~0.11 Å, W=C by ~0.10 Å, W=O by 0.036 Å, but W—P by only ~0.004 Å (average)].

Finally, we emphasize that these molecular oxo–alkylidene complexes of tungsten(VI) are closely related to certain heterogeneous tungsten(VI) and molybdenum(VI) catalysts used industrially for olefin metathesis reactions.[10-13]

Acknowledgment. This work was supported by National Science Foundation Grant CHE80-23448 to M.R.C. We thank Professor R. R. Schrock for providing the sample.

Registry No. $W(=O)(=CHCMe_3)(PMe_3)_2Cl_2$, 76603-92-4.

Supplementary Material Available: Listings of observed and calculated structure-factor amplitudes, anisotropic thermal parameters, calculated positions for hydrogen atoms, and data-processing formulas (18 pages). Ordering information is given on any current masthead page.

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Iridium Carbonyl Clusters. 5.[1-4] Crystal Structure and Molecular Geometry of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$

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The bimetallic species $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ has been examined via a single-crystal X-ray diffraction study. This complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ [C_i^1, No. 2] with $a = 8.503$ (2) Å, $b = 9.238$ (2) Å, $c = 15.659$ (6) Å, $\alpha = 87.40$ (3)°, $\beta = 76.61$ (3)°, $\gamma = 73.12$ (2)°, $V = 1144.7$ (5) Å^3, and ρ(calcd) = 3.37 g cm^{-3} for $Z = 2$ and mol wt 1162.4. Diffraction data were collected with a Syntex $P2_1$ diffractometer, and the structure was refined to R_F = 3.6% for 2998 reflections with 3° < 2θ < 45° (Mo Kα radiation). The molecule is based upon a closed tetrahedral W_2Ir_2 core. Each iridium atom is linked to three terminal carbonyl ligands, while the two tungsten atoms are each associated with an η^5-cyclopentadienyl ligand and with two carbonyl ligands. There are some indications that the two most bent carbonyl ligands may have some "semibridging" character [W(1)–WC(11)–WO(11) = 167.2 (13)° with W(2)···WC(11) = 2.794 (14) Å; W(2)–WC(21)–WO(21) = 171.8 (12)° with Ir(1)···WC(21) = 2.835 (14) Å]. The metal–metal distances (Å) are Ir(1)–Ir(2) = 2.722 (1), W(1)–W(2) = 2.991 (1), Ir(1)–W(1) = 2.796 (1), Ir(1)–W(2) = 2.863 (1), Ir(2)–W(1) = 2.833 (1), and Ir(2)–W(2) = 2.847 (1).

Introduction

The "mixed-metal" cluster complexes $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ and $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ have recently been synthesized by Shapley and co-workers[5] as a prelude to studying the properties of bimetallic clusters as alumina-supported catalysts. We have previously reported the detailed molecular structure of the 1:3 (W:Ir) species $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$[1] and now report the results of a full X-ray structural analysis of the 2:2 species, $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$.[5] While these complexes are normal "60-electron" tetrahedral clusters, they are among the most crowded of the known tetranuclear derivatives.

Experimental Section

Collection of X-ray Diffraction Data for $(\eta^5\text{-}C_5H_5)W_2Ir_2(CO)_{10}$. The compound was provided by Professor J. R. Shapley in the form of opaque dark crystals. The crystal selected for data collection was close to spherical with an average dimension of 0.2 mm. The crystal was mounted and aligned on our Syntex $P2_1$ diffractometer, and intensity data were collected as described previously.[6] Details are given in Table I. The intensities were corrected for absorption with an empirical method based upon twofold interpolation (in 2θ and ϕ) between ψ-scans of close-to-axial reflections.

Table I. Experimental Data for the X-ray Diffraction Study of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$

(A) Crystal Parameters at 24 °C[a]

crystal system: triclinic	$V = 1144.7$ (5) Å^3
space group: $P\bar{1}$ (C_i^1, No. 2)	$Z = 2$
$a = 8.5028$ (24) Å	mol wt = 1162.4
$b = 9.2377$ (24) Å	ρ(calcd) = 3.37 g cm^{-3}
$c = 15.6588$ (64) Å	μ(Mo Kα) = 228.9 cm^{-1}
$\alpha = 87.40$ (3)°	
$\beta = 76.61$ (3)°	
$\gamma = 73.12$ (2)°	

