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The acylation of an acyl complex resulting in a labile OCO tridentate ligand

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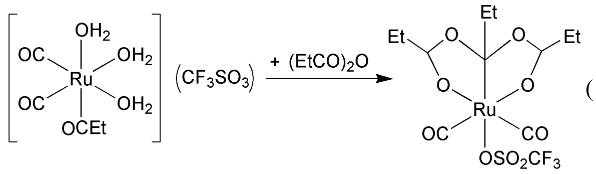
The reaction of propionic anhydride with [*fac*-Ru(C(O)Et)-$(CO)_2(H_2O)_3][CF_3SO_3]$ produces a new propylidin dipropionato group, which behaves as a tridentate ligand giving the neutral complex $Ru\{CEt(OC(O)Et)_2\}(CO)_2(CF_3SO_3)$.

The removal of coordinated H_2O from 18e organometallic aquo complexes may result in electronically and coordinatively unsaturated species, useful in synthetic chemistry and catalysis;[1] a variety of dehydrating agents can be used to induce coordinative unsaturation in a coordinatively saturated organometallic aquo complex. However, we found that the dehydration of the acyl aquo compound [*fac*-Ru(C(O)Et)$(CO)_2(H_2O)_3][CF_3SO_3]$ **1**[2] with propionic anhydride in propionic acid is accompanied by a remarkable addition of the anhydride onto the organometallic –C(O)Et group. A tridentate propylidin dipropionato ligand, unprecedented in the OCO combination of donor atoms, is thus formed. Two oxygen atoms of the tridentate ligand substitute two water molecules in the Ru(II) coordination sphere of **1**, the third water group being replaced by the triflate. Thus, the neutral complex $Ru\{CEt(OC(O)Et)_2\}(CO)_2(CF_3SO_3)$ **2** (ν_{CO} = 2073(s) and 2007(vs) cm^{-1}) is obtained in a quantitative yield†(eqn. (1)).



1 **2** (1)

The molecular structure‡ of **2** is shown in Fig 1. The coordination around ruthenium is distorted octahedral, the distortion being mainly due to the geometrical constraints acting in the two condensed ruthenadioxacyclopentane rings. The two pentagonal rings RuO(3)C(3)O(4)C(6) and Ru-C(6)O(5)C(9)O(6) are almost planar, the deviations from planarity being 0.114 and 0.054 Å, respectively. The dihedral angle between these two planes is 94.0°. The bite dimensions resulting from the use of three coordination sites are too small to achieve around Ru(II) the bond distances and angles required for an ideal octahedron. The tridentate ligand adopts a conformation that fulfils the usual Ru(OC(O)R) bond distance of 2.09 Å,[3] but produces a markedly short (2.033 Å) Ru–C(6) bond.[4] Moreover, the bond angles around the metal centre are severely distorted, as can be seen in Fig. 1, and the Ru–C(6) bond is bent towards the O(3) and O(6) atoms, the O(3)–Ru–C(6) and O(6)–Ru–C(6) angles being 79.3 and 80.0°, respectively. This strain anticipates the fragility and the lability of the tridentate ligand. Accordingly, **2**, which is sparingly soluble in propionic acid, dissolves as a non-electrolyte in tetrahydrofuran where it is converted back to **1** by an excess of water. On the other hand, under a CO atmosphere in anhydrous propionic acid, **2** is present in a P_{CO}-dependent equilibrium [eqn. (2)] with *mer*-$Ru\{CEt(OC(O)Et)_2\}(CO)_3(CF_3SO_3)$ **3**, the latter being characterized by IR absorptions at 2149(s), 2094(vs) and 2055(s) cm^{-1}.

