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**Preliminary communication**

# CLUSTER CHEMISTRY. ISOCYANIDE COMPLEXES OF RUTHENIUM AND HYDRIDORUTHENIUM CARBONYLS: CRYSTAL AND MOLECULAR STRUCTURE OF $Ru_3(CO)_{11}(CNBu\text{-}t)$

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## Summary

Reactions between t-BuNC and $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ afford $Ru_3(CO)_{12-n}(CNBu\text{-}t)_n$ ($n = 1$, 2 or 3) and $H_4Ru_4(CO)_{12-n}(CNBu\text{-}t)_n$ ($n = 1$, 2 or 4), respectively; an X-ray diffraction study of the molecular structure of $Ru_3(CO)_{11}(CNBu\text{-}t)$ shows the isocyanide ligand to occupy an axial position, while from the $^{13}C$ NMR spectrum, all CO groups are equivalent at low temperatures.

Monosubstituted derivatives of the trinuclear ruthenium carbonyl, $Ru_3(CO)_{12}$, are not readily obtained, although complexes such as $Ru_3(CO)_{11}L$ ($L = PR_3$ or $CNEt(CH_2)_2NEt$[LEt]) have been isolated from reactions between the carbonyl and $Pt(PR_3)_4$ [1] or the electron-rich olefin, $[LEt]_2$ [2], respectively. In contrast, we now report that $Ru_3(CO)_{12}$ reacts under mild conditions with t-butyl isocyanide to give $Ru_3(CO)_{11}(CNBu\text{-}t)$ (I) as dark red plate-like crystals, m.p. 114–116°C. The complex has $\nu(CO)$ absorptions at 2093w, 2047s, 2040s, 2016m, 1998m and 1995m $cm^{-1}$, and $\nu(CN)$ at 2170 $cm^{-1}$. The $^1H$ NMR spectrum contains only a sharp singlet at $\tau$ 8.47 ppm ($C\underline{Me}_3$), while in the $^{13}C$ NMR spectrum, signals at $\delta$ 30.1 and 59.0 ppm can be assigned to the alkyl group carbons, the eleven CO groups resonating as a singlet at 201.1 ppm. The latter signal remains unresolved at temperatures as low as −100°C, and this behaviour is similar to that of $Ru_3(CO)_{12}$, which also shows only one CO resonance at the lowest temperature studied (−100°C), at 198.9 ppm [3].

The crystal and molecular structures of I have been determined from a single crystal X-ray diffraction study*, and the molecular structure is shown in Fig. 1 together with some relevant bond lengths. The average Ru—Ru distance of 2.854(2) Å compares favourably with that found in $Ru_3(CO)_{12}$, 2.8515(4) Å [4]. The isocyanide ligand occupies an axial position on one of the ruthenium atoms with an Ru—C(isocyanide) distance of 1.99(2) Å.

The carbonyls on any two $Ru(CO)_4$ units, in $Ru_3(CO)_{12}$, are in an eclipsed arrangement when viewed along an Ru—Ru bond. However in the isocyanide complex I the ligands adopt a partially staggered configuration (Fig. 1 and 2). This distortion can be derived from the $Ru_3(CO)_{12}$ structure by twisting each $Ru(CO)_4$ group in turn and in the same direction about the bisectors of the internal angles of the $Ru_3$ triangle. The twisting, which could be considered to be the first stage of a rotation similar to that proposed by Cotton and Troup as a pathway for complete scrambling of all CO groups in $Fe_3(CO)_{12}$ [5], results in a distortion of the ligand polyhedron from the twinned cuboctahedron of $Ru_3(CO)_{12}$ towards an icosahedral arrangement. In view of the fluxional behaviour in solution, it is likely that the solid state conformation represents a shallow energy minimum stabilised by crystal packing forces.

