

Direct Access to *cis*-1,2-Dihydro-1,2-diphosphetes from Butadiynes and Terminal Phosphinidene Complexes

Ngoc Hoa Tran Huy, Louis Ricard, and François Mathey*

Laboratoire "Hétéroéléments et Coordination", URA 1499 CNRS, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

Received June 10, 1997

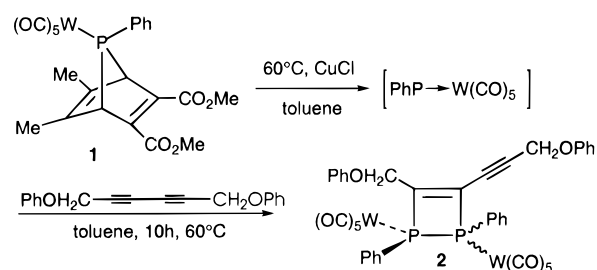
Summary: Transient terminal phosphinidene complexes $[RP \rightarrow W(CO)_5]$ ($R = Ph, Me, Bz, allyl$), as generated from the corresponding 7-phosphanorbornadiene complexes, react with substituted butadiynes to afford the corresponding 3-alkynyl-1,2-dihydro-1,2-diphosphete complexes by insertion of a second phosphinidene unit into the alkynyl-substituted P-C ring bond of the initially formed phosphirene complexes. According to the X-ray analysis of one of the products, the stereochemistry of the substituents on the P-P bond is *cis*.

Introduction

The chemistry of 1,2-dihydro-1,2-diphosphetes displays such versatility¹ that a number of groups have investigated their synthesis. The first described route involves the condensation of cyclopolyphosphines with alkynes.² Despite its simplicity, this approach gives only modest yields of thermally robust 1,2-dihydro-1,2-diphosphetes, together with several other larger rings. More recently, the related [2 + 2] cycloaddition of diphosphene complexes with alkynes has afforded a series of diphosphete complexes under much milder conditions and with better selectivity.³ Alternatively, 1,2-dihydro-1,2-diphosphetes can be obtained *via* the formal insertion of a phosphonium ion into a three-membered phosphirene ring,⁴ the reaction of sterically stabilized iminophosphines with phosphirenes,⁵ or the Zr-to-P metathetical exchange on 1-phospha-2-zircona-cyclobutenes.⁶ Many other approaches of more limited generality also exist.¹ While investigating the reaction of electrophilic terminal phosphinidene complexes with substituted butadiynes, we observed an unexpected insertion of the phosphinidene complexes into the initially formed phosphirene ring,⁷ leading to a series of new 1,2-dihydro-1,2-diphosphete complexes instead of the expected 2,2'-bis(phosphirenyl) species. This observation is the subject of this report.

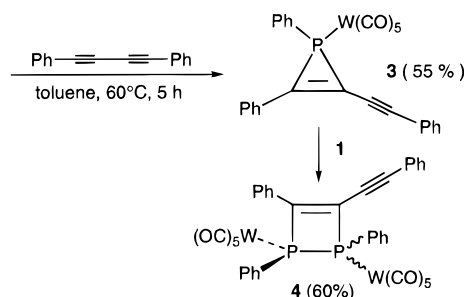
Results and Discussion

The phosphinidene complex $[PhP \rightarrow W(CO)_5]$ was generated from the corresponding 7-phenyl-7-phosphanorbornadiene complex **1** in the presence of CuCl as a catalyst at around 60 °C.⁷ Its reaction with 1,6-diphenoxy-2,4-hexadiyne afforded the 1,2-dihydro-1,2-diphosphete complex **2** as a pure isomer in 47% yield.



The NMR data of **2** are very characteristic. The ³¹P NMR spectrum shows the presence of two nonequivalent phosphorus atoms: AB system, δ 43.38 and 49.37, $\Sigma J(P-P) = 28.1$ Hz. One of the ¹³C resonances of the ring carbons appears at 156.6 ppm as a multiplet with $^1J(C-P) = 30.5$ Hz, $^2J(C-P) = 16.8$ Hz. The course of the reaction leading to **2** was monitored by ³¹P NMR; this showed the initial formation of a phosphirene complex ($\delta -123.4$) by [1 + 2] cycloaddition of the phosphinidene to the alkyne, followed by the insertion of a second phosphinidene unit into one of the intracyclic P-C bonds. The insertion reaction appears to be highly favored with respect to the [1 + 2] cycloaddition of the second alkyne unit; indeed, no trace of bis-phosphirene complex has been detected.

