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**Preliminary communication**

# Isomeric clusters differing only in the orientation of a bidentate ligand; synthesis and crystal structures of two isomers of $[HRu_5C(CO)_{14}(C_5H_4N)]$

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## Abstract

An X-ray diffraction study has confirmed that reaction of $[Ru_5C(CO)_{15}]$ (**1**) with an excess pyridine gives an equimolar mixture of two isomers of $[HRu_5C(CO)_{14}(C_5H_4N)]$ (**2a** and **2b**) that differ only in the orientation of a bridging ligand, along with a third minor product $[HRu_5C(CO)_{13}(C_5H_4N)(C_5H_5N)]$ (**3**); **2a** and **2b** undergo quantitative thermal decarbonylation to give the same unstable product $[HRu_5C(CO)_{13}(C_5H_4N)]$ (**4**), which can be recarbonylated quantitatively under mild conditions to regenerate equal proportions of the isomers **2a** and **2b**.

Metal cluster isomers are relatively rare in the solid state but several have now been structurally characterised. These have previously involved different sites for hydride or other monodentate ligands [1–3], alternative metal framework polyhedra [3], or isomerism of an organo ligand [4].

An X-ray structural study of $[HRu_5C(CO)_{14}(C_5H_4N)]$ (**2**) * shows cluster isomers differing only in the orientation of a bridging ligand (Fig. 1), and provides the

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* Crystal data for **2a**: $C_{20}H_5NO_{14}Ru_5$, $M = 988.06$, monoclinic, space group $P2_1/c$, $a$ 8.864(2), $b$ 17.962(5), $c$ 17.200(5) Å, $\beta$ 95.84(3)°, $U$ 2724.29 Å$^3$, $F(000) = 1856$, $\mu$(Mo-$K_\alpha$) 25.21 cm$^{-1}$, $Z = 4$, $D_c$ 2.41 g cm$^{-3}$. $R = 0.0281$ for 3995 reflections with $I/\sigma(I) > 3.0$.

Crystal data for **2b**: $C_{20}H_5NO_{14}Ru_5$, $M = 988.06$, triclinic, space group $P\bar{1}$ (No. 2), $a$ 19.095(5), $b$ 17.870(5), $c$ 9.479(3) Å, $\alpha$ 97.86(3), $\beta$ 106.52(4), $\gamma$ 63.02(2)°, $U$ 2763.39 Å$^3$, $F(000) = 1856$, $\mu$(Mo-$K_\alpha$) 24.86 cm$^{-1}$, $Z = 4$, $D_c$ 2.37 g cm$^{-3}$. $R = 0.0436$ for 4140 reflections with $I/\sigma(I) > 3.0$.

Data were collected for both compounds in the $\theta$-range 3–25° with a scan width of 0.80°. The H ligands in isomer **2a** and in both molecules of **2b** were located directly by difference-Fourier syntheses ($\sin\theta < 0.35$), and evidence for their positions were also obtained from potential energy minimization calculations [8] and examination of computed space filling models. Confirmation of the N-atom sites in the two isomers was obtained by reversal of the assignment of the coordinated N-atom and C-atom in each structure, which gave unreasonable thermal parameters on refinement.