(B) Measurement of Data

diffractometer	Syntex $P\bar{2}_1$
radiation	Mo Kα ($\bar{\lambda}$ 0.71073 Å)
monochromator	highly oriented graphite, equatorial mode ($2\theta_{mono} = 12.2°$)
reflctns measd	$h, \pm k, \pm l$
2θ range	3–45°
scan type	θ(crystal)–2θ(counter)
scan width	$[2\theta(K\alpha_1) - 0.8]°$ to $[2\theta(K\alpha_2) + 0.8]°$
scan speed	3.0°/min
bkgd measmnt	stationary crystal and counter at beginning and end of 2θ scan, each for half of the scan time
reflctns collected	3346 total, merged to 2998 independent reflections
std reflctn	three measured after each 97 reflections (006, 070, 411); no decay was observed over the period of data collection

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo$K\bar{\alpha}$ components of 24 reflections with 2θ between 20° and 30°. Reflections used were {620}, {540}, {533}, {504}, {457}, {439}, $\{4\bar{1}9\}$, {356}, {462}, {361}, $\{26\bar{4}\}$, and {163}.

Analysis of the standard reflections showed no evidence for crystal decay. All absorption-corrected intensities were therefore converted

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(1) Part 4, $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$: Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1981**, *20*, 4112.

(2) Part 3, $Ir_4(CO)_{10}$(diars): Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1980**, *19*, 2765.

(3) Part 2, $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$: Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1979**, *18*, 2451.

(4) Part 1, $Ir_4(CO)_{12}$: Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528.

(5) Shapley, J. P.; Hardwick, S. J.; Foose, D. S.; Stucky, G. D.; Churchill, M. R.; Bueno, C.; Hutchinson, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 7383.

(6) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

0020-1669/82/1321-1359$01.25/0

Table II. Final Positional and Thermal Parameters for Atoms in the $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ Molecule

atom	x	y	z	B_{iso}, Å^2
Ir(1)	0.21260 (6)	0.11061 (5)	0.22251 (3)	
Ir(2)	0.45209 (6)	0.25435 (5)	0.15923 (3)	
W(1)	0.30618 (6)	0.26727 (5)	0.34177 (3)	
W(2)	0.11022 (6)	0.43376 (5)	0.21368 (3)	
O(11)	−0.0430 (14)	0.0344 (12)	0.3733 (8)	
O(12)	0.5071 (13)	−0.1638 (11)	0.2319 (7)	
O(13)	0.1292 (15)	0.0109 (13)	0.0591 (8)	
O(21)	0.5896 (15)	0.5235 (13)	0.1294 (9)	
O(22)	0.7786 (13)	0.0244 (12)	0.1844 (7)	
O(23)	0.4778 (17)	0.1782 (13)	−0.0320 (7)	
WO(11)	−0.0645 (12)	0.4187 (12)	0.4361 (6)	
WO(12)	0.4031 (15)	0.5686 (12)	0.3421 (8)	
WO(21)	−0.2135 (13)	0.3336 (12)	0.2717 (8)	
WO(22)	0.1070 (16)	0.3495 (11)	0.0227 (7)	
C(11)	0.0481 (18)	0.0666 (16)	0.3168 (11)	
C(12)	0.3972 (17)	−0.0553 (15)	0.2266 (9)	
C(13)	0.1590 (17)	0.0498 (16)	0.1200 (10)	
C(21)	0.5328 (17)	0.4248 (15)	0.1456 (9)	
C(22)	0.6531 (18)	0.1072 (16)	0.1787 (9)	
C(23)	0.4655 (18)	0.2081 (15)	0.0387 (10)	
WC(11)	0.0677 (19)	0.3695 (15)	0.3922 (9)	
WC(12)	0.3652 (16)	0.4586 (15)	0.3373 (8)	
WC(21)	−0.0825 (17)	0.3605 (16)	0.2489 (9)	
WC(22)	0.1136 (17)	0.3725 (15)	0.0936 (9)	
C(1)	0.5225 (17)	0.0699 (15)	0.3846 (9)	3.4 (3)
C(2)	0.3767 (18)	0.0395 (16)	0.4184 (10)	3.8 (3)
C(3)	0.2680 (18)	0.1542 (16)	0.4781 (10)	3.7 (3)
C(4)	0.3581 (20)	0.2616 (17)	0.4794 (10)	4.4 (3)
C(5)	0.5168 (17)	0.2077 (15)	0.4188 (9)	3.4 (3)
C(6)	−0.0988 (18)	0.6551 (16)	0.2716 (10)	3.8 (3)
C(7)	−0.0754 (17)	0.6514 (14)	0.1780 (9)	3.1 (3)
C(8)	0.0852 (18)	0.6607 (15)	0.1419 (9)	3.5 (3)
C(9)	0.1658 (18)	0.6682 (15)	0.2111 (9)	3.6 (3)
C(10)	0.0497 (18)	0.6666 (16)	0.2889 (10)	3.8 (3)
H(1)	0.6153	0.0072	0.3437	4.5
H(2)	0.3499	−0.0479	0.4039	4.5
H(3)	0.1575	0.1590	0.5108	4.5
H(4)	0.3197	0.3521	0.5140	4.5
H(5)	0.6028	0.2571	0.4045	4.5
H(6)	−0.1974	0.6506	0.3137	4.5
H(7)	−0.1559	0.6439	0.1466	4.5
H(8)	0.1341	0.6620	0.0809	4.5
H(9)	0.2778	0.6732	0.2049	4.5
(10)	0.0689	0.6724	0.3458	4.5

