Notes

Synthesis of Novel O,P,C-Cage Complexes via Thermal C−O Ring Opening of an Oxaphosphirane $W(CO)_5$ Complex

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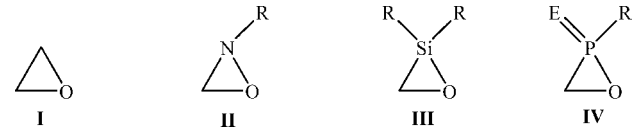
Summary: A facile and highly stereoselective synthesis of novel O,P,C-cage complexes via thermal C−O ring opening of an oxaphosphirane $W(CO)_5$ complex is described. All compounds were unambiguously characterized by elemental analysis, multinuclear NMR, IR, MS, and single-crystal X-ray diffraction studies.

Introduction

Epoxides **I** (oxiranes) (Chart 1) are important building blocks in organic synthesis and polymer chemistry.[1,2] In contrast, oxaziridines **II**, in which one of the CR_2 moieties is (formally) exchanged for an NR group, have received much less attention, which is also true for the silicon (**III**) and phosphorus analogues (**IV**) (Chart 1). The latter have been (mostly) claimed as reactive intermediates,[3] and up to now only one stable derivative of **III**[4] has been described; **IV** (E = lone pair) is still unknown. Theoretical calculations were recently performed on derivatives of **IV** (E = lone pair)[5] and **IV** (E = two R groups).[6] In 1978, $\sigma^4\lambda^5$-oxaphosphiranes **IV** (E = NR) were synthesized via a [2+1] cycloaddition reaction of an iminophosphine derivative and hexafluoroacetone.[7] Oxaphosphirane transition-metal complexes **IV** (E = $W(CO)_5$), first described in 1990 by Mathey and co-workers, were prepared by epoxidation of phosphaalkene complexes with *meta*-chloroperbenzoic acid.[8]

Chart 1. Epoxides I and Related Three-Membered Ring Systems II−IV (R denotes ubiquitous organic substituents; E denotes a lone pair, R_2, O, NR, or a $W(CO)_5$ group)



I **II** **III** **IV**

Later, thermal ring cleavage of a 2*H*-azaphosphirene $W(CO)_5$ complex in the presence of an aldehyde[9] or a ketone[10] enabled access to derivatives having *P*-alkyl substituents. Recent attempts to exploit this route using a *P*-C_5Me_5-substituted 2*H*-azaphosphirene complex and benzaldehyde failed, and a 1,3,4-dioxaphospholane complex with a symmetrical substitution pattern at the carbon centers was obtained instead.[11] Very recently, we gained novel access to *P*-bis(trimethylsilyl)methyl oxaphosphirane tungsten complexes using a transient Li/Cl phosphinidenoid tungsten complex, which reacted *in situ* with benz- or isobutyraldehyde.[12] To the best of our knowledge neither *P*- nor *C*-functional oxaphosphirane complexes are known so far. Here, the synthesis and structural characterization of the first *P*-functional oxaphosphirane complex and its selective transformation into novel O,P,C-cage complexes are described.

