

Equilibria Between Tri-ruthenium(carbonyl) Clusters with Face- and Edge-bridging Pentalene Ligands: Crystal and Molecular Structures of Two Isomers of $[\text{Ru}_3(\text{CO})_8\{1,3,5-(\text{Me}_3\text{Si})_3\text{C}_8\text{H}_3\}]$

By JUDITH A. K. HOWARD, SELBY A. R. KNOX, RONALD J. MCKINNEY, ROBERT F. D. STANSFIELD, F. GORDON A. STONE*, and PETER WOODWARD

(Department of Inorganic Chemistry, The University, Bristol BS8 1TS)

Summary The i.r. and ^1H n.m.r. spectra of pentalene $[\text{C}_8\text{H}_6, 2\text{-RC}_8\text{H}_5$ ($\text{R} = \text{SiMe}_3, \text{Me}, \text{Ph}$), and $1,3,5-(\text{Me}_3\text{Si})_3\text{-C}_8\text{H}_3$] complexes of the $\text{Ru}_3(\text{CO})_8$ cluster reveal the existence of equilibria between isomers; *X*-ray diffraction studies of the two forms of $[\text{Ru}_3(\text{CO})_8\{1,3,5-(\text{Me}_3\text{Si})_3\text{-C}_8\text{H}_3\}]$ show that this involves the pentalene ligand in an edge- or face-bridging configuration with respect to the tri-ruthenium cluster.

X-RAY crystallographic studies on the complexes $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_6)]$ (I) and $[\text{Ru}_3(\text{CO})_8\{1,5-(\text{Me}_3\text{Si})_2\text{C}_8\text{H}_4\}]$ (II) revealed that the pentalene ligands were directly bonded to only two metal atoms of an Ru_3 triangle.¹ Moreover, whereas the complex of unsubstituted pentalene (I) showed

fluxional behaviour [Scheme; process (ii)], the complex (II) of the unsymmetrically di-substituted pentalene did not, as expected, because a similar degenerate rearrangement is not possible.^{1,2} In contrast with (II), the symmetrically tri-substituted pentalene complex $[\text{Ru}_3(\text{CO})_8\{1,3,5-(\text{Me}_3\text{Si})_3\text{C}_8\text{H}_3\}]$ (III)³ is also fluxional, but with a free energy of activation ($9.2 \pm 0.2 \text{ kcal mol}^{-1}$) substantially less than that of (I) ($12.8 \pm 0.3 \text{ kcal mol}^{-1}$). In an attempt to understand this difference an *X*-ray diffraction study of (III) was undertaken. However, the crystal selected proved to be that of a minor isomer of (III), involving a new mode of co-ordination of a pentalene molecule to a metal cluster. Subsequent studies have established that this isomerism exists in general for $\text{Ru}_3(\text{CO})_8$ complexes of symmetrical pentalenes, and that in solution the two isomers are in equilibrium.

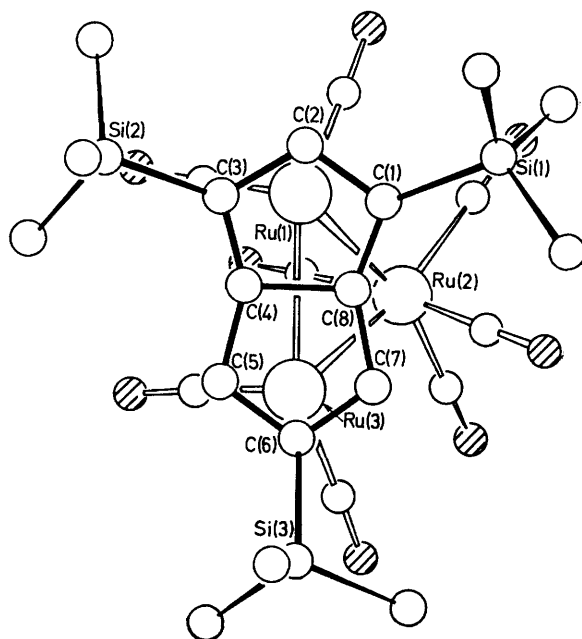
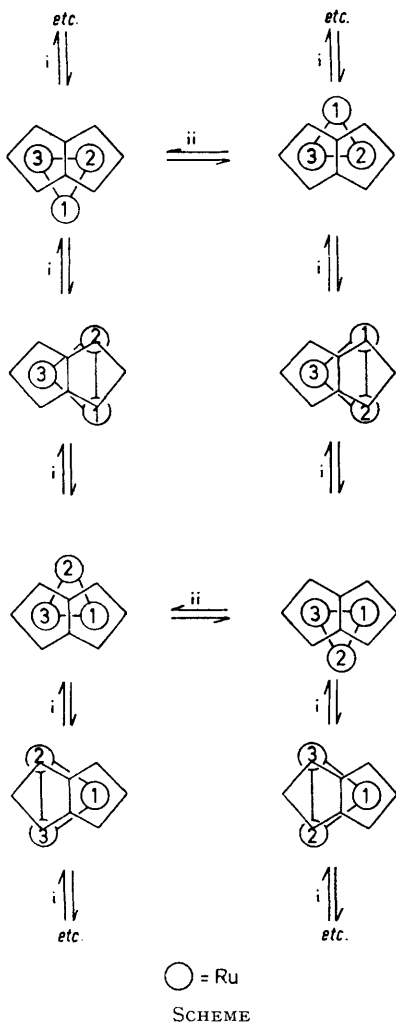


