

## Synthesis and Crystal Structure of a Dioxo Heterometallic Complex CpWOs<sub>3</sub>(CO)<sub>9</sub>(μ-O)<sub>2</sub>(μ-H) (Cp = η-C<sub>5</sub>H<sub>5</sub>)

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The dioxo complex CpWOs<sub>3</sub>(CO)<sub>9</sub>(μ-O)<sub>2</sub>(μ-H) (Cp = η-C<sub>5</sub>H<sub>5</sub>) has been prepared from CpWOs<sub>3</sub>(CO)<sub>12</sub>(μ-H) by treatment with Me<sub>3</sub>NO and then 95% ethanol; the crystal structure has been determined, suggesting the presence of unique bridging oxo ligands.

There is a growing interest in the synthesis of organometallic complexes containing oxygen donor ligands<sup>1</sup> since they can serve as both realistic model and potential catalyst for the oxygen transfer reactions. Many mononuclear and dinuclear oxide complexes have appeared in the literature.<sup>2</sup> Extension of the preparative work to polynuclear systems is of particular interest because the latter may provide a direct link between the so-called organometallic oxides<sup>1</sup> and the inorganic oxides or polyoxoanions.<sup>3</sup> Here we report the synthesis and structural characterization of a unique heterometallic carbonyl cluster oxide.

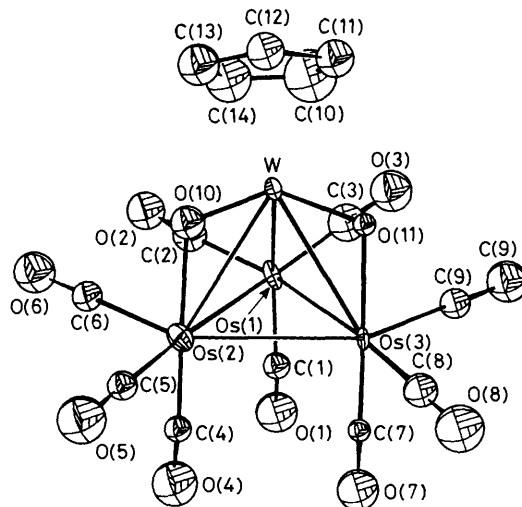
The tetrahedral cluster CpWOs<sub>3</sub>(CO)<sub>12</sub>(μ-H) (**1**) is readily available from the condensation of Os<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub> and CpW(CO)<sub>3</sub>H.<sup>4</sup> Treatment of complex (**1**) with 1 equiv. Me<sub>3</sub>NO in acetonitrile, followed by reaction with 95% ethanol or an acetone-water mixture, gave an orange solution. The solvent was removed under vacuum and the product purified by t.l.c. The i.r. spectrum (C<sub>6</sub>H<sub>12</sub>) in the carbonyl region shows absorption bands at 2098(s), 2074(vs), 2031(vs), 2017(s), 2010(sh), 1991(w), 1965(m), 1944(m) cm<sup>-1</sup> indicating the presence of terminal CO ligands. The <sup>1</sup>H n.m.r. (400 MHz, room temp., CDCl<sub>3</sub>) spectrum shows a Cp resonance at δ 6.37 (5H) and a hydride resonance at δ -15.5 (1H). The field desorption mass spectrum indicates an ion at *m/z* 1112, † corresponding to a composition of C<sub>14</sub>H<sub>6</sub>O<sub>11</sub>WOs<sub>3</sub>. Based on this spectroscopic data, a formulation of CpWOs<sub>3</sub>(CO)<sub>9</sub>(μ-O)<sub>2</sub>(μ-H) (**2**) is proposed for this complex. Orange crystals suitable for a single crystal X-ray diffraction study were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-heptane at room temperature.

The molecular structure of (**2**) is shown in Figure 1 together with some important bond parameters. ‡ The molecule has a tetrahedral WOs<sub>3</sub> core structure in which the tungsten atom is co-ordinated to a Cp ring, while each of the osmium atoms is linked to three terminal CO ligands. The bridging hydride has not been located on the difference Fourier map; however, it is proposed to associate with the Os(2)-Os(3) edge because it is the longest Os-Os bond in the molecule. An unusual feature of this molecule is the two bridging oxo ligands which are located on the two W-Os bonds of equal length. The bond

length of the oxygen centres (av. W-O = 1.79(3) Å, Os-O = 2.09(3) Å) is similar to that of the regular W=O→Os bonding mode proposed by Churchill,<sup>5</sup> and the average Os-O distance is compatible with the Os-O distance [2.06(2) Å] in Os<sub>6</sub>(μ<sub>3</sub>-O)(μ<sub>3</sub>-CO)(CO)<sub>18</sub>,<sup>6</sup> and [Os(CO)<sub>3</sub>(μ<sub>3</sub>-O)]<sub>4</sub>.<sup>7</sup> There is roughly a mirror plane across the W, Os(1) atoms, and the middle of the Os(2)-Os(3) vector; therefore, the molecular structure has a C<sub>s</sub> point symmetry within estimated standard deviation.

