DALTON

# Dinuclear thioether half-sandwich ruthenium(II) complexes of the types $[\{RuL'([9]aneS_3)\}_2(\mu\text{-}L)_n]^{2+}$ ($n = 1, L' = PPh_3; n = 2, L' = MeCN$), $[\{Ru([9]aneS_3)\}_2(\mu\text{-}L)_2]^{2+}$ and $[\{Ru([9]aneS_3)\}_2(\mu\text{-}L)_3]^+$ with heterocyclic thioamides L ($[9]aneS_3$ = 1,4,7-trithiacyclononane)

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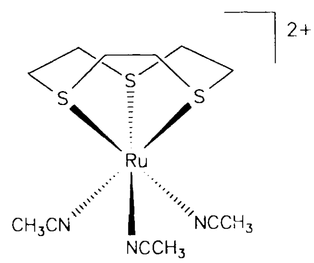
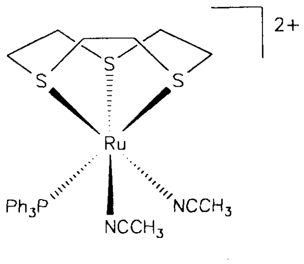
Reaction of $[Ru(MeCN)_3([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane) with 1,3-benzothiazol-2-thione (Hbtt) and pyridine-2-thione (Hpyt) in methanol in a 1 : 1 molar ratio afforded dinuclear complexes $[\{Ru([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}L)_2][CF_3SO_3]_2$ (L = btt or pyt) in which the ligands exhibit a tridentate $\mu\text{-}1\kappa S{:}2\kappa^2N,S$ bridging mode. Crystallization of the btt complex from acetonitrile yielded $[\{Ru(MeCN)([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}btt)_2][CF_3SO_3]_2$ with μ-S bridging ligands. A triply μ-S bridged complex $[\{Ru([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}btt)_3][CF_3SO_3]$ was obtained from $[Ru(MeCN)_3([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ and $btt^-$ in a 2:3 molar ratio. Fragments $(Ph_3P)([9]aneS_3\text{-}\kappa^3S)Ru^{II}$ can be bridged with tetra- or tri-dentate $dtuc^{2-}$ ($H_2dtuc$ = 2,4-dithiouracil) anions in $[\{Ru(PPh_3)([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}dtuc)]^{2+}$ and $[\{RuCl(PPh_3)([9]aneS_3\text{-}\kappa^3S)\}(\mu\text{-}dtuc)\{Ru(PPh_3)([9]aneS_3\text{-}\kappa^3S)\}]^+$. The structures of four complexes have been determined by X-ray crystallography.

We have recently reported the synthesis and structural characterization of the 1,4,7-trithiacyclononane ($[9]aneS_3$) ruthenium(II) complexes $[Ru(MeCN)_3([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **1** and $[Ru(MeCN)_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **2**, which are expedient starting materials for the preparation of further thioether half-sandwich complexes.[1] Two important advantages of **1** in comparison to the analogous areneruthenium(II) starting materials[2,3] $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ or the chloro-bridged complexes $[\{RuCl(\eta^6\text{-}C_6H_6)\}_2(\mu\text{-}Cl)_2]$, namely the increased stability and reduced bulkiness of the facial $([9]aneS_3\text{-}\kappa^3S)Ru^{II}$ fragment, are exemplified by the synthesis of the dinuclear complex $[\{Ru(\mu\text{-}S_2CNMe_2)([9]aneS_3\text{-}\kappa^3S)\}_2][CF_3SO_3]_2$, in which the bridging dimethyldithiocarbamate ligands exhibit respectively $\mu\text{-}1\kappa^2S,S'{:}2\kappa S$ and $\mu\text{-}1\kappa S{:}2\kappa^2S,S'$ co-ordination modes. In contrast, reaction of $[\{RuCl(\eta^6\text{-}C_6H_6)\}_2(\mu\text{-}Cl)_2]$ with dialkyldithiocarbamates leads to loss of the facial benzene ligand and formation of greenish brown paramagnetic solids,[4] which may be presumed to be a mixture of ruthenium(III) complexes such as $[Ru(S_2CNR_2)_3]$ and $[Ru_2(S_2CNR_2)_5]Cl$ (R = Me or Et).[5,6]

The formal analogy of the facial six-electron-donor ligand $[9]aneS_3$ to the $\eta^6\text{-}C_6H_6$ group is apparent. This prompted us to investigate whether novel dinuclear cations of the types $[\{RuL'([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}L)_2]^{2+}$ (L' = MeCN or $PPh_3$) or $[\{Ru([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}L)_3]^+$, with respectively two or three bridging anionic ligands L, can be isolated for the $([9]aneS_3\text{-}\kappa^3S)Ru^{II}$ fragment, for which only one such example, $[\{Ru(PPh_3)([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}Cl)_2]^{2+}$, has previously been reported.[7] In contrast to the previous paucity of such thioether half-sandwich ruthenium(II) species, a doubly hydroxo-bridged cation $[\{Ru(OH)(\eta^6\text{-}C_6H_6)\}(\mu\text{-}OH)_2\{Ru(\eta^6\text{-}C_6H_6)(H_2O)\}]^+$ has been characterized for the $(\eta^6\text{-}C_6H_6)Ru^{II}$ fragment, in addition to the well known chloro-bridged starting material $[\{RuCl(\eta^6\text{-}C_6H_6)\}_2(\mu\text{-}Cl)_2]$. Numerous examples of triply bridged dinuclear cations have been prepared for this organometallic half-sandwich, *e.g.* $[\{Ru(\eta^6\text{-}C_6H_6)\}_2(\mu\text{-}L)_3]^+$ for L = Cl,[3,8] OR (R = Me, Et or Ph),[9] or SEt.[10] Mixed-bridged complexes of the types $[\{Ru(\eta^6\text{-}C_6H_6)\}_2(\mu\text{-}L)_2(\mu\text{-}pz)]^+$ (L = Cl or OH; Hpz = pyrazole)[11] and $[\{Ru(\eta^6\text{-}arene)\}_2(\mu\text{-}L)(\mu\text{-}pz)_2]^+$ (L = Cl or OH; arene = *p*-cymene or $C_6H_6$)[11,12] have also been reported.



**1**



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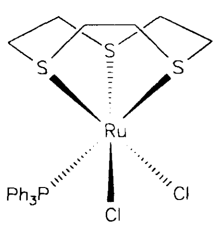


**3**

In the course of the present work we established that reaction of the tris(acetonitrile) complex **1** with NaSH, in a 1:2 or 2:3 molar ratio in methanol, leads to the formation of precipitates which are insoluble in common organic solvents. This led us to investigate the heterocyclic thioamides 1,3-benzothiazole-2-thione (Hbtt), pyridine-2-thione (Hpyt) and 2,4-dithiouracil (pyrimidine-2,4-dithione) ($H_2dtuc$). Analogous ambidentate ligands such as 1-methylimidazole-2-thione (Hmimt) or thiazole-2-thione (Htzt) have been successfully employed for the preparation of dinuclear $(\eta^6\text{-}arene)Ru^{II}$ complexes.[13]

## Experimental

Solvents were dried and distilled before use. Proton and $^{31}P$ ($H_3PO_4$ external standard) NMR spectra were recorded on a

Bruker AM-400 spectrometer, IR spectra as KBr discs on a Perkin-Elmer 1760 spectrometer and FAB mass spectra on a VG Autospec instrument employing 3-nitrobenzyl alcohol as the matrix. Elemental analyses were performed on a Carlo Erba 1106 instrument. Complexes **1**–**3** were prepared according to the literature procedures.[1,7,14] The compound [9]aneS$_3$ was obtained from Fluka and used as received.

### Syntheses

**[{Ru([9]aneS$_3$-κ$^3$*S*)}$_2$(μ-btt)$_2$][CF$_3$SO$_3$]$_2$ 4.** Compound **1** (0.141 g, 0.2 mmol) was added to Hbtt (0.033 g, 0.2 mmol) in MeOH (20 cm$^3$) in the presence of 1 mol dm$^{-3}$ NaOH (0.2 cm$^3$). After refluxing (2 h) and filtration the solution was reduced in volume to 5 cm$^3$ and left to stand at room temperature to afford a red-brown precipitate of complex **4**. The solid was filtered off and dried in vacuum (yield 86%, 0.103 g) (Found: C, 28.7; H, 2.4; N, 2.4. Calc. for $C_{28}H_{32}F_6N_2O_6Ru_2S_{12}$: C, 28.2; H, 2.7; N, 2.4%). FAB mass spectrum: *m*/*z* 1045 (70%, $[M - CF_3SO_3]^+$). $^1$H NMR (CD$_3$OD): δ 2.07 (2 H, m, [9]aneS$_3$), 2.23–2.38 (6 H, m, [9]aneS$_3$), 2.68 (2 H, m, [9]aneS$_3$), 2.82–3.16 (12 H, mm, [9]aneS$_3$), 3.23 (2 H, m, [9]aneS$_3$), 7.22 (2 H, m, btt), 7.37 (2 H, m, btt) and 7.90 (4 H, m, btt).

