

## Cluster Synthesis using a Methoxymethylidyne Template

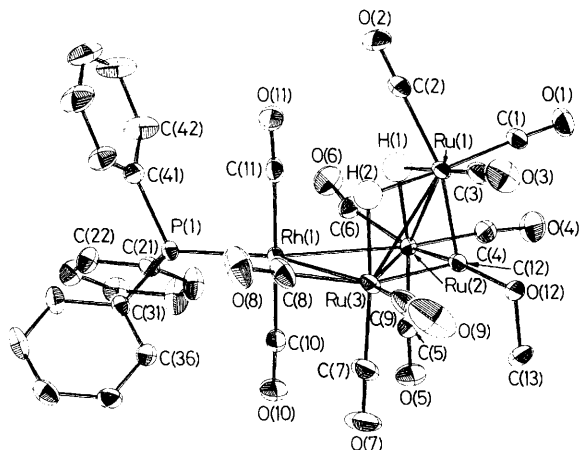
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$\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-COMe})\{\text{Rh}(\text{CO})_2\text{PPh}_3\}$  rearranges with loss of CO to form  $\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{10}\text{PPh}_3(\mu\text{-COMe})$  from which the Me group can be abstracted thus forming  $[\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{11}\text{PPh}_3]^-$ .

Many clusters are now known which incorporate a  $\mu_3$ -ligand, e.g.  $\text{C}_2\text{Bu}^t$ ,<sup>1</sup> PPh,<sup>2</sup> NR,<sup>3</sup> COMe,<sup>4</sup> S,<sup>5</sup> and in the subsequent reactions of these compounds this ligand usually remains co-ordinated in the same fashion. Exceptions to this have resulted in an increase in the connectivity of the capping unit

as observed for the site change of a PPh ligand from  $\mu_3$  to  $\mu_4$ .<sup>6</sup> In this Communication we report a reaction which results in a  $\mu_3$  to  $\mu$  co-ordination shift, hitherto unobserved, for the COMe ligand. Furthermore, we also report the unusual reaction of K-Selectride towards the so formed  $\mu\text{-COMe}$



**Figure 1.** The molecular structure of  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-COMe})\{\text{Rh}(\text{CO})_2\text{PPh}_3\}$  (2). Bond lengths (Å): Ru(1)–Ru(2), 2.880(1); Ru(1)–Ru(3), 2.865(1); Ru(2)–Ru(3), 2.834(1); Rh(1)–Ru(2), 2.895(1); Rh(1)–Ru(3), 2.872(1); Rh(1)–P(1), 2.301(1). Ru(1)–Ru(2)–Ru(3) and Rh(1)–Ru(2)–Ru(3) interplanar angle,  $118.0^\circ$ .

which results in Me abstraction highlighting the difference in reactivity induced by this co-ordination shift.

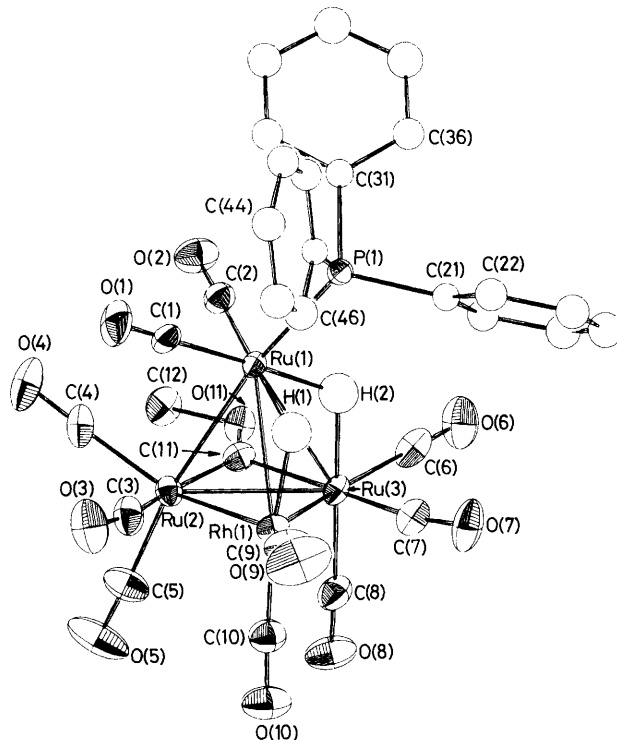
The anion  $[(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-COMe})]^-$  (1)<sup>7</sup> reacts with  $[\text{Rh}(\text{CO})_3(\text{PPh}_3)_2]\text{PF}_6$  in MeOH at  $-20^\circ\text{C}$  to form the bimetallic cluster  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-COMe})\{\text{Rh}(\text{CO})_2\text{PPh}_3\}$  (2) in 80% yield.