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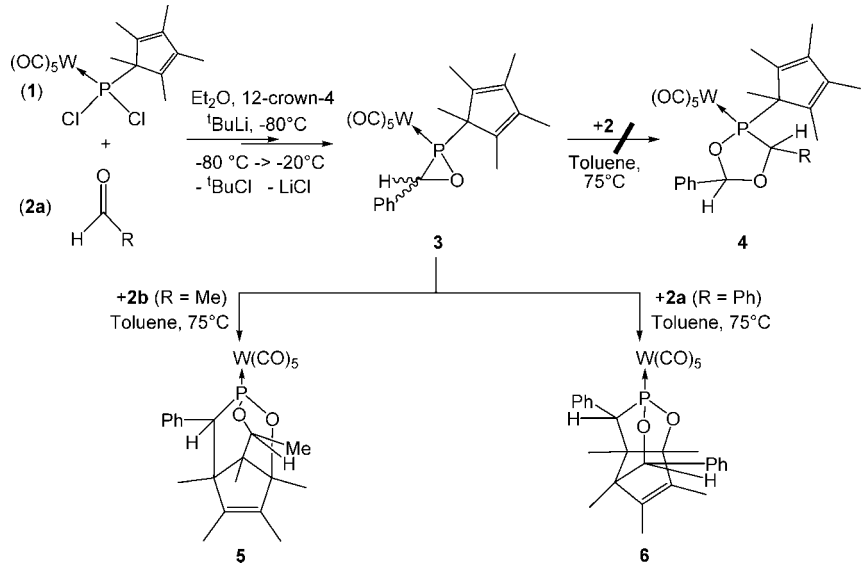
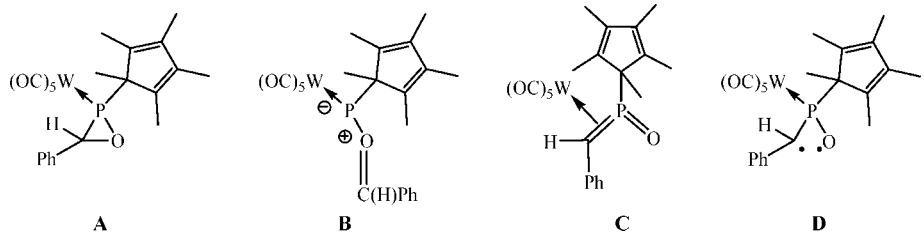
Scheme 1. Synthesis of Oxaphosphirane Complex 3 Using Dichloro(organo)phosphane Complex 1 and Benzaldehyde (2a), and Thermal Ring-Opening Reactions of 3



Scheme 2. Oxaphosphirane Complex 3 (A) and Isomeric Forms (B−D)



Results and Discussion

The reaction of dichloro(organo)phosphane complex **1**[13] with *tert*-butyllithium in diethyl ether at low temperature in the presence of 12-crown-4 and benzaldehyde (**2a**) afforded selectively the oxaphosphirane complex **3** (Scheme 1). We assume that an intermediate Li/Cl exchange reaction occurred in **1**, thus leading to a transient Li/Cl phosphinidenoid complex.[12] As we wished to gain access to asymmetrically substituted 1,3,4-dioxaphospholane complexes **4**, we studied the thermal reaction of complex **3** with aldehydes **2a**,**b** in toluene. To our surprise, we did not obtain the expected heterocycle complexes **4**. Instead, complexes **5** and **6** were obtained regioselectively, which have novel, different O,P,C-cage ligands, showing that an oxaphosphirane C−O ring opening had occurred (Scheme 1). It is also remarkable that the former *P*-C_5Me_5 group was transformed into a partially saturated ring that is incorporated into different polycyclic structures: Noteworthy is that a P−C bond cleavage must have occurred at one point.

Although we do not have direct evidence for primarily formed intermediates, the observation that complex **4** was not detected is important, and therefore we conclude that no valence isomerization (**A** → **B**) of **3** (**A**) to the intermediate phosphacarbonyl-ylide complex **B** had occurred. Further support stems from the observation that the related *P*-bis(trimethylsilyl)methyl derivative of complex **3**[9] does not react with aldehydes **2a**,**b** under the same conditions.[14] Therefore, a cleavage of the C−O bond in **3** (**A**) seems to occur, generating either the η^2-coordinated alkylidene(oxo)phosphorane complex **C** or the acyclic diradical complex **D** (Scheme 2), which rapidly react with the *P*-C_5Me_5 group.[15,16]

