Organometallic Thiol and Thiolato Complexes of Ruthenium(IV) †

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Reaction of the ruthenium(IV) chloro-bridged dimer [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(μ-Cl)}$_2$] **1** with a range of alkane- and arene-thiols in CH$_2$Cl$_2$ resulted in the formation of the simple, bridge-cleaved adducts [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2$(HSR)] (R = Et **2**, Me **3**, Pr^i **4**, Bu^t **5** or Ph **6**). Reaction of **1** with an excess of thiol in methanol gave doubly thiolate-bridged compounds [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(μ-SR)}$_2$] (R = Et **7**, Ph **12** or C$_6$F$_5$ **13**) each of which exists as two diastereoisomers but as a single geometrical isomer. In the case of **7** and **12** separation of the two diastereomeric forms proved possible because of their remarkably different solubilities in methanol, and their kinetic inertness. Reactions of **2** and **3** with **1** gave the mixed-bridge chloro/thiolato complexes [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl}$_2$(μ-Cl)(μ-SR)] (R = Me **9** or Et **8**). The unusual stereochemistry of these compounds is evident from analysis of their variable-temperature ^{1}H NMR spectra. The crystal structure of **8** has been determined. Reaction of **1** with H$_2$S in CH$_2$Cl$_2$ proceeds *via* the H$_2$S adduct [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2$(SH$_2$)] **10**, which rapidly reacts with further **1** with accompanying loss of HCl to give the singly SH-bridged complex [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl}$_2$(μ-Cl)(μ-SH)] **11**. Reaction of the EtSH compound **2** with a range of Ru^{II} and Rh^{III}-containing compounds enabled the isolation of a number of unusual mixed-valence and mixed-metal complexes containing one or two bridging ethanethiolate ligands. The ruthenium(IV)–rhodium(III) compounds [(η^3:η^3-C$_{10}$H$_{16}$)ClRu(μ-Cl)(μ-SEt)-RhCl(η^5-C$_5$Me$_5$)] and [(η^3:η^3-C$_{10}$H$_{16}$)ClRu(μ-SEt)$_2$RhCl$_2$(PMe$_2$Ph)$_2$] have been characterised by X-ray crystallography.

The chemistry of the organometallic ruthenium(IV) chloride-bridged dimer [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(μ-Cl)}$_2$] **1** [1,2] has been under extensive investigation by ourselves and others in recent years. [3–13] One intriguing point which has arisen several times in these studies but which has never been thoroughly investigated is the propensity of **1** to form neutral, bridge-cleaved adducts with ligands containing the thiol (SH) functionality {e.g. [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2$(HL)] (HL = benzothiazole-2-thiol, pyridine-2-thiol, [5] 6-methylpyridine-2-thiol or quinoline-2-thiol [8]) and [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2${SC(OH)Me}] [11] although in the latter case it is unclear whether the oxygen or sulfur of the thiocarboxylic acid is protonated}. These results contrast with similar observations made upon the analogous reactions involving ligands containing the hydroxyl functionality in which deprotonation invariably occurs to give compounds such as [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(L')] (L' = pyridin-2-olate, 6-methylpyridin-2-olate or quinolin-8-olate) [8] and [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(O$_2$CMe)] or [Ru(η^3:η^3-C$_{10}$H$_{16}$)(O$_2$-CCF$_3$)$_2$(OH$_2$)]. [11]

The observation of compounds such as [Ru(η^3:η^3-C$_{10}$-H$_{16}$)Cl$_2$(HL)] and [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2${SC(OH)Me}] is surprising in that co-ordination complexes of neutral thiols are relatively uncommon, [14,15] presumably because of the high acidity of the SH functionality, and many of those which are known are frequently unstable to air [15,16] or to loss of H$^+$ or H$_2$. [16,17]

Some thiol complexes of ruthenium(II) have been reported in recent years, [15,16] e.g. [Ru(η^5-C$_5$H$_5$){PPh$_2$(OMe)}$_2$(HSBu^t)]-[PF$_6$] {which oxidises in air to the paramagnetic ruthenium(III) species [Ru(η^5-C$_5$H$_5$){PPh$_2$(OMe)}$_2$(SBu^t)][PF$_6$] [15]} and very recently the crystal structure of the hydrogen sulfide-containing compound [Ru(H$_2$S)(PPh$_3$)(o-SC$_6$H$_4$SCH$_2$CH$_2$-SC$_6$H$_4$S-o)]·thf (thf = tetrahydrofuran) has been elucidated, although it also oxidises in air to form [{Ru(PPh$_3$)(o-SC$_6$H$_4$SCH$_2$CH$_2$SC$_6$H$_4$S-o)}$_2$(μ-S$_2$)]. [18]

In the case of the ruthenium(IV) thiol complexes [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2$(HL)] and [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2${SC(OH)Me}] it is unclear whether the SH functionality is actually bound to the metal centre since in each case the ligands involved are ambidentate and spectroscopic data are in many cases ambiguous.

We now report the results of our investigations into the reactions of complex **1** with a range of simple alkane- and arene-thiols in which there is little doubt about the co-ordination mode of the sulfur donors in the resulting thiol- and thiolato-metal compounds.

Experimental

Instrumental.—Infrared spectra were recorded on a Perkin-Elmer PE983 spectrometer between 4000 and 180 cm^{-1} as either KBr discs or Nujol mulls on CsI plates, NMR spectra on Varian VXR400 spectrometers at University College London and microanalyses were carried out by the departmental service. Mass spectra were run by the University of London Intercollegiate Research Service at the School of Pharmacy. Cyclic voltammetry measurements were performed using a Metrohm E506 potentiostat interfaced with a Metrohm E612 VA scanner and a Hewlett-Packard 7035B XY recorder. Electrolyte solutions were 0.2 mol dm^{-3} in tetra-*n*-butylammonium tetrafluoroborate. The solution was deaerated before the experiment and a stream of nitrogen passed throughout. The working electrode was a platinum wire (Metrohm EA285). A platinum wire was used as a pseudo-reference electrode and potentials were corrected relative to the ferrocene–ferrocenium couple (ferrocene was added at the end of each experiment). A massive platinum wire was used as the auxiliary electrode. All potentials are reported with respect to the Ag–AgCl couple against which ferrocene is oxidised at a potential of +0.60 V. All manipulations were carried out under nitrogen with degassed solvents using conventional Schlenk-line techniques, although no significant air sensitivity of the products was noted.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Materials.—The complex [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] was prepared by published literature methods.[1,13,15] Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc and was purified before use by dissolution in water and boiling to dryness. All other reagents and materials were obtained from the usual commercial sources.

Preparations.—[Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSEt)] **2**. The compound [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] **1** (0.22 g, 0.35 mmol) was stirred in CH_2Cl_2 (3 cm^3) with EtSH (0.2 cm^3, excess) for 5 min resulting in a rapid change from purple to orange-red. The volume of the solution was reduced to 0.5 cm^3 resulting in the deposition of the product as well formed orange-red crystals. Hexane (5 cm^3) was added to precipitate a further crop of product and the mixture was filtered off, washed thoroughly with hexane and dried under vacuum. Yield: 0.20 g, 0.54 mmol, 77% (Found: C, 38.55; H, 6.15; Cl, 20.15. Calc. for $C_{12}H_{22}Cl_2RuS$: C, 38.90; H, 6.00; Cl, 19.15%).

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSMe)] **3**. Compound **1** (0.17 g, 0.28 mmol) was stirred in CH_2Cl_2 (3 cm^3) for 1 min during which time a steady stream of MeSH was bubbled through the solution resulting in a change from purple to deep orange. The solvent was removed *in vacuo* and the resulting orange oil triturated with hexane to give the product as orange-red microcrystals which were filtered off, washed thoroughly with hexane and dried under vacuum. Yield: 0.16 g, 0.45 mmol, 80% (Found: C, 36.85; H, 5.75. Calc. for $C_{11}H_{20}Cl_2RuS$: C, 37.10; H, 5.65%).

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSPr^i)] **4**. Compound **1** (0.12 g, 0.19 mmol) was stirred in CH_2Cl_2 (3 cm^3) with Pr^{i}SH (0.15 cm^3, excess) for 5 min resulting in a rapid change from purple to deep orange. The solvent was removed *in vacuo* and the resulting orange solid washed thoroughly with hexane and dried under vacuum. Yield: 0.11 g, 0.29 mmol, 76% (Found: C, 40.60; H, 6.30. Calc. for $C_{13}H_{24}Cl_2RuS$: C, 39.95; H, 5.80%).

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSBu^t)] **5**. Compound **1** (0.14 g, 0.23 mmol) was stirred in CH_2Cl_2 (3 cm^3) with Bu^{t}SH (0.2 cm^3, excess) for 30 min resulting in a slow change from purple to deep red. Treatment of this solution as for **3** resulted in an orange solid found to be a mixture of complexes **5** and **1**. Attempts to obtain pure **5** by recrystallisation from diethyl ether resulted in an orange solution from which **1** rapidly precipitated.

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSPh)] **6**. Compound **1** (0.07 g, 0.11 mmol) was treated with PhSH (0.2 cm^3, excess) for 15 min as described for **2** resulting in the isolation of a brown solid. Yield: 0.07 g, 0.17 mmol, 77% (Found: C, 45.95; H, 5.30. Calc. for $C_{16}H_{22}Cl_2RuS$: C, 45.30; H, 5.40%).

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-SEt)}$_2$] **7**. (*a*) Compound **1** (0.18 g, 0.29 mmol) was stirred in MeOH (5 cm^3) with EtSH (0.4 cm^3, excess) for 36 h resulting in the gradual formation of a deep red solution and a brown precipitate which was filtered off and air dried. A second crop of precipitate was obtained by evaporation of the red solution to *ca.* 1 cm^3 and was filtered off and dried under vacuum. Combined yield: 0.11 g, 0.16 mmol, 55% (Found: C, 42.10; H, 6.15. Calc. for $C_{24}H_{42}Cl_2Ru_2S_2$: C, 43.15; H, 6.35%). The initial precipitate was found to consist almost entirely (> 90%) of a single diastereoisomer **7a**. The second crop consisted solely of **7b**.

(*b*) The compound [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSEt)] (0.08 g, 0.23 mmol) was stirred in MeOH (5 cm^3) for 36 h resulting in the formation of an orange-red solution and an orange precipitate which was filtered off. Evaporation of the solvent to *ca.* 1 cm^3 resulted in a further crop of brown precipitate. Combined yield: 0.05 g, 0.07 mmol, 64%. The orange precipitate was shown by ^{1}H NMR spectroscopy to consist of an almost equimolar mixture of isomers **7a** and **7b** whilst the second crop contained solely **7b**.

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl}$_2$(μ-Cl)(μ-SEt)] **8**. Compound **1** (0.26 g, 0.42 mmol) was stirred in MeOH (5 cm^3) with EtSH (0.2 cm^3, excess) for 16 h resulting in the gradual formation of a deep orange-red solution and an orange precipitate which was

filtered off and air dried. Yield: 0.12 g, 0.19 mmol, 45% (Found: C, 40.80; H, 5.80; Cl, 16.25. Calc. for $C_{22}H_{37}Cl_3Ru_2S$: C, 41.15; H, 5.80; Cl, 16.55%).

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl}$_2$(μ-Cl)(μ-SMe)] **9**. The compound [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSMe)] (0.13 g, 0.36 mmol) was stirred in MeOH (4 cm^3) for 20 h resulting in the gradual formation of a pale orange-brown solution and a dark brown precipitate which was filtered off and dried under vacuum. Yield: 0.09 g, 0.15 mmol, 83% (Found: C, 38.90; H, 5.50; Cl, 16.05. Calc. for $C_{21}H_{35}Cl_3Ru_2S$: C, 40.15; H, 5.60; Cl, 16.95%).

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl}$_2$(μ-Cl)(μ-SH)] **11**. Compound **1** (0.18 g, 0.29 mmol) was dissolved in CH_2Cl_2 (10 cm^3). A few drops of CH_2Cl_2 saturated with H_2S were added and the mixture was stirred for 5 min. Removal of the solvent *in vacuo* resulted in the formation of the product as a deep brown solid which was washed with diethyl ether and air dried. Yield: 0.14 g, 0.24 mmol, 83%. The complex could not be isolated in analytically pure form.

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-SPh)}$_2$] **12**. Compound **1** (0.07 g, 0.11 mmol) was stirred in MeOH (5 cm^3) with PhSH (0.1 cm^3, excess) for 24 h. The product was deposited gradually as a light brown precipitate which was filtered off and dried under vacuum. Yield: 0.08 g, 0.11 mmol, 97% (Found: C, 49.90; H, 5.15; Cl, 9.35. Calc. for $C_{32}H_{42}Cl_2Ru_2S_2$: C, 50.30; H, 5.55; Cl, 9.30%).

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-SC_6F_5)}$_2$] **13**. Compound **1** (0.06 g, 0.10 mmol) was stirred in MeOH (5 cm^3) with C_6F_5SH (0.2 cm^3, excess) for 1.5 h resulting in the rapid formation of a deep orange-brown solution and a red-brown precipitate. This material was filtered off, washed sparingly with methanol and air dried. Yield: 0.06 g, 0.06 mmol, 60% (Found: C, 40.45; H, 3.10. Calc. for $C_{32}H_{32}Cl_2F_{10}Ru_2S_2$: C, 40.75; H, 3.40%).

[(η^3:η^3-$C_{10}H_{16}$)ClRu(μ-Cl)(μ-SEt)RuCl(η^6-C_6H_6)] **14**. The compound [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSEt)] (0.13 g, 0.35 mmol) was stirred in MeOH (10 cm^3) with [{Ru(η^6-C_6H_6)Cl(μ-Cl)}$_2$] (0.09 g, 0.18 mmol) for 20 h. The product was deposited gradually as a yellow-orange precipitate which was filtered off and dried under vacuum. Yield: 0.13 g, 0.22 mmol, 63% (Found: C, 36.00; H, 4.70; Cl, 18.65. Calc. for $C_{18}H_{27}Cl_3Ru_2S$: C, 37.00; H, 4.65; Cl, 18.20%).