The analogous reaction of $[PhP \rightarrow W(CO)_5]$ (**1**) with 2 equiv of 1,4-diphenyl-1,3-butadiyne led to the phosphirene complex **3**, with only 6% of the corresponding 1,2-diphosphete **4**. The reaction was complete in 5 h, and **3** was isolated in 55% yield. The ³¹P NMR signal



of **3** appears at -133.9 ppm; the proposed structure was established by X-ray analysis (see later). The isolation of the phosphirene complex **3** allowed us to confirm unambiguously the feasibility of the insertion of phos-

* Abstract published in *Advance ACS Abstracts*, September 15, 1997.

(1) (a) Mathey, F.; Charrier, C.; Maigrot, N.; Marinetti, A.; Ricard, L.; Tran Huy, N. H. *Comments Inorg. Chem.* **1992**, *13*, 61. (b) Kummer, S.; Zenneck, U. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 1b, p 1157.

(2) (a) Mahler, W. *J. Am. Chem. Soc.* **1964**, *86*, 2306. (b) Ecker, A.; Schmidt, U. *Chem. Ber.* **1973**, *106*, 1453. (c) Charrier, C.; Guilhem, J.; Mathey, F. *J. Org. Chem.* **1981**, *46*, 3. (d) Charrier, C.; Maigrot, N.; Mathey, F.; Robert, F.; Jeannin, Y. *Organometallics* **1986**, *5*, 623. (e) Phillips, I. G.; Ball, R. G.; Cavell, R. G. *Inorg. Chem.* **1988**, *27*, 2269.

(3) Tran Huy, N. H.; Inubushi, Y.; Ricard, L.; Mathey, F. *Organometallics* **1997**, *16*, 2506.

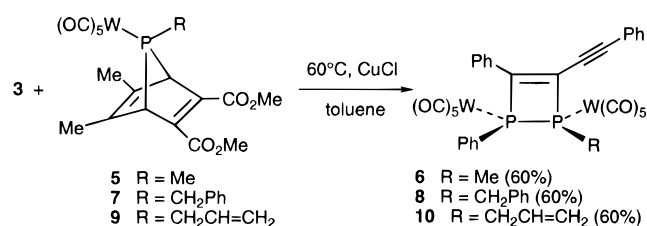
(4) Ricard, L.; Maigrot, N.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 548.

(5) Linck, M.; Niecke, E.; Nieger, M. *Chem. Ber.* **1994**, *127*, 313.

(6) Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365.

(7) Marinetti, A.; Mathey, F.; Fischer, J.; Mitscher, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484.

phosphinidene complexes into the P–C ring bond, leading to the corresponding diphosphete derivatives. Thus, the phosphirene complex **3** was allowed to react with an additional amount of 7-phosphanorbornadiene complex **1**. At 60 °C, in the presence of a catalytic amount of CuCl, the insertion of [PhPW(CO)₅] into the phosphirene **3** takes place, leading to the expected four-membered ring **4**, which was isolated in 60% yield. Only one isomer of **4** has been obtained, as in the case of **2**. The insertion reaction into **3** has been extended to other phosphinidene complexes. [MePW(CO)₅], as generated from the 7-methyl-7-phosphanorbornadiene complex **5**,⁷ reacts with **3** to afford the diphosphete complex **6**, which was isolated as a single isomer and fully characterized. This reaction is both regio- and stereoselective; the insertion was supposed to take place into the P–C ring bond bearing the acetylenic substituent, but an unambiguous structural assignment could not be inferred from the NMR data.



