4150 *Organometallics* **2006,** *25,* 4150−4154

Synthesis of $Ph_2PC{\equiv}C(CH_2)_5C{\equiv}CPPh_2$ Ligand and Its Complexation with Tungsten Carbonyls to Form a Dinuclear Paddle-Wheel and a Tetranuclear Tripodal Compound

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Received May 1, 2006

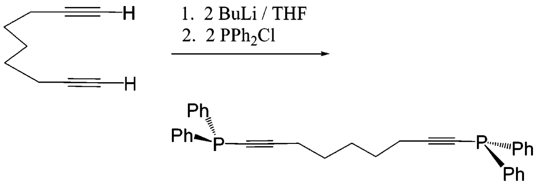
The multifunctional ligand bis(diphenylphosphino)-1,9-nonadiyne (**1**; abbreviated as dpndy) has been prepared by sequential treatment of $HC{\equiv}C(CH_2)_5C{\equiv}CH$ with BuLi and PPh_2Cl. Compound **1** reacts with $W(CO)_4(NCMe)_2$ to give $W(CO)_4(\eta^2\text{-dpndy})$ (**2**), while the reaction of **1** and $W(CO)_3(Me_3tach)$ (Me_3tach = 1,3,5-trimethyl-1,3,5-triazacyclohexane) produces $W(CO)_3(\eta^2\text{-dpndy})(\eta^1\text{-dpndy})$ (**3**), $[W(CO)_3(\eta^2\text{-dpndy})]_2(\mu,\eta^2\text{-dpndy})$ (**4**), and the paddle-wheel complex $[W(CO)_3]_2(\mu,\eta^2\text{-dpndy})_3$ (**5**). Further treatment of $W(CO)_3(Me_3tach)$ with **3** generates the tripodal compound $W(CO)_3[(\mu,\eta^2\text{-dpndy})W(CO)_3(\eta^2\text{-dpndy})]_3$ (**6**). The molecular structures of **2** and **5** have been determined by an X-ray diffraction study.

Introduction

Recent work on assembly of metal complexes (or ions) with suitable bridging ligands allows the preparation of well-defined inorganic supramolecular architectures in solution.[1−6] The tertiary diphosphine ligands, $R_2P{-}(L){-}PR_2$, have been interesting to chemists due to their various modes of coordination with metal atoms[7] and possible catalytic activities of many of their complexes.[8] They also stabilize a variety of ligands of interest to organometallic chemistry as their diphosphine complexes.[9] Most importantly, the electronic and steric properties of diphosphines can be altered in a systemic and predictable way over a wide range by varying the electron-donating ability and steric size of R and the configuration of L, which can be rigid in the $Ph_2P(C{\equiv}C)_nPPh_2$, $Ph_2P(C_6H_4)_nPPh_2$, and $Ph_2P(C_{10}H_6)_2PPh_2$ (BINAP) ligands or flexible in the $Ph_2P(CH_2)_nPPh_2$ and $(C_5H_4\text{-}PPh_2)_2Fe$ ligands.[10] In addition, the two phosphine groups can be incorporated into a medium-sized ring,[11] which offers unique opportunities to study the interactions between phosphorus atoms. As part of our interest in the design and coordination chemistry of multifunctional ligands,[12] herein we present the synthesis of a new diphosphine molecule, $Ph_2PC{\equiv}C(CH_2)_5C{\equiv}CPPh_2$, and its coordination to tungsten carbonyls.

Results and Discussion

Sequential treatment of 1,9-nonadiyne with 2 equiv of *n*-butyllithium and chlorodiphenylphosphine affords a slightly air-sensitive, colorless crystalline solid of bis(diphenylphosphino)-1,9-nonadiyne (**1**) in 48% yield (eq 1) after purification by column chromatography and crystallization from dichloromethane/*n*-hexane. The FAB mass spectrum of **1** presents the molecular ion peak at *m/z* 488. This compound is symmetric in that the ^1H NMR spectrum shows three multiplet signals in the range δ 7.71−7.04 (20H) for the phenyl protons and two broad signals at δ 2.04 (4H) and 1.23 (6H) for the methylene protons, and only one ^{31}P resonance signal is recorded at δ −31.96.



