

# The Synthesis, Molecular Structure and Interconversion of Two Novel Benzene-coordinated Pentaruthenium–Carbido Cluster Isomers $[\text{Ru}_5\text{C}(\text{CO})_{12}(\mu_3 : \eta^2 : \eta^2 : \eta^2\text{-C}_6\text{H}_6)]$ and $[\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)]$

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Two isomers of a benzene-coordinated pentaruthenium–carbido cluster,  $[\text{Ru}_5\text{C}(\text{CO})_{12}(\mu_3 : \eta^2 : \eta^2 : \eta^2\text{-C}_6\text{H}_6)]$  **1** and  $[\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)]$  **2** have been synthesised from  $[\text{Ru}_5\text{C}(\text{CO})_{15}]$  **3** and structurally characterised by single crystal X-ray diffraction; **1** is irreversibly converted to **2** on mild thermolysis.

We have previously reported the synthesis of cluster compounds containing either  $\eta^6$ - or  $\mu_3 : \eta^2 : \eta^2 : \eta^2$ -coordinated arene moieties.<sup>1–3</sup> In this communication we wish to report the synthesis of a pentaruthenium carbido cluster which exists in two isomeric forms, one containing  $\eta^6\text{-C}_6\text{H}_6$  and the other  $\mu_3 : \eta^2 : \eta^2 : \eta^2\text{-C}_6\text{H}_6$ .

Treatment of  $[\text{Ru}_5\text{C}(\text{CO})_{15}]$  **3** with two molar equivalents of  $\text{Me}_3\text{NO}$  in the presence of cyclohexa-1,3-diene results in coordination of the diene to the cluster core to give  $[\text{Ru}_5\text{C}(\text{CO})_{13}(\eta^4\text{-C}_6\text{H}_8)]$  **4**.<sup>†</sup> The reaction of **4** with an additional equivalent of  $\text{Me}_3\text{NO}$  affords a mixture of the benzene complexes  $[\text{Ru}_5\text{C}(\text{CO})_{12}(\mu_3 : \eta^2 : \eta^2 : \eta^2\text{-C}_6\text{H}_6)]$  **1**<sup>‡</sup> and  $[\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)]$  **2** (Scheme 1),<sup>§</sup> which may be separated by TLC. Mass spectrometry data for **1** and **2** are identical, however the <sup>1</sup>H NMR spectrum of **2** displays a singlet at  $\delta$  5.93, characteristic of an  $\eta^6$ -coordinated benzene ligand, whilst that of **1** has a singlet at  $\delta$  4.12, indicating a different coordination mode for the organic ligand in this cluster. In order to establish the nature of the differences between the isomers **1** and **2** single crystal analyses were carried out.<sup>¶</sup> The molecular structures of **1** and **2** are shown in Fig. 1 and 2, respectively.

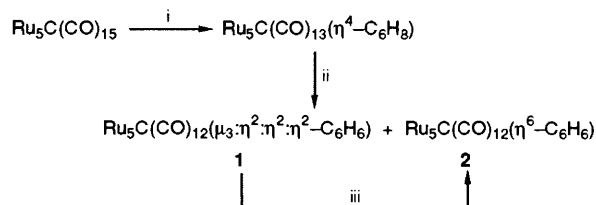
<sup>†</sup> Spectroscopic data for **4**: IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})/\text{cm}^{-1}$ : 2083m, 2051s, 2032w,sh and 2020s; <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  5.42 (m), 4.36 (m), 2.74 (m) and 1.80 (m); Electron impact mass spectrum (EI-MS)  $\text{M}^+$  (obs.) 959 (calc. 959). An X-ray structure analysis of this species is near to completion and will be reported elsewhere.

<sup>‡</sup> Spectroscopic data for **1**: IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})/\text{cm}^{-1}$ : 2085s, 2053s, 2024w,sh, 2014s and 1980w,br; <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  4.12 (s); EI-MS  $\text{M}^+$  (obs.) 931 (calc. 932).