Under the same conditions, the 7-benzyl-7-phosphanorbornadiene **7**⁸ and 7-allyl-7-phosphanorbornadiene **9**⁹ react with the phosphirene **3** to afford the corresponding 1,2-diphosphetes **8** and **10** in 60% yields. These reactions are also totally regio- and stereoselective. In order to establish into which P–C phosphirene bond the insertion of phosphinidene takes place, we performed the X-ray crystal structure analysis of **8** (Figure 1). As expected, the insertion of the benzylphosphinidene unit has taken place into the P–C(C≡CPh) ring bond. But quite unexpectedly, the insertion has produced exclusively the least stable stereoisomer with the two carbon and tungsten P–P substituents in the *cis* disposition.¹⁰ It must be emphasized that [PhPW(CO)₅] does not insert into the P–C bonds of other, C-alkyl- or -aryl-substituted phosphirene complexes under similar conditions. The presence of the acetylenic substituent appears to be crucial for the insertion to take place. The X-ray crystal structure analysis of the phosphirene complex **3** (Figure 2) gives some clue for the increased reactivity of **3** with respect to other phosphirene complexes. Indeed, the P–C₂ is somewhat longer than the P–C₁ bond: 1.806(3) vs 1.789(3) Å. It must be stressed that the intracyclic P–C bond lengths of [(triphenylphosphirene)W(CO)₅] are strictly identical (1.790(4) and 1.787(4) Å)⁷ to the length of P–C₁ in **3**. In the same vein, the C₂–C₃ bond of **3** is longer, at 1.320(4) Å, than the corresponding bond in [(Ph₂C₂PPh)W(CO)₅] (1.307(6) Å). Thus, it appears that the alkynyl substituent weakens the adjacent C=C and P–C bonds, probably through a conjugative destabilizing interaction. Any proposed insertion mechanism must rationalize both the regio- and stereoselectivity of

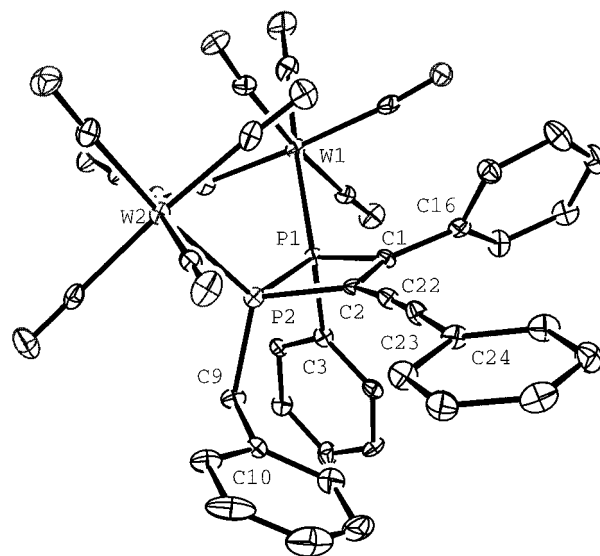


Figure 1. ORTEP drawing of one molecule of **8**, as determined by a single-crystal X-ray diffraction study. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W₁–P₁ 2.510(2), W₂–P₂ 2.482(2), P₁–C₁ 1.825(7), P₁–P₂ 2.283(3), P₁–C₃ 1.818(7), C₁–C₂ 1.35(1), C₁–C₁₆ 1.46(1), C₂–P₂ 1.831(7), C₂–C₂₂ 1.44(1), C₂₂–C₂₃ 1.19(1), P₂–C₉ 1.852(6); W₁–P₁–C₁ 118.5(2), W₁–P₁–P₂ 129.27(8), W₁–P₁–C₃ 116.4(2), C₁–P₁–P₂ 75.5(2), C₁–P₁–C₃ 106.0(3), P₂–P₁–C₃ 103.1(2), P₁–C₁–C₂ 104.5(5), C₁–C₂–P₂ 104.8(5), W₂–P₂–P₁ 122.0(7), W₂–P₂–C₉ 114.2(2), W₂–P₂–C₉ 119.2(2), P₁–P₂–C₉ 109.2(3), C₂–P₂–C₉ 108.6(3).