to (unscaled) $|F_o|$ values, following correction for Lorentz and polarization factors. Any reflection with $I_{net} < 0$ was assigned a value of $|F_o| = 0$.

Solution and Refinement of the Structure. All computations were done with our in-house Syntex XTL system. The analytical form[7a] of the scattering factors for neutral atoms were used throughout the analysis; both $\Delta f'$ and $i\Delta f''$ terms[7b] were included for all nonhydrogen atoms. The function minimized during the least-squares process was $\sum w(|F_o| - |F_c|)^2$, where the assigned weights are given by $w = [(\sigma(|F_o|))^2 + (p|F_o|)^2]^{-1}$ where $p = 0.015$. Data were placed on an approximate scale via a Wilson plot. The structure was solved by using a combination of Patterson, difference-Fourier, and least-squares refinement techniques. All nonhydrogen atoms were located. The cyclopentadienyl ring's hydrogen atoms were included in calculated positions with $d(C-H) = 0.95$ Å.[8]

With a correction for secondary extinction included ($c = 1.4 \times 10^{-7}$; see footnote 8 of ref 1), the final discrepancy indices[9] were $R_F = 3.6\%$, $R_{wF} = 3.8\%$, and GOF = 1.71 for 257 parameters refined against all 2998 reflections (none rejected). The residuals for those 2767 data with $|F_o| > 3.0\sigma(|F_o|)$ were $R_F = 3.2\%$, $R_{wF} = 3.7\%$, and GOF = 1.75.

A final difference-Fourier synthesis showed no significant features. The function $\sum w(|F_o| - |F_c|)^2$ showed no abnormal dependency on $|F_o|$, $(\sin \theta)/\lambda$, sequence number, identity or parity-class of the crystallographic indices; the weighting scheme is thus satisfactory. Positional and thermal parameters are collected in Table II.

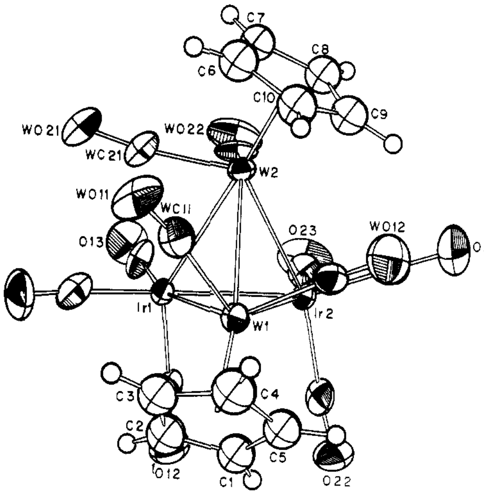

Figure 1. Labeling of atoms in the $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ molecule.

Table III. Interatomic Distances (Å) for $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$

