

A Reversible Skeletal Rearrangement in a Metal Cluster Complex: the Formation and Characterisation by I.R. Spectroscopy and X-Ray Crystallography of $\text{Ru}_5\text{C}(\text{CO})_{15}\cdot\text{MeCN}$

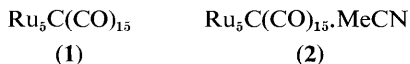
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The cluster complex $\text{Ru}_5\text{C}(\text{CO})_{15}$ reacts with acetonitrile to produce the adduct $\text{Ru}_5\text{C}(\text{CO})_{15}\cdot\text{MeCN}$ with a concomitant rearrangement of the Ru_5C unit from square-pyramidal to *arachno*-pentagonal bipyramidal geometry.

In a recent communication we reported¹ that the carbido-cluster $\text{Ru}_5\text{C}(\text{CO})_{15}$ (**1**) reacted with a variety of nucleophilic reagents (L) to produce 1 : 1 adducts of the type $\text{Ru}_5\text{C}(\text{CO})_{15}\text{L}$. In this communication we describe the formation and characterisation of one such adduct, *viz.*, $\text{Ru}_5\text{C}(\text{CO})_{15}\cdot\text{MeCN}$ (**2**), produced by the reaction of (**1**) with MeCN and which involves a rearrangement of the metal atom skeleton from a square-based pyramid to a bridged butterfly. Also described here are the details of an i.r. spectroscopic examination of (**2**) which clearly reveals the difference in the co-ordination about the carbon atoms in these two structures.



The square-pyramidal cluster (**1**) [$\nu_{\text{CO}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$: 2067s, 2034m, and 2015w] dissolves in acetonitrile to give an orange solution, the i.r. spectrum of which ($\nu_{\text{CO}}/\text{cm}^{-1}$: 2106w, 2068m, 2053vs, 2042m, 2021m, and 2010s) is indicative of a structural change, although it offers no specific information on the nature of the change. Rapid removal of the acetonitrile produces crystals of the adduct $\text{Ru}_5\text{C}(\text{CO})_{15}\cdot\text{MeCN}$ (**2**). The structure of the polycrystalline solid (**2**) was predicted by an examination of its i.r. spectrum, measured at ambient and liquid-nitrogen temperatures (Perkin-Elmer 325 spectrophotometer; CsI disc). The metal-carbido stretching i.r. absorptions for (**2**) were considerably different from those observed for the parent cluster (**1**), where the carbido atom occupies an exposed position capping the square face.¹ In contrast with the ruthenium-carbido stretching absorptions of (**1**), which occur in the 770–730 cm^{-1} region,² bands assigned to these modes are observed in the room-temperature spectrum of (**2**) at 817 s cm^{-1} and 674 m cm^{-1} , the higher-frequency band becoming asymmetric on cooling to *ca.* 95 K. The environment of the carbido atom in (**2**), as indicated by these Ru–C absorptions, is in fact closely analogous to the situation of the semi-interstitial carbido ligand in the derivatives $\text{HRu}_5\text{C}(\text{CO})_{15}\text{X}$, X = Cl, Br, which have been shown to possess the *arachno*-pentagonal bipyramidal (bridged butterfly) geometry² first recognised in the analogous osmium anion $[\text{Os}_5\text{C}(\text{CO})_{15}\text{I}]^-$ [ref. 3; *cf.* ν_{RuC} in $\text{HRu}_5\text{C}(\text{CO})_{15}\text{X}$ at 823 and 686 cm^{-1} , the former displaying a 5 cm^{-1} splitting at low temperature].² The C–N stretching mode of acetonitrile in (**2**) was observed (95 K spectrum) as a weak absorption at 2310 cm^{-1} , a frequency typical of linearly bonded MeCN.⁴ The i.r. data are thus consistent with (**2**) possessing the *arachno*-pentagonal bipyramidal structure, the MeCN ligand being presumed to co-ordinate to the unique ruthenium atom {*cf.* $[\text{Os}_5\text{C}(\text{CO})_{15}\text{I}]^-$ }.³

After the conclusion of the i.r. study a crystal suitable for X-ray structural analysis became available. The molecular structure of (**2**) is shown in Figure 1, along with some