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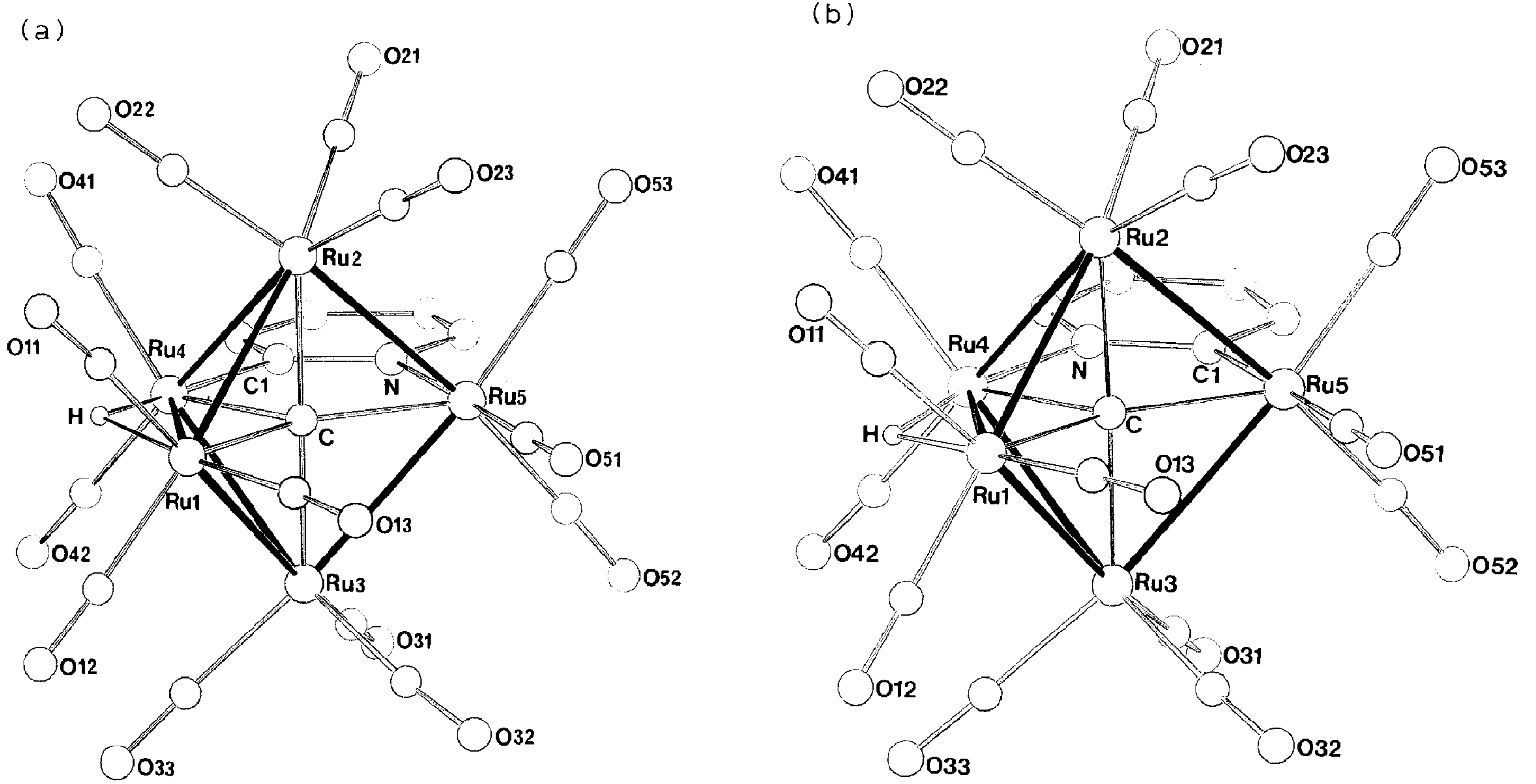

Fig. 1. Structures of the two isomers of [$HRu_5C(CO)_{14}(C_5H_4N)$]; (a) isomer **2a**; (b) one molecule of isomer **2b**. Principal bond lengths (Å) for isomer **2a** with the corresponding mean values for the two independent molecules of isomer **2b** in parentheses: Ru(1)–Ru(2) 2.877(1) (2.860(2)), Ru(1)–Ru(3) 2.882(1) (2.858(2)), Ru(1)–Ru(4) 2.895(1) (2.833(2)), Ru(2)–Ru(4) 2.833(1) (2.819(2)), Ru(2)–Ru(5) 2.876(1) (2.896(2)), Ru(3)–Ru(4) 2.823(1) (2.809(1)), Ru(3)–Ru(5) 2.876(1) (2.899(2)), Ru–N 2.169(4) (2.134(12)), Ru–C(1) 2.080(5) (2.131(15)). Non-bonded contacts (Å): Ru(1)...Ru(5) 4.05 (4.05), Ru(2)...Ru(3) 3.94 (3.95), Ru(4)...Ru(5) 3.57 (3.59).

first example of this type of isomerism in the solid state. The metal framework in each isomer may be described as a bridged 'butterfly' or as arachno-pentagonal bipyramidal, an expected structure for a 76 electron cluster ($S = 8$). [5] The hydride ligand bridges the Ru(1)–Ru(4) hinge bond in both compounds, and the Ru(4)...Ru(5) unbonded edge is bridged by the orthometallated pyridine via the nitrogen atom and the deprotonated carbon atom. Essentially, the two new ruthenium isomers differ only in the orientation of this aromatic ligand; in isomer **2a** the nitrogen atom is bonded to the bridging metal (Ru(5)–N 2.169(4) Å), whereas in isomer **2b** it is bonded to the hinge ruthenium atom (Ru(4)–N 2.134(12) Å). This difference has a large effect on the chemical shift of the hydride in the 1H NMR spectrum * which in **2a** is approximately 5 ppm upfield from that in **2b**.

The structure of isomer **2a** is essentially similar to that reported for the osmium analogue $[HOs_5C(CO)_{14}(C_5H_4N)]$, for which no evidence of a second isomer has been observed so far [6].

Lengthening of metal–metal bonds bridged by $\mu$-hydride ligands is a feature of many cluster compounds [2,7,8]. This is observed in isomer **2a**, in which the hydrido-bridged bond (Ru(1)–Ru(4) 2.895(1) Å) is the longest in the structure. In contrast, in isomer **2b** the equivalent 'hinge' bond, which is also hydrido-bridged, is much shorter in both independent molecules (mean 2.833(2) Å), the longest Ru–Ru bonds in this structure being those from the 'wing-tip' spanning ruthenium atom (mean lengths Ru(5)–Ru(2) 2.896(2) and Ru(5)–Ru(3) 2.899(2) Å). Relatively short H-bridged M–M distances have been observed previously; for example the $\mu$-H edge in $[Os_8H(CO)_{22}]^-$ (Os–Os 2.848(1) Å) and the $\mu_3$-H face in $[Os_8H(CO)_{22}I]$ (mean Os–Os 2.787 Å) [9].

