Synthesis and Chemical Reactivity of Tungsten P-Substituted Phospholes

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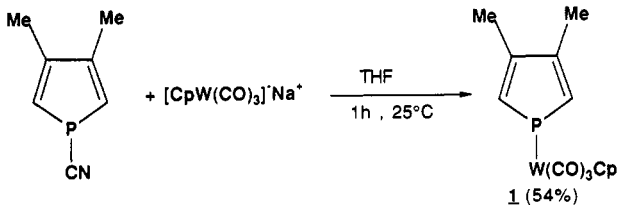
Two tungsten-substituted phospholes were prepared by reaction of $CpW(CO)_3Na$ with 1-cyano-3,4-dimethylphosphole and 1-bromo-2,5-diphenylphosphole, respectively. According to a X-ray crystal structure analysis, the 3,4-dimethyl-substituted compound is more planar and displays a higher electronic delocalization than an ordinary phosphole such as 1-benzylphosphole. In both cases, the lone pair at phosphorus retains a substantial nucleophilicity, with oxidation, sulfurization, and quaternization being easily achieved. Reaction with carboxylic acids leads to a tungsten-substituted 2,5-dihydrophosphole oxide via an initial protonation at phosphorus followed by a [1,5]-sigmatropic shift of hydrogen. [4 + 2] cycloadditions with *N*-phenylmaleimide are possible with the phosphole oxides or sulfides. The reaction with dimethyl acetylenedicarboxylate yields a spirocyclic compound containing a P—C=C—C(O)—W ring whose structure was established by X-ray analysis. The thermolysis of the 3,4-dimethyl-substituted phosphole leads to a normal μ-phosphido P_2W_2 dimer by loss of CO, whereas the more congested 2,5-diphenyl derivative gives a μ-phosphido, μ-hydrido complex with a W—W bond.

Introduction

Even though some phospholes with transition-metal substituents at phosphorus are known,[1,2] all of them are derived from the nonrepresentative 2,3,4,5-tetraphenylphospholyl ring and, apart from oxidation and thermolysis, no chemistry has been performed with any of them. We felt that is would be interesting to explore the reactivity of such species in some depth, since they can be considered as lying halfway between the covalent and weakly aromatic phospholes on one hand and ionic and highly aromatic alkali-metal phospholides on the other. Thus, a subtle interplay was expected between the reactivity of the phosphorus lone pair, the dienic system, and the P–metal bond. We report now on our results with two representative tungsten-substituted phospholes.

Results and Discussion

The first such phosphole 1 was easily obtained via the reaction of the appropriate tungsten anion with 1-cyano-3,4-dimethylphosphole[3] (eq 1). An inspection of the NMR

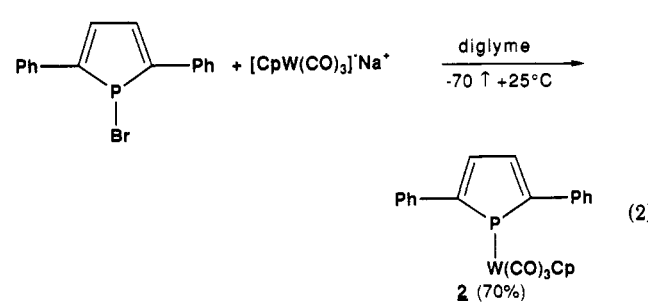


(1)

spectra clearly revealed that 1 has some special characteristics. The ^{31}P NMR resonance of 1 is observed at −105 ppm (vs H_3PO_4), and the $^1J(^{31}P-^{183}W)$ coupling is low at 55.1 Hz. The corresponding data for $CpW(CO)_3(PPh_2)$ are respectively −63.3 ppm and 52 Hz.[4] The abnormal high-field shift of the ^{31}P resonance of 1 is difficult to interpret. In contrast, the relatively high $^1J(C-P)$ coupling of 1 (17.2 Hz) is probably indicative of a higher P–C bond order in 1 than in ordinary phospholes. The data for the corresponding 3,4-dimethylphospholes are 4 Hz (P–Ph) and 2.4 Hz (P–H) versus 44 Hz for the fully delocalized P^- anion.[5] Also noteworthy is the shift to low fields of the α-carbons of 1: $\delta(^{13}C)$ +140.24 (1), +129.47 (P–Ph), and +124.56 ppm (P–H).[5] Strictly similar phenomena were observed for the NMR spectra of 2, which was prepared, for purposes of comparison, from 1-bromo-2,5-diphenylphosphole[6] (eq 2). The NMR data recorded for 2 follow the trends observed for 1: $\delta(^{31}P)$ (2) −98.8 (C_6D_6), $^J(^{31}P-$

Table I. Structural Comparison between 1, 3, 1-Benzylphosphole, and the 2,3,4,5-Tetramethylphospholide Ion

	1-benzylphosphole[7]	1	3	2,3,4,5-tetramethylphospholide[8]
P—C (ring), Å	1.786 (5) 1.780 (5)	1.772 (6) 1.769 (6)	1.795 (4) 1.794 (4)	1.750 (5) 1.752 (4)
C=C (ring), Å	1.343 (6) 1.343 (6)	1.372 (7) 1.37 (1)	1.363 (5) 1.363 (6)	1.396 (5) 1.396 (7)
C–C (ring), Å	1.438 (6)	1.447 (9)	1.439 (6)	1.424 (7)
ΣCPC, deg	302.7	319.6	315.1	



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(1) Braye, E. H.; Joshi, K. K. *Bull. Soc. Chim. Belg.* **1971**, *80*, 651.
(2) Abel, E. W.; Towers, C. *J. Chem. Soc., Dalton Trans.* **1979**, 814.
(3) Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796.
(4) Malisch, W.; Malisch, R.; Colquhoun, I. J.; McFarlane, W. *J. Organomet. Chem.* **1981**, *220*, C1.
(5) Charrier, C.; Mathey, F. *Tetrahedron Lett.* **1987**, *28*, 5025.
(6) Charrier, C.; Bonnard, H.; Mathey, F.; Neibecker, D. *J. Organomet. Chem.* **1982**, *231*, 361.

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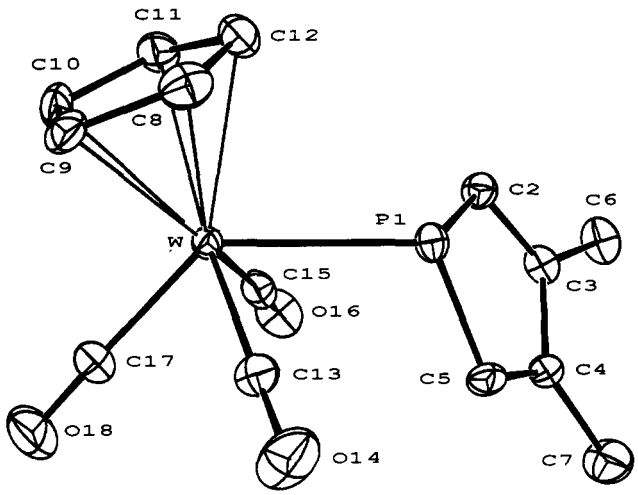
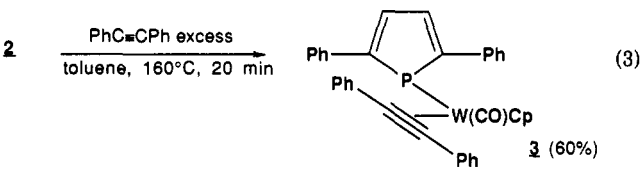


Figure 1. ORTEP drawing of 1 showing the thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Important bond distances (Å) and angles (deg): W–P_1 = 2.571 (2), P_1–C_2 = 1.772 (6), P_1–C_5 = 1.769 (6), C_2–C_3 = 1.372 (7), C_3–C_4 = 1.447 (9), C_4–C_5 = 1.37 (1); W–P_1–C_2 = 116.2 (2), W–P_1–C_5 = 112.7 (2), C_2–P_1–C_5 = 90.7 (3), P_1–C_2–C_3 = 111.0 (4), C_2–C_3–C_4 = 113.2 (6), C_3–C_4–C_5 = 112.7 (5), P_1–C_5–C_4 = 111.5 (4).