(A) Metal–Metal Distances			
Ir(1)–Ir(2)	2.722 (1)	Ir(2)–W(1)	2.833 (1)
Ir(1)–W(1)	2.796 (1)	Ir(2)–W(2)	2.847 (1)
Ir(1)–W(2)	2.863 (1)	W(1)–W(2)	2.991 (1)
(B) Metal–(Carbonyl Carbon) Distances			
Ir(1)–C(11)	1.902 (16)	W(1)–WC(11)	1.960 (16)
Ir(1)–C(12)	1.859 (14)	W(1)–WC(12)	1.967 (13)
Ir(1)–C(13)	1.915 (15)		
Ir(2)–C(21)	1.878 (14)	W(2)–WC(21)	1.908 (15)
Ir(2)–C(22)	1.928 (15)	W(2)–WC(22)	1.979 (14)
Ir(2)–C(23)	1.925 (15)		
(C) Short Metal···Carbonyl Contacts			
Ir(1)···WC(21)	2.835 (14)	W(2)···WC(11)	2.794 (14)
(D) Metal–(Cyclopentadienyl Carbon) Distances			
W(1)–C(1)	2.381 (14)	W(2)–C(6)	2.340 (15)
W(1)–C(2)	2.365 (14)	W(2)–C(7)	2.304 (13)
W(1)–C(3)	2.329 (14)	W(2)–C(8)	2.311 (14)
W(1)–C(4)	2.293 (14)	W(2)–C(9)	2.343 (14)
W(1)–C(5)	2.309 (15)	W(2)–C(10)	2.363 (14)
W(1)–Cp[a]	2.012	W(2)–Cp[a]	2.005
(E) Carbon–Oxygen Distances			
C(11)–O(11)	1.125 (20)	C(23)–O(23)	1.127 (19)
C(12)–O(12)	1.170 (17)	WC(11)–WO(11)	1.148 (19)
C(13)–O(13)	1.140 (19)	WC(12)–WO(12)	1.162 (18)
C(21)–O(21)	1.143 (19)	WC(21)–WO(21)	1.182 (19)
C(22)–O(22)	1.138 (19)	WC(22)–WO(22)	1.157 (18)
(F) Carbon–Carbon Distances			
C(1)–C(2)	1.335 (22)	C(6)–C(7)	1.433 (20)
C(2)–C(3)	1.404 (20)	C(7)–C(8)	1.378 (22)
C(3)–C(4)	1.421 (23)	C(8)–C(9)	1.422 (21)
C(4)–C(5)	1.423 (22)	C(9)–C(10)	1.382 (21)
C(5)–C(1)	1.387 (19)	C(10)–C(6)	1.385 (23)

[a] "Cp" is the centroid of the appropriate η^5-cyclopentadienyl ligand.

Description of the Structure

The crystal consists of discrete ordered units of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ which are mutually separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. Figure 1 shows the scheme used for labeling atoms, while Figures 2 and 3 provide stereoscopic views of the molecule. Interatomic distances and their estimated standard deviations (esd's) are collected in Table III, and interatomic angles are listed in Table IV.

The molecule is based upon a closed tetrahedral W_2Ir_2 core. There are the usual 60 valence electrons associated with a tetrahedral array (formally, we have two d^6 W(0) atoms, two

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(7) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4: (a) pp 99–101; (b) pp 149–150.

(8) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(9) $R_F = [\sum ||F_o| - |F_c|| / \sum |F_o|] \times 100$ (%). $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \times 100$ (%). GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ (NO = number of observations; NV = number of variables).

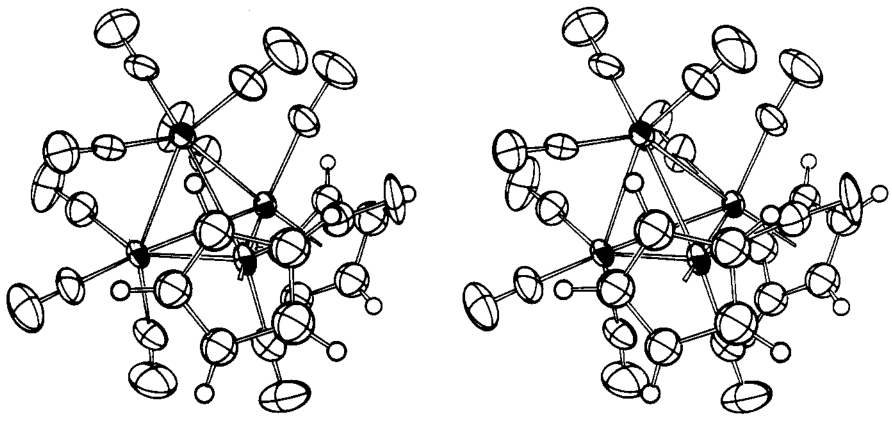


Figure 2. Stereoscopic view of the $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ molecule; tungsten atoms are on the right side.

