Preparation and Crystal Structure of the Dinuclear, Asymmetric Dioxo Complex $(\eta^5\text{-}C_5Me_5)(CO)_3W\text{–}W(O)_2(\eta^5\text{-}C_5Me_5)$

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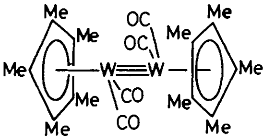
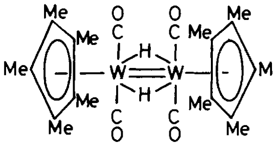
The dinuclear, asymmetric, dioxo complex $(\eta^5\text{-}C_5Me_5)(CO)_3W\text{–}W(O)_2(\eta^5\text{-}C_5Me_5)$ (**3**) can be prepared by air oxidation of $[(C_5Me_5)W(CO)_2]_2$ (**1**) or $(C_5Me_5)W(CO)_2(\mu\text{-}H)]_2$ (**2**); in this compound W^I is directly connected with W^V

Presently the various chemistry of oxo complexes is attracting great attention and application.[1,2] An easy approach to oxo complexes is the exposure of carbonyl complexes to air. In this manner the dinuclear complexes $[(C_5Me_5)W(CO)_2]_2$ (**1**) or $[(C_5Me_5)W(CO)_2(\mu\text{-}H)]_2$ (**2**) react with air to yield the title compound (**3**).

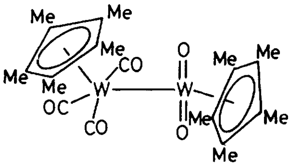
This result is not that of the reported reaction of (**1**) and oxygen to give complexes (**4**) and (**5**) as products.[1] We could not detect these species in our experiments. The Cr analogue $[(C_5Me_5)Cr(O)(\mu\text{-}O)]_2$, however, has been described.[3] Mononuclear dioxo complexes of tungsten and molybdenum containing cyclopentadienyl (Cp) ligands are known, *e.g.*



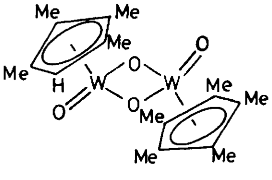
(1)



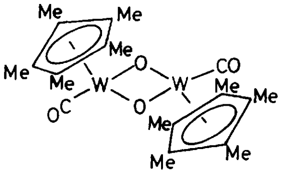
(2)



(3)



(4)



(5)

$CpW(O)_2CH_2SiMe_3$,[4] $CpW(O)_2Fc$ (Fc = ferrocenyl),[5] and $CpMo(O)_2Cl$.[6] We are not aware of any other dinuclear dioxo complex in which W^{I} is directly connected with W^{V}.

The formation of (**3**)† involves complexation of oxygen and elimination and uptake of carbon monoxide. The $(C_5Me_5)W(CO)_3$ fragment is isolobal with Me There are two independent molecules of (**3**) in the asymmetric unit. The two molecules are nearly identical with the exception of a rotational difference in the orientation of the η-C_5Me_5 ligand bonded to the W^{I} $(CO)_3$ fragment. The molecular geometry of one of these molecules is depicted in Figure 1. The $(C_5Me_5)W(CO)_3$ fragment is connected to the $(C_5Me_5)WO_2$ unit *via* a W–W bond. The two metal–metal distances in (**3**) [av. 2.877(3) Å] are shorter than the one in the dinuclear carbonyl complex $[CpW(CO)_3]_2$[7] or in the fulvalene complex $C_{10}H_8W_2(CO)_6$ [3.347(1) Å],[8] but they are still in the range of literature values for W–W single bonds [see ref. 8(26)]. Bond distances and bond angles of the $(C_5Me_5)W(CO)_3$ moiety are comparable to those in the $CpW(CO)_3$ unit in $[CpW(CO)_3]_2$,[7] except that the two carbonyl ligands of each molecule in (**3**) are bent towards the other tungsten atom occupying a semibridging position. The four such W–C contacts average 2.87(3) Å. The W^{V}=O distances [av. 1.73(2) Å] are in the same range as the corresponding metal–oxygen bond lengths [1.716(5) and 1.723(5) Å] in the monomolecular complex $CpW(O)_2CH_2SiMe_3$.[4]

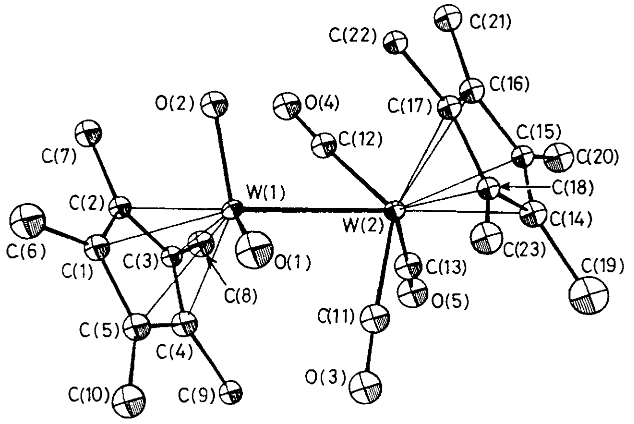


Figure 1. ORTEP[10] drawing of one of the two unique molecules of (**3**). Ellipsoids represent 50% probability surfaces. Selected average distances (Å) and angles (degrees) with estimated standard deviations [Z(1) and Z(2) are the centroids of the rings containing C(5) and C(15), respectively]. W^{V}–Z(1) 2.14, W^{L}–CO 1.95(2), W^{L}–Z(2) 2.00 Å; W^{L}–W^{V}–O 100(1), O–W^{V}–O 106(2), W^{V}–W^{L}–CO [corresponding to C(11) and C(12)] 70(1), W^{V}–W^{L}–CO [corresponding to C(13)] 120.1(4), OC–W^{L}–CO [corresponding to C(11) or C(12)–W(2)–C(13)] 84(2), OC–W^{L}–CO [corresponding to C(11)–W(2)–C(12)] 124(4)°.

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† *Spectroscopic data:* ^{1}H n.m.r. (90 MHz, $[^{2}H_6]$acetone, −20 °C) δ 2.02 (s) and 2.08 (s); ^{13}C n.m.r. (22.5 MHz, −20 °C) δ 103.5 (s), 119.5 (s, C_5Me_5), 10.9 (s), 12.2 [s, C_5Me_5, $^{1}J(C,H)$ 127.9 Hz]; 224.2 and 223.6 (CO); i.r.: $\nu_{(CO)}$ 1962(s), 1884(vs) (tetrahydrofuran); $\nu_{(W=O)}$ 936, 894 cm^{-1} (KBr); *m/z* 726 (M^+, rel. ^{184}W).

Acceptable elemental analyses were obtained for C and H; m.p. (decomp.) 122 °C.

Crystal data: $C_{23}H_{30}O_5W_2$, M = 754.2, space group $P2_1/c$, a = 29.106(5), b = 10.418(4), c = 15.703(4) Å, β = 105.66(2)°, Z = 8, D_c = 2.19 g cm^{-1}. Intensity data were obtained at −150 °C by 2θ–θ scans on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-K_α radiation (λ 0.71073 Å). The structure was solved by heavy atoms techniques. Least-squares refinement of 6088 independent observed reflections [$F_o \geqslant 5\sigma(F_o)$] gave R = 0.062. Due to crystallographic difficulties resulting from an irregularly shaped crystal and a high value of μ (96.3 cm^{-1}), only the tungsten atoms were refined anisotropically. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from ref. 9. Data were corrected for absorption. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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