$[Ru_2(\mu\text{-}4\text{-}F\text{-}C_6H_4CO_2)_2(CO)_5H_2O]$: Molecular Structure and Catalytic Activity

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The X-ray structure of the title complex, prepared from $Ru_3(CO)_{12}$ and 4-fluorobenzoic acid, indicates a core structure of Ru–Ru–di-μ-carboxylato with side ligation of one water molecule. The title complex is catalytically reactive in the addition of the above acid to diphenylacetylene to give vinyl esters.

The identification of catalytically active species is fundamental to the understanding of homogeneous transition metal catalysis. In conjunction with our recent report on the catalytic addition reaction of carboxylic acids to acetylenes using $Ru_3(CO)_{12}$ as a pre-catalyst [1], a study of the chemistry of carboxylic acids and $Ru_3(CO)_{12}$ seemed important. This subject was investigated by the groups of Lewis [2] and Schumann [3], whose findings led to the discovery of three types of related bridged-Ru carboxylato complexes:

(a) $[(\mu\text{-}O_2CR)(CO)_2Ru]_n$—insoluble polymers

(b) $[(\mu\text{-}O_2CR)(CO)_3Ru]_2$—unstable dimers; readily polymerize

(c) $[(\mu\text{-}O_2CR)(CO)_2(L)Ru]_2$—stable dimers; L = phosphines, amines, arsines.

While hitherto only aliphatic carboxylic acids have been explored, it became necessary in connection with our catalysis investigation to study the interaction between $Ru_3(CO)_{12}$ and aromatic acids. Thus, the reaction between 4-fluorobenzoic acid and $Ru_3(CO)_{12}$ gives a yellow complex which analyzes for 1† (reaction 1).

$$4\text{-F-}C_6H_4CO_2H + Ru_3(CO)_{12} \longrightarrow [Ru_2(4\text{-F-}C_6H_4CO_2)_2(CO)_5H_2O]0.5C_6H_6 \quad (1)$$

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The IR spectrum of the crude product is very similar to that of type b complexes [2, 3]. However, crystallization from benzene gives 1 having now a different IR spectrum (KBr) 3580, 3320, 2090, 2030, 1998, 1935, 1605, 1550 and 1410 cm^{-1}. Complex 1 was found to be reactive in the catalytic addition reaction of 4-fluorobenzoic acid and diphenylacetylene [1]. A mixture of a α-(4-fluorobenzoyloxy) stilbene and 1,1-diphenyl-2-(4-fluorobenzoyloxy)ethylene, a rearranged product, was obtained. The induction period noted in the above reaction with $Ru_3(CO)_{12}$ was eliminated when 1 was used. However the molecular formula of 1 presents a structural ambiguity and an X-ray study was undertaken (Fig. 1).

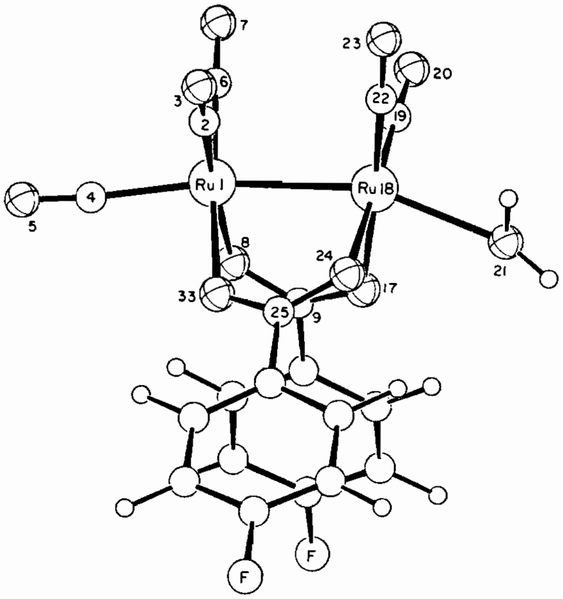

Fig. 1. Molecular structure of $[Ru_2(4\text{-F-}C_6H_4CO_2)_2(CO)_5\text{-}H_2O]$ (the crossed circles represent oxygen atoms). Selected bond lengths (Å) and angles (deg.) are: Ru(1)–Ru(18) = 2.649(2); Ru(1)–C(4) = 1.999(11); Ru(1)–O(8) = 2.119(6); Ru(18)–O(17) = 2.136(6); Ru(18)–O(21) = 2.299(6); Ru(18)–O(24) = 2.109(6); C(9)–O(17) = 1.271(10); C(25)–O(33) = 1.256(11); Ru(1)–C(2) = 1.883(11); Ru(1)–C(6) = 1.864(10); Ru(1)–O(33) = 2.113(6); Ru(18)–C(19) = 1.826(11); Ru(18)–C(22) = 1.831(11); C(9)–O(8) = 1.249(11); C(25)–O(24) = 1.267(11). C(4)–Ru(1)–Ru(18) = 171.1(3); Ru(1)–Ru(18)–O(21) = 159.8(2).

Crystal Data††

$[Ru_2(4\text{-F-}C_6H_4CO_2)_2(CO)_5H_2O]0.5C_6H_6$, M_r = 677.5: orthorhombic, space group *Pbcn* with a = 15.123(1), b = 15.646(11), c = 20.530(3) Å, $D_{calcd.}$ = 1.853 g cm^{-3} for $Z = 8$, $F(000) = 2648$; $\mu(MoK\alpha)$ = 12.86 cm^{-1}. Final anisotropic least-squares refinement of the non-hydrogen atoms converged at R = 0.045 and R_w = 0.050 for 2239 reflections with $I \geqslant 3\sigma(I)$ and $2\theta < 50°$. The diffraction intensities were measured on an Enraf-Nonius CAD4 diffractometer

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†Satisfactory elemental analysis was obtained.

††The atomic coordinates for this work are available on request from Prof. Y. Shvo.

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using graphite monochromatized MoKα radiation (λ = 0.7107 Å) and employing the $\omega-2\theta$ scan technique. An empirical method was used to correct the intensity data for absorption effects [4]. The structure was solved by phase refinement and weighted Fourier techniques using the MULTAN80 system of computer programs. The aromatic H-atoms were introduced in calculated positions; those of the H_2O ligand were found in difference maps, but are not entirely reliable.

The molecular structure has no internal symmetry. The coordination sphere around each one of the Ru atoms forms a distorted octahedron in a similar manner to that described by Schumann *et al.* [3], the two octahedra being differently oriented with respect to the Ru–Ru axis.

The crystal structure can be described as composed of layers of densely packed molecules of the complex that extend parallel to the (001) plane. Adjacent layers are separated by about 10 Å, their packing along the *c*-axis inducing channels that are occupied by benzene molecules (solvent of crystallization).

An infra-red study indicates that the primary product of reaction (1) is a complex of type b, $[Ru(\mu\text{-}4\text{-}F\text{-}C_6H_4CO_2)(CO)_3]_2$. However, it readily exchanges (on crystallization) one CO group with a water molecule and gives the stable complex **1**. The pronounced thermodynamic instability of complexes of type b with respect to c, or in the present case with respect to **1**, may be due to an excess of π-acid ligands (CO), which are bound to a metal in the (I) oxidation state. Nevertheless, unsymmetrical ligation around the Ru–Ru carboxylato core, such as displayed by **1** has not been previously observed in this class of complexes. However, Bianchi *et al.* [5] have recently reported a complex formulated as $Ru_2(CH_3CO_2)_2(CO)_5PBu_3$, which may have a molecular structure analogous to **1**.

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