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Synthesis of Bis((tricarbonylmetal)-η^5-cyclopentadienyl)methane Derivatives of Molybdenum and Tungsten. Molecular Structures of Bis((tricarbonyltungstenio)-η^5-cyclopentadienyl)methane and Its 2-Acyl Derivative

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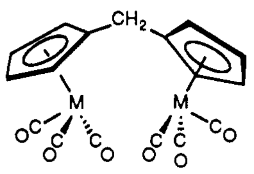
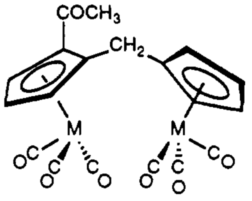
Bis((tricarbonylmetal)-η^5-cyclopentadienyl)methane derivatives of molybdenum and tungsten, **1** and **2**, respectively, have been prepared by reaction of the disodium salt of bis(cyclopentadienyl)methane with tris(acetonitrile)metal tricarbonyl complexes of molybdenum and tungsten. Oxidation of the resulting dianions gives compounds **1** and **2** in good yields. Variable-temperature studies of **1** and **2**, which have C_2 symmetry in the solid, reveal a fluxional twisting motion for which the ΔG^* of the tungsten complex is slightly larger than that of the molybdenum complex. An acyl derivative of **2** has been isolated from an incompletely neutralized batch of **2**. The pathway leading to this new material, **3**, is not yet clear. **2** has been characterized by X-ray crystallography: triclinic, $P\bar{1}$, a = 7.670 (4) Å, b = 7.757 (4) Å, c = 15.536 (9) Å, α = 86.22 (3)°, β = 81.87 (3)°, γ = 67.67 (3)°, V = 846.2 Å^3, Z = 2, and $R(F)$ = 4.96%. **3** was also characterized by crystallography: orthorhombic, $p2_12_12_1$, a = 8.254 (2) Å, b = 12.527 (3) Å, c = 18.103 (4) Å, V = 1871.7 Å^3, Z = 4, and $R(F)$ = 3.58%.

We have been involved in the synthesis of a large number of dinuclear compounds in which two cyclopentadienylmetal moieties are coupled by a methylene linkage between the cyclopentadienyl rings. This coupling forces the metals to remain in close proximity and has been shown (for rhodium) to promote reactions which lead to bridging of the two metals by groups such as CO,[1] SO_2,[2] and CH_2.[3] In extending these studies to dimers of the group VI metals, we anticipated that ring coupling might stabilize new bridging species and encourage reactions in which metal–metal cooperativity might be observed. In the present paper we shall describe the synthesis and characterization of two new dinuclear derivatives of molybdenum and tungsten of the general formula $CH_2[(\eta_5\text{-}C_5H_4)M(CO)_3]_2$ (M = Mo (**1**), W (**2**)) and an acyl derivative of the tungsten compound, **3**, which was isolated as a by-product. The X-ray molecular structure determinations of the two tungsten compounds are presented. A variable-temperature NMR study of **1** and **2** is reported. A matrix photochemical study of **1** and **2** has previously been reported.[4] Additional chemical and photochemical studies of these compounds will be described separately. The chromium analogue of these compounds has been reported in a patent by Lilga and Hallen[5].



1 (M = Mo)
2 (M = W)



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Results and Discussion

Synthesis and Spectroscopic Properties. Several ring-coupled, dinuclear derivatives of molybdenum and tungsten have been reported. Smart and Curtis[6] have described the synthesis of (η^5:η^5-fulvalene)hexacarbonyldimolybdenum and its reduction and subsequent reaction with methyliodide to yield the dimethyl derivative. This molybdenum compound and the analogous tungsten compound have been prepared by an alternative procedure by Vollhardt and his co-workers,[7] who have extensively investigated the chemistry of the dianions[8] and the photolysis of the neutral compounds,[8b,9] Wegner and Uski[10] have reported the synthesis of metal carbonyl derivatives of α,α-bis(cyclopentadienyl)-*m*-xylene and have examined the chemistry of the dianions. Two groups have reported bis((tricarbonylmetal)-η^5-cyclopentadienyl)dimethylsilane complexes for both molybdenum and tungsten.[11]

Bis(cyclopentadienyl)methane is readily prepared from sodium cyclopentadienide and dichloromethane by the method of Shaltegger[12a] as modified by Bergman and Bryndza.[12b,c] Reaction of this compound with sodium hydride in THF yields the corresponding dianion, which is reacted with $(CH_3CN)_3M(CO)_3$ (M = Mo, W) to give solutions that contain the $CH_2[CpM(CO)_3]_2$ dianions. Oxidation of these solutions with aqueous ferric sulfate and acetic acid as described by Manning and his co-workers[13]

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for $CpM(CO)_3$ anions, and subsequent purification of the recovered materials by column chromatography, gives the dinuclear compounds 1 and 2 for Mo and W, respectively. The compounds are prepared in good yield as dark red crystalline solids. Although both compounds are stable in air for extended periods, they are best stored in the cold under nitrogen. A sample of 1 was found to have undergone about 50% decomposition after storage of 6 months in air.