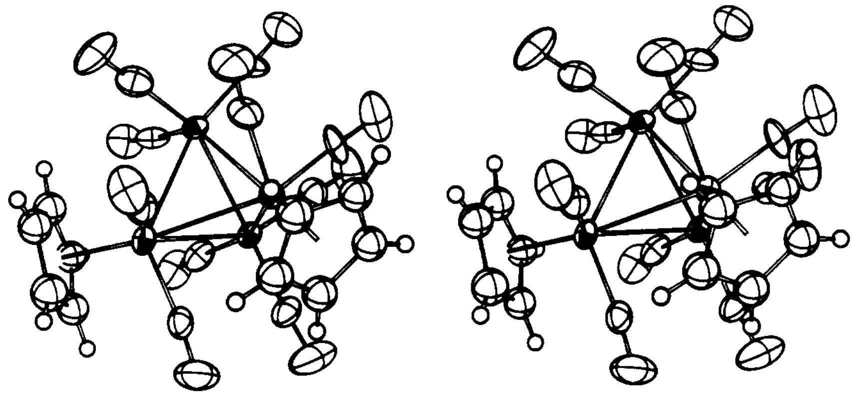
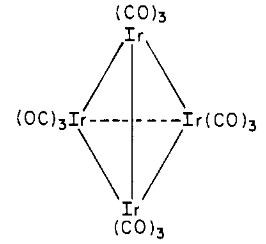
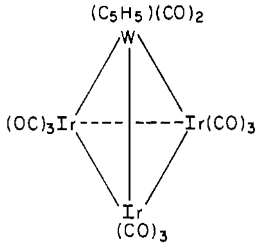


Figure 3. Stereoscopic view of the $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ molecule, with tungsten atoms at the lower front positions.

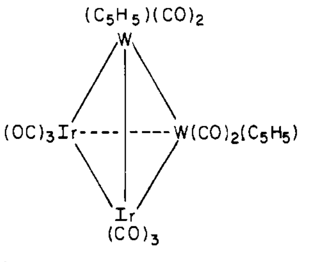
d^9 Ir(0) atoms, two electrons from each of the ten carbonyl groups, and five electrons from each of the η^5-cyclopentadienyl system). Each iridium atom is linked to three terminal carbonyl ligands, and each tungsten atom is bound to two carbonyl ligands; the structure is completed by η^5-cyclopentadienyl rings attached to each of the tungsten atoms. Within the framework of this description, each metal atom is associated individually with 18 outer-valence electrons (however, vide infra). The molecule thus becomes the third known member of the $(\eta^5\text{-}C_5H_5)_nW_nIr_{4-n}(CO)_{12-n}$ (n = 0–4) series (see **1–3**).



1, $Ir_4(CO)_{12}$[4]



2, $CpWIr_3(CO)_{11}$[1]



3, $Cp_2W_2Ir_2(CO)_{10}$ (this work)

The core structure of **3** may thus be regarded as derived from that of $Ir_4(CO)_{12}$ by substitution of two $Ir(CO)_3$ units by $(\eta^5\text{-}C_5H_5)W(CO)_2$ fragments. Metal–metal distances (Å) within the molecule are W(1)–W(2) = 2.991 (1), Ir(1)–Ir(2) = 2.722 (1), W(1)–Ir(1) = 2.796 (1), W(1)–Ir(2) = 2.833 (1), W(2)–Ir(1) = 2.863 (1), W(2)–Ir(2) = 2.847 (1) (average W(1)–Ir = 2.815, average W(2)–Ir = 2.855).

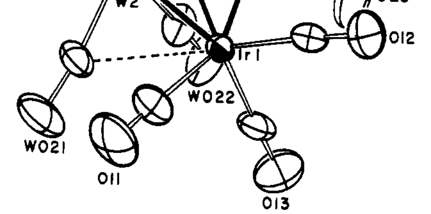


Figure 4. M···CO interactions in the $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ molecule.

However, this simple description ignores one aspect of the structure of $(\eta^5\text{-}C_5H_5)_2Ir_2W_2(CO)_{10}$—i.e., two of the W–C–O systems are appreciably nonlinear, possibly due to some "semi-bridging character" (see Figure 4).

