voltammograms reveal an initial reaction analogous to that observed for acetone and hexaammineosmium(II); the hexaammine 3+/2+ couple at −0.84 V is initially replaced by one at $E_{1/2}$ = −0.53 V, which, in light of the previous discussion, suggests the formation of $[Os(NH_3)_5(NHCHCH_3)]^{2+}$. This species rapidly decomposes, however, resulting in several electroactive products. Treatment of this reaction mixture with excess ether results in a precipitate whose infrared spectrum includes an intense absorption near 2200 cm^{-1}. This observation suggests that a coordinated nitrile may be one of the reaction products.[12] Schug et al.[6,13] have reported similar findings with $[Ru(NH_3)_6]^{3+}$, which under basic conditions reacts with aldehydes to give the corresponding Ru(II) nitrile complex. The oxidation of an imine to a nitrile would require either an external oxidant or elimination of hydrogen, however, neither of which have been detected.[14]

Acknowledgment. Support of this work by National Science Foundation Grants CHE85-11658 and CHE84-14329 (400-MHz NMR) and National Institutes of Health Grant GM13638-20 is gratefully acknowledged.

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(11) When this reaction is repeated without the addition of base, no reactivity is detected by cyclic voltammetry after 1 h, even upon addition of $[Os(NH_3)_6](OTf)_3$.

(12) E.g., the C–N stretch for $[Os(NH_3)_5(CH_3CN)](OTf)_2$ occurs at 2186 cm^{-1}: Sekine, M.; Harman, W. D.; Taube, H. *Inorg. Chem.*, in press. Also see ref 12.

(13) Schug, K.; Guengerich, C. P. *J. Am. Chem. Soc.* **1975**, *97*, 4135.

(14) For additional reports of imine complexes see: Joss, S.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 3487. Elsbernd, H.; Beattie, J. K. *J. Chem. Soc. A* **1970**, 2598. Lane, C. C.; Lester, J. E.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1971**, 1618.

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Structure of (Pentamethylcyclopentadienyl)((pentamethylcyclopentadienyl)oxy)dioxotungsten(VI), $(\eta^5\text{-}C_5Me_5)W(O)_2(OC_5Me_5)$. Structural Evidence for the Strong Trans Influence of the Oxo Ligand

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Received March 4, 1988

The chemistry of organometallic compounds containing oxo, alkoxo, and peroxo ligands is an area of increasing interest with potential relevance to selective catalytic oxidation of hydrocarbons. Compounds of the middle transition elements could exhibit reactivity that would provide a basis for catalytic systems, since these metals are less oxophilic than the early transition metals and yet readily attain high formal oxidation states. We have therefore recently explored synthetic routes to oxo derivatives of permethyltungstenocene, e.g. $(\eta^5\text{-}C_5Me_5)_2W{=}O$.[1] Herein we report the structure of $(\eta^5\text{-}C_5Me_5)W(O)_2(OC_5Me_5)$, obtained by the reaction of $(\eta^5\text{-}C_5Me_5)_2W{=}O$ with O_2. The two oxo ligands exhibit a strong trans influence resulting in a coordination geometry of the $\eta^{"5"}\text{-}C_5Me_5$ ligand, which is more properly described as $\eta^1,\eta^4\text{-}C_5Me_5$.

Experimental Section

(i) Preparation of $(\eta^5\text{-}C_5Me_5)W(O)_2(OC_5Me_5)$. A solution of $Cp^*{}_2W{=}O$ (200 mg) in pentane (10 cm^3) at −78 °C was placed under O_2 (1 atm) and was stirred as it was allowed to warm to room temperature. Upon reaching room temperature, the initially green solution became colorless. The solution was concentrated after 30 min and cooled to −78 °C, giving white (or very pale yellow) crystals of $(\eta^5\text{-}C_5Me_5)W(O)_2(OC_5Me_5)$ (200 mg, 93%). Anal. Found (calcd): C, 47.5 (47.8); H, 5.8 (6.0). The crystals used in the X-ray analysis were obtained by slow evaporation from a mixture of pentane and benzene.