[(η^3:η^3-$C_{10}H_{16}$)ClRu(μ-Cl)(μ-SEt)RuCl(η^6-C_6Me_6)] **15**. The compound [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSEt)] (0.084 g, 0.23 mmol) was stirred in MeOH (10 cm^3) with [{Ru(η^6-C_6Me_6)Cl(μ-Cl)}$_2$] (0.077 g, 0.12 mmol) for 2 h. The product was deposited gradually as a bright orange precipitate which was filtered off and dried under vacuum. Yield: 0.12 g, 0.18 mmol, 76% (Found: C, 42.85; H, 5.55; Cl, 16.70. Calc. for $C_{24}H_{39}Cl_3Ru_2S$: C, 43.15; H, 5.90; Cl, 15.90%).

[(η^3:η^3-$C_{10}H_{16}$)ClRu(μ-Cl)(μ-SEt)RhCl(η^5-C_5Me_5)] **16**. The compound [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSEt)] (0.10 g, 0.26 mmol) was treated with [{Rh(η^5-C_5Me_5)Cl(μ-Cl)}$_2$] (0.08 g, 0.13 mmol) as described for **14**, reaction time 2 h. The product was deposited as an orange-red precipitate which was filtered off and dried under vacuum. A further crop of product was obtained by reduction of the volume of the filtrate to *ca.* 1 cm^3 and was filtered off and washed with hexane–diethyl ether (4:1 v/v). Combined yield: 0.12 g, 0.19 mmol, 73% (Found: C, 40.70; H, 5.80; Cl, 17.60. Calc. for $C_{22}H_{36}Cl_3RhRuS$: C, 41.10; H, 5.65; Cl, 16.55%).

[(η^3:η^3-$C_{10}H_{16}$)ClRu(μ-SEt)$_2$RhCl$_2$(PMe$_2$Ph)$_2$] **17**. The complex *mer*-[RhCl$_3$(PMe$_2$Ph)$_3$] (0.046 g, 0.074 mmol) was stirred in methanol (10 cm^3) with Ag[BF$_4$] (0.015 g, 0.076 mmol) for 3 h. The resulting suspension was filtered through Celite and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSEt)] (0.027 g, 0.072 mmol) added to the filtrate. Stirring this for 2 h resulted in the formation of a red precipitate (shown by ^{1}H NMR spectroscopy to consist solely of **7**) and an orange solution. Reduction of the volume of the solvent to *ca.* 1 cm^3 and standing overnight gave large yellow needles of *mer*-[RhCl$_3$(PMe$_2$Ph)$_3$] and small red plates of [(η^3:η^3-$C_{10}H_{16}$)ClRu(μ-SEt)$_2$RhCl$_2$(PMe$_2$Ph)$_2$] (*ca.* 10% overall yield) which were separated manually for the purposes of the X-ray diffraction experiment. The ruthenium(IV)

complex [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(PMe_2Ph)] was also detected in the filtrate by NMR spectroscopy.

Crystallography.—(i) [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl}$_2$(μ-Cl)(μ-SEt)] **8**. *Crystal data.* $C_{22}H_{37}Cl_3Ru_2S$, $M = 642.14$, monoclinic, space group $P2_1/c$, $a = 12.521(3)$, $b = 13.039(5)$, $c = 15.158(4)$ Å, $\beta = 108.25(2)°$, $U = 2350$ Å^3 (by least-squares refinement of diffractometer angles for 24 automatically centred reflections in the range $17 \leqslant 2\theta \leqslant 24°$, $\lambda = 0.710\ 73$ Å), $Z = 4$, $F(000) = 1296$, $D_c = 1.81$ g cm^{-3}, μ(Mo-Kα) = 16.99 cm^{-1}. Red needle $0.4 \times 0.2 \times 0.1$ mm.

The ω–2θ technique was used to collect 4361 (3964 unique) data in the range $5 \leqslant 2\theta \leqslant 50°$ on a Nicolet R3mV diffractometer equipped with graphite-monochromated Mo-Kα radiation. Three standards monitored every 97 reflections showed no appreciable change in intensity throughout the data collection. Data were corrected for Lorentz and polarisation effects and for absorption based on additional azimuthal scan data. Omission of intensities $I \leqslant 3\sigma(I)$ gave 2736 observed data which were employed in the analysis.

The structure was solved by a combination of conventional direct methods and Fourier difference techniques. The asymmetric unit contained one complete molecule. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in idealised positions and allowed to ride on the atoms to which they were attached (C–H 0.96 Å, U_{iso} 0.08 Å^2). The final cycle of least-squares refinement included 253 parameters [weighting scheme applied: $w^{-1} = \sigma^2(F) + 0.000\ 521F^2$] and did not shift any parameter by more than 0.007 times its standard deviation, $R = 0.0422$, $R' = 0.0442$. The largest residual peak was 0.64 e Å^{-3}.

(ii) [(η^3:η^3-$C_{10}H_{16}$)ClRu(μ-Cl)(μ-SEt)RhCl(η^5-C_5Me_5)]· 2CHCl$_3$ **16**. *Crystal data.* $C_{22}H_{36}Cl_3RuRhS\cdot2CHCl_3$, $M = 881.71$, monoclinic, space group $P2_1/c$, $a = 11.617(2)$, $b = 20.504(3)$, $c = 15.394(2)$ Å, $\beta = 110.18(1)°$, $U = 3442$ Å^3 (by least-squares refinement of diffractometer angles for 31 automatically centred reflections in the range $22 \leqslant 2\theta \leqslant 32°$, $\lambda = 0.710\ 73$ Å), $Z = 4$, $F(000) = 1760$, $D_c = 1.70$ g cm^{-3}, μ(Mo-Kα) = 16.83 cm^{-1}. Red block $0.5 \times 0.4 \times 0.3$ mm.

The crystal was fixed in a thin-walled glass capillary with silicone grease. A total of 6542 (6001 unique) data were collected and corrected according to the method described for complex **8**. Omission of intensities $I \leqslant 3\sigma(I)$ gave 4252 observed data which were employed in the analysis.

The structure was solved and refined as described for complex **8**. The asymmetric unit contained one complete molecule and two molecules of chloroform of crystallisation, one of which is thermally disordered. The final cycle of least-squares refinement included 325 parameters [weighting scheme applied: $w^{-1} = \sigma^2(F) + 0.000\ 163F^2$] and the largest shift-to-error ratio was 0.001:1, $R = 0.0481$, $R' = 0.0479$. The largest residual peak was 1.40 e Å^{-3}.

(iii) [(η^3:η^3-$C_{10}H_{16}$)ClRu(μ-SEt)$_2$RhCl$_2$(PMe_2Ph)$_2$] **17**. *Crystal data.* $C_{30}H_{48}Cl_3P_2RhRuS_2$, $M = 845.17$, monoclinic, space group $P2_1/n$, $a = 11.343(3)$, $b = 14.586(4)$, $c = 21.350(6)$ Å, $\beta = 98.37(2)°$, $U = 3495$ Å^3 (by least-squares refinement of diffractometer angles for 29 automatically centred reflections in the range $17 \leqslant 2\theta \leqslant 26°$, $\lambda = 0.710\ 73$ Å), $Z = 4$, $F(000) = 2048$, $D_c = 1.61$ g cm^{-3}, μ(Mo-Kα) = 13.46 cm^{-1}. Red plate $0.4 \times 0.2 \times 0.05$ mm.

A total of 6617 (6022 unique) data were collected and corrected as described for complex **8**. Omission of intensities of $I \leqslant 3\sigma(I)$ gave 3480 observed data which were employed in the analysis.

The structure was solved and refined as described for complex **8**. The final cycle of least-squares refinement included 352 parameters [weighting scheme applied: $w^{-1} = \sigma^2(F) + 0.000\ 318F^2$] and did not shift any parameter by more than 0.001 times its standard deviation, $R = 0.0446$, $R' = 0.0444$. The largest residual peak was 0.53 e Å^{-3}.

All calculations were carried out using the SHELXTL PLUS

program package[19] on a MicroVax II computer. Final fractional atomic coordinates and selected bond lengths and angles are given in Tables 2–7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Mononuclear Thiol Adducts.—Addition of ethanethiol (EtSH) to a dichloromethane solution of complex **1** gives an almost immediate colour change from reddish purple to orange. Evaporation of the solvent leads to the deposition of air- and moisture-stable orange-red crystals of formula [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSEt)] **2** resulting from bridge cleavage and co-ordination of the thiol as a neutral, two-electron-donor ligand. The formulation is confirmed by the ^{1}H NMR spectrum (Table 1) which exhibits an allylic pattern similar to those observed for a range of neutral adducts [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2L] (L = CO, PPh$_3$, N$_2$C$_3$H$_4$, *etc.*)[13,20] with the ligand L occupying the equatorial site of the approximately trigonal-bipyramidal ruthenium ion. Evidence for the non-deprotonated nature of the ethanethiol ligand comes from the observation of a strong band assigned to v(SH) in the infrared spectrum of the complex at 2427 cm^{-1} (with a shoulder to lower wavenumber) and the occurrence of a sharp triplet ^{1}H NMR resonance [δ 3.46 ($^3J = 8.4$ Hz)] assigned to the SH proton {*cf.* [Ru(η^5-C_5H_5)(CO)(PPh$_3$)(HSBu^t)][PF$_6$], δ 2.08}. This resonance is presumably sharp as a consequence of strong intramolecular hydrogen bonding to the terminal chloride ligands which may also help to stabilise the complex. The observation of the shoulder on the v(SH) infrared band is thus likely to be due to the occurrence of antisymmetric and symmetric stretching modes of the S–H $\cdots$ Cl group. The FAB mass spectrum of this compound exhibits a clear molecular ion peak at m/z 370 (based on ^{102}Ru and ^{35}Cl) with the expected isotope distribution and associated fragmentation peaks corresponding to loss of the ethanethiol molecule, and one and two chloride ligands. In a similar fashion the adducts [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSR)] (R = Me **3**, Pr^i **4**, Bu^t **5** or Ph **6**) have also been synthesised, all of which display bands, with shoulders, assignable to v(SH) in their infrared spectra (2423 **3**, 2471 **4**, 2458 **5** and 2460 cm^{-1} **6**) and the corresponding ^{1}H NMR signals for the protons of the co-ordinated thiol (Table 1).

Whilst complexes **3** and **4** behave in a similar fashion to **2**, the broadness of the ^{1}H NMR signals for **5** and **6** suggest that they are in dynamic equilibrium. It is possible that this process results from weak binding of the thiols to the metal centre, leading to partial disproportionation of the complexes into free thiol and **1**. Indeed **5** was found to be very difficult to isolate free of **1** in the absence of an excess of Bu^{t}SH and it was noted that orange diethyl ether solutions of **5** rapidly yielded a pink precipitate of **1** on standing at room temperature, accompanied by the unmistakable odour of Bu^{t}SH. Similar effects have been noted in the case of bulky dialkyl sulfide adducts of (arene)ruthenium(II) compounds.[21] Attempts to synthesise [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(HSC$_6$F$_5$)] from the bulky pentafluorobenzenethiol resulted only in the recovery of unreacted **1**.

Another possible fluxional process which may account for the broadness of the lines in the ^{1}H NMR spectra of complexes **5** and **6** is inversion at the sulfur atom. Such processes are generally found to be fast on the NMR time-scale at room temperature in thiolate-bridged complexes (rate $> ca.$ 10^2 s^{-1}, $\Delta G^{\ddagger}$ $ca.$ 50 kJ mol^{-1})[14] but may be frozen out at low temperature. The ^{1}H NMR spectra of **2**–**6** were examined in the temperature range +20 to −80 °C. For compound **2**, at room temperature, the prochiral CH protons of the HSCH$_2$CH$_3$ ligand occur as a single multiplet (doublet of quartets, δ 2.89) consistent with rapid inversion of configuration at the sulfur and averaging of the magnetic environments for these nuclei. At −60 °C however, **2** and **3** displayed two sets of signals, both for

Table 1 Proton NMR data for new complexes [a]