^{183}W) = 65.9 Hz; $\delta(^{13}C_\alpha)$ +166.17 (C_6D_6) ^1J(C–P) = 17 Hz vs +151.58 (P–Ph) and 146.9 (P–H) ppm with ^1J(C–P) = 0 Hz.[5]

In order to assess the influence of the tungsten substituent on the structure of the phosphole ring more precisely, we recorded the X-ray crystal structures of 1 (Figure 1) and 3 (Figure 2), prepared from 2 by substitution of two carbonyl ligands (eq 3). The most significant



(3)

parameters of the phosphole rings of 1 and 3 are compared with those of 1-benzylphosphole[7] and lithium 2,3,4,5-tetramethylphospholide[8] in Table I. From this comparison, it is clear that 1 is significantly more planar at phosphorus and, hence, more aromatic than 1-benzylphosphole. On the other hand, 1 remains pyramidal and significantly less aromatic than the planar phospholide ion according to the alternating between short and long C–C bonds within the ring.[9] From another standpoint, the bond between phosphorus and tungsten is much shorter in 3 than in 1 in spite of a greater steric congestion which results from the 2,5-diphenyl substitution of the phosphole ring in the former case. The replacement of 2 CO by diphenylacetylene in 3 certainly plays a role in this strengthening of the P–W bond. Formally, the alkyne plays the role of a four-electron donor in this complex.[10] However, some contribution of the phosphole lone pair to the filling of the d orbitals of tungsten may release some

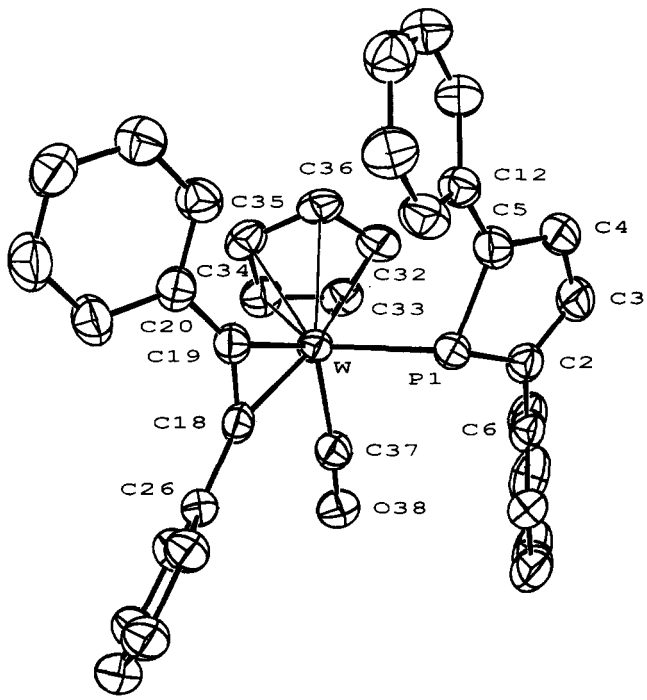
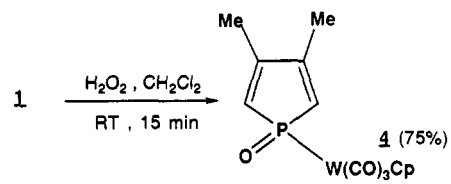


Figure 2. ORTEP drawing of 3 showing the thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Important bond distances (Å) and angles (deg): W–P_1 = 2.448 (1), W–C_{18} = 2.051 (4), W–C_{19} = 2.026 (4), P_1–C_2 = 1.795 (4), P_1–C_5 = 1.794 (4), C_2–C_3 = 1.363 (5), C_3–C_4 = 1.439 (6), C_4–C_5 = 1.363 (6), C_{18}–C_{19} = 1.331 (5); W–P_1–C_2 = 110.8 (1), W–P_1–C_5 = 112.9 (1), C_2–P_1–C_5 = 91.4 (2), P_1–C_2–C_3 = 109.7 (3), C_2–C_3–C_4 = 114.5 (4), C_3–C_4–C_5 = 114.5 (3), P_1–C_5–C_4 = 109.7 (3).

electron density toward the alkyne ligand. As a result, less delocalization operates within the phosphole ring of 3 than in the phosphole ring of 1. An additional adverse effect of 2,5-diphenyl substitution upon the electronic delocalization within the ring of 3 can also be envisaged.

The phosphorus–tungsten bonds in 1 and 2 proved to be remarkably stable. Oxidation and sulfurization of 1 take place under normal conditions (eqs 4 and 5). The



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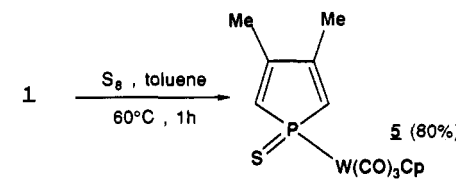


(5)

oxide slowly dimerizes upon standing or heating. Its abnormal stability toward [4 + 2] dimerization[11] is probably the result of the steric bulk of the tungsten substituent. In comparison with 1, both the oxide 4 and

(7) Coggon, P.; Engel, J. F.; McPhail, A. T.; Quin, L. D. *J. Am. Chem. Soc.* **1970**, *92*, 5779. Coggon, P.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1973**, 1888.

(8) Douglas, T.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1367.

(9) The question of phosphole aromaticity is reviewed in: Mathey, F. *Chem. Rev.* **1988**, *88*, 429. More recent references include: Baldridge, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 4204. Hughes, A. N.; Edgecombe, K. E. *Heterocycles* **1992**, *33*, 563.

(10) Structural data for the W(C≡C) unit are close to those already reported in the literature for a 4e alkyne donor; see for example: Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J. J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318.

(11) 1-Phenyl-3,4-dimethylphosphole oxide readily dimerizes at room temperature: Quin, L. D.; Wu, X.-P. *Heteroat. Chem.* **1991**, *2*, 359.