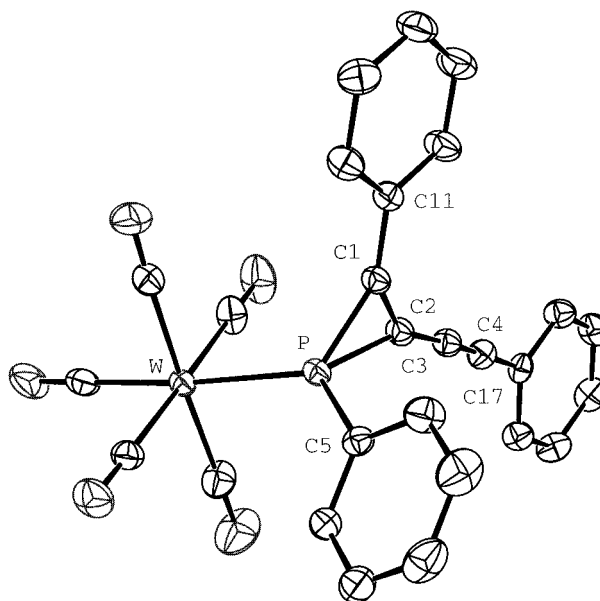


Figure 2. ORTEP drawing of one molecule of **3**, as determined by a single-crystal X-ray diffraction study. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P–C₁ 1.789(3), P–C₂ 1.806(3), C₁–C₂ 1.320(4), P–C₅ 1.823(3), P–W 2.4870(8), C₁–C₁₁ 1.449(4), C₂–C₃ 1.403(4), C₃–C₄ 1.198(5); C₁–P–C₂ 43.1(1), C₁–P–C₅ 107.9(1), C₂–P–C₅ 109.1(1), P–C₁–C₂ 69.1(2), P–C₂–C₁ 67.8(2), C₁–P–W 123.5(1), C₂–P–W 121.1(1), W–P–C₅ 125.0(1), C₁–C₂–C₃ 146.0(3), C₂–C₁–C₁₁ 143.2(3).

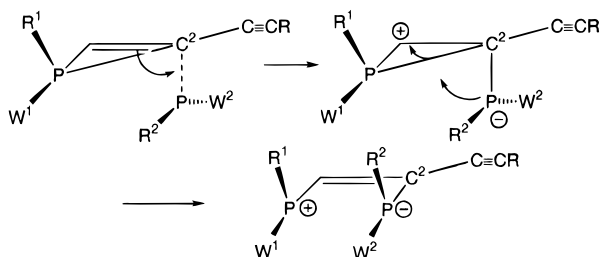
(8) Tran Huy, N. H.; Mathey, F. Unpublished results.

(9) Svava, J.; Marinetti, A.; Mathey, F. *Organometallics* **1986**, *5*, 1161.

(10) Maignot, N.; Ricard, L.; Charrier, C.; Le Goff, P.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, 129, 76.

the reaction. A direct insertion into the P–C ring bond is ruled out because it would certainly afford the less

Scheme 1. Proposed Mechanism for the Formation of *cis*-1,2-Dihydro-1,2-diphosphetes



hindered and more stable *trans* stereoisomers. Our proposal is summarized in Scheme 1. The activated $C^1=C^2$ double bond of the phosphirene ring is attacked by the incoming phosphinidene at the less hindered C^2 . The structural data show (Figure 2) that W^1 is farther away from C^2 than R^1 : $W^1 \cdots C^2$ separation of 3.753 vs 2.955 Å for $R^1(C^5) \cdots C^2$. Hence, the attack takes place on the W^1 side of the phosphirene ring. The orientation of the phosphinidene places W^2 away from W^1 . Phosphirane carbocations are known to ring-open easily.¹¹ In our case, the opening of the phosphirane carbocation resulting from the initial attack places the two phosphorus atoms face to face with the required stereochemistry.

This series of reactions opens a new, convenient, and rather general access to symmetrically or unsymmetrically substituted *cis*-1,2-dihydro-1,2-diphosphetes. Moreover, it should be possible to introduce functional groups on the phosphorus atoms such as alkoxy,¹² alkoxycarbonyl,¹³ dialkylamino,¹⁴ and vinyl¹⁵ from the appropriate phosphinidene precursors, thus broadening the scope of this method.