Compound	δ				
	Terminal allyl	Internal allyl	Ethylinic	Methyl	Other
2 [Ru(η³:η³-C₁₀H₁₆)Cl₂(HSEt)]	4.69 (s, 2 H), 3.87 (s, 2 H)	4.89 (t, 2 H, ³J = 6.4)	3.06 (m, 2 H), 2.63 (m, 2 H)	2.32 (s, 6 H)	3.46 (t, 1 H, ³J = 8.4, SH), 2.89 (m, 2 H, SCH₂CH₃),[e] 1.50 (t, 3 H, ³J = 7.4, SCH₂CH₃)
3 [Ru(η³:η³-C₁₀H₁₆)Cl₂(HSMe)]	4.68 (s, 2 H), 3.87 (s, 2 H)	4.90 (t, 2 H, ³J = 6.2)	3.04 (m, 2 H), 2.64 (m, 2 H)	2.34 (s, 6 H)	3.51 (q, 1 H, ³J = 7.6, SH), 2.33 (d, 3 H, ³J = 7.6, SCH₃)
4 [Ru(η³:η³-C₁₀H₁₆)Cl₂(HSPrⁱ)]	4.72 (s, 2 H), 3.94 (s, 2 H)	4.96 (t, 2 H, ³J = 6.6)	3.09 (m, 2 H), 2.60 (m, 2 H)	S.32 (s, 6 H)	3.48 (br s, SH), 3.53 [d of spt, ³J = 6.7, 2.5, SCH(CH₃)₂], 1.48 [d, 3 H, ³J = 6.7, SCH(CH₃)₂], 1.47 [d, 3 H, ³J = 6.7, SCH(CH₃)₂]
5 [Ru(η³:η³-C₁₀H₁₆)Cl₂(HSBuᵗ)]	4.95 (s, 2 H), 4.15 (s, 2 H)	5.09 (m, 2 H)	3.12 (m, 2 H), 2.53 (m, 2 H)	2.32 (s, 6 H)	3.29 (br s, SH), 1.60 [br s, 9 H, SC(CH₃)₃]
6 [Ru(η³:η³-C₁₀H₁₆)Cl₂(HSPh)]	4.21 (s, 2 H), 3.81 (s, 2 H)	4.83 (t, 2 H, ³J = 5.6)	2.94 (m, 2 H), 2.62 (m, 2 H)	2.29 (s, 6 H)	7.52 (br m, 2 H, SC₆H₅),[e] 7.46 (br m, 3 H, SC₆H₅),[e] 5.56 (br s, 1 H, SH)[e]
7 [{Ru(η³:η³-C₁₀H₁₆)Cl(μ-SEt)}₂] (Two diastereoisomers)	5.18 (s 2 H), 4.87 (s, 2 H),[b] 4.72 (s, 2 H),[b] 4.04 (s, 2 H), 4.03 (s, 2 H), 3.88 (s, 2 H),[b] 3.60 (s, 2 H), 2.73 (s, 2 H)[b]	4.67 (m, 2 H), 4.42 (m, 2 H),[b] 3.26 (m, 2 H), 3.00 (m, 2 H)[b]	2.66 (m, 8 H),[b] 2.58 (m, 8 H)	2.56 (s, 6 H),[b] 2.40 (s, 6 H), 2.35 (s, 6 H), 2.33 (s, 6 H)[b]	2.68 (d of q, 2 H, ²J = 14.0, ³J = 7.2, SCH₂CH₃), 2.11 (d of q, 2 H, ²J = 15.2, ³J = 7.4, SCH₂CH₃),[b] 1.21 (d of q, 2 H, ²J = 14.0, ³J = 7.2, SCH₂CH₃), 1.10 (d of q, 2 H, ²J = 15.2, ³J = 7.4, SCH₂CH₃),[b] 0.84 (t, 6 H, ³J = 7.2, SCH₂CH₃), 0.79 (t, 6 H, ³J = 7.4, SCH₂CH₃)[b]
8a [{Ru(η³:η³-C₁₀H₁₆)Cl}₂(μ-Cl)(μ-SEt)] Cᵢ diastereoisomer	5.53 (s, 2 H), 5.05 (s, 2 H), 4.46 (s, 2 H), 3.93 (s, 2 H)	4.44 (m, 2 H), 3.49 (m, 2 H)	2.82–2.49 (m, 8 H)	2.34 (s, 6 H), 1.98 (s, 6 H)	3.39 (m, 1 H, ³J = 7.5, SCH₂CH₃), 2.80 (m, 1 H, SCH₂CH₃), 1.32 (t, 3 H, ³J = 7.5, SCH₂CH₃)
8b [{Ru(η³:η³-C₁₀H₁₆)Cl}₂(μ-Cl)(μ-SEt)] C₂ diastereoisomer	5.73 (s, 2 H), 4.69 (s, 2 H), 4.21 (s, 2 H), 4.12 (s, 2 H)	4.39 (m, 2 H), 3.21 (m, 2 H)	2.82–2.49 (m, 8 H)	2.29 (s, 6 H), 2.16 (s, 6 H)	3.36 (q, 2 H, ³J = 7.5, SCH₂CH₃), 1.36 (t, 3 H, ³J = 7.3, SCH₂CH₃)
9a [{Ru(η³:η³-C₁₀H₁₆)Cl}₂(μ-Cl)(μ-SMe)] 55 °C, Cᵢ diastereoisomer	5.44 (s, 2 H), 5.00 (s, 2 H), 4.42 (s, 2 H), 3.89 (s, 2 H)	4.37 (m, 2 H), 3.41 (m, 2 H)	2.81–2.30 (m, 8 H)	2.34 (s, 6 H), 1.98 (s, 6 H)	2.35 (s, 3 H, SCH₃)
9b [{Ru(η³:η³-C₁₀H₁₆)Cl}₂(μ-Cl)(μ-SMe)] 55 °C, C₂ diastereoisomer	5.71 (s, 2 H), 4.69 (s, 2 H), 4.18 (s, 2 H), 4.06 (s, 2 H)	4.37 (m, 2 H), 3.21 (m, 2 H)	2.81–2.30 (m, 8 H)	2.29 (s, 6 H), 2.17 (s, 6 H)	2.35 (s, 3 H, SCH₃)
9a −40 °C, Cᵢ diastereoisomer) (Two geometrical isomers)	5.52 (s, 1 H), 5.27 (s, 1 H), 5.12 (s, 1 H), 4.82 (s, 1 H), 4.36 (s, 1 H), 4.32 (s, 1 H), 3.93 (s, 1 H), 3.59 (s, 1 H)	4.35 (m, 1 H), 4.21 (m, 1 H), 3.39 (m, 1 H), 3.30 (m, 1 H)	2.81–2.34 (m, 8 H)	2.34 (s, 3 H), 2.30 (s, 3 H), 2.00 (s, 3 H), 1.92 (s, 3 H)	2.37 (s, 3 H, SCH₃)
9b −40 °C, C₂ diastereoisomer (One geometrical isomer)	5.69 (s, 2 H), 4.62 (s, 2 H), 4.13 (s, 2 H), 4.03 (s, 2 H)	4.28 (m, 2 H), 3.19 (m, 2 H)	2.81–2.34 (m, 8 H)	2.27 (s, 6 H), 2.13 (s, 6 H)	2.37 (s, 3 H, SCH₃)
10 [Ru(η³:η³-C₁₀H₁₆)Cl₂(SH₂)]	4.78 (s, 2 H), 3.98 (s, 2 H)	4.90 (t, 2 H, ³J = 6.0)	3.03 (m, 2 H), 2.64 (m, 2 H)	2.33 (s, 6 H)	7.78 (br s, 2 H, SH₂)
11a [{Ru(η³:η³-C₁₀H₁₆)Cl}₂(μ-Cl)(μ-SH)] (Two diastereoisomers)	5.67 (s, 2 H), 5.56 (s, 2 H), 4.87 (s, 2 H), 4.65 (s, 2 H), 4.47 (s, 2 H), 4.22 (s, 2 H), 4.01 (s, 2 H), 3.89 (s, 2 H)	4.72 (m, 4 H), 4.36 (m, 2 H), 3.23 (m, 2 H)	2.82–2.46 (m, 8 H)	2.44 (s, 6 H), 2.40 (s, 6 H), 2.37 (s, 6 H), 2.26 (s, 6 H)	−0.64 (s, 2 H, SH)
11b [{Ru(η³:η³-C₁₀H₁₆)Cl}₂(μ-Cl)(μ-SH)] (Two diastereoisomers)	5.22 (s, 2 H), 5.13 (s, 2 H), 4.92 (s, 2 H), 4.51 (s, 2 H), 4.46 (s, 2 H), 4.42 (s, 2 H), 3.62 (s, 2 H), 3.61 (s, 2 H)	4.66 (m, 2 H), 4.31 (m, 2 H), 3.98 (m, 2 H), 3.57 (m, 2 H)	2.82–2.46 (m, 8 H)	2.40 (s, 6 H), 2.34 (s, 6 H), 2.33 (s, 6 H), 2.30 (s, 6 H)	−0.34 (br s, 2 H, SH)

Table 1 (continued)

Compound	δ Terminal allyl	Internal allyl	Ethylinic	Methyl	Other
12 [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl-(μ-SPh)}$_2$] (Two diastereoisomers)	5.76 (s, 2 H), 5.55 (s, 2 H),^{b} 5.07 (s, 2 H),^{b} 4.97 (s, 2 H), 4.87 (s, 2 H),^{b} 4.35 (s, 2 H), 4.26 (s, 2 H), 3.11 (s, 2 H)^b	4.47 (dd, 2 H, ^3J = 8.1, 2.8), 4.33 (m, 2 H),^{b} 3.36 (dd, 2 H, ^3J = 7.5, 1.7), 2.82 (d, 2 H, ^3J = 6.8)^b	2.52–2.24 (m, 8 H), 2.11 (m, 4 H), 1.94 (m, 4 H)	2.43 (s, 6 H),^{b} 2.41 (s, 6 H),^{b} 2.37 (s, 6 H), 2.24 (s, 6 H)	7.32–7.03 (m, 20 H, SC$_6$H$_5$)^e
13 [{Ru(η^3:η^3-C$_{10}$H$_{16}$)-Cl(μ-SC$_6$F$_5$)}$_2$]	5.97 (s, 2 H), 5.67 (s, 2 H), 5.63 (s, 2 H),^{c} 5.31 (s, 2 H),^{c} 5.28 (s, 2 H), 5.22 (d, 2 H),^{c,d} 4.43 (s, 2 H), 3.25 (d, 2 H)^{c,d}	4.62 (m, 2 H),^{c} 4.59 (m, 2 H), 4.32 (m, 2 H), 3.11 (m, 2 H)^c	2.59 (m, 4 H),^{c} 2.59 (m, 4 H), 2.16 (m, 4 H),^{c} 2.16 (m, 4 H)	2.43 (s, 6 H),^{c} 2.43 (s, 6 H), 2.26 (s, 6 H),^{c} 2.25 (s, 6 H)	
14 [(η^3:η^3-C$_{10}$H$_{16}$)ClRu(μ-Cl)-(μ-SEt)RuCl(η^6-C$_6$H$_6$)] 60 °C (Two diastereoisomers)	6.18 (s, 1 H), 5.09 (s, 1 H), 4.87 (s, 1 H),^{b} 4.86 (s, 1 H),^{b} 4.56 (s, 1 H),^{b} 4.17 (s, 1 H), 4.15 (s, 1 H),^{b} 3.59 (s, 1 H)	4.56 (m, 1 H), 4.32 (m, 1 H),^{b} 3.81 (t, 1 H, ^3J = 6.5), 3.71 (m, 1 H)^b	2.96–2.42 (m, 2 × 4 H)	2.39 (s, 3 H), 2.24 (s, 3 H),^{b} 2.17 (s, 3 H), 2.16 (s, 3 H)^b	5.61 (s, 6 H, C$_6$H$_6$),^{b} 5.50 (s, 6 H, C$_6$H$_6$), 3.29 (dq, 1 H, ^2J = 11.5, ^3J = 7.3, SCH$_2$CH$_3$),^{b} 3.22 (dq, 1 H, ^2J = 11.6, ^3J = 7.2, SCH$_2$CH$_3$), 2.46 (dq, 1 H, ^2J = 12.4, ^3J = 7.3, SCH$_2$CH$_3$),^{b} 1.99 (dq, 1 H, ^2J = ca. 12, ^3J = ca. 7, SCH$_2$CH$_3$),^{f} 1.19 (t, 3 H, ^3J = 7.2, SCH$_2$CH$_3$), 1.18 (t, 3 H, ^3J = 7.3, SCH$_2$CH$_3$)^b
15 [(η^3:η^3-C$_{10}$H$_{16}$)ClRu(μ-Cl)-(μ-SEt)RuCl(η^6-C$_6$Me$_6$)] (Two diastereoisomers)	6.11 (s, 1 H),^{c} 4.97 (s, 1 H),^{c} 4.90 (s, 1 H), 4.87 (s, 1 H), 4.42 (s, 1 H), 4.01 (s, 1 H),^{c} 3.87 (s, 1 H), 3.34 (s, 1 H)^c	4.32 (m, 1 H),^{c} 4.15 (m, 1 H), 3.69 (m, 1 H),^{c} 3.57 (m, 1 H)	2.83–2.40 (m, 2 × 4 H)	2.35 (s, 3 H),^{c} 2.23 (s, 3 H), 2.12 (s, 3 H),^{c} 2.04 (s, 3 H)	3.31 (dq, 1 H, SCH$_2$CH$_3$),^{f} 3.19 (dq, 1 H, ^2J = 12.9, ^3J = 7.4, SCH$_2$CH$_3$),^{c} ca. 2.5 (m, 1 H, SCH$_2$CH$_3$),^{g} 2.06 (m, 1 H, SCH$_2$CH$_3$),^{c} 2.08 (s, 18 H, C$_6$Me$_6$, 1.99 (s, 18 H, C$_6$Me$_6$),^{c} 1.12 (t, 3 H, ^3J = 7.4, SCH$_2$CH$_3$), 1.08 (t, 3 H, ^3J = 7.4, SCH$_2$CH$_3$)^c
16 [(η^3:η^3-C$_{10}$H$_{16}$)ClRu(μ-Cl)-(μ-SEt)RhCl(η^5-C$_5$Me$_5$)] (Two diastereoisomers)	6.34 (s, 1 H), 4.92 (s, 1 H), 4.90 (s, 1 H), 4.81 (s, 1 H), 4.62 (s, 1 H), 4.06 (s, 1 H), 3.93 (s, 1 H), 3.53 (s, 1 H)	4.57 (t, 1 H, ^3J = 6.7), 4.30 (m, 1 H), 3.89 (t, 1 H, ^3J = 6.5), 3.86 (m, 1 H)	2.97–2.50 (m, 2 × 4 H)	2.35 (s, 3 H), 2.22 (s, 3 H), 2.21 (s, 3 H), 2.18 (s, 3 H)	3.48 (dq, 1 H, ^2J = 11.9, ^3J = 7.3, SCH$_2$CH$_3$), 3.33 (dq, 1 H, ^2J = 12.2, ^3J = 7.4, SCH$_2$CH$_3$), 2.71 (dq, 1 H, ^2J = 11.8, ^3J = 7.3, SCH$_2$CH$_3$), 2.17 (dq, 1 H, ^2J = ca. 11, ^3J = ca. 7, SCH$_2$CH$_3$),^{f} 1.64 (s, 15 H, C$_5$Me$_5$), 1.55 (s, 15 H, C$_5$Me$_5$), 1.16 (t, 3 H, ^3J = 7.3, SCH$_2$CH$_3$), 1.14 (t, 3 H, ^3J = 7.4, SCH$_2$CH$_3$)
17 [(η^3:η^3-C$_{10}$H$_{16}$)ClRu(μ-SEt)$_2$-RhCl$_2$(PMe$_2$Ph)$_2$]	6.03 (s, 1 H), 4.58 (s, 1 H), 3.49 (s, 1 H), 3.32 (s, 1 H)	4.66 (m, 1 H), 4.57 (m, 1 H)	2.90–2.70 (m, 4 H)	2.56 (s, 3 H), 2.12 (s, 3 H)	7.86 (m, 2 H, Ph), 7.82 (t, 2 H, ^3J = 8.1, PMe$_2$Ph), 7.46–7.32 (m, 6 H, PMe$_2$Ph), 2.96 (m, 1 H, SCH$_2$CH$_3$), ca. 2.5 (m, 1 H, SCH$_2$CH$_3$),^{h} 2.00 [d, 3 H, ^2J(P–H) = 10.6, PMe$_2$Ph], 1.69 [d, 3 H, ^2J(P–H) = 10.6, PMe$_2$Ph], 1.49 [d, 3 H, ^2J(P–H) = 10.5, PMe$_2$Ph], 1.18 (t, 3 H, ^3J = 7.0, SCH$_2$CH$_3$), 1.04 [d, 3 H, ^2J(P–H) = 10.6], 0.86 (m, 1 H, SCH$_2$CH$_3$), 0.69 (m, 1 H, SCH$_2$CH$_3$), −0.15 (t, 3 H, ^3J = 7.0, SCH$_2$CH$_3$)