**[{Ru([9]aneS$_3$-κ$^3$*S*)}$_2$(μ-pyt)$_2$][CF$_3$SO$_3$]$_2$ 5.** A solution of Hpyt (0.022 g, 0.2 mmol) in MeOH (20 cm$^3$) and 1 mol dm$^{-3}$ NaOH (0.2 cm$^3$) was refluxed for 2 h together with complex **1** (0.141 g, 0.2 mmol). After filtration and reduction in volume to 1 cm$^3$, the solution was left to stand at −40 °C to afford orange crystals of **5**·0.5MeOH which were filtered off and dried (yield 73%, 0.079 g) (Found: C, 26.2; H, 2.7; N, 2.3. Calc. for $C_{24}H_{32}F_6N_2O_6Ru_2S_{10}\cdot 0.5CH_3OH$: C, 26.7; H, 3.0; N, 2.6%). FAB mass spectrum: *m*/*z* 1081 (5, $M^+$) and 932 (70%, $[M - CF_3SO_3]^+$). $^1$H NMR (CD$_3$OD): δ 2.12–2.26 (4 H, mm, [9]aneS$_3$), 2.28–2.46 (4 H, mm, [9]aneS$_3$), 3.00–3.17 (4 H, mm, [9]aneS$_3$), 6.78 (2 H, d, pyt), 6.99 (2 H, dd, pyt), 7.51 (2 H, dd, pyt) and 7.98 (2 H, d, pyt).

**[{Ru(MeCN)([9]aneS$_3$-κ$^3$*S*)}$_2$(μ-btt)$_2$][CF$_3$SO$_3$]$_2$ 6.** Compound **4** (0.060 g, 0.05 mmol) was dissolved in acetonitrile (4 cm$^3$). Slow evaporation of the solution provided red crystals of **6** in quantitative yield which were dried in vacuum (Found: C, 29.8; H, 2.6; N, 3.9. Calc. for $C_{32}H_{38}F_6N_4O_6Ru_2S_{12}$: C, 30.1; H, 3.0; N, 4.4%). FAB mass spectrum: *m*/*z* 1126 (6, $[M - CF_3SO_3]^+$) and 1045 (28%, $[M - CH_3CN - CF_3SO_3]^+$). $^1$H NMR (CD$_3$CN): δ 2.38 (6 H, s, CH$_3$CN), 2.35–2.48 (8 H, mm, [9]aneS$_3$), 2.55–2.68 (12 H, mm, [9]aneS$_3$), 2.88–2.97 (4 H, mm, [9]aneS$_3$), 7.39 (2 H, dd, btt), 7.47 (2 H, dd, btt) and 7.85 (4 H, m, btt).

**[{Ru([9]aneS$_3$-κ$^3$*S*)}$_2$(μ-btt)$_3$][CF$_3$SO$_3$] 7.** Compound **1** (0.141 g, 0.2 mmol) was refluxed for 3 h together with Hbtt (0.050 g, 0.3 mmol) in MeOH (20 cm$^3$) and 1 mol dm$^{-3}$ NaOH (0.3 cm$^3$). After filtration the solution was reduced in volume to 10 cm$^3$ and left to stand at 4 °C to afford a red precipitate of complex **7** which was washed with diethyl ether (yield 51%, 0.062 g) (Found: C, 33.4; H, 2.8; N, 3.7. Calc. for $C_{34}H_{36}F_3N_3O_3Ru_2S_{13}$: C, 33.7; H, 3.0; N, 3.5%). FAB mass spectrum: *m*/*z* 1212 (8, $[M + H]^+$) and 1062 (75%, $[M - CF_3SO_3]^+$). $^1$H NMR [(CD$_3$)$_2$SO]: δ 2.52 (12 H, m, [9]aneS$_3$), 2.65 (12 H, m, [9]aneS$_3$), 7.40 (3 H, dd, btt), 7.45 (3 H, dd, btt), 7.82 (3 H, d, btt) and 7.97 (3 H, d, btt).

**[Ru(btt)$_2$([9]aneS$_3$-κ$^3$*S*)] 8.** A solution of Hbtt (0.067 g, 0.4 mmol) in MeOH (20 cm$^3$) and 1 mol dm$^{-3}$ NaOH (0.4 cm$^3$) was heated at 60 °C for 1 h together with complex **1** (0.141 g, 0.2 mmol) leading to the formation of a red-brown precipitate. This was filtered off, washed with diethyl ether and dried in vacuum to provide **8** in 82% yield (0.101 g) (Found: C, 37.8; H, 2.7; N, 4.1. Calc. for $C_{20}H_{20}N_2RuS_7$: C, 39.1; H, 3.3; N, 4.6%). FAB mass spectrum: *m*/*z* 614 (78%, $M^+$). $^1$H NMR [(CD$_3$)$_2$SO]: δ 2.50–2.80 (8 H, mm, [9]aneS$_3$), 3.09 (2 H, m, [9]aneS$_3$), 3.41–3.47 (2 H, m, [9]aneS$_3$), 7.13, 7.24, 7.36, 7.43 (4 H, 4dd, btt), 7.55, 7.65, 7.79 and 7.95 (4 H, 4 d, btt).

**[Ru(pyt)(PPh$_3$)([9]aneS$_3$-κ$^3$*S*)][CF$_3$SO$_3$] 9.** The compound Hpyt (0.017 g, 0.15 mmol) was dissolved in MeOH (10 cm$^3$) in the presence of 1 mol dm$^{-3}$ KOH (0.15 cm$^3$). After addition of complex **2** (0.138 g, 0.15 mmol) and refluxing for 3 h the solution was filtered, reduced in volume to 3 cm$^3$ and left to stand at −18 °C to afford a yellow precipitate of **9** in 84% yield (0.061 g) (Found: C, 44.5; H, 3.8; N, 1.5. Calc. for $C_{30}H_{31}F_3NO_3PRuS_5$: C, 44.9; H, 3.9; N, 1.7%). FAB mass spectrum: *m*/*z* 803 (6, $M^+$) and 654 (100%, $[M - CF_3SO_3]^+$). NMR (CDCl$_3$): $^1$H, δ 0.45, 1.99, 2.18, 2.36 (4 H, 4m, [9]aneS$_3$), 2.70 (4 H, m, [9]aneS$_3$), 2.88, 3.20, 3.36, 3.44 (4 H, 4m, [9]aneS$_3$), 6.32 (1 H, dd, pyt), 6.59 (1 H, d, pyt), 7.11 (1 H, dd, pyt), 7.18 (1 H, d, pyt) and 7.32–7.40 (15 H, mm, PPh$_3$); $^{31}$P, δ 39.15 (s).