Experimental Section

All reactions were performed under nitrogen; the solvents were purified, dried and degassed by standard techniques. 1H , ^{13}C , and ^{31}P NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13, 50.32, and 81.01 MHz, respectively. All chemical shifts are reported in ppm downfield from internal TMS (1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method.

[1,2-Diphenyl-3-(phenoxypropynyl)-4-(phoxymethyl)-1,2-dihydro-1,2-diphosphete]decacarbonylditungsten (2). A solution of 7-phosphanorbornadiene complex **1** (3.3 g, 5×10^{-3} mol), 1,6-diphenoxy-2,4-hexadiyne (2 g, 7.6×10^{-3} mol), and 200 mg of CuCl as a catalyst in toluene (20 mL) was heated at 60 °C for 10 h. After evaporation, the residue was chromatographed on silica gel (70–230 mesh Merck) with hexane/ CH_2Cl_2 as the eluent; 1.7 g of **2** was isolated as a dark orange powder (yield 47%): ^{31}P NMR ($CDCl_3$) δ 43.88 (d, $\Sigma J(P-P) = 28$ Hz), 49.37 (d); 1H NMR ($CDCl_3$) δ 4.7 (s, 4H, CH_2OPh), 6.9–7.3 (m, 20H, Ph); ^{13}C NMR ($CDCl_3$) δ 56.41 (s, CH_2), 66.77 (d, $^2J(C-P) = 4.4$ Hz, CH_2), 81.11 (dd, $^2J(C-P) = 21.3$ Hz, $^3J(C-P) = 9.1$ Hz, $-C \equiv C-CH_2OPh$), 98.87 (d, $^3J(C-P) = 3.3$ Hz, $-C \equiv C-CH_2OPh$), 156.56 (dd, $^1J(C-P) = 30.5$ Hz, $^2J(C-P) = 16.8$ Hz, $C=C$), 195.26 (d, $^2J(C-P) = 6.3$ Hz, CO *cis*), 198.2 (d, $^2J(C-P) = 18.2$ Hz, CO *trans*); mass, m/z (relative

intensity) 1126 (M^+ , 18), 1042 ($M^+ - 3CO$, 34), 902 ($M^+ - 8CO$, 59), 846 ($M^+ - 10CO$, 100).

[1,2-Diphenyl-3-phenethynylphosphirene]penta-carbonyltungsten (3). A solution of 7-phosphanorbornadiene complex **1** (3.3 g, 5×10^{-3} mol), 1,4-diphenyl-1,3-butadiyne (2 g, 1×10^{-2} mol), and 200 mg of CuCl in toluene (20 mL) was heated at 60 °C for 5 h. After evaporation, the residue was chromatographed on silica gel with hexane/ CH_2Cl_2 as the eluent. The first fraction was eluted with hexane; 700 mg of diyne in excess was recovered. The second fraction was eluted with hexane/ CH_2Cl_2 (10/1); 1.7 g of phosphirene **3** was isolated as a light yellow powder (yield 55%): ^{31}P NMR ($CDCl_3$) δ -133.99 ($^1J(P-W) = 273.8$ Hz); mass m/z (relative intensity) 638 (M^+ , 12), 578 ($M^+ - 2CO$, 8), 550 ($M^+ - 3CO$, 19), 522 ($M^+ - 4CO$, 29), 494 ($M^+ - 5CO$, 100). Anal. Calcd for $C_{27}H_{15}O_5PW$: C, 51.10; H, 2.36. Found: C, 50.39; H, 2.41.

The third fraction was eluted with hexane/ CH_2Cl_2 (10/2); 100 mg of 1,2-dihydro-1,2-diphosphete **4** was obtained and characterized as described hereafter.

