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Preliminary communication

CLUSTER CHEMISTRY. PARTIAL HYDROGENATION OF COORDINATED ISOCYANIDE ON A RUTHENIUM CLUSTER CARBONYL.

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Summary. Addition of dihydrogen to $Ru_3(CO)_{11}(CNBu^t)$ affords $HRu_3(CO)_9(HC{:}NBu^t)$ as the major product; this complex and four other minor products were identified from their IR, NMR and mass spectra.

In a remarkably facile reaction, dihydrogen reacts directly with $Ru_3(CO)_{12}$ in a boiling hydrocarbon solvent at *ca.* 120° to give $H_4Ru_4(CO)_{12}$ in high yield.[1] There have been few reported extensions of this reaction other than those mentioned in the original account, although it is an important example of the activation of molecular hydrogen by metal cluster complexes.

We have studied the reaction of dihydrogen with $Ru_3(CO)_{12}(CNBu^t)$, which occurs under somewhat milder conditions than those employed for $Ru_3(CO)_{12}$. For example, a reaction carried out in refluxing cyclohexane for 90 minutes under dihydrogen (1 atm.) afforded five products in a combined yield of *ca.* 80%, which have been separated by extensive

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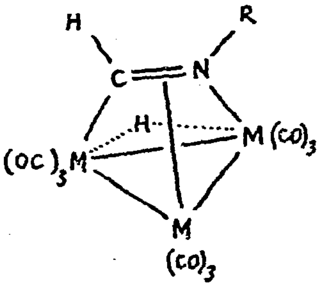
chromatography on Florisil. Three minor products were readily identified as the tetranuclear hydrido complexes $H_4Ru_4(CO)_{12-n}(CNBu^t)_n$ (n = 0-2) by comparison of their IR, ^1H NMR and mass spectra with those of authentic samples.[1,2]

The major product isolated from this reaction formed yellow plates, m.p. *ca.* 100° (dec.), with ν(CO) at 2093m, 2067s, 2038s, 2020s, 1998s, 1995m and 1986m cm^{-1}, which were identified as $HRu_3(CO)_9(HC{:}NBu^t)$ from the following evidence. The IR spectrum does not contain any ν(CN) absorption between 2100-2200 cm^{-1}, and resonances in the ^1H NMR spectrum occur at τ 0.55s (1,C*H*), 8.84s (9,C*Me*$_3$) and 28.01s (1,Ru*H*). The mass spectrum contains 13 ion clusters between *m/e* 305-642, the highest ion cluster and microanalyses (C,H,N) confirming the molecular formula.

Consideration of possible structures for this complex suggested that (I) represents the best arrangement of non-hydrogen atoms which accords with the spectroscopic evidence. A formimidoyl ligand is bonded to all three metal atoms, acting as a 4e (2σ + π) donor; the absence of a ν(CN) band, and the lowest field ^1H resonance are both consistent with the presence of this ligand. The metal-bonded hydrogen must occupy a bridging position (chemical shift), but this cannot be determined at present. An analogous osmium complex, $HOs_3(CO)_9(HC{:}NPh)$ (II) with similar spectral properties, has recently been structurally characterised.[3]

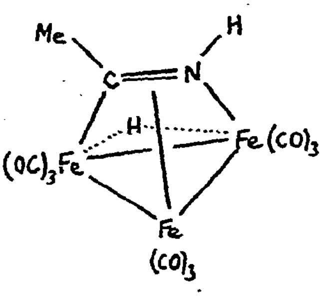
The fifth complex, obtained in very small amount, was shown to be $HRu_3(CO)_8(CNBu^t)(HC{:}NBu^t)$ [ν(CN), 2162w; ν(CO), 2075m, 2072m, 2053vw, 2033s, 2013vs, 1996m, 1992s, 1985m, 1971w, 1963w cm^{-1}; ^1H NMR: τ 0.54s (C*H*), 8.50s, 8.86s (C*Me*), 27.69s (Ru*H*); parent ion cluster centred on *m/e* 697], formally derived from (I) by replacement of a CO group by the isocyanide ligand.

Our results are of interest in relation to the homogeneous reduction of heteronuclear triple bonds. The formation of formimidoyl ligands from isocyanide has been reported in the case of the osmium complex (II) mentioned above, the formation of which is suggested to proceed via an insertion-rearrangement reaction. The stepwise reduction of acetonitrile



(I) $M = Ru$, $R = Bu^t$

(II) $M = Os$, $R = Ph$



(III)

on an Fe_3 cluster has been demonstrated, via (III) as one of the characterised intermediates.[4] Thus examples of partial hydrogenation of the C≡N bond by addition of isocyanide (or nitrile) to a metal hydride, or of dihydrogen to a coordinated isocyanide, have now been described; there is also one report of formation of a similar ligand from a saturated ligand (NMe_3) on $Os_3(CO)_{12}$.[5]

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