

# Reactive intermediates from carbonylation of ruthenium(I) carbonyl carboxylates. Isolation, molecular structures and chemical properties of dinuclear unbridged ruthenium carbonyl trifluoroacetates

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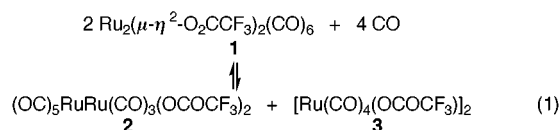
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Carboxylato-bridged Ru(I) carbonyl complexes are activated by CO towards both disproportionation and reaction with dihydrogen, through the intermediacy of the unbridged metal-metal bonded valence isomers  $(OC)_5RuRu(CO)_3(OCOFR_3)_2$  and  $[Ru(CO)_4(OCOFR_3)]_2$ .

Catalysis chemistry involving carboxylato-bridged Ru(I) carbonyl complexes of formula  $Ru_2(\mu-\eta^2-O_2CR)_2(CO)_6$  includes the acid-cocatalyzed water gas shift reaction<sup>1</sup> (WGS) and the related Reppe olefin carbonylation,<sup>2</sup> CO hydrogenation<sup>3</sup> and syngas homologation of aliphatic carboxylic acids.<sup>4</sup> Furthermore, in the presence of tertiary phosphines, carboxylato-bridged Ru(I) carbonyl complexes are used as catalytic precursors for the addition of carboxylic acids to alkynes,<sup>5</sup> the hydrogenation of carboxylic acids<sup>6</sup> and esters,<sup>7</sup> and the hydroformylation of alkenes.<sup>8</sup> Concerning the nature of the species promoting the activation of simple molecules and organic substrates in these catalytic processes, the present study highlights the unsaturation of  $Ru_2(\mu-\eta^2-O_2CR)_2(CO)_6$  complexes, vacant coordination sites being generated by the rearrangement of the bridging carboxylato ligands. Thus,  $Ru_2(\mu-\eta^2-O_2CCF_3)_2(CO)_6$  **1** was found to reversibly add two CO ligands yielding hitherto unknown dinuclear unbridged ruthenium carbonyl carboxylates. The rate of CO uptake is markedly affected by the medium: in toluene, forcing conditions (150 °C,  $P_{CO} = 120$  atm) are required to convert **1** to a nearly equimolar mixture of  $(OC)_5RuRu(CO)_3(OCOFR_3)_2$  **2** [ $\nu_{CO}$  (Nujol mull) 2173m, 2116s, 2102m, 2075s, 2053m and 2023m  $cm^{-1}$ ] and  $[Ru(CO)_4(OCOFR_3)]_2$  **3** [ $\nu_{CO}$  (Nujol mull) 2133s, 2093vs, 2077s and 2051s  $cm^{-1}$ ]<sup>†</sup> [eqn. (1)].

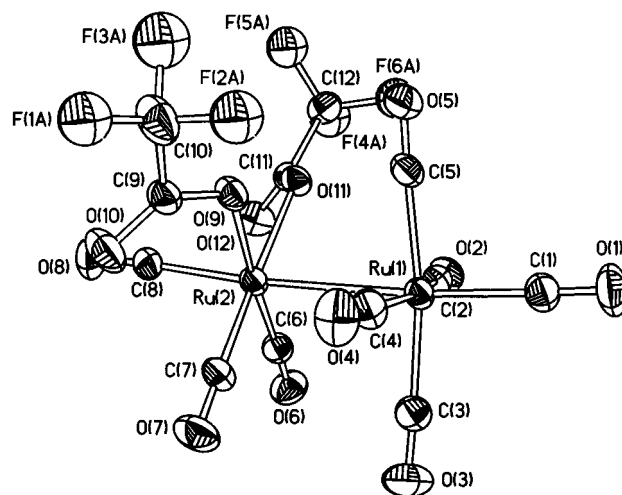


Remarkably, with trifluoroacetic acid as solvent, reaction (1) is an equilibrium at room temperature. Presumably, hydrogen bonding between bridging carboxylato ligands and solvent molecules assists the conversion of the bridging carboxylato ligand to its monodentate arrangement. Gas volumetric measurements and IR analysis show that **1**, **2** and **3** are present in a 1:2.5:4 molar ratio in a 0.046 M trifluoroacetic acid solution of **1** under CO at atmospheric pressure.