Compounds 1 and 2 have been characterized by IR, ^1H and ^{13}C NMR, and UV/visible spectroscopy, elemental analysis, and/or mass spectroscopy, and all data are consistent with their formulation as dinuclear, metal–metal bonded complexes. 1 was found to give consistently poor elemental analyses, suggesting that this compound retains solvent even after long-term storage under vacuum. A high resolution mass spectrum unambiguously established the elemental composition of this compound.

The room-temperature ^1H NMR spectra of both 1 and 2 show broad singlets for the ring protons and a sharp singlet for the bridging methylene protons. The molecular structure of 2 (vide infra) suggests that the cyclopentadienyl rings are twisted in such a way that a more complex ring resonance pattern might be expected. Indeed, a preliminary low-temperature NMR experiment on 2 in deuterated acetone demonstrated that the two ring proton resonances broaden as the temperature is lowered, and four resonances are observed at −80 °C. The methylene proton resonance remains a singlet at this temperature.

A detailed, variable-temperature ^1H NMR study of 1 and 2 was conducted in $CDCl_3$. At −33 °C low-temperature-limiting spectra were observed in which all four ring resonances of 1 were resolved, while two of the four ring resonances overlapped in the spectrum of 2. In both cases the methylene resonances were found to be singlets at −33 °C. For 1, ΔG^* values of 55.9 and 57.7 kJ/mol were calculated for the α and β protons, respectively. For 2, a ΔG^* values of 59.2 kJ/mol was calculated for both the α and β protons. The slightly higher value of ΔG^* for the third-row element as compared to the second-row element is consistent with fluxional barriers observed for $CH_2[(\eta^5\text{-}C_5H_4)M(CO)]_2(\mu\text{-}CO)$ where M = Rh and Ir,[14] and $CH_2[(\eta^5\text{-}C_5H_4)M(CO)_2]_2(\mu\text{-}RC{\equiv}CR)$, where M = Mo and W.[15] The ΔG^* values for compounds 1 and 2 are less than those reported by Heck and co-workers,[11c] 60.6 and 67.8 kJ/mol, for the analogous $SiMe_2$-coupled compounds in toluene.

A set of ^{13}C NMR spectra of 1 were recorded at −33, 24, and 47 °C, respectively. In the low-temperature spectrum, three carbonyl resonances can be observed at 234.8, 230.8, and 224.1 ppm, five ring proton resonances, 112.4 (ipso), 99.3, 88.7, 87.4, and 86.9 ppm, and a resonance for the methylene carbon at 27.5 ppm. At 24 °C, only the lowest of the carbonyl resonances is still observed, the ipso carbon, a single broad resonance at 87.4 ppm, and the methylene resonance. At 47 °C, the carbonyl resonances cannot be observed, and a broad new resonance is found at about 93 ppm in the ring region. In addition, the ipso carbon, a sharp resonance at 87.3 ppm, and the methylene resonance are observed. We believe that at about 24 °C the cis carbonyl resonances have been averaged by the torsional motion of the molecule while the trans resonance is still observed. The disappearance of all of the carbonyl resonances at 47 °C may indicate that a carbonyl scrambling motion which mixes the cis and trans carbonyl groups may be involved. A ^{13}CO-labeling experiment will be carried out to clarify the behavior of these carbonyls. The averaging behavior of the ring resonances indicates that the α carbons can be identified with the resonances at 99.3 and 87.4 ppm, and the β carbon resonances at 88.7 and 86.9 ppm. It is likely that the coalescence temperature of the α carbons is about 24 °C, accounting for the appearance of a single broad carbon resonance (in addition to the ipso) at this temperature. The coalescence for the β carbons is masked by the resonance of the α carbons. Calculation of ΔG^* for the α carbons by using 24 °C for T_c gives a value of 53.4 kJ/mol, which is at least consistent with the values calculated by using the proton resonances.

The low-temperature-limiting spectra of 1 and 2, along with a knowledge of the solid-state structure of these compounds, vide infra, indicate that the fluxional motion of these compounds involves a torsional twisting of the cyclopentadienyl rings relative to the methylene bridge, which keeps the environment of the methylene protons constant while altering that of the ring proton sets α and β to the bridge. This is in contrast to the behavior of $CH_2[(\eta^5\text{-}C_5H_4)M(CO)]_2(\mu\text{-}CO)$, where M = Rh and Ir, and $CH_2[(\eta^5\text{-}C_5H_4)M(CO)_2]_2(\mu\text{-}RC{\equiv}CR)$, where M = Mo and W. In these latter cases, the bridging methylene group is found to have an AB quartet at the low-temperature limit, indicating that it is flipping from side to side during the fluxional motion.

