Synthesis and S-Centred Reactivity of $(C_5Me_5)_3Ru_3S_4^+$

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Addition of $(C_5Me_5)Ru^+$ to $(C_5Me_5)_2Ru_2S_4$ affords $(C_5Me_5)_3Ru_3S_4^+$; this cluster displays *S*-centred reactivity towards a range of electrophiles (H^+, SO_2, Me^+, Et^+) to give adducts with solid-state structures containing $Ru_3(\mu_3\text{-}S_2)(\mu_3\text{-}S)(\mu\text{-}SR)$ cores.

The only known ruthenium sulfide, RuS_2, is comprised of octahedrally coordinated Ru centres interconnected by persulfide ligands.[1] There has been much interest in RuS_2 as a catalyst for hydrodesulfurization and photochemical water splitting.[2,3] In both processes it is plausible that the sulfur ligands in RuS_2 are involved in substrate binding. We were intrigued by the possibility that soluble ruthenium persulfide clusters might also prove highly reactive towards small molecules.

In evaluating possible routes to Ru_x persulfido clusters we were attracted by the metalloligand approach whereby small metal sulfido compounds are deployed as ligands towards other metals. Noteworthy applications of this strategy have included the metallation of MoS_4^{2-}, $Fe_2S_2(CO)_6$ and $(C_5R_5)_2V_2S_4$.[4] We report here the application of this cluster construction methodology for the preparation of an unusual family of reactive Ru_3S_4 clusters. Our results define a potentially general route to reactive metal sulfido clusters *via* the addition of $(C_5Me_5)Ru^+$ to $L_2M_2S_4$ species, for which there are numerous examples.[4a]

The reaction of $[(C_5Me_5)Ru(MeCN)_3]PF_6$[5] with $(C_5Me_5)_2Ru_2S_4$[6] in refluxing MeCN affords high yields of the red species $[(C_5Me_5)_3Ru_3S_4]PF_6$ ([**1**]PF_6), eqn. (1); the empirical formula was confirmed by microanalysis and mass spectrometry.†

(1)

The observation of a single line in the ^1H NMR spectrum (25 to −40 °C, 500 MHz, CD_3CN) is consistent with a C_{3v} $M_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)$ core typical of clusters with this stoichiometry (Scheme 1).[7] Interestingly, however, the reactivity of this species indicates otherwise. We have not been able to obtain single crystals of well-ordered salts of $\mathbf{1}^+$ but the cell data are at least consistent with the proposed molecularity.‡

The structure of $\mathbf{1}^+$ can be partly inferred from the structures of its derivatives. The adduct $\mathbf{1}\cdot SO_2^+$ was prepared by both addition of SO_2 to a MeCN solution of [**1**]PF_6 as well as air oxidation of the latter. This cluster features an isosceles Ru_3 core featuring two Ru–Ru bonds.§ These metals are joined by triply bridging sulfido and persulfido ligands (Fig. 1). The SO_2 is bound to an otherwise doubly bridging sulfide. The geometry at S(1) is consistent with SO_2 serving as a Lewis acid, the long S–SO_2 distance of 2.469 Å being comparable to SO_2 adducts of other metal sulfides.[8]

The lability of salts of $\mathbf{1}\cdot SO_2^+$ precluded detailed spectroscopic characterisation in solution, hence we examined the more robust *S*-alkylated derivatives. Solutions of $\mathbf{1}PF_6$ quickly give a green colour upon addition of ROTf (R = Me, Et) to give the salts [**1**·R](PF_6)(OTf), isolated as analytically pure black microcrystals.¶ Significantly the *S*-alkylated clusters are unreactive towards further equivalents of ROTf. ^1H NMR spectra of these derivatives indicate C_s structures with two types of C_5Me_5 groups (2:1) and one *S*-alkyl group. A crystallographic determination‖ confirmed that $\mathbf{1}\cdot Et^{2+}$ is very similar to $\mathbf{1}\cdot SO_2^+$ in terms of the symmetry and connectivity of the $Ru_3S_4^{4+}$ core. The electrophiles in both $\mathbf{1}\cdot Et^{2+}$ and $\mathbf{1}\cdot SO_2^+$ are oriented towards the persulfide face of the Ru_3 triangle. In each case, the S–S bond in the persulfido group is *ca.* 0.15 Å longer than typical S–S bonds. *E.g.* $(C_5Me_5)_2Ru_2S_4$ has S–S distances of 2.02 and 2.04 Å.[9] The S–S distances in the adducts of $\mathbf{1}^+$ are more similar to that seen in the mineral RuS_2 (2.179 Å) which adopts the pyrite structure.[1]

