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Annelation of Phosphole-Substituted Fischer Carbene Complexes by Alkynes

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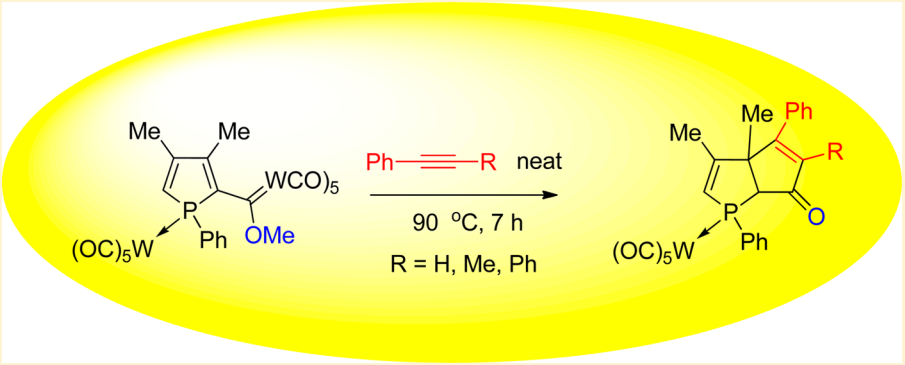
Supporting Information



ABSTRACT: The reaction of 1-phenyl-2-lithio-3,4-dimethylphosphole with $W(CO)_6$ at −90 °C followed by methyl triflate at room temperature gives the complex [(phosphol-2-yl)methoxycarbene]pentacarbonyltungsten (**1**). This complex reacts with sulfur to give the corresponding complex [methyl (phosphol-2-yl)thiocarboxylate]pentacarbonyltungsten (**2**), in which tungsten has migrated from the carbene to phosphorus. The reaction of **3** with alkynes at 90 °C gives the corresponding phospholene-annelated cyclopentenones **5** without the need for a nickel catalyst. In one case, an intermediate vinylketene rearranges by an intramolecular Diels−Alder reaction to give the tricyclic compound **6**. All of the products have been characterized by X-ray crystal structure analysis.

INTRODUCTION

In contrast to furans, thiophenes, and pyrroles, phospholes are essentially nonaromatic[1] as a result of the pyramidality of the heteroatom. Their weak aromatic stabilization energy (ASE)[2] mainly results from a σ^*/π hyperconjugation between the exocyclic P−R bond and the dienic system. From a practical standpoint, this weak ASE means that access to functional phospholes is far less simple than for the classical heteroles. In a different field, Fischer carbene complexes have seen an extraordinary development of their applications in organic synthesis.[3] Combining the chemistry of Fischer carbene complexes with phospholes was thus quite appealing, and our preliminary results[4] immediately showed unique interactions between the phosphole dienic system and the carbene−metal bond with no equivalent in the furan, thiophene, and pyrrole derivatives.[5] In this report, we wish to describe additional examples of this nonconventional chemistry, including an annelation of the phosphole ring by reaction with alkynes.

RESULTS AND DISCUSSION

In our preceding report, we described the phosphole-carbene derivative as a P−$W(CO)_5$ complex, but the ^{31}P monitoring of the crude reaction mixture also showed a peak corresponding very probably to the free species. By using only 1 equiv of $W(CO)_6$ per phosphole instead of 2 equiv as in our previous experiments, we managed to change the ratio between the free and complexed species and to isolate the tervalent phosphole carbene **1** (eq 1).

At 316.94 ppm, the ^{13}C carbenic chemical shift of **1** is practically identical with that of its P−$W(CO)_5$ complex (**3**). The X-ray crystal structure of **1** is shown in Figure 1. The structural parameters of **1** and its P−$W(CO)_5$ complex are quite similar. The C═W bond is slightly longer in **1** than in **3** (2.202(2) vs 2.173(4) Å), and the ring−carbene bond is slightly shorter (1.462(3) vs 1.475(6) Å), but these data are probably not significant.

In order to test the reactivity of the trivalent phosphorus in **1**, we performed the reaction with sulfur under mild conditions (room temperature, overnight). To our surprise, tungsten shifted from carbon to phosphorus and a thiocarboxylate was formed (eq 2).