Both could be starting points for multistep reactions leading finally to complexes **5** and **6**. The following arguments disfavor other conceivable primary steps: (1) homolytic $P-C^{Cp^*}$ bond cleavage reactions of related three-membered *P*-heterocyclic ligands having *P*-C_5Me_5 substituents such as phosphiranes and 1*H*-phosphirenes are unknown, and (2) intermolecular [4 + 2] cycloaddition reactions of such *P*-bonded C_5Me_5 groups have not been observed before.[17] Recently, an interesting ring enlargement of a *P*-bonded C_5Me_5 group (of a dinuclear μ_2-phosphinidene complex) has been observed to occur during reaction with a phosphaalkyne derivative, leading finally to a 1,2-diphospha-cyclooctatetraene complex.[18]

The molecular structures of complexes **3**, **5**, and **6** were unambiguously established by elemental analysis, NMR and IR spectroscopy, and single-crystal X-ray diffraction studies (Figure

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(16) In principle, complex **8** could be formed directly via homolytic C−O bond cleavage from **3**; we are currently trying to calculate the different barriers for the P−C, P−O, and C−O cleavage reactions in oxaphosphirane complexes. For the problem of C−C vs C−O bond cleavage in oxiranes, see: Tian, F.; Baker, J. M.; Smart, B. E. *J. F. Chem.* **2002**, *114*, 107–111.

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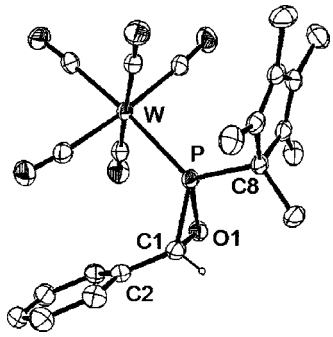

Figure 1. Structure of complex **3** (50% probability level; hydrogen atoms except H1 are omitted for clarity). Selected bond lengths [Å] and angles [deg]: W−P 2.4694(7), P−O(1) 1.667(2), P−C(1) 1.805(3), P−C(8) 1.855(3), O(1)−C(1) 1.468(3), O(1)−P−C(1) 49.84(11), C(1)−O(1)−P 69.97(15), O(1)−C(1)−P 60.20(14).

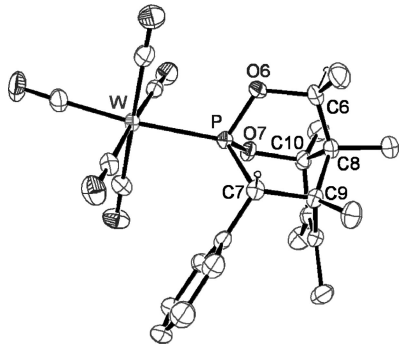

Figure 2. Structure of complex **5** (50% probability level; hydrogen atoms except H6 and H7 are omitted for clarity). Selected bond lengths [Å] and angles [deg]: W−P 2.453(6), P−O(6) 1.606(17), P−O(7) 1.601(14), P−C(7) 1.845(2), O(6)−C(6) 1.475(3), O(7)−C(10) 1.501(3), C(6)−C(8) 1.529(3), C(7)−C(9) 1.584(3); O(6)−P-O(7) 101.92(8), O(6)−P-C(7) 99.16(9), O(7)−P-C(7) 104.38(9), C(6)−O(6)−P 115.66(14), C(10)−O(7)−P 116.71(12), C(9)−C(7)−P 109.75(13), O(6)−C(6)−C(8) 112.49(19).

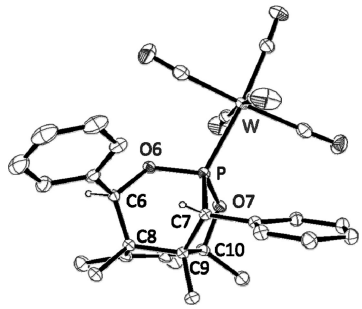

Figure 3. Structure of complex **6** (50% probability level; hydrogen atoms except H6 and H7 are omitted for clarity). Selected bond lengths [Å] and angles [deg]: W−P 2.457(4), P−O(6) 1.614(11), P−O(7) 1.609(10), P−C(7) 1.829(14), O(6)−C(6) 1.451(15), O(7)−C(10) 1.488(17), C(6)−C(8) 1.579(19), C(7)−C(9) 1.564(19), O(6)−P−O(7) 106.80(6), O(6)−P−C(7) 100.24(6), O(7)−P−C(7) 94.29(6), C(6)−O(6)−P 124.51(9), C(10)−O(7)−P 112.58(8), C(9)−C(7)−P 98.43(9), O(6)−C(6)−C(8) 112.16(10).