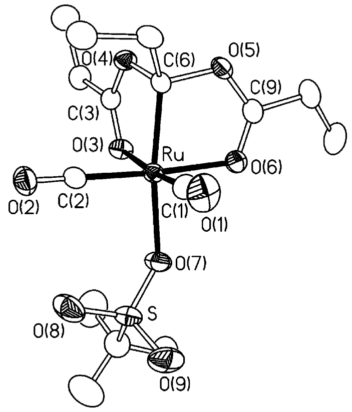


Fig. 1 View of the molecular structure of **1**. Ellipsoids are at 30% probability. Relevant bond distances (Å) and angles (°): Ru–C(1) 1.861(6), Ru–C(2) 1.868(4), Ru–C(6) 2.033(4), Ru–O(3) 2.111(3), Ru–O(6) 2.107(3), Ru–O(7) 2.176(3), C(2)–Ru–C(1) 88.2(2), C(2)–Ru–C(6) 96.4(2), C(1)–Ru–C(6) 94.4(2), C(2)–Ru–O(3) 91.2(2), C(1)–Ru–O(3) 173.6(2), C(6)–Ru–O(3) 79.3(2), C(2)–Ru–O(6) 175.9(2), C(1)–Ru–O(6) 94.0(2), C(6)–Ru–O(6) 80.0(2), O(3)–Ru–O(6) 86.2(1), C(2)–Ru–O(7) 96.9(2), C(1)–Ru–O(7) 98.2(2), C(6)–Ru–O(7) 162.0(2), O(3)–Ru–O(7) 88.3(1), O(6)–Ru–O(7) 86.2(1), C(3)–O(3)–Ru 111.7(3), O(3)–C(3)–O(4) 122.8(4), C(3)–O(4)–C(6) 115.6(3), O(4)–C(6)–Ru 107.7(3), C(9)–O(6)–Ru 112.5(3), O(6)–C(9)–O(5) 122.1(4), C(9)–O(5)–C(6) 117.3(3), O(5)–C(6)–Ru 107.4(3).

$$\underset{\mathbf{2}}{Ru\{CEt(OC(O)Et)_2\}(CO)_2(CF_3SO_3)} + CO \rightleftarrows \underset{\mathbf{3}}{mer\text{-}Ru\{CEt(OC(O)Et)_2\}(CO)_3(CF_3SO_3)} \quad (2)$$

On these grounds, **2** behaves as an unsaturated species, and its application as precursor in some catalytic reactions is being investigated.

The acylation here reported is similar to that converting aldehydes into 1,1′-diesters[5] but no examples of such an addition are known in organometallic chemistry. It constitutes a rare case[6] of an acyl group being modified while the C–M σ-bond is maintained. Such a transformation can activate an acyl to further carbonylation reaction[7] and constitutes an approach to a double carbonylation of alkyl complexes. In the field of catalytic reactions promoted by ruthenium carbonyls, the hydrogenation of carbon monoxide to C_2 products in anhydrous acetic acid[8] could reasonably consist of an activation to carbonylation *via* acylation of a formyl intermediate.

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Notes and references

† Compound **1**[2] (6.92 g, 16.6 mmol) was suspended, under an argon atmosphere, in 50 ml of anhydrous propionic acid containing 14 ml (108 mmol) of propionic anhydride. By warming at 65 °C a clean solution was obtained; upon addition of 100 ml of diethyl ether **2** was precipitated as colorless crystals. Yield: 7.49 g (91.6%). IR (Nujol mull): ν_{CO} 2073(s) and 2007(vs) cm^{-1}. ^1H NMR (200 MHz, THF-d_8): δ 2.75 (4H, q), 2.40 (2H, q), 1.2 (9H, t). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 192.62 (s), 188.09 (s), 144.36 (s), 119.31 (q), 38.77 (s), 26.42 (s), 8.95 (s), 8.69 (s). Anal. Calc. (found) for $C_{12}H_{15}F_3O_9RuS$: C, 29.21 (29.16); H, 3.04 (2.99); Ru, 20.49 (20.52)%.

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‡ *Crystallography*: for **2**: a colourless prism, slightly flattened on $(\bar{1}\ 0\ 1)$ of approximate dimensions $0.40 \times 0.36 \times 0.18$ mm was sealed in a glass capillary under a pure argon atmosphere, and the intensity data were collected on a Bruker P4 diffractometer using Mo-Kα graphite-monochromated radiation ($\lambda = 0.71073$ Å). Cell parameters were calculated on the accurately centred setting angles of 33 strong reflections with $5.3 \leqslant \theta \leqslant 12.6°$. *Crystal data*: $C_{12}H_{15}F_3O_9RuS$, $M_r = 493.37$, $T = 293(2)$ K, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.597(2)$, $b = 10.299(2)$, $c = 14.314(3)$ Å, $\beta = 101.64(1)°$, $V = 1818.9(6)$ Å^3, $Z = 4$, $D_c = 1.802$ g cm^{-3}, μ(Mo-Kα) = 1.048 mm^{-3}, $F(000) = 984$. The intensities of 4101 reflections with $2.4 \leqslant \theta \leqslant 25°$ were collected. After merging equivalent reflections and after correction for Lorentz, polarisation, and absorption effects with an empirical method,[9a] an internal R value $[\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma(F_o^2)]$ of 0.0467 was obtained.

The structure was solved by standard direct and Fourier methods and refined by full-matrix least-squares procedures. The hydrogen atoms were placed in calculated positions and allowed to ride on the connected carbon atoms. In the final refinement cycle anisotropic thermal parameters were used for all heavy atoms, giving a conventional R factor (F_o) of 0.0357, calculated for 236 parameters on 2367 observed reflections $[I > 2\sigma(I)]$ and a value of 0.0612 for all 3195 data. The residual peaks in the final difference Fourier map range between 0.79 and -0.47 e Å^{-3}. The calculations were performed *via* the SHELX97 program[9b] contained in the WINGX[9c] suite. CCDC reference number 170235. See http://www.rsc.org/suppdata/b1/b110259c/ for crystallographic files in .CIF or other electronic format.

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