Registry No. **1a**, 38834-51-4; **1b**, 38834-27-4; **1c**, 38834-28-5; **1d**, 35399-67-8; **2**, 12427-42-8; **3a**, 59653-72-4; **3b** (3-Me), 117340-20-2; **3b** (2-Me), 117340-28-0; **3b** (4-Me), 117340-29-1; **3c**, 117340-21-3; **3d**, 65643-59-6; **3e**, 117340-22-4; **3f** (3-Me), 117340-23-5; **3f** (2-Me), 117340-30-4; **3f** (4-Me), 117340-31-5; **3g**, 117340-24-6; **3h**, 117340-25-7; **4a**, 52193-26-7; **4b**, 94791-67-0; **5a**, 117340-26-8; **5b**, 117340-27-9; $AlMe_3$, 75-24-1; $AlEt_3$, 97-93-8; $Mn(CO)_5Br$, 14516-54-2; $[(benzene)Mn(CO)_3][PF_6(AlMe_3)_6]\cdot$19.0toluene, 117340-13-3; $[(p\text{-xylene})Mn(CO)_3][PF_6(AlMe_3)_6]\cdot$15toluene, 117340-15-5; $[(mesitylene)Mn(CO)_3][PF_6(AlMe_3)_6]\cdot$16toluene, 117340-17-7; $[Co(C_5H_5)_2][PF_6(AlMe_3)_6\cdot$15.4toluene, 117340-19-9; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; mesitylene, 108-67-8.

Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters for **3d**, **5a** and **5b** and important torsion angles for **5a** and **5b** (4 pages); listings of observed and calculated structure factors for **3d**, **5a**, and **5b** (77 pages). Ordering information is given on any current masthead page.

The First Group 6 (η^2-Olefin)(η^4-diene)M(CO)$_3$ Complexes: Photochemical Synthesis and Structure of *mer*-Tricarbonyl(η^2-olefin)(η^4-norbornadiene)tungsten Compounds

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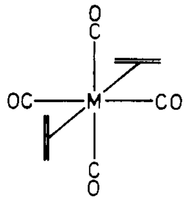
The photoreactions of (η^4-norbornadiene)W(CO)$_4$ (3) with (*Z*)-cyclooctene and ethene yield *mer*-(η^2-(*Z*)-cyclooctene)(η^4-norbornadiene)W(CO)$_3$ (4) and *mer*-(η^2-ethene)(η^4-norbornadiene)W(CO)$_3$ (5), respectively. Single-crystal X-ray diffraction analyses of 3 and 5 establish distorted octahedral coordination geometries, in the case of 5 with a *mer*-W(CO)$_3$ structure and a trans-orthogonal orientation of the ethene and one of the norbornadiene C=C units. The W—C distances of the latter are shorter, by 0.1 Å, than those of the other C=C unit, trans to a CO group. Crystals of 3 are monoclinic, space group $P2_1/c$, with a = 9.744 (2) Å, b = 9.929 (1) Å, c = 11.394 (1) Å, β = 91.16 (1)°, and Z = 4. The structure was solved and refined to R = 0.031 and R_w = 0.035 by using 4790 independent reflections. Crystals of 5 are monoclinic, space group $P2_1/n$, with a = 8.225 (1) Å, b = 12.571 (2) Å, c = 11.327 (1) Å, β = 92.51 (1)°, and Z = 4. The structure was solved and refined to R = 0.035 and R_w = 0.041 by using 3395 independent reflections. 4 and 5 were characterized by elemental analysis and UV-vis, IR, and ^{1}H and ^{13}C NMR spectroscopy. The *trans*-(η^2-C=C)$_2$M substructure of 4 and 5 provides for optimum metal (d_π)→olefin (π^*) back-donation, thus accounting for the extraordinary stability of the complexes. Moreover, it is associated with unusually large ^{13}C NMR coordination shifts of the olefinic carbon atoms, which may serve as a general criterion for recognizing the relative positions of olefinic units and CO groups in octahedral complexes. The dynamic behavior reveals that olefin rotation occurs with E_a = 58 kJ mol^{-1} (4) and E_a = 54.8 kJ mol^{-1} (5).

Introduction

Group 6 metal carbonyls undergo sequential photosubstitution of two CO groups for monoolefin ligands, yielding (η^2-olefin)M(CO)$_5$ and, ultimately, stable *trans*-(η^2-olefin)$_2$M(CO)$_4$ (1),[1-7] with orthogonal arrangement of the two monoolefin units. Labile[5,6] *cis*-(η^2-olefin)$_2$M(CO)$_4$ isomers (2) are suspected to be involved as intermediate products.[7]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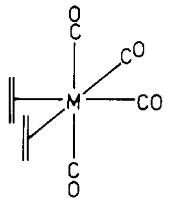
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Further CO photosubstitution, with introduction of a third olefin ligand, has not yet been accomplished. However, such an undertaking might have a good chance of success when starting with a (η^4-diene)M(CO)$_4$ complex, bearing in mind the stabilizing diene chelate effect.