Table I. Crystal and Intensity Collection Data

formula: $WO_3C_{20}H_{30}$
fw: 502.31
cryst color: pale yellow
habit: irregular, chunky
a = 14.987 (2) Å
b = 7.459 (1) Å
c = 19.422 (3) Å
β = 110.59 (1)°
V = 2032.5 (5) $Å^3$
Z = 4
λ = 0.71073 Å
space group: $P2_1/n$
cryst size: 0.19 × 0.19 × 0.47 mm
graphite monochromator
CAD-4 diffractometer
2θ range: 2–50°
absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$
μ = 60.22 cm^{-1} (μr_{max} = 1.63)
θ–2θ scan
octants colled: $\pm h,k,\pm l$; $\pm h,-k,l$
no. of reflcns measd: 12144
no. of indep reflcns: 3556
no. of reflcns with $F_o^2 > 0$: 3373
no. of reflcns with $F_o^2 > 3\sigma(F_o^2)$: 2861
goodness of fit for merging data: 1.14
final R index: 0.0318
final goodness of fit: 1.57

Table II. Final Parameters for the Heavy Atoms (×10^4)

atom	x	y	z	U_{eq},[a] $Å^2$
W	4288.7 (1)	1542.3 (2)	1912.0 (1)	345 (0.4)
O(1)	3766 (2)	3217 (4)	1146 (2)	478 (9)
O(2)	4932 (2)	17 (5)	1612 (2)	660 (10)
O(3)	3350 (2)	371 (5)	1992 (2)	623 (9)
C(1)	3121 (3)	3125 (6)	393 (2)	440 (12)
C(2)	3518 (3)	2003 (6)	−79 (2)	420 (11)
C(3)	2881 (3)	743 (6)	−412 (2)	422 (11)
C(4)	2055 (3)	871 (6)	−163 (2)	407 (11)
C(5)	2192 (3)	2197 (6)	321 (2)	425 (11)
C(6)	2977 (5)	5079 (8)	135 (4)	638 (17)
C(7)	4460 (5)	2398 (11)	−154 (4)	670 (17)
C(8)	2938 (5)	−607 (10)	−967 (3)	625 (17)
C(9)	1226 (4)	−382 (10)	−422 (4)	625 (16)
C10)	1585 (5)	2830 (12)	730 (4)	678 (18)
C(11)	5203 (3)	1718 (6)	3162 (2)	393 (10)
C(12)	5807 (3)	2481 (7)	2804 (2)	412 (11)
C(13)	5381 (3)	4077 (6)	2472 (2)	418 (11)
C(14)	4542 (3)	4363 (6)	2646 (2)	414 (11)
C(15)	4449 (3)	2933 (6)	3080 (2)	393 (10)
C(16)	5403 (5)	35 (8)	3618 (3)	614 (16)
C(17)	6718 (4)	1665 (12)	2796 (4)	674 (17)
C(18)	5712 (5)	5327 (11)	2003 (4)	749 (19)
C(19)	3867 (5)	5930 (8)	2407 (5)	679 (19)
C(20)	3687 (5)	2694 (12)	3411 (4)	685 (18)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i{}^*a_j{}^*)(\vec{a}_i\cdot\vec{a}_j)]$.

(ii) X-ray Structure Analysis. The crystals were thick needles, clear to pale yellow, and were cleaved with a razor blade to give irregular chunks that were mounted in capillary tubes. The maximum dimensions of the crystal used for data collection, measured with a micrometer microscope, were about 0.19 × 0.19 × 0.47 mm, but the grease used to fix the crystal in the capillary obscured the edges and both the size and the shape of the crystal may have been incorrectly estimated. The data (Table I) were collected on a CAD-4 diffractometer using monochromated Mo Kα radiation, and the cell dimensions were obtained from 25 reflections with 11.5° < θ < 14°. Three equivalent quadrants ($\pm h,k,l$; $\pm h,k,-l$; $\pm h,-k,l$) were collected to θ = 25°, with θ–2θ scans at 4° (in θ)/min. With data uncorrected for absorption, the GOF for merging equivalent reflections was 1.16; with corrected data (μ = 60.22 cm^{-1}), 1.21. Structure refinements based on both data sets indicated that the absorption corrections were probably too large, so the final data set was based on μ = 45 cm^{-1}; the GOF of merging was 1.14.

The structure was derived from Patterson and Fourier maps. The conformations of the methyl groups were indicated clearly and unambiguously on difference maps calculated in the planes of the H atoms, which were then positioned so as to complete regular tetrahedra with C–H = 1.0 Å; they were then included in the refinements (with isotropic B's). Full-matrix minimization of $\sum w(F_o^2 - F_c^2)^2$ was based on 338 parameters, including an isotropic extinction parameter g:[2a] final value

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(1) Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.*, submitted for publication.

(2) (a) Larson, E. C. *Acta Crystallogr.* **1967**, *23*, 664 (eq 3). (b) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974.

