Preliminary Communication

Synthesis and electrochemistry of organometallic ethanethiolato bridged complexes of ruthenium(IV)

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Abstract

Reaction of the ruthenium(IV) chloro-bridged dimer [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$], 1, with ethanethiol (EtSH) in CH_2Cl_2 gives the bridged-cleaved adduct [Ru(η^3:η^3-$C_{10}H_{16}$)Cl$_2$(SHEt)], 2. Stirring of two molar equivalents of 2 in methanol with one equivalent of 1 gives the binuclear, mixed chloro/thiolato bridged compound [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl}$_2$(μ-Cl)(μ-SEt)], 3. The related doubly thiolato bridged complex [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-SEt)}$_2$], 4, is formed by treatment of 1 with an excess of EtSH, or by prolonged stirring of 2 alone in methanol. Compounds 2–4 have been studied by cyclic voltammetry. Compound 2 undergoes only irreversible oxidation, whereas in the case of both 3 and 4 the observation of significant return waves is consistent with a greater stability of the primary redox products.

1. Introduction

Several compounds derived from the organometallic ruthenium(IV) dimer [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$], 1 [1,2] with multidentate ligands, such as pyridine-2-thiol, containing the thiol (SH) functionality have been reported [3–5]. It is clear in many cases that the ligand (L) forms simple adducts [Ru(η^3:η^3-$C_{10}H_{16}$)Cl$_2$(L)] in which the SH proton is retained, although spectroscopic data do not reveal whether the SH functionality is actually bound to the metal centre. In general, however, thiol complexes are uncommon [6,7] and are often unstable towards air, or with respect to loss of H$^+$ or H$_2$ [7–9]. We now report some compounds of ethanethiol which are representative of those obtained so far in our study of the reactions of 1 with simple

alkyl and aryl thiols. In these compounds there is no ambiguity about the binding mode of the thiol function to the metal centre.

2. Results and discussion

2.1. Synthesis and structures

Reaction of 1 with two equivalents of EtSH in CH_2Cl_2 results in an immediate colour change from purple to orange-red. Removal of the solvent *in vacuo* results in the deposition of red crystals of formula [Ru(η^3:η^3-$C_{10}H_{16}$)Cl$_2$(SHEt)], 2. The presence of the SH proton is clearly established by infrared and ^{1}H NMR data. The remainder of the ^{1}H NMR spectrum is sharp, and consistent with coordination of the thiol into one of the equatorial sites of the trigonal bipyramidal ruthenium ion [10] *. The resonance due to the prochiral –CH_2CH$_3$ protons of the ethyl group would be expected to appear as the AB portion of the spectrum of an ABX$_3$ spin system as a consequence of the chirality of the "Ru(η^3:η^3-$C_{10}H_{16}$)" fragment, in a similar way to that observed for other ligands containing prochiral centres such as PF$_2$NMe$_2$ and O$_2$CCH_2F [5,10,11]. In fact, only a single, symmetrical, multiplet is observed, consistent with equivalence of the two