1, 2, and 3). The NMR data of oxaphosphirane complex **3** are closely related to those of the *P*-bis(trimethylsilyl)methyl derivative[9] reported recently, although the ^{31}P resonance of **3** (δ = 31.6 ppm; ^{1}J(W,P) = 309.0 Hz) is upfield shifted by a $\Delta\delta$ value of 10 ppm, and also the oxaphosphirane ring carbon resonance is found at 55.5 ppm (J(P,C) = 17.5 Hz), which is in the upfield region. The ^{31}P{^{1}H} NMR data of the polycycles **5** and **6** are very similar to each other (δ = 152.7 ppm, ^{1}J(W,P) = 334.4 Hz (**5**) and δ = 155.1 ppm, ^{1}J(W,P) = 334.4 Hz (**6**)) but different from the expected 1,3,4-dioxaphospholanes, which show values at approximately 138 ppm and phosphorus−tungsten coupling constants of 280−285 Hz. The structural differences of the cages of **5** and **6** are revealed through the phosphorus−hydrogen couplings with the C(Ph)H proton: whereas the ^{31}P and ^{1}H NMR spectra of **6** clearly showed a coupling constant of 12.8 Hz, a much smaller coupling constant of 4.5 Hz was determined (only) from the ^{1}H NMR spectrum of **5**.

The solid state structures of **5** and **6**, shown in Figures 1 and 2, unambiguously confirm the constitutions. The main differences between **5** and **6** are found within the particular cage moieties but shall not be discussed further; the geometries at phosphorus are quite similar and the P−O is ca. 1.61 Å and P−C bond distances are ca. 1.83 Å; such values are also found for polycyclic phosphite and O,P,C-cage compounds.[19] The bond angle sums $\sum$ °P of the PR_3 units are 305.5° (**5**) and 301.3° (**6**), respectively.

Conclusions

Herein, we describe facile synthesis of the first *P*-functional oxaphosphirane complex and its use in thermal reactions that lead to the regioselective formation of novel O,P,C-cage ligands. It illustrates nicely the versatility of *P*-bonded C_5Me_5 groups in P,C-cage synthesis[20] and broadens the applicability using aldehydes as new cooperative building blocks. Current studies are devoted to elucidate the mechanism, especially with regard to the discussed reactive intermediates, and to explore the chemistry of the uncoordinated O,P,C-cage ligands.

Experimental Section

All operations were performed in an atmosphere of purified and dried argon. Solvents were distilled from sodium. NMR data were recorded on a Bruker Avance 300 spectrometer at 30 °C using C_6D_6 (**3**) or $CDCl_3$ (**5**, **6**) as solvent and internal standard; shifts are given relative to tetramethylsilane (^{13}C: 75.5 MHz) and 85% H_3PO_4 (^{31}P: 121.5 MHz). Mass spectra were recorded on a Kratos MS 50 spectrometer (EI, 70 eV); only *m*/*z* values are given. Elemental analyses were performed using an Elementa (Vario EL) analytical gas chromatograph. Infrared spectra were collected on FT-IR Nicolet 380. Melting points were obtained on a Büchi 535 capillary apparatus. X-ray crystallographic analysis of **3**, **5**, and **6**: Data were collected on a Nonious KappaCCD diffractometer at 123 K using Mo Kα radiation (λ = 0.71073 Å) (**3**, **5**) and a Bruker SMART diffractometer at 133 K (**6**). The structures were refined by full-matrix least-squares on F^2 (SHELXL-97[21]). All non-hydrogens were refined anisotropically. The hydrogen atoms were included in calculated positions using a riding model.