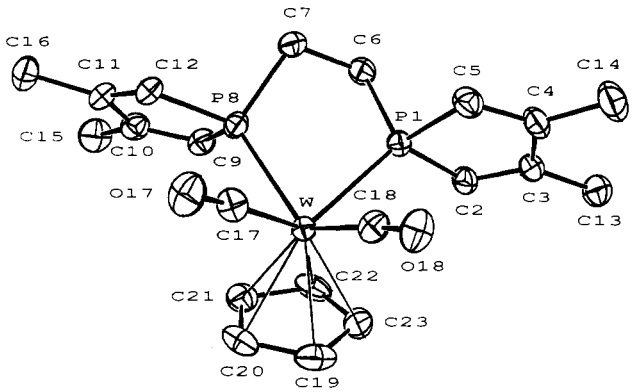
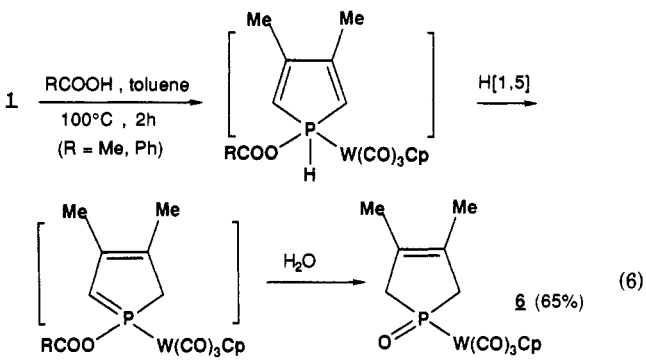


Figure 3. ORTEP drawing of **8** showing the thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Important bond distances (Å) and angles (deg): W–P_1 = 2.4765 (8), W–P_8 = 2.4707 (9), P_1–C_2 = 1.777 (3), P_1–C_5 = 1.784 (4), P_1–C_6 = 1.831 (4), C_2–C_3 = 1.351 (5), C_3–C_4 = 1.494 (5), C_4–C_5 = 1.356 (5), C_6–C_7 = 1.533 (5), C_7–P_8 = 1.836 (4), P_8–C_9 = 1.808 (4), P_8–C_{12} = 1.790 (3), C_9–C_{10} = 1.338 (5), C_{10}–C_{11} = 1.488 (5), C_{11}–C_{12} = 1.355 (5); P_1–W–P_8 = 75.87 (3), W–P_1–C_2 = 117.1 (1), W–P_1–C_5 = 119.1 (1), W–P_1–C_6 = 113.3 (1), C_2–P_1–C_5 = 92.2 (2), C_2–P_1–C_6 = 105.2, C_5–P_1–C_6 = 107.4 (2), W–P_8–C_7 = 112.7 (1); W–P_8–C_9 = 116.1 (1), W–P_8–C_{12} = 123.3 (1), C_7–P_8–C_9 = 104.6 (2), C_7–P_8–C_{12} = 105.3 (2), C_9–P_8–C_{12} = 91.7 (2).

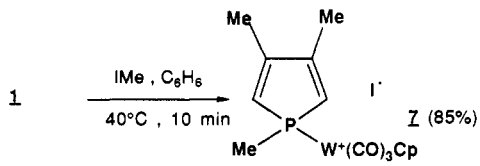
the sulfide **5** display a higher P–W coupling and a shift to high fields of the α-carbons.

Protonation by carboxylic acids leads to a phospholene oxide via a H [1,5]-sigmatropic shift as in the case of normal phospholes[12] (eq 6). The two α-CH_2 groups of **6** appear



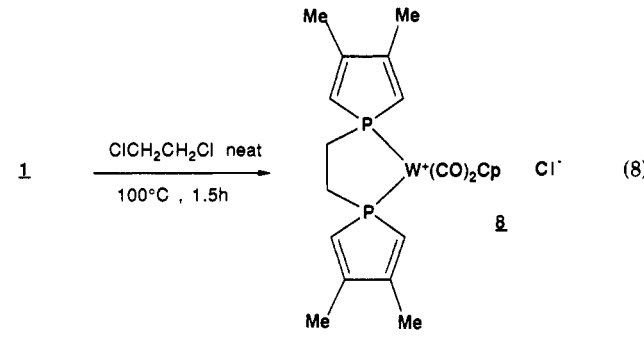
(6)

as a characteristic doublet at 53.71 ppm (^1J(C–P) = 39.8 Hz) in the ^{13}C NMR spectrum ($CDCl_3$). Quaternization by methyl iodide also follows the expected pathway (eq 7), giving a product where the ^1J(P–W) coupling is now substantially higher, at 164 Hz.



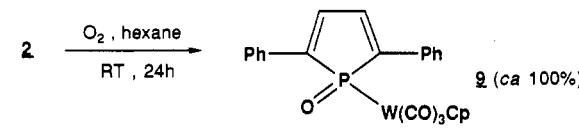
(7)

Phosphole **1** is even able to react with the two C–Cl bonds of 1,2-dichloroethane (eq 8). The chelate **8** was isolated in the pure state and characterized by X-ray crystal structure analysis (Figure 3). The P–W bond is significantly shorter in **8** than in **1**, and the alternation between short and long C–C bonds within the ring is stronger in the former case.



(8)

The phosphorus lone pair of **2** displays a similar reactivity. The oxide **9** and the sulfide **10** were easily obtained as shown in eqs 9 and 10.



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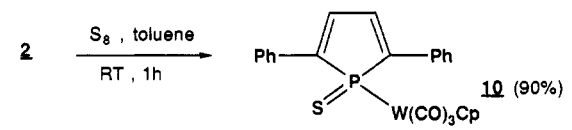
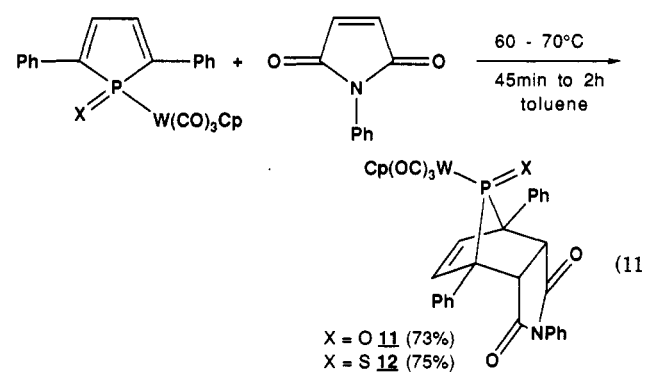


(10)

In contrast to the high nucleophilicity of their phosphorus lone pairs, the dienic systems of **1** and **2** show a rather low reactivity. Only their *P*-oxides or -sulfides such as **9** and **10** are able to undergo clean [4 + 2] cycloadditions with dienophiles, exemplified by eq 11. The ^{31}P resonances



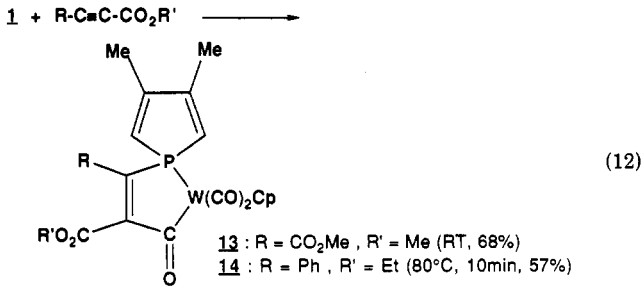
(11)

of **11** and **12** show shifts to low fields which are characteristic of the 7-phosphanorbornene skeleton: δ(^{31}P) (**12**) +167.5 (C_6D_6); δ(^{31}P) (**13**) +183 (C_6D_6). The endo position of *N*-phenylmaleimide is demonstrated by the inspection of the ^{1}H NMR spectra of **11** and **12**. In both cases, the protons at the junction are not (or are only weakly) coupled to phosphorus. Thus, they are in the exo position: see the comparison between the ^{1}H NMR spectra of the endo and exo [4 + 2] dimers of 1-phenyl-3,4-dimethylphosphole sulfide.[13] The geometry at the bridges of **11** and **12** is postulated for steric reasons.

