Heteronuclear Cluster Formation: The Synthesis and Structure of the Chloro-bridged Tetranuclear Complex [$TlCl_2Ru(PPh_3)([9]aneS_3)]_2(PF_6)_2$ Incorporating a [$RuCl_2Tl_2Cl_2Ru$] Ladder ([9]aneS_3 = 1,4,7-Trithiacyclononane)

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Treatment of [$RuCl_2(PPh_3)([9]aneS_3)$], formed in high yield by reaction of [$RuCl_2(PPh_3)_3$] with [9]aneS_3, with $TlPF_6$ in CH_2Cl_2 at 273 K affords the yellow hetero-cluster species [$TlCl_2Ru(PPh_3)([9]aneS_3)]_2(PF_6)_2$ incorporating a [$RuCl_2Tl_2Cl_2Ru$] ladder; dissolution of [$TlCl_2Ru(PPh_3)([9]aneS_3)]_2(PF_6)_2$ in acetone leads to precipitation of TlCl and the formation of the orange chloro-bridged dimer [$RuCl(PPh_3)([9]aneS_3)]_2(PF_6)_2$.

The macrocycle [9]aneS_3 has been shown to be an effective six-electron capping ligand for a range of transition metal centres.[1–4] [9]aneS_3 is, therefore, the thioether S-donor analogue of cyclopentadienyl, aryl, tris(pyrazolyl)borate and triphos [$(Ph_2PCH_2)_3CMe$], and might be expected to form a range of half-sandwich organometallic and coordination compounds. We have reported previously the synthesis and properties of the low-valent complexes [$M([9]aneS_3)(alkene)_2]^+$ (M = Rh, Ir),[5] and describe herein the first examples of half-sandwich complexes of [9]aneS_3 with Ru^{II}, and the formation of an unusual heteronuclear Ru_2Tl_2 cluster.

Treatment of [$RuX_3(PR_3)_3$] (X = Cl, PR_3 = PMe_2Ph, PEt_2Ph, $PEtPh_2$; X = Br, PR_3 = $PEtPh_2$) with [9]aneS_3 in EtOH or CH_2Cl_2 affords [$RuCl(PR_3)_2([9]aneS_3)]^+$, while reaction of [$RuX_2(PPh_3)_3$] (X = Cl, Br) with [9]aneS_3 gives [$RuX_2(PPh_3)([9]aneS_3)$] in high yield.† The bright yellow complex [$RuCl_2(AsPh_3)([9]aneS_3)$] can be prepared by reaction of [$RuCl_3(AsPh_3)_2(MeOH)$] with [9]aneS_3 in refluxing EtOH. [$RuX_2(PPh_3)([9]aneS_3)$] is a particularly useful starting material for the synthesis of chiral complexes of the type [$RuX(PPh_3)(L)([9]aneS_3)]^+$. Thus, reaction of [$RuX_2(PPh_3)([9]aneS_3)$] with $TlPF_6$ in the presence of coordinating solvents or ligands gives [$RuX(PPh_3)(L)([9]aneS_3)]^+$ (X = Cl, L = NCMe, NCPh, PMe_2Ph, $P(OMe)_2Ph$, CO, CS, py; X =