^{a} In CDCl$_3$, J(H–H) in Hz, 400 MHz, 293 K, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, spt = septet, dq = doublet of quartets, m = multiplet, br = broad; resonances and coupling constants assigned with the aid of homonuclear decoupling experiments where appropriate. ^{b} Due to the diastereoisomer which is least soluble in methanol. ^{c} Resonance due to most abundant isomers. ^{d} Resonance split by long-range coupling to ^{19}F, ca. 2.5 Hz. ^{e} Broadness of signal makes measurements of coupling constant uncertain. ^{f} Coupling obscured by overlapping signals. ^{g} Due to the low relative abundance of the second diastereoisomer (ca. 10%) this resonance could not be unambiguously located. ^{h} Resonance obscured by overlapping signals.

the allylic protons of the dimethyloctadienediyl ligand and for the co-ordinated thiol, occurring in a ratio of ca. 5:4. Furthermore, in the case of **2** the prochiral SCH$_2$CH$_3$ protons

were observed as four distinct multiplets (δ 2.98, 2.81, 2.66 and 2.42) indicating that inversion at the sulfur atom is slow at this temperature. These observations are consistent with the

presence of two diastereoisomers as shown in Fig. 1, which interconvert rapidly at room temperature by inversion of configuration at the sulfur atom.

In general, these results indicate that complex **1** does indeed form stable adducts with thiols, which co-ordinate as neutral ligands *via* the sulfur atom. The binding is apparently stronger in the case of the less sterically bulky thiols possibly as a consequence of stabilising hydrogen-bonding interactions.

Binuclear Thiolate-bridged Complexes.—Stirring complex **1** in methanol for 36 h with an excess of EtSH resulted in the formation of an air- and moisture-stable red-brown precipitate of $[\{Ru(\eta^3:\eta^3-C_{10}H_{16})Cl(\mu-SEt)\}_2]$ **7** which did not exhibit a band assignable to $v(SH)$ in its infrared spectrum. The ^1H NMR spectrum of this material was surprising in that it did not exhibit the eight terminal allyl and four methyl resonances expected for the two diastereoisomers of binuclear compounds with inequivalent axial sites. Instead, only half this number of resonances were observed [δ 4.87, 4.72, 3.88 and 2.73 (terminal allyl) and 2.56 and 2.33 (methyl)] consistent with the presence of only a single diastereoisomer. The possibility of the two expected diastereoisomers of **7** being of greatly different stabilities (as suggested for $[\{Ru(\eta^3:\eta^3-C_{10}H_{16})Cl(\mu-SCN)\}_2]^7$) was considered, but concentration of the filtrate from the synthesis of **7** resulted in the precipitation of a brown solid consisting solely of a second compound exhibiting a similar, but distinct, ^1H NMR spectrum [*e.g.* δ 5.18, 4.04, 4.03 and 3.60 (terminal allyl) and 2.40 and 2.35 (methyl)]. Taken together these two species represent the expected two diastereoisomers **7a** and **7b** respectively and, whilst these two materials are formed, or at least isolated, in similar amounts (and hence may be assumed to be of similar stabilities), they differ markedly in their solubility in methanol such that, under the slow-precipitation conditions employed, pure samples of each were fortuitously isolated.

In principle complex **7** (and indeed **1**) may exist as two geometrical isomers (each of which would exist as a pair of diastereoisomers) with respectively cisoid and transoid arrangements of the terminal chloride ligands (types **I** and **II** respectively, Fig. 2). Compound **1** exists solely as the transoid pair of diastereoisomers[2] which is almost certainly the more stable arrangement by virtue of the lesser proximity of the bulky bis(allyl) ligands to one another. Unlike the two diastereo-
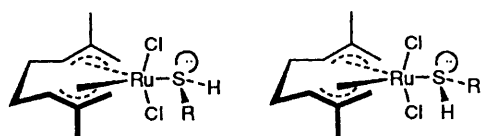
isomers of **1**,[3] complexes **7a** and **7b** do not interconvert rapidly at room temperature (hence the two forms may be readily isolated) and so it is possible that either geometrical isomer of **7** might possess at least kinetic stability. In practice, however, we do not find evidence for the existence of any other compounds except the diastereoisomers **7a** and **7b**, which possess transoid arrangements of the chloride ligands analogous to **1** (the two SEt groups are equivalent in the ^1H NMR spectrum of **7**). The possibility that **7** exists with bridging chloride and terminal thiolate ligands is considered to be less likely.

A further possibility for isomerism in complex **7** exists as the sulfur atom may invert. Bridging thiolate ligands generally adopt a pyramidal geometry at sulfur and hence the possibility of *syn* and *anti* isomers exists, given a planar 'Ru_2S_2' core, Fig. 3.[14] At temperatures down to $-90\ ^\circ C$, however, the ^1H NMR spectrum of **7** remained unchanged. Also the fact that the two distinct multiplets may be resolved in each diastereoisomer for the diastereotopic SCH_2CH_3 protons indicates that inversion at sulfur is slow at room temperature (fast sulfur inversion would interconvert the two diastereotopic protons) and hence **7** exists as only one of these two possible forms (probably the *anti* isomer,[22] to minimise unfavourable steric interactions between the two ethyl groups).

The reaction of complex **1** with EtSH in methanol was repeated using a range of different stoichiometries. It was found that reactions involving low concentrations of **1** and only a small excess of EtSH resulted in the precipitation of an almost equimolar mixture of **7a** and **7b**. Those involving a substantial excess (at least 50-fold) of EtSH resulted in the selective precipitation of **7a**, whilst **7b** remained in solution as noted above. Interestingly, reactions involving relatively large concentrations of **1** gave an orange precipitate of a different product $[\{Ru(\eta^3:\eta^3-C_{10}H_{16})Cl\}_2(\mu-Cl)(\mu-SEt)]$ **8** which, from integration of its ^1H NMR spectrum, contained only a single bridging ethanethiolate anion per binuclear unit. Simple mixed-bridge complexes, especially with substitution-labile ligands such as chloride, are relatively uncommon in the literature and, in the case of ruthenium chemistry, only one other system has come to our attention: irradiation of $[\{Ru(\eta^5-C_5H_5)(CO)(\mu-SC_6F_5)\}_2]$ results in isomerisation to give $[(OC)(\eta^5-C_5H_5)Ru-(\mu-CO)(\mu-SC_6F_5)Ru(\eta^5-C_5H_5)(SC_6F_5)]$ and, ultimately, decarbonylation to form the triply bridged species $[\{Ru(\eta^5-C_5H_5)\}_2(\mu-CO)(\mu-SC_6F_5)_2].^{23}$ In a related reaction irradiation of $[Ru(\eta^5-C_5H_5)(CO)(SR)]$ (R = Me or Ph) gives, as a minor product, $[Ru_3(\eta^5-C_5H_5)(CO)_2(SR)_3]$ in which two of the metal centres are bridged by one carbonyl and one thiolate ligand.[24] Mixed chloride–thiolate-bridged compounds are known for palladium however, for example, the mixed-bridge compound $[\{PdCl(PMe_2Ph)\}_2(\mu-Cl)(\mu-SEt)]$ is formed on heating a mixture of the analogous dichloride- and dithiolate-bridged complexes in chloroform.[25] Chloro/benzeneseleno-

Fig. 1 Two diastereomeric forms of $[Ru(\eta^3:\eta^3-C_{10}H_{16})Cl_2(HSR)]$ **2–6**

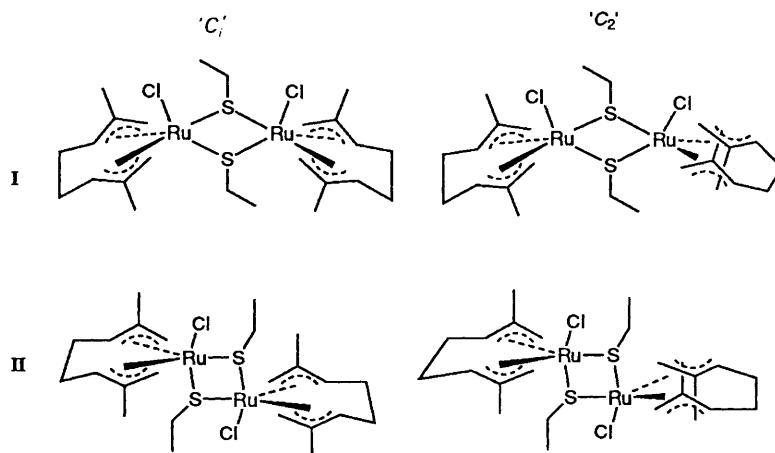**Fig. 2** Possible geometrical isomers of the ethanethiolate-bridged compounds $[\{Ru(\eta^3:\eta^3-C_{10}H_{16})Cl(\mu-SEt)\}_2]$

lato analogues on platinum have also recently been reported.[26]

Assuming the SEt unit to adopt a bridging position in complex **8**, the possibility exists for up to three geometrical isomers (each of which will have a pair of diastereoisomers), two exhibiting a cisoid arrangement of the two terminal chloride ligands and one a transoid geometry (Fig. 4, I–III respectively). Intuitively, and by analogy with **1**, the transoid pair of diastereoisomers, **III**, would be expected to be more stable and indeed the ^{1}H NMR spectrum of the complex is consistent with the presence of only a single pair of diastereoisomers (e.g. eight terminal allyl signals). A single-crystal structure determination was undertaken in order to verify the geometry of this compound.

The crystal and molecular structure of complex **8** is shown in Fig. 5. Atomic coordinates and bond lengths and angles are given in Tables 2 and 3 respectively. The geometry of **8** is a striking one in that it is in fact the cisoid isomer of type **I** (i.e. terminal chloride trans to bridging chloride, Fig. 4) that is observed in the crystal (cf. [{PdCl(PMe$_2$Ph)}$_2$(μ-Cl)(μ-SEt)][25] in which terminal and bridging chloride ligands are cis). This geometry results in the thiolate ligand occupying equatorial sites on both of the approximately trigonal-bipyramidal metal centres. A cisoid arrangement of terminal chloride ligands of this type is unique among the wide variety of bis(allyl)ruthenium(IV) compounds which have been structurally characterised, and the oxalate-bridged compound [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl}$_2$(μ-O$_4$C$_2$)][12] is the only example to exhibit even traces of cisoid isomers of this type. Furthermore, the crystallographically observed diastereoisomer of **8** possesses approximate overall C$_2$ molecular symmetry (if one ignores the ethyl group of the thiolate ligand). All binuclear complexes containing two 'Ru(η^3:η^3-C$_{10}$H$_{16}$)' fragments, including **8**, exhibit diastereoisomers of either 'C_i' (meso, **8a**) or 'C_2' (rac, **8b**)
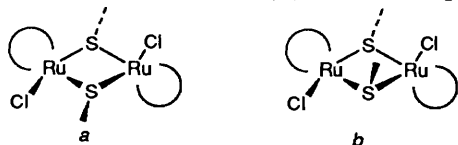
Fig. 3 The anti (a) and syn (b) isomers of [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(μ-SR)}$_2$]

type symmetry[3] but with the exception of [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(μ-SCN)}$_2$][7] it has always been the C_i form which has been observed crystallographically[2,4,6,12] [the labels C_i and C_2 are retained for comparison with other binuclear compounds containing the Ru(η^3:η^3-C$_{10}$H$_{16}$) fragment although in some cases the actual molecular point group may vary[13]].

