¹³C NMR (CDCl₃): δ 14.83 (d, $J_{C-P} = 3.7$ Hz, Me), 15.28 (d, $J_{C-P} =$

2.7 Hz, Me), 38.61 (s, OMe), 41.05 (d, $J_{C-P} = 10.3$ Hz, P-CH₂), 51.71 (d, $J_{C-P} = 21.2$ Hz, P-CH), 53.76 (d, $J_{C-P} = 7.7$ Hz, OMe), 54.12 (dd, $J_{C-P} = 21.3$ and 5.8 Hz, P-CH), 55.18 (s, P-CH), 56.28 (s, P-CH), 56.50 (d, $J_{C-P} = 18.6$ Hz, P-CH), 74.96 (s, C), 98.32 (d, $J_{C-P} = 8.7$ Hz, =C), 118.37 (s, =CH₂), 122.94 (dd, =CH), 123.62 (s, =CH), 133.40 (d, $J_{C-P} = 10.5$ Hz, =CMe), 138.75 (d, $J_{C-P} = 14.6$ Hz, =CMe), 141.13 (d, $J_{C-P} = 14.7$ Hz, vinyl =CH), 152.52 (s, =COO), 172.76 (s, CO₂Me), 195.75 (d, $J_{C-P} = 7.6$ Hz, *cis*-CO), 196.26 (d, $J_{C-P} = 6.8$ Hz, *cis*-CO), 197.89 (d, $J_{C-P} = 27.0$ Hz, *trans*-CO), 198.91 (d, $J_{C-P} = 28.6$ Hz, *trans*-CO), 197.89 (d, $J_{C-P} = 27.0$ Hz, *trans*-CO). Anal. Calcd for C₃₀H₂₄O₄P₂W₂: 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, ϕ and ω scans, Mo K α radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 150$ K, structure solution with SIR97,¹² refinement against F^2 in SHELXL97¹³ with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters.

Data collection for **7**: colorless plate, $0.20 \times 0.14 \times 0.12$ mm; monoclinic, $P2_1/c$, $a = 17.0670(10)$ Å, $b = 13.4710(10)$ Å, $c = 16.3210(10)$ Å, $\beta = 115.1700(10)^\circ$; $V = 3396.1(4)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.030$ g cm⁻³, $\mu = 6.930$ cm⁻¹, $F(000) = 1976$, $\theta_{\text{max}} = 30.03^\circ$, hkl ranges -24 to $+24$, -18 to $+16$, -22 to $+22$, 16 351 data collected, 9903 unique data ($R_{\text{int}} = 0.0256$), 7814 data with $I > 2\sigma(I)$, 437 parameters refined, $\text{GOF}(F^2) = 1.008$, 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, $0.20 \times 0.20 \times 0.14$ mm; triclinic, $P\bar{1}$, $a = 8.3200(10)$ Å, $b = 10.2930(10)$ Å, $c = 14.1890(10)$ Å, $\alpha = 91.3990(10)^\circ$, $\beta = 95.9020(10)^\circ$, $\gamma = 112.7390(10)^\circ$, $V = 1112.00(19)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.709$ g cm⁻³, $\mu = 5.293$ cm⁻¹, $F(000) = 560$, $\theta_{\text{max}} = 29.99^\circ$, hkl ranges -11 to $+11$, -14 to $+14$, -19 to $+19$, 9450 data collected, 6434 unique data ($R_{\text{int}} = 0.0190$), 6049 data with $I > 2\sigma(I)$, 257 parameters refined, $\text{GOF}(F^2) = 1.058$, 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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(12) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single-crystal data.

(13) Sheldrick, G. M. SHELXL-97; Universität Göttingen, Göttingen, Germany, 1997.