0020-1669/88/1327-3262$01.50/0

Table III. Hydrogen Atom Parameters

atom	10^3x	10^3y	10^3z	B, Å^2
H(6a)	356 (4)	567 (7)	17 (3)	5.5 (14)
H(6b)	256 (3)	510 (7)	−38 (3)	5.1 (12)
H(6c)	261 (4)	576 (8)	37 (3)	6.3 (16)
H(7a)	491 (4)	250 (9)	30 (3)	6.8 (17)
H(7b)	464 (5)	155 (10)	−51 (5)	11.9 (26)
H(7c)	445 (5)	359 (9)	−31 (4)	8.6 (21)
H(8a)	345 (4)	−38 (8)	−115 (3)	7.4 (17)
H(8b)	299 (5)	−170 (9)	−80 (4)	9.4 (24)
H(8c)	236 (4)	−55 (7)	−141 (3)	6.1 (14)
H(9a)	136 (5)	−144 (9)	−22 (4)	9.1 (22)
H(9b)	70 (5)	9 (9)	−26 (4)	9.3 (20)
H(9c)	87 (4)	−42 (8)	−95 (3)	6.4 (14)
H(10a)	190 (5)	294 (9)	124 (4)	8.7 (19)
H(10b)	129 (5)	393 (9)	52 (4)	9.0 (22)
H(10c)	110 (5)	212 (9)	68 (4)	7.7 (20)
H(16a)	574 (4)	20 (9)	410 (4)	8.6 (19)
H(16b)	481 (4)	−67 (8)	361 (3)	7.5 (16)
H(16c)	582 (4)	−82 (8)	346 (3)	6.3 (15)
H(17a)	724 (4)	173 (7)	332 (3)	6.9 (15)
H(17b)	664 (4)	53 (8)	262 (3)	5.7 (16)
H(17c)	693 (4)	218 (9)	246 (4)	7.8 (20)
H(18a)	626 (4)	485 (8)	192 (3)	6.0 (16)
H(18b)	530 (5)	562 (10)	148 (4)	10.9 (22)
H(18c)	604 (5)	648 (9)	234 (4)	10.0 (21)
H(19a)	380 (5)	637 (9)	200 (4)	8.5 (22)
H(19b)	409 (5)	686 (10)	270 (4)	10.5 (25)
H(19c)	321 (6)	576 (10)	257 (5)	13.9 (29)
H(20a)	398 (5)	303 (10)	396 (4)	10.6 (22)
H(20b)	313 (5)	347 (9)	323 (4)	8.9 (20)
H(20c)	345 (4)	161 (8)	330 (4)	7.2 (19)

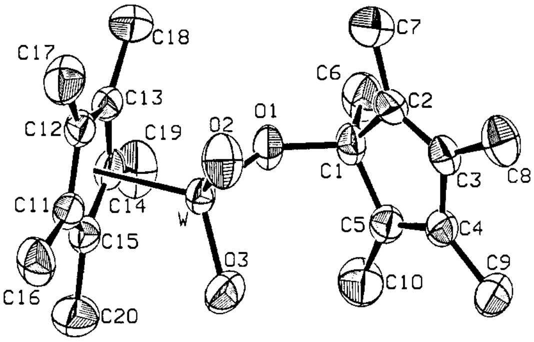

Figure 1. Molecular structure of $(\eta^5\text{-C}_5\text{Me}_5)\text{W(O)}_2(\text{OC}_5\text{Me}_5)$.

0.144 (12) × 10^{-6}. At convergence, the maximum shift-to-σ ratios were 0.15 for a heavy atom and 0.37 for H. Variances of the individual intensities were based on counting statistics plus an additional term, $0.014I^2$; final variances of the averaged intensities were obtained by standard propagation of error plus another additional term $0.014\langle I\rangle^2$. Calculations were done with programs of the CRYM crystallographic computing system and ORTEP. Scattering factors, including $\Delta F'$ for W, were taken from ref 2a. Final parameters are given in Tables II and III.

In view of our concerns about the absorption problem, we also carried out preliminary refinements (no hydrogen atoms were included) based on (i) the data fully corrected for absorption, with μ = 60.22 cm^{-1}, and (ii) data uncorrected for absorption. In each case both R and GOF were about 20% larger than for the partially corrected (μ = 45 cm^{-1}) data. It is probable, then, that our measurements of the crystal, perhaps its shape as well as its size, were incorrect, and that the U_{ij} values (which were very sensitive to absorption effects) are not to be trusted. We are comforted, however, in that the coordinates from all three refinements were in agreement within 1 esd in all cases; there is no reason to doubt the molecular dimensions.

