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LETTER

Organometallic carboxylato compounds of ruthenium(IV)

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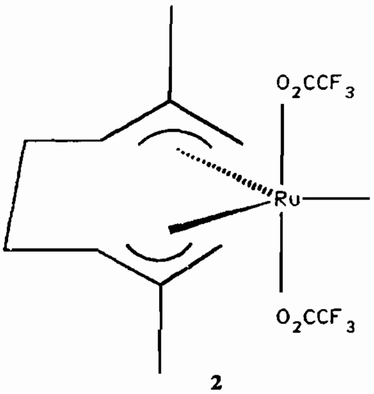
Since the discovery of [(η^3:η^3-$C_{10}H_{16}$)RuCl(μ-Cl)]$_2$ (1) in 1965 [1, 2] its chemistry, in comparison to that of the related compounds [(η^6-arene)RuCl(μ-Cl)]$_2$ [3, 4], has been relatively neglected. Recent interest in the organometallic chemistry of metals in relatively high formal oxidation states [5, 6] has however revived interest in this compound.

Compound **1** exists as two diastereoisomers of C_i and C_2 symmetry [7] which arise as a consequence of the chirality of the '(η^3:η^3-$C_{10}H_{16}$)Ru^{2+}' fragment. This feature is reflected in the ^1H NMR spectrum of **1** which shows twice the number of expected resonances [76]. The geometry about the metal atom is loosely described as trigonal bipyramidal [8] with the axial sites being occupied by one bridging and one terminal chloride ligand. The number of resonances in the ^1H NMR spectrum of **1** is further redoubled as a consequence of the inequivalence of these axial sites thus giving, for example, eight resonances for the terminal allyl protons and four resonances for the allylic methyl groups [7]. The sensitivity of the NMR spectra of the bis(allyl) ligand to the geometry about the metal centre makes this technique an excellent probe for studying ligand substitution reactions at the ruthenium(IV) centre.

Carboxylates, particularly trifluoroacetates, have been shown in (arene)ruthenium(II) chemistry [9, 10] to make particularly good leaving groups rendering (arene)ruthenium trifluoroacetate complexes useful precursors to a wide range of arene(ruthenium) complexes. We now report the synthesis and ^1H NMR characterisation of three bis(allyl)-ruthenium(IV) carboxylates and highlight the differences in reactivity compared with their ruthenium(II) analogues.

In common with the analogous [(η^6-arene)RuCl(μ-Cl)]$_2$ complexes (arene = benzene, *p*-cymene, hexamethylbenzene) [9], reaction of **1** with 2 molar equivalents of silver acetate at room temperature in acetone/water gives a chelate complex, [(η^3:η^3-$C_{10}H_{16}$)RuCl(O_2CCH_3)] (3) in 70% yield. The complex exhibits four terminal allyl singlets (δ 5.51, 4.65, 4.63, 3.56 ppm) and two methyl resonances (δ 2.29, 2.12 ppm) in its ^1H NMR spectrum, indicative of the inequivalent axial sites of the trigonal bipyramidal ruthenium centre. In contrast the analogous reaction with a 4:1 mole ratio of silver trifluoroacetate produces a complex displaying only half this number of ^1H NMR resonances, i.e. two terminal allyl singlets (δ 5.68, 4.23 ppm) and a single methyl resonance (δ 2.12 ppm). A sharp peak of integral 2H is also observed at 7.11 ppm. The IR spectrum of this material displays two broad bands at 3362 and 3196 cm^{-1} in addition to bands due to ν(CO) at 1703, 1670 and 1421 cm^{-1}, and ν(CF) at 1196 and 1143 cm^{-1}. From this data and in conjunction with microanalytical and mass spectroscopic measurements the complex is identified as the novel water solvate [(η^3:$\eta^3$$C_{10}H_{16}$)Ru($O_2CCF_3$)$_2$($OH_2$)] (2). Differences in reactivity of the two carboxylate ligands must be a consequence of the different electronic properties of the substituent groups.

Compound **2** decomposes above 140 °C but will sublime intact at *c.* 80 °C under reduced pressure with no trace of displacement of the water molecule. Refluxing **2** in dichloromethane containing anhydrous magnesium sulfate results in recovery of the starting material. Interestingly **2** is also obtained from refluxing **1** in trifluoroacetic acid. From these observations we infer the water ligand to be extremely tightly bound to the metal centre, an observation supported by its low substitutional lability. Preliminary results indicate displacement of the water ligand by pyrazene to be *c.* 50% complete after 24 h at room temperature.