[1,2,3-Triphenyl-4-phenethynyl-1,2-dihydro-1,2-diphosphete]decacarbonylditungsten (4). A solution of phosphirene complex **3** (1 g, 1.57×10^{-3} mol), 7-phosphanorbornadiene complex **1** (1 g, 1.5×10^{-3} mol), and 60 mg of CuCl in toluene (10 mL) was heated at 60 °C for 3 h. After evaporation, the residue was chromatographed on silica gel with hexane/ CH_2Cl_2 (10/2) as the eluent; 300 mg of phosphirene complex **3** were recovered, and then 1 g of complex **4** was isolated as yellow powder (yield 60%, based on the phosphirene consumed): ^{31}P NMR ($CDCl_3$) δ 38.88 and 41.16 ($\Sigma J(P-P) = 33.85$ Hz); ^{13}C NMR ($CDCl_3$) δ 86.92 (dd, $^2J(C-P) = 21.9$ Hz, $^3J(C-P) = 8.6$ Hz, $C \equiv CPh$), 103.06 (pseudotriplet, $^3J(C-P) \approx ^4J(C-P) \approx 3.0$ Hz, $C \equiv CPh$), 154.28 (dd, $^1J(C-P) = 33.1$ Hz, $^2J(C-P) = 15.1$ Hz, $C=C$), 196.49 (d, $^2J(C-P) = 6.2$ Hz, CO *cis*), 198.99 (d, $^2J(C-P) = 27.2$ Hz, CO *trans*); mass m/z (relative intensity) 1066 (M^+ , 35), 982 ($M^+ - 3CO$, 72), 870 ($M^+ - 7CO$, 96), 786 ($M^+ - 10CO$, 100). Anal. Calcd for $C_{38}H_{20}O_{10}P_2W_2$: C, 42.77; H, 1.8. Found: C, 42.83; H, 2.01.

[1-Methyl-2,3-diphenyl-4-phenethynyl-1,2-dihydro-1,2-diphosphete]decacarbonylditungsten (6). A solution of phosphirene complex **3** (0.3 g, 0.5×10^{-3} mol), 7-phosphanorbornadiene complex **5** (1 g, 1.6×10^{-3} mol), and 60 mg of CuCl in toluene (10 mL) was heated for 2.5 h. The same purification as above gave 300 mg of **6** as a yellow powder (yield 60%): ^{31}P NMR ($CDCl_3$) δ 25.96 (d, $\Sigma J(P-P) = 29.22$ Hz, P-Me), 34.67 (d, P-Ph); 1H NMR ($CDCl_3$) δ 1.56 (pseudotriplet, 3H, Me), 7.55 (m, 18H, Ph); ^{13}C NMR ($CDCl_3$) δ 21.66 (d, $^1J(C-P) = 7.4$ Hz, CH_3), 85.42 (dd, $^2J(C-P) = 23.1$ Hz, $^3J(C-P) = 9.0$ Hz, $-C \equiv CPh$), 102.45 (pseudotriplet, $^3J(C-P) \approx ^4J(C-P) \approx 3.3$ Hz, $-C \equiv CPh$), 151.14 (dd, $^1J(C-P) = 33.3$ Hz, $^2J(C-P) = 14.4$ Hz, $C=C$), 196.08 (d, CO *cis*), 198.20 (d, CO *trans*); mass m/z (relative intensity) 1004 (M^+ , 15), 920 ($M^+ - 3CO$, 45), 864 ($M^+ - 5CO$, 32), 808 ($M^+ - 7CO$, 81), 724 ($M^+ - 10CO$, 100). Anal. Calcd for $C_{33}H_{18}O_{10}P_2W_2$: C, 39.44; H, 1.79. Found: C, 40.13; H, 1.67.

[1-Benzyl-2,3-diphenyl-4-phenethynyl-1,2-dihydro-1,2-diphosphete]decacarbonylditungsten (8). Same procedure as above with **7** (yield 60%): ^{31}P NMR ($CDCl_3$) δ 39.80 (d, $\Sigma J(P-P) = 35.86$ Hz), 41.69 (d); ^{13}C NMR ($CDCl_3$) δ 41.2 (s, CH_2Ph), 86.38 (dd, $^2J(C-P) = 21.7$ Hz, $^3J(C-P) = 9.2$ Hz, $-C \equiv CPh$), 102.8 (s, $-C \equiv CPh$), 151.05 (dd, $^1J(C-P) = 32.4$ Hz, $^2J(C-P) = 15.0$ Hz, $C=C$); mass m/z (relative intensity) 1080 (M^+ , 6), 996 ($M^+ - 3CO$, 26), 912 ($M^+ - 6CO$, 29), 856 ($M^+ - 8CO$, 32), 800 ($M^+ - 10CO$, 100). Anal. Calcd for $C_{39}H_{22}O_{10}P_2W_2$: C, 43.33; H, 2.02. Found: C, 42.62; H, 2.09.