The IR spectra of 1 and 2 contain at least four terminal carbonyl stretching bands that are almost identical in position with those reported for the fulvalene analogues.[6,7] Mass spectra of 1 and 2 contain clusters of peaks corresponding to the parent masses and fragmentation species for the loss of one to all six carbonyl groups. Relative intensities of the $M^+ - nCO$ fragments indicate that a $CH_2Cp_2M_2(CO)_2$ species is relatively stable for both compounds and that the molybdenum compound is somewhat more prone to lose all six of its carbonyl groups than is the tungsten.

Wavelength maxima for the $d \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions for compounds 1 and 2 are intermediate between those values reported for the cyclopentadienyl derivatives, $Cp_2M_2(CO)_6$,[16] and the fulvalene compounds.[7] Since the W–W bond lengths increase in the series $CH_2Cp_2 < Cp <$ fulvalene, it is unlikely that the shifts in the absorption maxima correspond to simple metal–metal bond elongation.

In one preparation of 2 the workup of the reaction was interrupted and a solution of 2 and incompletely neutralized acetic acid in THF was stored (5 °C) for a period of several weeks. When the workup was completed, and the product purified by column chromatography, two new bands in addition to 2 were observed on the column. One of these bands was successfully recovered, and the red crystalline product, 3, was examined by IR and ^1H NMR spectroscopy. The IR spectrum of this trace material contained a set of terminal carbonyl stretching bands identical with those of 2 as well as a new, less intense band at 1684 cm^{-1}. At 25 °C the ^1H NMR spectrum of this compound contained a set of broadened resonances for the ring hydrogens, a well-defined AB pattern for the methylene group, and a sharp singlet at high field (2.39 ppm). The integration was consistent with seven ring protons, a methylene bridge, and a methyl group, respectively. Increasing the temperature to 47 °C caused the broad resonances to split and sharpen into seven distinct ring

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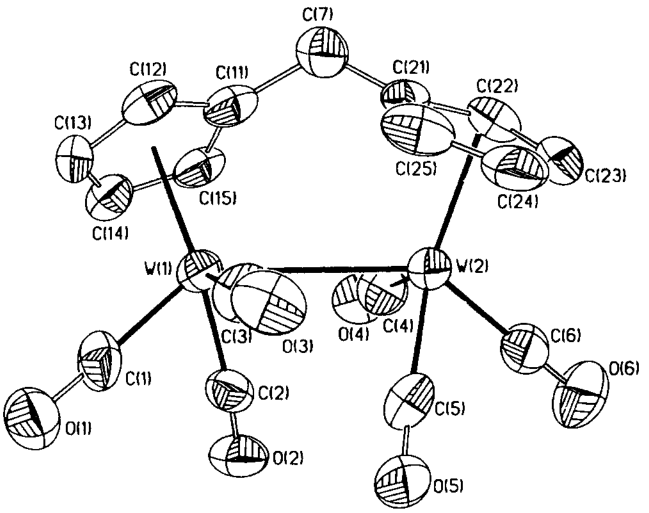

Figure 1. Molecular structure of 2 drawn with 40% probability ellipsoids.

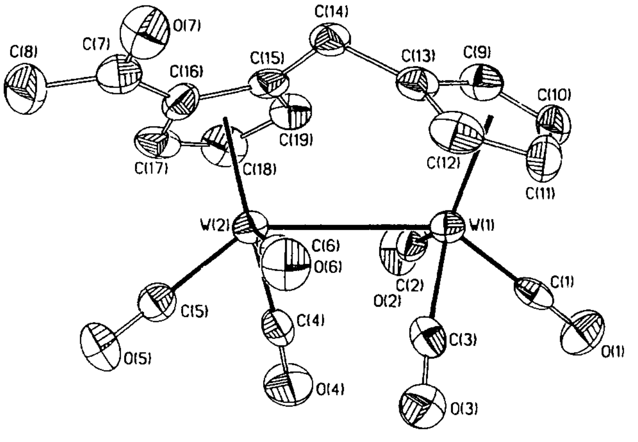

Figure 2. Molecular structure of 3 drawn with 40% probability ellipsoids.

resonances. Further work is now ongoing to understand the dynamics of this process. The NMR singlet and IR band at 1684 cm^{-1} suggested a ring-bound acetyl group although the location of the acetyl group could not be determined by NMR spectroscopy. A molecular structure determination of this compound was conducted to establish the structure of the compound, vide infra, and confirmed that one ring is acylated adjacent to the bridging methylene. Repeated attempts to acylate 2 under a variety of Friedel–Crafts conditions with acetyl chloride and acetic anhydride have failed to generate additional samples of these ring-acylated compounds.