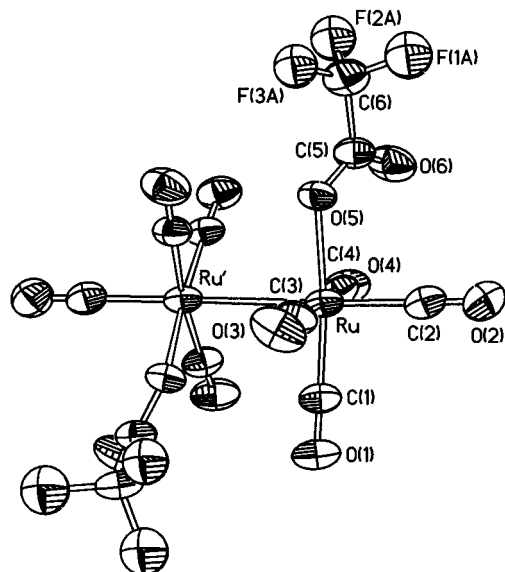
The molecular structures<sup>‡</sup> of **2** and **3** are shown in Fig. 1 and 2, respectively. Binuclear Ru carbonyl complexes without bridging ligands are rare, only anionic  $[Ru(CO)_4]_2^{2-}$ <sup>9</sup> and neutral  $[Ru(CO)_4(GaCl_2 \cdot THF)]_2^{10}$  and  $[Ru(CO)_4(SnMe_3)]_2^{11}$  being structurally characterized. Compounds **2** and **3** show Ru–Ru distances of 2.836 and 2.853 Å, respectively, indicating a strong metal–metal bond, as compared to the dinuclear compound  $[Fe(CO)_4(CO_2CMe_3)_2]_2$ ,<sup>12</sup> with an Fe–Fe distance of 2.840 Å.

Compound **2**, in which the  $Ru(CO)_5$  moiety acts as a donor ligand towards the Ru(II) 16-electron centre, is stable both in the solid state and in diethyl ether solution and constitutes the first structurally characterized adduct of the  $Ru(CO)_5$  donor unit. Such an interaction stabilizes  $Ru(CO)_5$  towards decarbonylation; however, upon adding an equimolar amount of  $CF_3CO_2Cs$  to a 0.02 M THF solution of **2**, free  $Ru(CO)_5$  is immediately released into solution where it slowly converts to  $Ru_3(CO)_{12}$ . According to eqn. (2), the eighteen-electron complex  $Ru(CO)_5$  is substituted by the trifluoroacetato ligand yielding the anionic Ru(II) carbonyl complex **4** which was identified spectroscopically [ $\nu_{CO}$  (THF) 2142m, 2089s, 2072s  $cm^{-1}$ ].<sup>1</sup>

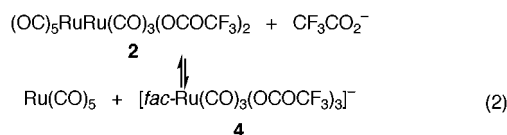
On these grounds, we conclude that exposure of a solution containing carboxylato-bridged Ru(I) carbonyl complexes to CO can result in equilibrium (1) and then in an irreversible