**[{Ru(PPh$_3$)([9]aneS$_3$-κ$^3$*S*)}$_2$(μ-dtuc)]X$_2$ (X = CF$_3$SO$_3$ 10a or Cl 10b) and [{RuCl(PPh$_3$)([9]aneS$_3$-κ$^3$*S*)}(μ-dtuc){Ru(PPh$_3$)([9]aneS$_3$-κ$^3$*S*)}]Cl 11.** Compound **2** (0.138 g, 0.15 mmol) was added to H$_2$dtuc (0.011 g, 0.075 mmol) in MeOH (20 cm$^3$) in the presence of 1 mol dm$^{-3}$ NaOH (0.15 cm$^3$). After refluxing for 2 h the solution was filtered and the solvent removed. The resulting solid was redissolved in CHCl$_3$ (2 cm$^3$) and the solution covered with hexane (5 cm$^3$) to afford a yellow microcrystalline precipitate of **10a**·CHCl$_3$ within 3 d (yield 83%, 0.103 g). Complex **10b** was prepared under identical conditions using H$_2$dtuc and **3**. After filtration of the reaction solution, this was reduced in volume to 3 cm$^3$ and left to stand for 12 h to afford **10b** (yield 83%, 0.108 g). A second fraction, harvested after 2 d more, contained both yellow crystals of **10b** and orange crystals of **11**·H$_2$O·0.5MeOH (ratio *ca.* 45:55). The latter could be separated manually with difficulty and were suitable for an X-ray structural analysis. Complex **10a**·CHCl$_3$ (Found: C, 40.1; H, 3.0; N, 1.4. Calc. for $C_{54}H_{56}F_6N_2O_6P_2Ru_2S_{10}\cdot CHCl_3$: C, 40.1; H, 3.5; N, 1.7%): FAB mass spectrum *m*/*z* 1528 (7, $M^+$) and 1379 (81%, $[M - CF_3SO_3]^+$); NMR (CDCl$_3$), $^1$H, δ 0.33, 0.94, 1.41 (3 H, 3m, [9]aneS$_3$), 2.0–2.9 (16 H, mm, [9]aneS$_3$), 3.00–3.45 (5 H, mm, [9]aneS$_3$), 5.71 (1 H, d, dtuc), 6.42 (1 H, d, dtuc), and 7.2–7.5 (30 H, mm, PPh$_3$); $^{31}$P, δ 35.60 and 36.28 (2s, 2P). Complex **10b** (Found: C, 47.9; H, 3.7; N, 1.6. Calc. for $C_{52}H_{56}Cl_2N_2P_2Ru_2S_8$: C, 48.0; H, 4.3; N, 2.2%): FAB mass spectrum: *m*/*z* 1265 (100%, $[M - Cl]^+$); $^{31}$P NMR (CDCl$_3$), δ 35.53, 36.42 (2s, 2P); second fraction (**10** + **11**), δ 34.79, 35.09 (2P, 2s, *ca.* 55%), 35.51, 36.44 (2P, 2s, *ca.* 45%).

**[RuCl(H$_2$imt)(PPh$_3$)([9]aneS$_3$-κ$^3$*S*)]Cl 12 (H$_2$imt = imidazole-2-thione).** The compounds H$_2$imt (0.020 g, 0.2 mmol) and **3** (0.123 g, 0.2 mmol) were refluxed for 2 h in MeOH (15 cm$^3$). After removal of the solvent, followed by addition of CHCl$_3$ (1 cm$^3$) and subsequent filtration, the resulting solution was covered with hexane (3 cm$^3$) to afford orange-yellow crystals of complex **12**·0.5CHCl$_3$ at −18 °C (yield 90%, 0.139 g) (Found: C, 42.3; H, 4.0; N, 4.0. Calc. for $C_{27}H_{31}Cl_2N_2PRuS_4\cdot 0.5CHCl_3$: C, 42.7; H, 4.1; N, 3.6%). FAB mass spectrum: *m*/*z* 679 (75%, $[M - Cl]^+$). NMR (CD$_3$OD): $^1$H, δ 1.99, 2.12, 2.38 (3 H, 3m, [9]aneS$_3$), 2.55 (2 H, m, [9]aneS$_3$), 2.62, 2.70 (2 H, 2m, [9]aneS$_3$), 2.82 (2 H, m, [9]aneS$_3$), 2.93 (1 H, m, [9]aneS$_3$), 3.05 (2 H, m, [9]aneS$_3$), 7.02 (2 H, s, H$_2$imt), 7.34 (9 H, m, PPh$_3$) and 7.68 (6 H, m, PPh$_3$); $^{31}$P, δ 34.00 (s).

**[Ru(H$_2$imt)(MeCN)(PPh$_3$)([9]aneS$_3$-κ$^3$*S*)][CF$_3$SO$_3$]$_2$ 13.** Compound **2** (0.092 g, 0.1 mmol) and H$_2$imt (0.010 g, 0.1 mmol) were refluxed for 2 h in MeOH (10 cm$^3$). The solution was then reduced in volume to 3 cm$^3$ and left to stand at 4 °C to provide orange crystals of **13** (yield 88%, 0.087 g) (Found: C, 37.8; H, 3.4; N, 5.0. Calc. for $C_{31}H_{34}F_6N_3O_6RuPS_6$: C, 37.9; H, 3.5; N, 4.3%). FAB mass spectrum: *m/z* 834 (65, $[M - CF_3SO_3]^+$) and 793 (81%, $[M - CH_3CN - CF_3SO_3]^+$). NMR ($CD_3OD$): $^1$H, δ 1.46, 2.08, 2.43, 2.54 (4 H, 4m, [9]ane$S_3$), 2.00 (3 H, s, $CH_3CN$), 2.75 (2 H, m, [9]ane$S_3$), 2.96 (4 H, m, [9]ane$S_3$) 3.03, 3.12 (2 H, m, [9]ane$S_3$), 7.22 (2 H, s, $H_2$imt), 7.50 (9 H, m, $PPh_3$) and 7.60 (6 H, m, $PPh_3$); $^{31}$P, δ 34.31 (s).

**[Ru($H_2$imt)$_2$($PPh_3$)([9]ane$S_3$-$\kappa^3$*S*)][$CF_3CO_3$]$_2$ 14.** The compounds $H_2$imt (0.020 g, 0.2 mmol) and **2** (0.092 g, 0.1 mmol) were refluxed in MeOH (10 cm$^3$) for 2 h and the solution volume subsequently reduced to 1 cm$^3$. Addition of $CHCl_3$ (3 cm$^3$) led to the formation of an orange microcrystalline precipitate of complex **14**·$CHCl_3$ within 3 d (yield 62%, 0.072 g) (Found: C, 34.5; H, 3.1; N, 4.5. Calc. for $C_{32}H_{35}F_6N_4O_6PRuS_7$·$CHCl_3$: C, 34.1; H, 3.1; N, 4.8%). FAB mass spectrum: *m/z* 893 (27, $[M - CF_3SO_3]^+$), 793 (12, $[M - H_2imt - CF_3SO_3]^+$) and 643 (69%, $[M - H_2imt - 2CF_3SO_3]^+$). NMR ($CD_3OD$); $^1$H, δ 1.80, 2.43 (2 × 2 H, 2m, [9]ane$S_3$), 2.61, 2.69 (2 × 4 H, 2m, [9]ane$S_3$), 6.91 (4 H, s, $H_2$imt), 7.48 (9 H, m, $PPh_3$) and 7.58 (6 H, m, $PPh_3$); $^{31}$P, δ 31.89 (s).

### X-ray crystallography

Crystal and refinement data for complexes **5**·0.5MeOH, **6**·MeCN, **11**·$H_2O$·0.5MeOH and **13** are provided in Table 1. Diffracted intensities were collected on a Siemens P4 four-circle diffractometer with Mo-Kα radiation (λ = 0.710 73 Å) at 295 K in the ω-scan mode for **5**, **11** and **13** and the ω–2θ scan mode for **6**. In each case three control intensities were monitored after collection of 100 reflections; no significant alterations in their intensities were recorded. Semiempirical absorption corrections were applied on the basis of ψ-scan data. The structures were solved by a combination of Patterson and Fourier-difference syntheses and refined by full-matrix least squares with the SHELXTL PLUS set of programs.[15] The asymmetric unit of **5** contains two $CF_3SO_3^-$ anions, one of which [S(88), C(88)] displays a rotational disorder about the S–C bond, leading to two sets for O [O(881)–O(883), O(884)–O(886)] and F atoms [F(881)–F(883), F(884)–F(886)] with site-occupation factors (s.o.f.s) of 0.5. A methanol solvent molecule [O(77), C(77)] contained in the unit cell is also disordered with an s.o.f. of 0.5. Anisotropic thermal parameters were introduced for all non-hydrogen atoms of the dication of **5**, the sulfur atoms of the $CF_3SO_3^-$ anions and the methanol C and O atoms. With the exception of the C and N atoms of a solvent acetonitrile molecule, all non-hydrogen atoms in **6** were refined anisotropically. This was also the case for the Ru, Cl, S, P, O(water), N, C(dtuc) and C([9]ane$S_3$) atoms of **11**. The asymmetric unit of this complex also contains two disordered water molecules [O(88), O(99)] and a disordered methanol molecule [C(77), O(77)], all atoms of which exhibit s.o.f.s of 0.5. All non-hydrogen atoms in **13** were assigned anisotropic thermal parameters. Hydrogen atoms of the cations of **5**, **6**, **11** and **13** were included in the refinements at geometrically calculated positions with joint isotropic thermal parameters. Final *R* factors are listed in Table 1 with weighting schemes $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$ for $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. Scattering factors and corrections for anomalous dispersion were taken from ref. 16. Fractional atomic coodinates for the refined crystal structures are listed in Table 3, selected bond lengths (Å) and angles in Table 2.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