Synthesis of Complex 3. To a solution of 230 mg (0.41 mmol) of **1** in 5 mL of diethyl ether were added 74 μL (0.46 mmol) of 12-crown-4 and then 46 μL (0.46 mmol) of benzaldehyde. The solution was cooled to −80 °C, and a solution, prepared from 0.3 mL (0.46 mmol) of *tert*-butyllithium (1.5 mol/L in pentane) and 5 mL of diethyl ether at −80 °C, was added dropwise. The solutions were then stirred for 90 min while gently warming to −20 °C. The

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solvents were then removed *in vacuo* (ca. 0.01 bar), and the residue was extracted with 20 mL of *n*-pentane. The product was purified by column chromatography (Al_2O_3, −10 °C) using (1) petroleum ether and (2) a mixture of petroleum ether with diethyl ether (95:5). After evaporation the crude product was washed with *n*-pentane at −70 °C.

3: pale yellow solid; yield 54 mg (0.09 mmol, 22%); mp 103 °C (dec). ^{1}H NMR: δ 0.83 (d, 3H, ^3J(P,H) = 11.3 Hz, Cp*(C1)-CH_3), 1.65 (m, 6H, Cp*-CH_3), 1.68 (s, 3H, Cp*-CH_3), 1.93 (s, 3H, Cp*-CH_3), 4.23 (s, 1H, POCH), 7.05−7.37 (m, 5H, Ph). ^{13}C{^{1}H} NMR: δ 9.5 (d, J(P,C) = 3.2 Hz, Cp*-CH_3), 10.1 (d, J(P,C) = 2.3 Hz, Cp*-CH_3), 10.2 (d, J(P,C) = 1.3 Hz, Cp*-CH_3), 10.6 (d, J(P,C) = 1.6 Hz, Cp*-CH_3), 12.0 (d, J(P,C) = 4.8 Hz, Cp*(C^1−CH_3), 55.5 (d, J(P,C) = 17.5 Hz, PCO), 63.0 (d, ^1J(P,C) = 10.0 Hz, Cp*(C1)), 125.0 (d, J(P,C) = 2.9 Hz, Ph), 127.2 (d, J(P,C) = 2.3 Hz, Ph), 127.5 (d, J(P,C) = 2.3 Hz, Ph), 131.6 (d, J(P,C) = 7.4 Hz, Cp*), 134.0 (s, Ph), 136.8 (d, J(P,C) = 1.6 Hz, Cp*), 140.7 (d, J(P,C) = 6.1 Hz, Cp*), 143.0 (d, J(P,C) = 7.8 Hz, Cp*), 194.8 (d, ^2J(P,C) = 8.4 Hz, J(W,C) = 125.2 Hz, *cis*-CO), 197.3 (d, ^2J(P,C) = 37.5 Hz, *trans*-CO). ^{31}P{^{1}H} NMR: δ = 31.6 (s_{Sat}, ^1J(W,P) = 309.0 Hz). MS: *m*/*z* (%): 596 (17) [$(M)^+$]. IR (KBr; ν(CO)): $\tilde{\nu}$ 1937 (m), 1992 (s), 2074 (s) [cm^{-1}]. Aanl. Calcd: C 44.32 H 3.55. Exptl: C 44.39 H 3.69. X-ray crystallographic analysis: Suitable pale yellow single crystals were obtained from concentrated *n*-pentane solutions upon slow cooling to 4 °C. $C_{22}H_{21}O_6PW$; crystal size 0.60 × 0.40 × 0.40 mm^3, triclinic, $P(-1)$, a = 9.4880(5) Å, b = 10.3300(4) Å, c = 13.0830(6) Å, α = 101.576(2)°, β = 109.730(2)°, γ = 103.089(2)°, V = 1120.65(9) $Å^3$, Z = 2, $2\theta_{max}$ = 58°, collected (independent) reflections = 12 415 (5728), R_{int} = 0.0426, μ = 5.260 mm^{-1}, 276 refined parameters, R_1 (for $I > 2\sigma(I)$) = 0.0256, wR_{21} (for all data) = 0.0609, max./min. residual electron density = 1.788/−1.822 e $Å^{-3}$.

