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Nucleophilic addition to ruthenium activated tetramethylthiophene

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Abstract

The reaction of $[\{Ru(\eta^5\text{-TMT})(\mu\text{-Cl})Cl\}_2]$ (TMT = tetramethylthiophene) with the thioether ligand [9]aneS$_3$ (1,4,7-trithiacyclononane) gives a new cationic sandwich complex $[Ru(\eta^5\text{-TMT})(\kappa^3\text{-[9]aneS}_3)]^{2+}$. Reaction of this complex with ethoxide gives the complex ion $[Ru(\eta^4\text{-}C_4Me_4S\text{-2-OEt})(\kappa^3\text{-[9]aneS}_3)]^{+}$ in which the carbon at the '2' position on the thiophene ligand is attacked but otherwise the ring remains intact and coordinates to the metal in an η^4 fashion, as confirmed by the X-ray structure determination of $[Ru(\eta^4\text{-}C_4Me_4S\text{-2-OEt})(\kappa^3\text{-[9]aneS}_3)][PF_6]$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Thioether [9]aneS$_3$; Thiophene; Nucleophilic attack

1. Introduction

The conversion of petroleum to hydrocarbons is a multi-step process. Key among these steps is the removal of sulfur contaminants from the crude oil. This process, hydrodesulfurisation (HDS), is heterogeneously catalyzed by metal sulfides deposited on a support. While Mo and W are the essential components of the catalyst, activity can be further increased by the addition of late transition metals, particularly those belonging to group 8, as promoters [1–4]. While the role of the promoter is not well understood it is believed that enhanced activity may be due to the creation of new sites with different physico-chemical properties from those found in unpromoted catalysts. The fact that one of the more difficult groups of sulfur contaminants to remove are the thiophenes has led several authors to pursue model studies for the industrial heterogeneous process on molecular, thiophene coordinated, late transition metals [5–9]. In particular Rauchfuss et al. have extensively studied the reactivity of η^5-coordinated thiophenes in complexes of the type $[Ru(\eta^5\text{-thiophene})(\eta^6\text{-arene})]^{2+}$ [10–12]. Electrochemical or chemical reduction can be used to generate the corresponding Ru(0) compounds $[Ru(\eta^4\text{-thiophene})(\eta^6\text{-arene})]$ [10] which have an extensive chemistry including undergoing protonation reactions to give complexes such as $[Ru(\eta^4\text{-2,5-}Me_2C_4H_2S\text{-2-H})(\eta^6\text{-}C_6Me_6)]^{+}$, which was identified by X-ray crystallography [10] and is notable in that the added proton is *endo* with respect to the metal. If however the sandwich complexes, $[Ru(\eta^5\text{-thiophene})(\eta^6\text{-arene})]^{2+}$, are subjected to either base hydrolysis or aminolysis then the thiophene tends to undergo attack resulting ultimately in C–S bond cleavage [11,12]. Interestingly, in the case of base hydrolysis it is known that the initial attack occurs at the sulfur atom. In each of these studies a π-bonded arene is present as the inert ancillary supporting ligand. We were interested to investigate whether there was any variation in the chemistry of the complexed thiophene ligand upon changing the nature of the auxiliary ligand. To that end we have prepared a number of new $[Ru(\eta^5\text{-TMT})(L_3)]^{2+}$ complexes (TMT = tetramethylthiophene; L_3 = [2.2]-paracyclophane, trispyrazolylmethane, [9]aneS$_3$) and report here some results of our investigations into the reactivity of one of these, namely $[Ru(\eta^5\text{-TMT})(\kappa^3\text{-[9]aneS}_3)][PF_6]_2$.

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2. Results and discussion

Treatment of an aqueous suspension of [{Ru(η^5-TMT)(μ-Cl)Cl}$_2$] [13,14] with two mole equivalents of [9]aneS$_3$ results in the formation of a yellow solution over a period of 2 h. Subsequent addition of an excess of aqueous $NH_4[PF_6]$ to the reaction mixture gives a yellow precipitate of [Ru(η^5-TMT)(κ^3-[9]aneS$_3$)][PF$_6$]$_2$ in good yield (72%). The ^{1}H-NMR spectrum of this compound displays two sharp resonances, δ 2.38 and 2.44 ppm, due to the methyl substituents on the thiophene ring and a third singlet, δ 3.24 ppm, due to the methylene protons on the [9]aneS$_3$ ligand. Integration of the NMR spectrum and microanalysis confirm the proposed formulation of the product. The ^{13}C-{^{1}H}-NMR spectrum also exhibits only a single resonance for the methylene carbon atoms, consistent with the rapid rotation of the π-bonded ring about the metal–ligand axis.