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* ^{1}H NMR data for [Ru(η^3:η^3-$C_{10}H_{16}$)Cl$_2$(SHEt)], 2 (400 MHz, CDCl$_3$, 293 K, J_{H-H}/Hz): δ 4.69 (s, 2H), 3.87 (s, 2H) – terminal allyl; 4.89 (t, 2H, ^3J = 6.4) – internal allyl; 3.06 (m, 2H), 2.63 (m, 2H) – –CH_2CH_2–; 2.32 (s, 6H) – Me; 3.46 (t, 1H, ^3J = 8.4, SH), 2.89 (m, 2H, CH_2CH$_3$), 1.50 (t, 3H, ^3J = 7.4, CH$_2$CH_3) ppm – ligand. [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl}$_2$(μ-Cl)(μ-SEt)], 3: 5.73 (s, 2H), 4.69 (s, 2H), 4.21 (s, 2H), 4.12 (s, 2H) – terminal allyl; 4.39 (m, 2H), 3.21 (m, 2H) – internal allyl; 2.82–2.49 (m, 8H) – –CH_2CH_2–; 2.29 (s, 6H), 2.16 (s, 6H) – Me; 3.36 (q, 2H, ^3J = 7.5, SCH_2CH$_3$), 1.36 (t, 3H, ^3J = 7.3, SCH$_2$CH_3) – ligand, C_2 isomer; 5.53 (s, 2H), 5.05 (s, 2H), 4.46 (s, 2H), 3.93 (s, 2H) – terminal allyl; 4.44 (m, 2H), 3.49 (m, 2H) – internal allyl; 2.82–2.49 (m, 8H) – –CH_2CH_2–; 2.34 (s, 6H), 1.98 (s, 6H) – Me; 3.39 (m, 1H, ^3J = 7.5, SCH_2CH$_3$), 2.80 (m, 1H, SCH_2CH$_3$), 1.32 (t, 3H, ^3J = 7.5, SCH$_2$CH_3)$_3$ – ligand, C_i isomer. [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl}$_2$(μ-Cl)(μ-SEt)], 4 (2 diastereoisomers): 5.18 (s, 2H), 4.87 (s, 2H), 4.72 (s, 2H), 4.04 (s, 2H), 4.03 (s, 2H), 3.88 (s, 2H), 3.60 (s, 2H), 2.73 (s, 2H) – terminal allyl; 4.67 (m, 2H), 4.42 (m, 2H), 3.26 (m, 2H), 3.00 (m, 2H) – internal allyl; 2.66 (m, 8H), 2.58 (m, 8H) – –CH_2CH_2–; 2.56 (s, 6H), 2.40 (s, 6H), 2.35 (s, 6H), 2.33 (s, 6H) – Me; 2.68 (d of q, 2H, ^2J = 14.0, ^3J = 7.2, SCH_2CH$_3$), 2.11 (d of q, 2H, ^2J = 15.2, ^3J = 7.4 SCH_2CH$_3$), 1.21 (d of q, 2H, ^2J = 14.0, ^3J = 7.2 SCH_2CH$_3$), 1.10 (d of q, 2H, ^2J = 15.2, ^3J = 7.4, SCH_2CH$_3$), 0.84 (t, 6H, ^3J = 7.2, SCH$_2$CH_3), 0.79 (t, 6H, ^3J = 7.4, SCH$_2$CH_3) – ligand.
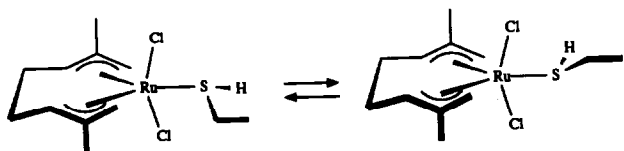

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Fig. 1. Isomers of [Ru(η^3: η^3-C$_{10}$H$_{16}$)Cl$_2$(SHEt)], 2 resulting from slow inversion at the sulphur atom.

Fig. 2. Possible geometrical isomers of [{Ru(η^3: η^3-C$_{10}$H$_{16}$)Cl}$_2$(μ-Cl)(μ-SEt)], 3.

prochiral protons. This indicates that, in common with that in many metal thiolate compounds [6], inversion of configuration at the sulphur atom is fast at room temperature. Cooling the NMR probe to below −60°C results in a doubling of the number of resonances for the *bis*(allyl) (2,7-dimethylocta-2,6-diene-1,8-diyl) ligand and allows observation of two different sets of signals, present in a ratio of approximately 5 : 4, which are sharp at −80°C, consistent with the presence of the two isomers shown in Fig. 1. Two sharp triplet resonances are also observed for the S*H* protons at this temperature, but the signal for the prochiral −C*H*$_2$CH$_3$ part of the ligand splits into four multiplets (δ 2.98, 2.81, 2.66 and 2.42 ppm), consistent with the pair of signals expected from each isomer.

Reaction of a concentrated solution of 1 in methanol with a small excess of EtSH resulted in the deposition of an orange solid, [{Ru(η^3: η^3-C$_{10}$H$_{16}$)Cl}$_2$(μ-Cl)(μ-SEt)], 3. This compound was also synthesised more straightforwardly by reaction of 2 with 0.5 mol equivalents of 1 in methanol (Scheme 1). Compounds containing mixed bridges, especially those with labile ligands such as chloride (*cf.* the ready cleavage of the chloride bridges in 1 [10]), are relatively rare, often
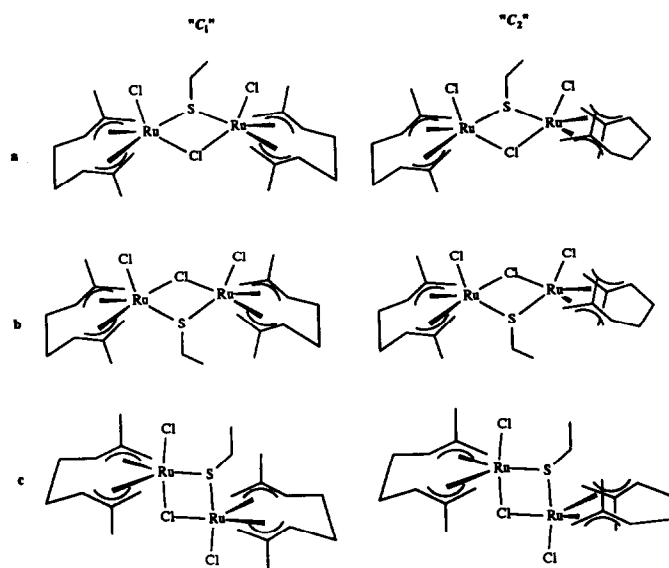
because the reactions proceed entirely to homo-bridged analogues. One other system involving mixed bridge ruthenium thiolato species has been reported, UV irradiation of [{Ru(η^5-C$_5$H$_5$)(CO)(μ-SC$_6$F$_5$)}$_2$] resulting in isomerisation to give [(η^5-C$_5$H$_5$)(CO)Ru(μ-CO)(μ-SC$_6$F$_5$)Ru(SC$_6$F$_5$)(η^5-C$_5$H$_5$)] and, ultimately, by decarbonylation, the triply bridged species [{Ru(η^5-C$_5$H$_5$)}$_2$(μ-CO)(μ-SC$_6$F$_5$)$_2$] [12].