1

(1)

The linear acetylene backbone in the parent $Ph_2PC{\equiv}CPPh_2$ molecule (dppa) constrains the two phosphine moieties to bridge between metal centers.[13] Compound **1** consists of two rigid

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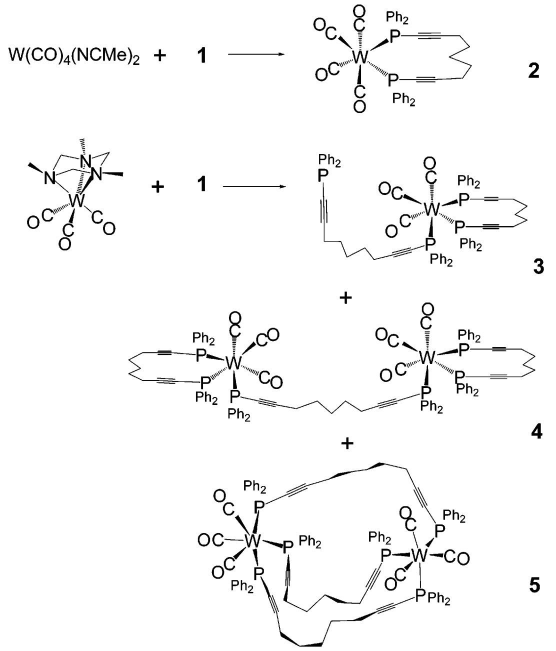
Scheme 1



$C{\equiv}CPPh_2$ groups linked by a flexible pentylene chain and might serve as both a bridging and a chelating agent.[14] Thus, the reaction of $Mo(CO)_4(NCMe)_2$ and $Ph_2PC{\equiv}CPPh_2$ was shown to produce $[Mo(CO)_4]_2(\mu,\eta^2\text{-dppa})_2$ predominantly,[15] while $W(CO)_4(NCMe)_2$ reacts with **1** to generate the chelated complex $W(CO)_4(\eta^2\text{-dpndy})$ (**2**) as the major product (Scheme 1). Compound **2** forms air-stable, yellow crystals. The $^{31}P\{^1H\}$ NMR spectrum presents one sharp singlet at δ −5.46 with appropriate ^{183}W satellites. Coordination of the dpndy ligand makes the methylene proton resonances resolved, shown in Figure 1, which can be assigned on the basis of coupling patterns. The spectral data are in agreement with a C_s symmetry for **2** in solution. The molecular structure of **2**, depicted in Figure 2, shows that the dpndy ligand chelates the $W(CO)_4$ moiety in a cis position. The C5−P1−W angle of 112.70(9)° and the C13−P2−W angle of 111.82(9)° are only slightly deviated from the ideal value of 109.5°, indicating little strain within the metallacycle, while the obtuse P1−W−P2 bite angel of 98.56(2)° is likely arising from steric repulsions between the bulky PPh_2 groups. The W−CO distances to the C3 (1.982(3) Å) and C4 (2.000(3) Å) atoms are slightly but significantly shorter than those to the C1 (2.034(3) Å) and C2 (2.026(3) Å) atoms, consistent with the stronger net donor capacity of the PPh_2R ligand compared with CO.[16] The four acetylene carbon atoms (C5, C6, C12, and C13) are coplanar to within 0.03 Å, which makes a dihedral angle of 72° with the P1−W−P2 plane. The $P{-}C{\equiv}C{-}C$ links are slightly bowed from linearity, as indicated by the $C{\equiv}C{-}P$ angles (174.5(3)° to P1 and 169.4(3)° to P2) and the $C{\equiv}C{-}C$ angles (176.0(3)° to C7 and 177.3(3)° to C11).