Molecular Structures of 2 and 3. The structures of 2 and 3 are shown in Figures 1 and 2, respectively, and a view of 2 along the W–W vector is shown in Figure 3. Except for the acetyl group, this view is nearly superimposable on that of 3. In fact, there are no chemically significant differences between the frameworks of structures 2 and 3.

The effects of coupled cyclopentadienyl rings are evident when the structures of 2 and 3 are compared with analogous uncoupled and coupled compounds. For the uncoupled analogue, the Cp rings assume a trans geometry; in 2 and 3, the CNT–W–W–CNT′ (CNT = centroid) torsion angles are 47.8 (6) and 47.1 (4)°, respectively. Coupling has also caused a small *decrease* in the M–M distances; in 2 and 3 these values are 3.166 (1) and 3.175 (1) Å, whereas in $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ this distances is 3.222 (1) Å. $Me_2Si[\eta^5\text{-}C_5H_4W(CO)_3]_2$ has been found to have an

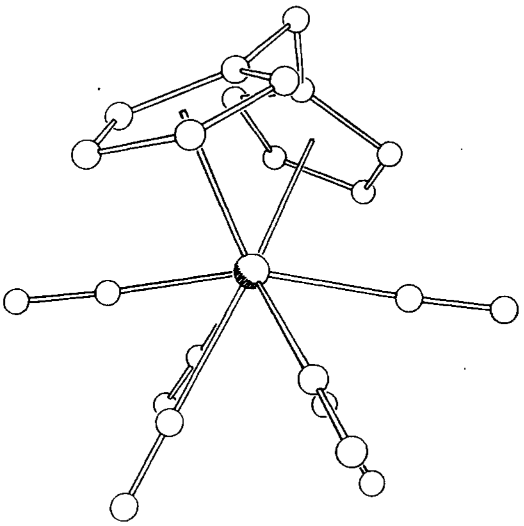

Figure 3. Structure of 2 viewed along the W–W vector, showing a ~47° dihedral angle relationship between the Cp rings.

intermediate compression to a W–W distance of 3.196 (1) Å[11b]. Not unexpectedly, the tightly constrained fulvalene complex $(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)W_2(CO)_6$ has a W–W distance that is conspicuously elongated to 3.347 (1) Å.[8b] For the CH_2-coupled complex crowding about the W–W bond is partially relaxed by the assumption of a ~47° CNT–W–W–CNT torsion angle, which is not possible for the fulvalene complex. It is not clear at this time why ring coupling should result in shorter M–M distances than for the uncoupled compounds, but similar trends are observed in the rhodium series $[\eta^5\text{-}C_5H_5Rh(CO)]_2(\mu\text{-}CO)$ (Rh–Rh = 2.681 Å),[17] $CH_2[\eta^5\text{-}C_5H_4Rh(CO)]_2(\mu\text{-}CO)$ (Rh–Rh = 2.650 Å),[18] and $C_2H_4[\eta^5\text{-}C_5H_4Rh(CO)]_2(\mu\text{-}CO)$ (Rh–Rh = 2.675 Å)[19] and in the ruthenium compounds $[\eta^5\text{-}C_5H_5Ru(CO)]_2(\mu\text{-}CO)_2$ (Ru–Ru = 2.735 Å)[20] and $Me_2Si[\eta^5\text{-}C_5H_4Ru(CO)]_2(\mu\text{-}CO)_2$ (Ru–Ru = 2.7042 Å).[19]

Experimental Section

Bis(cyclopentadienyl)methane was prepared by the procedure described by Shaltegger[12a] as modified by Bergman and Bryndza.[12b] $(CH_3CN)_3M(CO)_3$,[21] M = Mo and W, were prepared by literature procedures. Molybdenum and tungsten hexacarbonyls were purchased from Strem. All reactions were conducted under nitrogen, and solvents were freshly distilled from appropriate drying agents under nitrogen or argon.

Infrared spectra were recorded on a Perkin-Elmer Model 1750 FTIR instrument. NMR spectra were recorded on an IBM 300-MHz NMR spectrometer. UV/visible spectra were recorded on a Beckman DU 7 spectrometer. Mass spectra were recorded on a Finnigan Model 4610 mass spectrometer operating in the electron-impact mode. Routine product analyses were conducted by using a Gow-Mac HPLC instrument with a silica gel column and 3:7 THF–petroleum ether as an eluant. Elemental analyses were conducted by Galbraith Laboratories, Inc., of Knoxville, TN.

