

## Facile Preparation, Characterization, and X-Ray Crystal Structure of $[\text{Ru}_3\{\mu_3\text{-}\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2\}(\mu_3\text{-O})(\mu_2\text{-H})(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2\text{-SO}_4)]$ , a High-valent Hydrido-Oxo Cluster of Ruthenium

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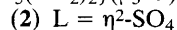
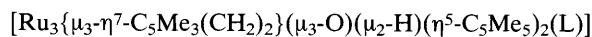
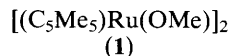
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The reaction of  $\text{KHSO}_5$  with  $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{OMe})]_2$  (**1**) in a two-phase medium such as  $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$  or in methanol produces in high yield the novel cluster  $[\text{Ru}_3\{\mu_3\text{-}\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2\}(\mu_3\text{-O})(\mu_2\text{-H})(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2\text{-SO}_4)]$  (**2**) characterized by an X-ray crystal structure determination in which two adjacent methyl groups of a  $\text{C}_5\text{Me}_5$  ligand have been activated and are co-ordinated to two ruthenium atoms giving rise to a novel  $\mu_3$ -bridging  $\eta^7$ -dimethylene-trimethylcyclopentadiene ligand; the generality of this reaction is demonstrated by the production of a similar cluster,  $[\text{Ru}_3\{\mu_3\text{-}\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2\}(\mu_3\text{-O})(\mu_2\text{-H})(\eta^5\text{-C}_5\text{Me}_5)_2(\text{OCOC}_6\text{H}_4\text{Cl})_2]$  (**3**), from the reaction of (**1**) with *m*-chloroperbenzoic acid.

Despite the present high interest in platinum metal organometallic chemistry,<sup>1</sup> that of high-valent derivatives has remained little explored so far, especially for those compounds containing oxo ligands.<sup>2</sup> The discovery by Hermann *et al.*<sup>3</sup> of the existence and rich reactivity of  $(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_3$  has stimulated a new impetus for the preparation of high-valent oxo complexes containing a cyclopentadienyl or pentamethylcyclopentadienyl ligand. As far as ruthenium is concerned, oxo complexes are known with nitrogen<sup>4</sup> or carboxylate co-ligands.<sup>5</sup> Furthermore, Groves *et al.* have recently shown that a porphyrin ruthenium(IV) oxo complex is able to activate molecular oxygen and to oxygenate organic substrates.<sup>5c</sup> Finally, it is noteworthy that although the cluster chemistry of ruthenium has been extensively studied, it is almost exclusively devoted to low-valent carbonyl derivatives.<sup>6</sup>

As part of our interest in the chemistry of the  $(\text{C}_5\text{Me}_5)\text{Ru}$  fragment,<sup>7</sup> we have attempted to prepare oxo pentamethylcyclopentadienyl ruthenium derivatives for which we expected that oxygen-transfer reactions would take place readily. We describe in this note the facile high-yield synthesis of a novel, high-valent, carbonyl-free, hydrido-oxo cluster of ruthenium.

The reaction of  $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{OMe})]_2$  (**1**) with  $\text{KHSO}_5$  (1 equiv.) in a  $\text{H}_2\text{O-CH}_2\text{Cl}_2$  two-phase medium or in methanol led to an immediate colour change from cherry-red to orange-brown. Recrystallization from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  afforded yellow-brown crystals of the title compound (**2**) in high yield (70%).<sup>†</sup>