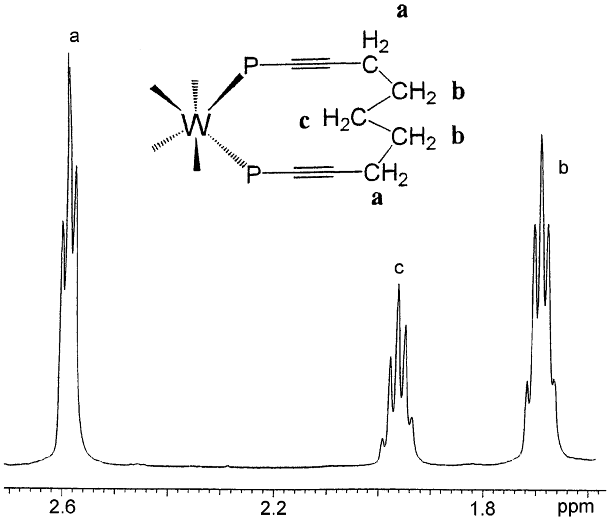


Figure 1. ^1H NMR spectrum of **2** in the methylene resonance region.

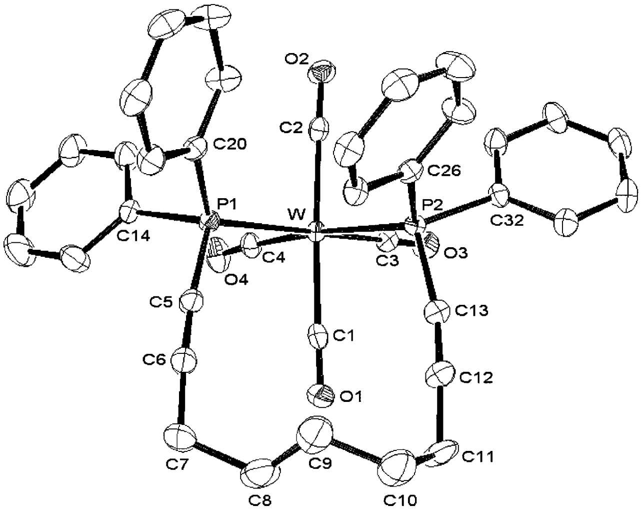


Figure 2. Molecular structure of **2**. Selected bond distances (Å): W−P1 = 2.5255(7), W−P2 = 2.5150(6), W−C1 = 2.034(3), W−C2 = 2.026(3), W−C3 = 1.982(3), W−C4 = 2.000(3), C5−C6 = 1.193(4), C12−C13 = 1.190(4). Selected bond angles (deg): P1−W−P2 = 98.56(2), P1−W−C3 = 174.27(7), P2−W−C4 = 172.75(8), C1−W−C2 = 177.7(1), C5−P1−W = 112.70(9), C6−C5−P1 = 174.3(3), C5−C6−C7 = 176.0(3), C13−P2−W = 111.82(9), C12−C13−P2 = 169.4(3), C13−C12−C11 = 177.3(3).

Since no dinuclear products were isolated from the reaction of **1** and $W(CO)_4(NCMe)_2$, the trisubtituted complex $W(CO)_3(Me_3tach)$ (Me_3tach = 1,3,5-trimethyl-1,3,5-triazacyclohexane) was prepared to react with **1** in a 2:3 ratio at room temperature, producing $W(CO)_3(\eta^2\text{-dpndy})(\eta^1\text{-dpndy})$ (**3**; 22%), $[W(CO)_3(\eta^2\text{-dpndy})]_2(\mu,\eta^2\text{-dpndy})$ (**4**; 31%), and $[W(CO)_3]_2(\mu,\eta^2\text{-dpndy})_3$ (**5**; 5%) after separation by TLC and crystallization. Compounds **3**−**5** form air-stable, yellow crystalline solids and have been properly characterized by elemental analysis and mass, IR, and NMR spectroscopies. The IR spectra of these compounds in the carbonyl region display two strong absorptions around 1940 and 1840 cm^{-1}, a pattern in agreement with a *facial*-$W(CO)_3LLL'$ configuration.[17]

The molecular ion peak at *m/z* 1244 for **3** is the combination of $W(CO)_3$ and two dpndy species. The $^{31}P\{^1H\}$ NMR spectrum presents a 2P doublet at δ −0.96 (J_{P-P} = 24 Hz) with ^{183}W satellites (J_{P-W} = 234 Hz), a 1P triplet at δ −2.87 with ^{183}W satellites, and a 1P singlet at δ −32.8. Thus an octahedral *facial*-$W(CO)_3PPP'$ configuration can be constructed for **3**, with the tungsten atom being chelated by a dpndy ligand and coordinated by one phosphorus atom of another dpndy ligand.