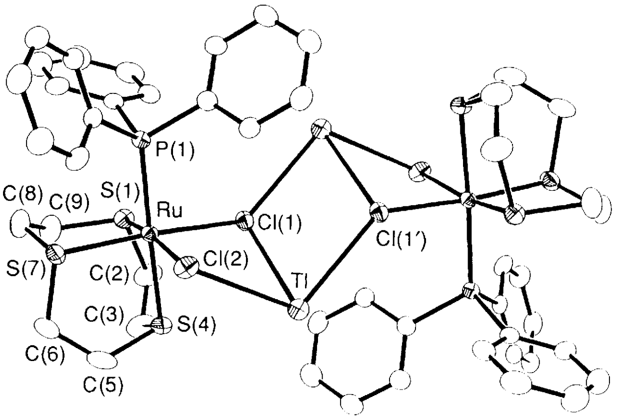

Fig. 1 The single crystal X-ray structure of [$TlCl_2Ru(PPh_3)([9]aneS_3)]_2^{2+}$ with numbering scheme adopted. H atoms are omitted for clarity. Tl–Cl(1) 3.0734(11), Tl–Cl(1′) 3.0014(11), Tl–Cl(2) 3.0026(12), Ru–Cl(1) 2.4416(12), Ru–Cl(2) 2.4526(12), Ru–S(1) 2.2804(13), Ru–S(4) 2.3501(13), Ru–S(7) 2.2821(13), Ru–P(1) 2.3539(12) Å. The primed atom is related to its unprimed equivalent by inversion through (0,1,1).

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† All complexes reported herein have been fully characterised using elemental analysis, IR, NMR, electronic and FAB mass spectroscopy, and in the case of [$RuCl(PEtPh_2)_2([9]aneS_3)]^+$ and [$RuCl(PPh_3)(NCMe)([9]aneS_3)]^+$ by single crystal X-ray diffraction.[4]

Br, L = PMe$_2$Ph, py; py = pyridine).[4]† Interestingly, the complex [RuCl(PPh$_3$)$_2$([9]aneS$_3$)]$^+$ could not be prepared under these conditions, presumably owing to the steric hindrance of the relatively large phosphine ligands. We were interested in the reactions of [RuX$_2$(PPh$_3$)([9]aneS$_3$)] with TlPF$_6$ in the absence of coordinating ligands, particularly with regard to the possibility of forming oligomers of the [Ru([9]aneS$_3$)]$^{2+}$ fragment.

Reaction of [RuCl$_2$(PPh$_3$)([9]aneS$_3$)] with TlPF$_6$ in CH$_2$Cl$_2$ at 273 K leads to the formation of a yellow complex. Elemental analysis of the product indicated a stoichiometry [RuCl$_2$(PPh$_3$)([9]aneS$_3$)]·TlPF$_6$, while FAB mass spectroscopy showed a molecular ion peak at M$^+$ = 819 assigned to [^{102}Ru^{35}Cl$_2$(PPh$_3$)([9]aneS$_3$)^{205}Tl]$^+$ with the correct isotopic distribution; IR and NMR spectroscopy confirmed the presence of [9]aneS$_3$, PPh$_3$ and PF$_6^-$ counter-ion. Crystals of the complex were obtained from CD$_3$NO$_2$ and a single crystal X-ray structural determination was undertaken. The crystal structure‡ confirms the presence of Ru and Tl within a tetranuclear cluster (Fig. 1). Two octahedral [RuCl$_2$(PPh$_3$)([9]aneS$_3$)] units are bridged *via* the coordinated Cl$^-$ ligands to two Tl$^+$ ions to form a highly unusual RuCl$_2$Tl$_2$Cl$_2$Ru ladder structure. The cluster incorporates two μ^2-Cl$^-$ and two μ^3-Cl$^-$ bridges with the two halves of the cation related by an inversion centre; ∠Cl(1)TlCl(2) 69.36(3), ∠Cl(1)TlCl(1′) 72.61(3), ∠Cl(2)TlCl(1′) 107.38(3)°. There are no apparent M–M interactions: Tl···Ru = 4.0596(4) Å. The [9]aneS$_3$ ligand is coordinated facially to Ru^{II} with the Ru–S bond *trans* to PPh$_3$ [2.3501(13) Å] being longer than those *trans* to Cl$^-$ [2.2804(13), 2.2821(13) Å]; additionally, there is a potential long-range interaction between Tl and S(4) at 3.6481(13) Å. Although there are a number of documented heterometallic Tl-containing species in the literature,[6–8] most of them incorporate direct M–Tl bonding rather than the bridged M–halide–Tl units observed in our structure. Mingos and coworkers have reported the structure of [Pt$_3$(CO)$_3$(PCy$_3$)$_3$Tl][Rh(C$_8$H$_{12}$)Cl$_2$] (Cy = cyclohexyl) incorporating direct Pt–Tl bonding and an additional Rh···Cl···Tl interaction.[7] Schmidbauer and coworkers have reported [(C$_6$H$_3$Me$_3$)$_6$Tl$_4$][GaBr$_4$]$_4$, an adduct of [GaBr$_4$]$^-$ with [Tl(C$_6$H$_3$Me$_3$)]$^+$ and [Tl(C$_6$H$_3$Me$_3$)$_2$]$^+$. This species incorporates an array of Ga···Br···Tl bridges.[8] The use of TlPF$_6$ to remove coordinated Cl$^-$ from metal complexes is well documented. The formation of [TlCl$_2$Ru(PPh$_3$)([9]aneS$_3$)]$_2$(PF$_6$)$_2$ suggests that the first step in the reaction involves interaction of Tl$^+$ with the Cl$^-$ within the coordination sphere of the parent complex.

