

**Ru<sub>4</sub>(CO)<sub>10</sub>(C=CHPr<sup>1</sup>)(OH)(PPh<sub>2</sub>): A Tetranuclear Ruthenium Carbonyl Cluster with  $\mu_4$ -Vinylidene and Face-bridging Hydroxo-groups; X-Ray Crystal Structures of Ru<sub>4</sub>(CO)<sub>10</sub>(C=CHPr<sup>1</sup>)(OR)(PPh<sub>2</sub>) (R = H or Et)**

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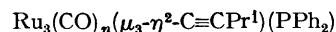
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*Summary* Fragmentation of Ru<sub>3</sub>(CO)<sub>11</sub>(Ph<sub>2</sub>PC≡CPr<sup>1</sup>) in wet THF or THF-EtOH generates the tetranuclear carbonyl clusters Ru<sub>4</sub>(CO)<sub>10</sub>(C=CHPr<sup>1</sup>)(OR)(PPh<sub>2</sub>) (R=H, Et) which have been shown by X-ray diffraction to consist of 'butterfly' arrangements of metal atoms with multi-site bound  $\mu_4$ -vinylidene and face-bridging OH or OR groups.



(1) R = H

(2) R = Et



(3) n = 9

(4) n = 8

WE report the synthesis and characterisation of the tetranuclear carbonyl clusters of ruthenium Ru<sub>4</sub>(CO)<sub>10</sub>(C=CHPr<sup>1</sup>)(OR)(PPh<sub>2</sub>) (**1**, R=H; **2**, R = Et) containing face-bridging hydroxo- or alkoxo-ligands and multi-site bound vinylidene groups. The proposed involvement of surface hydroxy-groups in the reduction of CO to methane, catalysed by alumina-supported subvalent metal carbonyl species,<sup>1</sup> suggests that more attention should be directed to the significance of low-valent, polynuclear hydroxo-species. To our knowledge, (**1**) provides the first example of a polynuclear carbonyl cluster in which a face-bridging hydroxo-ligand has been structurally identified. Although a number of compounds with terminal or doubly bridging vinylidene [C=C(H)R] ligands are now known<sup>2-8</sup> and their interesting chemistry is under closer scrutiny, cluster-bound vinylidene species are relatively rare,<sup>9</sup> the only other example of  $\mu_4$ -bonding known to us being in the mixed-metal cluster (C<sub>5</sub>H<sub>5</sub>)NiRu<sub>3</sub>(CO)<sub>9</sub>[C=C(H)Bu<sup>t</sup>].<sup>10</sup>

Ru<sub>4</sub>(CO)<sub>10</sub>(C=CHPr<sup>1</sup>)(OH)(PPh<sub>2</sub>) was prepared by bubbling a rapid stream of N<sub>2</sub> through a solution of Ru<sub>3</sub>(CO)<sub>11</sub>(Ph<sub>2</sub>PC≡CPr<sup>1</sup>) [synthesised from Ru<sub>3</sub>(CO)<sub>12</sub> and Ph<sub>2</sub>PC≡CPr<sup>1</sup> in dry heptane<sup>11</sup>] in wet tetrahydrofuran (THF) followed by chromatography on Florisil. The three major bands eluted successively with heptane-benzene mixtures gave compounds (**3**) (30%), (**4**) (10%), and (**1**) (30%). Compounds (**3**) and (**4**), with open and closed triangular structures, respectively, have been fully characterised by X-ray diffraction and are reported elsewhere.<sup>11</sup> A similar synthetic procedure using THF with 10% ethanol afforded (**3**), (**4**), (**2**) (30%), and an unidentified yellow cluster (**5**).

Red crystals of (**1**) and (**2**) have characteristic i.r. spectra [ $\nu(\text{CO})(\text{C}_6\text{H}_{12})$ , (**1**): 2071vs, 2036vs, 2023vs, 2007s, 2001m, sh, 1980m, 1977m, 1963w, and 1953w cm<sup>-1</sup>; (**2**): 2068s, 2035s, 2021s, 2005s, 2000m, sh, 1987m, 1976s, 1960w, and 1952w cm<sup>-1</sup>] and <sup>31</sup>P chemical shifts [ $\delta(\text{C}_6\text{D}_6; \text{H}_3\text{PO}_4)$ , (**1**): + 179.1 p.p.m.; (**2**): + 183.6 p.p.m.] typical of phosphido-groups bridging two strongly bonded ruthenium atoms.<sup>11</sup>