Consideration of the ligand arrangement in **3** suggests that it may also be viewed as an adduct formed between triply bonded $[\eta^5\text{-}C_5H_5W(CO)_2]_2$ and an "acetylene-like" $Ir_2(CO)_6$ moiety. In particular the structure shows one carbonyl group on W(1) that is distinctly nonlinear (W(1)–WC(11)–WO(11) = 167.2 (13)°) and interacts weakly with W(2) (W(2)···WC(11) = 2.794 (14) Å). A "semibridging" carbonyl is a characteristic feature displayed in the structures of the acetylene adducts $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4(C_2R_2)$ (M = Mo, R

Table IV. Bond Angles (Deg) for $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$

	(A) Angles Involving the Metal Atoms		
Ir(2)-Ir(1)-W(1)	61.77 (2)	Ir(1)-W(1)-Ir(2)	57.82 (2)
W(1)-Ir(1)-W(2)	63.79 (2)	Ir(2)-W(1)-W(2)	58.46 (2)
Ir(2)-Ir(1)-W(2)	61.24 (2)	Ir(1)-W(1)-W(2)	59.20 (2)
Ir(1)-Ir(2)-W(1)	60.40 (2)	Ir(1)-W(2)-Ir(2)	56.93 (2)
W(1)-Ir(2)-W(2)	63.54 (2)	Ir(2)-W(2)-W(1)	58.00 (2)
Ir(1)-Ir(2)-W(2)	61.83 (2)	Ir(1)-W(2)-W(1)	57.01 (2)
	(B) Metal-Metal-Carbon Angles		
Ir(2)-Ir(1)-C(11)	150.46 (47)	Ir(1)-Ir(2)-C(21)	153.02 (43)
C(12)	83.86 (43)	C(22)	101.66 (43)
C(13)	104.62 (45)	C(23)	93.46 (45)
W(1)-Ir(1)-C(11)	88.87 (47)	W(1)-Ir(2)-C(21)	101.93 (43)
C(12)	89.77 (43)	C(22)	89.94 (43)
C(13)	163.71 (45)	C(23)	153.47 (45)
W(2)-Ir(1)-C(11)	104.43 (47)	W(2)-Ir(2)-C(21)	92.59 (43)
C(12)	142.91 (43)	C(22)	152.97 (43)
C(13)	102.50 (45)	C(23)	101.56 (45)
Ir(1)-W(1)-WC(11)	89.97 (43)	Ir(1)-W(2)-WC(21)	69.66 (43)
WC(12)	133.66 (39)	WC(22)	78.19 (41)
Ir(2)-W(1)-WC(11)	123.13 (43)	Ir(2)-W(2)-WC(21)	126.30 (43)
WC(12)	83.32 (39)	WC(22)	79.51 (41)
W(2)-W(1)-WC(11)	64.86 (43)	W(1)-W(2)-WC(21)	98.35 (43)
WC(12)	80.04 (39)	WC(22)	129.57 (41)
Ir(2)-Ir(1)···WC(21)	100.19 (29)	Ir(1)-W(2)···WC(11)	74.22 (30)
W(1)-Ir(1)···WC(21)	84.15 (29)	Ir(2)-W(2)···WC(11)	97.30 (30)
W(2)-Ir(1)···WC(21)	39.11 (29)	W(1)-W(2)···WC(11)	39.42 (30)
	(C) Semibridging (?) Metal-Carbon-Metal Angles		
Ir(1)···WC(21)-W(2)	71.22 (43)	W(2)···WC(11)-W(1)	75.72 (46)
	(D) Carbon-Metal-Carbon Angles		
C(11)-Ir(1)-C(12)	100.3 (6)	C(21)-Ir(2)-C(22)	98.3 (6)
C(11)-Ir(1)-C(13)	103.7 (6)	C(21)-Ir(2)-C(23)	100.5 (6)
C(12)-Ir(1)-C(13)	97.9 (6)	C(22)-Ir(2)-C(23)	100.6 (6)
WC(11)-W(1)-WC(12)	91.8 (6)	WC(21)-W(2)-WC(22)	85.1 (6)
C(11)-Ir(1)···WC(21)	71.7 (5)	WC(21)-W(2)···WC(11)	71.6 (5)
C(12)-Ir(1)···WC(21)	169.9 (5)	WC(22)-W(2)···WC(11)	148.6 (5)
C(13)-Ir(1)···WC(21)	90.0 (5)		
	(E) Metal-Carbon-Oxygen Angles		
Ir(1)-C(11)-O(11)	176.4 (14)	Ir(2)-C(21)-O(21)	173.5 (13)
Ir(1)-C(12)-O(12)	176.1 (12)	Ir(2)-C(22)-O(22)	174.6 (13)
Ir(1)-C(13)-O(13)	178.7 (13)	Ir(2)-C(23)-O(23)	178.0 (14)
W(1)-WC(11)-WO(11)	167.2 (13)	W(2)-WC(21)-WO(21)	171.8 (12)
W(1)-WC(12)-WO(12)	173.9 (12)	W(2)-WC(22)-WO(22)	174.0 (13)
W(2)···WC(11)-WO(11)	117.0 (10)	Ir(1)···WC(21)-WO(21)	117.0 (10)
	(F) Carbon-Carbon-Carbon Angles		
C(5)-C(1)-C(2)	109.0 (13)	C(10)-C(6)-C(7)	107.0 (13)
C(1)-C(2)-C(3)	110.9 (14)	C(6)-C(7)-C(8)	107.5 (12)
C(2)-C(3)-C(4)	105.6 (13)	C(7)-C(8)-C(9)	108.7 (13)
C(3)-C(4)-C(5)	107.1 (13)	C(8)-C(9)-C(10)	106.8 (13)
C(4)-C(5)-C(1)	107.4 (13)	C(9)-C(10)-C(6)	109.9 (13)