**Fig. 1** The molecular structure of **2**. The molecule possesses an approximate mirror plane, although this is not an operation of the space group. Only the most populated positions of the disordered  $CF_3$  groups have been represented. The ellipsoids are at 30% probability. Selected bond lengths (Å) and angles (°): Ru(1)–C(4) 1.964(9), Ru(1)–C(3) 1.964(9), Ru(1)–C(2) 1.966(8), Ru(1)–C(5) 1.991(9), Ru(1)–C(1) 2.016(8), Ru(1)–Ru(2) 2.8526(8), Ru(2)–C(6) 1.875(8), Ru(2)–C(7) 1.891(8), Ru(2)–C(8) 1.969(8), Ru(2)–O(11) 2.109(5), Ru(2)–O(9) 2.118(5); C(4)–Ru(1)–C(3) 89.6(4), C(4)–Ru(1)–C(2) 166.4(3), C(3)–Ru(1)–C(2) 89.4(3), C(4)–Ru(1)–C(5) 89.9(3), C(3)–Ru(1)–C(5) 171.2(3), C(2)–Ru(1)–C(5) 89.0(3), C(4)–Ru(1)–C(1) 96.7(3), C(3)–Ru(1)–C(1) 95.5(3), C(2)–Ru(1)–C(1) 96.9(3), C(5)–Ru(1)–C(1) 93.3(3), C(4)–Ru(1)–Ru(2) 83.4(2), C(3)–Ru(1)–Ru(2) 89.3(2), C(2)–Ru(1)–Ru(2) 83.1(2), C(5)–Ru(1)–Ru(2) 81.9(2), C(1)–Ru(1)–Ru(2) 175.2(3), C(6)–Ru(2)–C(7) 89.3(3), C(6)–Ru(2)–C(8) 90.4(3), C(7)–Ru(2)–C(8) 93.2(3), C(6)–Ru(2)–O(11) 94.2(3), C(7)–Ru(2)–O(11) 174.8(3), C(8)–Ru(2)–O(11) 90.7(3), C(6)–Ru(2)–O(9) 176.4(3), C(7)–Ru(2)–O(9) 93.2(3), C(8)–Ru(2)–O(9) 92.0(3), O(11)–Ru(2)–O(9) 83.18(19), C(6)–Ru(2)–Ru(1) 91.0(2), C(7)–Ru(2)–Ru(1) 91.5(2), C(8)–Ru(2)–Ru(1) 175.1(2), O(11)–Ru(2)–Ru(1) 84.58(13), O(9)–Ru(2)–Ru(1) 86.35(14).



**Fig. 2** The molecular structure of **3**. The molecule possesses a twofold axis of symmetry. Only the most populated positions of the disordered  $\text{CF}_3$  groups have been represented. The ellipsoids are at 30% probability. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Ru–C(1) 1.885(11), Ru–C(4) 1.946(12), Ru–C(3) 1.947(11), Ru–C(2) 1.982(16), Ru–O(5) 2.104(6), Ru–Ru' 2.836(2); C(1)–Ru–C(4) 89.3(5), C(1)–Ru–C(3) 89.7(4), C(4)–Ru–C(3) 174.1(5), C(1)–Ru–C(2) 94.7(5), C(4)–Ru–C(2) 92.8(5), C(3)–Ru–C(2) 93.1(5), C(1)–Ru–O(5) 173.7(4), C(4)–Ru–O(5) 93.6(4), C(3)–Ru–O(5) 86.8(3), C(2)–Ru–O(5) 90.6(4), C(1)–Ru–Ru' 87.5(4), C(4)–Ru–Ru' 88.7(4), C(3)–Ru–Ru' 85.4(4), C(2)–Ru–Ru' 177.3(4), O(5)–Ru–Ru' 87.1(2).  $' = -x + 1/2, -y + 3/2, z$ .



disproportionation [eqn. (2)], in the presence of the free carboxylato ligand.

We showed that the disproportionation of **1** constitutes the key step of some catalytic processes such as  $\text{CF}_3\text{CO}_2\text{H}$ -catalyzed WGS<sup>1</sup> and the related Reppe olefin carbonylations.<sup>2</sup> It now appears that the reaction is a consequence of the carbonylation of **1** giving the reactive adduct **2**. Presumably, this conclusion is general and applies also to carboxylato-bridged Ru(II) carbonyl complexes other than **1**: for instance,  $\text{Ru}_2(\eta^2\text{-O}_2\text{CMe})_2(\text{CO})_6$ , which is indefinitely stable in an acetato-acetic acid solution, was found to absorb CO and to disproportionate at room temperature and atmospheric pressure.

Finally, the present findings can help to elucidate the dihydrogen activation promoted by carboxylato-bridged Ru(II) carbonyl complexes, a step common to several catalytic processes involving ruthenium. Both in toluene and in trifluoroacetic acid, **1** fails to react with dihydrogen even under harsh conditions. However, two distinct reaction pathways are encountered under 120 atm of  $\text{H}_2\text{--CO}$  ( $v/v = 1:1$ ), as a function of the solvent: in toluene at 130  $^\circ\text{C}$ ,  $\text{Ru}(\text{CO})_5$  and trifluoroacetic acid are quantitatively formed within 1 h while in trifluoroacetic acid catalytic hydrogenation of the solvent to 2,2,2-trifluoroethanol occurs. While the catalytic reaction, which has few precedents in homogeneous catalysis,<sup>13</sup> is under investigation, it is evident that dihydrogen activation by **1** requires CO. An interpretation for this could be given by considering the nature of **2** and **3**, namely the species present under CO. A radical pathway initiated by Ru–Ru bond fission in **3**<sup>14</sup> or, alternatively a  $\text{H}_2$  heterolytic splitting promoted by the Ru(II) centre of **2** can then be envisaged. In this connection, the chemistry of these ruthenium(II) containing species is reminiscent of the dihydrogen activation processes promoted by cobalt carbonyl species, which have been reported in earlier studies

from these laboratories.<sup>15</sup> It thus appears that the formation of rather weak metal–metal bonds is required.

