A Dirhodium(II) Complex with Trifluoroacetamidato Ligands

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A dirhodium(II) complex with trifluoroacetamidato bridging ligands has been prepared and its chemistry investigated.

During recent years dimeric metal–metal bonded complexes of Rh^{II} such as those found in the tetrakis-μ-carboxylato-dirhodium(II) complexes (**1**) have received considerable attention.[1–5] However, despite detailed theoretical and experimental studies it is still not clear to what extent the structural properties[1] and chemical reactivity[2–5] of the dirhodium(II) complexes are intrinsic to the Rh_2^{4+} moiety or to what degree they depend on the constraints placed on the dirhodium(II) centre by the bridging ligand. In order to answer this question we are studying new complexes in which the Rh_2^{4+} structure remains intact but the bridging ligands have been substantially altered from those previously reported in the literature.[6]

We now report the synthesis and physical properties of a new dirhodium(II) complex which is similar to $Rh_2(O_2CCR)_4$ but has trifluoroacetamidato in place of carboxylato bridging ligands. This compound provides new examples of Rh^{II} metal–metal bonded dimers which are stable, have good solubility characteristics, and can be altered chemically by substitution on the amide carbon and nitrogen atoms. Because of the presence of the mixed N,O, bridging groups there is also the possibility of isolating isomers in which the two individual rhodium ions in the complex are in the same or different chemical environments.

$Rh_2(O_2CCR)_4$ $Rh_2(HNOCCF_3)_4$
(1) **(2)**

Tetrakis-μ-acetato-dirhodium(II) reacts in molten trifluoroacetamide at 160—165 °C for 2 h to produce a product with the formula $Rh_2(HNOCCF_3)_4$, **(2)**. Excess of trifluoroacetamide was removed by vacuum sublimation and the product recrystallized from methanol–water.† The parent ion mass of **(2)**, determined by liquid chromatography–mass spectrometry in the negative ion mode, was 653 which corresponds to the dirhodium complex with one nitrogen proton lost. The ^1H n.m.r. spectrum of **(2)** shows the presence of N–H protons (broad peak centred at δ 6.71) but no methyl protons. The ^{19}F n.m.r. spectrum shows one peak which is shifted 2.0 p.p.m. downfield from the absorbance of the free ligand.

The light blue desolvated complex forms axial adducts with ligands containing a wide variety of donor atoms. The colour change associated with adduct formation is quite different from that observed for the rhodium(II) carboxylates. With oxygen donor ligands the complex is reddish purple, with CO reddish orange, and with pyridine, dimethyl sulphoxide, and R_3P yellow adducts are formed. When **(2)** is added to a methanol solution saturated with a chloride salt a blue chloride adduct precipitates. This adduct is not soluble in water but when the solid is added to methanol without chloride ions a reddish purple solution forms indicating the loss of the chloride ions and formation of the methanol adduct.

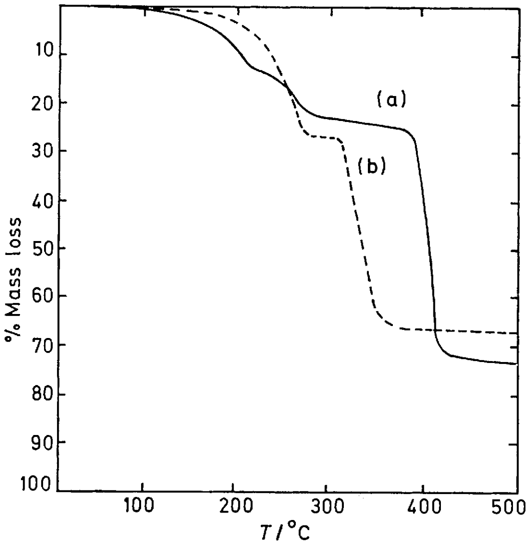

Figure 1. Thermal decomposition of (a) $Rh_2(HNOCCF_3)_4\cdot 2C_5H_5N$ and (b) $Rh_2(OOCCH_3)_4\cdot 2C_5H_5N$.

The mass loss on thermal decomposition of the bis pyridine adducts of the amidato bridged complex and rhodium(II) acetate is shown in Figure 1. The complex $Rh_2(HNOCCF_3)_4\cdot 2C_5H_5N$ displays a step-wise loss of the two pyridines whereas both pyridines are lost from the corresponding rhodium(II) acetate adduct in one step. The desolvated amidato bridged complex is also considerably more stable thermally than rhodium(II) acetate.