Protonation experiments confirm the nucleophilic character of $\mathbf{1}^+$. Addition of HOTf to solutions of $\mathbf{1}^+$ gives a green species which shows a 2:1 C_5Me_5 pattern in its ^1H NMR spectrum (the SH signal was not observed), as seen for $\mathbf{1}\cdot R^{2+}$. Protonation can also be effected with p-$MeC_6H_4SO_3H$ (pK_a −1.74), but not CH_3CO_2H (pK_a 4.7). Aqueous ammonia cleanly converts $\mathbf{1}\cdot H^{2+}$ back to $\mathbf{1}^+$ [eqn. (2)].

$$(C_5Me_5)_3Ru_3S_4^+ \underset{NH_3}{\overset{H^+}{\rightleftharpoons}} (C_5Me_5)_3Ru_3S_3(SH)^{2+} \qquad (2)$$

Two types of $(C_5R_5)_3M_3S_4$ clusters are known (Scheme 1). The clusters, including $(C_5R_5)_3V_2CoS_4$ and $(C_5R_5)_3Mo_2FeS_4^+$, adopt core structures with an edge-bridging persulfido ligand (type *A* in Scheme 1).[10] $(C_5R_5)_3Mo_3S_4$ on the other hand features a symmetrical C_{3v} core and no persulfides (type

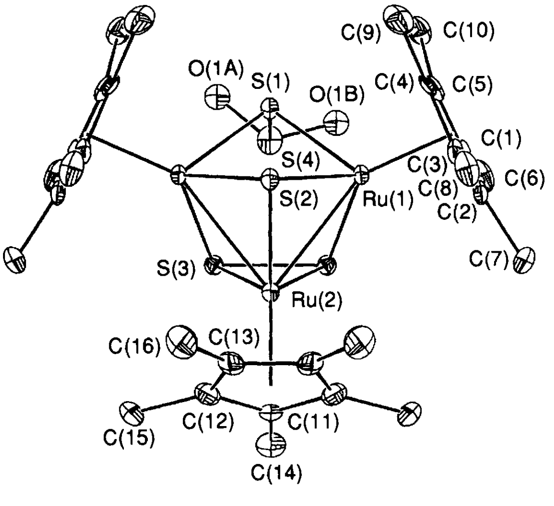
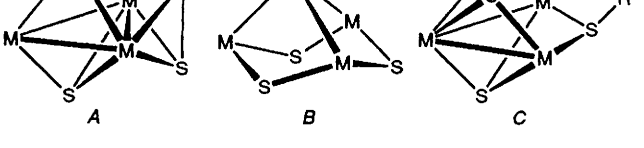


Fig. 1 Structure of the cation in [**1**·SO_2]PF_6 with thermal ellipsoids drawn at the 35% probability level. Atoms Ru(2), S(1) and S(4) define the crystallographically imposed symmetry plane. Selected bond angles (Å) and distances (°): Ru(1)–Ru(2) 2.8618(9), Ru(1)···Ru(1′) 3.4300(9), S(3)–S(3) 2.174(4), S(1)–S(4) 2.469(4), S(4)–O(1) 1.436(8), Ru(2)–S(2) 2.267(3), Ru(3)–S(3) 2.310(2), Ru(1)–S(2) 2.328(2), Ru(1)–S(1) 2.349(2), Ru(1)–S(3) 2.241(2), Ru(1)–Ru(2)–Ru(1′) 73.84(3), O(1a)–S(4)–O(1b), 116.8(6). The corresponding bonding Ru–Ru distances in [**1**·Et](PF_6)(OTf) are 2.870(2) and 2.886(2) Å and the S–S bond length [corresponding to S(3)–S(3′)] in [**1**·SO_6]PF_6 is 2.210(3) Å.