[Ru(η^5-TMT)(κ^3-[9]aneS$_3$)][PF$_6$]$_2$ reacts in alcohols with a number of nucleophiles (Y^-), including hydride, alkoxides, and cyanide salts, to give the corresponding complexes, [Ru(η^4-C$_4$Me$_4$S-2-Y)(κ^3-[9]aneS$_3$)][PF$_6$], in which the carbon at the '2' position on the tetramethylthiophene ligand is believed to have undergone *exo* attack. The most stable of these is formed by the attack of an alkoxide ion on the thiophene ligand, and the characterisation of a representative compound is presented below.

The reaction between [Ru(η^5-TMT)(κ^3-[9]aneS$_3$)][PF$_6$]$_2$ and a freshly prepared solution of sodium ethoxide in ethanol proceeds smoothly to give an orange-yellow suspension. Addition of water, extraction with dichloromethane, evaporation to dryness, and subsequent recrystallisation from chloroform/hexane gives the product, [Ru(η^4-C$_4$Me$_4$S-2-OEt)(κ^3-[9]aneS$_3$)][PF$_6$], in moderate yield (26%). The ^{1}H-NMR spectrum of this material exhibits four signals, δ 1.33, 1.86, 2.06, 2.28 ppm, for the methyl groups on the thiophene derived ligand together with the triplet and quartet, δ 1.18 and 3.28 ppm, of the ethoxy functionality. The protons of the [9]aneS$_3$ ligand give rise to a series of ill-resolved multiplet signals in the range δ 2.0–3.1 ppm. Attack on the tetramethylthiophene ligand at any of the ring carbon atoms results in the loss of symmetry in the cation which should, as a consequence, result in the observation of 12 proton signals due to the [9]aneS$_3$ ligand. Although these are not resolved in the proton NMR spectrum examination of the ^{13}C-{^{1}H}-NMR spectrum clearly reveals that there are six signals, δ 31.7, 32.7, 33.8 33.9, 34.4, 36.6 ppm, due to the carbon atoms of the [9]aneS$_3$ ligand. Confirmation that it is the carbon in the '2' position which is attacked is obtained from the crystal structure determination of [Ru(η^4-C$_4$Me$_4$S-2-OEt)(κ^3-[9]aneS$_3$)][PF$_6$] (Fig. 1).

The structure consists of a κ^3-coordinated [9]aneS$_3$ ligand on the ruthenium(II) ion together with the thiophene derived ligand which coordinates in a planar η^4 fashion to the metal through the atoms S(1), C(2), C(3), and C(4) (maximum deviation from plane 0.04 Å, C(3)). The structure determination clearly demonstrated that the incoming nucleophile has added in an *exo* fashion. The sp^3 hybridised carbon, C(1), is 0.63 Å out of the plane, with a non-bonded Ru···C(1) distance of 2.86 Å and a dihedral angle between the planes [S(1)C(2)C(3)C(4)] and [S(1)C(1)C(2)] of 35.7°. The metal to ligand distances are somewhat longer than those reported previously in the η^4-thiophene complex, [Mn(CO)$_3$(η^4-C$_4$H$_5$S-2-CN)] [15], as would be expected for a second row metal, but similar to those found in the *endo* complex [Ru(η^6-C$_6$Me$_6$)(η^4-2,5-Me$_2$C$_4$H$_2$S-2-H)][PF$_6$] [10], and the only other crystallographically characterized η^4-C$_3$S thiopheneyl, [Rh(η^5-C$_5$Me$_5$)(η^4-C$_4$Me$_4$S-2-OH)][OTf] [16]. The ethoxy substituent on the ligand adopts a conformation which places the methylene carbon, C(9), over the centroid of the π-bonded connectivity, 2.85 Å. The bonds from the metal to the sulfurs of the [9]aneS$_3$ ligand are dissimilar, with two long, 2.345(2) and 2.326(2) Å, and one short