Results and Discussion

Irradiation of (η^4-norbornadiene)W(CO)$_4$ (3)[8] in the presence of excess olefin ((*Z*)-cyclooctene, ethene) results in the formation of the *mer*-(η^2-olefin)(η^4-norbornadiene)W(CO)$_3$ complexes (4, olefin = (*Z*)-cyclooctene; 5, olefin = ethene; eq 1), which are the first representatives

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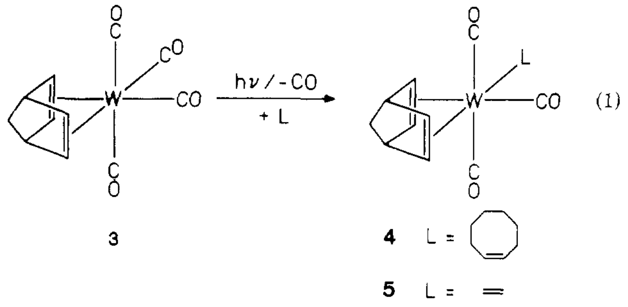
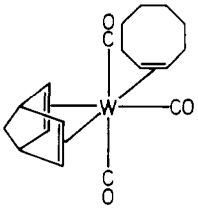


(1)

of this type of compound. Complexes 4 and 5 are stable in solution at least up to +90 °C. The CO stretching vibrational patterns [4, 2019.5 (w), 1942.5 (st), 1932.5 (m) cm^{-1}; 5, 2028 (w), 1951.5 (vst, slightly broadened) cm^{-1}; in *n*-hexane] establish the *mer* geometry of the $W(CO)_3$ moiety (vide infra) rather than the alternative *fac* structure, which would give rise to three bands of nearly equal intensities.

The *mer* structure of 4 and 5 parallels that of (η^4-norbornadiene)(triphenylphosphine)$Cr(CO)_3$.[9,10] However, it contrasts with the preferential photodissociation of an axial CO group of 3, concluded from photoinduced incorporation of ^{13}CO into group 6 (η^4-norbornadiene)M$(CO)_4$ complexes,[11,12] and with the exclusive axial CO photodissociation observed for (η^4-1,3-diene)$Cr(CO)_4$ in low-temperature matrices.[13] Thus we suspect, in accord with current flash photolysis and low-temperature experiments,[14] that the *fac* isomer is involved as a labile intermediate in the formation of 4 and 5.

The $^{13}C\{^1H\}$ NMR spectrum of 4, at ambient temperature and 25.2 MHz, exhibits two sets of four resonance lines each, assigned to the norbornadiene and the (*Z*)-cyclooctene ligand, respectively, and two lines with 1:2 intensity ratio in the carbonyl region (Table I). This pattern would be in accordance with C_s symmetry, i.e., with the monoolefin in the upright orientation, its C=C axis being parallel to those of norbornadiene. However, the shape of one of the (*Z*)-cyclooctene resonances (C-5) as a markedly broadened signal, and its disappearance when the spectrum is recorded at 100.6 MHz, points toward a fluxional process to be operative, most probably involving rotation about the metal–olefin bond. Indeed, lowering the temperature causes this process to be frozen out. The low-temperature-limiting spectrum at 223 K and 100.6 MHz (Figure 1B, Table I) shows a total number of 18 lines, indicating that not only are the carbon atoms of the (*Z*)-cyclooctene ligand inequivalent in the static structure but also those of norbornadiene and the CO groups. Hence it follows that the mirror plane of (*Z*)-cyclooctene does not coincide with that of the *mer*-(η^4-norbornadiene)$W(CO)_3$ fragment; i.e., the spectrum is consistent with the position of the monoolefin C=C axis perpendicular to the norbornadiene double bonds. The $^1J(^{183}W-^{13}C)$ coupling constants, taken from the low-temperature spectrum (Figure 1B), amount to 157 Hz for the equatorial CO group and 137/124 Hz for the axial CO groups, in close agreement with those observed for 3 (163.5 Hz, 117.7 Hz; cf ref 12).



4

Raising the temperature results in coalescence in pairs of all ^{13}C resonances of 4, except those of the unique equatorial CO group and the norbornadiene CH_2 bridge, in accord with the assumption that the underlying process implicates rotation by 180° about the metal–((*Z*)-cyclooctene) bond. At 363 K and 100.6 MHz all signals have reappeared, that of C-5 still being somewhat broad (Figure 1A). Variable-temperature spectra and line-shape analyses[15] of the C-1, C-2, and axial CO $^{13}C\{^1H\}$ NMR signals yield $E_a = 58.0 \pm 1.7$ kJ mol^{-1}, $\Delta H^{\ddagger} = 55.7 \pm 1.8$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 16 \pm 7$ J mol^{-1} K^{-1}. The (*Z*)-cyclooctene signals, particularly those of C-5 and one pair of CH_2 groups, exhibit additional broadening at lower temperatures (Figure 1B), which most probably originates from conformational dynamics of the eight-membered ring.[16] Consequently, those signals are not included in the line-shape analysis.