Red, air-stable crystals of (2) were grown by slow diffusion of MeOH into a  $\text{CH}_2\text{Cl}_2$  solution at  $-20^\circ\text{C}$ , and the crystal structure determined.<sup>†</sup> The molecular structure of (2) is

<sup>†</sup> *Crystal data:* (2),  $\text{C}_{31}\text{H}_{20}\text{O}_{12}\text{PRhRu}_3$ ,  $M = 1021.48$ , monoclinic,  $P2_1/c$  (No. 14),  $a = 13.661(2)$ ,  $b = 18.030(2)$ ,  $c = 15.323(3)$  Å,  $\beta = 111.17(2)^\circ$ ,  $U = 3519$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.928$  g cm<sup>-3</sup>,  $D_m$  (floatation) =  $1.90(1)$  g cm<sup>-3</sup>,  $F(000) = 1976$ ,  $\mu(\text{Mo-K}\alpha) = 17.64$  cm<sup>-1</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å. Data were collected using an Enraf-Nonius CAD4 diffractometer with a graphite monochromator on a crystal at room temperature ( $0.55 \times 0.35 \times 0.15$  mm) mounted in a thin wall capillary. 6184 Unique reflections ( $1.5 < \theta < 25^\circ$ ) were recorded of which 4740 with  $F > 3\sigma(F)$  were used for refinement. Structure solved using the Patterson facility in SHELX-86<sup>8</sup> to locate the 4 metal atoms and subsequent Fourier syntheses using SHELX-76.<sup>9</sup> Full-matrix least-squares refinement converged to  $R = 0.030$  (440 parameters), anisotropic (Ru, Rh, P, C, O) and isotropic (H),  $w = 1/[\sigma^2(F) + 0.0002F^2]$ ,  $R_w = 0.033$ , empirical absorption, non-rigid phenyl rings, calculated phenyl H-atom co-ordinates [ $d(\text{CH}) = 0.95$  Å]. Hydride H atoms were located from difference electron-density syntheses towards the end of refinement and their positions refined with a fixed thermal parameter ( $0.08$  Å<sup>2</sup>).

*Crystal data:* (3),  $\text{C}_{30}\text{H}_{20}\text{O}_{11}\text{PRhRu}_3$ ,  $M = 993.47$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 9.560(3)$ ,  $b = 21.438(6)$ ,  $c = 16.391(3)$  Å,  $\beta = 93.55(2)^\circ$ ,  $U = 3353$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.967$  g cm<sup>-3</sup>,  $D_m$  (floatation) =  $1.91(1)$  g cm<sup>-3</sup>,  $F(000) = 1920$ ,  $\mu(\text{Mo-K}\alpha) = 18.49$  cm<sup>-1</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å. Data were collected using an Enraf-Nonius CAD4 diffractometer equipped with graphite monochromator on a crystal at room temperature ( $0.4 \times 0.25 \times 0.1$  mm) mounted in a thin wall capillary. 4109 Unique reflections ( $1.5^\circ < \theta < 22^\circ$ ) were recorded of which 2980 with  $F > 3\sigma(F)$  were used for refinement. Structure solved by direct methods<sup>9</sup> and Fourier techniques and refined by full-matrix least-squares to  $R = 0.042$  (332 parameters), anisotropic (Ru, Rh, P, carbonyl, COME C and O) and isotropic (H and phenyl C),  $w = 1/[\sigma^2(F) + 0.0005F^2]$ ,  $R_w = 0.048$ , empirical absorption, non-rigid phenyl rings, calculated phenyl H-atom co-ordinates [ $d(\text{CH}) = 0.95$  Å]. Hydride H atoms were located from difference electron-density syntheses towards the end of refinement and their positions refined with a fixed thermal parameter ( $0.08$  Å<sup>2</sup>).

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.** The molecular structure of  $\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{10}\text{PPh}_3(\mu\text{-COMe})$  (3). Bond lengths (Å): Ru(1)–Ru(2), 2.794(1); Ru(1)–Ru(3), 2.931(1); Ru(1)–Rh(1), 2.915(1); Ru(2)–Ru(3), 2.844(1); Ru(2)–Rh(1), 2.783(1); Ru(3)–Rh(1), 2.762(1); Ru(1)–P(1), 2.350(2).

