Double Deprotonation, Ring-opening and C–C Bond Formation in a Coordinated Crown Thioether. Formation and Structure of an Areneruthenium(II) Ethenethiolate, $[\overline{\mathrm{Ru(SCH{=}CH_2)(\eta^6\text{-}C_6Me_5CH_2CH_2CH_2SCH_2CH_2S)}}]$

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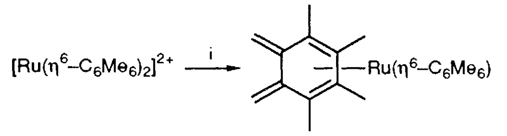
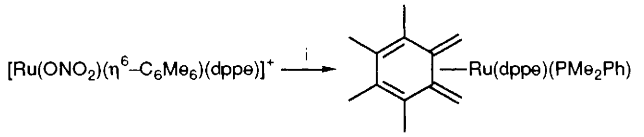
Treatment of $[\mathrm{Ru(\eta^6\text{-}C_6Me_6)([9]aneS_3)](PF_6)_2}$ ($\mathrm{[9]aneS_3}$ = 1,4,7-trithiacyclononane) with an excess of potassium *tert*-butoxide gives an η^1-*S*-bonded ethenethiolate complex, $[\overline{\mathrm{Ru(SCH{=}CH_2)(\eta^6\text{-}C_6Me_5CH_2CH_2CH_2SCH_2CH_2S)}}]$, which is characterised by single crystal X-ray analysis; it is formed as a result of deprotonation at two of the methylene carbon atoms of $\mathrm{[9]aneS_3}$ and cleavage of two C–S bonds, followed by deprotonation at one of the $\mathrm{C_6Me_6}$ methyl groups.

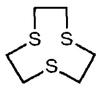
Cationic η^6-hexamethylbenzeneruthenium(II) complexes can be deprotonated by strong bases such as potassium *tert*-butoxide to give tetramethyl-*o*-xylyleneruthenium(0) complexes.[1,2] Depending on the precursor, the resulting *o*-xylylene may be coordinated through either its *endo*- or *exo*-pair of double bonds. Thus, $[\mathrm{Ru(\eta^6\text{-}C_6Me_6)_2}]^{2+}$ gives $[\mathrm{Ru(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}}\textit{endo}\mathrm{\text{-}C_6Me_4(CH_2)_2\}}]$ (Scheme 1),[1] whereas $[\mathrm{Ru(ONO_2)(\eta^6\text{-}C_6Me_6)(dppe)]NO_3}$ (dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) in the presence of $\mathrm{PMe_2Ph}$ gives $[\mathrm{Ru\{\eta^4\text{-}}\textit{exo}\mathrm{\text{-}C_6Me_4(CH_2)_2\}(dppe)(PMe_2Ph)}]$ (Scheme 2).[2] We report here an attempt to apply this technique to the preparation of tetramethyl-*o*-xylyleneruthenium(0) complexes containing 1,4,7-trithiacyclononane, $\mathrm{[9]aneS_3}$ **1**, a ligand that prefers to occupy the three facial sites of an octahedron. It forms stable homoleptic complexes with the later transition elements that are far more stable than those of monodentate or bidentate thioethers,[3,4] but although the half-sandwich cations $[\mathrm{Fe(\eta^5\text{-}C_5H_5)([9]aneS_3)}]^+$,[5] $[\mathrm{Os(1\text{-}Me\text{-}4\text{-}Pr^iC_6H_4)([9]aneS_3)}]^{2+}$,[6] $[\mathrm{M([9]aneS_3)(cod)}]^+$ (M = Rh, Ir; cod = cycloocta-1,5-diene)[7] and $[\mathrm{Rh([9]aneS_3)(C_2H_4)_2}]^+$,[7] have been structurally



Scheme 1 *Reagents*: i, KOBu^t



Scheme 2 *Reagents*: i, KOBu^t, PMe$_2$Ph



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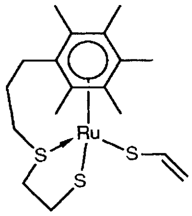
characterised, little attention has been paid to the chemistry of its organo-transition metal complexes.