## Results and Discussion

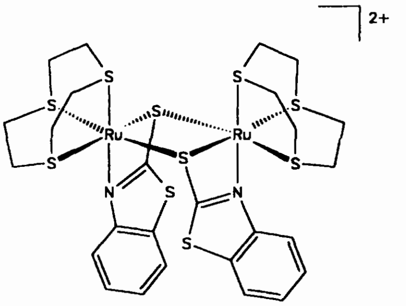
The co-ordination chemistry of heterocyclic thioamides is a topic of current interest.[17] Recently tzt$^-$, mimt$^-$ and btt$^-$ have been employed in a μ-1κ*N*:2κ*S* or $\mu_3$-1κ*N*:2κ*S*:3κ*S* bridging manner in the construction of di-, tri- and tetra-nuclear complexes such as [{Rh(μ-tzt)(CO)($PPh_3$)}$_2$], [(cod)$_2$Rh$_2$(μ-btt)$_2$Ag($ClO_4$)] (cod = cycloocta-1,5-diene), [Rh$_3$($\mu_3$-btt)$_2$(CO)$_2$($PPh_3$)$_2$(tfbb)] [$ClO_4$] {tfbb = tetrafluorobenzobarrelene (tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene)} or [{Cu($\mu_3$-mimt)}$_4$].[18] An alternative bridging mode was established for a polymeric cadmium(II) complex $^1_\infty$[Cd(μ-btt)$_2$], in which Cd atoms separated at an average distance of 3.09 Å are linked *via* btt$^-$ anions displaying a μ-1κ*S*:2κ$^2$*N*,*S* co-ordination.[19] Whereas the first of the bridging tzt$^-$ ligands in [{Ru($\eta^6$-$C_6H_6$)}(μ-tzt)$_2${RuCl($\eta^6$-$C_6H_6$)}]Cl exhibits a similar tridentate co-ordination mode, the second is restricted to a bidentate μ-1κ*N*:2κ*S* pattern.[14] It seems reasonable to assume that non-bonding interactions between adjacent *cis*-sited $\eta^6$-$C_6H_6$ ligands or ring strain in a potential (RuS)$_2$ four-membered ring prevent the adoption of the μ-1κ*S*:2κ$^2$*N*,*S* bridging mode by both tzt$^-$ ligands in this complex. As such an (RuS)$_2$ ring is indeed observed in the dithiocarbamate complex [{Ru(μ-$S_2CNMe_2$)([9]ane$S_3$-$\kappa^3$*S*)}$_2$][$CF_3SO_3$]$_2$, it was of interest to establish the co-ordination behaviour of heterocyclic thioamides such as btt$^-$ or pyt$^-$ in similar dinuclear complexes of the type $[\{Ru([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}L)_2]^{2+}$ (L = btt **4** or pyt **5**).

Both complexes **4** and **5** display an $[M - CF_3SO_3]^+$ ion in their FAB mass spectra, corresponding to a dinuclear formulation for *M*. The occurrence of only one set of ligand signals in the $^1$H NMR spectra of each complex in $CD_3OD$ is in accordance with the adoption of identical tridentate modes by the individual bridging heterocyclic thioamides btt$^-$ and pyt$^-$. This interpretation was confirmed by the X-ray structural analysis of **5**, the effectively $C_2$-symmetrical cation of which is depicted in Fig. 1. Complexes **4** and **5** provide the first examples of dinuclear complexes with half-sandwich fragments to contain exclusively μ-1κ*S*:2κ$^2$*N*,*S* bridging heterocyclic thioamides. This finding emphasizes once again the reduced steric demands of the facially co-ordinated ([9]ane$S_3$-$\kappa^3$*S*)Ru$^{II}$ fragment in comparison to organometallic half-sandwich fragments such as ($\eta^6$-$C_6H_6$)Ru$^{II}$. The central four-membered ring in **5** is effectively planar as illustrated by the atom deviations of only ±0.045 Å from the best least-squares plane [Ru ··· Ru(a) 3.61 Å]. In an interesting contrast, the analogous (RuS)$_2$ ring in [{Ru(μ-$S_2CNMe_2$)([9]ane$S_3$-$\kappa^3$*S*)}$_2$]-[$CF_3SO_3$]$_2$ is markedly non-planar (deviations ±0.143 Å),[1] leading to a much shorter (presumably stabilizing) intramolecular S(7) ··· S(7a) interaction of 3.37 Å in comparison with that of 4.08 Å in **5**. Significant differences are also observed for the Ru–S bond distances in the (RuS)$_2$ rings of these complexes, that within the chelate ring being shorter in the dithiocarbamate complex ([Ru–S 2.416(1) and 2.452(1) Å] with the opposite state of affairs being valid in **5** (average Ru–S 2.454 and 2.430 Å). The lengthening of this chelate bond length in **5** is presumably a result of the increased ring strain in this complex caused by the marked difference in the Ru–S and Ru–N distances of the (RuS)$_2$ ring. A comparison of the geometry of the cation[13] [{Ru($\eta^6$-$C_6H_6$)}(μ-tzt)$_2${RuCl($\eta^6$-$C_6H_6$)}]$^+$ with that of **5** also provides evidence for the high extent of endocyclic strain in the latter complex. Thus the Ru–S–Ru angle for the tridentate bridging tzt$^-$ ligand in the dinuclear ($\eta^6$-$C_6H_6$)Ru$^{II}$ complex is 22.3° larger than that in **5** [95.5 (2)°]. At the same time non-chelate Ru–S distances of 2.361(3) and 2.395(3) Å in the former complex are much shorter than the analogous bond lengths in the four-membered (RuS)$_2$ ring of **5** (average 2.430 Å).

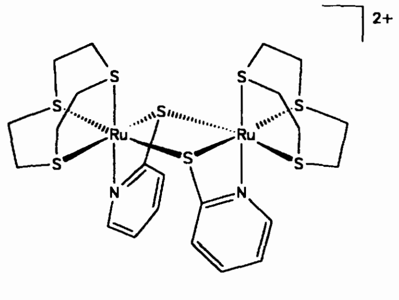
These findings prompted us to investigate the reaction of complex **4** with an excess of the sterically very undemanding acetonitrile. Substitution of one of the co-ordination sites of the

**Table 1** Crystal and refinement data for complexes **5**, **6**, **11** and **13**

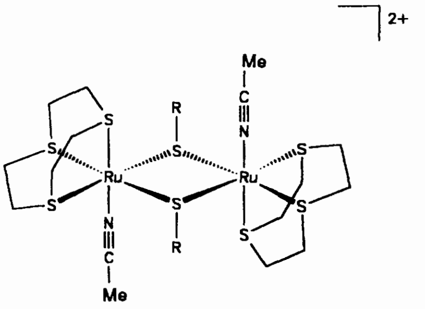
| | **5** | **6** | **11** | **13** |
|---|---|---|---|---|
| Formula | $C_{24}H_{32}F_6N_2O_6Ru_2S_{10}\cdot0.5CH_3OH$ | $C_{32}H_{38}F_6N_4O_6Ru_2S_{12}\cdot CH_3CN$ | $C_{52}H_{56}Cl_2N_2P_2Ru_2S_8\cdot H_2O\cdot0.5CH_3OH$ | $C_{31}H_{34}F_6N_3O_6PRuS_6$ |
| $M$ | 1097.3 | 1316.6 | 1334.5 | 983.0 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ |
| $a$/Å | 8.208(1) | 12.730(5) | 12.993(6) | 8.663(2) |
| $b$/Å | 12.558(2) | 13.459(5) | 30.749(9) | 11.761(3) |
| $c$/Å | 21.246(3) | 14.919(3) | 15.581(4) | 19.746(6) |
| $\alpha$/° | 75.91(1) | 83.51(3) | | 82.71(2) |
| $\beta$/° | 79.31(1) | 81.32(2) | 102.57(3) | 89.31(2) |
| $\gamma$/° | 78.21(1) | 78.86(2) | | 84.08(2) |
| $U$/Å$^3$ | 2058.1(7) | 2469.9(14) | 6076(4) | 1984.9(9) |
| $Z$ | 2 | 2 | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.771 | 1.770 | 1.459 | 1.645 |
| $F$(000) | 1098 | 1324 | 2724 | 996 |
| Crystal size/mm | 0.22 × 0.30 × 0.46 | 0.38 × 0.44 × 0.54 | 0.31 × 0.43 × 0.62 | 0.24 × 0.34 × 0.56 |
| μ(Mo-Kα)/mm$^{-1}$ | 1.31 | 1.19 | 0.95 | 0.82 |
| Scan width/° | 2.00 | 1.70 | 1.20 | 1.40 |
| $2\theta_{max}$/° | 47.5 | 50.0 | 50.0 | 50.0 |
| $hkl$ Ranges | 0–9, −14 to 13, −24 to 23 | 0–15, −15 to 16, −17 to 17 | 0–15, 0–36, −18 to 18 | 0–10, −13 to 14, −23 to 23 |
| Maximum, minimum transmission | 0.45, 0.40 | 0.26, 0.24 | 0.37, 0.32 | 0.45, 0.39 |
| Reflections collected | 7089 | 8849 | 11 378 | 7727 |
| Independent reflections | 6590 | 8661 | 10 646 | 7049 |
| $R_{int}$ | 0.022 | 0.029 | 0.027 | 0.021 |
| Observed reflections [$I > 2\sigma(I)$] | 3558 | 6994 | 5796 | 4121 |
| No. parameters | 412 | 575 | 448 | 504 |
| $R$ | 0.078 | 0.031 | 0.074 | 0.052 |
| $R'$ | 0.085 | 0.042 | 0.078 | 0.057 |
| $g$ in weighting scheme | 0.0003 | 0.0003 | 0.0003 | 0.0005 |
| Maximum, minimum in $\Delta F$ synthesis/e Å$^{-3}$ | 1.20, −1.28 | 1.02, −0.57 | 1.55, −0.68 | 0.72, −0.45 |

