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products have thus far prevented isolation of the material as a pure solid. Addition of acetic acid generates the known diacetate[15] and 2 equiv of arene.

A more tractable organo derivative was prepared by reaction of the dichloride with $LiCH_2SiMe_3$; the resulting *cis*-dialkyl **5** was isolated in quantitative yield and has been fully characterized.[9] Although crystalline **5** is very air-sensitive, it can be stored at room temperature in a fluorescent-lit, nitrogen-filled drybox for many months. Benzene solutions exposed to fluorescent room lighting for several hours decompose to a myriad of products, as indicated by proton NMR spectroscopy. Once again, ligands coordinated to the (OEP)Zr moiety are heavily shielded in the proton NMR spectrum. Singlets at δ -4.18 (4 H) and δ -1.80 (18 H) correspond to the methylene and trimethylsilyl groups, respectively. The cis structure indicated by the appearance of diastereotopic methylenes for the OEP ligand has been confirmed in the solid state by X-ray crystallography (Figure 1).[16]

The Zr–C bond distances (2.285 (4), 2.289 (4) Å) are identical, within experimental error, to those in $Cp_2Zr(CH_2SiMe_3)_2$,[17] and C–Si distances and Zr–C–Si angles are unexceptional. Evidence for the increased steric demand of the OEP ligand versus the Cp_2 moiety may be inferred from the C(37)–Zr–C(41) angle, which is significantly more acute than the corresponding parameter in $Cp_2Zr(CH_2SiMe_3)_2$ [82.7 (1)° and 97.8 (1)°, respectively]. The plane defined by the four nitrogens is exact, although the porphyrin ligand as a whole is both domed and ruffled. The Zr lies 0.93 Å above the N_4 plane and appears to sit closer to one side of the ring, such that Zr–N distances range from 2.236 (3) and 2.232 (3) Å on one side to 2.250 (3) and 2.248 (3) Å on the other. Note, however, that these differences are small and may not be significant given the esd's involved.

Treatment of benzene solutions of **5** with excess carbon monoxide or 2,6-xylyl isocyanide led to rapid, complex reactions from which no pure products have yet been isolated. Protonolysis with acetic acid rapidly forms the diacetate and tetramethylsilane in high yield. Reaction of **5** with hydrogen (1 atm, 20 °C) produces 2 equiv of tetramethylsilane and a dark green paramagnetic solution, the nature of which is still under investigation.[18] Compound **5** was unreactive toward ethylene (2 atm) over 24 h at room temperature; however, when hydrogen (2 atm) was added to these solutions, a smooth hydrogenation occurred over several hours to produce 8–10 equiv of ethane per mole of Zr. NMR spectra taken during this period were highly informative, revealing the formation of two ethyl-containing metalloporphyrins **6** and **7**.[9] Proton chemical shifts for the zirconium-bound ethyl groups are similar to those found in related *trans*-diethyl metalloporphyrins.[10,19,20] NMR spectra of the deuterated analogues **6**-d and **7**-d_2 are similar except that the $ZrCH_2CH_2D$ groups each give rise to two sets of triplets. Monitoring the course of the hydrogenation showed that all three compounds (**5**–**7**) were present at an early stage, but that the concentration of the diethyl **7** grew as **5** and **6** were consumed. Over the course of several hours at room temperature, the diethyl complex **7** decomposed and ethane production ceased.

Hydrogenation of propene under similar conditions proceeds via the *n*-propyl derivatives **8** and **9**.[9] We found no spectroscopic evidence for the participation of species resulting from Markownikov addition. The presumed hydride intermediates in these hydrogenation reactions were not detected spectroscopically; presumably, the rate of olefin insertion was rapid compared to that for Zr–C bond hydrogenolysis.[21,22]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society and the Exxon Education Foundation for funding.

Supplementary Material Available: Characterization data for all new compounds and details of the structure determination of **5**, including tables of crystal and data collection parameters, temperature factor expressions, positional parameters, intramolecular distances and angles, and least-squares planes (15 pages); listing of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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Alkyne–Alkyne Coupling with $W(PhC{\equiv}CPh)_3(CO)$. Crystal Structure of $W(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2(CO)$

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Reactions of metal carbonyls with alkyne derivatives are known to give a wide variety of organometallic and organic products.[1-4] It has been shown that $Mo(CO)_6$ or $(diglyme)Mo(CO)_3$ reacts with diphenylacetylene to yield hexaphenylbenzene and several molybdenum tetraphenylcyclobutadiene complexes.[5] In contrast, the analogous reaction with either $W(CO)_6$ or $W(CO)_3(NCCH_3)_3$ only leads to the formation of tris(alkyne) complexes of the type $W(RC{\equiv}CR')_3(CO)$.[6] It appears that the $W(RC{\equiv}CR')_3(CO)$ stoichiometry is particularly stable, as suggested by theoretical analyses.[7,8] Thus, further reaction with alkynes is likely to be retarded. We wish to report that under harsh conditions, however, $W(PhC{\equiv}CPh)_3(CO)$ will couple with diphenylacetylene, forming a cyclobutadiene complex.