General Procedure for the Synthesis of Complexes 5 and 6. To a solution of 208 mg (0.35 mmol) of **3** in 1.5 or 2.8 mL of toluene was added 1.5 mL (26.5 mmol) of acetaldehyde (**5**) or 39 μL (0.38 mmol) of benzaldehyde (**6**), and the reaction mixtures were stirred at 75 °C for 4 h. The solvents were removed *in vacuo* (ca. 0.01 bar), and the residues were extracted with 15 mL of petroleum ether. After evaporation the crude product was washed with *n*-pentane at −20 °C.

5: colorless solid; yield 152 mg (0.237 mmol, 68%); mp 218 °C (dec). Selected NMR data: ^{1}H NMR: δ 0.71 (q, J(H,H) = 1.1 Hz, 3H, C^{cage}-CH_3), 0.89 (s, 3H, C^{cage}-CH_3), 1.30 (d, J(P,H) = 0.9 Hz, 3H, C^{cage}-CH_3), 1.42 (s, 3H, C^{cage}-CH_3), 1.66 (d, J(H,H) = 6.9 Hz, 3H, C(H)-CH_3), 1.71 (q, J(H,H) = 1.1 Hz, 3H, C^{cage}-CH_3), 2.87 (d, J(P,H) = 4.5 Hz, 1H, C(H)Ph), 4.66 (dq, J(P,H) = 3.0 Hz (d), J(H,H) = 6.9 Hz (q), 1H, C(H)Me), 7.16−7.37 (m_c, 5H, Ph). ^{13}C{^{1}H} NMR: δ 8.8 (s, C^{cage}-CH_3), 11.0 (s, C^{cage}-CH_3), 16.4 (d, J(P,C) = 1.9 Hz, C^{cage}-CH_3), 16.9 (d, J(P,C) = 2.3 Hz, C^{cage}-CH_3), 18.4 (d, J(P,C) = 2.3 Hz, C(H)CH_3), 18.7 (d, J(P,C) = 4.2 Hz, C^{cage}-CH3), 49.0 (d, J(P,C) = 22.3 Hz, C^{cage}), 54.3 (d, J(P,C) = 4.2 Hz, C^{cage}), 54.7 (d, J(P,C) = 21.7 Hz, C(H)Ph), 74.9 (d, J(P,C) = 6.8 Hz, C(H)CH_3), 93.2 (d, J(P,C) = 6.5 Hz, C^{cage}), 126.2 (d, J(P,C) = 1.6 Hz, Ph (C21/23)), 127.1 (s, p-Ph (C22)), 127.5 (d, J(P,C) = 1.3 Hz, Ph), 129.3 (d, J(P,C) = 9.4 Hz, Ph), 130.9 (d, J(P,C) = 10.7 Hz, Ph), 133.0 (s, C^{cage}), 129.3 (d, J(P,C) = 9.4 Hz, Ph), 141.5 (s, C^{cage}), 194.5 (d_{Sat}, J(W,C) = 125.8 Hz, J(P,C) = 9.7 Hz, *cis*-CO), 198.5 (d, J(P,C) = 32.7 Hz, *trans*-CO). ^{31}P NMR: δ 152.7 (br, s_{Sat}, ^1J(W,P) = 334.4 Hz). MS: *m*/*z* (%): 640 (62) [$(M)^+$]. IR (KBr; ν(CO)): $\tilde{\nu}$ 1924 (s), 1955 (s), 1991 (m), 2075 (m) [cm^{-1}]. Anal. Calcd: C 45.02 H 3.94. Exptl: C 44.96 H 3.96. X-ray crystallographic analysis: Suitable colorless single crystals were obtained from concentrated *n*-pentane/diethyl ether solutions upon slow cooling to 4 °C. $C_{24}H_{25}O_7PW$; crystal size 0.40 × 0.40 × 0.30 mm^3, monoclinic, $P2_1/n$, a = 10.4536(2) Å, b = 15.8144(4) Å, c = 14.8700(4) Å, β = 99.6078(15)°, V = 2423.79(10) $Å^3$, Z = 4, $2\theta_{max}$ = 60°, collected (independent) reflections = 26 294 (7065), R_{int} = 0.0479, μ = 4.873 mm^{-1}, 304 refined parameters, R_1 (for $I > 2\sigma(I)$) = 0.0224, wR_{21} (for all data) = 0.0438, max./min. residual electron density = 1.699/−1.139 e $Å^{-3}$.