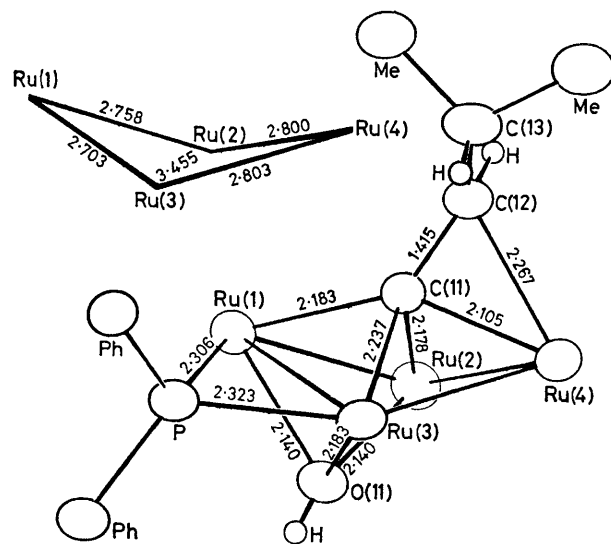


FIGURE. A perspective view of the molecular structure of  $\text{Ru}_4(\text{CO})_{10}(\text{C}=\text{CHPr})(\text{OH})(\text{PPh}_2)$  (**1**) showing the atomic numbering and selected bond lengths (Å). 50% thermal ellipsoids are drawn except for hydrogens which are scaled appropriately.

Structural details were provided by a single crystal X-ray analysis of (**1**)<sup>†</sup> (Figure). The four ruthenium atoms adopt a 'butterfly' arrangement, with four strong Ru-Ru bonds and two open edges [ $\text{Ru}(1)\text{-Ru}(4) = 4.1244(6)$  and  $\text{Ru}(2)\text{-Ru}(3) = 3.4559(6)$  Å]. The dihedral angle between the planes defined by  $\text{Ru}(1)\text{-Ru}(2)\text{-Ru}(3)$  and  $\text{Ru}(2)\text{-Ru}(3)\text{-Ru}(4)$  is  $38.51^\circ$ . One remarkable feature of the structure is the  $\mu_4\text{-}\eta^2$ -vinylidene group which appears to be  $\sigma$ -bonded to  $\text{Ru}(1)$ ,  $\text{Ru}(2)$ , and  $\text{Ru}(3)$ , and  $\eta$ -bonded to  $\text{Ru}(4)$ . Co-ordination of  $\text{C}(11)$  to all four metal atoms is in many respects similar to the  $\mu_4$ -bonding of the methynyl carbon atom in the tetranuclear methoxycarbonylmethylidyne complex  $[\text{Et}_4\text{N}][\text{Fe}_4(\text{CO})_{12}(\text{C})(\text{CO}_2\text{Me})]$ ,<sup>12</sup> although in

the latter only one carbon atom is involved in the interactions with the cluster. By analogy with the recently demonstrated conversion of  $\mu_2$ -vinylidenes into carbynes via  $\text{H}^+$  addition,<sup>7</sup> generation of  $\mu_4$ -methylidyne species from (**1**) or (**2**) via proton addition to the  $\mu_4$ -vinylidene ligands appears to be an attractive proposition.