$W(PhC{\equiv}CPh)_3(CO)$[6a] (200 mg, 0.26 mmol) and diphenylacetylene (135 mg, 0.76 mmol) were mixed and sealed in a glass

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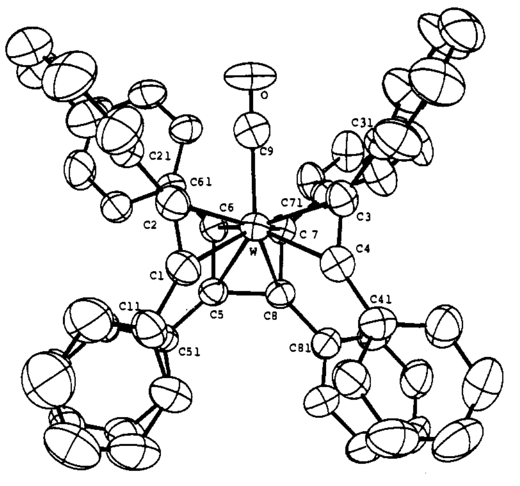


Figure 1. Molecular structure of W(η^4-C_4Ph_4)(PhC≡CPh)$_2$(CO) with hydrogen atoms artificially omitted.

tube under vacuum (0.1 mmHg). The tube was heated to 120 °C, at which temperature diphenylacetylene melted, forming a dark-red solution immediately. After 25 min, the tube was cooled to room temperature and opened in air. The residue was applied to TLC and eluted with *n*-hexane/dichloromethane (3:1 v/v). Crystallization of the material forming the orange-red band from *n*-hexane yielded air-stable, red crystals of W(η^4-C_4Ph_4)(PhC≡CPh)$_2$(CO)[9] (102 mg, 0.11 mmol, 41%). For comparison, the reaction was conducted in refluxing toluene under nitrogen, but produced W(η^4-C_4Ph_4)(PhC≡CPh)$_2$(CO) in low yields (<10%).

The molecular structure of W(η^4-C_4Ph_4)(PhC≡CPh)$_2$(CO)[10] is illustrated in Figure 1. The structure consists of discrete molecules with each tungsten unit bonded to one terminal CO (∠W–C9–O = 177.5 (5)°), one tetraphenylcyclobutadiene, and two diphenylacetylenes. The hydrocarbon ligands are essentially in an eclipsed form with respect to the W–C9–O axis, as evidenced by their torsional angles.[11] The cyclobutadiene ring (C5∼C8) is planar with the maximum atomic displacement from plane being 0.008 (8) Å. The two alkyne ligands are themselves coplanar to within 0.026 (9) Å. The interplanar angle between the plane of cyclobutadiene and that of the two alkynes is 15.3 (4)°. Apparently, the coordinated CO ligand is sterically forcing the alkyne ligands and the cyclobutadiene ring from being parallel, such that C1C2 is tilted from the W–C9–O vector by 7.38°, C4C3 by 8.21°, C5C6 by 12.49°, and C8C7 by 11.78°. Furthermore, taking the centers of the alkynes (cen1 and cen2), the center of cyclobutadiene (cen3), and the terminal CO ligand, the coordination about the tungsten atom can be described as a distorted tetrahedron (Figure 2).[12]