FIGURE 1. Molecular structure of (IIIa). $\text{Ru}(1)\text{-Ru}(2) = 2.827(1)$, $\text{Ru}(2)\text{-Ru}(3) = 2.810(1)$, $\text{Ru}(1)\text{-Ru}(3) = 2.933(1)$; Ru-C distances: $\text{C}(1\text{-}3)$ and $\text{C}(5\text{-}7) = 2.240(4)$; $\text{C}(4)\text{-C}(8) = 2.489(4)$; mean $\text{C-C} = 1.445(5)$ Å.

Crystallisation of a sample of $[\text{Ru}_3(\text{CO})_8\{1,3,5-(\text{Me}_3\text{Si})_3\text{-C}_8\text{H}_3\}]$ from hexane affords two kinds of crystal, which gave the same mass spectrum but had different i.r. spectra in the carbonyl stretching region [(IIIa), yellow prisms, m.p. 135°C (decomp.), $\nu_{\text{CO}}(\text{max})(\text{hexane})$ 2 087s, 2 028m,

2 012vs, 2 002s, 1 996w, 1 984w, 1 954m, and 1 943w cm^{-1} ; (IIIb), orange-red prisms, m.p. 135 °C (decomp.), $\nu_{\text{CO}}(\text{max})$ 2 072s, 2 037s, 2 001s, 1 993m, 1 975w, 1 969w, and 1 943w cm^{-1}].

When hexane solutions of either isomer were allowed to stand at room temperature for several minutes i.r. bands due to the other appeared, and ultimately an equilibrium mixture was obtained with the yellow form predominating. The ^1H n.m.r. spectrum (30 °C) of an equilibrium mixture revealed two sets of resonances; the more intense peaks are attributable to (IIIa) (87%) [τ (CDCl_3) 4.05 (1H, s), 6.53 (2H, s), 9.62 (9H, s), and 9.89 (18H, s)], and peaks of lower intensity to (IIIb) (13%) [τ 4.54(1H, s), 5.92 (2H, s), 9.70 (18H, s), and 9.78 (9H, s)]. Measurement of the change in equilibrium constant with temperature for (IIIa) \rightleftharpoons (IIIb) gave for this process $\Delta H^\circ = 0.9$ (± 0.1) kcal mol^{-1} and $\Delta S^\circ = 0.7$ (± 0.3) $\text{cal K}^{-1} \text{mol}^{-1}$. Single-crystal X-ray diffraction studies were undertaken for both isomers.

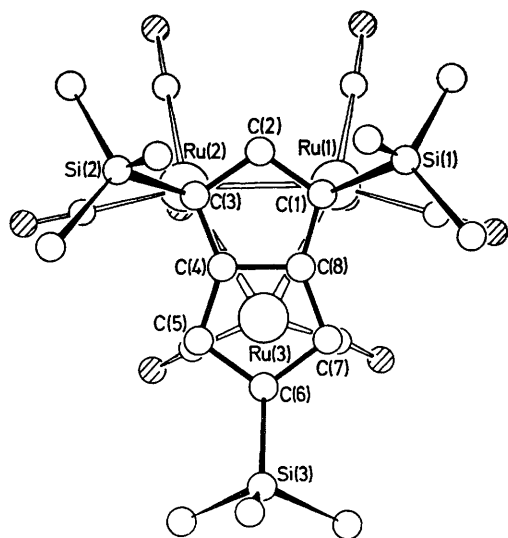


FIGURE 2. Molecular structure of (IIIb). Ru(1)–Ru(2) = 2.792(1), Ru(2)–Ru(3) = 2.861(1), Ru(1)–Ru(3) = 2.850(1); Ru(1)–C(1) = Ru(2)–C(3) = 2.255(7), C(2)–Ru(1) = C(2)–Ru(2) = 2.64; mean Ru(3)–C(4–8) = 2.236(6) Å; mean C–C = 1.444(5) Å.