Regarding the $^{13}C\{^1H\}$ NMR spectrum of complex 5, variation of the temperature should affect the ethene signals only. In fact, at any temperature in the range from 353 to 223 K (Table I) a set of four lines (with 2:1:2:2 intensity ratio) is observed for the norbornadiene unit, whereas the two ethene ^{13}C resonances observed in the low-temperature-limiting spectrum undergo coalescence and reappear as a single line upon raising the temperature. Line-shape analysis yields the following activation parameters (which closely resemble those of 4): $E_a = 54.8$ kJ mol^{-1}, $\Delta H^{\ddagger} = 52.6$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -3$ J mol^{-1} K^{-1}. The height of the barrier for olefin rotation in compounds 4 and 5 is similar to that observed for *trans*-(η^2-olefin)$_2$W$(CO)_4$ complexes,[2,17] which reflects the energy difference between the orthogonal and the parallel arrangement of the two C=C units. Accordingly, the transition state of the fluxional process in 4 and 5 should involve the upright position of the monoolefin double bond, parallel to the norbornadiene C=C units.

The X-ray diffraction structure analysis of 5 (Figure 2, Tables II and III) not only confirms the general structural features concluded from the infrared CO stretching vibrational pattern and the ^{13}C NMR data but also in addition provides the metal—(C=C) bond distances which are of interest with regard to the bonding situation. For comparison, the structure of (η^4-norbornadiene)$W(CO)_4$ (3) (Figure 3, Tables IV and V) is reported.

The structures of both complexes represent distorted octahedral arrangements of the ligands around the metal. The C–W–C angles in the *trans*-$W(CO)_2$ units of 3 and 5 deviate from 180° by 12.4° and 8.4°, respectively. More pronounced deviations from the ideal octahedral geometry result from the strain imposed by the limited chelate angle

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Table I. $^{13}C\{^1H\}$ NMR Data[a] for 3–5

compd	T/K	C-1	C-2	C-3	C-4	C-5	CH$_2$	CO-ax	CO-eq
3	298	68.78	48.76		67.16			204.31	209.74
4	363	76.26	48.94	39.74	64.55	56.58	26.98, 31.79, 35.27	205.84	213.52
	223	75.85	47.28	39.39	64.23	49.67	26.19, 30.31, 34.48	204.46	214.35
		77.85	49.18	39.45		61.04	26.35, 32.10, 34.74	206.70	
5	353	72.43	49.12	37.98	64.06	32.09		204.60	209.75
	223	73.00	48.45	37.69	63.73	27.13 35.63		204.33	210.44

[a] δ/ppm in toluene-d_8 at 100.6 MHz; note the numbering scheme given in Figure 1, which differs from those in the X-ray diffraction analyses.

Table II. Selected Bond Distances (Å) in 5

W–C1	2.303 (7)	O3–C13	1.14 (1)
W–C2	2.303 (6)	C1–C2	1.39 (1)
W–C4	2.405 (7)	C1–C6	1.55 (1)
W–C5	2.404 (7)	C2–C3	1.53 (1)
W–C8	2.228 (8)	C3–C4	1.52 (1)
W–C9	2.306 (8)	C3–C7	1.53 (1)
W–C11	2.014 (7)	C4–C5	1.41 (1)
W–C12	2.033 (7)	C5–C6	1.54 (1)
W–C13	2.045 (7)	C6–C7	1.55 (1)
O1–C11	1.158 (9)	C8–C9	1.48 (1)
O2–C12	1.13 (1)		

Table III. Selected Bond Angles (deg) in 5[a]

C13–W–C12	87.6 (3)	C6–C1–W	100.7 (4)
C13–W–C11	171.6 (3)	C2–C1–W	72.4 (4)
C13–W–C9	87.3 (3)	C3–C2–C1	107.1 (6)
C13–W–C8	86.8 (3)	C3–C2–W	100.6 (4)
C13–W–C5	109.9 (3)	C1–C2–W	72.4 (4)
C13–W–C4	75.8 (3)	C7–C3–C4	102.0 (6)
C13–W–C2	76.4 (3)	C7–C3–C2	101.5 (6)
C13–W–C1	111.5 (3)	C4–C3–C2	102.0 (5)
C11–W–C9	84.3 (3)	C5–C4–C3	104.9 (6)
C11–W–C8	87.2 (3)	C5–C4–W	72.8 (4)
C11–W–C5	76.1 (3)	C3–C4–W	96.8 (4)
C11–W–C4	110.3 (3)	C6–C5–C4	106.2 (6)
C11–W–C2	111.5 (3)	C6–C5–W	96.9 (4)
C11–W–C1	76.4 (3)	C4–C5–W	73.0 (4)
C5–W–C4	34.2 (2)	C7–C6–C5	99.8 (6)
C5–W–C1	60.9 (2)	C7–C6–C1	101.7 (5)
C4–W–C2	60.4 (2)	C5–C6–C1	101.2 (6)
C2–W–C1	35.2 (2)	C6–C7–C3	93.1 (6)
D3–W–D2	63.9	C9–C8–W	73.8 (4)
D3–W–C12	94.3	C8–C9–W	68.1 (4)
D2–W–D1	110.1	O1–C11–W	178.4 (6)
D1–W–C12	91.7	O2–C12–W	179.5 (6)
C6–C1–C2	104.7 (6)	O3–C13–W	177.9 (7)

[a] D1 is the midpoint of C8–C9. D2 is the midpoint of C4–C5. D3 is the midpoint of C1–C2.