Electrochemical or chemical oxidation of **(1)** has been shown by *X*-ray photoelectron spectroscopy to yield a stable species in which both $Rh^{II/III}$ atoms are identical on the time-scale of the experiment.[7] The mixed-valence species $[Rh_2(HNOCCF_3)_4]^+$ appears to be generated by oxidation of $Rh_2(HNOCCF_3)_4$ in a similar manner to that observed for the rhodium(II) carboxylates.[3,8] In nonbonding, or weakly bonding solvents, **(2)** undergoes a reversible one-electron oxidation between 1.07 and 1.15 V *vs.* standard calomel electrode (S.C.E.). This is shown in Figure 2 (a) where the solvent is acetonitrile and $E_{1/2}$ = 1.09 V. No other oxidation or reduction process was observed

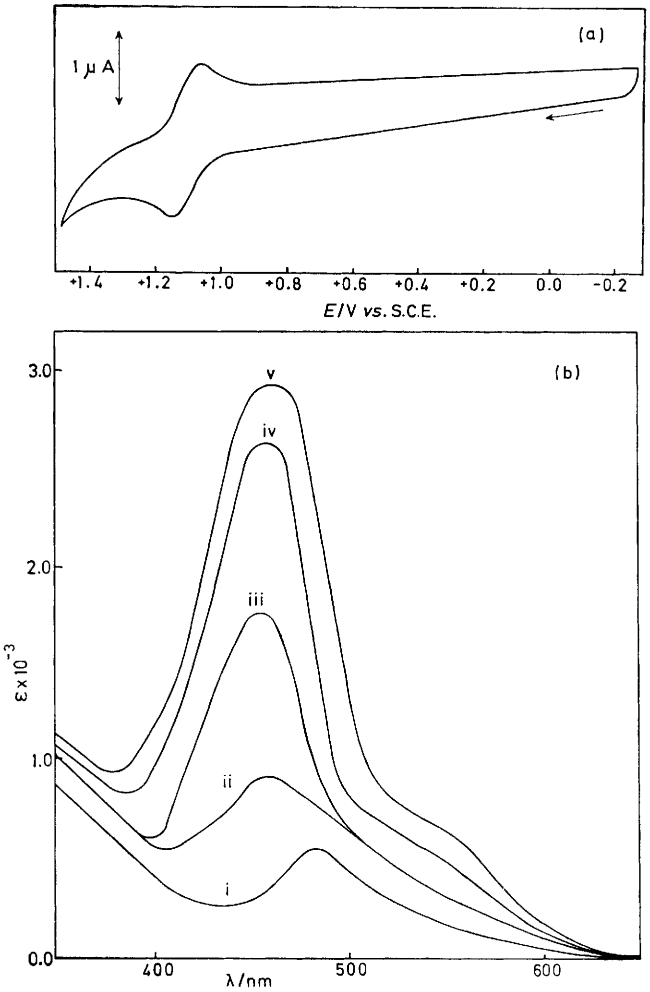

Figure 2. (a) Cyclic voltammogram of $Rh_2(ONHCCF_3)_4$ **(2)** in MeCN with 0.1 M Bu_4N^+ ClO_4^-; [**(1)**] = *ca.* 4.9 × 10^{-4} M; scan rate, 0.100 V/s. (b) Electronic absorption spectra obtained during the oxidation of **(2)**, conditions as in (a), with *E* applied = +1.300 V/S.C.E. Total oxidation times: i, 0 s; ii, 10 s; iii, 35 s; iv, 80 s; v, 515 s.

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† A satisfactory elemental analysis of the product was obtained.

in the potential range of +1.5 to −1.6 V. The single oxidation process was diffusion controlled as shown by characteristically constant plots of $i_p/v^{1/2}$ and $E_{1/2}$ with increase in potential scan rate. In addition, the difference in anodic and cathodic peak potential, $E_{pa} - E_{pc}$, was equal to 59 ± 5 mV suggesting the abstraction of a single electron. This value was confirmed by controlled-potential oxidation at +1.3 V and rereduction at +0.80 V. Application of the controlled potential yielded a value of 0.97 ± 0.04 electrons for oxidation and 0.92 ± 0.02 electrons for rereduction.

Monitoring of the electronic absorption spectra during the controlled potential oxidation yielded the spectra shown in Figure 2(b). A large increase in ϵ_{max} and a shift toward shorter wavelengths was observed on going from **(2)** to the cation $[Rh_2(HNOCCF_3)_4]^+$. This transition was totally reversible, since the spectrum obtained after controlled potential reduction of the oxidized species was identical to the starting spectrum. It is interesting and surprising that the potential for oxidation of **(2)** was almost identical to that observed for **(1)** when R = C_2H_5.[3] This suggests that the electron density on the Rh centres is equal in the two complexes and that the effects of the change from C_2H_5 to CF_3 as substituent and the replacement of an oxygen bridging atom by nitrogen are equal but opposite. Previous electrochemical studies have shown that an approximate 750 mV anodic shift of potential is observed in Rh reduction potentials on going from a C_2H_5 to a CF_3 substituent.[3] Thus, the reversible potential of 1.09 V for oxidation of **(2)** implies a 750 mV cathodic stabilization component of the redox potential upon changing the bridging atom.

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