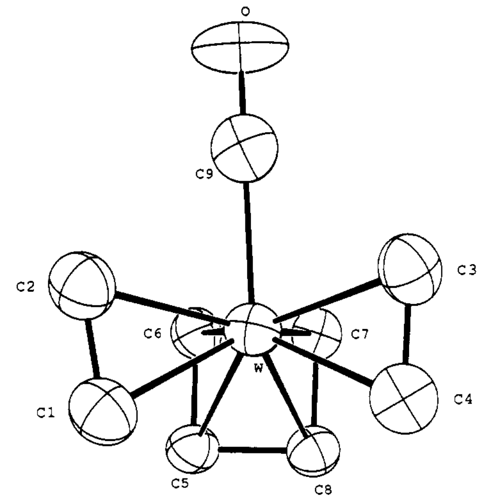
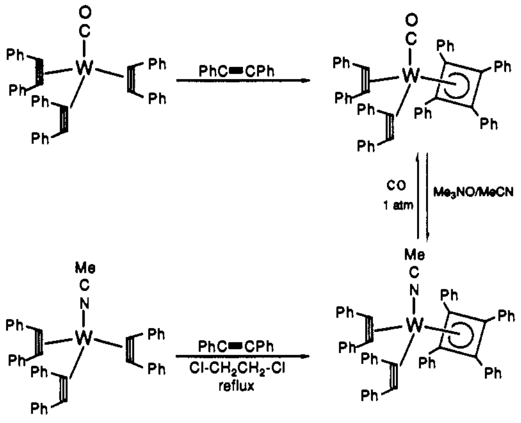


Figure 2. W(C_4)(C_2)$_2$CO core of the molecule, showing the distorted tetrahedral coordination for the tungsten atom.

Scheme I



The W–C9 and C9–O distances associated with the carbonyl group are 2.018 (7) and 1.130 (9) Å, respectively, which are comparable with those found in W(PhC≡CPh)$_3$(CO),[13] where W–C = 1.99 Å and C–O = 1.16 Å. The alkyne C≡C vectors are tilted to the WCO group; this gives rise to slight differences between the upper and lower C–W distances, such that W–C2 = 2.112 (6), W–C1 = 2.100 (6), W–C3 = 2.127 (6), and W–C4 = 2.097 (6) Å. The two alkyne C≡C lengths are about equal, 1.304 (±0.001) Å, and the phenyl groups are bent back from the C≡C axis by angles averaging 139.8° (range, 137.4–141.7°).

The cyclobutadiene group is bonded to the tungsten atom asymmetrically, with W–C6 = 2.271 (6) Å and W–C7 = 2.224 (6) Å being significantly shorter than W–C5 = 2.363 (6) Å and W–C8 = 2.343 (6) Å. The phenyl groups connected to the cyclobutadiene ring are exo to W. Thus they are bent away from the cyclobutadiene plane by angles ranging from 23.0 (±1.3)° for C6, C7 to 13.7 (±0.5)° for C5, C6; this reflects a large CO steric influence on the phenyl groups syn to CO but probably a very limited influence on those anti to CO. The cyclobutadiene C–C bond distances, ranging from 1.455 to 1.491 Å, closely resemble those found for other cyclobutadiene–metal complexes.[5b,5c,14]

The geometry of W(η^4-C_4Ph_4)(PhC≡CPh)$_2$(CO) should lead to chemically inequivalent C≡C carbons and cyclobutadiene ring carbons. Thus, the ^{13}C NMR spectrum at room temperature

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(9) Data: mp 224–226 °C dec; mass spectrum (fast atom bombardment), *m/z* 924 (M^+, ^{184}W), 896 (M^+ – CO), 718 (M^+ – CO – C_2Ph_2), 540 (M^+ – CO – 2C_2Ph_2); IR (KBr) 2030 (ν CO), 1595 (ν C≡C) cm^{-1}; ^1H NMR (CD_2Cl_2, 25 °C) δ 7.25–6.77 (m, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 214.9 (CO), 175.9, 158.9 (≡C), 140.6, 138.7, 135.1, 133.2, 131.4, 130.1, 129.3, 128.2, 127.9, 127.4, 126.5, 125.1 (Ph), 83.8 (C_4Ph_4). Anal. Calcd for $C_{57}H_{40}WO$: C, 74.03; H, 4.36. Found: C, 74.33; H, 4.60.

(10) The crystal of W(η^4-C_4Ph_4)(PhC≡CPh)$_2$(CO) found suitable for X-ray analysis was grown by slow evaporation of a dichloromethane/hexane solution at 25 °C. Crystal data are as follows: triclinic, space group $P\bar{1}$, a = 10.961 (1) Å, b = 11.086 (2) Å, c = 18.579 (4) Å, α = 97.46 (1)°, β = 75.64 (1)°, γ = 104.13 (1)°, V = 2115.1 (6) Å^3, Z = 2, d_{calcd} = 1.452 g cm^{-3}, $F(000)$ = 927.81. Diffraction data (Mo Kα, $2\theta_{max}$ = 44.9°) were collected on a Nonius diffractometer, using the $\theta/2\theta$ scan mode. The structure was refined to R = 3.2% and R_w = 3.8% for 532 parameters against 4896 ($I \geq 2\sigma(I)$) out of 5512 unique reflections.