The reaction is quasi-quantitative. The thiocarbonyl group of **2** appears at 204.6 ppm in the ^{13}C NMR spectrum, and the P−W coupling is 225 Hz. The X-ray crystal structure is shown in Figure 2. The thiocarboxylate and the dienic system are practically coplanar (interplane angle 6.97°). We have found a similar reaction in the literature involving sulfur, CO, and a

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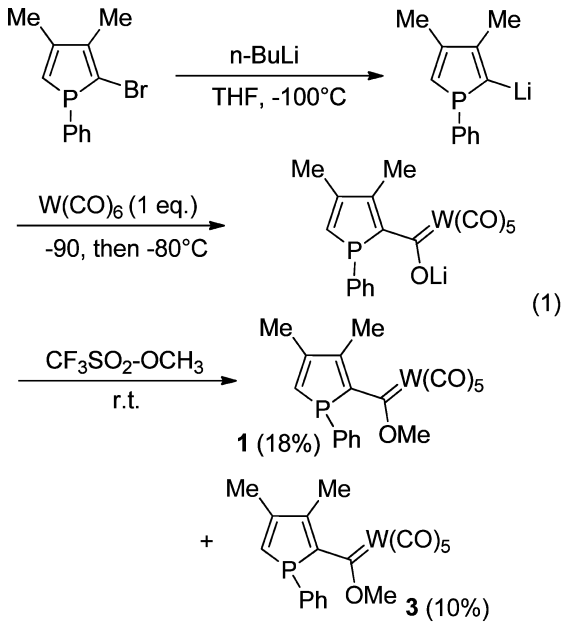


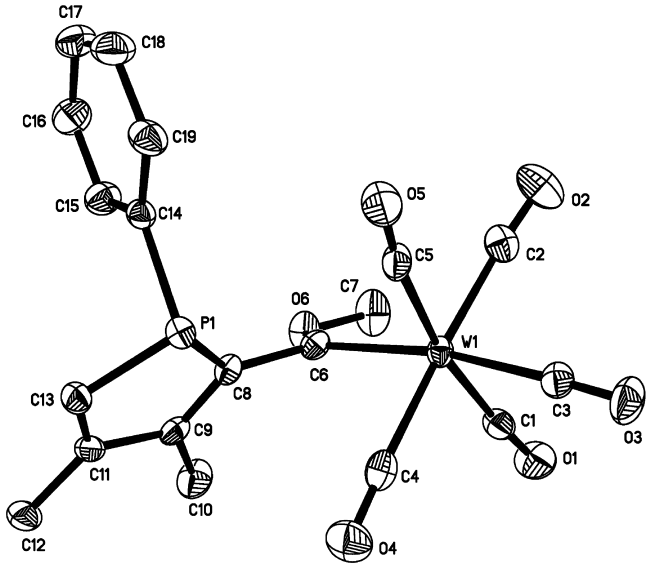
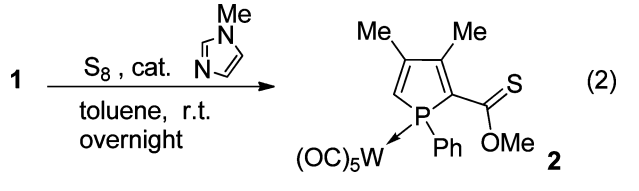


Figure 1. X-ray crystal structure of the phosphole-substituted Fischer carbene complex **1**. Main distances (Å) and angles (deg): P−C14 1.836(3), P−C8 1.820(2), P−C13 1.785(3), C8−C9 1.373(3), C9−C11 1.470(4), C11−C13 1.347(4), C8−C6 1.462(3), C6−O6 1.327(3), C6−W1 2.202(2); C8−P−C13 90.04(11), O6−C6−C8 106.7(2), O6−C6−W1 130.62(17), C8−C6−W1 122.19(17).



Fischer carbene−$Cr(CO)_5$ complex leading to a thiocarboxylate and $Cr(CO)_6$.[6] Here, the intramolecular P-ligand plays the role assigned to CO in the published work. This result shows that the carbene unit is more reactive than the tricoordinate phosphorus.