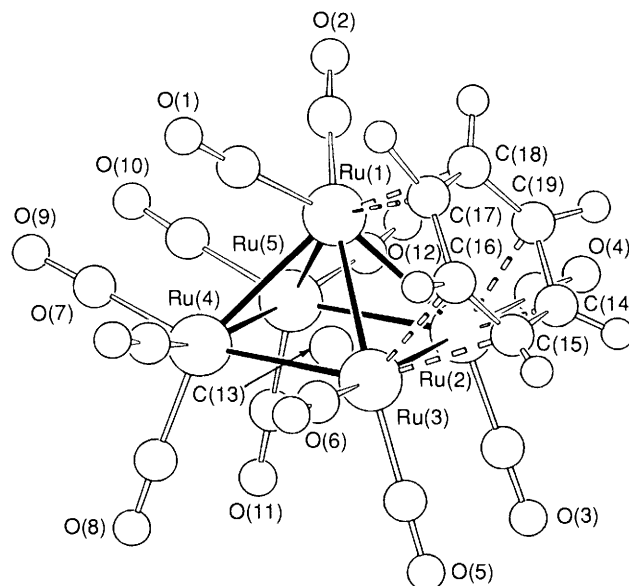
<sup>§</sup> Spectroscopic data for **2**: IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})/\text{cm}^{-1}$ : 2077m, 2048s, 2033m,sh and 2010s; <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  5.93 (s); EI-MS  $\text{M}^+$  (obs.) 931 (calc. 932).

<sup>¶</sup> Crystal data for **1** and **2**:  $\text{C}_{19}\text{H}_6\text{O}_{12}\text{Ru}_5$ ;  $M = 931.7$ ; **1**: (face-capping) triclinic, space group  $P\bar{1}$ ,  $a = 9.525(2)$ ,  $b = 14.574(3)$ ,  $c = 9.484(4)$  Å,  $\alpha = 96.29(2)^\circ$ ,  $\beta = 112.37(3)^\circ$ ,  $\gamma = 82.33(2)^\circ$ ,  $U = 1204 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 2.57 \text{ g cm}^{-3}$ ,  $F(000) = 872$ ,  $\mu(\text{Mo-K}\alpha) = 28.40 \text{ cm}^{-1}$ ,  $3 < \theta < 28^\circ$ , final  $R$  value 0.040,  $R_w = 0.040$  for 4114 out of 6415 independent reflections [ $I > 2\sigma(I)$ ]; **2** (terminal benzene), monoclinic,  $P2_1/c$ ,  $a = 15.26(2)$ ,  $b = 16.675(9)$ ,  $c = 19.016(9)$  Å,  $\beta = 96.04(7)^\circ$ ,  $U = 4812 \text{ \AA}^3$ ,  $Z = 8$ ,  $D_c = 2.57 \text{ g cm}^{-3}$ ,  $F(000) = 3488$ ,  $\mu(\text{Mo-K}\alpha) = 28.43 \text{ cm}^{-1}$ ,  $2.5 < \theta < 25^\circ$ , final  $R$  value 0.058,  $R_w = 0.060$  for 3951 out of 7726 independent reflections [ $I > 2\sigma(I)$ ]. Two independent molecules are present in the asymmetric unit of **2**: structural parameters discussed in the text are given as pairs of chemically corresponding values in the two molecules. Data common to both species: diffraction data collected by the  $\omega$ -2 $\theta$  scan method. All non-H atoms allowed to vibrate anisotropically. The H atoms in **2** were added in calculated positions [C–H 1.08 Å] and refined 'riding' on their respective C atoms; those in **1** were found in the final Fourier maps and refined with C–H bond length constraints. The structures were solved by direct methods and refined by full-matrix least-squares.<sup>8</sup> Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