Scheme 1

B in Scheme 1).[11] The structures of $\mathbf{1}\cdot\mathrm{Et}^{2+}$ and $\mathbf{1}\cdot\mathrm{SO_2}^{+}$, type *C* in the Scheme, resemble neither type *A* nor type *B*. This suggests that $\mathbf{1}^{+}$ itself may adopt a new M_3S_4 structure. The significance of structure/reactivity correlations in these clusters is illustrated by our finding that $(C_5Me_5)_3Mo_3S_4{}^{+}$,** a stoichiometric analogue of $\mathbf{1}^{+}$, is completely unreactive towards both MeOTf and concentrated HCl.

A new class of M_3S_4 clusters has been discovered which displays novel, S-centred reactivity. These findings suggest that discussions of the reactivity of RuS_2 should consider a substrate-binding role for the sulfido ligands.[12] Our studies also show that the $(C_5Me_5)Ru^{+}$ is a promising building block for cluster synthesis.

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Footnotes

† ^1H NMR $[(CD_3)_2CO]$: δ 1.93 (s). $^{13}C\{^1H\}$ NMR $[(CD_3)_2CO]$: δ 11.24, 100. UV–VIS (nm, CH_3CN): 326(sh), 432, 496. FABMS (*m/z*): 839 (M^+), 807 ($M^+ - S$). Similar procedures gave the Cl^-, OTf^-, $SbF_6{}^-$ and $BF_4{}^-$ salts.

‡ $C_{30}H_{45}F_6PRu_3S_4\cdot C_3H_6O$ orthorhombic, $P2_12_12_1$: $a = 8.876(3)$, $b = 21.426(7)$, $c = 22.807(8)$ Å, $V = 4337(3)$ Å^3, $Z = 4$; 4614 reflections collected (198 K, Mo-Kα, $2 < 2\theta < 50°$; Enraf-Nonius CAD4 diffractometer).

§ $C_{31}H_{45}F_3O_6Ru_3S_4$, orthorhombic, *Pnma*: $a = 20.089(4)$, $b = 21.597(6)$, $c = 8.559(2)$ Å, $V = 3713(2)$ Å^3, $Z = 4$. Of 3350 reflections collected (198 K, Mo-Kα, $2 < 2\theta < 25°$; Enraf-Nonius CAD4 diffractometer) 2236 $[F_o > 4\sigma(F_o)]$ 3350 were refined to $R = 0.0441$, $R_w = 0.08$. The oxygen atoms in the SO_2 and the O and F atoms in the OTf^- were disordered.

¶ $[(C_5Me_5)_3Ru_3S_3(SMe)](PF_6)CF_3SO_3$: Dark-green crystals in 81% yield from CH_2Cl_2–THF. ^1H NMR (CD_3CN): δ 2.09 (s, 15 H), 1.87 (s, 30 H), 0.80 (s, 3 H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 109.6, 109, 21.3 (CH_3), 12.3 $[C_5(CH_3)_5]$, 11.3 $[C_5(CH_3)_5]$. UV–VIS (nm, MeCN): 332, 432, 622. FABMS (*m/z*): 854 (M^+), 807 (M^+ − SMe). CV (mV, *vs.* Ag/AgCl, MeCN): +1240, −200, −740. $[(C_5Me_5)_3Ru_3S_3(SEt)](PF_6)CF_3SO_3$: ^1H NMR (CD_3CN): δ 2.096 (s), 1.864 (s), 1.273 (q), 0.730 (t).

|| Monoclinic crystals, $P2_1/n$: $a = 13.095(7)$, $b = 15.672(8)$, $c = 21.104(1)$ Å, $\beta = 90.53(4)°$, $V = 4313(3)$ Å^3. Of 7195 unique reflections (193 K, Mo-Kα: $3 < 2\theta < 52°$; Stoe Stadi II diffractometer), 6330 $[F_o > 3\sigma(F_o)]$ were refined to $R = 0.0547$, $R_w = 0.0575$. The F atoms in the $PF_6{}^-$ and the F and O atoms in the OTf^- were disordered.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

** We have confirmed the solid-state structure of C_{3v} $[(C_5Me_5)_3Mo_3S_4]Cl$: H. Krautscheid, unpublished results.

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