= H, Et, Ph; M = W, R = H),[10] with which the structure of **3** is closely related.

Compound **3** also is the formal dimer of triply bonded $(\eta^5\text{-}C_5H_5)W(CO)_2{\equiv}Ir(CO)_3$ units. The present complex is the stable Ir_2W_2 analogue of the Co_2Mo_2 intermediate proposed by Curtis[11] to explain the products resulting from the reaction of $Co_2(CO)_8$ with $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$.

To a first approximation, this cluster is about as crowded as would be an $M_4(CO)_{15}$ tetrahedral cluster (of which there are no known examples).[12] This suggests that the higher members of the $(\eta^5\text{-}C_5H_5)_nW_nIr_{4-n}(CO)_{12-n}$ series—i.e., $(\eta^5\text{-}C_5H_5)_3W_3Ir(CO)_9$ and $(\eta^5\text{-}C_5H_5)_4W_4(CO)_8$—are likely to be sterically unobtainable.

The second possible "semibridging" carbonyl ligand is different from the first in that it spans a tungsten and iridium atom (as opposed to two tungsten atoms). The W(2)-WC(21)-WO(21) angle of 171.8 (13)° is smaller than the strictly terminal carbonyl angles on the iridium and tungsten atoms (which are all close to linear). The Ir–C–O angles range from 173.5 (13) to 178.7 (13)°, while the remaining $W\text{–}C\text{–}O_{term}$ angles span from 173.9 (12) to 174.0 (13)°. The Ir(1)···W-C(21) distance is 2.835 (13) Å. Although no "semibridging" carbonyl groups are required from the point of view of electronic reorganization,[13] we suggest that one or both of the W(1)-WC(11)···W(2) and W(2)-WC(21)···Ir(1) systems might be regarded as involving a weakly "semibridging" carbonyl group.[14,15] This would be consistent with the observation of a rather low-frequency carbonyl stretch in the infrared spectrum of the complex ($\nu_{C\text{–}O}$ = 1833 w cm^{-1}).

The consideration of the W(1)-[WC(1)-WO(1)]···W(2) and W(2)-[WC(21)-WO(21)]···Ir(1) systems as weakly

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(10) Ginley, D. S.; Bock, C. R.; Wrighton, M. S.; Fischer, B; Tipton, D. L.; and Bau, R. *J. Organomet. Chem.* **1978**, *157*, 41.

(11) Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23.

(12) An η^5-cyclopentadienyl ligand is generally regarded as occupying about the same cone angle of space as would $2^1/_2$ carbonyl ligands.

(13) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 1233–1234. Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

(14) Curtis et al. define the "asymmetry parameter" (α) as $\alpha = (d_2 - d_1)/d_1$ where d_2 is the long M···C distance and d_1 is the short M–C distance in an $M_2(CO)$ fragment. For the W(1)–WC(11)···W(2) system, α = 0.425, and for the W(2)–WC(21)···Ir(1) system, α = 0.486. These fall in the range 0.1 < α < 0.6 which Curtis et al. regard as the "semibridging" regime.

(15) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096.

"semibridging" leads to the following electronic reorganization: (a) some electron density is transferred from W(1) to W(2) and (b) some electron density is transferred from W(2) to Ir(1). The net result of these two transfers is that W(1) becomes slightly "electron poor" and Ir(1) becomes slightly "electron rich". This appears to be compensated by direct transfer of electron density from Ir(1) to W(1). Thus, the Ir(1)–W(1) bond length of 2.796 (1) Å is substantially shorter than any of the other Ir–W bond lengths in the molecule [viz, Ir(1)–W(2) = 2.863 (1), Ir(2)–W(1) = 2.833 (1), Ir(2)–W(2) = 2.847 (1) Å].