The complex [Ru(η^6-C$_6$Me$_6$)([9]aneS$_3$)](PF$_6$)$_2$ **2**, obtained as yellow crystals in 86% yield by displacement of the labile acetone ligands of [Ru(η^6-C$_6$Me$_6$)(OCMe$_2$)$_3$](PF$_6$)$_2$[8] by [9]aneS$_3$, reacts with KOBu^t (>3 mol per mol Ru) in tetrahydrofuran at room temperature to give an air-stable, dark-red solid in *ca.* 50% yield, the composition of which corresponds with the formula [Ru{η^4-C$_6$Me$_4$(CH$_2$)$_2$}([9]aneS$_3$)]; the NMR (^{1}H, ^{13}C) spectra, however, are clearly inconsistent with this formulation. Thick needles of diffraction quality were obtained from dichloromethane–diethyl ether after five days at −20 °C. Single crystal X-ray analysis† shows the compound to be a half-sandwich areneruthenium(II) complex [Ru(SCH=CH$_2$)(η^6-C$_6$Me$_5$CH$_2$CH$_2$CH$_2$SCH$_2$CH$_2$S)] **3**, the structure of which is illustrated in Fig. 1. The nine-membered ring in **2** has now been opened; salient features are the presence of coordinated ethenethiolate, and the linking of a CH$_2$ group on the η^6-arene with a CH$_2$CH$_2$ unit derived from [9]aneS$_3$ to give a novel arene-thioether-thiolate ligand. As a consequence of the formation of the bridge, carbon atom C(6) is pulled *ca.* 3° towards the ruthenium atom from the plane formed by the remaining arene carbon atoms. The Ru–S distances to the thiolate and thioether sulfur atoms in the chelate ring do not differ significantly [Ru–S(1) 2.3664(10) Å, Ru–S(2) 2.3549(6) Å], but both are larger than the corresponding distance of 2.4155(8) Å in the ethenethiolate ligand. Consistent with the structure, the ^{1}H NMR spectrum of **3**‡ shows five singlets between δ 1.93 and 2.10 arising from the inequivalent methyl groups on the η^6-arene ring, an AMX pattern in the region δ 4.5–6.5 characteristic of a vinyl group,



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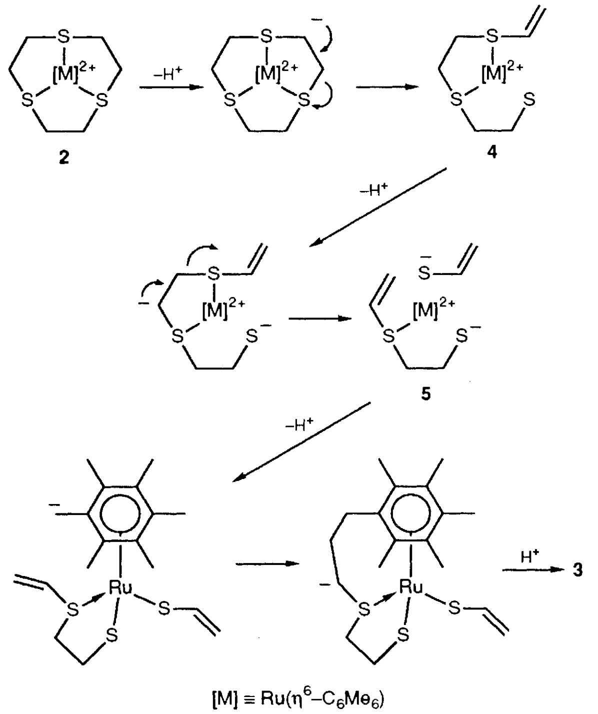

[M] ≡ Ru(η^6-C$_6$Me$_6$)

Scheme 3

and complex multiplets between δ 1.55 and 3.23 due to the methylene groups. The corresponding ^{13}C NMR resonances are also clearly discernible. The IR spectrum of **3** shows a strong band at 1556 cm^{-1} assignable to ν(C=C) of coordinated SCH=CH$_2$, *cf.* 1580 cm^{-1} in free ethenethiol.[9]

The acidity of the CH$_2$ protons in [9]aneS$_3$ and of the Me protons in C$_6$Me$_6$ is likely to be enhanced in a dication such as that in **2**, and this suggests a plausible mechanism for the formation of **3** (Scheme 3). Abstraction of one proton from [9]aneS$_3$ causes cleavage of an adjacent C–S bond and forms the chelate vinylthioether-thiolate complex **4**; this process is analogous to the reversible, Et$_3$N-induced deprotonation of [M([9]aneS$_3$)$_2$]$^{3+}$ (M = Co, Rh, Ir) to give [M(SCH$_2$CH$_2$SCH$_2$CH$_2$SCH=CH$_2$)([9]aneS$_3$)]$^{2+}$.[10] Repetition of the process at a thioether CH$_2$ group breaks a second C–S bond giving complex **5**, which contains the unique ethenethiolate ligand, SCH=CH$_2$, and the bidentate vinylthioether-thiolate ligand CH$_2$=CHSCH$_2$CH$_2$S$^-$. The vinyl group of the latter is well placed to undergo an intramolecular Michael addition with the carbanion **6** formed by removal of a third proton, this time from a methyl group on the η^6-arene ring; the nucleophilic behaviour of the exocyclic methylene carbon atom in [Fe(η^5-C$_5$H$_5$)(η^5-C$_6$Me$_5$CH$_2$)], generated either by hydrogen-atom abstraction from [Fe(η^5-C$_5$H$_5$)(η^6-C$_6$Me$_6$)] or by deprotonation of [Fe(η^5-C$_5$H$_5$)(η^6-C$_6$Me$_6$)]$^+$, is well established.[11] Reprotonation of the resulting carbanion then gives **3**. Evidence for the formation of intermediates **4** and **5** will be presented in the full publication.