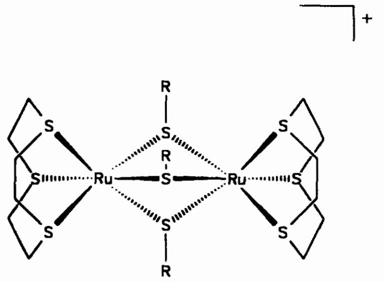


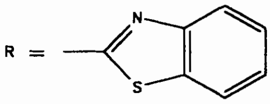
**4**



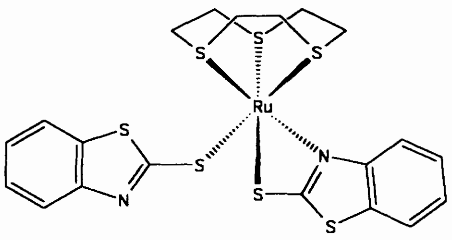
**5**







**6** **7**



**8**

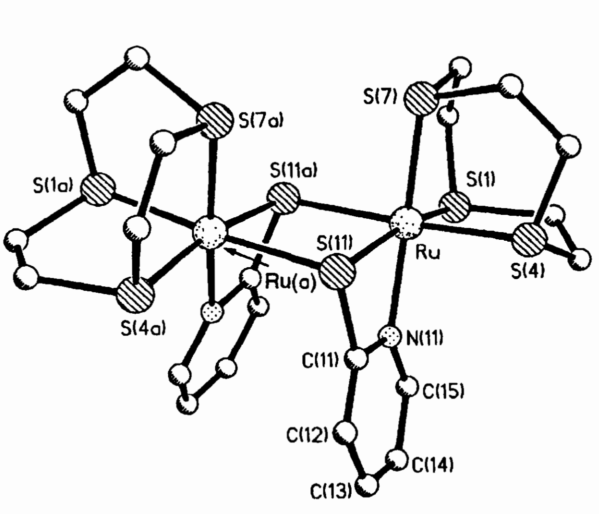


**Fig. 1** Structure of the cation $[\{Ru([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-pyt})_2]^{2+}$ **5**

tridentate bridging btt$^-$ ligands at each of the Ru atoms should lead to drastic reduction in ring strain for either a μ-S or μ-N,S co-ordination pattern in a resulting dinuclear cation $[\{Ru(MeCN)([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-btt})_2]^{2+}$ **6**. Slow crystallization of **4** from an acetonitrile solution at ambient temperature does indeed lead to the formation of **6** in effectively quantitative yield. The red crystals exhibit the expected $[M - CF_3SO_3]^+$ ion ($m/z$ = 1126) in their FAB mass spectrum. Loss of two acetonitrile ligands yields an ion $[M - 2MeCN - CF_3SO_3]^+$ ($m/z$ = 1045) at the same position as that observed for the molecular ion of **4**. A resonance at δ 2.38 (s) in the $^1$H NMR spectrum of **6** confirms the presence of symmetrically co-ordinated acetonitrile ligands. This spectrum also enables a distinction between the potential μ-S and μ-N,S co-ordination modes for the bridging heterocyclic thioamide. The registration of only three resonances at δ 7.39 (dd), 7.47 (dd) and 7.85 (m) for the btt$^-$ protons is in accordance with $C_i$ or $C_2$ symmetry for the dinuclear cation. Whereas a μ-N,S bridging mode must lead to three different *trans* sites for the S atoms of the facially co-ordinated thioether, only two such sites in a 2 : 1 relationship

**Table 2** Selected bond lengths (Å) and angles in complexes **5**, **6**, **11** and **13**

| | | | |
|---|---|---|---|
| Compound **5** | | | |
| Ru–S(1) | 2.287(5) | Ru(a)–S(1a) | 2.293(5) |
| Ru–S(4) | 2.299(5) | Ru(a)–S(4a) | 2.299(4) |
| Ru–S(7) | 2.287(6) | Ru(a)–S(7a) | 2.293(6) |
| Ru–S(11) | 2.458(5) | Ru(a)–S(11a) | 2.451(5) |
| Ru–S(11a) | 2.430(5) | Ru(a)–S(11) | 2.431(5) |
| Ru–N(11) | 2.05(2) | Ru(a)–N(11a) | 2.10(2) |
| S(11)–C(11) | 1.74(2) | S(11a)–C(11a) | 1.76(2) |
| N(11)–C(11) | 1.36(2) | N(11a)–C(11a) | 1.34(2) |
| Ru–S(11)–Ru(a) | 95.2(2) | Ru–S(11a)–Ru(a) | 95.5(2) |
| S(11)–Ru–S(11a) | 84.4(2) | S(11)–Ru(a)–S(11a) | 84.5(2) |
| S(11)–Ru–N(11) | 66.7(5) | S(11a)–Ru(a)–N(11a) | 67.5(4) |
| S(11a)–Ru–N(11) | 95.0(4) | S(11)–Ru(a)–N(11a) | 94.6(4) |
| Ru–S(11)–C(11) | 80.0(6) | Ru(a)–S(11a)–C(11a) | 79.2(7) |
| S(11)–C(11)–N(11) | 107.0(1) | S(11a)–C(11a)–N(11a) | 109.0(1) |
| Ru–N(11)–C(11) | 105.9(14) | Ru(a)–N(11a)–C(11a) | 103.6(14) |
| Compound **6** | | | |
| Ru–S(1) | 2.306(1) | Ru(a)–S(1a) | 2.313(1) |
| Ru–S(4) | 2.311(1) | Ru(a)–S(4a) | 2.313(1) |
| Ru–S(7) | 2.298(1) | Ru(a)–S(7a) | 2.311(1) |
| Ru–S(11) | 2.429(1) | Ru(a)–S(11a) | 2.424(1) |
| Ru–S(11a) | 2.435(1) | Ru(a)–S(11) | 2.438(1) |
| Ru–N(21) | 2.051(1) | Ru(a)–N(21a) | 2.069(3) |
| S(11)–C(11) | 1.770(3) | S(11a)–C(11a) | 1.763(3) |
| N(12)–C(11) | 1.288(4) | N(12a)–C(11a) | 1.307(4) |
| S(12)–C(11) | 1.761(4) | S(12a)–C(11a) | 1.746(4) |
| Ru–S(11)–Ru(a) | 98.5(1) | Ru–S(11a)–Ru(a) | 98.8(1) |
| S(11)–Ru–S(11a) | 81.3(1) | S(11)–Ru(a)–S(11a) | 81.4(1) |
| S(11)–Ru–N(21) | 93.8(1) | S(11a)–Ru(a)–N(21a) | 96.6(1) |
| S(11a)–Ru–N(21) | 84.3(1) | S(11)–Ru(a)–N(21a) | 86.9(1) |
| Ru–S(11)–C(11) | 115.6(1) | Ru(a)–S(11a)–C(11a) | 116.5(1) |
| Ru–S(11a)–C(11a) | 114.5(1) | Ru(a)–S(11)–C(11) | 108.4(1) |
| Compound **11** | | | |
| Ru–S(1) | 2.362(4) | Ru(a)–S(1a) | 2.352(4) |
| Ru–S(4) | 2.308(4) | Ru(a)–S(4a) | 2.318(4) |
| Ru–S(7) | 2.335(4) | Ru(a)–S(7a) | 2.291(4) |
| Ru–P(1) | 2.347(4) | Ru(a)–P(1a) | 2.325(4) |
| Ru–S(11) | 2.431(4) | Ru(a)–S(12) | 2.444(4) |
| Ru–N(12) | 2.11(1) | Ru(a)–Cl(a) | 2.456(4) |
| S(11)–C(11) | 1.70(1) | S(12)–C(12) | 1.73(1) |
| N(12)–C(11) | 1.36(2) | N(12)–C(12) | 1.34(2) |
| S(11)–Ru–P(1) | 93.0(1) | S(12)–Ru(a)–P(1a) | 89.7(1) |
| S(11)–Ru–N(12) | 111.1(9) | S(12)–Ru(a)–Cl(a) | 102.7(1) |
| Ru–S(11)–C(11) | 80.2(5) | Ru(a)–S(12)–C(12) | 118.2(4) |
| S(11)–C(11)–N(12) | 111.1(9) | S(12)–C(12)–N(12) | 119.5(9) |
| Ru–N(12)–C(11) | 101.4(7) | | |
| Compound **13** | | | |
| Ru–S(1) | 2.358(2) | Ru–S(4) | 2.325(2) |
| Ru–S(7) | 2.307(2) | Ru–S(11) | 2.450(2) |
| Ru–P | 2.362(2) | Ru–N(21) | 2.081(7) |
| S(11)–C(11) | 1.702(8) | C(11)–N(11) | 1.35(1) |
| C(11)–N(14) | 1.34(1) | | |
| S(11)–Ru–P | 87.0(1) | S(11)–Ru–N(21) | 94.5(2) |
| P–Ru–N(21) | 92.8(2) | Ru–S(11)–C(11) | 107.0(3) |
| Ru–N(21)–C(21) | 166.9(6) | S(11)–C(11)–N(11) | 128.3(7) |
| S(11)–C(11)–N(14) | 126.4(6) | N(11)–C(11)–N(14) | 105.2(7) |