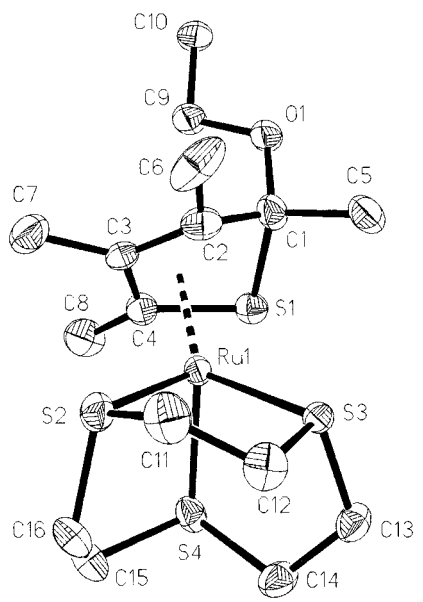

Fig. 1. The structure of the cation in [Ru(η^4-C$_4$Me$_4$S-2-OEt)(κ^3-[9]aneS$_3$)][PF$_6$] showing the atom labeling scheme. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): Ru(1)–S(1) 2.405(2), Ru(1)–C(2) 2.212(8), Ru(1)–C(3) 2.167(7), Ru(1)–C(4) 2.117(7), Ru(1)–S(2) 2.274(2), Ru(1)–S(3) 2.346(2), Ru(1)–S(4) 2.326(2), S(1)–C(1) 1.869(8), S(1)–C(4) 1.792(8), C(1)–C(2) 1.513(11), C(2)–C(3) 1.448(11), C(3)–C(4) 1.406(11), C(1)–O(1) 1.429(9), O(1)–C(9) 1.437(9), C(9)–C(10) 1.504(10). Selected interbond angles (°): S(2)–Ru(1)–S(3) 86.82(7), S(2)–Ru(1)–S(4) 87.83(7), S(3)–Ru(1)–S(4) 87.88(6), C(4)–S(1)–C(1) 92.7(3), S(1)–C(1)–C(2) 98.8(5), S(1)–C(1)–C(5) 109.0(6), S(1)–C(1)–O(1) 114.1(5), C(5)–C(1)–O(1) 104.5(6).

2.274(2) Å. It is notable that the short bond is formed approximately *trans* to the thiopheneyl sulfur, S(1)–Ru(1)–S(2) 160.94(7)°. A similar pattern of two shorter and one longer bond has been observed in other [9]aneS$_3$ compounds, such as [RuCl$_2$(DMSO)(κ^3-[9]aneS$_3$)] [17] and [RuCl$_2$(PPh$_3$)(κ^3-[9]aneS$_3$)] [18], and indeed even in complexes where each sulfur is *trans* to the same ligand, as in [Ru(CH$_3$CN)$_3$(κ^3-[9]aneS$_3$)]$^{2+}$, there is considerable variation in the Ru–S bond distances [17]. Having confirmed the stereochemistry of nucleophilic attack by X-ray crystallography the similarities between the NMR spectra of [Ru(η^4-C$_4$Me$_4$S-2-OEt)(κ^3-[9]aneS$_3$)][PF$_6$] and the other [Ru(η^4-C$_4$Me$_4$S-2-Y)(κ^3-[9]aneS$_3$)][PF$_6$] compounds strongly suggest that in each of these attack has occurred in an *exo* fashion on a carbon adjacent to the thiophene sulfur rather than *endo* as found in the protonation studies performed by Rauchfuss [10].

3. Experimental section

NMR spectra were recorded on a Varian VXR400 spectrometer and were referenced internally. Microanalyses were by the departmental service at University College London. Fast atom bombardment mass spectra were recorded by the University of London Intercollegiate Research Service based at the London School of Pharmacy. All manipulations were carried out under nitrogen with laboratory grade solvents using conventional Schlenk-line techniques. [{Ru(η^5-TMT)(μ-Cl)Cl}$_2$] was prepared by a published method [13].

