C–H Activation of Co-ordinated Crowns Thioethers: Deprotonation and Ring-opening of $[M([9]aneS_3)_2]^{3+}$ (M = Co, Rh, Ir). Crystal Structure of $[Rh(H_2C{=}CHS(CH_2)_2S(CH_2)_2S)([9]aneS_3)](PF_6)_2$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane)

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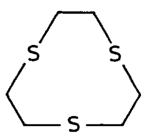
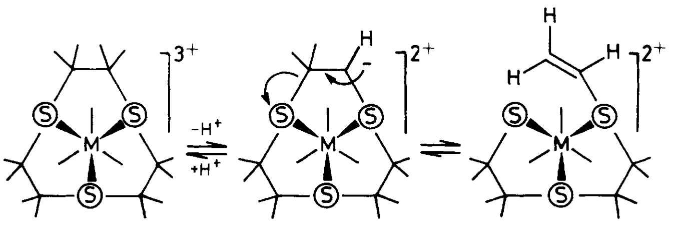
Addition of base to the complexes $[M([9]aneS_3)_2]^{3+}$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane; M = Co, Rh, Ir) leads to deprotonation at a methylene carbon, and subsequent re-arrangement of the carbanion affords a vinyl thioether complex *via* C–S bond cleavage; for M = Co this process is reversed in acidic medium to regenerate $[Co([9]aneS_3)_2]^{3+}$.

The synthesis and structure of the complexes $[M([9]aneS_3)_2]^{3+}$ (M = Co,[1] Rh,[2] Ir[3]) have been described. These octahedral complex cations show homoleptic hexathia co-ordination about the d^6 metal ion. The redox interconversion of $M^{I/II/III}$ species in which the trithia macrocycles can vary their co-ordination to accommodate these metal oxidation states has been achieved.[1—3] We report herein a new type of reaction of $[9]aneS_3$ with M^{III} centres involving C–H activation at the co-ordinated thioether followed by ring-opening *via* C–S bond cleavage to afford vinyl thioether complexes.

Addition of one molar equivalent of Et_3N to solutions of the complexes $[M([9]aneS_3)_2]^{3+}$ (M = Co, Rh, Ir) in MeCN or $MeNO_2$, or dissolution of $[M([9]aneS_3)_2]^{3+}$ in water at pH > 4 leads to a rapid change in colour of the solutions: from orange to green (λ_{max} 685 nm) for Co, from colourless to red (λ_{max} 474 nm) for Rh, and from colourless to yellow (λ_{max} 379 nm) for Ir.



[9]ane S_3



Scheme 1

Importantly for M = Co, this process is reversed under aqueous conditions at pH < 2, and the interconversion of orange to green species can be cycled readily by control of pH.

The ^1H n.m.r. spectra of the basic solutions each show resonances near δ_1 6.6 p.p.m. (dd, 1H) with a multiplet near δ_2 6.2 p.p.m. (2H). In addition, a series of multiplets is observed in the range δ 2.8—4.0 p.p.m. (20H) assigned to the methylene protons of co-ordinated [9]aneS$_3$. Selective decoupling experiments show that the resonances δ_1 and δ_2 are coupled to one another but not to any other proton. These data contrast with the ^1H n.m.r. spectra for the parent 3+ cations, which show symmetric multiplets in the δ 3.6 p.p.m. (24H) region (Figure 1). The ^{13}C n.m.r. spectra of the products confirm that symmetric binding of [9]aneS$_3$ to M^{III} has been perturbed. Resonances are observed in the region δ 28—43 p.p.m. assigned to 10 methylene C-centres of two [9]aneS$_3$ ligands. In addition, two resonances are observed at δ_A 126.67 (CH_2) and δ_B 118.45 p.p.m. (CH) for the Co system (D_2O), and at δ_A 128.84 (CH_2) and δ_B 122.07 p.p.m. (CH) for the Rh system (CD_3CN). For the Co system, selective decoupling experiments indicate that the proton (δ_1 6.5) is bound to the carbon (δ_B 118.45) and the protons (δ_2 6.2) to the carbon (δ_A 126.67). The n.m.r. data confirm that the complexes [M([9]aneS$_3$)$_2$]$^{3+}$ (M = Co, Rh, Ir) react under basic conditions to give the same type of products. F.a.b.-mass spectral data and elemental analysis of the isolated products confirm the stoicheiometry [M([9]aneS$_3$)([9]aneS$_3$−H)] (PF_6)$_2$.

