Cluster Chemistry. Synthesis and *X*-Ray Structure of $[Ru_5(CO)_{14}(CNBu^t)_2]$, containing an Unusual Open Ru_5 Cluster

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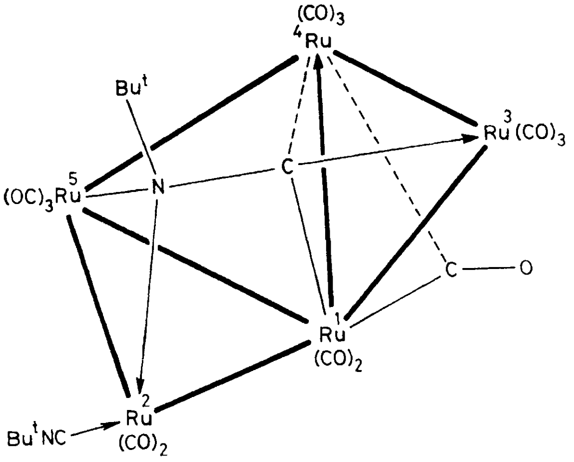
Summary Moderate heating converts $[Ru_3(CO)_{11}(CNBu^t)]$ into $[Ru_5(CO)_{14}(CNBu^t)_2]$, which has been shown by *X*-ray crystallography to contain an open 'swallow' cluster with one isocyanide ligand acting as a 6e donor, and bonded to all five metal atoms.

THERE is currently much interest in transformations of metal clusters, and in the extended interactions that are possible between unsaturated ligands and arrays of metal atoms, as an approach to the understanding of interactions of such molecules and metal surfaces, and hence of heterogeneously catalysed reactions. We report the formation of an unusual open five-atom cluster in which a μ_5-isocyanide ligand acts as a 6e donor.



(1)

Moderate heating of $[Ru_3(CO)_{11}(CNBu^t)]^1$ [for 16 h under nitrogen (*ca.* 0·5 atm), 120 °C] and purification by t.l.c. (Kieselgel G, light petroleum eluant) affords moderate yields of dark purple $[Ru_5(CO)_{14}(CNBu^t)_2]$ (**1**), which has been fully characterised by spectroscopic [molecular ion at *m/e* 1068; ν(CO) (cyclohexane) 2073w, 2044s, 2028m, 1999s, and 1995(sh); ν(CN) 2158vw cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$) 1·38 (s, CMe_3); ^{13}C n.m.r. δ($CDCl_3$) 29·4 (s, CMe_3), 30·3 (s, CMe_3), and 223·0 (s, CO) p.p.m.] and *X*-ray crystallographic techniques. In solution at ambient temperatures, all carbonyl groups are equivalent, while the two isocyanide ligands are distinguishable.

Crystal data: $C_{24}H_{18}N_2O_{14}Ru_5$, *M* 1063·8, monoclinic, space group $P2_1/c$; a = 10·598(2), b = 16·036(5), c = 19·159(8) Å, β = 93·11(2)°, U = 3251·3 Å^3; Z = 4, D_c = 2·188 g cm^{-3}; $F(000)$ = 1756e; μ(Mo-K_α) = 26·97 cm^{-1}.

The ruthenium atoms were located by direct methods using the SHELX system of programmes.[2] Successive difference Fourier syntheses revealed the remaining non-hydrogen atoms. All hydrogen atom positions were calculated geometrically (C–H = 0·965 Å). The methyl groups of the $CNBu^t$ ligand co-ordinated to Ru(2) are disordered. The structure was refined by block-matrix least-squares techniques using unit weights to give a final residual R of 0·0227 for 2948 independent reflexions [$I \geqslant 2·5\,\sigma(I)$, $1·5° \leqslant \theta \leqslant 20°$, Enraf-Nonius CAD-4 diffractometer].†