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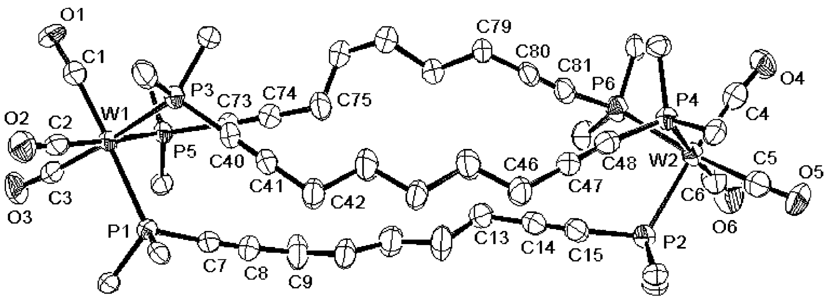


Figure 3. Molecular structure of **5**. The C_6H_5 groups have been artificially omitted, except the ipso carbon atoms, for clarity. Selected bond distances (Å): W1−P1 = 2.528(2), W1−P3 = 2.532(2), W1−P5 = 2.525(2), W1−C1 = 1.978(7), W1−C2 = 1.966(8), W1−C3 = 1.969(7), W2−P2 = 2.507(2), W2−P4 = 2.535(2), W2−P6 = 2.529(2), W2−C4 = 1.950(8), W2−C5 = 1.989(8), W2−C6 = 1.946(8). Selected bond angles (deg): P1−W1−P3 = 90.62(5), P1−W1−P5 = 90.63(6), P3−W1−P5 = 94.98(6), P2−W2−C4 = 171.8(2), P6−W2−C5 = 172.4(2), P4−W2−C6 = 177.6(2), P2−W2−P4 = 92.86(6), P2−W2−P6 = 94.01(6), P4−W2−P6 = 89.11(6), C8−C7−P1 = 177.1(6), C7−C8−C9 = 176.1(8), C14−C15−P2 = 167.1(7), C13−C14−C15 = 177.8(8), C41−C40−P3 = 178.1(7), C40−C41−C42 = 178.4(8), C47−C48−P4 = 173.2(6), C46−C47−C48 = 177.7(8), C74−C73−P5 = 168.3(7), C73−C74−C75 = 174.5(9), C80−C81−P6 = 173.1(6), C79−C80−C81 = 176.4(7).

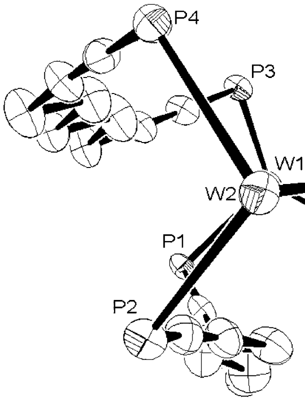
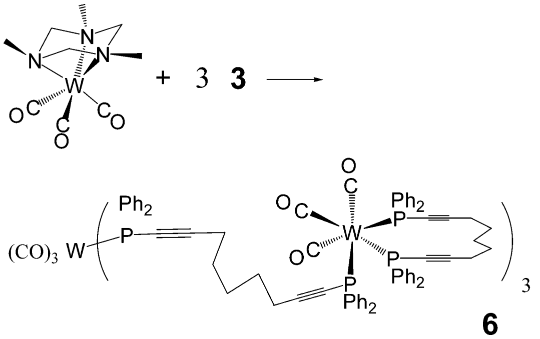


Figure 4. Projection of **5** down the W2−W1 vector to show the paddle-wheel arrangement of the ligands.

The molecular ion peak of **4** at *m*/*z* 2000 suggests a dinuclear $[W(CO)_3]_2(dpndy)_3$ species. The $^{31}P\{^1H\}$ NMR spectrum contains two sets of resonance signals: a 4P doublet at δ −1.51 with ^{183}W satellites and a 2P triplet at δ −3.58 with ^{183}W satellites. Apparently, compound **4** consists of two identical $W(CO)_3(\eta^2$-dpndy) moieties bridged by a dpndy ligand.