Dissolution of [TlCl$_2$Ru(PPh$_3$)([9]aneS$_3$)]$_2$(PF$_6$)$_2$ in acetone or MeNO$_2$ leads to precipitation of TlCl and the formation of the orange chloro-bridged dimer [RuCl(PPh$_3$)([9]aneS$_3$)]$_2$(PF$_6$)$_2$. The single crystal structure of the complex‡ shows (Fig. 2) two Cl$^-$ ligands [Ru–Cl = 2.4654(10), 2.4945(10) Å], bridging [Ru(PPh$_3$)([9]aneS$_3$)]$^{2+}$ units, Ru–S(*trans* to Cl) = 2.2880(10), 2.2817(10), Ru–S(*trans* to P) = 2.3456(10) Å, Ru···Ru = 3.7768(6), Cl···Cl = 3.2151 Å. The two halves of the dimer are related by a crystallographic inversion centre. Dissolution of [TlCl$_2$Ru(PPh$_3$)([9]aneS$_3$)]$_2$(PF$_6$)$_2$ in more strongly coordinating solvents or in the presence of donor ligands (L) leads to the formation of the mononuclear species [RuCl(PPh$_3$)(L)([9]aneS$_3$)]$^+$.

The results described herein suggest that the first step in the thalliation of metal–halide bonds involves the interaction of Tl$^+$ with the M–Cl bond to form an M–Cl–Tl bridge, and that the synthesis of mixed main group–transition metal clusters might be readily achieved using this methodology. Current work is aimed at developing these electrophilic Ru^{II} complexes of [9]aneS$_3$ towards C–H bond activation and organic transformations.

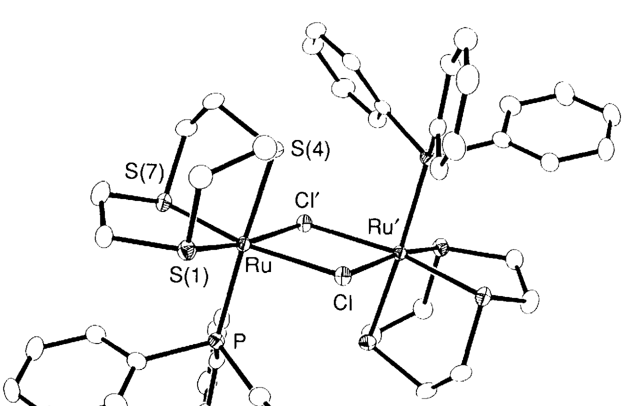

Fig. 2 The single crystal X-ray structure of [RuCl(PPh$_3$)([9]aneS$_3$)]$_2^{2+}$ with numbering scheme adopted. H atoms are omitted for clarity. Ru–S(1) 2.2880(10), Ru–S(4) 2.3456(10), Ru–S(7) 2.2817(10), Ru–Cl 2.4654(10), Ru–Cl′ 2.4945(10), Ru–P 2.3741(10) Å. The primed atom is related to its unprimed equivalent by inversion through (½,0,½).