In our previous work, we described the curious reaction of styrene with the P−$W(CO)_5$ complex of **1** (**3**). As a logical

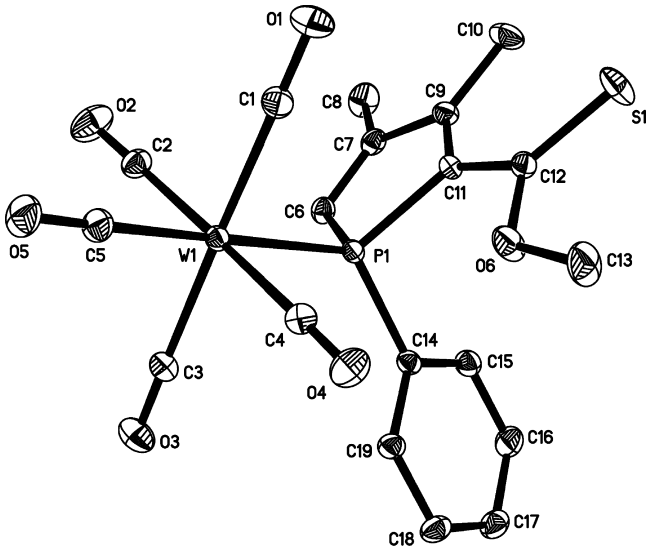
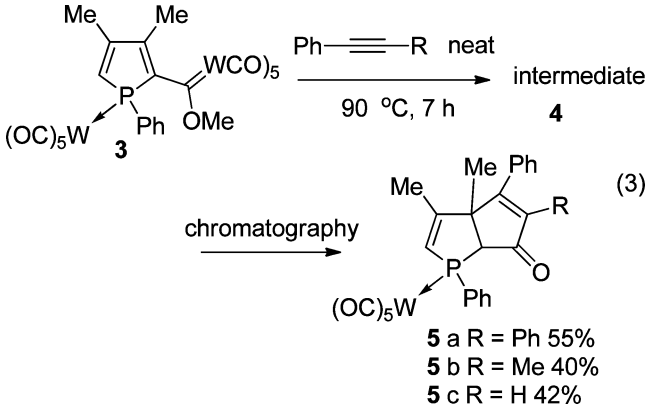


Figure 2. X-ray crystal structure of thioester **2**. Main distances (Å) and angles (deg): P−W 2.5062(6), P−C11 1.820(2), P−C6 1.789(2), P−C14 1.825(3), C6−C7 1.343(4), C7−C9 1.480(4), C9−C11 1.373(3), C11−C12 1.451(3), C12−S 1.635(3), C12−O6 1.352(3); C6−P−C11 90.70(11), C11−C12−O6 109.3(2), C12−C11−P 121.16(17), O6−C12−S 122.34(19).

extension of this work, we decided to investigate the reaction of **3** with alkynes. Once again, compound **3** displays a chemistry which is different from that of other heteroaryl derivatives of Fischer carbene complexes. In all of the cases, the major final product is a cyclopentenone (eq 3).



All three cyclopentenones display a ketonic carbonyl in their ^{13}C NMR spectrum: **5a,** $\delta(^{13}CO)$ 199.84, J_{C-P} = 3.9 Hz; **5b,** $\delta(^{13}CO)$ 200.94, J_{C-P} = 3.6 Hz; **5c**, $\delta(^{13}CO)$ 200.08, J_{C-P} = 3.9 Hz. All of these species have been characterized by X-ray crystal structure analysis. The structure of **5a** is depicted in Figure 3 as an example. The O−C−C−P dihedral angle is 75.84°. The cyclopentenone lies on the phenyl side of the phosphole plane; the Ph−P−C−CO dihedral angle is 22.75°. These cyclopentenones are not the initial products of the reaction. The crude mixture contains intermediates **4**: **4a**, $\delta(^{31}P)$ −2.25, J_{P-W} = 234 Hz; **4b**, $\delta(^{31}P)$ −3.33, J_{P-W} = 238 Hz; **4c**, $\delta(^{31}P)$ −4.66, J_{P-W} = 234 Hz. These intermediates are hydrolyzed during the chromatographic purification. We propose the mechanism given in eq 4 to rationalize these observations.