In common with all other binuclear compounds containing the "Ru(η^3: η^3-C$_{10}$H$_{16}$)" fragment [10,13–15], the ^{1}H NMR spectrum * of 3 demonstrates that it exists as two diastereoisomers, which are for convenience labelled "C_i" (*meso*) and "C_2" (*rac*) (by analogy with the molecular symmetry of the corresponding isomers of 1 [10]) although 3 does not actually belong to these molecular point groups. In principle 3 could exist as up to 3 geometrical isomers (each of which could exist as two diastereoisomers) with either *cisoid* (Fig. 2(a), 2(b)) or *transoid* (Fig. 2(c)) arrangements of the terminal chloride ligands. By analogy with observations on 1 and related species [2,14,15], the *transoid* pair of diastereoisomers would be expected. It should be noted however, that if the mechanism for the formation of 3 from reaction of 2 with 1 is an associative one, involving initial bridging of an EtS group between the equatorial sites on each metal ion, then the *cisoid* isomer shown in Fig. 2(a) might be expected to be the kinetic product.

As for 2, compound 3 shows fluxionality in the room temperature NMR spectrum. At 25°C inversion at the sulphur atom is fast, giving rise to eight averaged terminal allyl resonances (four for each diastereoiso-
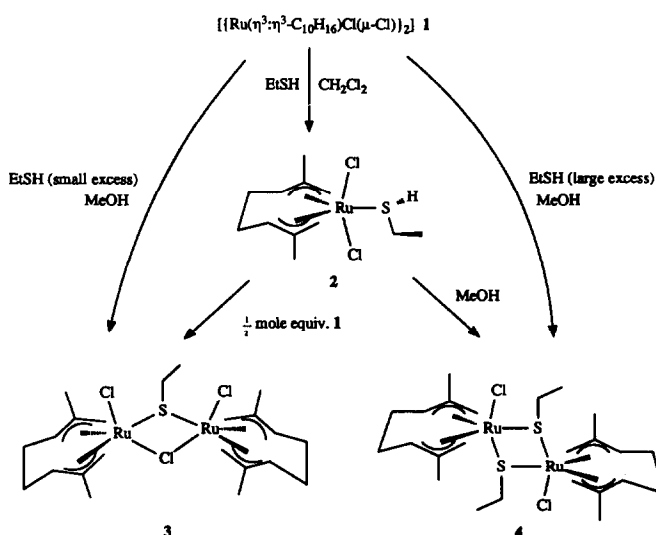
Scheme 1. Reactions of [{Ru(η^3: η^3-C$_{10}$H$_{16}$)Cl(μ-Cl)}$_2$], 1 with ethanethiol.

mer). Lowering the temperature to $-60°C$ results in the splitting of *four* of these resonances into two sets of approximately equal intensity, while the other four remain unchanged; *i.e.* the resonances for only one diastereoisomer of **3** split at low temperature. The remainder of the spectrum is also consistent with this observation. Since it seems reasonable that both diastereoisomers should undergo inversion at sulphur at similar rates, the observation implies that the symmetry of one diastereoisomer is such that the two possible orientations of the ethyl group of the thiolate ligand are degenerate at low temperature and hence do not cause a splitting of the NMR resonances. Such symmetry is exhibited only by isomers of the "C_2" type possessing *cisoid* arrangements of the terminal chloride ligands. In other words, **3** exists in one of the two *cisoid* forms shown in Fig. 2(a) and 2(b), not as the expected *transoid* isomer (Fig. 2(c)). Preliminary results of a single crystal structure determination clearly demonstrate this to be the case and unequivocally show the structure to be of the S-*equatorial* (Fig. 2(a)) type.