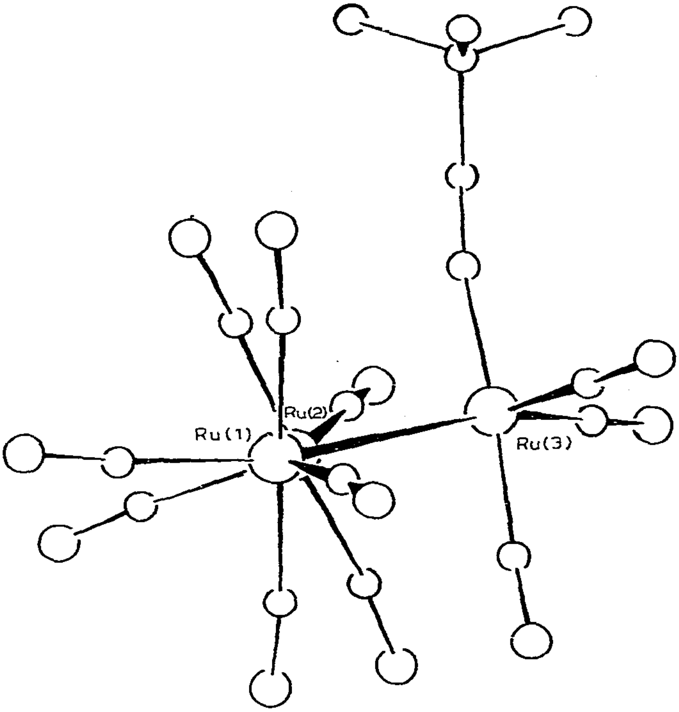

Fig. 1. Molecular structure of $Ru_3(CO)_{11}(CNBu\text{-}t)$. Bond lengths (Å), e.s.d. in parentheses: Ru(1)—Ru(2) 2.866(2), Ru(1)—Ru(3) 2.853(2), Ru(2)—Ru(3) 2.844(3), Ru(3)—C(1) 1.99(2), C(1)—N 1.16(3), Ru—CO 1.84—1.93(3), C—O 1.11—1.19(4).

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*Crystal data: Space group $P2_1/c$, $a$ 11.922(3), $b$ 12.064(5), $c$ 16.597(5) Å, $\beta$ 67.21(2)°, $D_c$ 2.07 g cm$^{-3}$ for $Z = 4$, Mo-$K_\alpha$ radiation (Nb filter), $R$ = 0.058 for 1969 independent reflections. The crystal structure is disordered to the extent that ~ 10% of the molecules have been rotated through 180° about an axis perpendicular to and passing through the centre of the $Ru_3$ triangle. Mays and Gavens [8] were unable to refine the structure of a sample of $Ru_3(CO)_{11}(CNBu\text{-}t)$ which they had prepared because of the disorder.

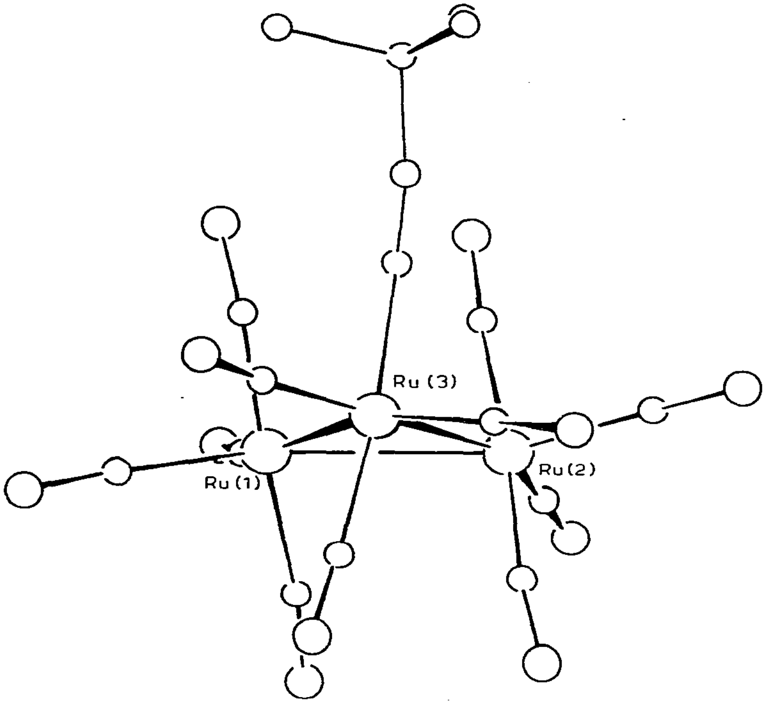

Fig. 2.