Compound **5** is isomeric to **4** to present the same molecular ion peaks and elemental analysis. However, the ^1H NMR spectrum of **5** is complicated, and only one ^{31}P resonance is recorded at δ 5.39 with ^{183}W satellites. A single-crystal X-ray diffraction study was conducted to reveal the structure of **5**. The crystals contain solvent molecules (dichloromethane and diethyl ether). There are two independent but structurally similar complexes in the asymmetric unit, and one is depicted in Figure 3, which consists of two facially substituted $W(CO)_3$ groups bridged by three dpndy lignads to show a cryptand-like cage. The coordination of each tungsten atom is a distorted octahedral such that the C−W−C angles range from 83.2(3)° to 88.6(3)° and the P−W−P angles are in the range 89.11(6)−94.98(6)°. The W−P−$C_{(acetylene)}$ angles range from 114.4(2)° to 119.2(2)°, consistent with steric strain arising from *syn*-coordination of three phosphine groups. The P−C≡C−C backbones are slightly bowed, as indicated by the P−C≡C angles (167.1(7)−178.1(7)°) and the C≡C−C angles (174.5(9)−178.4(8)°). Interestingly, the rigid C≡C units constrain the dpndy ligands in a paddle-wheel arrangement, shown in Figure 4. There is a large void at the center, such that the W1···W2 distances is 15.17 Å and the distances between the middle methylene carbon atoms are 5.13 Å on average. It is plausible that compound **5** is derived from **4** by opening of the chelated rings. Since heating **4** gives no reaction, compound **5** is more likely formed by direct assembling of $W(CO)_3(Me_3tach)$ and the ligands in the solution.



6

(2)

Compound **3** contains a pendent phosphine group and may act as an organomatallic ligand for further structural construction.[18] Thus, reaction of $W(CO)_3(Me_3tach)$ with 3 equiv of **3** in dichloromethane at ambient temperature affords a tetratungsten tripodal macromolecule, $W(CO)_3[(\mu,\eta^2$-dpndy)$W(CO)_3(\eta^2$-dpndy)$]_3$ (**6**), in 54% yield after purification by TLC and crystallization. Compound **6** forms a pale yellow, air-stable solid. There are two strong carbonyl stretching absorptions at 1940 and 1844 cm^{-1}, indicating a *facial*-$W(CO)_3$ arrangement for all tungsten atoms. The coordination modes of dpndy ligands in **6** can be assigned on the basis of the $^{31}P\{^1H\}$ NMR spectrum shown in Figure 5. The phosphorus resonance pattern resembles that recorded for **3**, except that the singlet peak at δ −32.8 for **3** is shifted downfield to δ −2.67 and accompanied with ^{183}W satellites for **6**. We are not able to obtain suitable crystals of **6** for an X-ray diffraction study. The energy-minimized configuraton constructed for **6** suggests a disklike feature for the tripodal framework (Chart 1), likely due to great steric bulk of the terminal η^2-dpndy groups. The complex is estimated to be 38 Å wide, where the distance between the central and the peripheral tungsten atoms is ca. 14 Å.

In conclusion, the new diphosphine ligand, dpndy, has been prepared and reacted with substituted tungsten carbonyls to generate a variety of complexes, which are of interest within the context of coordination and supramolecular chemistry. Previously, alkyne−alkyne coupling to generate carbocycles was demonstrated in the $W_2(CO)_6(Ph_2PC{\equiv}CPPh_2)_3$[19] and $[PtCl_2(Ph_2$-