6: colorless solid; yield 50 mg (0.071 mmol, 20%); mp 170−171 °C. Selected NMR data: ^{1}H NMR: δ 0.66 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 4.08 (s, 1H, C(H)Ph), 5.12 (d, J(P,H) = 12.8 Hz, 1H, C(H)Ph), 7.20−7.38 (m_c, 10H, Ph). ^{13}C{^{1}H} NMR: δ 10.1 (s, C^{cage}-CH_3), 10.6 (s, C^{cage}-CH_3), 18.6 (d, J(P,C) = 5.4 Hz, C^{cage}-CH_3), 19.0 (s, C^{cage}-CH_3), 21.1 (d, J(P,C) = 4.2 Hz, C^{cage}-CH_3), 55.8 (s, C^{cage}), 56.1 (d, J(P,C) = 22.1 Hz, C^{cage}-Ph), 60.1 (d, J(P,C) = 3.6 Hz, C^{cage}), 87.6 (d, J(P,C) = 13.1 Hz, C^{cage}-Ph), 104.0 (d, J(P,C) = 9.5 Hz, C^{cage}), 127.5 (s, Ph), 127.8 (s, Ph), 128.5 (s, Ph), 128.9 (s, Ph), 134.9 (d, J(P,C) = 5.4 Hz, C^{cage}), 135.4 (s, C^{cage}), 138.4 (s, C^{cage}), 138.6 (d, J(P,C) = 1.2 Hz, C^{cage}), 195.5 (d_{Sat}, J(W,C) = 125.8 Hz, J(P,C) = 9.5 Hz, *cis*-CO), 198.6 (d, J(P,C) = 33.4 Hz, *trans*-CO). ^{31}P NMR: δ 155.1 (d_{Sat}, J(W,P) = 334.4 Hz, J(P,H) =12.7 Hz); MS: *m*/*z* (%): 702 (100) [$(M)^+$]. IR (KBr; ν(CO)): $\tilde{\nu}$ 1929 (s), 1935 (s), 1983 (m), 2074 (m) [cm^{-1}]. Anal. Calcd: C 49.59 H 3.87. Exptl: C 49.58 H 3.99. X-ray crystallographic analysis: Suitable colorless single crystals were obtained from concentrated diethyl ether solutions. $C_{29}H_{27}O_7PW$, crystal size 0.27 × 0.21 × 0.15 mm, triclinic, space group $P(-1)$, a = 8.8233(8) Å, b = 10.7260(10) Å, c = 15.0798(14) Å, α = 92.218(4)°, β = 105.029(4)°, γ = 93.583(4)°, U = 1373.4(2) $Å^3$, Z = 2, $2\theta_{max}$ 61°, collected (independent) reflections 29 773 (8358), R_{int} = 0.022, μ = 4.31 mm^{-1}, 348 refined parameters, R_1 (for $I > 2\sigma(I)$) = 0.0152, wR_{21} (for all data) = 0.0375, max./min. residual electron density = 1.14/−0.36 e $Å^{-3}$.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data of **3**, **5**, and **6** have also been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-647516 (**3**), CCDC-663345 (**5**), and CCDC-671764 (**6**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data _request/cif.

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