This proposed mechanism is exactly similar to that of a cyclopentenone synthesis from alkenyl Fischer carbenes and

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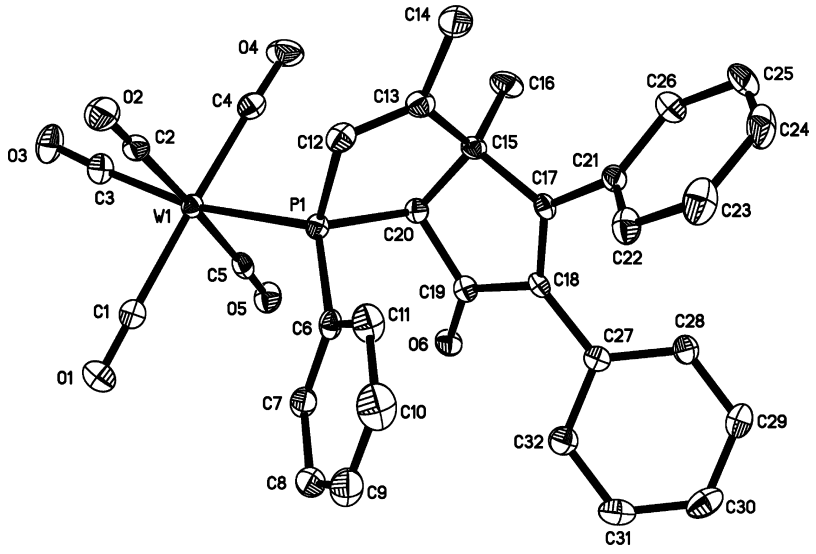
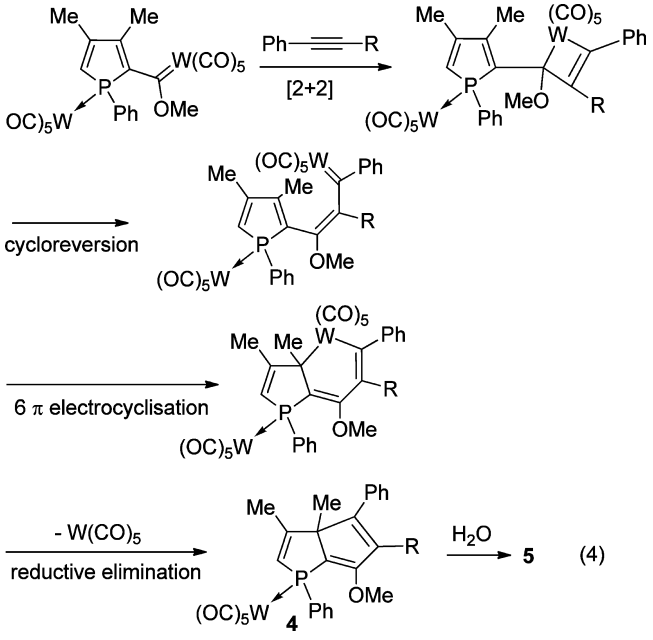


Figure 3. X-ray crystal structure of cyclopentenone **5a**. Main distances (Å) and angles (deg): P−W 2.4985(6), P−C6 1.832(2), P−C12 1.794(2), P−C20 1.860(2), C12−C13 1.325(4), C13−C15 1.525(3), C15−C17 1.537(3), C17−C18 1.349(3), C18−C19 1.480(3), C19−C20 1.509(3), C19−O6 1.215(3); C12−P−C20 91.36(11), C18−C19−C20 107.54(18), C19−C20−P 112.17(16).



alkynes as proposed recently by Barluenga.[7] The only difference is that the synthesis of Barluenga needs a nickel(0) catalyst. It is clear that this annelation reaction works with phospholes because the ring is not aromatic, in contrast to those of thiophenes, furans, and pyrroles. In the case of phenylpropyne, the cyclopentenone **5b** is accompanied by the secondary product **6**, which we have been able to isolate and to characterize by X-ray crystal structure analysis (Figure 4). Some time ago, Moser described what he calls the interrupted Dötz reaction, in which a Fischer carbene complex reacts with an alkyne to give a vinylketene.[8] On this basis, we propose the mechanism given in eq 5 for the formation of **6**.

The tricyclic compound **6** probably results from an intramolecular [4 + 2] cycloaddition between the vinylketene and the phosphole double bond.