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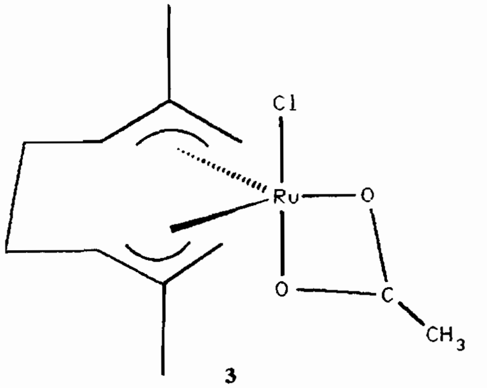

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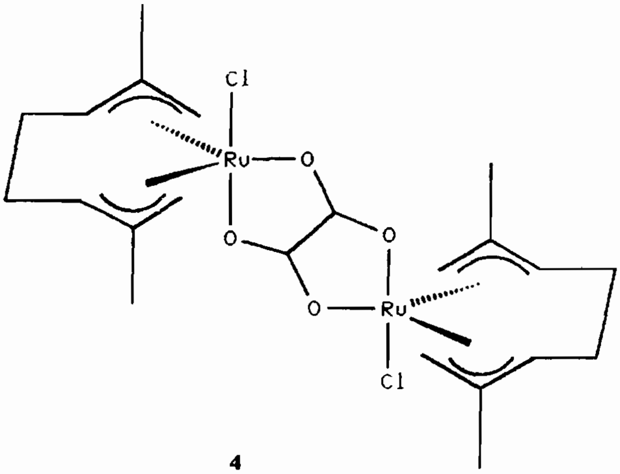

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Reaction of **1** with a 1:2 mole ratio of silver trifluoroacetate, surprisingly, also gives **2**, along with a large quantity of unreacted starting material.

Reaction of **1** with silver oxalate in both 1:2 and 1:4 mole ratios produces, as the sole product, the binuclear bridged species $[\{(\eta^3{:}\eta^3\text{-}C_{10}H_{16})RuCl\}_2(\mu_2\text{-}O_2CCO_2)]$ (**4**) the ^1H NMR spectrum of which displays eight terminal allyl resonances (δ 5.32, 5.19, 4.52, 4.43, 4.33, 4.18, 3.36, 3.24 ppm) and four methyl resonances (δ 2.33, 2.30, 2.19, 2.15 ppm). This observation is consistent with the presence of two diastereoisomers, of C_i and C_2 symmetry, similar to those observed for **1**. The oxalate ligand also raises the possibility of linkage isomerism since it may bind to a metal centre in either monodentate fashion or bidentately, through either a three or four atom linkage. Preliminary results of a single crystal X-ray diffraction study indicate a bidentate mode of coordination through a four atom linkage so forming two fused five membered rings. This is the normal mode of coordination for binuclear oxalato bridged systems [11, 12].

Compounds **2**, **3** and **4** exhibit three different modes of coordination for the carboxylate ligands. Compound **2** can be contrasted with the ruthenium(II) compound $[(\eta^6\text{-}C_6H_6)RuCl(O_2CCF_3)]$ which is formed by analogous synthetic routes [9] and in which the trifluoroacetate ligand exhibits bidentate coordination. Work is in progress with a number of chlorinated carboxylates to determine the 'crossover' point, in terms of the electronic effects of the substituent groups, between monodentate and bidentate coordination modes and investigations into the reactivity of the compounds described in this short report are being undertaken.

Acknowledgements

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References

1 L. Porri. M.C. Gallazzi, A. Colombo and G. Allegra, *Tetrahedron Lett., 47* (1965) 4187.
2 A. Colombo and G. Allegra, *Acta Crystallogr., Sect. B, 27* (1971) 1653.
3 P. M. Maitlis, *Chem. Soc. Rev., 10* (1981) 1.
4 M. A. Bennett, *Comprehensive Organometallic Chemistry*, Vol. IV, Pergamon, Oxford, 1982, Ch. 32.
5 C. Che, W. Cheng and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, (1987) 418.
6 W. A. Hermann, *Angew. Chem., Int. Ed. Engl., 27* (1988) 1297.
7 D. N. Cox and R. Roulet, *Inorg. Chem., 29* (1990) 1360.
8 J. G. Toerien and P. H. van Rooyen, *J. Chem. Soc., Dalton Trans.*, (1991) 1563.
9 D. A. Tocher, R. O. Gould, T. A. Stephenson, M. A. Bennett, J. P. Ennett, T. W. Matheson, L. Sawyer and V. K. Shah, *J. Chem. Soc., Dalton Trans.*, (1983) 1571.
10 E. C. Morrison, C. A. Palmer and D. A. Tocher, *J. Organomet. Chem., 349* (1988) 405.
11 H. D. Hausen, K. Mertz and J. Weidlein, *J. Organomet. Chem., 67* (1974) 7.
12 R. Deyrieux and A. Peneloux, *Bull. Soc. Chim. Fr.*, (1969) 2675.