Synthesis of $CH_2[CpM(CO)_3]_2$ (M = Mo (1), W (2)). Bis(cyclopentadienyl)methane, 2.2 g (15 mmol), is taken up in 20 mL of THF, and the solution is added slowly to 1.0 g (42 mmol) of sodium hydride in 20 mL of THF. The mixture is permitted to react at room temperature for 5 h and is transferred by Cannula to a fritted addition funnel. The air-sensitive sodium salt is added dropwise to a THF solution of $(CH_3CN)_3Mo(CO)_3$ (prepared from 6.6 g (25 mmol) of $Mo(CO)_6$ in refluxing acetonitrile over about

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Table I. Crystal Data for $(\eta^5\text{-}C_5H_4)CH_2(\eta^5\text{-}C_5H_4)W_2(CO)_6$ (2) and $(\eta^5\text{-}C_5H_4)CH_2(\eta^5\text{-}C_5H_4)W_2(CO)_6$ (3)[a]

	2	**3**
	(a) Crystal Parameters	
formula	$C_{17}H_{10}O_6W_2$	$C_{19}H_{12}O_7W_2$
cryst system	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
a, Å	7.670 (4)	8.254 (2)
b, Å	7.757 (4)	12.527 (3)
c, Å	15.536 (9)	18.103 (4)
α, deg	86.22 (3)	90
β, deg	81.87 (3)	90
γ, deg	67.67 (3)	90
V, Å^3	846.3 (5)	1871.8 (1)
Z	2	4
D(calc), g cm^{-3}	2.660	2.555
μ(Mo Kα), cm^{-1}	139.1	125.9
temp, K	293	293
cryst size, mm	0.03 × 0.26 × 0.34	0.15 × 0.15 × 0.28
cryst color	deep red orange	deep red
	(b) Data Collection	
diffractometer	Nicolet R3m/μ	*b*
monochromator	oriented graphite	*b*
radiation	Mo Kα	*b*
wavelength, Å	0.71073	*b*
2θ limits, deg	$4 \le 2\theta \le 52$	$4 \le 2\theta \le 50$
scan technique	ω	ω
std rflns	3 std/197 rflns	*b*
decay	<1% variation	<2% variation
octants collcd	$\pm h, \pm k, l$	$\pm h, +k, l$
no. of rflns collcd	2665	3578
no. of independt rflns	2513	3296
no. of independt rflns, $F_o \ge 3\sigma(F_o)$	1955	2970
R(int), %	1.36	3.73
T(max)/T(min)	2.89	1.63
	(c) Refinement	
$R(F)$, %	4.96	3.58
$R_w(F)$, %	6.14	4.65
GOF	1.327	1.077
Δ/σ	0.03	0.05
$\Delta(\rho)$, e Å^{-3}	1.84	1.61
N_o/N_v	8.61	11.33

[a] Unit cell parameters obtained from the least-squares best fit of 25 reflections (20° ≤ 2θ ≤ 26°). [b] Same as for **2**.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 2

	x	y	z	U^a
W(1)	2166 (1)	3969 (1)	1467 (1)	51 (1)
W(2)	1421 (1)	2721 (1)	3421 (1)	54 (1)
O(1)	884 (18)	7793 (22)	477 (10)	90 (7)
O(2)	−2253 (15)	5103 (18)	1647 (9)	78 (6)
O(3)	3014 (16)	6625 (19)	2610 (9)	84 (7)
O(4)	−569 (17)	815 (20)	2401 (9)	81 (6)
O(5)	−1229 (22)	6991 (20)	3534 (9)	96 (7)
O(6)	−2058 (21)	2742 (27)	4747 (11)	115 (9)
C(1)	1342 (25)	6325 (28)	857 (12)	67 (8)
C(2)	−632 (22)	4701 (23)	1626 (11)	60 (7)
C(3)	2627 (26)	5636 (24)	2204 (11)	67 (8)
C(4)	157 (24)	1603 (29)	2769 (14)	75 (9)
C(5)	−257 (26)	5474 (30)	3464 (11)	71 (8)
C(6)	−762 (23)	2724 (34)	4242 (13)	82 (10)
C(7)	5434 (24)	−250 (25)	2251 (12)	69 (8)
C(11)	4727 (21)	918 (26)	1480 (12)	63 (7)
C(12)	5410 (20)	2143 (22)	970 (11)	57 (6)
C(13)	4439 (23)	2814 (27)	248 (10)	69 (8)
C(14)	3073 (25)	2069 (32)	284 (12)	79 (9)
C(15)	3194 (22)	874 (27)	1013 (12)	70 (8)
C(21)	4623 (19)	684 (29)	3114 (13)	72 (8)
C(22)	3695 (21)	−64 (25)	3833 (12)	64 (7)
C(23)	3219 (27)	1171 (35)	4522 (13)	87 (10)
C(24)	3810 (26)	2677 (41)	4266 (15)	107 (12)
C(25)	4619 (24)	2396 (30)	3428 (16)	78 (9)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