At this stage, it is clear that the unique chemistry of phospholyl-substituted carbene complexes such as **1** and **3** is due to the close proximity of a reactive diene and a carbenic center.

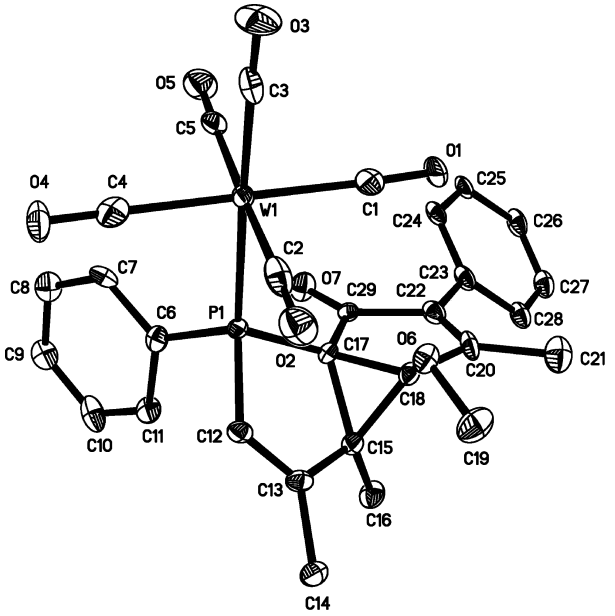


Figure 4. X-ray crystal structure of tricyclic compound **6**. Main distances (Å) and angles (deg): P−W 2.5045(18), P−C6 1.837(7), P−C12 1.811(7), P−C17 1.822(7), C12−C13 1.329(10), C13−C15 1.496(9), C15−C17 1.562(10), C15−C18 1.546(9), C18−O6 1.429(9), C18−C20 1.505(10), C20−C22 1.341(11), C22−C29 1.493(10), C29−O7 1.209(9), C29−C17 1.504(10); C12−P−C17 90.7(3), C15−C17−C18 60.4(4), C18−C17−C29 105.4(6), C17−C29−C22 107.5(6).

EXPERIMENTAL SECTION

Oven-dried glassware (105 °C) was used and cooled under a nitrogen atmosphere. All reactions were carried out with distilled dry solvents and under a N_2 atmosphere. Commercially available diphenylacetylene, 1-phenyl-1-propyne, and phenylacetylene were used without purification. Silica gel (230−400 mesh) was used for the chromatographic separations. NMR spectra were recorded on a JEOL ECA 400, JEOL ECA 400 SL, or Bruker BBFO2 400 MHz spectrometer.

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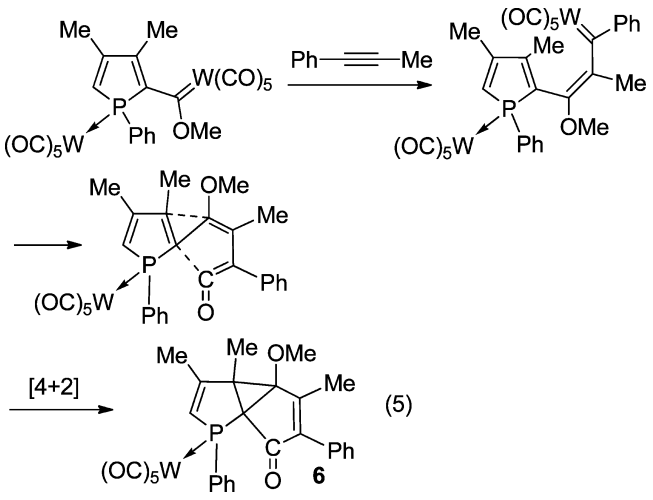

All spectra were recorded at 298 K. Proton decoupling was applied for ^{13}C and ^{31}P spectra. X-ray crystallographic analyses were performed on a Bruker X8 APEX CCD diffractometer or a Bruker Kappa CCD diffractometer.