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## Notes and references

† Compound **1** (0.8 g, 1.38 mmol) was suspended in 50 ml of toluene in a glass ampoule which was placed in a stainless-steel autoclave, pressurized with CO up to 120 atm and heated to 150  $^\circ\text{C}$  in a thermostatted oil bath. After slow cooling and gas venting, the glass ampoule was found to contain pale yellow crystals of two different shapes, while only traces of carbonyl complexes were detected by IR spectroscopy in the liquid phase. The air stable crystals were selected according to their shape. The X-ray single-crystal study showed  $(\text{OC})_5\text{RuRu}(\text{CO})_3(\text{OCOCF}_3)_2$  **2** to constitute the stick-shaped crystals and  $[\text{Ru}(\text{CO})_4(\text{OCOCF}_3)]_2$  **3** to form prismatic shaped crystals. The diffractometric measurements were carried out with a Siemens P4 diffractometer using Mo- $\text{K}\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$ . The intensity data were corrected for Lorentz and polarisation effects and for absorption by using a  $\psi$ -scan method.<sup>16</sup> Calculations were carried out with the SHELX97<sup>17</sup> program. In both studies, the disordered  $\text{CF}_3$  groups were refined as distributed with fixed geometry in two limiting positions. At the end of both refinements residual peaks and holes of ca.  $\pm 1 \text{ e } \text{\AA}^{-3}$  were present in the  $\text{CF}_3$  regions of the difference Fourier maps.

‡ *Crystal data*: **2**, colourless crystals,  $\text{C}_{12}\text{F}_6\text{O}_{12}\text{Ru}_2$ ;  $M = 652.3$ ,  $T = 293(2)$  K,  $a = 8.151(1)$ ,  $b = 15.740(1)$ ,  $c = 15.857(1)$   $\text{\AA}$ ,  $\beta = 95.46(1)^\circ$ , monoclinic  $P2_1/c$  (no. 14),  $U = 2025.2(3)$   $\text{\AA}^3$ ;  $Z = 4$ ;  $\mu = 1.603 \text{ mm}^{-1}$ ; crystal size =  $0.35 \times 0.18 \times 0.09$  mm. 3565 independent reflections were collected ( $R_{\text{int}} = 0.0184$ ). Final reliability factors for 273 parameters:  $R_1 = 0.0481$  calculated for 2826 reflections with  $I > 2\sigma(I)$ ,  $wR_2 = 0.1140$  calculated for all 3565 reflections in the refinement; GOF = 1.018.  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ , GOF =  $\{\sum [w(F_o^2 - F_c^2)^2] / (N - P)\}^{1/2}$ , where  $N$ ,  $P$  are the numbers of observations and parameters, respectively.

**3**, light yellow crystals,  $\text{C}_{12}\text{F}_6\text{O}_{12}\text{Ru}_2$ ;  $M = 652.3$ ,  $T = 293(2)$  K,  $a = 9.020(1)$ ,  $b = 12.716(2)$ ,  $c = 17.748(2)$   $\text{\AA}$ , orthorhombic  $Pccn$  (no. 56),  $U = 2035.7(5)$   $\text{\AA}^3$ ;  $Z = 4$ ;  $\mu = 1.595 \text{ mm}^{-1}$ ; crystal size =  $0.28 \times 0.21 \times 0.13$  mm. 1595 independent reflections were collected ( $R_{\text{int}} = 0.0208$ ). Final reliability factors for 137 parameters:  $R_1 = 0.0536$  calculated for 964 reflections with  $I > 2\sigma(I)$ ,  $wR_2 = 0.1557$  calculated for all 1595 reflections in the refinement; GOF = 1.028. CCDC 182/1401. See <http://www.rsc.org/suppdata/cc/1999/2043/> for crystallographic files in .cif format.

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