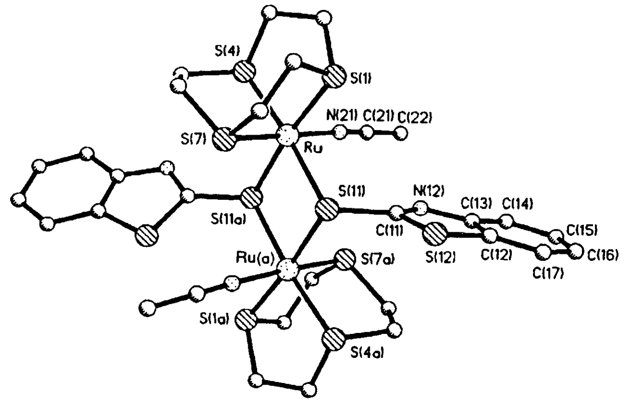


**Fig. 2** Structure of the cation $[\{Ru(MeCN)([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}btt)_2]^{2+}$ **6**

are expected for a μ-S bridged dimer. The relative simplicity of the signal pattern for the thioether protons, namely three multiplets in an intensity relationship 2 : 3 : 1, is strong evidence for the μ-S co-ordination pattern. Confirmation is provided by the X-ray structural analysis of **6**·MeCN (Fig. 2). The central $(RuS)_2$ four-membered ring is planar (atom deviations ± 0.06 Å) with a Ru ⋯ Ru(a) distance of 3.69 Å, longer than that of 3.61 Å in **5**. Comparison of the exocyclic bond lengths S(11)–C(11) and S(11a)–C(11a) in **6** [1.770(3), 1.763(3) Å] with the analogous distance in free Hbtt [1.662(4) Å][20] suggests that these can be regarded as essentially single bonds in the dinuclear complex. In contrast to **5** (2-*syn*) the $btt^-$ ligands in **6** display a 2-*anti* orientation with a dihedral angle of 40.0° between their respective planes. Both isomeric forms are possible for **5** and **6**.

Complex **6** represents the first example of a dimeric μ-S bridged complex to contain the $([9]aneS_3\text{-}\kappa^3S)Ru^{II}$ fragment. It was, therefore, of interest to establish whether a triply-bridged dinuclear cation $[\{Ru([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}btt)_3]^+$ **7** can also be prepared. The reaction of **1** with $btt^-$ was carried out at reflux in methanol in a 2 : 3 molar ratio. After filtration and volume reduction, the resulting solution was left to stand at 4 °C to afford a red precipitate of **7**, which was characterized by elemental analysis, FAB mass and $^1H$ NMR spectroscopy. The recorded ion $[M - CF_3SO_3]^+$ ($m/z$ = 1062) corresponds to the formulation of **7** as a triply μ-S bridged dinuclear complex. Conclusive evidence for the necessary $C_3$ symmetry in solution is provided by the $^1H$ NMR resonance pattern of the thioether ligands, for which only two multiplets at δ 2.52 (12 H) and 2.65 (12 H) are observed. The bridging $btt^-$ ligands are magnetically equivalent and give rise to only one set of four signals. Complex **7** represents the first example of a dinuclear triply bridged $([9]aneS_3\text{-}\kappa^3S)Ru^{II}$ complex. The employment of the relatively bulky $btt^-$ ligands prevents formation of insoluble polymeric products as observed for the reaction between **1** and NaSH. Reaction of **2** with $btt^-$ in methanol at a 1 : 2 or higher molar ratio leads to the precipitation of the red-brown complex $[Ru(btt)_2([9]aneS_3\text{-}\kappa^3S)]$ **8**, which exhibits the expected molecular ion $M^+$ at $m/z$ = 614. The 1 : 2 ratio of the thioether and $btt^-$ ligands in **8** is confirmed by the integral values of their $^1H$ NMR signals. The presence of two sets of resonances for the thioamide protons is in accordance with the adoption of different co-ordination modes (κ*S* and $\kappa^2N,S$) by these ambidentate ligands.

The introduction of a sterically demanding $PPh_3$ ligand at each Ru centre enables the isolation[7] of the doubly μ-Cl bridged complex $[\{Ru(PPh_3)([9]aneS_3\text{-}\kappa^3S)\}_2(\mu\text{-}Cl)_2]^{2+}$. However, the presence of $PPh_3$ prevents the formation of dinuclear complexes with bulkier bridging ligands such as heterocyclic thioamides. Instead reaction of anions such as $btt^-$ or $pyt^-$ with **2** produces monomeric complexes $[Ru(btt)(PPh_3)([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]$[1] and **9**. We, therefore, chose to look at the $dtuc^{2-}$ dianion as a potential bridging ligand. This sulfur analogue of uracil is capable of forming two N,S coordinated four-membered chelate rings as in $[\{Ti(C_5Me_5)_2\}_2(\mu\text{-}dtuc)]$.[21] The adoption of such a $\mu\text{-}1\kappa^2N,S{:}2\kappa^2N',S'$ co-ordination mode should allow the formation of dinuclear complexes with effectively no steric interaction between $(Ph_3P)([9]aneS_3\text{-}\kappa^3S)Ru^{II}$ fragments. However, employment of the ambidentate dianion $dtuc^{2-}$ has often been found to lead to insoluble polymeric products.[22]

Reaction of complex **2** or $[RuCl_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)]$[7]