Tervalent Phospholyl-Substituted Fischer Carbene Complex 1. 1-Phenyl-2-bromo-3,4-dimethylphosphole[9] (1.00 g, 3.74 mmol) was dissolved in THF (15 mL) in a Schlenk tube and cooled to −100 °C. Then, *n*-BuLi (2.6 mL, 1.6 M in Hex, 4.11 mmol) was added dropwise into the solution. The reaction mixture was stirred for 0.5 h at −100 °C. To the mixture was added $W(CO)_6$ (1.3161 g, 3.74 mmol), and it was then stirred at −90 °C for 0.5 h followed by −80 °C for 0.5 h. The reaction mixture was slowly warmed to room temperature. Subsequently, methyl trifluoromethanesulfonate (0.42 mL, 3.74 mmol) was added. The crude mixture was purified using chromatography at −20 °C with a 4/1 hexane/DCM eluent mixture. A dark red oil of compound **1** (0.3730g, 18%) was obtained before its P-$W(CO)_5$ complex **3** (0.3284, 10%). Hexane was added, and pure red crystalline **1** was obtained at −25 °C.

^{31}P NMR (CD_2Cl_2): δ 13.66 ppm. ^1H NMR (CD_2Cl_2): δ 2.09 (d, $^4J_{H-P}$ = 3.2 Hz, 3H, Me), 2.12 (dd, $^4J_{H-P}$ = 4.4 Hz, 3H, Me), 4.41 (s, 3H, OMe), 6.73 (d, $^2J_{H-P}$ = 38.8 Hz, 1H, =CH−P), 7.24−7.32 (m, 5H, Ph). ^{13}C NMR (CD_2Cl_2): δ 16.97 (s, Me), 18.28 (d, $^3J_{C-P}$ = 1.9 Hz, Me), 68.99 (s, OMe), 129.23 (d, J_{C-P} = 7.7 Hz, Ph), 130.37 (s, Ph), 130.55 (d, J_{P-C} = 14.0 Hz, P−C(Ph)), 134.13 (d, J_{P-C} = 4.8 Hz, P−CH=), 134.37 (d, J_{C-P} = 19.7 Hz, Ph), 143.61 (d, J_{C-P} = 16.6 Hz, P−C=), 150.23 (d, J_{C-P} = 7.7 Hz, C−Me), 167.56 (d, J_{C-P} = 2.8 Hz, C−Me), 198.39 (s, C−$W(CO)_5$ *cis* C=O), 205.22 (s, C−$W(CO)_5$ *trans* C=O), 316.94 (d, J_{C-P} = 30.1 Hz, C=W). Exact mass: calcd for $C_{19}H_{15}O_6PW$, 554.0116; found, 554.0115.

Sulfuration of 1. Red solid **1** (0.020 g, 0.036 mmol) was dissolved in toluene (5 mL), and sulfur powder (0.0012g, 0.036 mmol) was added. A small drop of *N*-methylimidazole was added, and the reaction mixture was stirred overnight at room temperature. The mixture was purified by flash chromatography with a 4/1 hexane/dichloromethane mixture. Thiocarboxylate **2** (0.0696 g, 95%) was obtained as an orange oil. Crystallization with pentane was achieved at −25 °C.

^{31}P NMR (CH_2Cl_2): δ 20.96 ppm (J_{P-W} = 225.4 Hz). ^1H NMR ($CDCl_3$): δ 2.28 (d, $^4J_{H-P}$ = 0.9 Hz, 3H, Me), 2.64 (s, 3H, Me), 4.02 (s, 3H, OMe), 6.68 (d, $^2J_{H-P}$ = 35.7 Hz, 1H, =CH−P), 7.38−7.49 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.64 (d, $^3J_{C-P}$ = 6.7 Hz, Me), 17.98 (d, $^3J_{C-P}$ = 9.5 Hz, Me), 57.97 (s, OMe), 128.44 (s, Ph), 128.92 (d, J_{C-P} = 68.0 Hz, P−C(Ph)), 129.07 (d, J_{C-P} = 11.5 Hz, Ph), 131.09 (s, Ph), 132.25 (d, J_{C-P} = 13.4 Hz, Ph), 137.04 (d, J_{C-P} = 40.3 Hz, P−CH=), 144.15 (d, J_{C-P} = 45.0 Hz, P−C−C(S)OMe), 150.02 (d, J_{C-P} = 5.8 Hz, C−Me), 158.69 (d, J_{C-P} = 14.4 Hz, C−Me), 196.51 (d, J_{C-P} = 5.7 Hz, $W(CO)_5$ *cis* C=O), 198.67 (d, J_{C-P} = 21.1 Hz, $W(CO)_5$ *trans* C=O), 204.60 (d, J_{C-P} = 16.3 Hz, C=S). Exact mass: calcd for $C_{17}H_{11}O_6PSW$, 557.9524; found, 557.9539.