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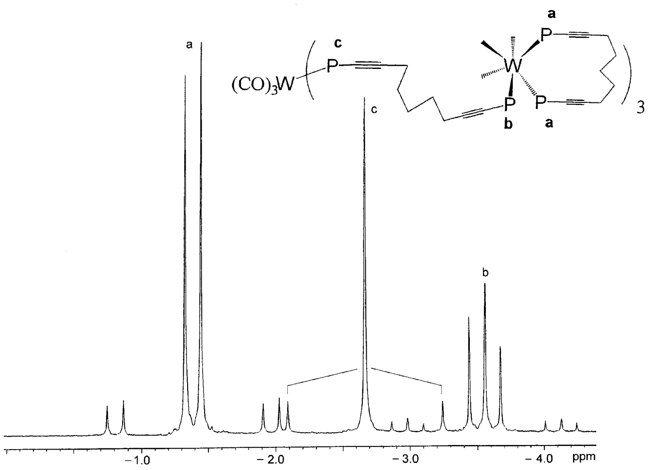
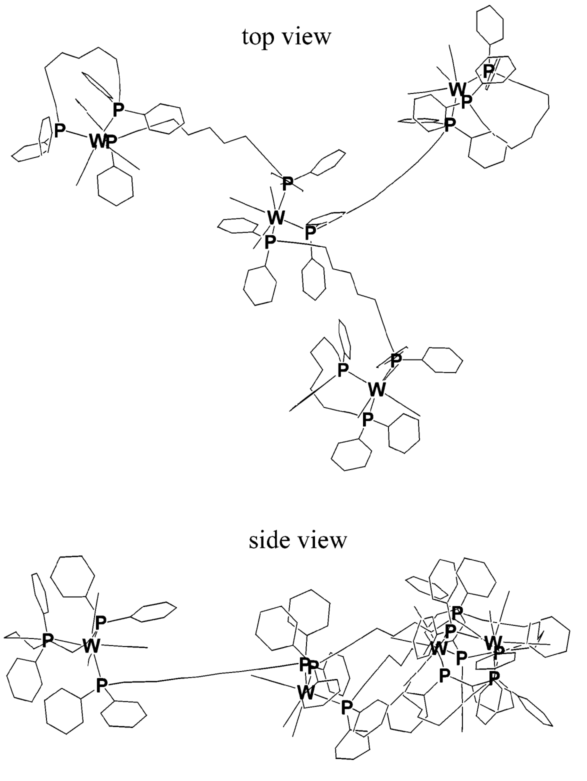


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of **6** in CD_2Cl_2 at 22 °C.

Chart 1



$PC{\equiv}C-C{\equiv}CPPh_2)]_n$ (n = 2, 3)[20] systems. There are several free alkyne moieties in **2**−**6**, and their similar reactivity is currently under investigation.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of dinitrogen with standard Schlenk techniques. $W(CO)_4(NCMe)_2$[21] and $W(CO)_3(Me_3tach)$[22] were prepared by literature methods. 1,9-Nonadiyne, PPh_2Cl, and BuLi (1.6 M in hexane) were purchased from Aldrich. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). ^1H and ^{31}P NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer. Fast-atom-bombardment (FAB) mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

Preparation of 1. 1,9-Nonadiyne (344 mg, 2.87 mmol) and THF (50 mL) were placed in an oven-dried 100 mL Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper. The flask was placed in a cold bath at −20 °C, and BuLi (3.8 mL, 6.08 mmol) were introduced slowly via a syringe. The resulting mixture was stirred at −20 °C for 20 min, warmed to room temperature to stir for another 20 min, and then cooled to 0 °C in an ice bath. PPh_2Cl (1.35 g, 6.1 mmol) was added into the flask via a syringe over a period of 15 min, and the solution was warmed to room temperature and stirred for 6 h. The volatile materials were removed under vacuum, and the crude products were purified by column chromatography (silica gel, 3 × 25 cm). The column was first flashed with 150 mL of dichloromethane/*n*-hexane (1:9, v/v) and then eluted with 200 mL of dichloromethane/*n*-hexane (1:1, v/v). The eluant was evaporated to dryness on a rotary evaporator, and the residue was crystallized from dichloromethane/*n*-hexane to afford colorless crystals of $Ph_2PC{\equiv}C(CH_2)_5C{\equiv}CPPh_2$ (**1**; 673 mg, 48%). Anal. Calcd for $C_{33}H_{30}P_2$: C, 81.13; H, 6.19. Found: C, 81.01; H, 5.96. MS (FAB): *m/z* 488 (M^+). ^1H NMR (C_6D_6, 23 °C): δ 7.71 (m, 8H), 7.11 (m, 8H), 7.04 (m, 4H, Ph), 2.04 (br, 4H, $CH_2C{\equiv}C$), 1.23 (br, 6H, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 23 °C): δ −31.96.