Both isomers **2a** and **2b** are converted quantitatively (as determined by IR) to $[HRu_5C(CO)_{13}(C_5H_4N)]$ (**4**) on prolonged heating in heptane (Scheme 1). However, the decarbonylation of **2a** is twice as fast as that of **2b**, indicating a greater kinetic stability for isomer **2b**. When kept at room temperature in heptane solution in air, **4** decomposes to give a mixture that includes small but equimolar amounts of **2a** and **2b**. Treatment of a hot solution of **4** for 10 min with CO regenerates **2a** and **2b** in equimolar proportions and no other detectable products, indicating that this reaction is kinetically controlled.

The reaction of pentanuclear clusters with pyridine and its derivatives provides interesting scope for further investigation. There are parallels to the types of

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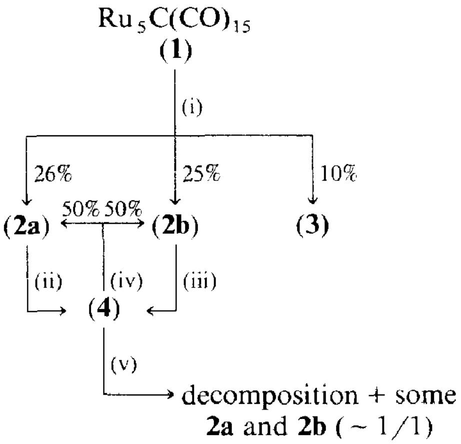
* Selected spectroscopic data (IR in hexane, NMR in $CDCl_3$ (**2a**) or $CD_2Cl_2$ (**2b**, **3**, **4**), coupling constants in Hz, all $^1H$ unless stated otherwise. Compound **2a**; IR: $\nu(CO)$ 2099m, 2072s, 2055vs, 2029m, 2016s, 2006m, 1999m, 1991w, 1967m, 1937vw $cm^{-1}$; $^1H$ NMR: $-25.83$ (s), 6.46 (dt, $^3J(H-H)$ 5.8, $^4J(H-H)$ 1.7), 6.87 (dt, $^3J(H-H)$ 7.5, $^4J(H-H)$ 1.7), 7.28 (dd, $^3J(H-H)$ 7.5, $^4J(H-H)$ 1.7), 8.42 (dd, $^3J(H-H)$ 5.8, $^4J(H-H)$ 1.7). Compound **2b**; IR: $\nu(CO)$ 2099m, 2072s, 2055vs, 2029m, 2016s, 2006m, 1999m, 1991w, 1967m, 1937vw $cm^{-1}$; $^1H$ NMR: $-20.90$ (s), 6.42 (dt, $^3J(H-H)$ 5.7, $^4J(H-H)$ 1.8), 6.83 (dt, $^3J(H-H)$ 7.8, $^4J(H-H)$ 1.8), 7.45 (dd, $^3J(H-H)$ 7.8, $^4J(H-H)$ 1.8), 8.22 (dd, $^3J(H-H)$ 5.7, $^4J(H-H)$ 1.8). For **2a**, peak intensity of $2016 > 2072$ $cm^{-1}$ and $2006 > 1999$ $cm^{-1}$; for **2b**, $2072 > 2016$ $cm^{-1}$ and $2006 > 1999$ $cm^{-1}$. Compound **3**; IR: $\nu(CO)$ 2092m, 2058s, 2039vs, 2021m, 2007m, 1996w, 1978vw, 1971w $cm^{-1}$; $^1H$ NMR: $-21.56$ (br s), 7.06 (m), 7.49 (m, 2H), 8.20 (m). Compound **4**; IR: $\nu(CO)$ 2087m, 2052s, 2044s, 2031s, 2010sh, 2000m, 1993m, 1969m, 1957w $cm^{-1}$; $^1H$ NMR: $-21.31$ (s), 6.44 (dt, $^3J(H-H)$ 5.8, $^4J(H-H)$ 1.5), 6.85 (dt, $^3J(H-H)$ 7.5, $^4J(H-H)$ 1.5), 7.87 (dd, $^3J(H-H)$ 5.8, $^4J(H-H)$ 1.5), 8.84 (dd, $^3J(H-H)$ 7.5, $^4J(H-H)$ 1.5), 7.5–7.6 (m, 3H, $C_5H_5N$), 8.0–8.1 (m, 2H, $C_5H_5N$).



Scheme 1. Reactions of [$Ru_5C(CO)_{15}$] (1) with pyridine; (i) excess pyridine, $CH_2Cl_2$, 40 °C, 5 h; (ii) 98 °C, heptane, 24 h; (iii) 98 °C, heptane, 48 h; (iv) CO(g), heptane, 80 °C, 10 min; (v) air, heptane, ambient temperature, several days.

bonding and reactivity observed in the reactions of trinuclear analogues, but the pentanuclear clusters have a greater flexibility in terms of metal core rearrangement.

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