A second novel feature of (**1**) is the presence of a triply bridging hydroxo-ligand above the  $\text{Ru}(1)\text{-Ru}(2)\text{-Ru}(3)$  face. The hydrogen atom of the OH ligand was located in a difference Fourier map and its presence further confirmed by the observation of a sharp  $\nu(\text{O-H})$  band at  $3502\text{ cm}^{-1}$  [ $\nu(\text{O-D})$   $2551\text{ cm}^{-1}$ ]. The hydroxy-oxygen atom [ $\text{O}(11)$ ] is almost symmetrically placed with respect to  $\text{Ru}(1)$ ,  $\text{Ru}(2)$ , and  $\text{Ru}(3)$  [ $\text{Ru}(1)\text{-O}(11) = 2.140(4)$ ,  $\text{Ru}(2)\text{-O}(11) = 2.140(3)$ ,  $\text{Ru}(3)\text{-O}(11) = 2.183(3)$  Å] despite the absence of an  $\text{Ru}(2)\text{-Ru}(3)$  bond. A single-crystal X-ray analysis of (**2**)<sup>‡</sup> has confirmed a closely similar polyhedral stereochemistry to that in (**1**) but with a  $\mu_3$ -OEt ligand capping the  $\text{Ru}(1)\text{-Ru}(2)\text{-Ru}(3)$  face. We are unaware of any structurally characterised polynuclear carbonyl clusters with face-bridging OH or OR groups, although  $\mu_3$ -oxo- or hydroxo-bridges between non-bonded metals are known.<sup>13</sup> The absence of (**1**) and (**2**) from fragmentation of  $\text{Ru}_3(\text{CO})_{11}\text{-}(\text{Ph}_2\text{PC}\equiv\text{CPr}^1)$  in dry non-hydroxylic solvents, and the synthesis of  $\text{Ru}_4(\text{CO})_{10}(\text{C}=\text{CDPr}^1)(\text{OD})(\text{PPh}_2)$  and  $\text{Ru}_4(\text{CO})_{10}\text{-}(\text{C}=\text{CDPr}^1)(\text{OC}_2\text{D}_5)(\text{PPh}_2)$  using  $\text{D}_2\text{O}$  and  $\text{C}_2\text{D}_5\text{OD}$ , confirmed that the OR group and the vinylidene hydrogen are probably derived from water or alcohol. Interestingly, the non-bonded distance between  $\text{O}(11)$  and  $\text{C}(11)$  is only  $2.565(6)$  Å in (**1**), much less than the sum of the Van der Waals radii for carbon (1.65–1.70 Å) and oxygen (1.50 Å). The possibility of accomplishing proton transfer from the triply bridging OH group to the multi-site bound vinylidene group in (**1**) would be of obvious significance in the context of catalytic hydrogenation.<sup>1</sup>

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<sup>†</sup> Crystal data:  $\text{C}_{27}\text{H}_{19}\text{O}_{11}\text{PRu}_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ ,  $M = 993.76$ , triclinic, space group  $\text{P}\bar{1}$ ,  $a = 9.943(1)$ ,  $b = 12.709(2)$ ,  $c = 14.108(2)$  Å;  $\alpha = 78.90(1)$ ,  $\beta = 93.02(1)$ ,  $\gamma = 98.71(1)^\circ$ ;  $Z = 2$ ,  $D_m = 1.91$ ,  $D_c = 1.909\text{ g cm}^{-3}$ ;  $F(000) = 962$ ,  $\mu(\text{Mo-K}\alpha) = 17.5\text{ cm}^{-1}$ . From a total of 6010 unique reflections ( $3.2 \leq 2\theta \leq 50^\circ$ ) measured on a Syntex P2<sub>1</sub> diffractometer with graphite monochromated Mo-K $\alpha$  radiation, 4685 had  $I \geq 3\sigma(I)$  and were used to solve and refine the structure to  $R$  and  $R_w$  values of 0.030 and 0.035, respectively. All non-hydrogen atoms were refined anisotropically and hydrogen atoms other than those of solvent were refined with isotropic coefficients.

<sup>‡</sup> Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

<sup>§</sup> Crystal data:  $\text{C}_{29}\text{H}_{23}\text{O}_{11}\text{PRu}_4$ ,  $M = 982.75$ , triclinic, space group  $\text{P}\bar{1}$ ,  $a = 9.917(2)$ ,  $b = 12.720(2)$ ,  $c = 14.043(2)$  Å;  $\alpha = 75.88(1)$ ,  $\beta = 94.74(1)$ ,  $\gamma = 103.02(1)^\circ$ ;  $Z = 2$ ,  $D_m = 1.90$ ,  $D_c = 1.951\text{ g cm}^{-3}$ ,  $F(000) = 952$ ,  $\mu(\text{Mo-K}\alpha) = 18.34\text{ cm}^{-1}$ . A total of 4603 observed [ $I \geq 3\sigma(I)$ ] reflections from 5911 measured were used in refinement of the structure to  $R$  and  $R_w$  values of 0.029 and 0.034, respectively. Bond lengths are:  $\text{Ru}(1)\text{-Ru}(2)$  2.740(1),  $\text{Ru}(1)\text{-Ru}(3)$  2.690(1),  $\text{Ru}(2)\text{-Ru}(4)$  2.811(1),  $\text{Ru}(3)\text{-Ru}(4)$  2.803(1),  $\text{Ru}(1)\text{-O}$  2.131(7),  $\text{Ru}(2)\text{-O}$  2.147(7), and  $\text{Ru}(3)\text{-O}$  2.183(7) Å.

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<sup>13</sup> See for example: E. W. Abel, W. Harrison, R. A. N. McLean, W. C. Marsh, and J. Trotter, *Chem. Commun.*, 1970, 1531.