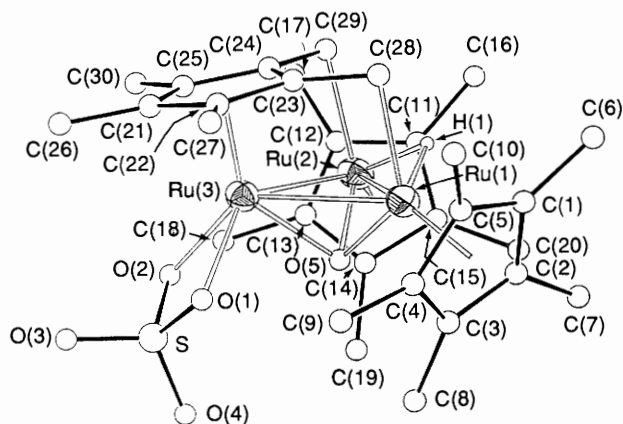


The structure of (**2**) was determined by X-ray diffraction and is shown in Figure 1.<sup>‡</sup> It consists of a triangle of ruthenium atoms containing  $\mu_3$ -oxo and  $\mu_2$ -hydrido bridges. Each metal atom is also co-ordinated to a pentamethylcyclopentadienyl ligand and Ru(3) completes its co-ordination sphere with a chelated  $\eta^2$ -sulphate group. Furthermore, two adjacent methyl groups of the pentamethylcyclopentadienyl ligand bonded to Ru(3) have been activated to form a unique example of a new  $\mu_3\text{-}\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2$  ligand. This is basically deduced from the typical  $\text{Ru-C}(\text{sp}^3)$  bond distances observed [ $\text{Ru}(1)\text{-C}(28)$  2.151(5), and  $\text{Ru}(2)\text{-C}(29)$  2.150(6) Å] and the long interatomic separations  $\text{Ru}(1) \cdots \text{C}(23)$  and  $\text{Ru}(2) \cdots \text{C}(24)$ , 2.640(5) and 2.639(4) Å respectively. The Ru-H distances are classical for a bridging hydride. Interestingly, the Ru-Ru distances, whether hydride bridged or not, are close to those found for the related hydrido-oxo carbonyl clusters.<sup>9</sup> The cluster can thus be considered as composed of an 'inorganic' ruthenium(IV) moiety co-ordinated to three oxygen atoms and bound to two 'organometallic' ruthenium(III) fragments linked together.

A precedent for this type of co-ordination of  $\text{C}_5\text{Me}_5$ , although the example was  $\mu_2\text{-}\eta^6$ , has been described by Bottomley<sup>10</sup> *et al.* in a dinuclear titanium complex; they discussed in particular the  $\eta^1$ ;  $\eta^5$  vs.  $\eta^2$ ;  $\eta^4$  mode of bonding.

<sup>‡</sup> *Crystal data:*  $\text{C}_{30}\text{H}_{44}\text{O}_5\text{Ru}_3\text{S}\cdot\text{CH}_2\text{Cl}_2$ , monoclinic,  $P2_1/a$ ,  $Z = 4$ ,  $a = 14.709(1)$ ,  $b = 14.810(1)$ ,  $c = 16.098(1)$  Å,  $\beta = 105.60(1)^\circ$ ;  $V = 3377.6(4)$  Å<sup>3</sup>;  $M = 904.88$ ;  $D_c = 1.779$  g cm<sup>-3</sup>;  $F(000) = 1816$ ,  $\mu(\text{Mo-K}\alpha) = 15.56$  cm<sup>-1</sup>; Siemens AED diffractometer,  $\omega/2\theta$  scan technique and graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å),  $3 \leq 2\theta \leq 48^\circ$ , 5157 unique reflections, 4104 observed with  $F \geq 4.0\sigma(F)$ . Data were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by Patterson and Fourier methods and refined by block-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. The SHELX system of computer programs was used (G. M. Sheldrick, Program for Crystal Structure Determination, Cambridge, 1976). The hydride ligand and the hydrogens bonded to C(28) and C(29) were clearly located and refined isotropically; other hydrogen atoms were placed at their geometrically calculated positions and refined riding on their carbon atoms with a common thermal parameter. A constrained model of disorder for the dichloromethane molecule was established to interpret the residual electron density observed. Final  $R$  and  $R_w$  values were 0.031 and 0.030. 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.