The bond lengths and angles in isomer **8b** are, in general, as expected for a complex of this type. The bis(allyl) ligands adopt the usual local C$_2$ symmetry and all the Ru–C distances are

Table 2 Atomic coordinates ($\times 10^4$) for [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl}$_2$-(μ-Cl)(μ-SEt)] **8**

Atom	x	y	z
Ru(1)	4239(1)	1904(1)	7597(1)
Ru(2)	1223(1)	2732(1)	6305(1)
Cl(1)	5367(2)	951(2)	6893(1)
Cl(2)	344(2)	2351(2)	4711(1)
Cl(3)	2649(1)	2816(1)	7792(1)
S	2873(2)	1955(1)	6037(1)
C(1)	3515(7)	431(5)	7822(5)
C(2)	4084(7)	830(6)	8681(5)
C(3)	5225(7)	1027(6)	8827(5)
C(4)	5957(8)	1583(6)	9644(6)
C(5)	5655(8)	2692(7)	9619(6)
C(6)	5125(6)	3049(5)	8646(5)
C(7)	5608(6)	3013(6)	7939(6)
C(8)	4846(7)	3260(6)	7070(6)
C(9)	3504(8)	1128(7)	9361(5)
C(10)	6803(7)	2736(7)	8061(7)
C(11)	1936(7)	4099(6)	5835(6)
C(12)	1207(7)	4426(6)	6301(5)
C(13)	87(7)	4080(6)	5923(5)
C(14)	−781(7)	4272(8)	6384(6)
C(15)	−552(8)	3611(8)	7239(7)
C(16)	148(7)	2706(7)	7211(6)
C(17)	−169(7)	1916(7)	6561(6)
C(18)	695(7)	1216(7)	6623(6)
C(19)	1568(7)	5061(6)	7154(6)
C(20)	−1296(8)	1841(9)	5876(7)
C(21)	2572(8)	681(6)	5545(5)
C(22)	3154(10)	497(8)	4836(6)

'Ci'   'C2'

I

II

III
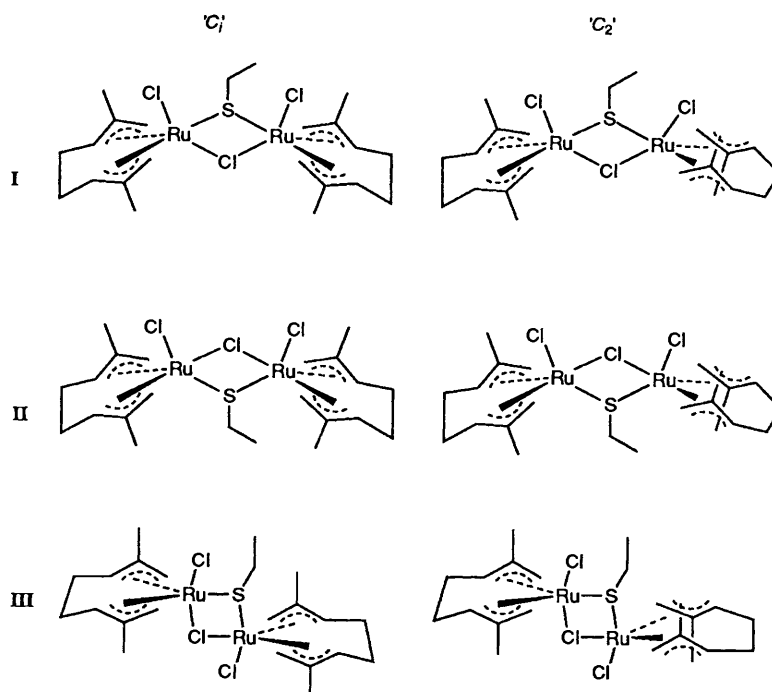
Fig. 4 Possible geometrical isomers of the thiolate-bridged compound [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl}$_2$(μ-Cl)(μ-SEt)}] **8**

Table 3 Selected bond lengths (Å) and angles (°) for [{Ru(η³:η³-C₁₀H₁₆)Cl}₂(μ-Cl)(μ-SEt)] 8

Ru(1)–Cl(1)	2.370(3)	Ru(1)–Cl(3)	2.415(2)
Ru(1)–S	2.448(2)	Ru(1)–C(1)	2.195(7)
Ru(1)–C(2)	2.213(8)	Ru(1)–C(3)	2.206(7)
Ru(1)–C(6)	2.210(7)	Ru(1)–C(7)	2.177(7)
Ru(1)–C(8)	2.173(8)	Ru(2)–Cl(2)	2.373(2)
Ru(2)–Cl(3)	2.400(2)	Ru(2)–S	2.446(2)
Ru(2)–C(11)	2.210(8)	Ru(2)–C(12)	2.209(8)
Ru(2)–C(13)	2.222(8)	Ru(2)–C(16)	2.205(10)
Ru(2)–C(17)	2.179(9)	Ru(2)–C(18)	2.185(9)
S–C(21)	1.812(8)	C(1)–C(2)	1.375(10)
C(2)–C(3)	1.399(12)	C(2)–C(9)	1.487(14)
C(3)–C(4)	1.479(10)	C(4)–C(5)	1.492(12)
C(5)–C(6)	1.490(10)	C(6)–C(7)	1.386(13)
C(7)–C(8)	1.400(10)	C(7)–C(10)	1.495(12)
C(11)–C(12)	1.384(14)	C(12)–C(13)	1.413(11)
C(12)–C(19)	1.482(11)	C(13)–C(14)	1.486(14)
C(14)–C(15)	1.506(14)	C(15)–C(16)	1.478(14)
C(16)–C(17)	1.394(12)	C(17)–C(18)	1.396(13)
C(17)–C(20)	1.470(12)	C(21)–C(22)	1.494(16)
Cl(1)–Ru(1)–Cl(3)	160.5(1)	Cl(1)–Ru(1)–S	85.1(1)
Cl(3)–Ru(1)–S	75.6(1)	S–Ru(1)–C(1)	88.7(2)
Cl(1)–Ru(1)–C(2)	101.9(2)	Cl(3)–Ru(1)–C(2)	87.3(2)
S–Ru(1)–C(2)	122.5(2)	Cl(1)–Ru(1)–C(7)	85.4(2)
Cl(3)–Ru(1)–C(7)	105.1(2)	S–Ru(1)–C(7)	118.1(2)
C(1)–Ru(1)–C(7)	151.2(3)	C(2)–Ru(1)–C(7)	119.3(3)
C(3)–Ru(1)–C(7)	87.3(3)	C(6)–Ru(1)–C(7)	36.8(3)
Cl(2)–Ru(2)–Cl(3)	159.6(1)	Cl(2)–Ru(2)–S	83.7(1)
Cl(3)–Ru(2)–S	75.9(1)	Cl(2)–Ru(2)–C(12)	101.9(2)
Cl(3)–Ru(2)–C(12)	87.7(2)	S–Ru(2)–C(12)	114.9(2)
C(11)–Ru(2)–C(12)	36.5(3)	Cl(2)–Ru(2)–C(17)	86.4(2)
Cl(3)–Ru(2)–C(17)	104.8(2)	S(1)–Ru(2)–C(17)	126.3(2)
C(11)–Ru(2)–C(17)	151.4(3)	C(12)–Ru(2)–C(17)	118.8(3)
C(13)–Ru(2)–C(17)	87.1(3)	C(16)–Ru(2)–C(17)	37.1(3)
Ru(1)–Cl(3)–Ru(2)	105.2(1)	Ru(1)–S–Ru(2)	102.8(1)
Ru(1)–S–C(21)	111.4(2)	Ru(2)–S–C(21)	111.7(3)
C(6)–C(7)–C(8)	112.7(7)	Ru(1)–C(7)–C(10)	123.5(5)
C(6)–C(7)–C(10)	125.1(7)	C(8)–C(7)–C(10)	122.2(9)
Ru(1)–C(8)–C(7)	71.4(5)	Ru(2)–C(11)–C(12)	71.7(5)
Ru(2)–C(12)–C(11)	71.8(5)	S–C(21)–C(22)	110.9(7)
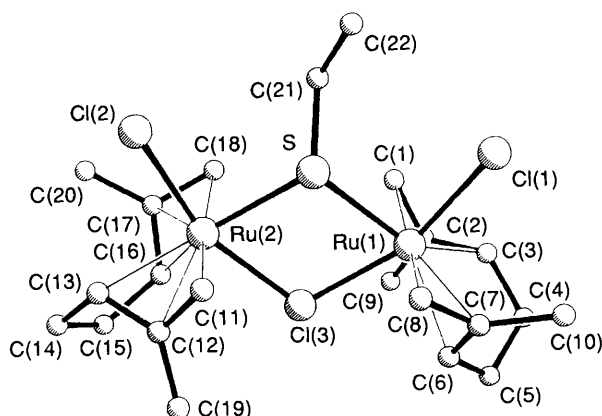
Fig. 5 Crystal structure of [{Ru(η³:η³-C₁₀H₁₆)Cl}₂(μ-Cl)(μ-SEt)] 8 showing the atom numbering scheme adopted

approximately equal within experimental error. The distances from the ruthenium atoms to the terminal chloride ligands [average 2.371(3) Å] are comparable with those observed for 1 (2.386 Å), while the distances to the bridging chloride ligand, Ru–Cl(3), are longer [2.400(2) and 2.415(2) Å], although markedly shorter than the asymmetric bridges in compound 1 (2.561 and 2.467 Å). Similarly the two Ru–S distances are equal within experimental error [average 2.447(2) Å] and are similar to those observed for doubly bridged ruthenium(II) thiolate compounds, e.g. 2.458(1) and 2.413(1) Å in [{Ru(SPh)-

(S₂CNMe₂)(CO)(PPh₃)}₂].[22] These distances are notably longer than those observed both for terminal Ru–SR bonds (e.g. 2.274(1) Å in [Ru(η⁵-C₅H₅){PPh₂(OMe)}₂(SBuⁱ)][PF₆][15] and 2.333(4) Å in [Ru(SC₆F₅)₂(PPh₃)₂][27]) and the corresponding bonds in the doubly bridged diruthenium(IV) complex [{Ru(SPh)(S₂CNMe₂)(CO)(PPh₃)}₂]⁴⁺ [2.405(3) and 2.310(3) Å] in which a metal–metal bond is postulated. The Ru–S distances are also shorter in the triply bridged diruthenium(II) species [{Ru(η⁶-p-MeC₆H₄CHMe₂)}₂(μ-SPh)₃][PF₆] (average 2.39 Å)[27] and in general it seems that 8b is close to the upper limit of 'normal' bridging Ru–S distances.

The separation between the two metal atoms in complex 8b is 3.825(1) Å, which is comparable to that observed for 1[2] and [{Ru(SPh)(S₂CNMe₂)(CO)(PPh₃)}₂][15] (3.983 and 3.683 Å respectively) and too long for any significant metal–metal interaction. Notably, on oxidation of [{Ru(SPh)(S₂CNMe₂)-(CO)(PPh₃)}₂][15] to [{Ru(SPh)(S₂CNMe₂)(CO)(PPh₃)}₂]⁴⁺ the metal–metal distance is reduced to 2.876 Å without significant distortion of the thiolate bridges, and a formal double bond is postulated.

Even a cursory examination of the structure of complex 8 reveals that the two bulky organic fragments are brought into closer proximity to one another than would be the case in a transoid isomer of type III (Fig. 4) and it is surprising therefore that 8 should adopt a cisoid geometry. The fact that, unlike 1 and the pyrazine adduct [{Ru(η³:η³-C₁₀H₁₆)Cl₂}₂(μ-pyz)],[4,13] the two diastereoisomers of 7 are separable and do not interconvert in solution at room temperature suggests that thiolate-bridged complexes such as 7 and 8 are significantly more kinetically inert than their chloride-bridged analogue. It is possible therefore that 8 is a kinetic product which does not rapidly rearrange to the more usual transoid geometry. If this is the case it suggests an interesting mechanism for the formation of 8, and its relationship to 2 and 7.

A suggested mechanism for the formation of complexes 7 and 8 is shown in Scheme 1. The first step involves bridge cleavage of 1 to give the adduct 2. Under the conditions for the formation of 7 a large excess of EtSH is present and so formation of 2 is probably rapid compared to elimination of HCl. Hence, it is more likely that after elimination of HCl the resulting transient solvate species will dimerise to give 7 rather than react with an additional molecule of 1. In contrast, the concentration of 1 is large relative to that of 2 under the conditions in which 8 is formed. The sulfur atom in 2 still possesses an uncomplexed lone pair which may react with a further mole of 1 to give a transient thiol-bridged species with the sulfur atom occupying the *equatorial* sites on both molecules {cf. formation of the trinuclear rhodium and iridium species [M₃(μ₃-SPh)(diene)₃]⁺ [diene = cycloocta-1,5-diene (cod), bicyclo[2.2.1]hepta-2,5-diene (nbd), etc.] from the binuclear precursors [M₂(μ-SPh)(diene)₂][28]}. Elimination of HCl then results in the formation of 8 in the observed cisoid arrangement. Support for this mechanism comes from the self-reaction of 2 in methanol. Stirring 2 alone in methanol for 36 h results in the clean formation of an orange-red precipitate consisting solely of an approximately equimolar mixture of 7a and 7b. Evaporation of the filtrate gave a further crop of pure 7b consistent with the previously observed relative solubilities of 7a and 7b. No trace of 8 was observed in the products from this reaction. Conversely, stirring 2 with 0.5 mol equivalent of 1 in methanol for 24 h resulted in the formation of 8 as the major product (ca. 70% of the isolated yield). Some traces of 7 (and unreacted 1) were observed resulting from dimerisation of 'Ru(η³:η³-C₁₀H₁₆)Cl(SEt)' units. The mechanism shown in Scheme 1 implies that 8 is not an intermediate in the conversion of 2 into 7 but is rather a side product and thus might not be expected to convert into 7 if stirred with an excess of EtSH. In fact stirring 8 with an excess of EtSH in methanol for 20 h does result in *partial* conversion of 8 into 7 (the isolated product proved to be a 1:2 mixture of 7:8).