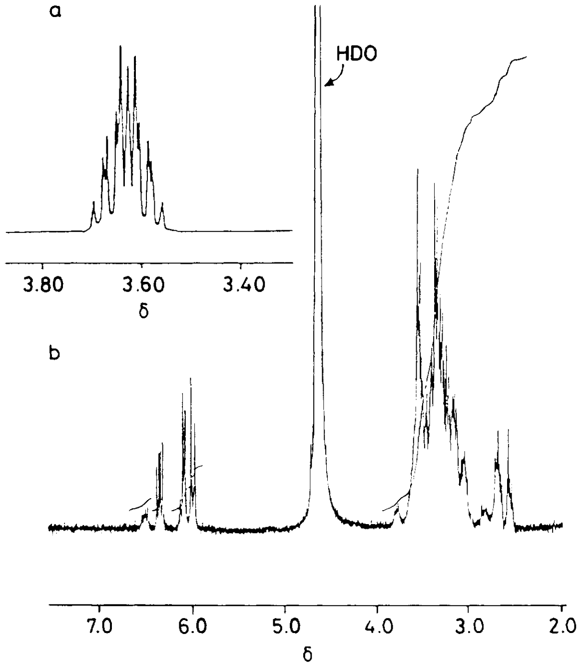


Figure 1. ^1H N.m.r. spectra of (a) [Co([9]aneS$_3$)$_2$]$^{3+}$ and (b) [Co($H_2C{=}CHS(CH_2)_2S(CH_2)_2S$)([9]aneS$_3$)]$^{2+}$.

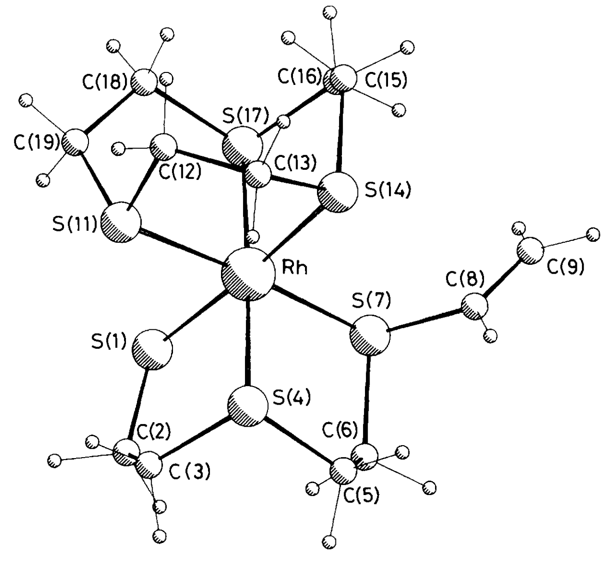


Figure 2. *X*-Ray crystal structure of [Rh($H_2C{=}CHS(CH_2)_2S(CH_2)_2S$)([9]aneS$_3$)]$^{2+}$ with numbering scheme adopted.