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† *Crystal data* for **3**: C$_{18}$H$_{28}$S$_3$Ru, M_r = 441.67, triclinic, $P\bar{1}$, a = 8.017(1), b = 9.028(1), c = 14.349(1) Å, α = 100.87(1)°, β = 91.92(1)°, γ = 113.62(1)°, U = 927.6 Å^3, Z = 2, D_c = 1.581 Mg m^{-3}, Philips PW 1100 diffractometer, λ(Cu-Kα) = 1.5418 Å, μ = 100.5 cm^{-1}, F(000) = 456, specimen 0.19 × 0.08 × 0.11 mm, 3092 unique reflections [$4 < 2\theta < 128°$], 194 unobserved [$I < 3\sigma(I)$], R_F = 0.020, R_w = 0.033. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 1.93, 1.95, 2.01, 2.07, 2.10 (each s, 15H, C$_6$Me$_5$), 1.55–1.70 (m, 1H), 1.81–1.90 (m, 1H), 2.10–2.28 (m, 4H), 2.39–2.66 (m, 3H), 3.23 (dt, 1H, sep 10.3, 3.9 Hz)(CH$_2$), 4.76 (dd, 1H, *J* 9.6, 1.8 Hz), 5.03 (dd, 1H, *J* 16.8, 2.0 Hz), 6.40 (dd, 1H, *J* 16.8, 9.7 Hz) (CH=CH$_2$). ^{13}C{^{1}H}NMR (75 MHz, CD$_2$Cl$_2$) δ 14.69, 14.89, 14.94, 15.03, 16.78 (C$_6$*Me*$_5$), 24.39, 26.60, 26.79, 31.10, 45.35 (CH$_2$), 92.26, 94.32, 98.67, 102.96 (*C*$_6$Me$_5$), 109.01 (=CH$_2$), 144.29 (=CH). MS(EI, 70 eV) *m/z* 442.2 (M$^+$).

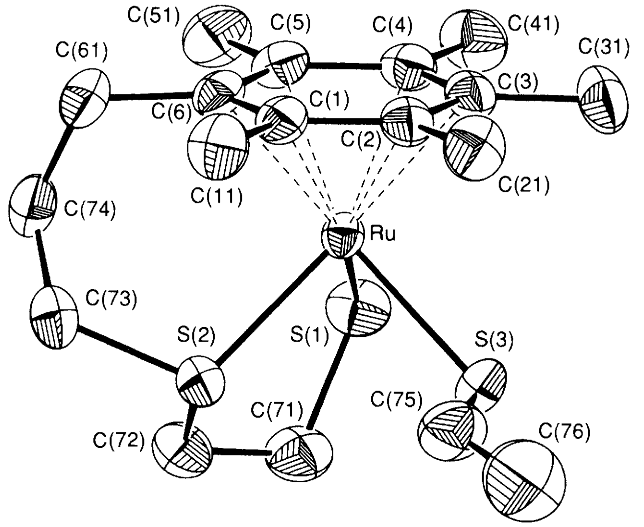

Fig. 1 Molecular structure of $[\overline{\mathrm{Ru}(\mathrm{SCH{=}CH_2})(\eta^6\text{-}\mathrm{C_6Me_5CH_2}\text{-}\mathrm{CH_2CH_2SCH_2CH_2S}})]$ **3**. Ellipsoids indicate 50% probability levels and hydrogen atoms are deleted. Selected bond lengths (Å) and angles (°): Ru–S(1) 2.3664(10), Ru–S(2) 2.3549(6), Ru–S(3), 2.4155(8), Ru–C(1) 2.242(3), Ru–C(2) 2.234(3), Ru–C(3) 2.224(2), Ru–C(4) 2.214(3), Ru–C(5) 2.224(3), Ru–C(6) 2.204(3), S(1)–C(71) 1.821(3), S(2)–C(72) 1.832(4), S(3)–C(75) 1.745(5), C(75)–C(76) 1.298(7), S(3)–C(75)–C(76) 127.7(5).

Facile cleavage of C–S bonds is known to occur in thiolate ligands attached to niobium[12] and molybdenum,[13] and in the addition of nucleophiles to η^5-thiophenes.[14] The results reported here suggest that irreversible, base-induced C–S bond cleavage may be a common feature in the chemistry of coordinated macrocyclic thioethers and may limit the extent to which such ligands can be attached to electron-rich transition metal centres.

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