Given these results we were surprised to find that stirring the

$$[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$$

1
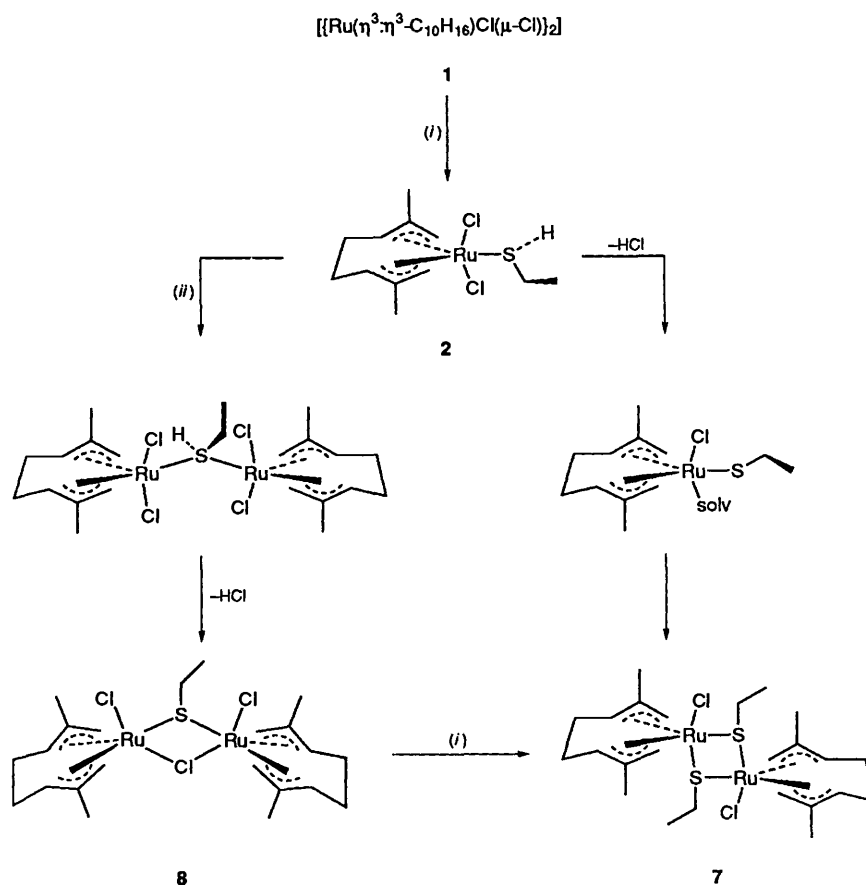
Scheme 1 Suggested mechanism for the reaction of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ **1** with ethanethiol. (*i*) EtSH; (*ii*) **1**

analogous methanethiol adduct **3** in methanol for 20 h resulted in the isolation of the *singly* methanethiolate-bridged compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\}_2(\mu\text{-}Cl)(\mu\text{-}SMe)]$ **9** and not $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}SMe)\}_2]$ as anticipated. The reason for this reactivity may be the volatility of methanethiol itself (b.p. 6 °C) which may slowly dissociate from **3** (as occurs very readily for **5** and, to some extent, **4**) and pass into the vapour phase, resulting in a deficiency of thiolate ligand in solution.

Consistent with the formulation proposed above, the ^{1}H NMR spectrum of complex **9** recorded at $+55$ °C bears a very strong resemblance to that of **8** in the terminal allyl region and is markedly dissimilar to that of **7**. Furthermore, although the expected eight terminal allyl and four methyl resonances are observed [δ 5.71, 5.44, 5.00, 4.69, 4.42, 4.18, 4.06 and 3.89 (terminal allyl), and 2.34, 2.29, 2.17 and 1.98 (methyl)] only a single signal is present for the methyl group of the methanethiolate ligand (δ 2.35), integrating for three protons per binuclear unit (this observation is ascribed to accidental degeneracy of the two signals expected). At room temperature a significant broadening of a number of the resonances was noted, and lowering the temperature to -40 °C resulted in the appearance of a new set of signals ostensibly consistent with the presence of three isomeric binuclear forms of **9**, one of which was apparently present in approximately twice the abundance of the other two. This dynamic behaviour is interpreted in terms of inversion at the pyramidal bridging sulfur atom in **9**, a process analogous to that observed for **2** and **3** (the bridging SMe in **9** may safely be assumed to be pyramidal by analogy with the crystal structure of **8** in which the S–Et bond lies 40.3° out of the 'Ru₂SCl' plane). At high temperature the inversion at sulfur is rapid giving rise to an ^{1}H NMR spectrum consistent with approximately equimolar quantities of the two expected diastereoisomeric forms of **9** [*meso*, **9a** (analogous to the C_i isomer of **1**) and *rac*, **9b** (C_2)]. At low temperature the

resonances for *one* of these diastereoisomers split into two sets of signals corresponding to the two possible orientations of the sulfur methyl group, Fig. 6. Inversion at sulfur would be expected to occur at an approximately equal rate for both **9a** and **9b**. However, consideration of the structures of the two diastereoisomers reveals that in the case of cisoid (type **I** or **II**, Fig. 4) isomers of the C_2 form of **9** (**9b**) the '$\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\}_2(\mu\text{-}Cl)$' core possesses two-fold rotational symmetry and thus inversion at sulfur is a degenerate process and is not expected to produce any splitting in the number of resonances for this diastereoisomer, hence it is only those signals due to the *meso* form of **9** (**9a**) which split at low temperature. This fortuitous circumstance enables the two sets of signals observed in the fast-exchange regime to be assigned to their respective diastereoisomers without the need for a crystal structure determination. Full high- and low-temperature NMR data for **9** with assignments are given in Table 1.

Examination of the low-temperature ^{1}H NMR spectrum of complex **8** revealed that it too exhibits parallel dynamic behaviour with the signals for only one diastereoisomer splitting at low temperature (-60 °C).

In contrast to the formation of complexes **2–6**, reaction of **1** with H₂S in dichloromethane does not result in the isolation of the bridge-cleaved adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(SH_2)]$ **10**. Instead loss of HCl occurs to give a compound related to **8** and **9**, $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\}_2(\mu\text{-}Cl)(\mu\text{-}SH)]$ **11**. Unfortunately the reaction is not a clean one and the compound could not be isolated free of decomposition products apparently arising from further reaction of **11** with the excess of H₂S. Presumably the small size of the H₂S ligand renders the rapid coupling of the initially formed adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(SH_2)]$ **10** with **1** (which is present in abundance in CH₂Cl₂ solution at the start of the reaction) and the relatively high acidity of H₂S results in loss of HCl even in the relatively non-polar solvent medium.
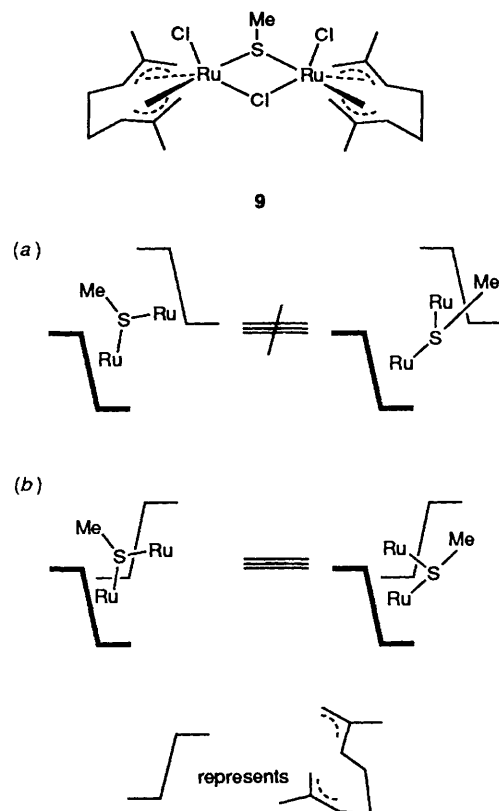
9

(a)

(b)

represents

Fig. 6 Possible orientations of the SMe unit with respect to the bis(allyl) ligands in [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl}$_2$(μ-Cl)(μ-SMe)] **9**: (a) C_i isomer; (b) C_2 isomer

Apart from its lack of analytical purity, the identification of **11** was also complicated by its existence as cisoid and transoid geometrical isomers, **11a** and **11b** (each of which exists as two diastereoisomers), as indicated by the ^{1}H NMR spectrum of the mixture (Table 1). Both **11a** and **11b** exhibit unambiguous resonances assigned to the proton of the SH ligand (δ -0.64 **11a** and -0.34 **11b**, chemical shifts consistent with those observed for other complexes containing SH$^-$ ligands in the bridging mode[29,30]). The presence of the SH ligand was also confirmed by the appearance of a band assigned to v(SH) at 2463 cm^{-1} in the infrared spectrum of the isomeric mixture.

The course of the reaction of complex **1** with H$_2$S was followed by ^{1}H NMR spectroscopy. Addition of a [^{2}H]chloroform solution of **1** to an NMR tube containing a large excess of H$_2$S dissolved in the same solvent at -78 °C followed by immediate recording of the (room temperature) spectrum resulted in the observation of a set of signals (Table 1) entirely consistent with the H$_2$S adduct [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2$(SH$_2$)] **10** as the sole initial product. Re-recording the spectrum after ca. 15 min indicated that substantial decomposition had occurred. In a similar experiment a small excess of an H$_2$S-saturated solution was added to a CDCl$_3$ solution of **1**. In this case, after initial formation of **10**, periodic re-recording of the spectrum demonstrated the conversion of **10** into an equimolar mixture of **11a** and **11b** along with some quantities of decomposition products which did not contain the 'Ru(η^3:η^3-C$_{10}$H$_{16}$)' fragment. With time the signals for **11b** decreased in intensity relative to those for **11a** until, after 1.5 h the sample consisted almost entirely ($>90\%$) of **11a**.

It seems likely from comparison of the ^{1}H NMR spectra of complexes **8** and **9** with those of **11a** and **11b** that **11a** possesses a structure similar to the cisoid, type **I** (Fig. 4) geometry, of **8** and **9**. Compound **11b** is therefore probably related to the isomers of type **II** or **III**. Rapid deprotonation in the case of the SH$_2$ compound **10** may well result in a departure from the associative mechanism outlined in Scheme 1, and hence formation of **11b**

may also occur via reaction of fragments such as 'Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(SH)' with the large quantities of **1** in CH$_2$Cl$_2$ solution. In this case no axial/equatorial selectivity would be expected and hence a mixture of cisoid and transoid isomers.

Unfortunately, reaction of complex **1** in methanol under an atmosphere of MeSH or H$_2$S, or with Pr^{i}SH or Bu^{t}SH, in a similar way to the synthesis of **7**, did not result in the isolation of the doubly bridged compounds [{Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(μ-SR)}$_2$] (R = H, Me, Pr^i or Bu^t). Instead, brown precipitates were obtained which exhibited no signals for the bis(allyl) ligand in their ^{1}H NMR spectra, consistent with complete displacement of η^3:η^3-C$_{10}$H$_{16}$ by thiolate. Stirring the Pr^{i}SH adduct **4** alone in methanol resulted in the formation of a complex mixture of products including a significant amount of **1**. This observation is attributed to the substitution lability of the more bulky thiol ligand.

Conversely, doubly bridged complexes [{Ru(η^3:η^3-C$_{10}$H$_{16}$)-Cl(μ-SR)}$_2$] (R = Ph **12** or C$_6$F$_5$ **13**) were obtained from the reaction of **1** with benzenethiol and pentafluorobenzenethiol respectively. In the case of **13** the highly acidic nature of the thiol resulted in a very rapid reaction which had gone to completion in ca. 1.5 h. This contrasts to the formation of **7**–**9** in which reaction times of 24–36 h were employed. As with **7**, the two diastereoisomers of **12** were found to possess significantly different solubilities such that when the reaction was first carried out the light brown precipitate isolated from the reaction mixture was found to consist of a single diastereoisomer. Repetition of the reaction using a smaller excess of PhSH resulted in the precipitation of both diastereoisomers in a ratio of approximately 2:1 (97% combined yield).

Synthesis of Mixed-valence and Mixed-metal Complexes.— The mechanism for the formation of compounds such as **8** depicted in Scheme 1 suggests that if thiol adducts, such as **2**, were treated with other dichloride dimers rather than **1** it may be possible to generate mixed-valence or mixed-metal compounds without extensive scrambling, especially if the resulting products were relatively kinetically inert as is apparently the case for **7** and **8**.

The reaction of complex **2** in methanol with the (arene)-ruthenium(II) dichloride dimer [{Ru(η^6-C$_6$H$_6$)Cl(μ-Cl)}$_2$] was investigated. Consistent with the mechanism shown in Scheme 1, the mixed-valence (Ru^{II}Ru^{IV}) complex [(η^3:η^3-C$_{10}$H$_{16}$)-ClRu(μ-Cl)(μ-SEt)RuCl(η^6-C$_6$H$_6$)] **14** was isolated in good yield with no trace of the formation of either **7** or **8**. It is noteworthy that the ruthenium(II) centre is chiral and so the complex exists as two diastereoisomers in a way analogous to the diruthenium(IV) compounds. The two isomers, **14a** and **14b**, are readily observed in the ^{1}H NMR spectrum (e.g. two singlets for co-ordinated benzene at δ 5.61 and 5.50) and were isolated in varying ratios consistent with solubility effects analogous to those found for **7**. Like the singly methanethiolate-bridged complex **9**, portions of the ^{1}H NMR spectrum of **14** are broad at room temperature (in particular, resonances due to the ethyl group of the thiolate ligand, along with the highest-field terminal allyl resonance and a signal for one of the methyl groups). Warming the NMR probe to $+60$ °C resulted in a sharpening of the resonances to give a spectrum consistent with the proposed formulation. Oddly, even at this elevated temperature, *four* multiplet resonances are observed for the prochiral SCH$_2$CH$_3$ protons (δ 3.29, 3.22, 2.46 and 1.99). These resonances collapse to a pair of AB patterns ($^2J = 11.5$ and 12.4 Hz) on selective irradiation of the resonance due to the methyl (SCH$_2$CH$_3$) portion of the ethanethiolate ligand (δ 1.18) implying that the two protons are unique even though inversion at the bridging sulfur atom is expected to be fast (i.e. an ABX$_3$ spin system is observed even at high temperature). This is a result of the asymmetric nature of the '(allyl)ClRuSClRuCl-(arene)' core in which there are four distinct domains within which the methylenic protons may lie. These domains are interconverted in pairs by inversion at sulfur but each pair

remains distinct. Lowering the temperature from $+60$ to $-40\,^{\circ}\text{C}$ does not result in any splitting of the resonances. Instead portions of the spectrum broaden and then sharpen once more to give a similar spectrum to that observed at high temperature.