3.1. [Ru(η^5-TMT)(κ^3-[9]aneS$_3$)][PF$_6$]$_2$

The compound [{Ru(η^5-TMT)(μ-Cl)Cl}$_2$] (0.25 g, 0.4 mmol) was suspended in H$_2$O (10 cm^3) to which 1,4,7-trithiacyclononane (0.15 g, 0.8 mmol) was added. The mixture was stirred for 2 h and then filtered through celite. The celite was washed with water (10 cm^3) and the washings combined with the yellow filtrate. Addition of an excess of aqueous NH$_4$[PF$_6$] resulted in the precipitation of a yellow solid. This was collected by filtration and washed with cold water (25 cm^3) and diethylether (50 cm^3), then dried in vacuo. Yield 0.41 g, 72%. Mass spectrum (FAB): m/z 567 [M–PF$_6$]; 422 [M–2PF$_6$]. Elemental Analysis: Found C 23.6, H 3.4%. Calc. for C$_{14}$H$_{24}$F$_{12}$P$_2$RuS$_4$: C 23.2, H 3.0%. ^{1}H-NMR data (400 MHz, d^6-acetone, 298 K): δ 2.38 (s, 6H), 2.44 (s, 6H) methyl resonances; δ 3.24 (s, 12H) [9]aneS$_3$ methylenes. ^{13}C-{^{1}H}-NMR data (100 MHz, d^6-acetone, 298 K): δ 11.5, 12.8 methyl resonances; δ 106.9, 108.6 TMT ring resonances; δ 36.2 [9]aneS$_3$ methylenes.

3.2. [Ru(η^4-C$_4$Me$_4$S-2-OEt)(κ^3-[9]aneS$_3$)][PF$_6$]

A fresh solution of NaOEt in EtOH was prepared (0.01 g Na, 25 cm^3 absolute ethanol). This was degassed by three repetitions of freeze–pump–thaw cycles. [Ru(η^5-TMT)(κ^3-[9]aneS$_3$)][PF$_6$]$_2$ (0.05 g, 0.07 mmol) was added and the mixture stirred for 1 h to give an orange-yellow suspension. Water (15 cm^3) was added and the product extracted with CH$_2$Cl$_2$ (3 × 30 cm^3). The volume of the combined extracts was reduced to 30 cm^3 and then dried over potassium carbonate. After removing the drying agent the solution was evaporated to dryness. Recrystallisation from chloroform/hexane gave the product as a dark orange solid which was filtered off and dried in vacuo. Yield 0.11 g, 26%. Mass spectrum (FAB): m/z 467 [M–PF$_6$]. Elemental Analysis: Found C 30.1, H 4.5%. Calc. for C$_{16}$H$_{29}$F$_6$OPRuS$_4$·H$_2$O: C 30.5, H 5.0%. ^{1}H-NMR data (400 MHz, CDCl$_3$, 298 K): δ 1.33 (s, 3H), 1.86 (s, 3H), 2.06 (s, 3H), 2.28 (s, 3H) methyl resonances; δ 1.18 (t, 3H), 3.28 (q, 2H) ethoxide; δ 2.0–3.1 series of 12 broad overlapping multiplets, total integral 12H, methylenes. ^{13}C-{^{1}H}-NMR data (100 MHz, CDCl$_3$, 298 K): δ 12.5, 13.7, 15.4, 16.1 methyl resonances; δ 63.3, 80.4, 98.0, 115.9 thiopheneyl ring resonances; δ 23.3 60.8 ethoxide; δ 31.7, 32.7, 33.8 33.9, 34.4, 36.6 [9]aneS$_3$ resonances.

3.3. Crystal data

C$_{16}$H$_{29}$F$_6$OPRuS$_4$, $M = 611.7$, monoclinic, space group $P2_1/c$, $a = 9.2692(2)$, $b = 17.0596(6)$, $c = 14.9350(4)$ Å, $\beta = 104.780(2)°$, $U = 2283.5(1)$ Å^3, $Z = 4$, 4421 unique data (19 911 measured, $2\theta \leq 52°$, $R_{int} = 0.034$), 318 parameters, $R_1 = 0.0723$ [$F^2 > 2\sigma(F^2)$], wR_2 (all data) = 0.1614. The crystal was mounted on a glass fibre and cooled to −173°C on the diffractometer. All crystallographic measurements were carried out with a Nonius Kappa CCD diffractometer equipped with graphite monochromated Mo–K$_\alpha$ radiation using φ rotations with 2° frames and a detector to crystal distance of 25 mm. Integration was carried out by the program DENZO-SMN [19]. Data were corrected for Lorentz and polarization effects, and for the effects of absorption using the program SCALEPACK [19]. The structure was solved by direct methods (SHELX-97 [20]) and developed using alternating cycles of least-squares refinement and difference Fourier synthesis (SHELX-97 [20]). All non-hydrogen atoms were refined anisotropically whilst the hydrogen atoms were fixed in idealized positions and allowed to ride on the atom to which they were attached. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. The six fluorines of the hexafluorophosphate anion are disordered over two sites, which were refined with relative occupancies of 55:45. Calculations were carried out on a Silicon

Graphics Indy workstation and IBM-PC compatible personal computers.

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