3 days). The resulting red solution was refluxed for 3 h and then cooled to room temperature. A solution of 4.0 g of iron(III) sulfate and 3.0 mL of acetic acid in 50 mL of water is added slowly to the red solution. After all of the aqueous solution is added, the reaction mixture is transferred to a separatory funnel and the water layer removed. The THF solution is dried over magnesium sulfate and then filtered and stripped of solvent with a rotary evaporator. The resulting red semisolid is taken up in methylene chloride and chromatographed on a 20 cm × 2 cm neutral alumina column. Elution with methylene chloride gave a single bright red band, which was stripped of solvent to give a red powder. Recrystallization from dichloromethane–heptane gave **1** as red crystals: mp 226–228 °C dec with gas evolution; yield 1.40 g, 28%. Anal. Calcd for $C_{17}H_{10}Mo_2O_6$: C, 40.64; H, 1.99. Found: C, 39.96; H, 2.12. High-resolution mass spectroscopy: theory (^{98}Mo, ^{98}Mo), *m/e* 505.8585; found *m/e* 505.8585; error 0.4%. IR (CH_2Cl_2): 2016, 1962, 1914, 1881 cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$): δ 5.27 (8 H, s), 3.55 (2 H, s). MS: *m/e* 502 (10, M$^+$), 474 (9, M$^+$ − CO), 446 (10, M$^+$ − 2CO), 418 (11, M$^+$ − 3CO), 390 (58, M$^+$ − 4CO), 362 (18, M$^+$ − 5CO), 334 (82, M$^+$ − 6CO), 306 (29), 280 (29), 230 (20). UV/vis (CH_2Cl_2): 529.0 (947), 383.5 nm (12063).

2 is prepared similarly beginning with 8.8 g (25 mmol) of $W(CO)_6$. **2** is recovered as a brick red powder: mp 250 °C dec; yield 1.72 g, 28%. Anal. Calcd for $C_{17}H_{10}W_2O_6$: C, 30.09; H, 1.48. Found: C, 30.15; H, 1.61. High-resolution mass spectroscopy: theory, *m/e* 678.9452; found, *m/e* 678.9436; error 2.4 ppm. Average error across the M$^+$ mass envelope is 4.8 ppm. IR (CH_2Cl_2): 2012, 1958, 1908, 1872 cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$): δ 5.30 (8 H, s), 3.89 (2 H, s). MS: *m/z* 678 (42, M$^+$), 650 (9, M$^+$ − CO), 622 (43, M$^+$ − 2CO), 594 (17, M$^+$ − 3CO), 566 (100, M$^+$ − 4CO), 538 (66, M$^+$ − 5CO), 510 (42, M$^+$ − 6CO), 480 (15), 457 (27). UV/vis (CH_2Cl_2): 512.5 (733), 350.0 nm (6468).

In one preparation of **2**, a partially neutralized reaction mixture was stored for several weeks. When workup of this material was completed, two additional bands were found on the column. One band was successfully isolated and gave a small number of red crystals, **3**. IR (CH_2Cl_2): 2015, 1963, 1913, 1870 (sh), 1684 cm^{-1}. ^{1}H NMR ($CDCl_3$): 298 K, δ 5.73 (broad s, 2 H), 5.57 (broad s, 1 H), 5.49 (broad s, 1 H), 5.40 (broad s, 1 H), 5.22 (broad s, 1 H), 5.12 (broad s, 1 H), 4.77 and 4.06 (1 H, AB quartet, J_{A-B} = 14.8 Hz), 2.39 (3 H, s); 320 K, δ 5.74 (m, 1 H), 5.70 (m, 1 H), 5.55 (t, 1 H), 5.48 (t, 1 H), 5.43 (m, 1 H), 5.29 (m, 1 H), 5.13 (m, 1 H), 4.80 and 4.03 (AB quartet, J_{A-B} = 14.71 Hz, 2 H), 2.39 (s, 3 H).