Our suggestion would clearly extend the range of M···CO contacts that have customarily been regarded as yielding significant bonding interactions. The "semibridging" carbonyl ligands in this complex would appear principally to relieve steric stress in the molecule.

Other distances in the molecule are within the expected ranges: C–O = 1.125 (20)–1.182 (19), W–C(cyclopentadienyl) = 2.293 (16)–2.381 (14),[16] and C–C(cyclopentadienyl) = 1.335 (22)–1.433 (20) Å.

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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes and anisotropic thermal parameters (15 pages).

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Synthesis, Characterization, and Molecular Structure of Oxo(porphyrinato)chromium(IV) Complexes

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The reaction of chloro(5,10,15,20-tetraphenylporphyrinato)chromium(III) [Cr(TPP)Cl] with iodosylbenzene and base (*tert*-butyl hydroperoxide, *m*-chloroperoxybenzoic acid, or sodium hypochlorite) produced the corresponding oxochromium(IV) complex (**2**). This diamagnetic compound had an intense band in the IR at 1025 cm^{-1}, which shifted to 981 cm^{-1} upon ^{18}O substitution. The visible spectrum showed bands at 430 and 544 nm. The oxochromium(IV) complex reacted with triphenylphosphine to give triphenylphosphine oxide and chromium(II), which reacted with methylene chloride to give Cr(TPP)Cl or with **2** to give a μ-oxo chromium(III) dimer, **5**. Crystallization of oxo(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(IV) from benzene–hexane gave diffractable single crystals: space group $P2_1/c$, $Z = 4$, $a = 17.342$ (6) Å, $b = 16.964$ (7) Å, $c = 15.804$ (6) Å, $\beta = 112.52$ (3), $V = 4295$ (3) Å^3. Least-squares refinement based on 2309 observed data with $I > 3\sigma(I)$ gave $R_1 = 0.068$, $R_2 = 0.072$. The Cr–O bond length was 1.572 (6) Å, the average Cr–N distance was 2.032 (7) Å and the chromium cation was 0.469 Å above the average pyrrole nitrogen plane. The porphyrin ring was distinctly saddle shaped with the pyrrole β-carbons displaced 0.340 and 0.568 Å above and below the mean pyrrole nitrogen plane.

Introduction

Transition-metal oxo complexes are useful reagents for the oxidation of organic molecules.[1] There are relatively few examples of such species in ligand encinctures which may control the electronic and steric environment of the high-valent metal center. While oxo–metalloporphyrin complexes of titanium(IV),[2] vanadium(IV),[3] molybdenum(IV),[4] and molybdenum(V)[5] have been prepared and structurally characterized, these compounds have not been shown to be effective oxidizing agents. In 1979 we demonstrated that chloro(5,10,15,20-tetraphenylporphyrinato)iron(III) [Fe(TPP)Cl] was an effective catalyst for oxygen transfer from iodosylbenzene to organic substrates.[6] An oxo–iron intermediate was proposed as the oxygen-transfer agent.[7,8] Cr(TPP)Cl[9] and Mn(TPP)Cl[10,11] were also shown to be active catalysts, and in the case of the chromium porphyrin, a reactive intermediate was formed which we have characterized as a chromium(V) porphyrinate (**1**).[12] On standing, **1** decomposed to an unusually stable, oxochromium(IV) complex,[13] the synthesis, structure, and characterization of which we describe herein.

Experimental Section

General Data. Thiophene-free benzene was distilled from potassium. Tetrahydrofuran was distilled from LAH/triphenylmethane, and alkane solvents were purified by treatment with sulfuric acid followed by distillation from potassium. Methylene chloride was distilled from P_2O_5 and filtered through solid potassium carbonate. Deuteriochloroform (100% Merck) was treated with solid potassium carbonate prior to use to remove acidic impurities. Elemental analyses were performed by Spang Microanalytical Laboratory. Mass spectra were obtained on a Finnegan Model 4021 GC mass spectrometer. Infrared spectra were determined by a Beckmann Model 4240. NMR spectra were obtained on JEOL FX-90Q and Bruker WM 360 NMR spectrometers. Visible spectra were determined on a Cary-17 or a Varian/Cary 219 spectrophotometer. Magnetic susceptibility mea-

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