Table IV. Selected Bond Distances (Å) in 3

W–C1	2.409 (5)	O3–C10	1.185 (8)
W–C2	2.403 (6)	O4–C11	1.139 (7)
W–C4	2.419 (5)	C1–C2	1.380 (8)
W–C5	2.412 (6)	C1–C6	1.556 (8)
W–C8	2.006 (5)	C2–C3	1.540 (8)
W–C9	2.032 (5)	C3–C4	1.548 (8)
W–C10	1.971 (6)	C3–C7	1.548 (9)
W–C11	2.045 (5)	C4–C5	1.399 (8)
O1–C8	1.124 (7)	C5–C6	1.512 (8)
O2–C9	1.143 (7)	C6–C7	1.535 (9)

Table V. Selected Bond Angles (deg) in 3[a]

C11–W–C10	84.2 (2)	C6–C1–C2	105.6 (5)
C11–W–C9	167.6 (2)	C6–C1–W	97.6 (3)
C11–W–C8	87.7 (2)	C2–C1–W	73.1 (3)
C11–W–C5	112.4 (2)	C3–C2–C1	106.9 (5)
C11–W–C4	78.8 (2)	C3–C2–W	98.9 (3)
C11–W–C2	79.8 (2)	C1–C2–W	73.6 (3)
C11–W–C1	113.1 (2)	C7–C3–C4	99.6 (4)
C10–W–C9	86.0 (2)	C7–C3–C2	100.5 (5)
C10–W–C8	94.3 (2)	C4–C3–C2	102.6 (4)
C9–W–C8	85.5 (2)	C5–C4–C3	105.2 (5)
C9–W–C5	77.6 (2)	C5–C4–W	72.9 (3)
C9–W–C4	111.2 (2)	C3–C4–W	98.0 (3)
C9–W–C2	111.3 (2)	C6–C5–C4	106.9 (5)
C9–W–C1	78.0 (2)	C6–C5–W	98.8 (4)
C5–W–C4	33.7 (2)	C4–C5–W	73.5 (3)
C5–W–C2	70.1 (2)	C7–C6–C5	100.6 (5)
C5–W–C1	59.8 (2)	C7–C6–C1	100.4 (4)
C4–W–C2	60.0 (2)	C5–C6–C1	103.3 (4)
C4–W–C1	70.7 (2)	C6–C7–C3	93.6 (5)
C2–W–C1	33.3 (2)	O1–C8–W	176.2 (5)
D2–W–D1	62.8	O2–C9–W	177.1 (5)
D2–W–C10	106.0	O3–C10–W	178.2 (5)
D1–W–C8	96.9	O4–C11–W	175.8 (5)

[a] D1 is the midpoint of C1–C2. D2 is the midpoint of C4–C5.

of the norbornadiene ligand. The angles subtended by tungsten with the midpoints of the norbornadiene C=C bonds are 62.8° (**3**) and 63.9° (**5**), while the adjacent and opposite angles around the metal are correspondingly widened (cf. Tables III and V).

The fundamental structural features of **5**, i.e., the *mer*-W(CO)$_3$ skeleton and the position of the ethene double bond perpendicular to the norbornadiene C=C units, are obvious from Figure 2. The most noticeable alteration in going from **3** to **5** is a substantial shortening, by 0.1 Å, of the W—C bond distances of that norbornadiene C=C unit which occupies the position trans to the ethene ligand. By contrast, bonding of the other part of norbornadiene to the metal remains virtually unchanged. Obviously, in the trans-orthogonal (η^2-C=C)$_2$M substructure the metal–olefin bond is distinctly stronger than in the *trans*-(η^2-C=C)M(CO) moiety. We interpret this in terms of optimum metal (d_π)→olefin (π^*) back-donation,[18-20] which accounts for the extraordinary stability not only of **4** and **5** but also of type **1** compounds in comparison with (η^2-olefin)M(CO)$_5$ complexes.[4,7] A corresponding elongation of the C(1)=C(2) distance, as it should be expected from the Dewar–Chatt–Duncanson model of the metal–olefin bond, is not observed. Minor alterations of distances and angles should not be overstressed, particularly in view of the observed differences between chemically equivalent parts of complex **3**.

The olefin coordination shifts, $\Delta\delta = \delta$(free olefin) − δ(coordinated olefin), in **4** and **5** deserve particular consideration. As the most remarkable feature we note the large difference between the two C=C units of norbornadiene, which are separated by ca. 36 ppm: $\Delta\delta$ = 103.5 (**4**) and 105.4 ppm (**5**) vs $\Delta\delta$ = 66.9 (**4**) and 70.7 ppm (**5**). The latter values are close to that of (η^4-norbornadiene)W(CO)$_4$, $\Delta\delta$ = 74.4 ppm (Table VI). Thus, we assign the