Variable-Temperature NMR Studies. Variable-temperature NMR studies were conducted in $CDCl_3$ over the temperature range 240–330 K. Spectra were recorded at 5 K intervals over this range. Both compounds **1** and **2** were found to exhibit low-temperature-limiting spectra at 240 K. The exchange of ring proton pairs α and β to the bridge can be treated as simple uncoupled, two-site exchanges so that the conventional rate expression

$$k = \pi\delta\nu/2$$

can be used without correction.[22]

1: ^{1}H NMR (240 K) δ 5.54 (α), 5.35 (β), 5.21 (β), 4.96 (α), 3.53 (CH_2); T_C(α protons) = 287 K, $\Delta G^{\ddagger}$ = 55.9 kJ/mol; T_C(β protons) = 279 K, $\Delta G^{\ddagger}$ = 57.7 kJ/mol; ^{13}C NMR (240 K) δ 234.8 (trans CO), 230.8 (cis CO), 224.1 (cis CO), 112.3 (ipso ring C), 99.3 (α ring C), 88.7 (β ring C), 87.4 (α ring C), 86.9 (β ring C), 27.5 (CH_2).

2: ^{1}H NMR (240 K) δ 5.61 (α proton), 5.48 (β proton), 5.16 (α and β proton), 3.91 (CH_2); T_C(α protons) = 300 K, $\Delta G^{\ddagger}$ = 59.2 kJ/mol; T_C(β protons) = 296 K, $\Delta G^{\ddagger}$ = 59.2 kJ/mol.

X-ray Structure Determinations. Crystallographic data are collected in Table I. Satisfactory crystals of both **2** and **3** were obtained by recrystallization from dichloromethane and heptane. Preliminary photographic characterization showed that **2** possessed $\bar{1}$ Laue symmetry with no higher symmetry observed, and **3**, *mmm* symmetry. The space group for **2** was initially assumed and proved to be correct by the refinement process. The preferred enantiomorph for **3** was unambiguously determined by refinement

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[22] Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for 3

	x	*y*	*z*	U^a
W(1)	1543 (1)	923 (1)	5403 (1)	39 (1)
W(2)	2161 (1)	−813 (1)	6649 (1)	40 (1)
O(1)	1375 (14)	3413 (7)	5350 (7)	70 (4)
O(2)	4558 (14)	1717 (9)	6328 (6)	70 (4)
O(3)	−1579 (16)	1374 (8)	6310 (6)	72 (4)
O(4)	2102 (19)	1223 (8)	7682 (6)	90 (5)
O(5)	87 (15)	−1647 (9)	7976 (6)	73 (4)
O(6)	−1365 (12)	−1155 (8)	6075 (6)	62 (4)
O(7)	1444 (14)	−3690 (8)	5730 (6)	67 (4)
C(1)	1463 (14)	2495 (10)	5364 (6)	41 (4)
C(2)	3401 (18)	1385 (9)	6015 (7)	46 (4)
C(3)	−404 (18)	1178 (10)	6001 (7)	48 (4)
C(4)	2144 (22)	499 (10)	7277 (7)	61 (5)
C(5)	903 (19)	−1321 (10)	7506 (8)	49 (4)
C(6)	−78 (16)	−963 (11)	6250 (7)	49 (4)
C(7)	2156 (18)	−3445 (11)	6271 (8)	53 (4)
C(8)	2272 (26)	−4155 (12)	6910 (9)	85 (7)
C(9)	2992 (20)	230 (10)	4372 (7)	54 (5)
C(10)	2002 (21)	1048 (10)	4141 (7)	59 (5)
C(11)	355 (21)	723 (11)	4253 (7)	61 (5)
C(12)	410 (19)	−314 (11)	4576 (8)	61 (5)
C(13)	2068 (17)	−645 (10)	4661 (7)	49 (4)
C(14)	2656 (19)	−1721 (9)	4928 (7)	51 (4)
C(15)	3431 (16)	−1709 (9)	5685 (7)	44 (4)
C(16)	3149 (17)	−2444 (10)	6285 (7)	49 (4)
C(17)	4135 (18)	−2079 (13)	6900 (8)	59 (5)
C(18)	4976 (16)	−1176 (13)	6661 (9)	64 (5)
C(19)	4610 (16)	−931 (11)	5928 (7)	52 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Selected Bond Distances and Angles for 2

(a) Bond Distances (Å)

W(1)–W(2)	3.166 (1)	C(1)–O(1)	1.20 (2)
W(1)–CNT(1)[a]	2.04 (1)	C(2)–O(2)	1.16 (2)
W(2)–CNT(2)	2.02 (1)	C(3)–O(3)	1.17 (3)
W(1)–C(1)	1.92 (2)	C(4)–O(4)	1.18 (3)
W(1)–C(2)	1.98 (2)	C(5)–O(5)	1.13 (2)
W(1)–C(3)	1.94 (2)	C(6)–O(6)	1.17 (3)
W(2)–C(4)	1.94 (2)	C(7)–C(11)	1.49 (3)
W(2)–C(5)	2.03 (2)	C(7)–C(21)	1.50 (3)
W(2)–C(6)	1.96 (2)		