Even though they display a remarkable stability, the tungsten coordination spheres of **1** and **2** are able to react with selected reagents. An interesting example has been found with electron-poor alkynes (eq 12). The formula of **13** has been established by an X-ray crystal structure analysis (Figure 4). Due to the blocked conformation of the molecule, the two sides of the phosphole ring become inequivalent. Both the ^{1}H and ^{13}C NMR spectra reflect

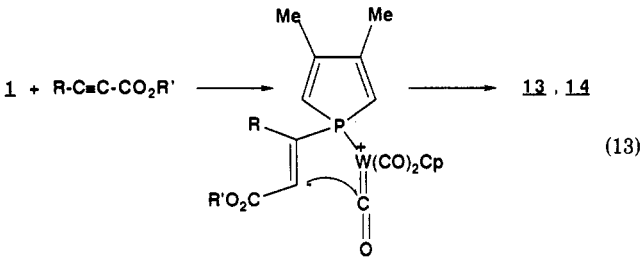
(12) Quin, L. D.; Belmont, S. E.; Mathey, F.; Charrier, C. *J. Chem. Soc., Perkin Trans. 2* **1986**, 629.

(13) Santini, C. C.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 5809.



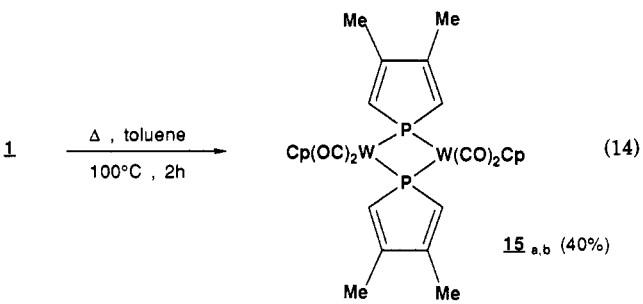
(12)

this inequivalence. The mechanism almost certainly involves the initial formation of a zwitterion via the nucleophilic attack of the phosphorus lone pair of 1 on the C≡C triple bond[14] (eq 13).



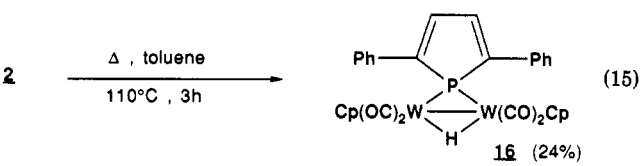
(13)

Finally, the thermolysis of 1 and 2 has also been investigated. In the former case, a classical μ-phosphido dimer was obtained (eq 14) as a mixture of two isomers (cis and trans Cp groups). These two isomers display ^{31}P



(14)

resonances at the very high fields which are expected for μ-phosphido complexes without metal–metal bonds: $\delta(^{31}P)$ −199.7 (minor) and −214.6 (major) in $CDCl_3$. The case of the highly congested **2**, where a μ-phosphido, μ-hydrido complex was produced, is more exciting (eq 15). The



(15)

hydride bridge appears at −16.38 ppm in C_6D_6 with a J(H–P) coupling of 24.7 Hz and a $J(^1H–^{183}W)$ coupling of 40 Hz. The presence of the W–W bond induces a strong shift to low fields of the ^{31}P resonance: $\delta(^{31}P)$ (**16**) +95 in C_6D_6. Toluene is probably the source of the hydride ligand in **16**.

In conclusion, we can state that, in spite of their more planar structures suggesting a higher electronic delocalization within the ring than "ordinary" phospholes, the tungsten P-substituted phospholes described here display a higher nucleophilicity at phosphorus and behave like their organic counterparts in most of their reactions.

(14) See: Hudson, H. R. *The Chemistry of Organophosphorus Compounds*; Wiley: Chichester, England, 1990; Vol. 1, p 419.

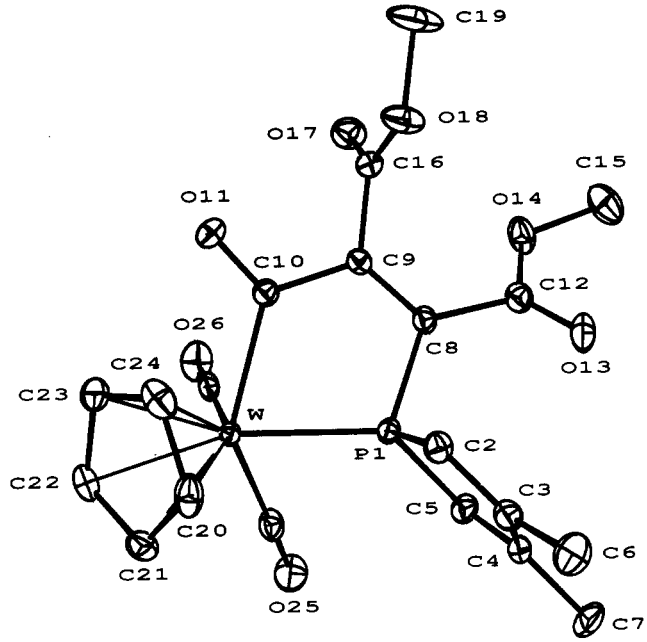


Figure 4. ORTEP drawing of **13** showing the thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Important bond distances (Å) and angles (deg): W–P_1 = 2.4196 (6), W–C_{10} = 2.208 (3), P_1–C_2 = 1.794 (3), P_1–C_5 = 1.794 (2), P_1–C_8 = 1.827 (3), C_2–C_3 = 1.349 (3), C_3–C_4 = 1.486 (4), C_4–C_5 = 1.351 (4), C_8–C_9 = 1.338 (3), C_9–C_{10} = 1.519 (3), C_{10}–O_{11} = 1.224 (3); P_1–W–C_{10} = 74.30 (6), W–P_1–C_2 = 117.51 (8), W–P_1–C_5 = 126.28 (9), W–P_1–C_8 = 107.38 (7), C_2–P_1–C_5 = 91.8 (1), C_2–P_1–C_8 = 103.1 (1), C_5–P_1–C_8 = 108.1 (1), P_1–C_8–C_9 = 112.5 (2), P_1–C_8–C_{12} = 122.8 (2), C_8–C_9–C_{10} = 118.9 (2), C_8–C_9–C_{16} = 125.5 (2), W–C_{10}–C_9 = 122.5 (2), W–C_{10}–O_{11} = 122.0 (2), C_9–C_{10}–O_{11} = 115.5 (2).

Experimental Section

All reactions were carried out under argon, and silica gel (70–230 mesh) was used for chromatographic separations. NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from internal TMS (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P). Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 spectrometer by the direct inlet method. Elemental analyses were performed by the "Service d'analyse du CNRS" at Gif-sur-Yvette, France.