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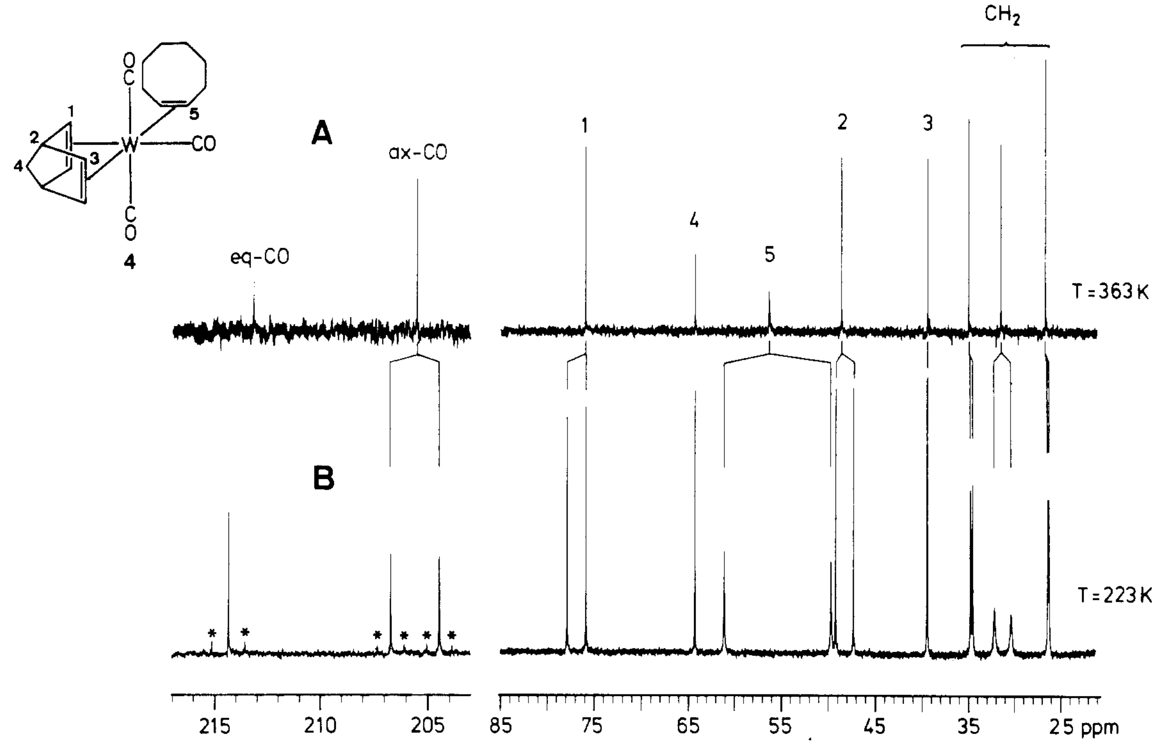

Figure 1. $^{13}C\{^1H\}$ NMR spectra of 4 at 363 K (A) and 223 K (B) in toluene-d_8 (100.6 MHz). Asterisks indicate satellites originating from $^1J(^{183}W-^{13}C)$. Note that the numbering scheme differs from that of the X-ray structure analysis.

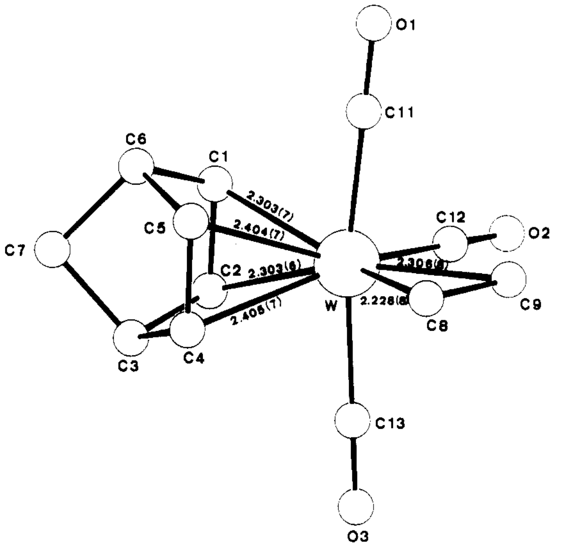

Figure 2. Structure of 5 in the crystal.

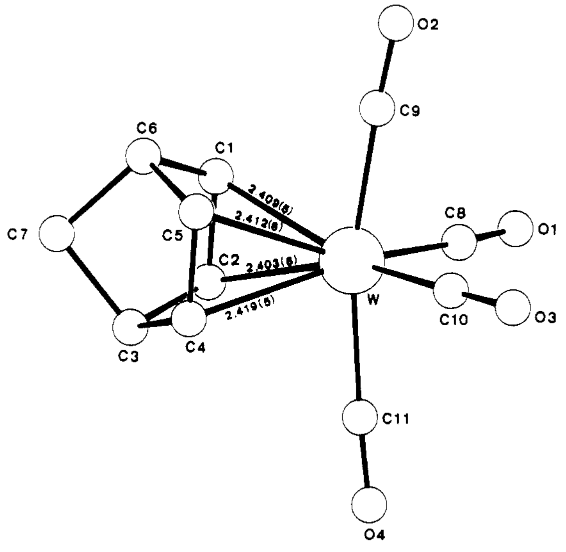

Figure 3. Structure of 3 in the crystal.

lower field norbornadiene signals of 4 and 5 to the double bond in the trans position to the equatorial CO group and the signals at higher field to the double bond trans to the monoolefin. With regard to the origin of this effect, we suspect that the coordination shift correlates with the degree of metal (d_π)→olefin (π^*) back-donation. Certainly, a C=C unit in the trans position to the strongly π-accepting CO ligand receives less d_π-electron density from the metal than in a position trans orthogonal to a second olefin.[18-20] An analogous case is represented by the coordination shifts of (*Z*)-cyclooctene (Table VI) in (η^2-(*Z*)-cyclooctene)W(CO)$_5$ ($\Delta\delta$ = 42.3 ppm),[4] on the one hand, and in 4 ($\Delta\delta$ = 73.8 ppm) and *trans*-(η^2-(*Z*)-cyclooctene)$_2$W(CO)$_4$ ($\Delta\delta$ = 72.7 ppm),[4] on the other hand, which differ by 30 ppm and once again demonstrate the validity of the above reasoning.