Cyclopentenone 5a. Complex **3**[4] (0.0426g, 0.049 mmol) was placed in an oven-dried NMR tube under a stream of N_2. Diphenylacetylene (neat) was added, and the tube was sealed and heated at 90 °C for 7 h. Upon completion of the reaction, CH_2Cl_2 was added to the crude mixture,; ^{31}P NMR showed a major signal at −2.25 ppm. Purification by column chromatography with a 4/1 mixture of hexane and dichloromethane gave product **5a** as a yellow oil (0.0194 g, 55%).

^{31}P NMR (CD_2Cl_2): δ 14.27 ppm (J_{P-W} = 243.3 Hz). ^1H NMR (CD_2Cl_2): δ 1.56 (s, 3H, Me), 1.80 (s, 3H, Me), 3.83 (s, 1H, C*H*), 6.04 (d, $^2J_{H-P}$ = 36.0 Hz, 1H, =CH-P), 6.09−6.11 (m, 2H, Ph), 6.90−6.94 (m, 2H, Ph), 7.00−7.08 (m, 3H, Ph), 7.35−7.38 (m, 3H, Ph), 7.48−7.53 (m, 3H, Ph), 7.59−7.61 (m, 2H, Ph). ^{13}C NMR (CD_2Cl_2): δ 18.50 (d, $^3J_{C-P}$ = 11.6 Hz, Me), 25.24 (d, $^3J_{C-P}$ = 5.4 Hz, Me), 64.98 (s, *C*−Me), 66.65 (d, $^1J_{C-P}$ = 19.4 Hz, *C*−H), 122.49 (d, J_{C-P} = 42.6 Hz, P−CH=), 133.10 (d, J_{C-P} = 29.9 Hz, P−C(Ph)), 136.7 (s, =*C*−Ph), 140.51 (s, =*C*−Ph), 160.13 (d, J_{C-P} = 3.8 Hz, =*C*−Me), 197.36 (d, J_{C-P} = 7.4 Hz, $W(CO)_5$ *cis* C=O), 199.84 (d, J_{C-P} = 3.9 Hz, C=O), 200.20 (d, J_{C-P} = 23.0 Hz, $W(CO)_5$ *trans* C=O). Exact mass: calcd for $C_{32}H_{23}O_6PW$, 718.0742; found, 718.0783.

Cyclopentenone 5b and Tricyclic Product 6. The same procedure as for **5a** was used with 1-phenyl-1-propyne. The crude mixture contains mainly two products at −3.33 (**4b**) and 5.0 ppm. Elution with a mixture of hexane and dichloromethane (4/1) gave the product at 5 ppm, which evolved overnight to give **6** (0.0028 g, 9%), while **4b** (−3.33 ppm) gave **5b** (0.0118 g, 40%), which was eluted with a 3/2 hexane/dichloromethane mixture.

Data for **5b** are as follows. ^{31}P NMR ($CDCl_3$): δ 13.12 ppm (J_{P-W} = 241.8 Hz). ^1H NMR ($CDCl_3$): δ 0.92 (s, 3H, Me), 1.60 (s, 3H, Me), 1.64 (s, 3H, Me), 3.68 (s, 1H, C−*H*), 5.97 (d, $^2J_{H-P}$ = 35.7 Hz, 1H, =CH−P), 7.04−7.07 (m, 2H, Ph), 7.38−7.54 (m, 8H, Ph). ^{13}C NMR (CD_2Cl_2): δ 8.14 (s, Me), 18.18 (d, $^3J_{C-P}$ = 11.6 Hz, Me), 24.58 (d, $^3J_{C-P}$ = 5.3 Hz, Me), 64.39 (s, *C*−Me), 65.90 (d, $^1J_{C-P}$ = 19.8 Hz, *C*−H), 121.56 (d, J_{C-P} = 42.2 Hz, P−CH=), 132.33 (d, J_{C-P} = 28.5 Hz, P−C(Ph)), 135.3 (s, PhC=*C*−Me), 137.77 (s, =*C*−Ph), 159.26 (d, J_{C-P} = 3.8 Hz, =*C*−Me), 196.59 (d, J_{C-P} = 7.2 Hz, $W(CO)_5$ *cis* C=O), 199.38 (d, J_{C-P} = 23.1 Hz, $W(CO)_5$ *trans* C=O), 200.94 (d, J_{C-P} = 3.6 Hz, C=O). Exact mass: calcd fo $rC_{27}H_{21}O_6PW$, 656.0585; found, 656.0586.