(η^1(*P*)-3,4-Dimethylphospholyl)(η^5-cyclopentadienyl)tricarbonyltungsten (1). The (η^5-cyclopentadienyl)tricarbonyltungsten sodium salt (7 g, 2×10^{-2} mol) in THF (35 mL) was added at room temperature to a solution of 1-cyano-3,4-dimethylphosphole[3] (2.8 g, 2×10^{-2} mol) in THF (15 mL). After 1 h at room temperature, the reaction mixture was filtered over Celite and evaporated. The residue was crystallized from ether: mp 168 °C dec; yield 4.8 g (54%); ^{31}P NMR (CD_2Cl_2) δ −105.2, $^1J(^{31}P–^{183}W)$ = 55.1 Hz; ^1H NMR (CD_2Cl_2, C_6D_6) δ 2.14 (d, ^4J(H–P) = 3.6 Hz, 6 H, Me), 5.09 (d, ^3J(H–P) = 1.2 Hz, 5 H, Cp), 6.65 (d, ^2J(H–P) = 40.9 Hz, 2 H, =CHP); ^{13}C NMR (CD_2Cl_2, C_6D_6) δ 17.85 (s, Me), 92.73 (s, Cp), 140.23 (d, ^1J(C–P) = 17.2 Hz, =CHP), 145.70 (d, ^2J(C–P) = 5.8 Hz, Me–*C*); mass spectrum (^{184}W) *m/z* 444 (M^+, 20%), 388 (M^+ − 2CO, 34%), 360 (M^+ − 3CO, 100%); IR (CH_2Cl_2) ν(CO) 2010 s, 1935 sh, 1920 vs cm^{-1}.

(η^1(*P*)-2,5-Diphenylphospholyl)(η^5-cyclopentadienyl)tricarbonyltungsten (2). The (η^5-cyclopentadienyl)tricarbonyltungsten sodium salt (10.5 g, 3×10^{-2} mol) in diglyme (60 mL) was added to a solution of 1-bromo-2,5-diphenylphosphole[6] (9.5 g, 3×10^{-2} mol) in C_6H_6/diglyme (50:50, 60 mL) at −70 °C. The resulting mixture was warmed to room temperature with stirring,

and after evaporation, the residue was chromatographed with CH_2Cl_2 on a short column of silica gel (50 g). A yellow (orange) crystalline product was crystallized from pentane/CH_2Cl_2 (95:5): mp 173 °C; yield 12.0 g (70%); ^{31}P NMR (C_6D_6) δ −98.8, $^1J(^{31}P-^{183}W)$ = 65.9 Hz; ^1H NMR (C_6D_6) δ 4.25 (s, 5 H, Cp), 7.10–7.50 (m, 12 H); ^{13}C NMR (C_6D_6) δ 91.9 (s, Cp), 131.11 (d, ^2J(C–P) = 6.1 Hz, C_β), 140.42 (d, ^2J(C–P) = 18.36 Hz, C(Ph)), 166.17 (d, ^1J(C–P) = 17.0 Hz, C_α); mass spectrum (^{184}W) *m/z* 556 (M + O − CO, 45%), 500 (M + O − 3CO, 100%); IR (CH_2Cl_2) ν(CO) 2010 s, 1930 vs cm^{-1}. Anal. Calcd for $C_{24}H_{17}O_3PW$: C, 50.75; H, 3.01. Found: C, 50.83; H, 2.87.

(η^1(*P*)-2,5-Diphenylphospholyl)(η^2-1,2-diphenylethyne)-(η^5-cyclopentadienyl)carbonyltungsten (3). In a sealed tube, 570 mg (1 × 10^{-3} mol) of phospholyltungsten **2** with 360 mg (2 × 10^{-3} mol) of 1,2-diphenylethyne were warmed in toluene (1 mL) at 160 °C for 20 min. The solution was cooled and chromatographed with CH_2Cl_2–hexane (50:50). The burgundy red complex **3** was crystallized from hexane/CH_2Cl_2 (95:5): mp 168 °C; yield 410 mg (60%); ^{31}P NMR ($CDCl_3$) δ 0.9, $^1J(^{31}P-^{183}W)$ = 263.6 Hz; ^1H NMR ($CDCl_3$) δ 4.78 (d, J(H–P) = 0.8 Hz, 5 H, Cp), 6.90–7.54 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ 93.15 (s, Cp), 136.56 (s, C ipso *Ph*C≡C), 139.74 (d, ^2J(C–P) = 18 Hz, C ipso), 140.82 (s, C ipso *Ph*C≡C), 162.21 (s, C_α), 195.87 (s, *C*≡C), 200.53 (s, C≡*C*) 224.61 (s, CO); mass spectrum (^{184}W) *m/z* 661 (M − CO − H, 30%), 484 [M − (CO + PhC≡CPh), 100%]; IR (CH_2Cl_2) ν(CO) 1953 s cm^{-1}.

(η^1(*P*)-3,4-Dimethylphosphole *P*-oxide)(η^5-cyclopentadienyl)tricarbonyltungsten (4). To 4.5 g (1 × 10^{-2} mol) of phospholyltungsten **1** in CH_2Cl_2 (50 mL) was added 3 mL of H_2O_2 (20% aqueous) at room temperature. After it was stirred for 15 min, the heterogeneous solution was decanted, washed twice with H_2O, dried over Na_2SO_4, and evaporated. The resulting oil was purified by chromatography with AcOEt/methanol (90:10): yield 3.5 g (75%); ^{31}P NMR ($CDCl_3$) δ 60.9, $^1J(^{31}P-^{183}W)$ = 125.4 Hz; ^1H NMR ($CDCl_3$) δ 2.01 (s, 6 H, Me), 5.74 (s, 5 H, Cp), 6.01 (d, ^2J(H–P) = 32.66 Hz, 2 H, CH); ^{13}C NMR ($CDCl_3$) δ 15.86 (d, ^3J(C–P) = 15.75 Hz, Me), 92.46 (s, Cp), 129.47 (d, ^1J(C–P) = 63.63 Hz, C_α), 143.90 (d, ^2J(C–P) = 16.91 Hz, C_β), 214.84 (d, ^2J(C–P) = 22.93 Hz, CO), 221.62 (s, CO); mass spectrum (^{184}W) *m/z* 432 (M − CO, 50%), 376 (M − 3CO, 100%); IR (CH_2Cl_2) ν(CO) 2025 m, 1932 vs cm^{-1}.

(η^1(*P*)-3,4-Dimethylphosphole *P*-sulfide)(η^5-cyclopentadienyl)tricarbonyltungsten (5). Phospholyltungsten **1** (450 mg, 1 × 10^{-3} mol) was heated in toluene (2 mL) with 32 mg of S_8 (1 × 10^{-3} mol) for 1 h. The solvent was removed in vacuo and the sulfide isolated from the residual oil by chromatography with AcOEt/CH_2Cl_2 (80:20). **5** was crystallized from hexane/CH_2Cl_2 (80:20): mp 196 °C; yield 400 mg (80%); ^{31}P NMR (CH_2Cl_2) δ 15.4, $^1J(^{31}P-^{183}W)$ = 126.6 Hz; ^1H NMR ($CDCl_3$) δ 2.08 (s, 6 H, Me), 5.74 (s, 5 H, Cp), 6.18 (d, ^2J(H–P) = 36.31 Hz, 2 H, CH); ^{13}C NMR ($CDCl_3$) δ 16.26 (d, ^3J(C–P) = 15.1 Hz, Me), 94.58 (s, Cp), 133.97 (d, ^1J(C–P) = 54.12 Hz, C_α), 144.62 (d, ^2J(C–P) = 13.09 Hz, C_β), 213.87 (d, ^2J(C–P) = 10.96 Hz, CO), 221.72 (s, CO); mass spectrum (^{184}W) *m/z* 448 (M − CO, 58%), 392 (M − 3CO, 100%); IR (CH_2Cl_2) ν(CO) 2030 s, 1940 broad cm^{-1}. Anal. Calcd for $C_{14}H_{13}O_3PSW$: C, 39.52; H, 2.77; P, 6.51. Found: C, 39.14; H, 2.75; P, 6.10.

