

Surface Organometallic Chemistry: Synthesis and X-Ray Structure of $\text{Ru}_3(\text{CO})_8(\mu\text{-OC}_6\text{H}_4\text{OMe-2})_2$, an Oxygen Stabilized Triruthenium Cluster

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The preparation and X-ray structure of $\text{Ru}_3(\text{CO})_8(\mu\text{-OC}_6\text{H}_4\text{OMe-2})_2$ is reported; this is the first example of an oxygen stabilized triruthenium cluster, with four oxygens formally contributing ten electrons, and which is a model of an oxide bound metal particle.

Interaction between molecular clusters and surfaces leads to 'sub-carbonyl' complexes in which surface oxygen atoms of an oxide replace carbonyl groups.¹ It is thought that several surface oxygens interact with the cluster framework. Molecular models of the cluster-oxide interaction (and more generally metal-support interaction) with several co-ordinated oxygen atoms are necessary to understand such chemistry.

We report the preparation and X-ray structure of the first example of an oxygen stabilized triruthenium cluster² which is a model of an oxide bound metal particle or molecular cluster, $\text{Ru}_3(\text{CO})_8(\mu\text{-OC}_6\text{H}_4\text{OMe-2})_2$ (1).

Compound (1) is obtained in good yield from the reaction between guaiacol, 2-(MeO)C₆H₄OH (0.36 mmol), and $\text{Ru}_3(\text{CO})_{12}$ (0.15 mmol) in CH_2Cl_2 or CHCl_3 , in the presence of anhydrous Me_3NO (0.36 mmol).³ It can be recrystallised from pentane- CH_2Cl_2 as yellow-orange crystals.† The X-ray structure (Figure 1)‡ indicates that the two phenoxy ligands are simultaneously co-ordinated to two ruthenium atoms with a $\mu_2\text{-O}$ atom behaving as a three-electron donor. The average Ru- $\mu\text{-O}$ distance (2.125 Å) is approximately the same distance as observed in the triply bridged $[\text{Ru}_2(\text{C}_6\text{H}_6)_2(\mu\text{-OMe})_3]^+$ ion (average 2.085 Å)⁴ or the Os-O distances (average 2.085 Å) in the cluster $\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})_2$.⁵ Each methoxy group is apparently co-ordinated to one ruthenium atom, however the distances between the methoxy oxygen and the ruthenium atoms are significantly long [Ru(1)-O(120) 2.298(3), Ru(2)-O(220) 2.285(3) Å].

While the methoxy-ruthenium distances are approximately 0.1 Å longer than any previously observed Ru-O bond,⁶ there must be some weak bonding interaction otherwise the cluster is electron deficient. In a formal sense, if there is no significant metal-metal interaction between Ru(1) and Ru(2)⁷ [Ru(1)-

Ru(2) 3.012(1), Ru(1)-Ru(3) 2.739(1), Ru(2)-Ru(3) 2.729(1) Å], each methoxy oxygen can be considered to be a two-electron donor (*vide infra*). This would make the cluster electron precise with four oxygen atoms in the molecule formally contributing ten electrons. It should be noted that the geometry around each ruthenium is approximately octahedral.

The absence of hydride in the molecule is supported by the absence of a Ru-H resonance in the ¹H n.m.r. spectrum and by the mass spectrum.† The rigidity and equivalence of the two ligands is also consistent with the ¹H n.m.r. spectra.

Rigid guaiacol co-ordination to the cluster is suggested by the shielding of the protons of the methoxy groups, δ_{OMe} 3.68 vs. 3.87 for the free ligand. An ABCD pattern is observed for the phenyl protons. Spectral simulation reveals that the proton in the *ortho* position with respect to the methoxy group is weakly coupled to this group [$J(\text{OMe-H}_D)$ 0.2 Hz]. This