[1-Allyl-2,3-diphenyl-4-phenethynyl-1,2-dihydro-1,2-diphosphete]decacarbonylditungsten (10). Same procedure as above with **9** (yield 60%): ^{31}P NMR ($CDCl_3$) δ 35.52 (d, $\Sigma J(P-P) = 35.8$ Hz), 38.36 (d); 1H NMR ($CDCl_3$) δ 2.7 (m, 2H, PCH_2), 5.2–5.6 (m, 3H, $-CH=CH_2$), 7.6 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 40.82 (s, $-CH_2-$), 86.23 (dd, $^2J(C-P) = 21.3$ Hz, $^3J(C-P) = 9.3$ Hz, $-C \equiv CPh$), 102.77 (pseudotriplet, $^3J(C-P) \approx ^4J(C-P) \approx 3.4$ Hz, $-C \equiv CPh$), 151.37 (dd, $^1J(C-P) = 33.3$

(11) Tran Huy, N. H.; Mathey, F. *Synlett* **1995**, 353.

(12) Alcaraz, J.-M.; Svava, J.; Mathey, F. *Nouv. J. Chim.* **1986**, *10*, 321.

(13) Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796.

(14) (a) Deschamps, B.; Ricard, L.; Mathey, F. *Polyhedron* **1989**, *8*, 2671. (b) Deschamps, B.; Mathey, F. *Synthesis* **1995**, 941.

(15) Tran Huy, N. H.; Ricard, L.; Mathey, F. *Organometallics* **1991**, *10*, 3958.

Table 1. Table of Crystallographic Data

	3	8
formula	C ₂₈ H ₁₅ O ₅ PW	C ₃₉ H ₂₂ O ₁₀ P ₂ W ₂
space group	P1 (No. 2)	P2 ₁ /n (No. 14)
data collection temp (K)	123	123
<i>a</i> (Å)	10.249(2)	15.666(2)
<i>b</i> (Å)	11.856(2)	12.488(2)
<i>c</i> (Å)	12.422(2)	19.927(4)
α (deg)	101.92(3)	
β (deg)	108.93(2)	110.34(1)
γ (deg)	100.85(1)	
<i>V</i> (Å ³)	1342.0(1)	3655.0(2)
<i>Z</i>	2	4
<i>d</i> _{calc} (g/cm ³)	1.598	1.963
μ (cm ⁻¹)	44.8	65.7
max 2θ	60.0	52.6
no. of reflns measd	8219	8014
no. of reflns included	6429	4485
no. of params refined	327	479
unweighted agreement factor	0.028	0.030
weighted agreement factor	0.034	0.029
GOF	1.09	1.01
convergence, largest shift/error	0.03	0.00

Hz, ²*J*(C–P) = 13.8 Hz, C=C), 196.17 (m, CO *cis*), 197.84 (m, CO *trans*); mass: *m/z* (relative intensity) 1030 (M⁺, 8), 946

(M⁺ – 3CO, 23), 834 (M⁺ – 7CO, 49), 778 (M⁺ – 9CO, 53), 750 (M⁺ – 10CO, 100).

X-ray Structure Determinations. All data sets were collected on an Enraf Nonius CAD4 diffractometer using Mo Kα (*λ* = 0.710 73 Å) and a graphite monochromator. The crystal structures were solved by direct methods (SIR92) and refined with the Enraf Nonius OpenMOLEN package using reflexions having *F*² < 3.0σ(*F*²). The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. Crystal data are assembled in Table 1.

Acknowledgment. The authors thank the CNRS and Ecole Polytechnique for financial support.

Supporting Information Available: X ray structure determination for **3** and **8**, including tables of positional parameters, bond distances and angles for non-hydrogen atoms, and β_{*ij*} values (8 pages). Ordering information is given on any current masthead page.

OM970487T