Analogous reaction of complex 2 with [{Ru(η⁶-C₆Me₆)Cl-(μ-Cl)}₂] gave a related mixed-valence, mixed-bridge complex [(η³:η³-C₁₀H₁₆)ClRu(μ-Cl)(μ-SEt)RuCl(η⁶-C₆Me₆)] 15 as the sole product, in 76% yield after only 2 h. Like 14, complex 15 also exists as two diastereoisomers (15a, 15b) isolated in a ratio of *ca.* 9:1.

Similarly, reaction of complex 2 with [{Rh(η⁵-C₅Me₅)Cl(μ-Cl)}₂] gives the mixed-metal (Ru^IVRh^III) complex [(η³:η³-C₁₀H₁₆)ClRu(μ-Cl)(μ-SEt)RhCl(η⁵-C₅Me₅)] 16 (analogous to 14 and 15) cleanly in 73% isolated yield. The room-temperature ¹H NMR spectrum is sharp and demonstrates that, like 14 and 15, complex 16 also exists as two diastereoisomers (ratio *ca.* 1:1) for similar reasons. An ABX₃ pattern is observed for the protons of the ethanethiolate ligands in each diastereoisomer, again reflecting the asymmetric nature of the core of the molecule. To confirm the geometry of this class of compound a single-crystal structure determination was undertaken upon the chloroform solvate 16·2CHCl₃. The crystal and molecular structure is shown in Fig. 7, atomic coordinates and bond lengths and angles are given in Tables 4 and 5. The structure represents a juxtaposition of the *facial* arrangement of the halide/chalcogenide ligands about the rhodium(III) centre and the *meridional* geometry of the ruthenium(IV) ion. The 'RuSClRh' ring is essentially planar, whilst the geometry at sulfur is pyramidal (the S–Et vector is inclined at an angle of 35.5° to the RuSClRh plane). In general the bond lengths and angles are similar to those observed in 8 although the distance from the ruthenium to the bridging chloride, Cl(3), is notably longer [2.453(2) as against 2.408(2) Å (average)], and is closer to the distances observed for 1.² The bridging chloride ligand is equidistant from both metal centres, but the sulfur atom is significantly closer to the rhodium than to the ruthenium ion [Ru–S 2.462(2), Rh–S 2.395(2) Å], possibly reflecting unfavourable S···Cl(1) steric interactions, and the slightly 'softer' nature of the rhodium(III) centre. The intermetal separation of 3.749(1) Å indicates that no significant ruthenium–rhodium interaction is present.

A second mixed-metal complex was prepared in the following manner. Compound 2 was stirred in a methanolic solution of *trans,mer*-[RhCl₂(OH₂)(PMe₂Ph)₃]⁺ {generated *in situ* from *mer*-[RhCl₃(PMe₂Ph)₃] as the tetrafluoroborate salt by action of Ag[BF₄] in methanol} in the hope of synthesising the cationic complex [(η³:η³-C₁₀H₁₆)ClRu(μ-Cl)(μ-SEt)RhCl-(PMe₂Ph)₃][BF₄] by displacement of the substitution-labile aqua ligand.³¹ This approach proved unsuccessful and the ruthenium(IV) complex 7 was obtained as the major product, resulting from self-reaction of 2. After removal of the red precipitate of 7 the filtrate was concentrated and allowed to

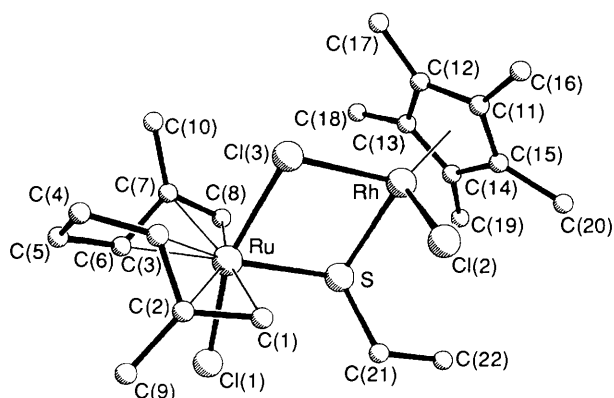stand overnight resulting in the formation of two sets of crystals, large yellow needles which rapidly desolvated and small red plates. These two sets of crystals were separated manually. The former were shown to consist of *mer*-[RhCl₃(PMe₂Ph)₃] whilst the latter displayed an ¹H NMR spectrum consistent with a compound containing bis(allyl), ethanethiolate and tertiary phosphine ligands. In order to characterise this material a single-crystal structure determination was undertaken. This revealed the product to be the unusual, neutral mixed-metal (Ru^IVRh^III) compound [(η³:η³-C₁₀H₁₆)ClRu(μ-SEt)₂RhCl₂-(PMe₂Ph)₂] 17 in which the two metal centres are bridged by *two* ethanethiolate ligands. The geometry of 17 is shown in Fig. 8, fractional atomic coordinates are given in Table 6 and bond
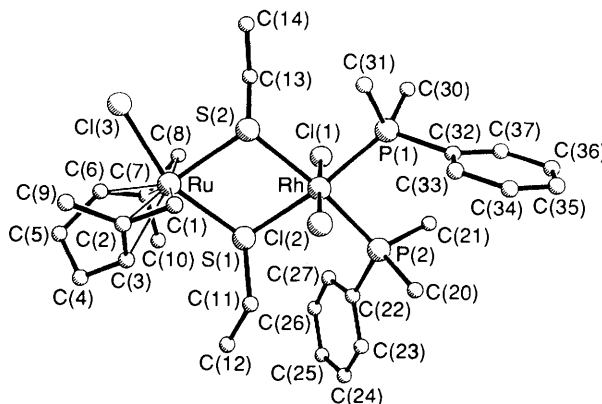
Fig. 8 Crystal structure of the mixed-metal doubly thiolate-bridged complex [(η³:η³-C₁₀H₁₆)ClRu(μ-SEt)₂RhCl₂(PMe₂Ph)₂] 17

Table 4 Atomic coordinates ($\times 10^4$) for [(η³:η³-C₁₀H₁₆)ClRu(μ-Cl)-(μ-SEt)RhCl(η⁵-C₅Me₅)]·2CHCl₃ 16·2CHCl₃

Atom	x	y	z
Ru	8 284(1)	473(1)	2 104(1)
Rh	8 276(1)	2 037(1)	840(1)
Cl(1)	10 066(2)	129(1)	3 354(2)
Cl(2)	7 670(2)	2 623(1)	1 966(1)
Cl(3)	6 908(2)	1 135(1)	846(1)
S	9 665(2)	1 356(1)	1 996(1)
C(1)	7 786(8)	1 067(4)	3 108(5)
C(2)	7 307(8)	435(4)	3 120(5)
C(3)	6 493(7)	227(4)	2 260(5)
C(4)	6 022(9)	−462(4)	2 049(7)
C(5)	7 029(10)	−935(4)	2 075(7)
C(6)	8 073(9)	−610(4)	1 905(6)
C(7)	8 024(10)	−318(4)	1 064(7)
C(8)	9 064(10)	55(4)	1 116(7)
C(9)	7 725(9)	−2(4)	3 967(6)
C(10)	6 906(12)	−345(5)	199(6)
C(11)	7 598(7)	2 775(3)	−229(5)
C(12)	7 507(7)	2 163(4)	−665(5)
C(13)	8 718(7)	1 887(4)	−402(5)
C(14)	9 551(7)	2 341(4)	177(5)
C(15)	8 847(8)	2 889(4)	297(5)
C(16)	6 560(9)	3 235(5)	−325(6)
C(17)	6 373(8)	1 840(5)	−1 282(5)
C(18)	9 056(11)	1 281(4)	−789(7)
C(19)	10 910(8)	2 272(6)	541(6)
C(20)	9 334(10)	3 503(4)	821(6)
C(21)	10 242(8)	1 811(5)	3 074(5)
C(22)	11 110(9)	2 330(5)	3 001(6)
C(50)	4 565(8)	2 459(4)	1 071(6)
Cl(50)	4 204(3)	1 957(2)	1 849(2)
Cl(51)	4 098(3)	3 245(2)	1 124(3)
Cl(52)	3 919(3)	2 148(2)	−30(2)
C(60)	2 909(10)	255(5)	3 153(8)
Cl(60)	2 899(5)	432(2)	2 049(3)
Cl(61)	3 744(6)	777(4)	3 920(4)
Cl(62)	3 269(6)	−542(2)	3 339(4)

Fig. 7 Crystal structure of the mixed-metal singly thiolate-bridged complex [(η³:η³-C₁₀H₁₆)ClRu(μ-Cl)(μ-SEt)RhCl(η⁵-C₅Me₅)] 16

Table 5 Selected bond lengths (Å) and angles (°) for $[(\eta^3:\eta^3-C_{10}H_{16})ClRu(\mu-Cl)(\mu-SEt)RhCl(\eta^5-C_5Me_5)]\cdot2CHCl_3$ **16**·2CHCl₃

Ru–Cl(1)	2.395(2)	Ru–Cl(3)	2.453(2)	C(2)–C(9)	1.516(11)	C(3)–C(4)	1.511(12)
Ru–S	2.462(2)	Ru–C(1)	2.197(9)	C(4)–C(5)	1.509(15)	C(5)–C(6)	1.484(16)
Ru–C(2)	2.228(10)	Ru–C(3)	2.233(9)	C(6)–C(7)	1.410(14)	C(7)–C(8)	1.409(15)
Ru–C(6)	2.243(8)	Ru–C(7)	2.225(9)	C(7)–C(10)	1.507(13)	C(11)–C(12)	1.410(10)
Ru–C(8)	2.196(12)	Rh–Cl(2)	2.406(2)	C(11)–C(15)	1.416(10)	C(11)–C(16)	1.496(13)
Ru–Cl(3)	2.440(2)	Rh–S	2.395(2)	C(12)–C(13)	1.439(11)	C(12)–C(17)	1.488(11)
Rh–C(11)	2.174(7)	Rh–C(12)	2.192(6)	C(13)–C(14)	1.415(10)	C(13)–C(18)	1.486(13)
Rh–C(13)	2.166(9)	Rh–C(14)	2.159(9)	C(14)–C(15)	1.439(12)	C(14)–C(19)	1.488(11)
Rh–C(15)	2.140(8)	S–C(21)	1.819(8)	C(15)–C(20)	1.496(11)	C(21)–C(22)	1.496(15)
C(1)–C(2)	1.414(12)	C(2)–C(3)	1.401(10)				

Cl(1)–Ru–Cl(3)	160.9(1)	Cl(1)–Ru–S	82.4(1)	Cl(2)–Rh–C(13)	157.6(2)	Cl(3)–Rh–C(13)	104.4(2)
Cl(3)–Ru–S	78.6(1)	Cl(1)–Ru–C(2)	86.2(2)	S–Rh(1)–C(13)	105.6(2)	C(11)–Rh–C(13)	64.2(3)
Cl(3)–Ru–C(2)	102.8(2)	S–Ru–C(2)	125.1(2)	C(12)–Rh–C(13)	38.6(3)	Cl(2)–Rh–C(14)	127.9(2)
C(1)–Ru–C(2)	37.3(3)	Cl(1)–Ru–C(7)	103.2(2)	Cl(3)–Rh–C(14)	140.8(2)	S–Rh–C(14)	97.1(2)
Cl(3)–Ru–C(7)	86.9(2)	S–Ru–C(7)	114.7(3)	C(11)–Rh–C(14)	64.5(3)	C(12)–Rh–C(14)	64.0(3)
C(1)–Ru–C(7)	155.1(4)	C(2)–Ru–C(7)	120.2(4)	C(13)–Rh–C(14)	38.2(3)	Cl(2)–Rh–C(15)	94.6(2)
C(3)–Ru–C(7)	90.7(4)	C(6)–Ru–C(7)	36.8(4)	Cl(3)–Rh–C(15)	155.6(2)	S–Rh–C(15)	123.1(2)
Cl(2)–Rh–Cl(3)	91.3(1)	Cl(2)–Rh–S	92.6(1)	C(11)–Rh–C(15)	38.3(3)	C(12)–Rh–C(15)	63.8(3)
Cl(3)–Rh–S	80.1(1)	Cl(2)–Rh–C(11)	94.4(2)	C(13)–Rh–C(15)	64.6(3)	C(14)–Rh–C(15)	39.1(3)
Cl(3)–Rh–C(11)	117.6(2)	S–Rh–C(11)	160.7(2)	Ru–Cl(3)–Rh	100.0(1)	Ru–S–Rh	101.0(1)
Cl(2)–Rh–C(12)	126.0(2)	Cl(3)–Rh–C(12)	93.8(2)	Ru–S–C(21)	111.1(3)	Rh–S–C(21)	108.8(3)
S–Rh–C(12)	141.2(2)	C(11)–Rh–C(12)	37.7(3)	S–C(21)–C(22)	110.0(7)		

Table 6 Atomic coordinates ($\times 10^4$) for $[(\eta^3:\eta^3-C_{10}H_{16})ClRu(\mu-SEt)_2RhCl_2(PMe_2Ph)_2]$ **17**