Preparation of 2. Compound **1** (75 mg, 0.15 mmol) and $W(CO)_4(NCMe)_2$ (53 mg, 0.14 mmol) were placed in an oven-dried 50 mL Schlenk flask under a dinitrogen atmosphere. Dichloromethane (10 mL) was added into the flask, and the solution was stirred at room temperature for 48 h. The solution was concentrated to ca. 2 mL under vacuum and then subjected to TLC with dichloromethane/*n*-hexane (1:4, v/v) as eluant. Isolation of the material forming the first yellow band gave yellow crystals of $W(CO)_4(\eta^2\text{-dpndy})$ (**2**; 56 mg, 51%) after crystallization from dichloromethane/*n*-hexane. Anal. Calcd for $C_{37}H_{30}O_4P_2W$: C, 56.65; H, 3.85. Found: C, 56.80; H, 3.95. IR (CH_2Cl_2, νCO): 2012 (m), 1922 (s), 1898 (s) cm^{-1}. MS (FAB): *m/z* 784 (M^+, ^{184}W). ^1H NMR (CD_2Cl_2, 23 °C): δ 7.60 (m, 8H), 7.27 (m, 12H, Ph), 2.59 (t, 4H, J_{H-H} = 6 Hz, $CH_2C{\equiv}C$), 1.96 (p, 2H, J_{H-H} = 7 Hz), 1.69 (p, 4H, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ −5.46 (s; with ^{183}W satellites J_{P-W} = 239 Hz).

Reaction of 1 and $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$. $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$ (43 mg, 0.11 mmol) and compound **1** (80 mg, 0.16 mmol) were placed in an oven-dried 50 mL Schlenk flask under a dinitrogen atmosphere. Dichloromethane (16 mL) was added into the flask, and the solution was stirred at room temperature for 48 h. The solution was concentrated to ca. 2 mL under vacuum and then subjected to TLC with dichloromethane/*n*-hexane (1:1, v/v) as eluant. Three major pale yellow bands were developed. Isolation of the material forming the first band afforded $W(CO)_3(\eta^2\text{-dpndy})(\eta^1\text{-dpndy})$ (**3**; 30 mg, 22%), the second band afforded $[W(CO)_3(\eta^2\text{-dpndy})]_2(\mu,\eta^2\text{-dpndy})$ (**4**; 34 mg, 31%), and the third band afforded $[W(CO)_3]_2(\mu,\eta^2\text{-dpndy})_3$ (**5**; 6 mg, 5%).

Characterization of 3. Anal. Calcd for $C_{69}H_{60}O_3P_4W$: C, 66.57; H, 4.86. Found: C, 66.14; H, 4.87. IR (CH_2Cl_2, νCO): 1940 (s), 1842 (s) cm^{-1}. MS (FAB): *m/z* 1244 (M^+, ^{184}W). ^1H NMR (CD_2Cl_2, 23 °C): δ 7.73 (m, 4H), 7.61 (m, 12H), 7.30 (m, 24H, Ph), 2.46 (t, 2H, J_{H-H} = 7 Hz), 2.15 (m, 4H), 1.94 (t, 2H, J_{H-H} = 8 Hz, $CH_2C{\equiv}C$), 1.59 (m, 2H), 1.50 (m, 4H), 1.42 (m, 4H), 1.27 (m, 2H, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ −0.96 (d, 2P, J_{P-P} = 24 Hz; with ^{183}W satellites J_{P-W} = 234 Hz), −2.87 (t, 1P, J_{P-P} = 24 Hz; with ^{183}W satellites J_{P-W} = 232 Hz), −32.8 (s, 1P).

Characterization of 4. Anal. Calcd for $C_{105}H_{90}O_6P_6W_2$: C, 63.01; H, 4.53. Found: C, 62.96; H, 4.94. IR (CH_2Cl_2, νCO): 1940 (s), 1844 (s) cm^{-1}. MS (FAB): *m/z* 2000 (M^+, ^{184}W). ^1H NMR

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(CD_2Cl_2, 23 °C): δ 7.73 (m, 8H), 7.60 (m, 16H), 7.28 (m, 36H, Ph), 2.16 (m, 8H), 1.98 (t, 4H, $J_{H-H} = 7$ Hz, $CH_2C{\equiv}C$), 1.52 (m, 6H), 1.39 (m, 4H), 1.25 (m, 8H, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ −1.51 (d, $J_{P-P} = 24$ Hz; with ^{183}W satellites $J_{P-W} = 235$ Hz), −3.58 (t, $J_{P-P} = 24$ Hz; with ^{183}W satellites $J_{P-W} = 232$ Hz).