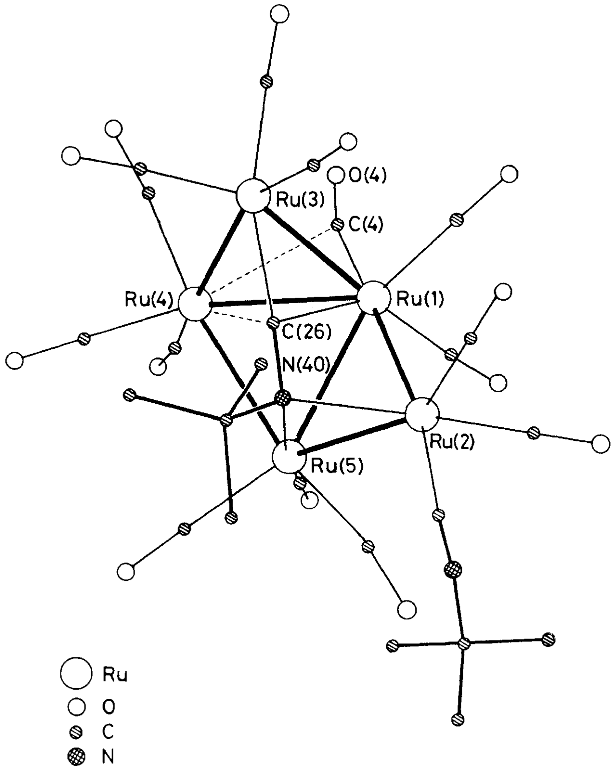


FIGURE. PLUTO[3] plot of the structure of $[Ru_5(CO)_{14}(CNBu^t)_2]$. Important bond distances and angles: Ru(1)–Ru(2), 2·784(1); Ru(1)–Ru(3), 2·833(1); Ru(1)–Ru(4), 2·776(1); Ru(1)–Ru(5), 2·778(1); Ru(2)–Ru(5), 2·745(1); Ru(3)–Ru(4), 2·767(1); Ru(4)–Ru(5), 2·864(1), Ru(1)–C(4), 1·898(7); Ru(1)–C(26), 2·156(5); Ru(3)–C(26), 1·923(7); Ru(4)–C(4), 2·653; Ru(2)–N(40), 2·128(4); Ru(5)–N(40) 2·151(1); C(26)–N(40), 1·375(8) Å; Ru(1)–C(4)–O(4), 164·5(6)°.

The molecular structure of complex (**1**) is shown in the Figure, which also includes selected bond distances and angles. There are a number of features of unusual interest in this molecule. Firstly, the five metal atoms form an open array of three edge-joined triangles, bent at these edges to form a swallow-shaped cluster, with Ru–Ru distances in the range 2·74—2·86 Å. Each metal atom is attached to three terminal 2e donor ligands (14 CO groups and one $CNBu^t$ ligand).

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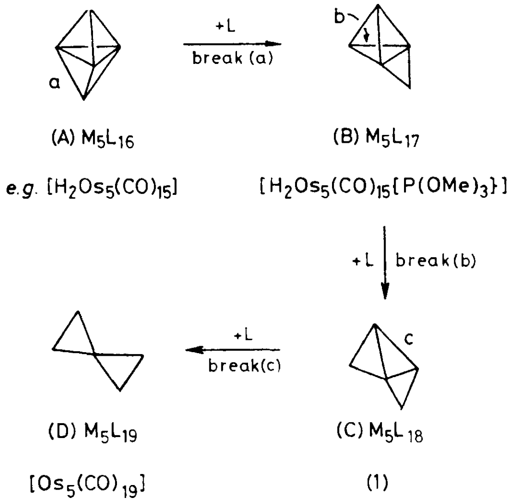
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The attachment of the second isocyanide ligand is also noteworthy. The cluster electron count requires that this ligand should act as a 6e donor if the cluster is electron-precise, and this unprecedented situation is achieved, formally at least, by N(40) acting as a 3e bridging atom to Ru(2)–Ru(5), while C(26) interacts with Ru(1) and Ru(3), also as a 3e donor. The C(26)–N(40) bond length [1·375(8) Å] and the Bu^t–N–C angle [122·2(5)°] are consistent with a reduction of the CN bond order.

This formal electron book-keeping results in Ru(4) being electron-deficient and Ru(1) electron-rich. However, if the interaction between these two metals takes the form of a donor bond from Ru(1) to Ru(4), this anomaly is removed. This interpretation is also supported by the geometry of the Ru(1)–C(4)–Ru(4) and Ru(1)–C(26)–Ru(4) interactions. Although the Ru(4)–C(4) and Ru(4)–C(26) distances are too long to be considered single bonds, the angles subtended by the two metal atoms at these carbon atoms [75·1(2) and 72·9°, respectively] show that they can be considered to be new examples of *semibridging* interactions. Their function is to allow a redistribution of electron density over this part of the cluster.[4]

This metal cluster is related to the *closo*-polyhedron (A) found in [$Os_5(CO)_{16}$][5] and [$H_2Os_5(CO)_{15}$];[6] the latter is known to react with $P(OMe)_3$ to give an adduct with an edge-bridged tetrahedron (B),[7] while the former affords [$Os_5(CO)_{19}$] with the open cluster (D) by direct reaction with CO.[8] Complex (**1**) occupies an intermediate position, and completes a series of M_5 clusters (A)—(D) formally related by successive addition of 2e donor ligands and concomitant cleavage of one 2e metal–metal bond (Scheme).

The Ru–Ru bond distances are distributed into two groups of five between 2·745 and 2·784 Å, and two considerably longer bonds of 2·833 and 2·864 Å. The former are in the range found for Ru–Ru bonds in [$Ru_3(CO)_{12}$] or [$Ru_3(CO)_{11}$(CNBu^t)],[1] the shortest of these being the result of the presence of the μ-NBu^t group. The lengthening of the Ru(1)–Ru(3) and Ru(4)–Ru(5) bonds recalls the situation in [$Os_5(CO)_{16}$], where bonds to the unique $Os(CO)_4$ group are longer than the other Os–Os bonds; however, in the present case, there is no such obvious explanation.



Scheme

We note that pyrolysis of [$Os_3(CO)_{11}$(CNBu^t)] affords [$Os_6(CO)_{16}$(CNBu^t)$_2$], which has the same metal skeleton as [$Os_6(CO)_{18}$]; in contrast, addition of isocyanide to the latter affords the adduct [$Os_6(CO)_{18}(CNR)_2$], in which the μ_2-CNR ligand acts as a 4e donor, with a rearranged metal skeleton.[9]

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