<sup>†</sup> Satisfactory analytical and spectroscopic data have been obtained for compounds (**2**) and (**3**); compound (**2**), <sup>1</sup>H NMR [200 MHz, (CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$  2.58 (s, 3H), 2.25 (d,  $J$  5.5 Hz, 2H), 1.90 (s, 30H), 0.89 (s, 6H), 0.76 (d,  $J$  5.5 Hz, 2H), and -23.19 (s, 1H); <sup>13</sup>C NMR [50 MHz, (CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$  97.55 (s), 96.72 (s), 96.48 (s), 89.78 (s), 10.8 (q,  $J$  127.37 Hz), 10.2 (q,  $J_{\text{CH}}$  128.87 Hz), 9.10 (q,  $J_{\text{CH}}$  129.87 Hz), and -0.40 (t,  $J_{\text{CH}}$  151.10 Hz); compound (**3**), <sup>1</sup>H NMR [200 MHz, (CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$  2.31 (s, 3H), 2.19 (d,  $J$  5.3 Hz, 2H), 1.87 (s, 30H), 0.91 (s, 3H), 0.75 (d,  $J$  5.3 Hz, 2H), and -25.62 (s, 1H).



**Figure 1.** The structure of the trinuclear complex (**2**). Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.829(2), Ru(1)–Ru(3) 2.695(2), Ru(2)–Ru(3) 2.708(2), Ru(1)–O(5) 1.964(4), Ru(2)–O(5) 1.972(4), Ru(3)–O(5) 2.006(3), Ru(1)–H(1) 1.76(5), Ru(2)–H(1) 1.82(5), Ru(3)–O(1) 2.103(4), Ru(3)–O(2) 2.106(3), Ru(3)–C(21) 2.182(4), Ru(3)–C(22) 2.173(4), Ru(3)–C(23) 2.209(5), Ru(3)–C(24) 2.215(5), Ru(3)–C(25) 2.153(5), Ru(1)–C(28) 2.151(5), Ru(2)–C(29) 2.150(6), Ru(2)–Ru(1)–Ru(3) 58.65(5), Ru(1)–Ru(2)–Ru(3) 58.20(5), Ru(1)–Ru(3)–Ru(2) 63.15(6), Ru(1)–C(28)–C(23) 92.3(3), Ru(2)–C(29)–C(24) 92.3(4), Ru(1)–H(1)–Ru(2) 104(2).

The  $^1\text{H}$  NMR spectra recorded in  $[\text{D}_6]\text{acetone}$  are in agreement with the solid-state structure. Thus, a hydride resonance is observed at  $\delta -23.2$ , while the methylene protons on C(28) and C(29) appear as an AB pattern at  $\delta 0.76$  and  $2.24$  ( $J_{\text{HH}}$  3.5 Hz), the two equivalent  $\text{C}_5\text{Me}_5$  rings as a singlet at  $\delta 1.90$ , and the three remaining methyl groups on the  $\text{C}_5\text{Me}_3(\text{CH}_2)_2$  ligand linked to Ru(3) as two singlets at  $\delta 2.57$  and  $0.90$  (integration ratio 1:2). Finally, the  $^{13}\text{C}$  NMR spectrum shows the methylene carbon atoms at  $\delta -0.4$ , the methyl carbon atoms of the  $\text{C}_5\text{Me}_5$  groups at  $\delta 10.2$  [on Ru(1) and Ru(2)],  $9.1$  [C(22) and C(25)], and  $10.8$  [C(21)], and the ring carbon atoms at  $\delta 97.55$ ,  $96.72$ ,  $96.48$ , and  $89.78$ .

A similar reaction was carried out with *m*-Cl- $\text{C}_6\text{H}_4\text{C}(\text{O})\text{OOH}$ . The reaction was found to give a similar cluster product, although it contained two monodentate  $\text{ClC}_6\text{H}_4\text{CO}_2^-$  anions (**3**).<sup>†</sup>

We cannot at this stage propose a satisfactory mechanism. However, the high-yield synthesis of these clusters starting with various single-oxygen donor reagents indicated that they are thermodynamically very stable. Note that a bis- $\mu_3$ -methoxo-bridged triruthenium cluster was recently described by Koelle *et al.*;<sup>11</sup> however the relationship with our compound is difficult to visualize. We are presently trying to obtain intermediates of this reaction. Preliminary reactivity studies indicate that (**2**) does not react with  $\text{PPh}_3$ ,  $\text{H}_2$ , or CO but does react with acids and phenylacetylene.

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