Discussion

The molecular structure of $(\eta^5\text{-C}_5\text{Me}_5)\text{W(O)}_2(\text{OC}_5\text{Me}_5)$ is shown in Figure 1; bond lengths and angles are in Table IV. The tungsten atom is approximately tetrahedrally coordinated by the $\eta^5\text{-C}_5\text{Me}_5$ ligand and the three oxygen atoms. The W–O(1) distance is typical of a single bond; W–O(2) and W–O(3) are typical of double bonds.[3] O(1) is bonded to a pentamethylcyclopentadienyl ligand at C(1). The hybridization at C(1) is sp^3, and the double bonds in that ring are localized (C(2)–C(3) = C(4)–C(5) = 1.332 (5) Å and C(3)–C(4) = 1.483 (6) Å). C(1) is about 0.08 Å from the plane of the other four ring atoms, and its methyl group C(6) is 1.36 Å from the plane.

Table IV. Selected Distances and Angles

	Distances (Å)		
W–O(1)	1.889 (3)	C(1)–C(5)	1.516 (6)
W–O(2)	1.720 (4)	C(1)–C(6)	1.532 (8)
W–O(3)	1.709 (3)	C(2)–C(3)	1.333 (7)
W–CpC	2.116 (2)	C(3)–C(4)	1.483 (6)
W–C(11)	2.334 (4)	C(4)–C(5)	1.331 (7)
W–C(12)	2.428 (5)	C(11)–C(12)	1.439 (6)
W–C(13)	2.487 (5)	C(11)–C(15)	1.412 (6)
W–C(14)	2.494 (5)	C(12)–C(13)	1.397 (7)
W–C(15)	2.427 (5)	C(13)–C(14)	1.428 (6)
O(1)–C(1)	1.443 (5)	C(14)–C(15)	1.396 (6)
C(1)–C(2)	1.510 (6)	C–H (av)	0.960 (13)[b]
	Angles (deg)		
O(2)–W–O(1)	107.3 (2)	C(5)–C(1)–O(1)	112.4 (4)
O(3)–W–O(1)	106.4 (1)	C(6)–C(1)–O(1)	104.7 (4)
O(3)–W–O(2)	105.7 (2)	C(6)–C(1)–C(2)	111.7 (4)
CpC–W–O(1)	104.6 (1)	C(6)–C(1)–C(5)	112.6 (4)
CpC–W–O(2)	116.1 (1)	C(2)–C(1)–C(5)	103.6 (4)
CpC–W–O(3)	116.0 (1)	C–C–H (av)	112.2 (6)[b]
C(1)–O(1)–W	135.3 (3)	H–C–H (av)	106.4 (11)[b]
C(2)–C(1)–O(1)	112.0 (4)		

[a] "CpC" is the centroid ring C(11)–C(15). [b] The esd of the average value, as calculated both from the scatter among the different values and from the internal esd's.

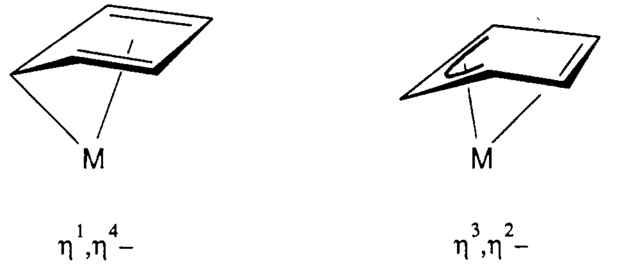

Figure 2. Asymmetric bonding modes of an $\eta^{"5"}$-cyclopentadienyl ligand.

In principle, a cyclopentadienyl ligand can bond to a single transition-metal center in a variety of modes. In this respect, the bonding between the tungsten atom and the $\eta^5\text{-C}_5\text{Me}_5$ ligand, atoms C(11)–C(20), is particularly interesting: while the bonding is primarily η^5 in character, there is some unmistakable η^1 component. We note the following:

(i) C(11)—but not its methyl group, C(16)—is displaced from the plane of the other ring atoms, toward W, by about 0.05 Å. Thus, C(11) is appreciably pyramidal, and the W–C(11) distance of 2.334 (4) Å is about 0.1 Å shorter than W–C(12) and W–C(15) and about 0.15 Å shorter than W–C(13) and W–C(14). Indeed, W–C(11) is only 0.13 Å longer than the value of 2.20 Å that seems to be typical of a W–C(aliphatic) single bond and that we have found for the W–C distance to an $\eta^1\text{-C}_5\text{Me}_5$ ligand.[4]

(ii) There appears to be considerable localization of the double bonds in the $\eta^5\text{-C}_5\text{Me}_5$ ligand: the C(12)–C(13) and C(14)–C(15) bonds at 1.396 (4) Å, while considerably longer than a pure double bond or the corresponding bonds in the $\eta^1\text{-C}_5\text{Me}_5$ ligand bonded to oxygen, are significantly shorter than the other ring bonds.