(11) Torsional angles between the hydrocarbon ligands and the WCO group: C9–W–C1–C2 = 3.3 (3)°, C9–W–C2–C1 = −176.9 (3)°, C9–W–C3–C4 = −178.6 (5)°, C9–W–C4–C3 = 1.5 (3)°, C9–W–C5–C6 = 8.5 (3)°, C9–W–C6–C5 = −172.7 (5)°, C9–W–C7–C8 = −179.2 (5)°, and C9–W–C8–C7 = 1.0 (3)°.

(12) Distances: W–cen1(C1C2) = 2.003 (7) Å, W–cen2(C3C4) = 2.009 (7) Å, W–cen3 = 2.055 (7) Å, and W–C9 = 2.018 (7) Å. Angles: cen1–W–cen2 = 106.2 (2)°, cen1–W–cen3 = 120.1 (2)°, cen1–W–C9 = 96.2 (2)°, cen2–W–cen3 = 124.5 (2)°, cen2–W–C9 = 96.7 (2)°, and cen3–W–C9 = 106.3 (2)°.

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exhibits two resonances at δ 175.9 and δ 158.9 for the alkyne $C{\equiv}C$ carbons. On the other hand, the cyclobutadiene carbons give a single sharp signal at δ 83.8, revealing that the cyclobutadiene ligand is fluxional with facile ring rotation. This signal broadens at −50 °C, but a slow-exchange spectrum is not recorded due to poor solubility for the complex at lower temperatures.

Solid $W(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2(CO)$ is thermally robust to 220 °C, suggesting a stable electronic configuration for the complex. Since terminal CO and η^4-cyclobutadiene ring are normally considered as two- and four-electron donors, respectively, the remaining two alkyne ligands must supply six electrons, presumably from two $\pi(\parallel)$ and one $\pi(\perp)$ orbitals,[7] to the neutral tungsten atom to satisfy the 18-electron rule. Therefore, the actual structure is best regarded as a resonance hybrid with two canonical forms involving one four-electron-donor ($\pi(\parallel) + \pi(\perp)$) and one two-electron-donor ($\pi(\parallel)$) alkyne ligands. The results are reflected on the $C{\equiv}C$ bond lengths and ^{13}C NMR shifts, which are found in between those measured for two- and four-electron-donating alkyne complexes.[15]

Recently we prepared a complex, $W(PhC{\equiv}CPh)_3(NCCH_3)$, which underwent facile ligand substitution with bulky phosphines to yield $W(PhC{\equiv}CPh)_3L$, where L = PPh_3 or $CH_2(PPh_2)_2$.[16] On the contrary, diphenylacetylene reacts with $W(PhC{\equiv}CPh)_3(NCCH_3)$, affording $W(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2(NCCH_3)$[17] in 79% yield; the same product is obtained by treating $W(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2(CO)$ with Me_3NO in acetonitrile solution. Moreover, carbonylation of $W(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2(NCCH_3)$ yields $W(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2(CO)$ quantitatively (Scheme I).

King[7] has shown that in a W(alkyne)$_3$ unit of either D_{3h} or C_{3v} symmetry, the three alkyne ligands can donate a total of only 10 electrons to the tungsten atom. A pathway dissociating CO or $NCCH_3$ from $W(PhC{\equiv}CPh)_3(CO)$ or $W(PhC{\equiv}CPh)_3(NCCH_3)$ to generate an unstable, 16-electron species $[W(PhC{\equiv}CPh)_3]$ is plausible. Alternatively, association of a diphenylacetylene would cause severe steric crowding around the tungsten atom, which could be released through alkyne–alkyne coupling to yield the observed products. However, it remains uncertain whether the tetraphenylcyclobutadiene group is derived from the coordinated $PhC{\equiv}CPh$ ligands or the added diphenylacetylene is involved. The details are presently under investigation.

Acknowledgment. This research was supported by the National Science Council of the Republic of China.

Registry No. $W(PhC{\equiv}CPh)_3(CO)$, 12120-72-8; $PhC{\equiv}CPh$, 501-65-5; $W(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2(CO)$, 138899-90-8; $W(PhC{\equiv}CPh)_3(NCCH_3)$, 138899-91-9; $W(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2(NCCH_3)$, 138899-92-0.

