Ligand Substitution of $Ru_3(CO)_{12}$ with 2,2′-Bipyridine (bipy). *X*-Ray Crystal Structure of $Ru_3(CO)_{10}(bipy)$

Tapani Venäläinen, Jouni Pursiainen, and Tapani A. Pakkanen

Department of Chemistry, University of Joensuu, SF-80101 Joensuu 10, Finland

The reaction of $Ru_3(CO)_{12}$ with 2,2′-bipyridine (bipy) in hexane gives in high yield $Ru_3(CO)_{10}(bipy)$, containing two asymmetrically bridging carbonyl groups *trans* to the perpendicularly co-ordinated bipyridine ligand.

2,2′-Bipyridine (bipy) is a common ligand in metal complexes,[1] one of the most studied bipyridine complexes being $Ru(bipy)_3{}^{2+}$ which has interesting photocatalytic properties.[2] On the other hand transition metal clusters have been shown to form catalytically active precursors in C_1-chemistry.[3] The chemistry and catalytic properties of bipyridine substituted clusters have not been developed extensively, and only a few examples are available. The $Ru_3(CO)_{12}$–bipyridine mixture acts as a catalyst precursor for the reduction of nitrobenzene to aniline with good conversion,[4] but the nature of catalytically active species is not known. While $Ru_3(CO)_{10}(bipy)$ has been synthesized and a structure with three bridging carbonyls has been suggested,[5] $HOs_3(CO)_9(bipy)$ remains the only structurally characterized cluster containing bipy;[6] spectroscopic evidence is available for $Rh_6(CO)_{14}(bipy)_2$.[7] We report here a high yield synthesis and the crystal structure of $Ru_3(CO)_{10}(bipy)$.†‡

We have previously described the disubstitution by triphenylphosphine of the mixed-metal cluster $FeRu_2(CO)_{12}$ which leads to semibridged carbonyls.[8] Ligand substitution by phosphine and phosphite on $Ru_3(CO)_{12}$ does not cause any tendency to bridging,[9] whereas substitution by the nitrogen-containing ligands 1,2-diazine and bipy does. $Ru_3(CO)_{10}$(1,2-diazine) has three equatorial bridged carbonyls and the ligand is above the metal plane bonded axially by nitrogen atoms to different ruthenium atoms.[10]

The structure of $Ru_3(CO)_{10}(bipy)$ is shown in Figure 1. The ligand substitution occurs perpendicular to the metal triangle leading to the formation of two carbonyl bridges. The excess electron density arising from donation from the basic ligand is balanced by the unsymmetrical bridging carbonyl groups. The bridged Ru–Ru distance (2.758 Å) is shorter than the others (2.824 and 2.849 Å). The structure of $HOs_3(CO)_9(bipy)$ is totally different with the bipyridine ligand above the metal plane and co-ordinated with one Os–C and two N–Os bonds.

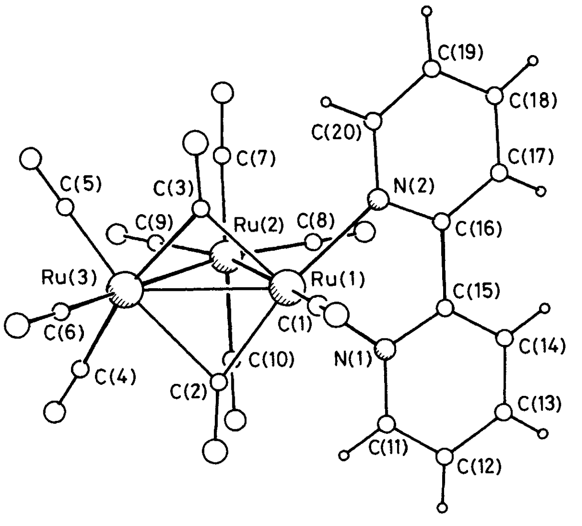

Figure 1. The molecular structure of $Ru_3(CO)_{10}(bipy)$. Selected bond lengths: Ru(1)–Ru(2) 2.849, Ru(1)–Ru(3) 2.758(1), Ru(2)–Ru(3) 2.824(1), Ru(1)–N(2) 2.177(4), Ru(1)–C(2) 2.027(5), Ru(3)–C(2) 2.112(5), Ru(1)–C(3) 1.961(5), and Ru(3)–C(3) 2.240(5) Å.

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† 2,2′-Bipyridine (0.31 mmol) and $Ru_3(CO)_{12}$(0.31 mmol) in refluxing n-hexane gave after 30 min a reddish precipitate which was filtered off. The orange air-stable product (ν_{CO} 2075m, 2060w, 2033vs, 2000vs, 1995vs, br, 1970m, and 1742w) was recrystallized at 0 °C from CH_2Cl_2 (total yield 90%).

‡ *Crystal data:* $C_{20}H_8O_{10}N_2Ru_3$, $M = 739.52$, monoclinic, space group $P2_1/n$, $a = 8.023(2)$, $b = 18.612(4)$, $c = 15.160(3)$ Å, $\beta = 95.50(2)°$, $U = 2253(1)$ Å^3, $F(000) = 1415$. 4401 intensities in the range $5° \leqslant 2\theta \leqslant 50°$ were recorded on a Nicolet R3m diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\ 69$ Å). 2882 absorption-corrected data with $I \geqslant 2.5\sigma(I)$ were used to locate all the non-hydrogen atoms by direct methods and Fourier synthesis. The hydrogen atoms were placed in idealized positions and refinement converged at $R = 0.0280$, $R_w = 0.0295$. 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 present structure is the first example of a fully characterized ruthenium–bipyridine cluster indicating that the chemistry of bipyridine clusters may be further developed and could lead to interesting catalytic systems.

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