Recent literature data on (η^4-norbornadiene)$_2$Mo(CO)$_2$[21,22] are in accord with the above notions. The two norbornadiene ligands are arranged in such a way that two C=C units, one of each norbornadiene, adopt trans-orthogonal (η^2-C=C)$_2$M geometry. In this substructure the average Mo–C distance is shorter, by 0.2 Å, and the coordination shift is larger, by 32.8 ppm, than in the two *trans*-(η^2-C=C)Mo(CO) units. In case of the analogous tungsten complex (cf. Table VI) the difference of the respective coordination shifts amounts to 38.2 ppm.[22] Thus it appears that ^{13}C NMR data can be taken as a general criterion in recognizing the positions of olefinic units and CO groups in octahedral group 6 metal complexes.

As a concluding remark we wish to emphasize that carbene ligands, owing to their single-faced nature,[19] be-

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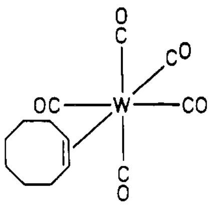
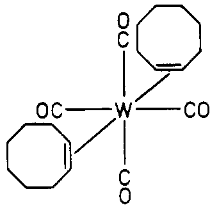
(21) Chow, T. J.; Wu, M.-Y.; Liu, L.-K. *J. Organomet. Chem.* **1985**, *281*, C33.

(22) Chow, T. J.; Chao, Y.-S.; Liu, L.-K. *J. Am. Chem. Soc.* **1987**, *109*, 797.

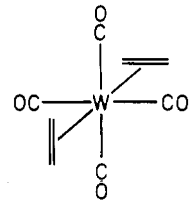
Table VI. Upfield Coordination Shifts ($\Delta\delta^a$) of C=C Units in Complexes 3–9



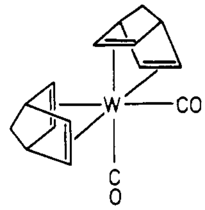
6



7



8



9

compd	norbornadiene	(Z)-cyclooctene		ethene
3	74.4			
4	66.9, 103.5		73.8	
5	70.8, 105.2			91.2
6^4		42.3		
7^4			72.7	
8^7				92.0
9^{22}	69.7, 107.9			

^{a} $\Delta\delta = \delta$(free olefin) − δ(coordinated olefin).

have much the same way as olefins do. This is demonstrated by the structures of *trans*-(carbene)(η^2-olefin)W(CO)$_4$ complexes,[23,24] where the olefin axis lies in the carbene plane. This implies orthogonal disposition of their π-acceptor orbitals and, consequently, optimum metal→ligand π-back-donation. From the increasing number of such examples it becomes obvious that such arrangements of two single-faced ligands generally can be expected when π-back-donation makes a substantial contribution to the metal–ligand bonds, unless chelate effects command a different geometry.

Experimental Section

Photoreactions were performed in an immersion well apparatus (solidex glass, λ ≥ 280 nm) with a Philips HPK 125-W mercury lamp. Anaerobic conditions were assured by Schlenk techniques throughout, using argon as the inert gas. Solvents (Merck, extra pure grade) were used as received. Characterization of products: elemental analyses, Microanalytical Laboratory Dornis and Kolbe, Mülheim a.d. Ruhr, FRG; melting points, Reichert-Kofler apparatus; mass spectra, Varian MAT CH 5 instrument; NMR spectra, Bruker AM 400 and WH 270 instruments (assignments are based on DEPT and 2D measurements); IR spectra, Perkin-Elmer 580 instrument in combination with Data Station 3600; UV–vis spectra, Perkin-Elmer 320 instrument.

Table VII. Crystallographic Data of 3 and 5 and Details of Data Collection

	3	5
formula	$C_{11}H_8O_4W$	$C_{12}H_{12}O_3W$
M_r	388.0	388.1
space group	$P2_1/c$	$P2_1/n$
a, Å	9.744 (2)	8.225 (1)
b, Å	9.929 ((1)	12.571 (2)
c, Å	11.394 (1)	11.327 (1)
β, deg	91.16 (1)	92.51 (1)
V, Å^3	1102.1	1170.1
Z	4	4
d_{calcd}, g/cm^3	2.34	2.20
μ(Mo), cm^{-1}	106.98	100.71
F(000), e	720	728
T, °C	20.0	20.0
cryst dimens (max), mm	0.09 × 0.45 × 0.52	0.43 × 0.37 × 0.46
radiatn (Mo Kα)	0.71069	0.71069
scan mode	Ω–2θ	Ω–2θ
scan range (θ)	1.79, 34.82	1.62, 29.95
hkl range	±15,±15,+18	±11,+17,+15
reflctns meased	9608	3696
reflctns unique	4790	3395
reflctns obsd ($I > 2.0\sigma(I)$)	3350	2675
param varied	145	145
max shift/esd (last cycle)	0.11	0.001
R^a	0.031	0.035
$R_w{}^b$	0.035	0.041
ρ(max), e/Å^3	1.43	1.55

$^a R = (\sum||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$.