The bonding mode of the oxo ligands can be easily understood by utilizing the concept of electron counting: the two bridging oxo ligands combined have acted as six electron donor in an electron precise, 60 electron tetrahedral cluster. Their donor ability (as three electron donor) is clearly different from that of the above mentioned W=O → Os oxo ligand (as a four electron donor).<sup>5</sup> This observation can be explained in terms of the resonance of the trivalent W=O → Os and the divalent W-O-Os bonding forms. In fact, we have determined the structure of an isostructural oxo-alkylidene complex, CpWOs<sub>3</sub>(CO)<sub>9</sub>(μ-O)(μ-CHTol)(μ-H),<sup>8</sup> its structure can be envisioned by simply replacing one oxo ligand in (**2**) with an analogous bridging alkylidene.

Being consistent with the solid state structure, the <sup>13</sup>C n.m.r. spectrum (100.6 MHz, -65 °C, CD<sub>2</sub>Cl<sub>2</sub>) of a 20% <sup>13</sup>C enriched sample displays five CO resonances at δ 193.6, 181.5,



**Figure 1.** The molecular structure of (**2**). Bond lengths (Å): Os(1)-Os(2), 2.831(4); Os(1)-Os(3), 2.838(4); Os(2)-Os(3), 2.987(3); W-Os(1), 2.610(3); W-Os(2), 2.887(3); W-Os(3), 2.887(3); W-O(10), 1.78(3); Os(2)-O(10), 2.12(4); W-O(11), 1.803(25); and Os(3)-O(11), 2.06(3). Bond angles (°): Os(3)-Os(2)-C(5), 117(1); Os(2)-Os(3)-C(8), 117(1); Os(1)-Os(2)-C(6), 90(1); Os(1)-Os(3)-C(9), 89(1).

† The *m/z* value is referenced to <sup>186</sup>W and <sup>192</sup>Os.

‡ Crystal data for C<sub>14</sub>H<sub>6</sub>O<sub>11</sub>WOs<sub>3</sub>, *M* = 1104.27, monoclinic, space group *C*2/c, *a* = 31.057(22), *b* = 10.446(9), *c* = 12.388(16) Å, β = 103.56(9)°, *U* = 3906.98 Å<sup>3</sup>, *Z* = 8, *D*<sub>c</sub> = 3.756 mg/cm<sup>3</sup>, *F*(000) = 3438.30, CAD 4 diffractometer with graphite-monochromated Mo-*K*<sub>α</sub> radiation, λ = 0.7093 Å, μ(Mo-*K*<sub>α</sub>) = 25.53 mm<sup>-1</sup>. ψ scan absorption correction has been made and 3437 unique reflections were measured and 2748 reflections with *I* > 3σ(*I*) were used in refinement. Refinement of the positional and anisotropic thermal parameters for tungsten and osmium atoms and the positional and isotropic thermal parameters for all other non-hydrogen atoms converged to *R*<sub>F</sub> = 0.076 and *R*<sub>w</sub> = 0.095. 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.

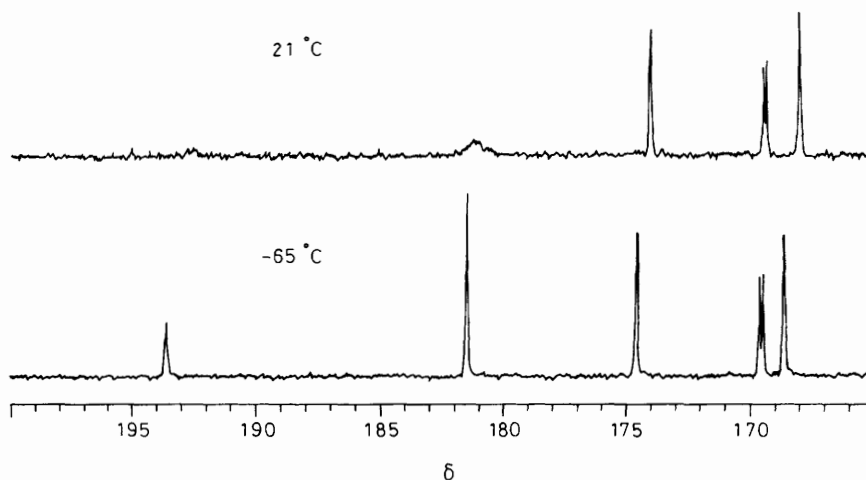


Figure 2.  $^{13}\text{C}$  N.m.r. spectra of (2) in the range of CO resonances.

174.6, 169.5 ( $J_{\text{C-H}}$  13 Hz) and 168.6 with an intensity ratio of 1:2:2:2:2 (Figure 2). On warming up to room temperature, the resonances at  $\delta$  193.6 and 181.5 broaden and coalesce into baseline, suggesting a fast exchange between these two sites and leading us to assign these to the axial and equatorial CO's on the unique  $\text{Os}(\text{CO})_3$  unit, respectively. The rest of the resonances are due to the CO's on the Os atoms associated with the bridging oxygen and hydride; the resonance at  $\delta$  169.5 is assigned to the CO ligands *trans* to the bridging hydride by the characteristic  $J_{\text{C-H}}$  coupling.

The oxo ligand is clearly not originated from the  $\text{Me}_3\text{NO}$  used: addition of  $\text{Me}_3\text{NO}$  (3 equiv.) in the first stage, or thermolysis in a carefully dried toluene solution in the second stage generated intractable product instead.

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