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‡ *Crystal data* for C$_{48}$H$_{54}$Cl$_4$P$_2$Ru$_2$S$_6$Tl$_2^{2+}$2PF$_6^-$·4CD$_3$NO$_2$. *M* = 2184.15, triclinic, space group $P\bar{1}$, *a* = 10.2202(23), *b* = 10.7668(18), *c* = 16.4498(24) Å, α = 96.206(15), β = 100.971(16), γ = 90.862(14)°, *V* = 1765.4 Å^3 [from 2θ values of 42 reflections measured at ±ω (2θ = 31–32°, λ = 0.71073 Å), *T* = 150 ± 0.1 K], *Z* = 1, D_c = 2.053 g cm^{-3}, μ(Mo-Kα) = 5.45 mm^{-1}. A yellow column (0.08 × 0.16 × 0.43 mm) was mounted on a Stoë STADI-4 four-circle diffractometer. Data collection at 150 K using Mo-Kα X-radiation (λ = 0.71073 Å), ω–2θ scans and the learnt-profile method[9] gave 4620 unique reflections (2θ$_{max}$ 45°), of which 4193 with $F \geqslant 4\sigma(F)$ were used in all calculations. A correction for *ca.* 5% linear isotropic decay was incorporated in the data reduction. Following solution by heavy-atom methods, the structure was refined by full-matrix least-squares (on *F*),[10] with anisotropic thermal parameters for all non-H atoms except that F and O atoms with occupancies of 0.5 or less were treated isotropically. Phenyl rings were refined with idealised D_{6h} symmetry. H atoms were included in fixed, calculated positions except for those in the solvent CD$_3$ groups which were treated as part of rigid groups.[10] Disorder affects both the PF$_6^-$ anions and the solvent; it was modelled by allowing split occupancies for the equatorial F atoms and the O atoms. At isotropic convergence, corrections for absorption were applied empirically using DIFABS.[11] At final convergence, *R* = 0.0251, R_w = 0.0321, *S* = 1.053 for 439 parameters and the final Δ*F* synthesis showed no Δρ beyond ±0.72 e Å^{-3}. A secondary extinction parameter refined to 1.4 × 10^{-8}.

Crystal Data for C$_{48}$H$_{54}$Cl$_2$P$_2$Ru$_2$S$_6^{2+}$2PF$_6^-$·2CH$_3$NO$_2$. *M* = 1570.18, monoclinic, space group $P2_1/n$, *a* = 14.5986(24), *b* = 13.1911(23), *c* = 15.6282(17) Å, β = 103.425(9)°, *V* = 2927.3 Å^3 [from 2θ values of 31 reflections measured at ±ω (2θ = 24–26°, λ = 0.71073 Å)], *Z* = 2, D_c = 1.781 g cm^{-3}, *T* = 150 ± 0.1 K, orange tablet, 0.085 × 0.23 × 0.23 mm, μ = 0.994 mm^{-1}, *F*(000) = 1584. Data collection under the conditions described above yielded 4461 absorption-corrected reflections, 3631 unique (R_{int} 0.030), giving 3222 with $F \geqslant 4\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed. A Patterson synthesis located the Ru and iterative cycles of least-squares refinement and difference Fourier synthesis located all remaining non-H atoms. Four of the F atoms in the PF$_6^-$ anion were found to be disordered over two orientations, the major component having occupancies of 0.84–0.95. The F atoms of the minor component were refined with a common U_{iso} of 0.08 Å^2 and occupancies ranging from 0.05 to 0.16; all other non-H atoms were refined (by least-squares on *F*)[10] with anisotropic thermal parameters. Phenyl rings were constrained to refine with idealised D_{6h} symmetry. H atoms were included at fixed, calculated positions, excepting those of the solvate methyl group which was refined as a rigid group: a common U_{iso} of 0.0408(22) Å^2 was refined for all H atoms. At final convergence *R*, R_w = 0.0293, 0.0434 respectively, *S* = 1.312 for 354 refined parameters and the final Δ*F* synthesis showed no Δρ above 0.47 or below −0.69 e Å^{-3}.

Atomic scattering factors were inlaid,[10] or taken from ref. 12. Molecular geometry calculations utilised CALC[13] and the Figures were produced by XP.[14] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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