(η^1(*P*)-3,4-Dimethyl-2,5-dihydrophosphole *P*-oxide)(η^5-cyclopentadienyl)tricarbonyltungsten (6). A solution of 450 mg (1 mmol) of **1** in toluene (2 mL) with 0.12 mL of CH_3COOH (2 mmol) was heated at 100 °C for 2 h. The solution was chromatographed with AcOEt/MeOH (90:10). The white solid was crystallized from hexane/toluene (20:80): mp 160 °C; yield 300 mg (65%); ^{31}P NMR ($CDCl_3$) δ 66.1, $^1J(^{31}P-^{183}W)$ = 128.4 Hz; ^1H NMR ($CDCl_3$) δ 1.71 (s, 6 H, Me), 2.95 (m, 4 H, CH_2), 5.73 (s, 5 H, Cp); ^{13}C NMR ($CDCl_3$) δ 16.76 (d, ^3J(C–P) = 19.73 Hz, Me), 53.71 (d, ^1J(C–P) = 39.8 Hz, CH_2), 92.98 (s, Cp), 129.75 (d, ^2J(C–P) = 4.23 Hz, *C* Me), 215.17 (d, ^2J(C–P) = 24.60 Hz, CO), 220.15 (d, ^2J(C–P) = 5.5 Hz, CO); mass spectrum (^{184}W) *m/z* 434 (M − CO, 34%), 378 (M = 3CO, 100%); IR (CH_2Cl_2/$CDCl_3$) ν(CO) 2025 s, 1945 m, 1928 s cm^{-1}. Anal. Calcd for $C_{14}H_{15}O_4PW\cdot H_2O$: C, 35.04; H, 3.57. Found: C, 35.09; H, 3.59.

(η^5-Cyclopentadienyl)(η^1(*P*)-1,3,4-trimethylphosphole)-tricarbonyltungsten Iodide (7). A solution of 450 mg (1 mmol) of **1** in dry benzene (4 mL) with 0.2 mL of IMe was warmed to 40 °C for 10 min. The red product was recrystallized from CH_2Cl_2/Et_2O (50:50): mp 200 °C; yield 500 mg (85%); ^{31}P NMR ($CDCl_3$) δ −5.41, $^1J(^{31}P-^{183}W)$ = 164.0 Hz; ^1H NMR ($CDCl_3$) δ 2.14 (d, ^2J(H–P) = 11.43 Hz, 3 H, PMe), 2.22 (s, 6 H, CMe), 6.17 (s, 5 H, Cp), 6.72 (d, ^2J(H–P) = 37.42 Hz, CH); ^{13}C NMR ($CDCl_3$) δ 15.93 (d, ^1J(C–P) = 33.66 Hz, PMe), 17.55 (d, ^3J(C–P) = 14.51 Hz, C*Me*), 93.56 (s, Cp), 127.03 (d, ^1J(C–P) = 55.16 Hz, CH), 154.05 (d, ^2J(C–P) = 11.0 Hz, *C*Me), 212.03 (d, ^2J(C–P) = 22.60 Hz, CO), 215.87 (s, CO); mass spectrum (^{184}W) *m/z* 558 (M − CO, 10%), 487 (M − (3CO + Me), 40%), 374 (M − (3CO + I), 100%); IR (CH_2Cl_2) ν(CO) 2045 s, 1975 m, 1950 s. Anal. Calcd for $C_{15}H_{16}IO_3PW$: C, 30.74; H, 2.75; I, 21.65. Found: C, 31.16; H, 2.73; I, 21.84.

(η^5-Cyclopentadienyl)[η^1(*P*):η^1(*P*')-1,2-bis(3,4-dimethylphospholyl)ethane]dicarbonyltungsten Chloride (8). Phospholyltungsten **1** (450 mg, 1 mmol) in dichloroethane (1 mL) was stirred for 1.5 h at 100 °C in a closed tube. Precipitation of the crude complex **8** was achieved by addition of Et_2O (5 mL). Recrystallization from hexane/CH_2Cl_2 (80:20) gave a yellow crystalline product: mp >270 °C; yield 200 mg (35% from **1**); ^{31}P NMR ($CDCl_3$) δ 45.8, $^1J(^{31}P-^{183}W)$ = 222.9 Hz; ^{1} NMR ($CDCl_3$) δ 1.82 (m, 2 H, CH_aH_b), 2.16 (s, 6 H, Me), 2.68 (m, 2 H, CH_aH_b), 5.74 (s, 5 H, Cp), 6.42 (d, 2 H, ^2J(H–P) = 34.71 (Hz, CH_α), 7.24 (d, ^2J(H–P) = 34.59 Hz, $CH_{\alpha'}$); ^{13}C NMR ($CDCl_3$) δ 17.65 (d, ^3J(C–P) = 5.84 Hz, CH_3), 28.11 (pseudo t, CH_2), 89.92 (s, Cp); mass spectrum (^{184}W) *m/z* 562 (M − CO, 5%), 534 (M − 2CO, 16%), 395 [M − (phosphole CH_2CH_2 + CO_2), 100%]; IR (CH_2Cl_2, $CDCl_3$) ν(CO) 1970 s, 1900 s, cm^{-1}. Anal. Calcd for $C_{21}H_{25}ClO_2P_2W$: C, 42.44; H, 3.94; Cl, 5.77. Found: C, 42.69; H, 4.27; Cl, 6.00.

(η^1(*P*)-2,5-Diphenylphosphole *P*-oxide)(η^5-cyclopentadienyl)tricarbonyltungsten (9). Phospholyltungsten **2** (570 mg, 1 mmol) in hexane (5 mL) was stirred in air for 24 h at room temperature. The yellow precipitate was chromatographed with AcOEt/MeOH (90:10) on a short column: ^{31}P NMR (C_6D_6) δ 67.7, $^1J(^{31}P-^{183}W)$ = 146.5 Hz; ^1H NMR (C_6D_6) δ 4.94 (s, 5 H, Cp), 6.16 (d, ^3J(H–P) = 38.53 Hz, 2 H, CH), 7.0–7.9 (m, 10 H, Ph); ^{13}C NMR (C_6D_6) δ 91.75 (s, Cp), 125.18 (d, ^2J(C–P) = 23.55 Hz, C_β), 136.67 (d, ^2J(C–P) = 12.93 Hz, C ipso), 146.74 (d, ^1J(C–P) = 54.56 Hz, C_α), 216.87 (d, ^2J(C–P) = 21.98 Hz, CO), 222.75 (d, ^2J(C–P) = 4.26 Hz, CO); mass spectrum (^{184}W) *m/z* 556 (M − CO, 30%), 500 (M − 3CO, 100%); IR (CH_2Cl_2) ν(CO) 2025 m, 1950–1935 s, broad cm^{-1}.