When **1** reacts with a substantial excess ($\geq$ 10-fold) of EtSH, or when **2** is simply stirred alone in methanol for 24 h a precipitation of the doubly ethanethiolato bridged compound [{Ru($\eta^3 : \eta^3$-C$_{10}$H$_{16}$)Cl(μ-SEt)}$_2$], **4** occurs. The ^{1}H NMR spectrum * of **4** is consistent with its existence as a single pair of diastereoisomers, even though the possibility of both *cisoid* and *transoid* forms exists. In this case the structure may be definitively assigned to the *transoid* form, since in a *cisoid* isomer the two SEt groups would be inequivalent, resulting in, for example, a total of four triplet signals for the methyl groups of the SEt ligands on the pair of diastereoisomers, contrary to observation. Interestingly *four* signals are observed for the diastereotopic $-CH_2$CH$_3$ protons, each integrating for two protons per diastereoisomer. Selective homonuclear decoupling experiments revealed that the diastereotopic protons within each ethyl group are inequivalent and coupled to one another ($^2J_{H-H} = ca.$ 15 Hz) implying *slow* inversion at sulphur even at room temperature, an finding contrary to that observed for **2** and **3**. In keeping with this observation the ^{1}H NMR spectrum of **4** was invariant at all temperatures between $+20°C$ and $-80°C$. Hence the EtS bridges in **4** must be locked into the most thermodynamically stable conformation.

2.2. Electrochemistry

Thiolato compounds of ruthenium are often electrochemically active. For example, a recent report describes the reversible oxidation of the doubly thiolato-bridged Ru^{II} dithiocarbamate compound [{Ru(μ-SPh)(S$_2$CNMe$_2$)(CO)(PPh$_3$)}$_2$] to [{Ru(μ-SPh)(S$_2$CNMe$_2$)(CO)(PPh$_3$)}$_2$]$^{4+}$ [16]. The four-electron oxida-

tion is accompanied by a decrease in the metal-metal distance from 3.683(1) to 2.876(2) Å.

Thiol adducts such as **2** often exhibit irreversible oxidations to compounds containing thiolate anions, *e.g.* [Ru(Cp)(PPh$_2$OMe)$_2$(SH^{t}Bu)][PF$_6$] is oxidised in air to the paramagnetic Ru^{III} species [Ru(Cp)(PPh$_2$OMe)$_2$(S^{t}Bu)][PF$_6$] [17] and the H$_2$S compound [Ru(SH$_2$)(PPh$_3$)('S$_4'$)][('S$_4'$)$^{2-}$ = 2,2'-(ethylenedithio)*bis*-(thiophenolate)] reacts with oxygen to form [{Ru(PPh$_2$)('S$_4'$)}$_2$(μ-S$_2$)] [18].

Compounds **2–4** were examined by cyclic voltammetry (0.2 M [^{n}Bu$_4$N][BF$_4$], CH$_2$Cl$_2$). Compounds derived from **1** often exhibit irreversible reductions at fairly high negative potentials (upwards of *ca.* -1.0 V *vs.* Ag/AgCl) [13,15] attributed to loss of the *bis*(allyl) ligand and, in the case of **1**, formation of solvato Ru^{2+} ions [19]. As for those compounds, complexes **2–4** all exhibit two reduction waves (*ca.* -1.2 and -1.7 V) that are irreversible over a variety of scan speeds (100–600 mV s^{-1}). There is some evidence for coupled oxidation waves, at *ca.* $+0.1$ and $+0.3$ V respectively, on the return scan for **3** and **4**. Compound **2** also exhibits an oxidation wave at $+1.52$ V (irreversible over a variety of scan speeds even at $-40°C$), possibly due to the loss of the thiol proton and the transient formation of Ru^V species such as [Ru($\eta^3 : \eta^3$-C$_{10}$H$_{16}$)Cl$_2$(SEt)].

At room temperature compound **3** exhibits two irreversible one-electron oxidation waves ($+1.27$ and -1.46 V). Cooling the cell to $-40°C$, however, results in the superposition of these waves ($+1.36$ V) and the observation of a significant return wave ($I_{pa}/I_{pc} = 0.69$), indicating that the primary redox product has a significant lifetime at this temperature.

The doubly bridged compound **4** also exhibits two one-electron oxidations ($+1.15$ V and *ca.* $+1.39$ V) both of which are electrochemically quasi-reversible (peak-to-peak separation $>$ 59 mV) even at room temperature. Peak current ratios are also less than unity for both processes, consistent with instability of the primary redox products. The current ratio is significantly less for the second process. The fact that some chemical reversibility is observed in these systems, in contrast to findings on all *bis*(allyl)ruthenium(IV) species previously studied, might be attributed to the flexibility of the thiolate bridges, which enables the metal centres to move relatively large distances towards each other without introducing significant steric strain in the cationic products [16].

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