Data for **6** are as follows. ^{31}P NMR ($CDCl_3$): δ 13.21 ppm (J_{P-W} = 238.1 Hz). ^1H NMR (CD_2Cl_2): δ 1.68 (s, 3H, Me), 2.31 (s, 3H, Me), 2.33 (s, 3H, Me), 3.69 (s, 3H, OMe), 6.07 (d, $^2J_{H-P}$ = 37.6 Hz, 1H, =CH-P), 7.24−7.30 (m, 2H, Ph), 7.35−7.46 (m, 3H, Ph), 7.49−7.51 (m, 3H, Ph), 7.68−7.74 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 12.49 (s, Me), 15.30 (s, Me), 18.87 (d, $^3J_{C-P}$ = 11.3 Hz, Me), 48.75 (d, $^2J_{C-P}$ = 31.7 Hz, P−*C*), 59.59 (s, OMe), 70.14 (s, *C*−Me), 84.27 (s, *C*−OMe), 128.63 (d, J_{C-P} = 45.3 Hz, P−CH=), 132.69 (d, J_{C-P} = 34.6 Hz, P−C(Ph)), 138.86 (d, J_{C-P} = 6.4 Hz, =*C*−Me), 150.75 (s, Ph−*C*=CMe), 161.08 (s, PhC=*C*−Me), 194.56 (d, J_{C-P} = 3.3 Hz, C=O), 196.86 (d, J_{C-P} = 7.5 Hz, $W(CO)_5$ *cis* C=O), 199.51 (d, J_{C-P} = 22.7 Hz, $W(CO)_5$ *trans* C=O). Exact mass: calcd for $C_{29}H_{23}O_7PW$, 698.0691; found, 698.0698.

Cyclopentenone 5c. The same procedure as for **5a** was used with phenylacetylene. The crude mixture contained **4c** (−4.66 ppm) and **5c**. Chromatography as usual gave pure **5c** (0.014 g, 42%).

^{31}P NMR ($CDCl_3$): δ 13.49 ppm (J_{P-W} = 244.1 Hz). ^1H NMR ($CDCl_3$): δ 1.72 (s, 3H, Me), 1.77 (s, 3H, Me), 3.69 (s, 1H, C-*H*), 5.34 (s, 1H, =C−*H*), 5.98 (d, $^2J_{H-P}$ = 35.2 Hz, 1H, =CH−P), 7.17−7.20 (m, 2H, Ph), 7.42−7.44 (m, 6H, Ph), 7.48−7.52 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 18.46 (d, $^3J_{C-P}$ = 11.6 Hz, Me), 25.33 (d, $^3J_{C-P}$ = 5.2 Hz, Me), 66.17 (s, *C*-Me), 67.16 (d, $^2J_{C-P}$ = 19.2 Hz, *C*−H), 122.89 (d, J_{C-P} = 42.3 Hz, P−CH=), 131.47 (s, =*C*−H), 132.31 (d, J_{C-P} = 30.2 Hz, P−C(Ph)) 135.89 (s, =*C*−Ph), 158.25 (d, J_{C-P} = 3.8 Hz, =*C*−Me), 196.85 (d, J_{C-P} = 7.1 Hz, $W(CO)_5$ *cis* C=O), 199.52 (d, J_{C-P} = 23.1 Hz, $W(CO)_5$ *trans* C=O), 200.08 (d, J_{C-P} = 3.9 Hz, C=O). Exact mass: calcd for $C_{26}H_{19}O_6PW$, 642.0429; found, 642.0443.

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■ ASSOCIATED CONTENT

Supporting Information

Figures giving NMR spectra of the compounds prepared in this work and CIF files giving X-ray crystallographic data for compounds **1**, **2**, **5a**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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