(η^1(*P*)-2,5-Diphenylphosphole *P*-sulfide)(η^5-cyclopentadienyl)tricarbonyltungsten (10). A solution of 11.4 g (2 × 10^{-2} mol) of phospholyltungsten **2** in toluene (50 mL) with 0.64 g of sulfur (2 × 10^{-2} mol) was stirred for 1 h at room temperature. After concentration under vacuum at room temperature, the residue was chromatographed with CH_2Cl_2. A yellow solid was recovered, which decomposed on heating: yield 10.8 g (90%); ^{31}P NMR (C_6D_6) δ 25.4, $^1J(^{31}P-^{183}W)$ = 146.48 Hz; ^1H NMR (C_6D_6) δ 4.57 (d, J(H–P) = 0.5 Hz, 5 H, Cp), 6.20 (d, ^3J(H–P) = 32.23 Hz, 2 H, CH), 7.0–8.15 (m, 10 H, Ph); ^{13}C NMR (C_6D_6) δ 137.38 (d, ^2J(C–P) = 13.64 Hz, C ipso), 149.31 (d, ^1J(C–P) = 44.40 Hz, C_α), 215.58 (d, ^2J(C–P) = 19.80 Hz, CO), 233.16 (s, CO); mass spectrum (^{184}W) *m/z* 572 (M − CO, 32%), 516 (M − 3CO, 100%); IR (CH_2Cl_2) ν(CO) 2030 s, 1950 vs broad cm^{-1}. **11** was too unstable for correct elemental analysis.

Cycloadduct of Oxide 9 with *N*-Phenylmaleimide (11). A toluene solution (10 mL) of oxide **9** (1.17 g, 2 mmol) and *N*-phenylmaleimide (1.0 g, 6 mmol) was stirred at 70 °C for 45 min. After the solvent was removed, the residue was chromatograhed with AcOEt/MeOH (90:10): yield 1.10 g (73%) of a mixture of endo (M) and exo (m) isomers (M:m = 80:20); ^{31}P NMR (C_6D_6) M (m) δ 167.5 (164.5), $^1J(^{31}P-^{183}W)$ = 200.2 Hz (200.2 Hz); endo ^1H NMR (C_6D_6) δ 4.43 (5 H, Cp), 4.92 (s, 2 H, CH), 6.54 (d, ^3J(H–P) = 7.68 Hz, =CH), 6.90–7.7 (m, 15 H, Ph); ^{13}C NMR (C_6D_6) δ 49.48 (d, ^2J(C–P) = 11.39 Hz, CH), 70.58 (d, ^1J(C–P) = 20.22 Hz, *C*Ph), 91.16 (s, Cp), 133.08 (d, ^2J(C–P) = 8.97 Hz, =CH), 136.99 (s, C ipso), 174.81 (d, ^3J(C–P) = 10.9 Hz,

Table II. Summary of X-ray Results for Compounds 1, 3, 8, and 13

	1	3	8	13
formula	$C_{14}H_{13}O_3PW$	$C_{36}H_{27}OPW$	$C_{22}H_{25}O_2P_2W{\cdot}CHCl_3$	$C_{20}H_{19}O_7PW$
space group	*Cc*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	12.449 (1)	12.137 (2)	8.449 (1)	8.055 (1)
b, Å	7.260 (1)	12.081 (2)	13.319 (2)	8.083 (1)
c, Å	15.650 (2)	19.313 (3)	13.977 (2)	15.820 (1)
α, deg			109.05 (1)	99.96 (1)
β, deg	96.47 (1)	99.27 (1)	102.93 (1)	91.50 (1)
γ, deg			105.94 (1)	98.57 (1)
V, Å^3	1405.46 (51)	2794.70 (1.43)	1341.92 (87)	1001.71 (38)
Z	4	4	2	2
d_{calc}, g/cm^3	2.099	1.641	1.699	1.943
μ, cm^{-1}	85.1	43.0	48.3	60.1
F_{000}	840	1360	670	568
max 2θ, deg	60.0	50.0	60.0	60
no. of observns used	2038	4053	7185	5298
p	0.06	0.05	0.08	0.04
R	0.024	0.022	0.026	0.019
R_w	0.034	0.032	0.047	0.027
GOF	1.03	1.03	1.07	1.03

C=O), 215.95 (d, ^2J(C-P) = 21.92 Hz), 222.49 (s, CO); mass spectrum (^{184}W) *m/z* 757 (M, 10%), 729 (M - CO, 28%), 500 (M - (3CO + *N*-phenylmaleimide), 100%); IR (CH_2Cl_2/decalin) ν(CO) 2030 s, 1960 vs, 1943 vs cm^{-1}.

Cycloadduct of Sulfide 10 with *N*-Phenylmaleimide (12). A toluene solution (10 mL) of sulfide **10** (600 mg, 1 mmoL) and *N*-phenylmaleimide (700 mg, 4 mmol) was stirred at 60 °C for 2 h. The solvent was removed under vacuum and the residue chromatographed with CH_2Cl/AcOEt (90:10). An orange powder was isolated: yield 600 mg (75%); ^{31}P NMR (C_6D_6) δ 183.0, $^1J(^{31}P-^{183}W)$ = 195.3 Hz; ^{1}H NMR (C_6D_6) δ 4.27 (s, 5 H, Cp), 4.98 (s, 2 H, CH), 6.59 (d, ^3J(H-P) = 8.98 Hz, =CH), 7.0–7.8 (m, 15 H, Ph); ^{13}C NMR (C_6D_6) δ 49.43 (d, ^2J(C-P) = 15.20 Hz, CH), 70.38 (d, ^1J(C-P) = 15.30 Hz, *C*Ph), 93.23 (s, Cp), 135.41 (d, ^2J(C-P) = 15.23 Hz, =CH), 174.69 (d, ^3J(C-P) = 11.04 Hz, C=O), 215.54 (d, ^2J(C-P) = 19.31 Hz, CO), 223.57 (s, CO); IR (CH_2Cl_2 decalin) ν(CO) 2035 s, 1965 vs, 1942 vs cm^{-1}. Anal. Calcd for $C_{34}H_{24}NO_5PSW$: C, 52.82; H, 3.12. Found: C, 53.10; H, 3.30.