(iii) The orientation of the $\eta^5\text{-C}_5\text{Me}_5$ ligand, with C(11) trans to the single bond W–O(1) (see Figure 1), is such that a small change (up to 8°) in the effective direction of the W–$(\eta^5\text{-C}_5\text{Me}_5)$

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(3) (a) Legzdins, P.; Rettig, S. J.; Sanchez, L. *Organometallics* **1985**, *4*, 1470–1471. (b) Faller, J. W.; Yinong, M. *Organometallics* **1988**, *7*, 559–561. (c) Churchill, M. R.; Missert, J. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 3388–3391. (d) Churchill, M. R.; Rheingold, A. L. *Inorg. Chem.* **1982**, *21*, 1357–1359. (e) Bino, A.; Gibson, D. *Inorg. Chem.* **1984**, *23*, 109–115.

(4) Parkin, G.; Schaefer, W. P.; Bercaw, J. E., manuscript in preparation.

bond—from the ring centroid toward C(11)—serves to make the bonding about W more nearly tetrahedral (see Table IV).

These observations suggest that the W–(η^5-C_5Me_5) interaction is a mixture of η^5- and η^1-bonding and that the ligand is more aptly described as bonding in an η^1,η^4-fashion. Points i and ii mitigate against η^3,η^2-bonding. So far as we are aware, (C_5Me_5)W(O)$_2$(OC_5Me_5) is the first structurally characterized example of a compound with an (η^1,η^4-) pentamethylcyclopentadienyl ligand (Figure 2).

We note that many of these same features are observed in the structure of the related compound (η^5-C_5Me_5)(η^1-C_5Me_5)W(O)$_2$, which differs from (η^5-C_5Me_5)W(O)$_2$(OC_5Me_5) in that the W atom is directly bonded to the η^1-C_5Me_5 ligand rather than being bonded through an oxygen atom.[4] In each of the two independent molecules in that structure, the W atom is appreciably closer (at about 2.32 Å) to one of the atoms of η^5-C_5Me_5 than to the other four, and in each case that ring atom is trans to the W–C single bond of the η^1-C_5Me_5 ligand. However, there was appreciable (C_5Me_5)–(C_5Me_5) crowding in that compound and the accuracy was considerably lower than we report here, so other details of the geometry of the $\eta^{"5"}$-C_5Me_5 ring are not as clear.

The origin of the asymmetry of the bonding of the η^5-C_5Me_5 ligand in (η^5-C_5Me_5)(η^1-C_5Me_5)W(O)$_2$ and (η^5-C_5Me_5)W(O)$_2$(OC_5Me_5) is the strong trans influence of two oxo ligands. The ligands trans to each oxo ligand may be viewed to be the double-bond components of the η^5-C_5Me_5 ligand. The strong W=O bonding weakens the trans tungsten–ligand bonding, and thus lengthening of the bonds to these four carbon atoms (C(12), C(13), C(14), and C(15)) results. The W–C(11) bonding (trans to the OC_5Me_5 ligand with relatively much less trans influence) remains strong, as the bond length indicates. Other evidence that the oxo ligand exerts a strong trans influence is provided by the structures of (η^5-C_5Me_5)Re(O)Cl_2 and (η^5-C_5Me_5)Re(O)(CH_3)$_2$.[5] In these examples, the presence of only one oxo ligand results in the lengthening of two Re–ring carbon bonds, so that only one double-bond component within the pentamethylcyclopentadienyl ligand obtains. Thus, by extension, the rhenium–(C_5Me_5) bonding for these structures takes on some η^3,η^2 (i.e. allyl, olefin) character.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE-8600875) and by Shell Companies Foundation, which are gratefully acknowledged. G.P. acknowledges support through a NATO Postdoctoral Fellowship administered through the Science and Engineering Research Council (U.K.), and W.P.S., support from the Exxon Educational Foundation.

Registry No. (η^5-C_5Me_5)W(O)$_2$(OC_5Me_5), 115795-91-0; $Cp^*{}_2W$=O, 115795-92-1.

Supplementary Material Available: For (η^5-C_5Me_5)W(O)$_2$(OC_5Me_5), tables of anisotropic displacement parameters and complete distances and angles (3 pages); a listing of structure factors (15 pages). Ordering information is given on any current masthead page.

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(5) (a) Herrmann, W. A.; Okuda, J. *J. Mol. Catal.* **1987**, *41*, 109–122. (b) Herrmann, W. A.; Herdtweck, E.; Floel, M.; Kulpe, J.; Kusthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165–1182.