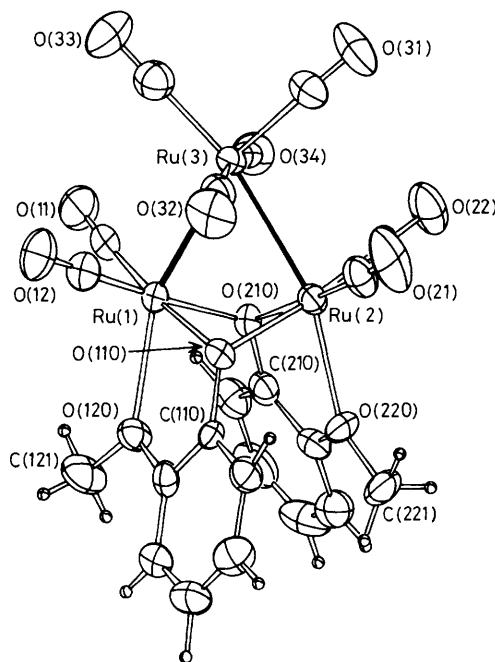


Figure 1. X-Ray structure of (1). Important bond lengths (Å) and angles (°): Ru(1)-Ru(3) 2.739(1), Ru(2)-Ru(3) 2.729(1), Ru(1)-Ru(2) 3.012(1), Ru(1)-O(110) 2.111(3), Ru(1)-O(210) 2.138(3), Ru(2)-O(110) 2.153(3), Ru(1)-O(120) 2.298(3), Ru(2)-O(220) 2.285(3), O(110)-O(210) 2.694(4); O(110)-Ru(1)-O(210) 78.7(1), Ru(1)-O(110)-Ru(2) 89.9(1), Ru(1)-O(210)-Ru(2) 90.7(1).

† Selected data: I.r. (pentane) $\nu(\text{CO})$ 2107m, 2040s, 2019s, 1991m, 1940s cm^{-1} ; chemical ionisation mass spectrum: m/z 774 (¹⁰¹Ru) and consecutive loss of 8 CO ligands in agreement with the pattern expected for a Ru_3 cluster.⁸ ¹³C N.m.r. (CDCl_3) δ_c 153.0 (*ipso*), 61.6 (OMe); in free ligand δ_c 145.7 (*ipso*), 55.6 (OMe).⁹

‡ Crystal data for (1): $\text{C}_{22}\text{H}_{14}\text{O}_{12}\text{Ru}_3$, $M = 773.7$, orthorhombic, space group $Pbca$ (D_{2h}^{15} , No. 61), $a = 11.143(6)$, $b = 15.363(2)$, $c = 30.037(8)$ Å, $Z = 8$, $U = 5142.0$ Å³, $D_c = 2.005$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 17.7$ cm^{-1} , $R_F = 0.025$, $R_{wF} = 0.042$ for 2902 absorption-corrected reflections $I > 3\sigma(I)$ of 3992 unique reflections ($4^\circ \leq 2\theta \leq 50^\circ$) collected at -50°C on an Enraf-Nonius CAD-4 diffractometer with no significant decay during data collection. All crystallographic computations were carried out on a PDP 11/44 computer using SDP (Structure Determination Package). 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.

coupling probably comes from a steric interaction between the methoxy group and the closest carbonyl ligand co-ordinated to ruthenium, forcing the methoxy group to move towards the phenyl group. Very good agreement is found between the real and simulated ^1H n.m.r. spectra using the observed chemical shift and coupling constants. § The ^{13}C n.m.r. spectra show that only the chemical shift of the *Cipso* [C(110), C(210)] and Me carbons are affected by bonding.^{9†}

This compound can be considered as a model for binding between a molecular cluster and surface oxygens of an oxide support, where carbonyl groups have been replaced by surface oxygen atoms.¹ The two bridging oxygen atoms hold the cluster to the surface and the weaker oxygen-metal bonds are susceptible to nucleophilic attack, as in the first step of a catalytic process.^{10,11}

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§ ^1H N.m.r. phenyl region: δ_{H} 6.95 [$J(\text{H}_\text{A}\text{H}_\text{B})$ 7.93, $J(\text{H}_\text{A}\text{H}_\text{C})$ 1.54, $J(\text{H}_\text{A}\text{H}_\text{D})$ 0.21 Hz, H_A], 6.76 [$J(\text{H}_\text{B}\text{H}_\text{C})$ 7.46, $J(\text{H}_\text{B}\text{H}_\text{D})$ 1.46 Hz, H_B], 6.47 [$J(\text{H}_\text{C}\text{H}_\text{D})$ 8.15 Hz, H_C], 6.26 [$J(\text{OMeH})$ 0.2 Hz, H_D].