(b) Bond Angles (deg)

CNT(1)–W(1)–W(2)	109.0 (2)	C(1)–W(1)–C(2)	78.0 (8)
CNT(2)–W(2)–W(1)	107.0 (2)	C(1)–W(1)–C(3)	76.1 (8)
CNT(1)–W(1)–C(1)	116.8 (7)	C(2)–W(1)–C(3)	104.9 (7)
CNT(1)–W(1)–C(2)	128.2 (8)	C(4)–W(2)–C(5)	104.8 (8)
CNT(1)–W(1)–C(3)	126.5 (7)	C(4)–W(2)–C(6)	76.7 (9)
CNT(2)–W(2)–C(4)	125.1 (1)	C(5)–W(2)–C(6)	78.1 (9)
CNT(2)–W(2)–C(5)	129.8 (7)	C(11)–C(7)–C(21)	115 (1)
CNT(2)–W(2)–C(6)	115.5 (7)		

(c) Torsion Angle (deg)

CNT(1)–W(1)–W(2)–CNT(2)	47.8 (6)

[a] CNT = centroid of Cp ring.

Table V. Selected Bond Distances and Angles for 3

(a) Bond Distances (Å)

W(1)–W(2)	3.175 (1)	C(2)–O(2)	1.19 (2)
W(1)–CNT(1)[a]	2.02 (1)	C(3)–O(3)	1.15 (2)
W(2)–CNT(2)	2.01 (1)	C(4)–O(4)	1.17 (2)
W(1)–C(1)	1.97 (1)	C(5)–O(5)	1.16 (2)
W(1)–C(2)	1.98 (1)	C(6)–O(6)	1.13 (2)
W(1)–C(3)	1.96 (1)	C(13)–C(14)	1.51 (2)
W(2)–C(4)	2.00 (1)	C(14)–C(15)	1.51 (2)
W(2)–C(5)	1.97 (1)	C(16)–C(7)	1.50 (2)
W(2)–C(6)	1.99 (1)	C(7)–O(7)	1.18 (2)
C(1)–O(1)	1.15 (1)	C(7)–C(8)	1.46 (2)

(b) Bond Angles (deg)

CNT(1)–W(1)–W(2)	109.4 (3)	C(1)–W(1)–C(3)	80.2 (5)
CNT(2)–W(2)–W(1)	105.2 (4)	C(2)–W(1)–C(3)	106.2 (5)
CNT(1)–W(1)–C(1)	114.2 (4)	C(4)–W(2)–C(5)	79.3 (6)
CNT(1)–W(1)–C(2)	128.6 (4)	C(4)–W(2)–C(6)	106.1 (6)
CNT(1)–W(1)–C(3)	125.0 (5)	C(5)–W(2)–C(6)	76.5 (6)
CNT(2)–W(2)–C(4)	128.9 (4)	C(13)–C(14)–C(15)	115 (1)
CNT(2)–W(2)–C(5)	119.5 (4)	C(16)–C(7)–O(7)	120 (1)
CNT(2)–W(2)–C(6)	123.9 (4)	C(16)–C(7)–C(8)	117 (1)
C(1)–W(1)–C(2)	75.8 (5)	O(7)–C(7)–C(8)	122 (1)

(c) Torsion Angle (deg)

CNT(1)–W(1)–W(2)–CNT(2)	47.1 (4)

[a] CNT = centroid of Cp ring.

of both hands. Both data sets were empirically corrected for absorption by using 252 data (seven reflections 10° increments). Crystals of 2 formed thin plates, and severe edge effects were evident in the ψ-scan data. Therefore, the data for 2 were fit to a laminar model, and those reflections making a glancing angle of less than 3.5° to the major face [001] were discarded (42 ψ-scan data and 870 general reflections). An ellipsoidal model was used for 3.

Both structures were solved by direct methods and completed by difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were treated as idealized, updated isotropic contributions.

Computations used the SHELXTL (5.1) library (G. Sheldrick, Nicolet Corp., Madison, WI). Atomic coordinates for 2 and 3 are given in Tables II and III, respectively. Selected bond distances and angles are given in Tables IV and V. Additional crystallographic data are available as supplementary data.

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Registry No. 1, 130971-53-8; 2, 130971-54-9; 3, 136630-25-6; bis(cyclopentadienyl)methane, 79249-50-6; $(CH_3CN)_3Mo(CO)_3$, 15038-48-9; $W(CO)_6$, 14040-11-0.

Supplementary Material Available: For 2 and 3, tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (7 pages); listings of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.