The Synthesis and Structure of Tetra-μ-acetatodiruthenium(II,II)–Bis(tetrahydrofuran)

Alan J. Lindsay,[a] Robert P. Tooze,[a] Majid Motevalli,[b] Michael B. Hursthouse,[b] and Geoffrey Wilkinson[a]

[a] *Chemistry Department, Imperial College, London SW7 2AY, U.K.*
[b] *Chemistry Department, Queen Mary College, London E1 4NS, U.K.*

Interaction of $[Ru_2(O_2CMe)_4]Cl$ with Grignards acting as reducing agents in ethers has led to isolation of the yellow-brown complex $Ru_2(\mu\text{-}O_2CMe)_4{\cdot}(C_4H_8O)_2$ whose structure has been determined by *X*-ray crystallographic analysis; the complex is the first carboxylate with a Ru_2^{4+} core.

Since the discovery of the carboxylate complexes $[Ru_2(\mu\text{-}O_2CR)_4]Cl$[1] various studies[2—5] have shown that in solution such species, formally II/III, can be reduced in a one-electron reduction.[6] However, it has been remarked (ref. 6, p. 197, 377) that 'these (neutral) complexes have yet to be isolated in the solid state' and 'it is well established that neither oxidation nor reduction of $[Ru_2(\mu\text{-}O_2CR)_4]^+$ ions to give stable (or at least isolable) products is feasible under normal chemical conditions.' A yellow complex of stoicheiometry $Ru(O_2CMe)_2(PPh_3)$ was isolated from the reaction of $[Ru_2(\mu\text{-}O_2CMe)_4]Cl$ with PPh_3 in methanol[2] but the substance was too insoluble for molecular weight studies and no structural information was obtained.

We now report the formation of the air sensitive yellow-

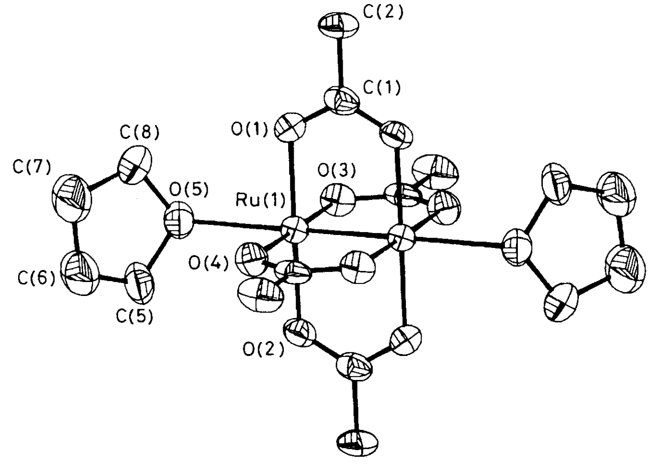

Figure 1. The molecular structure of tetra-μ-acetatodiruthenium(II) bis(tetrahydrofuran). Selected bond lengths are Ru–Ru, 2.260(2), Ru–O (acetate) 2.057(4)—2.064(5), Ru–O (tetrahydrofuran) 2.391(5) Å.

brown complex, $Ru_2(\mu\text{-}O_2CMe)_4\cdot(C_4H_8O)_2$, in the interaction of $[Ru_2(\mu\text{-}O_2CMe)_4]Cl$ with Grignard reagents such as Me_3SiCH_2MgCl in tetrahydrofuran (thf) or thf–Et_2O under reaction conditions similar to those employed in the preparation of Ru_2R_6 ($R = CH_2SiMe_3$, CH_2Bu^t)[7] but using only one equivalent of the Grignard, which merely acts as a soluble one-electron reducing agent. Although other reducing agents for $[Ru_2(\mu\text{-}O_2CMe)_4]Cl$ in organic solvents can be used, a more direct route to the Ru_2^{4+} species is the interaction of sodium acetate with the blue reduced ruthenium solutions in methanol.[8] This reaction gives the sparingly soluble methanol adduct which loses solvent on heating to give $Ru_2(\mu\text{-}O_2CMe)_4$.

These, and other carboxylate complexes have been fully characterised by elemental analyses and spectra. For the tetrahydrofuran adduct: mass spectrum (M^+ −2thf = 438), i.r. spectrum [$\nu_{asym.}(CO_2)$ 1560, $\nu_{sym.}$ (CO_2) 1440, $\Delta(\nu_{asym.}-\nu_{sym.})$ 120 cm^{-1} in Voltalef 3S mull], and electronic spectrum ($\lambda_{max.}$ 438 nm, ε 964 $dm^3\ mol^{-1}\ cm^{-1}$ in thf). No e.s.r. spectrum is observed in a 2-methyltetrahydrofuran glass at 77 K, although magnetic susceptibility measurements in the solid ($\mu_{eff.}$ 2.1 μ_B/Ru)[†] at 295 K and in 2% hexamethyldisiloxane–thf solution ($\mu_{eff.}$ 2.2 μ_B/Ru) at 305 K by Evans' method[9] confirm the paramagnetism. Electrochemical measurements in 0.2 M $Bu^n{}_4NPF_6$–thf at 295 K show that $Ru_2(\mu\text{-}O_2CMe)_4\cdot(C_4H_8O)_2$ undergoes a facile reversible one electron oxidation at +0.17 V;[‡] the comparable aquo ion, $[Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2]^+$ is known.[6]

The compound $Ru_2(\mu\text{-}O_2CMe)_4\cdot(C_4H_8O)_2$ has been structurally characterised by X-ray diffraction (Figure 1).[§] The Ru–Ru distance of 2.260(2) Å, which should formally correspond to a bond order of 2, lies between those found in the only other compounds containing the Ru_2^{4+} core, namely $Ru_2(hmp)_4\cdot CH_2Cl_2$ (hmpH = 2-hydroxy-6-methylpyridine) [2.238(1) Å][10] and Ru_2L_2 (L = tetra-aza[14]annulene), whose structure has not been fully reported by Goedken *et al.*,[11] [quoted to be 2.379(1) Å].[6] The Ru–Ru distance for $Ru_2(\mu\text{-}O_2CMe)_4\cdot(C_4H_8O)_2$ is slightly longer (*ca.* 0.012 Å) than that for its closest Ru_2^{5+} core analogue, $[Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2]BF_4$,[6] a result consistent with the former having one extra electron in a metal–metal antibonding orbital. The structural and magnetic data are thus in accord with the $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*3}$ electronic configuration proposed on the basis of an SCF-X_α-SW calculation for $Ru_2(\mu\text{-}O_2CH)_4$.[12]

Further in-depth synthetic, spectroscopic, and structural investigations are in progress on the carboxylate and related systems, as well as development of their reaction chemistry.

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[†] Non-S.I. units employed: μ_B = *ca.* 9.27×10^{-24} A m^2.

[‡] $E_{\frac{1}{2}}$ value is measured with respect to a saturated calomel reference electrode at which ferrocene is oxidised at +0.63 V.

[§] *Crystal data:* $C_{16}H_{28}O_{10}Ru_2$, M = 582.53, orthorhombic, space group *Pbcn*, a = 9.598(2), b = 15.803(3), c = 14.606(2) Å, U = 2215.4 $Å^3$, Z = 4, D_c = 1.746 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 12.67 cm^{-1}, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å. 1948 Unique intensity data measured, 1264 observed [$I > 2\sigma(I)$], R = 0.0296, non-hydrogen atoms anisotropic, hydrogens freely refined with isotropic refinement. 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.

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