Chelate Complex 13. Phospholyltungsten **1** (450 mg, 1 mmol) and dimethyl acetylenedicarboxylate (140 mg, 1 mmol) in C_6H_6 (1 mL) were stirred for 15 min. The red solution was chromatographed with CH_2Cl_2/AcOEt (90:10). Red crystals were obtained from CH_2Cl_2: mp 228 °C dec; yield 400 mg (68%); ^{31}P NMR ($CDCl_3$) δ 54.0, $^1J(^{31}P-^{183}W)$ = 308.4 Hz; ^{1}H NMR ($CDCl_3$) δ 2.21–2.24 (2 s, 6 H, Me), 3.64–3.77 (2 s, 6 H, OCH_3), 5.36 (s, 5 H, Cp), 5.95 (d, ^2J(H-P) = 37.93 Hz, 1 H, CH), 6.44 (d, ^2J(H-P) = 36.36 Hz, 1 H, CH); ^{13}C NMR ($CDCl_3$) δ 18.24 (d, ^3J(C-P) = 6.55 Hz, C*Me*), 18.50 (d, ^3J(C-P) = 5.42 Hz, C*Me*), 53.17–53.25 (2 s, OMe), 91.78 (s, Cp), 125.59 (d, ^1J(C-P) = 28.6 Hz, CH), 126.59 (d, ^1J(C-P) = 37.2 Hz, CH), 145.6 (d, ^1J(C-P) = 26 Hz, C=C), 154.96 (d, ^2J(C-P) = 9.10 Hz, C_βMe), 155.99 (d, ^2J(C-P) = 9.12 Hz, C_βMe), 164.28 (s, CO), 166.93 (d, ^2J(C-P) = 26.23 Hz, C=C), 169.13 (d, *J*(C-P) = 37.88 Hz, CO), 222.77 (d, ^2J(C-P) = 12.20 Hz, CO bridge), 225.40 (s, CO), 233.21 (d, ^2J(C-P) = 19.27 Hz, CO); mass spectrum (^{184}W) *m/z* 586 (M, 10%), 502 (M - 3CO, 32%), 358 (M - alkyne - 3CO, 100%); IR (CH_2Cl_2) ν(CO) 1955 s, 1880 s cm^{-1}.

Chelate Complex 14. A C_6H_6 solution (1 mL) containing 450 mg (1 mmol) of phospholyltungsten **1** and 220 mg (1 mmol) of phenyl propiolate was heated at 80 °C for 10 min. The mixture was chromatographed with CH_2Cl_2/AcOEt (90:10). The product was recrystallized from CH_2Cl_2/hexane (50:50): mp 230 °C dec; yield 350 mg (57%); ^{31}P NMR ($CDCl_3$) δ 59.6, $^1J(^{31}P-^{183}W)$ = 307.9 Hz; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, ^3J(H-H) = 7.08 Hz, 3 H, CH_2CH_3), 1.96 (s, 3 H, Me), 2.03 (s, 3 H, Me), 4.0 (q, 2 H, CH_2-CH_3), 5.39 (s, 5 H, Cp), 5.96 (d, ^2J(H-P) = 29.05 Hz, ^{1}H, CH), 6.33 (d, ^2J(H-P) = 29.12 Hz, 1 H, CH), 6.90–7.27 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.51 (s, CH_2CH_3), 17.8–18.39 (m, CH_3), 91.64 (s, Cp), 132.89 (s, C ipso), 155.40 (d, ^2J(C-P) = 8.69 Hz, C*Me*), 155.62 (d, ^2J(C-P) = 8.10 Hz, C*Me*), 156.22 (d, *J*(C-P) = 27.44 Hz, C=C), 166.1 (d, *J*(C-P) = 37.1 Hz, C=C), 167.55 (d, ^3J(C-P) = 29.29 Hz, CO_β), 223.52 (d, ^2J(C-P) = 10.68 Hz, CO bridge), 226.53 (s, CO), 234.78 (d, ^2J(C-P) = 19.59 Hz, CO); mass spectrum (^{184}W) *m/z* 618 (M, 6%), 534 (M - 3CO, 20%), 358 (M - phenyl propiolate - 3CO, 100%); IR (CH_2Cl_2) ν(CO) 1950 vs, 1875 vs cm^{-1}. Anal. Calcd for $C_{25}H_{23}O_5PW$: C, 48.58; H, 3.74. Found: C, 48.69; H, 3.87.

[Bis(μ_2(*P*)-3,4-dimethylphospholyl)bis(η^5-cyclopentadienyl)tetracarbonylditungsten (15). A solution of 450 mg (1 mmol) of **1** in toluene (1 mL) was heated at 100 °C for 2 h. The solution was chromatographed with CH_2Cl_2/AcOEt (90:10). Red crystals of an *a/b* mixture (90:10) of two diastereomers were obtained: yield 200 mg (40%); ^{31}P NMR ($CDCl_3$) δ −214.6 (**a**), $^1J(^{31}P-^{183}W)$ = 146 Hz, −199.7 [**b**], $^1J(^{31}P-^{183}W)$ = 141.1 Hz; ^{1}H NMR ($CDCl_3$) δ 2.21 [2.21 and 2.23] (s, 6 H, Me), 5.28 [4.87] (s, 5 H, Cp), 6.77 (pseudo t, 2 H, CH) [6.96 and 7.20 (d, ^2J(H-P) = 19.4 Hz)]; ^{13}C NMR ($CDCl_3$) **a** δ 17.6 (pseudo t), 91.24 (s, Cp), 140.98 (pseudo t, CH), 144.34 (s, *C*Me); mass spectrum (^{184}W) *m/z* 832 (M, 2%), 720 (M - 4CO, 44%), 609 (M - phospholyl - 4CO, 100%); IR (CH_2Cl_2) ν(CO) 1945 s, 1920 s, 1850 s cm^{-1}. Anal. Calcd for $C_{26}H_{26}O_4P_2W_2$: C, 37.53; H, 3.15. Found: C, 38.01; H, 3.09.

(μ_2-Hydrido)(μ_2(*P*)-2,5-diphenylphospholyl)bis(η^5-cyclopentadienyl)tetracarbonyltungsten (16). Phospholyltungsten **2** (600 mg, 1 mmol) in toluene (1 mL) was heated for 3 h at 110 °C. The crude mixture was chromatographed with CH_2Cl_2/hexane (60:40). The complex was recrystallized from hexane/CH_2Cl_2 (50:50): mp ≥250 °C dec; yield 200 mg (24%); ^{31}P NMR (C_6D_6) δ 95.0, $^1J(^{31}P-^{183}W)$ = 195.31 Hz; ^{1}H NMR (C_6D_6) δ −16.38 [^2J(H-P) = 24.76 Hz, $^1J(^1H-^{183}W)$ = 40.0 Hz], 4.68 (5 H, Cp), 6.93–7.37 (m, 12 H); ^{13}C NMR (C_6D_6) δ 88.91 (s, Cp), 134.80 (d, ^2J(C-P) = 15.41 Hz, C*Me*), 138.33 (d, ^2J(C-P) = 15.21 Hz, C ipso), 155.61 (d, ^1J(C-P) = 36.76 Hz, *C*Ph); mass spectrum (^{184}W) *m/z* 846 (M, 60%), 734 (M - 4CO, 100%); IR (CH_2Cl_2) ν(CO) 1930 vs, 1850 cm^{-1}. Anal. Calcd for $C_{30}H_{23}O_4PW_2$: C, 43.77; H, 2.73; P, 3.66. Found: C, 43.54; H, 3.0; P, 3.65.

X-ray Structure Determinations. All data were collected at −150 ± 0.5 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. The crystal structures were solved and refined using the Enraf-Nonius Molen package. The structures were solved by the Patterson method. Hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while anisotropic temperature factors were used for all other atoms. A non-Poisson weighting scheme was applied in all cases. Relevant crystallographic parameters are assembled in Table II.

Supplementary Material Available: Tables of experimental details for the X-ray structure determinations, positional and thermal parameters, and bond distances and angles for compounds **1**, **3**, **8**, and **13** (28 pages). Ordering information is given on any current masthead page.

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