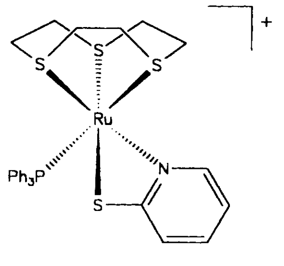
**Table 3** Fractional atomic coordinates ( × $10^4$) with estimated standard deviations (e.s.d.s) in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Compound **5** | | | | | | | |
| Ru | 6 534(2) | 1 315(1) | 2 986(1) | C(11a) | 2 767(18) | 2 947(16) | 2 948(10) |
| Ru(a) | 3 985(2) | 2 636(1) | 1 705(1) | C(12a) | 1 951(28) | 3 350(27) | 3 501(11) |
| S(1) | 6 012(6) | 575(5) | 4 085(2) | C(13a) | 1 367(32) | 4 474(30) | 3 442(16) |
| S(4) | 9 352(5) | 974(5) | 3 074(2) | C(14a) | 1 585(27) | 5 197(22) | 2 881(14) |
| S(7) | 6 820(6) | −438(4) | 2 801(3) | C(15a) | 2 351(24) | 4 804(20) | 2 342(12) |
| S(1a) | 1 295(5) | 2 654(4) | 1 541(2) | O(77) | 4 197(41) | 7 719(33) | 1 943(21) |
| S(4a) | 4 320(6) | 3 912(4) | 730(2) | C(77) | 2 567(47) | 8 275(33) | 1 781(24) |
| S(7a) | 4 912(6) | 1 254(4) | 1 125(2) | S(88) | 9 472(9) | 7 208(5) | 961(4) |
| S(11) | 6 873(5) | 2 495(4) | 1 879(2) | O(881) | 8 460(38) | 6 578(30) | 762(19) |
| S(11a) | 3 600(5) | 1 584(5) | 2 841(2) | O(882) | 11 218(19) | 6 793(29) | 1 020(19) |
| C(2) | 8 076(21) | 181(16) | 4 396(9) | O(883) | 8 618(39) | 7 342(31) | 1 616(10) |
| C(3) | 9 385(24) | 714(20) | 3 941(9) | O(884) | 10 350(38) | 7 154(31) | 305(9) |
| C(5) | 10 086(25) | −450(17) | 2 961(10) | O(885) | 10 388(41) | 6 628(27) | 1 489(13) |
| C(6) | 9 046(24) | −834(20) | 2 592(10) | O(886) | 7 865(25) | 6 915(32) | 955(18) |
| C(8) | 6 497(29) | −1 383(18) | 3 620(11) | C(88) | 9 189(27) | 8 684(9) | 694(11) |
| C(9) | 5 488(27) | −801(18) | 4 109(10) | F(881) | 7 595(27) | 9 047(26) | 594(16) |
| C(2a) | 919(26) | 3 829(21) | 876(12) | F(882) | 9 620(39) | 9 380(24) | 980(14) |
| C(3a) | 2 295(23) | 4 269(16) | 433(9) | F(883) | 10 191(34) | 8 656(25) | 120(12) |
| C(5a) | 5 457(26) | 3 118(18) | 156(11) | F(884) | 8 137(40) | 8 924(31) | 1 223(14) |
| C(6a) | 5 545(30) | 1 903(18) | 320(9) | F(885) | 10 592(34) | 8 935(31) | 809(18) |
| C(8a) | 3 077(28) | 794(22) | 1 052(16) | F(886) | 8 419(42) | 9 405(26) | 230(14) |
| C(9a) | 1 489(32) | 1 497(22) | 1 133(12) | S(99) | 1 486(11) | 7 396(7) | 4 574(5) |
| N(11) | 6 515(17) | 2 952(14) | 2 984(8) | O(991) | 2 045(33) | 8 435(15) | 4 305(13) |
| C(11) | 6 829(19) | 3 468(16) | 2 343(10) | O(992) | 431(30) | 7 038(22) | 4 208(12) |
| C(12) | 7 051(21) | 4 541(21) | 2 159(11) | O(993) | 1 545(35) | 6 863(22) | 5 262(7) |
| C(13) | 6 984(28) | 5 157(20) | 2 617(15) | C(99) | 3 166(22) | 6 277(14) | 4 438(11) |
| C(14) | 6 641(26) | 4 642(22) | 3 287(13) | F(991) | 4 347(25) | 6 455(16) | 4 743(9) |
| C(15) | 6 428(22) | 3 507(22) | 3 453(13) | F(992) | 2 579(24) | 5 338(16) | 4 702(10) |
| N(11a) | 2 967(16) | 3 666(16) | 2 373(7) | F(993) | 3 529(25) | 6 659(16) | 3 797(10) |
| Compound **6** | | | | | | | |
| Ru | 10 218(1) | 1 293(1) | 2 447(1) | S(11a) | 9 326(1) | 225(1) | 1 709(1) |
| S(1) | 11 245(1) | 2 166(1) | 3 110(1) | S(12a) | 6 993(1) | 60(1) | 2 540(1) |
| S(4) | 9 440(1) | 2 829(1) | 1 759(1) | N(12a) | 7 493(2) | 1 315(2) | 1 164(2) |
| S(7) | 8 900(1) | 1 555(1) | 3 675(1) | C(11a) | 7 917(3) | 621(3) | 1 757(2) |
| C(2) | 11 187(3) | 3 363(3) | 2 392(3) | C(12a) | 5 949(3) | 817(3) | 2 032(3) |
| C(3) | 10 075(3) | 3 798(3) | 2 146(3) | C(13a) | 6 368(3) | 1 439(3) | 1 309(3) |
| C(5) | 8 102(3) | 3 079(3) | 2 399(3) | C(14a) | 5 675(3) | 2 098(3) | 777(3) |
| C(6) | 8 080(3) | 2 804(3) | 3 419(3) | C(15a) | 4 583(4) | 2 112(3) | 998(4) |
| C(8) | 9 643(3) | 1 875(3) | 4 527(2) | C(16a) | 4 164(3) | 1 513(4) | 1 725(4) |
| C(9) | 10 400(3) | 2 598(3) | 4 155(2) | C(17a) | 4 838(3) | 848(3) | 2 255(3) |
| S(11) | 10 851(1) | −332(1) | 3 255(1) | N(21a) | 8 742(2) | −1 243(2) | 3 629(2) |
| S(12) | 12 864(1) | −1 288(1) | 4 040(1) | C(21a) | 8 032(3) | −1 203(3) | 4 201(3) |
| N(12) | 12 882(2) | −886(2) | 2 299(2) | C(22a) | 7 086(3) | −1 148(4) | 4 898(3) |
| C(11) | 12 259(3) | −787(2) | 3 060(2) | S(88) | 2 103(1) | 4 475(1) | −159(1) |
| C(12) | 14 062(3) | −1 697(3) | 3 344(3) | O(881) | 2 323(3) | 3 408(2) | 118(2) |
| C(13) | 13 909(3) | −1 412(3) | 2 444(3) | O(882) | 1 785(4) | 4 713(3) | −1 043(3) |
| C(14) | 14 756(3) | −1 690(3) | 1 745(3) | O(883) | 1 497(3) | 5 090(3) | 524(3) |
| C(15) | 15 723(4) | −2 233(4) | 1 982(4) | C(88) | 3 392(4) | 4 871(4) | −277(4) |
| C(16) | 15 859(4) | −2 503(4) | 2 882(4) | F(881) | 3 330(3) | 5 839(3) | −565(3) |
| C(17) | 15 040(3) | −2 242(4) | 3 582(4) | F(882) | 4 140(3) | 4 321(4) | −799(4) |
| N(21) | 11 402(2) | 1 066(2) | 1 356(2) | F(883) | 3 768(4) | 4 762(3) | 517(4) |
| C(21) | 12 052(3) | 900(3) | 755(3) | S(99) | 7 935(1) | 5 426(1) | 5 058(1) |
| C(22) | 12 899(4) | 652(4) | −1(3) | O(991) | 7 750(3) | 6 466(2) | 4 677(2) |
| Ru(a) | 9 941(1) | −1 394(1) | 2 525(1) | O(992) | 8 759(3) | 4 761(3) | 4 539(3) |
| S(1a) | 8 929(1) | −2 286(1) | 1 858(1) | O(993) | 7 933(3) | 5 309(3) | 6 022(2) |
| S(4a) | 10 739(1) | −2 925(1) | 3 210(1) | C(99) | 6 732(3) | 4 973(3) | 4 900(3) |
| S(7a) | 11 261(1) | −1 643(1) | 1 286(1) | F(991) | 6 747(3) | 4 032(3) | 5 247(3) |
| C(2a) | 9 010(3) | −3 484(3) | 2 580(3) | F(992) | 5 839(3) | 5 556(3) | 5 255(3) |
| C(3a) | 10 128(3) | −3 907(3) | 2 825(3) | F(993) | 6 646(3) | 4 970(3) | 4 031(2) |
| C(5a) | 12 080(3) | −3 184(3) | 2 570(3) | C(77) | 5 086(6) | 2 842(6) | 3 465(5) |
| C(6a) | 12 117(3) | −2 882(3) | 1 555(3) | C(771) | 4 728(8) | 3 685(7) | 2 834(7) |
| C(8a) | 10 530(3) | −1 979(3) | 442(2) | N(77) | 5 344(6) | 2 155(6) | 3 995(5) |
| C(9a) | 9 768(3) | −2 705(3) | 803(2) | | | | |
| Compound **11** | | | | | | | |
| Ru | −1 023(1) | 701(1) | 6 368(1) | C(55) | −370(12) | 1 153(5) | 9 640(10) |
| Cl | 4 018(3) | 592(1) | 2 700(3) | C(56) | −198(10) | 1 209(4) | 8 768(9) |
| S(7) | −2 115(3) | 816(1) | 7 355(2) | Ru(a) | −2 889(1) | 2 550(1) | 6 507(1) |
| S(1) | −2 542(3) | 443(1) | 5 379(2) | Cl(a) | −3 656(3) | 2 679(1) | 4 943(2) |
| S(4) | −785(3) | 2(1) | 6 911(3) | S(1a) | −1 303(3) | 2 847(1) | 6 276(3) |
| C(2) | −2 277(13) | −131(4) | 5 337(10) | S(4a) | −3 417(3) | 3 260(1) | 6 666(3) |
| C(3) | −1 830(11) | −333(4) | 6 218(10) | S(7a) | −2 147(3) | 2 537(1) | 7 982(2) |
| C(5) | −1 211(12) | −9(5) | 7 913(9) | C(1a) | −1 510(13) | 3 422(5) | 6 225(14) |