Supplementary Material Available: Tables of crystal data, atomic coordinates, bond lengths, bond angles, and torsional angles (8 pages). Ordering information is given on any current masthead page.

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(17) $W(PhC{\equiv}CPh)_3(NCCH_3)$ (540 mg, 0.71 mmol), diphenylacetylene (130 mg, 0.73 mmol), and 1,2-dichloroethane (10 mL) were refluxed under nitrogen for 15 min. The solvent was removed under vacuum, and the residue was separated by TLC. $W(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2(NCCH_3)$ (520 mg, 0.55 mmol, 79%) forms air-stable, orange-yellow crystals: mp 175–177 °C dec; mass spectrum (FAB), *m/z* 937 (M^+, ^{184}W), 896 ($M^+ - CH_3CN$), 718 ($M^+ - CH_3CN - C_2Ph_2$), 540 ($M^+ - CH_3CN - 2C_2Ph_2$); IR (KBr) 1591 (ν $C{\equiv}C$) cm^{-1}; ^1H NMR (CD_2Cl_2, 25 °C) δ 7.33–6.78 (m, Ph), 1.90 (s, CH_3CN); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 186.5, 174.8 (${\equiv}C$), 140.8, 139.6, 135.1, 129.9, 129.2, 128.3, 128.2, 127.8, 127.5, 127.4, 126.1, 125.8, 124.8 (Ph, $N{\equiv}C$), 86.2 (C_4Ph_4), 4.4 (CH_3). Anal. Calcd for $C_{58}H_{43}NW$: C, 74.28; H, 4.62; N, 1.49. Found: C, 74.49; H, 4.70; N, 1.47.

π Hydrogen Bonds as a Design Principal in Molecular Recognition

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We wish to report details of guest binding and the X-ray structures of two exceptionally high-efficiency hosts, **1-D** and **1-P**. We conclude that "tilted tee"[5] edge–face arene–arene interactions can be a dominating force in the stabilization of host–guest complexes in organic solvents.

While solvophobic forces dominate molecular recognition in aqueous medium, the situation is less clear in organic solvents. Multiple hydrogen bonding sites[1] and a variety of van der Waals contacts, including π–π and related dipole-induced dipole interactions associated with arene–arene interactions, have been exploited.[2] The remarkable use of physical encapsulation should be noted.[3]

We have reported the powerful molecular recognition behavior of a series of cyclophanes bearing a concave functionality which, having but one concave functionality, are nonetheless remarkably "sticky" toward aromatic hydrogen-bond-donating guests, primarily because of immobilization effects (Figure 1).[4]

Hosts **1-D** and **1-P**[6] are both extraordinarily efficient binders of *p*-nitrophenol ("PNP") in CD_2Cl_2, having K_{assoc} of 35000 M^{-1} for **1-D** and ca. 100 000 M^{-1}[4b] for **1-P**.[8] Competition binding experiments confirm the ca. 3:1 ratio of binding constants favoring **1-P** over **1-D**.[8] X-ray structures of the **1-D** and **1-P** PNP complexes are shown in Figure 2.[9]

The following observations lead us to the opening assertion.

(1) At 21 °C, the proton NMR spectrum of **1-D**:PNP (CD_2Cl_2, 1:2.5) shows the guest protons as broad singlets at δ 6.5 ($\nu_{1/2}$ = 50 Hz) and 7.15 ($\nu_{1/2}$ = 140 Hz). The aromatic protons of free *p*-nitrophenol appear as doublets at δ 6.93 and 8.15 (J = 9.1 Hz). Cooling the sample to −20 °C leads to separate but broad signals for the bound and free phenol. At −80 °C, well-resolved spectra are visible.

(2) At −40 °C, the *bound* PNP protons appear as four separate signals at 6.05, 5.95, 5.5, and 3.78 ppm. This upfield shift of 4.4 ppm is required by the binding model, wherein the two edges of *bound* PNP exist in quite different environments: H2 and H3 straddle the diyne spacer, while H5 and H6 lie over the *p*-xylene.

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(6) Host **1-P** was synthesized as previously reported in ref 4b. Host **1-D** was synthesized by analogous but much improved procedures to be reported.

(7) The association constant was determined by the procedure reported in ref 4b.

(8) The funnel-shaped pouch of **1-D** is probably responsible for its decreased $\Delta\delta$ and K_{assoc} relative to **1-P**.

(9) Data were taken on Syntex P-1 and Siemens P3F diffractometers. Hydrogen positions were determined by the Riding model, with fixed isotropic U in both cases.

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