Substitution of a second CO by t-BuNC was achieved using excess isocyanide under similar conditions, when $Ru_3(CO)_{10}(CNBu\text{-}t)_2$ [dark red crystals, m.p. 90–91°C, $\nu$(CO) 2065w, 2020s, 2007m, 1996w, 1990m and 1986m cm$^{-1}$; $\nu$(CN) 2155 cm$^{-1}$; $^1$H NMR $\tau$ 8.48s ppm, (C$\underline{Me}_3$); $^{13}$C NMR $\delta$ 30.2 (Me), 58.3 ($\underline{C}Me_3$), 144.1 ($\underline{C}$NBu-t) and 204.1 ppm (CO)] could be isolated. Other isocyanides RNC (e.g. R = cyclohexyl, $p$-$MeC_6H_4SO_2CH_2$, $p$-$MeOC_6H_4$) react similarly.

The cluster hydride also reacts readily with t-BuNC affording the complexes $H_4Ru_4(CO)_{12-n}(CNBu\text{-}t)_n$ ($n = 1$: $\nu$(CO) 2093w, 2067s, 2059vs, 2032vs, 2012s, 2004m, 1995w, 1992w, 1987w cm$^{-1}$; $\nu$(CN) 2168m cm$^{-1}$; $^1$H NMR $\tau$ 8.49s (C$\underline{Me}_3$), 28.0s (Ru$\underline{H}$) ppm; $n = 2$: $\nu$(CO) 2077m, 2071w, 2048s, 2023vs, 2012s, 1996s, 1988m, 1975s cm$^{-1}$; $\nu$(CN) 2156m cm$^{-1}$; $^1$H NMR $\tau$ 8.51s (C$\underline{Me}_3$), 27.7, 28.2 (Ru$\underline{H}$) ppm; $n = 4$: $\nu$(CO) 1990vs, 1973s, 1958s, 1944m cm$^{-1}$, $\nu$(CN) 2142s cm$^{-1}$). As found with derivatives of $Ru_3(CO)_{12}$ with a higher t-BuNC=Ru ratio, the tetrasubstituted complex is markedly air-sensitive, and decomposes rapidly in solution.

Mays and Gavens [6] have reported the preparation of similar osmium carbonyl complexes, and have described their facile condensation to isocyanide-substituted $Os_6$ cluster carbonyls; the structure of $Os_6(CO)_{16}(CNBu\text{-}t)_2$, obtained in this way, has been determined [7]. Thermal decomposition of $Ru_3(CO)_{11}(CNBu\text{-}t)$ in an inert solvent (cyclohexane at 80°C) affords two air-sensitive, purple complexes which from mass spectrometric evidence contain $Ru_5$ and $Ru_6$ clusters.

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## References

1 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc. Dalton, (1972) 2094.
2 M.F. Lappert and P.L. Pye, J. Chem. Soc. Dalton, (1977) 2172.
3 L. Milone, S. Aime, E.W. Randall and E. Rosenberg, J. Chem. Soc. Chem. Commun., (1975) 452.
4 M.R. Churchill, F.J. Hollander and J.P. Hutchinson, Inorg. Chem., 16 (1977) 2655.
5 F.A. Cotton and M.J. Troup, J. Amer. Chem. Soc., 96 (1974) 4155.
6 M.J. Mays and P.D. Gavens, J. Organometal. Chem., 124 (1977) C37.
7 C.R. Eady, P.D. Gavens, B.F.G. Johnson, J. Lewis, M.C. Malatesta, M.J. Mays, A.G. Orpen, A.V. Rivera, G.M. Sheldrick and M.B. Hursthouse, J. Organometal. Chem., 149 (1978) C43.
8 M.J. Mays and P.D. Gavens, personal communication.