Synthesis and Crystal Structure of (μ-H)$Ru_3(CO)_{10}$(μ-NH–CH_2Ph). An Example of Activation of the Carbon–Nitrogen Triple Bond

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The neutral complex (μ-H)$Ru_3(CO)_{10}$(μ-NH–CH_2Ph) was obtained by reductive co-ordination of benzonitrile to $Ru_3(CO)_{12}$ in the presence of acetic acid and its structure was elucidated by an *X*-ray analysis.

There has been considerable interest in the activation of the carbon–nitrogen triple bond, particularly for the catalytic hydrogenation of nitriles to amines, but also because of the analogy with the reduction of CO.[1] There are some reactions involving triple bonds which cannot be achieved using monometallic species but can be catalysed by transition metal clusters which permit a greater variety of interactions with the substrates.[2,3] For example, some iron carbonyl clusters,[4,5] $H_2Os_3(CO)_{10}$,[6,7] and $H_2Os_3(CO)_9PMe_2Ph$[6] have been reported to react with organic nitriles, but until now there have been no reports of the interaction of organic nitriles with neutral electronically saturated metal carbonyl clusters.

When a cyclohexane solution of $Ru_3(CO)_{12}$ and benzonitrile (molar ratio 1 : 5) was refluxed for 1 h in the presence of acetic acid, a number of compounds were formed, among which were $H_4Ru_4(CO)_{12}$ and two complexes formulated, by mass spectrometry, as $Ru_3(CO)_{10}$(L + 4H) (**1**) and $Ru_3(CO)_{10}$(L + 2H) (where L = benzonitrile).

(μ-H)$Ru_3(CO)_{10}$(μ-NH–CH_2Ph)
(**1**)

The dark yellow complex (**1**), obtained in 8—10% yield, was purified from the reaction mixture by t.l.c. and fully characterised by spectroscopy and by an *X*-ray analysis on crystals obtained from a concentrated hexane solution at −10 °C. Its i.r. spectrum in n-hexane shows absorption bands at 2100m, 2064vs, 2049vs, 2024vs, 2009s, 1999s, 1992m, 1980m, and 1965w cm^{-1}. The ^1H n.m.r. spectrum displays signals at τ 2.66 (5H), 4.95 (1H), 6.18 (2H), and 23.52 (1H); and the mass spectrum exhibits the molecular ion at m/z 693 which then loses all ten of its carbonyl groups.

Crystal data: $C_{17}H_9NO_{10}Ru_3$, $M = 690.47$, monoclinic, space group $P2_1/n$, $a = 11.547(6)$, $b = 20.185(9)$, $c = 9.407(5)$ Å, $\beta = 99.53(4)°$, $U = 2162(2)$ Å^3, $Z = 4$, $D_c = 2.121$ g cm^{-3}, $F(000) = 1320$, μ(Mo-K_α) = 20.82 cm^{-1}. The intensities of 4273 independent reflections were collected on

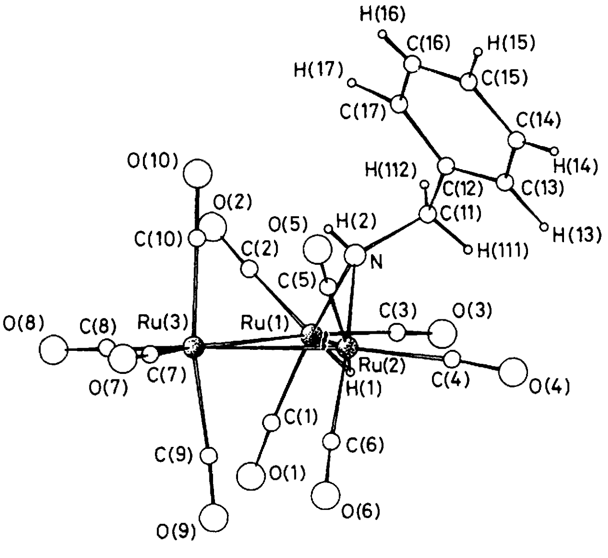

Figure 1. Molecular structure of the complex (μ-H)$Ru_3(CO)_{10}$-(μ-NH–CH_2Ph) (**1**). Important bond distances (Å) and bond angles (°): Ru(1)–Ru(2) 2.746(2), Ru(1)–Ru(3) 2.826(2), Ru(2)–Ru(3) 2.830(2), Ru(1)–N 2.088(5), Ru(2)–N 2.105(5), N–C(11) 1.483(8); Ru(2)–Ru(1)–Ru(3) 61.03(5), Ru(1)–Ru(2)–Ru(3) 60.90(5), Ru(1)–Ru(3)–Ru(2) 58.08(5), Ru(1)–N–Ru(2) 81.8(2), Ru(1)–N–C(11) 124.9(4), Ru(2)–N–C(11) 120.6(4).

a Siemens AED diffractometer (with θ in the range 3—26°), using Nb-filtered Mo-K_α radiation and the θ–2θ scan technique. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 3075 observed reflections having $I \geqslant 2\sigma(I)$ to an R value of 2.6%.†

The structure of (**1**) is shown in Figure 1 and significant bond distances and bond angles are given in the caption. The isosceles-triangular metal cluster is bonded to ten terminal carbonyl groups. The benzylamino ligand, formed by complete reduction of the benzonitrile triple bond with three hydrogen atoms, interacts with the cluster only through the nitrogen atom, which symmetrically bridges the shortest edge [Ru(1)–Ru(2)] of the metal triangle through two σ(N–Ru) bonds. The fourth hydrogen atom, gained by (**1**) through hydrogenation of the starting compound, is a hydride ligand bridging the same Ru(1)–Ru(2) edge of the cluster. The dihedral angles of the Ru(1)–H–Ru(2) and Ru(1)–N–Ru(2) planes with the metal triangle are 126.3 and 108.9°, respectively.

It is noteworthy that co-ordination of the benzonitrile to the well known and easily available neutral carbonyl cluster $Ru_3(CO)_{12}$ is accompanied by the addition of four hydrogen atoms; therefore, (**1**) may be considered as the closest precursor of benzylamine.

It must be stressed that the reaction between $Ru_3(CO)_{12}$ and benzonitrile is performed under mild reaction conditions and that the presence of the acid is necessary for the reaction to occur. On the contrary, $Fe_3(CO)_{12}$ reacts with benzonitrile both with or without acids to give $Fe_3(CO)_9L$ as previously described.[5] The same complex, though, is obtained in shorter reaction times when acetic acid is added.[8]

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8 Preliminary results, to be published.

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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 stucture factor table is available as Supplementary Publication No. SUP 23809 (18 pp.) from the British Library Lending Division. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, issue 3, p. xvii.