Atom	x	y	z	Atom	x	y	z
Ru	3898(1)	2398(1)	4853(1)	C(12)	5739(9)	4211(7)	3641(5)
Rh	1659(1)	3654(1)	3677(1)	C(13)	904(9)	1669(7)	4444(5)
Cl(1)	1295(2)	2361(1)	3017(1)	C(14)	53(13)	1435(8)	4855(8)
Cl(2)	1981(2)	4956(1)	4322(1)	C(20)	1750(8)	5729(5)	2857(4)
Cl(3)	3218(2)	1511(2)	5714(1)	C(21)	645(9)	4283(7)	2108(4)
P(1)	−369(2)	3939(2)	3643(1)	C(22)	3129(8)	4290(6)	2387(4)
P(2)	1806(2)	4500(2)	2767(1)	C(23)	3815(9)	4992(6)	2220(5)
S(1)	3736(2)	3246(2)	3864(1)	C(24)	4762(11)	4795(7)	1897(5)
S(2)	1733(2)	2734(1)	4627(1)	C(25)	4992(11)	3931(9)	1729(6)
C(1)	3783(8)	3658(6)	5417(4)	C(26)	4302(11)	3244(9)	1895(6)
C(2)	4887(8)	3253(6)	5613(4)	C(27)	3376(9)	3410(7)	2214(5)
C(3)	5609(8)	3141(6)	5147(5)	C(30)	−1345(8)	3124(7)	3185(5)
C(4)	6753(9)	2590(7)	5207(6)	C(31)	−809(8)	3882(6)	4418(4)
C(5)	6563(10)	1606(8)	5277(6)	C(32)	−1012(7)	5061(6)	3380(4)
C(6)	5302(8)	1312(7)	4994(6)	C(33)	−806(8)	5787(6)	3794(4)
C(7)	4822(9)	1326(6)	4349(5)	C(34)	−1319(9)	6642(7)	3634(5)
C(8)	3600(9)	1180(6)	4237(5)	C(35)	−2020(11)	6742(8)	3086(6)
C(9)	5226(10)	2954(8)	6280(5)	C(36)	−2237(11)	6042(9)	2658(6)
C(10)	5558(10)	1537(7)	3833(5)	C(37)	−1757(9)	5189(8)	2820(5)
C(11)	4553(8)	4332(6)	3882(4)				

lengths and angles in Table 7. The rhodium centre adopts an octahedral geometry with the chloride ligands mutually *trans*, whilst the tertiary phosphines are *trans* to the bridging ethanethiolate ligands (which form the shared edge of the two metal co-ordination spheres). The geometry about the ruthenium(IV) ion is of the usual distorted trigonal-bipyramidal type with the sulfur ligands occupying one axial and one equatorial site. The 'RuS₂Rh' ring is planar within experimental error (mean deviation 0.035 Å) whilst the two sulfur atoms are pyramidal, with the ethyl groups adopting an *anti* conformation [the S(1)–C(11) and S(2)–C(13) vectors are inclined at angles of 39.5 and 29.4° to the RuS₂Rh plane respectively]. The terminal Ru–Cl distance, 2.461(3) Å, is surprisingly long compared to the structures of **8** and **16** and indeed most other compounds of this type[2,7,12] and may reflect the fact that chloride is now *trans* to the bridging sulfur donor, rather than bridging chloride. It is notable that in the quinoline-2-thiolato chelate complex $[Ru(\eta^3:\eta^3-C_{10}H_{16})Cl(NC_9H_6S)]$ a similarly long Ru–Cl distance is observed *trans* to sulfur.[8] Consistent with the long Ru–Cl(3) bond, the axial Ru–S(1) distance is relatively short, 2.432(2) Å, whilst the equatorial Ru–S(2) distance is much longer, 2.482(2) Å. As with **16**, the Rh–S

distances are much shorter than Ru–S ones [Rh–S(1) 2.406(2) and Rh–S(2) 2.424(2) Å] presumably for similar reasons. The metal–metal separation is 3.778(1) Å.

The stoichiometry of complex **17** is a surprising one given that only 0.5 mol equivalent of ethanethiol per metal atom was present at the start of the reaction, and implies that the formation of **17** must be the result of a disproportionation process in which additional thiol becomes available. Attempts to optimise the yield by treatment of $[RhCl_2(OH_2)(PMe_2Ph)_3][BF_4]$ with an excess of EtSH prior to reaction with **2** met with only limited success. This modification resulted in the formation of a red precipitate consisting of a *ca.* 2:1 mixture of **7** and **17**. It is possible that the yield of **17** is fundamentally limited by the need to eliminate PMe₂Ph from the rhodium centre.

Electrochemistry.—A considerable amount of recent work has demonstrated that electrochemically active ruthenium compounds may have applications as redox catalysts (*e.g.* in the oxidation of small organic molecules) or, more interestingly, as chemotherapeutic agents, acting *via* the oxidative cleavage of DNA.[32–34] Ruthenium thiolates frequently display electrochemical activity associated with both the metal

Table 7 Selected bond lengths (Å) and angles (°) for $[(\eta^3:\eta^3\text{-}C_{10}H_{16})ClRu(\mu\text{-SEt})_2RhCl_2(PMe_2Ph)_2]$ **17**

Ru–Cl(3)	2.461(3)	Ru–S(1)	2.432(2)
Ru–S(2)	2.482(2)	Ru–C(1)	2.212(9)
Ru–C(2)	2.219(9)	Ru–C(3)	2.231(9)
Ru–C(6)	2.235(10)	Ru–C(7)	2.243(10)
Ru–C(8)	2.206(9)	Rh–Cl(1)	2.353(2)
Rh–Cl(2)	2.344(2)	Rh–P(1)	2.329(2)
Rh–P(2)	2.328(2)	Rh–S(1)	2.406(2)
Rh–S(2)	2.424(2)	P(1)–C(30)	1.811(10)
P(1)–C(31)	1.797(10)	P(1)–C(32)	1.846(9)
P(2)–C(20)	1.805(8)	P(2)–C(21)	1.809(9)
P(2)–C(22)	1.832(10)	S(1)–C(11)	1.832(9)
S(2)–C(13)	1.828(10)	C(1)–C(2)	1.393(13)
C(2)–C(3)	1.387(14)	C(2)–C(9)	1.484(13)
C(3)–C(4)	1.515(13)	C(4)–C(5)	1.461(16)
C(5)–C(6)	1.532(14)	C(6)–C(7)	1.405(15)
C(7)–C(8)	1.388(14)	C(7)–C(10)	1.507(16)
C(11)–C(12)	1.518(14)	C(13)–C(14)	1.437(20)
Cl(3)–Ru–S(1)	157.5(1)	Cl(3)–Ru–S(2)	80.8(1)
S(1)–Ru–S(2)	77.5(1)	Cl(3)–Ru–C(2)	85.9(3)
S(1)–Ru–C(2)	108.4(2)	S(2)–Ru–C(2)	114.3(3)
C(1)–Ru–C(2)	36.7(3)	Cl(3)–Ru–C(7)	102.2(3)
S(1)–Ru–C(7)	85.4(3)	S(2)–Ru–C(7)	124.3(3)
C(1)–Ru–C(7)	155.4(3)	C(2)–Ru–C(7)	121.4(4)
C(3)–Ru–C(7)	91.5(4)	C(6)–Ru–C(7)	36.6(4)
Cl(1)–Rh–Cl(2)	178.7(1)	Cl(1)–Rh–P(1)	92.2(1)
Cl(2)–Rh–P(1)	86.6(1)	Cl(1)–Rh–P(2)	87.3(1)
Cl(2)–Rh–P(2)	92.1(2)	P(1)–Rh–P(2)	94.0(1)
Cl(1)–Rh–S(1)	89.1(1)	Cl(2)–Rh–S(1)	92.2(1)
P(1)–Rh–S(1)	171.2(1)	P(2)–Rh–S(1)	94.7(1)
Cl(1)–Rh–S(2)	92.2(1)	Cl(2)–Rh–S(2)	88.5(1)
P(1)–Rh–S(2)	92.1(1)	P(2)–Rh–S(2)	173.8(1)
S(1)–Rh–S(2)	79.1(1)	Ru–S(1)–Rh	102.6(1)
Ru–S(1)–C(11)	116.6(3)	Rh–S(1)–C(11)	105.7(3)
Ru–S(2)–Rh	100.6(1)	Ru–S(2)–C(13)	109.7(3)
Rh–S(2)–C(13)	109.7(3)	S(1)–C(11)–C(12)	111.3(7)
S(2)–C(13)–C(14)	116.1(8)		

centre [15,16,18,22,35,36] and the thiolate ligands.[37] Oxidative coupling of thiolate ligands has also been found to occur extensively in iron thiolates.[38,39]

We have found that bis(allyl)ruthenium(IV) compounds derived from **1** generally do not display extensive redox behaviour, usually exhibiting only irreversible reductions, probably accompanied by loss of the bis(allyl) ligand.[12,13]

The ethane- and methane-thiol compounds **2** and **3** were examined by cyclic voltammetry (CH_2Cl_2–0.2 mol dm^{-3} [NBu^n_4][BF_4]). In common with observations upon other bis(allyl)ruthenium(IV) compounds, **2** and **3** as well as the other thiolate compounds examined (**7–9** and **11–13**) exhibited two reduction waves (ca. −1.2 and −1.7 V) which were irreversible over a variety of scan speeds (100–600 mV s^{-1}) consistent with irreversible loss of the bis(allyl) ligand. Compounds **2** and **3** also exhibited oxidation waves (ca. +1.5 V) both irreversible over a variety of scan speeds (even at −40 °C). This behaviour may be related to that of [$Ru(\eta^5\text{-}C_5H_5)\{PPh_2(OMe)\}_2(HSBu^t)$][$PF_6$] on oxidation to the ruthenium(III) complex [$Ru(\eta^5\text{-}C_5H_5)\{PPh_2(OMe)\}_2(SBu^t)$][$PF_6$].[15] However, given the complete lack of electrochemical oxidations exhibited by a range of other ruthenium(IV) products derived from **1**, and since this would involve the formation of an organometallic ruthenium(V) species [$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(SEt)$], we feel that a ligand-based intermolecular oxidative coupling to give disulfide products is more likely (cf. oxidation of [$Fe(\eta^5\text{-}C_5H_5)(SPh)(CO)_2$] by $NOPF_6$ to give [$\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}S_2Ph_2)$][$PF_6]_2$).

At room temperature the singly thiolate-bridged compound **8** exhibits two irreversible oxidation waves (+1.27 and +1.46 V). Cooling the cell to −40 °C, however, results in the observation of a single, two-electron oxidation (+1.36 V) exhibiting a significant return reduction wave (I_{pa}/I_{pc} = 0.69 at v = 200 mV

s^{-1}). For reasons outlined above this process is likely to be the result of formation of an unstable disulfide coupling product. Similar results were obtained for the singly bridged complexes **9** and **11** although the waves were not reversible even at low temperature.

The doubly bridged compound **7** also exhibits two one-electron oxidations at closely spaced potentials (+1.15 and +1.39 V) both of which exhibit re-reduction waves at room temperature [the former process (I_{pa}/I_{pc} = 0.81) is substantially more reversible than the latter, which only exhibits a trace of a return wave]. This behaviour is not inconsistent with oxidation to a metal–metal bonded ruthenium(V) species [$\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-SEt})\}_2$]$^{2+}$ (cf. the reversible four-electron oxidation of the doubly thiolate-bridged ruthenium(II) dithiocarbamate compound [$\{Ru(\mu\text{-SPh})(S_2CNMe_2)(CO)(PPh_3)\}_2$] to [$\{Ru(\mu\text{-SPh})(S_2CNMe_2)(CO)(PPh_3)\}_2$]$^{4+}$, accompanied by a decrease in the metal–metal distance from 3.683(1) to 2.876(2) Å[22]). We feel this to be unlikely however, given the relatively contracted nature of the high-oxidation-state metal orbitals, and the chemical reversibility in this case is more likely to be due to intramolecular disulfide formation, with the two thiolate ligands coupling to give [$\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\}_2(\mu\text{-}S_2Et_2)$]$^{2+}$. Similar results are also noted for the arenethiolate-bridged complexes **12** and **13** although return waves are only observed at low temperature.

The cyclic voltammograms of the singly EtS bridged mixed-valence and mixed-metal complexes **14–16** were also examined. In the case of **14** and **15** at room temperature (in addition to the usual pair of irreversible reduction waves, ca. −1.35 and −1.95 V) two irreversible oxidations are observed (+1.41 and +1.60, **14**; +1.22 and +1.66 V, **15**). In the case of **14**, at −20 °C, both of these oxidations are almost completely reversible, one-electron waves. At the same temperature compound **15** exhibits one reversible oxidation at +1.22 V, whilst the second wave remains irreversible. This behaviour is very similar to that observed for the other singly bridged complexes **8**, **9** and **11** and is likely to result from a related ligand-based process. This contention is further supported by the fact that the rhodium-containing complex **16** also exhibits irreversible oxidations [and the usual reductions associated with the bis(allyl)ruthenium(IV) fragment] at +1.39 and +1.73 V.

Conclusion

It has been demonstrated that neutral thiol adducts are rapidly formed from direct interaction of complex **1** with a variety of thiols under mild conditions. These materials are stable in the presence of air and moisture both in the solid state and in solution, but do eliminate HCl in polar solvents over periods of ca. 24 h to give the corresponding binuclear thiolate-bridged complexes. This chemistry has been exploited and it had been found that compounds containing one and two thiolate bridges may be synthesised by one or more of the three following general methods: (i) stirring the dichloride dimer **1** with an excess of thiol in methanol for ca. 24 h; in this way singly and doubly thiolate-bridged complexes may be synthesised depending upon the precise reaction conditions; (ii) self-reaction of the thiol adducts [$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(HSR)$] in methanol (doubly thiolate-bridged compounds); and (iii) stirring the thiol adducts [$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(HSR)$] with a half mol equivalent of dichloride dimers such as **1** in methanol for ca. 24 h (singly thiolate-bridged compounds).

Mechanistic studies suggest that in many cases non-labile kinetic products are cleanly isolated and this information has been used to synthesise a number of mixed-valence and mixed-metal Ru^{IV}–Ru^{II} and Ru^{IV}–Rh^{III} species with excellent selectivity. Thiolate-bridged compounds of the form [$\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-SR})\}_2$] exhibit electrochemical oxidations with some degree of chemical and electrochemical reversibility in contrast to all other complexes derived from **1**. These processes probably do not involve the ruthenium(IV) centre.

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