Single crystals of the red complex derived from the reaction of [Rh([9]aneS$_3$)]$^{3+}$ with Et_3N were isolated from MeCN/Et_2O. The single crystal *X*-ray structure[†] confirms[4] hexathia co-ordination about Rh^{III} (Figure 2). One [9]aneS$_3$ ligand is intact and bound facially to Rh^{III} with Rh–S(11) 2.315(4), Rh–S(14) 2.344(4), and Rh–S(17) 2.323(4) Å. The second [9]aneS$_3$, however, has undergone a ring-opening to afford a co-ordinated vinyl thioether moiety, S(7)–C(8)–C(9), with a terminal thiolate donor S(1): Rh–S(1) 2.350(4), Rh–S(4) 2.325(4), Rh–S(7) 2.356(4), and C(8)–C(9) 1.289(21) Å. The solid state structure is fully consistent with the ^1H and ^{13}C n.m.r. data, and suggests that analogous structures exist for the Co^{III} and Ir^{III} systems. Scheme 1 gives the proposed mechanism for the formation of this species. ^1H and ^{13}C n.m.r. spectroscopy of the vinyl thioether complexes indicate the presence of a minor isomer; the interconversion of isomers

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[†] *Crystal data* for: $C_{12}H_{23}S_6Rh^{2+}\cdot 2PF_6^-$, M = 752.6, monoclinic, space group $P2_1/a$, a = 13.226(5), b = 10.013(4), c = 18.966(7) Å, β = 95.55(3)°, U = 2500 Å^3 (from diffractometer angles for 23 centred reflections with 2θ = 26—34°, λ = 1.54184 Å, T = 298 K), Z = 4, D_c = 1.999 g cm^{-3}, μ(Cu-K_α) = 12.44 mm^{-1}. A deep red tablet (0.19 × 0.31 × 0.35 mm) was sealed in a Lindemann glass capillary tube and mounted on a Stoë STADI-4 four-circle diffractometer. Data collection to $2\theta_{max}$ = 90° using Cu-K_α *X*-radiation (λ = 1.54184 Å) gave 2305 absorption-corrected reflections, 1875 unique (R_{int} 0.029), of which 1549 with $F \geqslant 6\sigma(F)$ were used in all calculations. A Patterson synthesis located the Rh, and iterative cycles of least-squares refinement and difference Fourier synthesis[4] located all remaining non-H atoms. At isotropic convergence, final corrections for absorption were made using DIFABS.[5] Disorder in one PF_6^- counter-anion was successfully modelled and H atoms were included in fixed, calculated positions.[4] At final convergence, R = 0.0526, R_w = 0.0644, S = 1.225 for 242 parameters and the final ΔF synthesis showed no feature above 0.74 eÅ^{-3}. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

and fluxionality of these vinyl thioether complexes is under investigation. Deprotonation at a methylene carbon α to a co-ordinated thioether donor, followed by M–C bond formation has been reported previously.[6,7]

These results show that thioether crowns can be activated when co-ordinated to electropositive metal centres. The first step involves deprotonation at an α-methylene carbon centre. It seems likely that this type of reactivity will be general for other thioether macrocycles: we have found that $[M([9]aneS_3)]^{2+}$ (M = Pd, Pt), $[Pd([15]aneS_5)]^{2+}$, $[M([18]aneS_6)]^{n+}$ (M = Co, Rh, n = 3; M = Pd, Pt, n = 2), and $[Rh([12]aneS_4)Cl(AsPh_3)]^{2+}$ react similarly. We have recently reported the stabilisation of high valent complexes of Pd^{III},[3] Ag^{II},[8] Au^{III},[9] Fe^{III},[8,10] and Ni^{III}[8] with $[9]aneS_3$ under highly acidic conditions. It now seems clear that low pH conditions stabilise these highly charged cations by inhibiting deprotonation. We have also found that the vinyl thioether complex of Rh^{III} can be isolated as a by-product during the synthesis of $[Rh([9]aneS_3)_2]^{3+}$.[2] The yield of $[Rh([9]aneS_3)_2]^{3+}$ can be increased markedly by carrying out the reaction under acidic conditions to minimise the yield of ring-opened product. This is of particular relevance to the synthesis of thioether complexes, especially of inert metal ions. Deprotonation of $[9]aneS_3$ and related crowns, and reaction with electrophiles, represents a possible route for the *C*-functionalisation of thioether macrocycles.

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