Characterization of 5. Anal. Calcd for $C_{105}H_{90}O_6P_6W_2$: C, 63.01; H, 4.53. Found: C, 63.28; H, 4.51. IR (CH_2Cl_2, νCO): 1940 (s), 1844 (s) cm^{-1}. MS (FAB): *m/z* 2000 (M^+, ^{184}W). ^1H NMR (CD_2Cl_2, 23 °C): δ 8.16 (m, 24H), 7.02 (m, 36H, Ph), 2.10 (m, 6H), 1.94 (m, 6H, $CH_2C{\equiv}C$), 1.73 (m, 3H), 1.23 (m, 3H), 1.98 (m, 12H, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 5.39 (s; with ^{183}W satellites $J_{P-W} = 237$ Hz). The crystals found suitable for an X-ray diffraction study were grown from toluene/*n*-hexane at −15 °C.

Reaction of 3 and $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$. $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$ (5 mg, 0.0126 mmol), compound **3** (49 mg, 0.04 mmol), and dichloromethane (6 mL) were placed in an oven-dried 50 mL Schlenk flask under a dinitrogen atmosphere. The solution was stirred at room temperature for 48 h. The solvent was removed under vacuum, and the residue was applied on TLC, eluting with dichloromethane/*n*-hexane (2:1, v/v). Isolation of the material forming the fifth major band gave a pale yellow solid of $W(CO)_3[(\mu,\eta^2\text{-dpndy})W(CO)_3(\eta^2\text{-dpndy})]_3$ (**6**; 27 mg, 54%). Anal. Calcd for $C_{210}H_{180}O_{12}P_{12}W_4$: C, 63.01; H, 4.53. Found: C, 62.86; H, 4.36. IR (CH_2Cl_2, νCO): 1940 (s), 1844 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 23 °C): δ 7.69 (m, 12H), 7.60 (m, 36H), 7.23 (m, 72H, Ph), 2.10 (m, 18H), 1.96 (t, 6H, $J_{H-H} = 7$ Hz, $CH_2C{\equiv}C$), 1.47 (m, 12H), 1.28 (m, 24H, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ −1.39 (d, $J_{P-P} = 24$ Hz; with ^{183}W satellites $J_{P-W} = 235$ Hz), −2.67 (s; with ^{183}W satellites $J_{P-W} = 233$ Hz), −3.56 (t, $J_{P-P} = 24$ Hz; with ^{183}W satellites $J_{P-W} = 232$ Hz).

Structure Determination for 2 and 5. The crystals of **2** and **5** found suitable for X-ray analysis were each mounted in a thin-walled glass capillary and aligned on Bruker Smart ApexCCD (for **2**) and Nonius KappaCCD (for **5**) diffractometers, with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The θ range for data collection is 1.74−27.50° for **2** and 1.04−25.00° for **5**. Of the 41 104 and 133 620 reflections collected for **2** and **5**, 7315 and 34 028 reflections were independent, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-squares cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included with a riding model. All calculations were performed using the SHELXTL-97 package.[23] The data collection and refinement parameters are presented in Table 1.

Table 1. Crystallographic Data for 2 and 5

	2	**5**
chem formula	$C_{37}H_{30}O_4P_2W$	$C_{109.5}H_{101}ClO_7P_6W_2$
cryst syst	monoclinic	monoclinic
fw	784.40	2117.87
T, K	150(1)	150(1)
space group	$P2_1/n$	$P2_1/c$
a, Å	10.3289(6)	21.1762(6)
b, Å	13.7759(8)	22.3612(6)
c, Å	22.94106(13)	41.0111(10)
β, deg	102.810(1)	90.3001(8)
V, Å^3	3183.0(3)	19419.5(9)
Z	4	8
D_{calc}, g cm^{-3}	1.637	1.449
μ, mm^{-1}	3.769	2.550
R_1/wR_2	0.0224/0.0500	0.0478/0.1125
GOF on F^2	1.117	1.020

Acknowledgment. We are grateful for support of this work by the National Science Council of Taiwan.

Supporting Information Available: Crystal data of **2** and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0603722

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