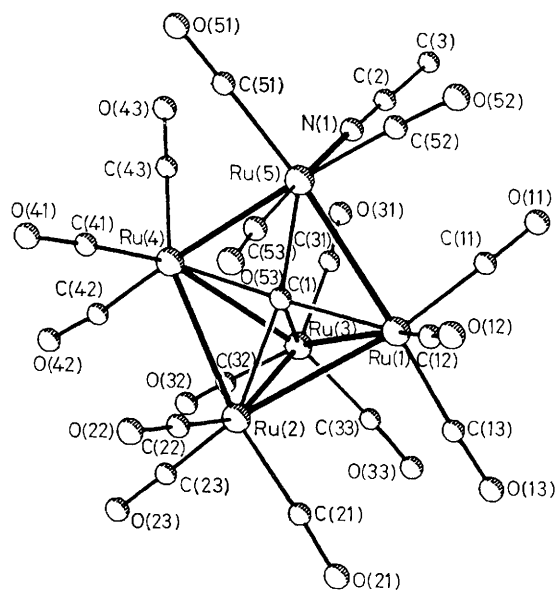


Figure 1. The molecular structure of (**2**). Important bond lengths: Ru(1)–Ru(2), 2.886(2); Ru(1)–Ru(3), 2.888(2); Ru(1)–Ru(5), 2.873(2); Ru(2)–Ru(3), 2.720(2); Ru(2)–Ru(4), 2.873(2); Ru(3)–Ru(4), 2.887(2); Ru(4)–Ru(5), 2.886(2); Ru(1)–C(1), 1.97(2); Ru(2)–C(1), 2.08(2); Ru(3)–C(1), 2.07(2); Ru(4)–C(1), 1.96(2); Ru(5)–C(1), 2.16(2); Ru(5)–N(1), 2.12(2); Ru(5)–C(53), 1.82(2) Å. Bond angles: Ru(5)–N(1)–C(2), 171(2); N(1)–C(2)–C(3), 178(2)°. Dihedral angle between planes Ru(1)Ru(2)Ru(3) and Ru(2)Ru(3)Ru(4) is 101(1)°.

important bond parameters.† The metal atoms Ru(1), Ru(2), Ru(3), and Ru(4) form a butterfly arrangement, with Ru(5) bridging the ‘wingtip’ atoms Ru(1) and Ru(4). The carbido atom is located above the centre of the Ru(2)–Ru(3) bond and is co-ordinated to all five ruthenium atoms. The acetonitrile ligand is bonded linearly to Ru(5), the shortness of the *trans* ruthenium-carbon bond being consistent with

† *Crystal data:* (**2**), $\text{C}_{18}\text{H}_3\text{NO}_{15}\text{Ru}_5$, $M = 978.56$, monoclinic, space group $P2_1/n$, $a = 14.116(6)$, $b = 18.167(7)$, $c = 10.276(4)$ Å, $\beta = 95.14(3)^\circ$, $U = 2624.6$ Å³, $Z = 4$, $D_c = 2.476$ g cm^{-3} , $F(000) = 1832$, graphite monochromated Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo}-K_\alpha) = 28.01$ cm^{-1} . Intensities were recorded on a Syntex $P2_1$ diffractometer to $2\theta_{\text{max}} = 45.0^\circ$ and were corrected for absorption. 1604 reflections [$F > 4\sigma(F)$] were used to solve (direct methods and Fourier difference techniques) the structure which was refined by blocked-cascade least squares (Ru, N, and O anisotropic, C isotropic, methyl H common isotropic) to $R = 0.047$ and $R_w = 0.039$. The atomic co-ordinates for (**2**) are available on request from the Director of the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

the weak π -acceptor character of this ligand. The geometry of (2) is generally similar to that of $[\text{Os}_5\text{C}(\text{CO})_{15}\text{I}]^-$.³ Exposed carbido atoms bonded to tetranuclear 'butterfly' metal clusters have been characterised for the species $[\text{Fe}_4(\mu\text{-H})\text{C}(\text{CO})_{12}]^-$ (ref. 5) and $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$ (ref. 6).

Donation of two electrons by the MeCN ligand brings about a change in the geometry of the Ru_5C unit; this change may be viewed as the result of the cleavage of one Ru-Ru bond in the square-based pyramidal structure of (1) to give one of the two possible cluster structures with seven metal-metal bonds, the *arachno*-pentagonal bipyramid. The ease with which this bond rearrangement may be reversed demonstrates the stability which a carbido atom may impart to the metal cluster whilst permitting considerable flexibility of the metal skeleton.

The formation of the adduct (2) also demonstrates how the choice of solvent for a particular reaction may be crucial in determining the nature of the substrate species and hence its reactivity. For example, hydrogenation of (1) proceeds differently in acetonitrile than in hydrocarbon solvents. It should be noted also that substitution of carbonyl groups in (1) by, for example, phosphines prevents its reaction with acetonitrile, indicating the delicate balance of factors dictating the stability of systems of this type.

Finally, we have demonstrated the successful prediction of cluster geometry in the adduct (2) by the application of vibrational spectroscopy, a technique which is especially useful in cases where crystals of the complexes suitable for X-ray structural analysis can be obtained only in favourable circumstances. The sensitivity of the metal-carbido stretch-

ing absorptions of metal cluster complexes containing either interstitial or exposed carbido atoms to cluster geometry has been noted now in a number of such systems.^{2,7,8}

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