Table VIII. Atomic Fractional Coordinates with Standard Deviations in Parentheses for 3

atom	*x*	*y*	*z*
W	0.2010 (1)	0.0945 (1)	0.2205 (1)
O1	−0.0823 (4)	0.0895 (4)	0.0865 (4)
O2	0.0232 (5)	0.1745 (6)	0.4400 (4)
O3	0.2453 (6)	0.4072 (4)	0.1906 (5)
O4	0.3461 (5)	0.0830 (5)	−0.0269 (4)
C1	0.1702 (6)	−0.1214 (5)	0.3128 (5)
C2	0.2415 (6)	−0.1439 (6)	0.2112 (5)
C3	0.3951 (6)	−0.1450 (6)	0.2456 (5)
C4	0.4228 (5)	0.0040 (5)	0.2780 (5)
C5	0.3504 (6)	0.0263 (6)	0.3810 (5)
C6	0.2814 (6)	−0.1051 (6)	0.4116 (5)
C7	0.3891 (7)	−0.2063 (7)	0.3702 (6)
C8	0.0206 (5)	0.0952 (5)	0.1325 (4)
C9	0.0895 (6)	0.1436 (7)	0.3629 (5)
C10	0.2309 (6)	0.2896 (7)	0.2024 (4)
C11	0.2943 (6)	0.0817 (5)	0.0617 (5)

***mer*-(η^2-(*Z*)-Cyclooctene)(η^4-norbornadiene)W(CO)$_3$ (4).** A solution of 3[8] (1.55 g, 4.0 mmol) and (*Z*)-cyclooctene (4.4 g, 40 mmol) in *n*-hexane (400 mL) is irradiated at ambient temperature for 80 min. After the solvent is evapòrated, the residue is chromatographed on silica, using *n*-hexane eluent and collecting the first, pale yellow band. Recrystallization from *n*-hexane (50 mL; 20 °C to −78 °C) yields 4 (1.25 g, 67%): pale yellow crystals; mp 85 °C. Anal. Calcd for $C_{18}H_{22}O_3W$: C, 45.98; H, 4.72; W, 39.10. Found: C, 45.88; H, 4.87; W, 38.88. MS: *m/z* (relative intensity) 470 (M$^+$, 21). ^{1}H NMR (toluene-d_8, 270 MHz, 298 K) δ 0.56/0.64 (m, 2 H, H-4/H-4′), 1.4 (m, 12 H), 1.90 (m, 2 H, H-5), 2.93 (m, 2 H, H-3), 3.33 (m, 2 H, H-2), 4.08 (m, 2 H, H-1). UV–vis (*n*-hexane): λ (ε) 245.5 nm (28200 L mol^{-1} cm^{-1}) 300 nm (sh, 6400 L mol^{-1} cm^{-1}).

***mer*-(η^2-Ethene)(η^4-norbornadiene)W(CO)$_3$ (5).** A solution of 3[8] (0.78 g, 2.0 mmol) in *n*-pentane (400 mL), saturated with ethene, is irradiated at −30 °C for 30 min while ethene is bubbled through. After the solvent is evaporated, the residue is flash-chromatographed at −20 °C on silica, using *n*-pentane eluent and collecting the colorless fractions, as monitored by IR spectroscopy. Small amounts of (η^2-ethene)W(CO)$_5$[7] and (η^2-ethene)$_2$W(CO)$_4$[7] are discarded, and the main fraction containing 5 is evaporated to dryness. Recrystallization from ethene-saturated *n*-pentane (10 mL; 20 °C to −78 °C) yields 5 (0.45 g, 64%): colorless cubes; mp 59 °C. Anal. Calcd for $C_{12}H_{12}O_3W$: C, 37.14; H, 3.12; W, 47.37. Found: C, 37.06; H, 3.03; W, 47.28. MS: *m/z* (relative intensity) 388 (M$^+$, 20). ^{1}H NMR (toluene-d_8, 298 K): δ 0.50/0.53 (m, 2 H, H-4/H-4′), 1.55 (m, 4 H, H-5), 2.88 (m, 2 H, H-3), 3.30 (m, 2 H, H-2), 4.10 (m, 2 H, H-1). UV–vis (*n*-hexane): λ (ε) 246.5 nm (27900 L mol^{-1} cm^{-1}), 300 nm (sh, 5900 L mol^{-1} cm^{-1}).

X-ray Diffraction Structure Analyses of 3 and 5. Crystals of 3 (recrystallized from *n*-hexane) and 5 (recrystallized from *n*-pentane) were mounted in glass capillaries under argon. X-ray

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(23) Angermund, K.; Grevels, F.-W.; Krüger, C.; Skibbe, V. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 904.

(24) Alvarez, C.; Pacreau, A.; Parlier, A.; Rudler, H.; Daran, J.-C. *Organometallics* **1987**, *6*, 1057.