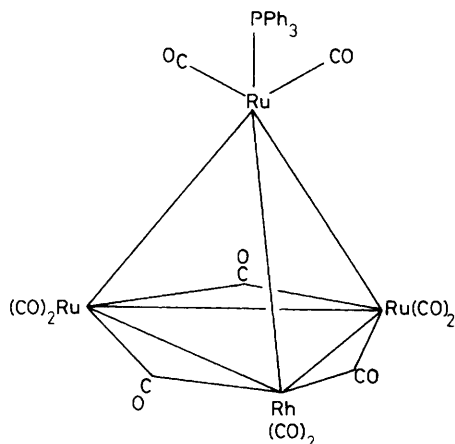
shown in Figure 1 and shows a 'butterfly' configuration of the  $\text{Ru}_3\text{Rh}$  metal core with the Rh occupying a 'wing tip' site. The COMe group retains its  $\mu_3$  co-ordination mode. The stoichiometric ratio of Ru : Ru : P was confirmed using E.D.X. (energy dispersion X-ray spectroscopy) and the assignment of the Rh atom is consistent with n.m.r. studies.

Complex (2) is unstable in tetrahydrofuran (thf) at room temperature and rearranges with loss of CO to give  $\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{10}\text{PPh}_3(\mu\text{-COMe})$  (3) which can be isolated by chromatographic separation on flash silica gel in 50% yield. E.D.X. again confirmed the stoichiometric ratio of Ru : Rh : P.

<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P n.m.r. studies show that in  $\text{CDCl}_3$ , (3) exists in two isomeric forms, which interconvert slowly on the n.m.r. timescale (from spin saturation <sup>1</sup>H n.m.r. studies), the PPh<sub>3</sub> being bound to ruthenium in one isomer (isomer A) and rhodium in the other (isomer B). At room temperature these isomers are found in the ratio of ca. 2.5:1, A:B. Red, air-stable crystals of (3) were grown by cooling a  $\text{CH}_2\text{Cl}_2$ /light petroleum solution and the crystal structure determined.<sup>†</sup> The location of the rhodium atom was determined from (i) <sup>13</sup>C n.m.r. which shows no rhodium coupling to the carbyne signal and (ii) <sup>31</sup>P solid state n.m.r. which shows no evidence of any rhodium–phosphorus coupling. This absence of rhodium–phosphorus coupling in the solid state identified the isomer crystallised as isomer A.

The molecular structure of (3) is shown in Figure 2. In contrast to (2), (3) has a tetrahedral  $\text{Ru}_3\text{Rh}$  metal core with the COMe ligand unexpectedly having converted to a  $\mu$ -bridging co-ordination.

The <sup>1</sup>H n.m.r. spectrum is assigned on the basis that the hydride ligands are averaged by rapid intramolecular exchange at room temperature with the hydrides in isomer A giving rise to a triplet owing to accidental equivalence of the couplings to rhodium and phosphorus. For isomer B the



**Figure 3.** Proposed molecular structure of the anion  $[\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{11}\text{PPh}_3]^-$  of **(4)** with hydride ligands omitted.

averaged rhodium and phosphorus couplings differ and a doublet of doublets is observed.

It has been suggested that the C–O bond in a  $\mu$ -bridging COMe ligand has some multiple bond character.<sup>10</sup> Consistent with this theory, the reaction of **(3)** with K-Selectride in thf leads predominantly to attack at the Me group of the  $\mu$ -COMe ligand to generate a carbonyl ligand in the product  $[\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{11}(\text{PPh}_3)]^-$  which has been isolated as the PPN salt  $[\text{PPN} = (\text{Ph}_3\text{P})_2\text{N}]$  (**4**) in 30% yield. Figure 3 shows the proposed structure of the anion of **(4)** which is consistent with n.m.r. studies.<sup>‡</sup> This structure has a similar geometry to that of

<sup>‡</sup>  $^{13}\text{C}\{^1\text{H}\}$  N.m.r.  $\delta(\text{CD}_2\text{Cl}_2, -90^\circ\text{C})$  266.7 (s, 1C, CO), 255.5 (d,  $J$  22, 2C, CO), 201.0 (s, 2C, CO), 200.2 (s, 2C, CO), 193.8 (s, 2C, CO), 192.5 (d,  $J$  74, 1C, CO), 183.0 (d of d,  $J$  64, 18, 1C, CO), 125–136 (Ph).

$\text{Rh}_4(\text{CO})_{12}$ .<sup>11</sup> The reaction leading to the formation of the anion of **(4)** can be contrasted with that of  $\text{H}_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-COMe})$  with K-Selectride where deprotonation to form  $[\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-COMe})]^-$  occurs.<sup>7</sup>

The reactions outlined can be considered as a new synthetic strategy for cluster building with the COMe ligand initially acting as a template which can be later converted to CO. The cluster anion thus formed can then be reacted further.

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