Crystals of (IIIa) are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 16.264(13)$, $b = 9.023(6)$, $c = 22.769(16)$ Å, $\beta = 97.95(6)^\circ$. Those of (IIIb) are also monoclinic, $P2_1/n$, $Z = 4$, $a = 11.490(2)$, $b = 18.646(6)$, $c = 15.381(7)$ Å, $\beta = 91.04(3)^\circ$. The structures were solved [$R = 0.040$ for (IIIa); $R = 0.038$ for (IIIb)] by conventional heavy atom methods from data collected {to $2\theta = 60^\circ$ for (IIIa) with 8013 observed reflections measured at 160 K; and to $2\theta = 50^\circ$ for (IIIb) with 3795 observed reflections measured at 298 K [$I_{\text{obs}} \geq 2.5 \sigma(I_{\text{obs}})$] on a Syntex $P2_1$ four-circle diffractometer with monochromatised Mo- K_α X-radiation.

The molecular structures, without the hydrogen atoms, are shown in Figures 1 and 2.

The fluxional isomer (IIIa) has the expected geometry, based on earlier studies,¹ with an asymmetric Ru_3 triangle bridged on the longest edge by the tris(trimethylsilyl)pentalene ligand. The mean plane of the latter is inclined at 51° to the Ru_3 plane, a result similar to that found for (I) despite the different activation energies of their fluxional motions.

Isomer (IIIb) has (Figure 2) both a different mode of attachment for the pentalene ligand and a different distribution of carbonyl groups from that seen previously. The C_8 -unit lies almost parallel to and effectively spans the ruthenium triangle, being η^5 -bonded to Ru(3) which carries only two CO groups, and η^1 -bonded to Ru(1) and Ru(2) through C(1) and C(3), respectively. Atoms Ru(1) and Ru(2) each carry three carbonyl groups, and are weakly bridged by C(2) from which they are equi-distant at 2.64 Å. The overall geometry of the pentalene is preserved but shows some slight changes in bond lengths and angles relative to (IIIa), necessary to accommodate the different bonding mode. Atom Si(3) attached to C(6) is effectively coplanar with the mean C_8 plane, whereas Si(1) and Si(2) are approximately 1 Å out of this plane away from the ruthenium triangle.

Revelation of this new mode of attachment of the pentalene ligand, and the facile equilibrium (IIIa) \rightleftharpoons (IIIb), led to a study of the spectra of several complexes in which substituted pentalenes are bonded to an $\text{Ru}_3(\text{CO})_8$ unit. It was found that though complexes [$\text{Ru}_3(\text{CO})_8\{2\text{-RC}_8\text{H}_5\}$] ($R = \text{H, Me, Ph, SiMe}_3$) of symmetrical pentalenes are predominantly edge-bonded, they have in their i.r. spectra low-intensity bands corresponding to face-bonded species. The ^1H n.m.r. spectra also revealed groups of low-intensity resonances attributable to isomers similar to (IIIb). Variable-temperature studies gave for (Ia) \rightleftharpoons (Ib), $\Delta H^\circ = 0.7$ (± 0.1) kcal mol^{-1} and $\Delta S^\circ = -1.0$ (± 0.3) $\text{cal K}^{-1} \text{mol}^{-1}$, and for the two isomers of [$\text{Ru}_3(\text{CO})_8\{2\text{-Me}_3\text{SiC}_8\text{H}_5\}$] $\Delta H^\circ = 0.6$ (± 0.1) kcal mol^{-1} and $\Delta S^\circ = -2.0$ (± 0.3) $\text{cal K}^{-1} \text{mol}^{-1}$.

These novel isomerisations are remarkable in requiring the shift of a hydrocarbon ligand from the edge of a metal cluster to a face (and *vice-versa*) with simultaneous carbonyl group migration between ruthenium atoms. For [$\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_6)$] a combination of the edge \rightleftharpoons face isomerisation (i) and the fluxional oscillation (ii) established for the edge-bonded isomer will allow the migration of the pentalene over *all* the faces and edges of the cluster (Scheme). For symmetrically substituted pentalenes the same scrambling is possible, though a more restricted motion is likely. It should be noted that the mobility of polyolefins on a metal surface may have features not unrelated to the behaviour described here.

We thank the S.R.C. for support.

(Received, 6th May 1976; Com. 498.)

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