Table IX. Atomic Fractional Coordinates with Standard Deviations in Parentheses for 5

atom	*x*	*y*	*z*
W	0.0873 (1)	0.1671 (1)	0.2847 (1)
O1	0.2465 (7)	0.0092 (5)	0.1046 (5)
O2	0.3602 (8)	0.1009 (7)	0.4757 (6)
O3	−0.0227 (9)	0.3413 (5)	0.4683 (7)
C1	−0.0571 (8)	0.0115 (6)	0.3039 (6)
C2	−0.1186 (8)	0.0853 (6)	0.3819 (5)
C3	−0.2679 (8)	0.1365 (6)	0.3196 (7)
C4	−0.1914 (9)	0.2029 (6)	0.2250 (7)
C5	−0.1319 (9)	0.1281 (6)	0.1442 (6)
C6	−0.1737 (9)	0.0175 (6)	0.1928 (6)
C7	−0.3384 (9)	0.0429 (7)	0.2480 (7)
C8	0.170 (1)	0.3006 (6)	0.1728 (7)
C9	0.3106 (9)	0.2724 (6)	0.2529 (8)
C11	0.1879 (8)	0.0679 (6)	0.1690 (6)
C12	0.2634 (8)	0.1247 (6)	0.4073 (6)
C13	0.0160 (9)	0.2805 (6)	0.4011 (6)

data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα X-radiation. Unit cell parameters were obtained by least-squares fits to the θ values of 75 automatically centered reflections. Data were corrected for Lorentz and polarization effects. Empirical absorption correction was performed for **5** and analytical absorption correction for **3**. $\sigma(F)$ was calculated from $\sigma(F) = [\sigma(I)^2 + (Ik)^2]^{1/2}/2F$, where $k = 0.02$.

The structures were solved by the heavy-atom method. Refinement was by full-matrix least-squares methods, where the function was minimized $\sum w(\Delta F)^2$ with $w = 1/\sigma^2(F)$ and $\Delta F = |F_o| - |F_c|$. The positions of the H atoms were calculated (d(C–H) = 0.95 Å) and included in the refinement with fixed positions and isotropic thermal parameters (U_H = 0.05 Å^2). A summary of data collection and processing parameters is given in Table VII. The results of the X-ray analyses are summarized in Tables II–V, VIII, and IX which give selected interatomic distances and angles and the final atomic coordinates. Figures 2 and 3 show the molecular structures.

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Registry No. **3**, 12129-25-8; **4**, 117686-87-0; **5**, 117686-88-1; *Z*-cyclooctene, 931-87-3; ethene, 74-85-1.

Supplementary Material Available: Detailed information on the crystal structures of **3** and **5** including figures of the molecular structures and tables of final atomic positional parameters, thermal parameters, and distances and angles (12 pages); listings of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

"Half-Open Metallocenes" of Iron, Ruthenium, and Osmium: Synthesis, Characterization, Photoelectron Spectroscopy, and Theoretical Calculations

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The "half-open ruthenocene" and "half-open osmocene" complexes, $M(C_5H_5)(2,4\text{-}C_7H_{11})$ (M = Ru, Os; C_7H_{11} = η^5-dimethylpentadienyl), have been prepared from reductions of $RuCl_3 \cdot nH_2O$ and Na_2OsCl_6, respectively, in the presence of slightly less than 1 equiv of cyclopentadiene and an excess of 2,4-dimethyl-1,3-pentadiene. An X-ray diffraction study of the ruthenium compound has revealed a structure analogous to that found for the isomorphous iron complex, with crystallographically imposed mirror plane symmetry. The structure was refined to agreement indices of R = 0.030 and R_w = 0.028 in space group D_{2h}^{16}—*Pnma* (No. 62), with a = 5.917 (2) Å, b = 13.124 (3) Å, c = 13.501 (4) Å, and Z = 4. The average Ru–C bond distance of 2.178 (3) Å to the cyclopentadienyl ligand was found to be similar to that for the 2,4-dimethylpentadienyl ligand, 2.168 (3) Å. $Ru(C_5H_5)(2,4\text{-}C_7H_{11})$ may readily be protonated by HBF_4, yielding $[HRu(C_5H_5)(2,4\text{-}C_7H_{11})]^+BF_4^-$. Variable-temperature NMR studies demonstrate that the added proton may readily exchange with the four hydrogen atoms attached to the terminal carbon atoms of the pentadienyl ligands. Photoelectron spectroscopy and theoretical calculations have been used to probe the electronic structures of the neutral compounds. On the basis of INDO–MO calculations we have correlated the energy levels and the wave functions of bis(pentadienyl)iron (**1**), (cyclopentadienyl)(pentadienyl)iron (**2**), and ferrocene (**3**). It is predicted that **2** is between **1** and **3** with respect to the energy of the HOMO and the 3d character of the wave functions. The He I and He II photoelectron (PE) spectra of the cyclopentadienyl 2,4-dimethylpentadienyl complexes of iron (**4**), ruthenium (**5**), and osmium (**6**) have been recorded. Assignments for the first bands are based upon INDO calculations on **4**, taking into account the differing Koopmans' defects in the framework of the Green's function technique, as well as relative intensity arguments involving the He I and He II spectra of **4**–**6**. The assignments have been supported through a comparison of the first bands of the PE spectrum of **4** with those of **5** and **6**.

Recently, the physical and theoretical natures of pentadienyl groups, and their metal complexes, have been of interest, especially relative to their better known cyclopentadienyl counterparts.[1] In our own earlier studies,

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