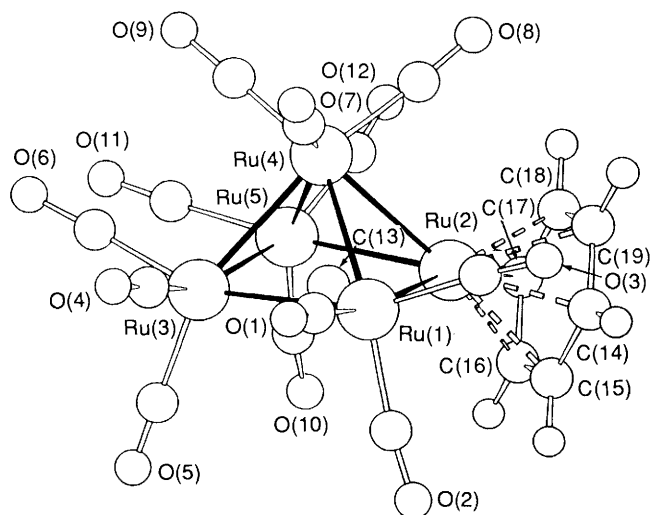
The solid state structures of **1** and **2** differ essentially in the coordination mode adopted by the benzene fragment. In **1** the benzene ligand is in face-capping position over a triangular face of the square pyramidal framework, while in **2** the ligand is  $\eta^6$ -coordinated to one basal Ru-atom, thus formally replacing a basal tricarbonyl unit in the structure of **3**.<sup>4</sup> It is worth stressing that, although both modes of coordination had been already observed in Ru-clusters such as  $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2 : \eta^2\text{-C}_6\text{H}_6)]$ <sup>5,6</sup>  $[\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2 : \eta^2\text{-C}_6\text{H}_6)]$ <sup>2</sup> and  $[\text{Ru}_3(\text{CO})_7(\mu_3 : \eta^2\text{-C}_2\text{Ph}_2\text{CO})(\eta^6\text{-C}_6\text{H}_6)]$ ,<sup>6</sup> never before has the isolation and structural characterization of such a pair of structural isomers been achieved. In this preliminary report the following aspects of the two structures are noteworthy: (i) the whole metal atom framework in **2** is heavily distorted with respect to the ideal geometry of **3**,<sup>4</sup> with



**Scheme 1** Reagents and conditions: i,  $\text{Me}_3\text{NO}$  (2 mol equiv.)– $\text{CH}_2\text{Cl}_2$  solution added dropwise to a  $\text{CH}_2\text{Cl}_2$  solution of **3** in the presence of cyclohexa-1,3-diene; ii,  $\text{Me}_3\text{NO}$  (1 mol equiv.)– $\text{CH}_2\text{Cl}_2$  solution added dropwise to a  $\text{CH}_2\text{Cl}_2$  solution of **4**; iii, reflux in hexane for 4 h.



**Fig. 1** Molecular structure of **1**, showing the labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond distances are discussed in the text.



**Fig. 2** Molecular structure of **2**, showing the labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Only one of the two independent molecules present in the asymmetric unit is shown. Relevant bond distances are discussed in the text.

Ru–Ru bonds ranging from 2.744(2), 2.732(2) to 2.865(2), 2.877(2) Å [compare with 2.800(2)–2.882(2) Å in **3**]; the C(carbide) atom is off-centred with respect to the middle of the square base and ‘pulled’ towards the benzene-bound Ru-atom [Ru(2)–C(13) 1.93(2), 1.86(2) vs. an average of 2.03(2), 2.06(2) Å]. (ii) The metal cluster in **1** is less distorted [Ru–Ru bonds in the range 2.800(1)–2.845(1) Å], and the C(carbide) occupies the centre of the square base. (iii) The C<sub>6</sub>H<sub>6</sub>-fragment in **1** clearly shows the ‘long’–‘short’ bond length alternation [mean 1.44(1), 1.36(1) Å, respectively] with ‘short’ bonds eclipsed over the Ru-atoms, as previously observed in [Ru<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-η<sup>2</sup>:η<sup>2</sup>:η<sup>2</sup>-C<sub>6</sub>H<sub>6</sub>)]<sup>5</sup> [mean 1.45(1), 1.40(1) Å]. (iv) Ru–C(benzene) distances are only slightly longer in **1** than in **2** [2.26(1) vs. 2.23(1), Å] and comparable with those in [Ru<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-η<sup>2</sup>:η<sup>2</sup>:η<sup>2</sup>-C<sub>6</sub>H<sub>6</sub>)]<sup>5</sup> [2.331(4) Å]

and in [Ru<sub>6</sub>C(CO)<sub>11</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(μ<sub>3</sub>-η<sup>2</sup>:η<sup>2</sup>:η<sup>2</sup>-C<sub>6</sub>H<sub>6</sub>)]<sup>2</sup> [2.306(3) Å].

The solid state structures of **1** and **2** are entirely consistent with the observed chemical shifts of their arene hydrogens,<sup>1,2,7</sup> thus suggesting the persistence of the two isomeric forms in solution. However, mild thermolysis (hexane 68 °C, 4 h) of **1** results in its quantitative and irreversible conversion to **2** indicated by IR monitoring of the reaction solution.

Further investigation into the possibility of the introduction of a second arene into the pentaruthenium system are underway with a view to providing analogues of the hexaruthenium–carbido bis-arene clusters.

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