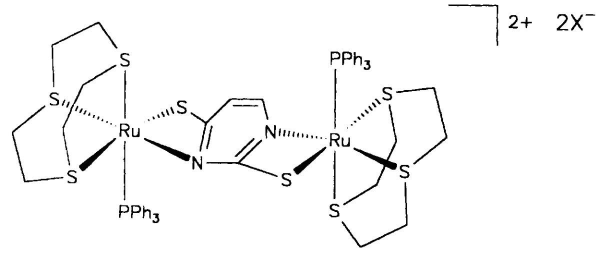
**Table 3** (*contd.*)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| C(6) | −2 121(14) | 300(5) | 7 956(10) | C(2a) | −2 574(12) | 3 579(5) | 6 129(10) |
| C(8) | −3 432(10) | 792(4) | 6 685(8) | C(5a) | −2 944(12) | 3 399(5) | 7 849(10) |
| C(9) | −3 596(11) | 424(5) | 5 974(10) | C(6a) | −2 768(11) | 3 009(5) | 8 413(9) |
| S(11) | −211(3) | 650(1) | 5 106(2) | C(8a) | −804(12) | 2 731(6) | 8 089(11) |
| S(12) | −2 151(3) | 1 819(1) | 6 502(2) | C(9a) | −430(13) | 2 760(7) | 7 336(13) |
| N(11) | −700(10) | 1 404(4) | 4 226(7) | P(1a) | −4 490(3) | 2 250(1) | 6 639(2) |
| N(12) | −1 206(8) | 1 272(3) | 5 598(6) | C(31a) | −5 562(10) | 2 651(4) | 6 383(8) |
| C(11) | −769(10) | 1 151(4) | 4 927(8) | C(32a) | −5 629(11) | 2 981(4) | 6 969(9) |
| C(12) | −1 644(10) | 1 665(4) | 5 606(8) | C(33a) | −6 432(12) | 3 292(5) | 6 734(10) |
| C(13) | −1 628(11) | 1 963(5) | 4 875(9) | C(34a) | −7 121(12) | 3 276(5) | 5 929(10) |
| C(14) | −1 181(13) | 1 810(5) | 4 206(10) | C(35a) | −7 057(12) | 2 942(5) | 5 326(10) |
| P(1) | 539(3) | 945(1) | 7 300(2) | C(36a) | −6 260(10) | 2 634(4) | 5 580(9) |
| C(31) | 1 019(10) | 1 505(4) | 7 154(8) | C(41a) | −4 563(10) | 2 008(4) | 7 705(8) |
| C(32) | 1 321(10) | 1 790(4) | 7 847(9) | C(42a) | −3 846(10) | 1 709(4) | 8 041(8) |
| C(33) | 1 755(12) | 2 185(5) | 7 734(10) | C(43a) | −3 880(12) | 1 479(5) | 8 810(10) |
| C(34) | 1 864(12) | 2 289(6) | 6 889(11) | C(44a) | −4 707(12) | 1 570(5) | 9 243(11) |
| C(35) | 1 525(11) | 2 022(5) | 6 185(10) | C(45a) | −5 427(13) | 1 882(5) | 8 919(11) |
| C(36) | 1 110(10) | 1 624(4) | 6 336(9) | C(46a) | −5 361(12) | 2 105(5) | 8 139(10) |
| C(41) | 1 776(10) | 650(4) | 7 297(8) | C(51a) | −5 040(9) | 1 792(4) | 5 916(8) |
| C(42) | 1 774(11) | 270(5) | 6 883(9) | C(52a) | −4 651(10) | 1 676(4) | 5 197(8) |
| C(43) | 2 759(12) | 52(5) | 6 920(10) | C(53a) | −5 114(11) | 1 335(5) | 4 655(9) |
| C(44) | 3 669(14) | 240(5) | 7 334(10) | C(54a) | −5 988(11) | 1 125(5) | 4 839(10) |
| C(45) | 3 675(14) | 610(5) | 7 756(10) | C(55a) | −6 372(11) | 1 221(5) | 5 542(9) |
| C(46) | 2 727(12) | 818(5) | 7 720(10) | C(56a) | −5 882(11) | 1 556(5) | 6 083(10) |
| C(51) | 455(10) | 926(4) | 8 468(8) | O(99) | 6 182(24) | 1 181(6) | 2 547(20) |
| C(52) | 969(11) | 603(4) | 9 014(9) | O(88) | 3 840(22) | 310(9) | 621(17) |
| C(53) | 813(13) | 574(5) | 9 844(11) | C(77) | 7 441(27) | 476(11) | 942(21) |
| C(54) | 170(13) | 843(5) | 10 141(11) | O(77) | 7 023(26) | 533(11) | 22(21) |
| Compound **13** | | | | | | | |
| Ru | 1 544(1) | 2 191(1) | 2 313(1) | C(42) | −1 796(9) | 2 573(7) | 3 596(4) |
| S(1) | 2 667(3) | 544(2) | 1 854(1) | C(43) | −2 765(10) | 2 357(8) | 4 151(5) |
| S(7) | 2 223(2) | 3 242(2) | 1 307(1) | C(44) | −2 805(11) | 3 035(9) | 4 671(5) |
| S(4) | 3 994(2) | 2 394(2) | 2 723(1) | C(45) | −1 863(11) | 3 921(9) | 4 635(4) |
| C(2) | 4 539(15) | 275(13) | 2 258(8) | C(46) | −883(9) | 4 127(7) | 4 088(4) |
| C(3) | 5 202(11) | 1 116(8) | 2 528(7) | C(51) | −1 226(8) | 4 731(6) | 2 241(4) |
| C(5) | 4 737(10) | 3 479(8) | 2 129(6) | C(52) | −2 265(9) | 5 508(7) | 2 535(5) |
| C(6) | 4 248(12) | 3 510(9) | 1 430(6) | C(53) | −3 323(10) | 6 252(8) | 2 132(6) |
| C(8) | 2 510(13) | 2 176(9) | 723(5) | C(54) | −3 406(9) | 6 250(7) | 1 459(6) |
| C(9) | 3 137(13) | 1 024(9) | 973(5) | C(55) | −2 394(10) | 5 496(7) | 1 152(5) |
| S(11) | −959(2) | 1 927(2) | 1 823(1) | C(56) | −1 310(9) | 4 737(7) | 1 548(4) |
| N(11) | −1 093(7) | −352(6) | 2 327(4) | S(77) | 7 268(3) | 1 834(2) | −221(2) |
| N(14) | −992(8) | −45(6) | 1 236(4) | O(771) | 8 734(7) | 1 138(5) | −117(3) |
| C(11) | −988(8) | 488(6) | 1 799(4) | O(772) | 6 393(9) | 1 812(7) | 392(5) |
| C(12) | −1 165(11) | −1 399(8) | 2 092(6) | O(773) | 6 458(13) | 1 726(7) | −827(5) |
| C(13) | −1 112(13) | −1 210(8) | 1 428(6) | C(77) | 7 767(12) | 3 257(9) | −353(5) |
| N(21) | 1 252(7) | 1 082(6) | 3 204(4) | F(771) | 6 550(10) | 4 024(6) | −348(5) |
| C(21) | 1 388(10) | 421(8) | 3 678(5) | F(772) | 8 745(10) | 3 495(6) | 99(5) |
| C(22) | 1 599(14) | −457(11) | 4 247(6) | F(773) | 8 495(13) | 3 489(8) | −927(4) |
| P | 254(2) | 3 792(2) | 2 770(1) | S(88) | 3 132(3) | 1 284(3) | 6 096(2) |
| C(31) | 1 524(8) | 4 826(6) | 3 009(4) | O(881) | 3 635(14) | 1 808(9) | 6 637(4) |
| C(32) | 1 554(9) | 5 902(7) | 2 641(5) | O(882) | 1 981(8) | 515(5) | 6 262(3) |
| C(33) | 2 592(12) | 6 646(9) | 2 827(6) | O(883) | 4 341(15) | 865(11) | 5 652(9) |
| C(34) | 3 591(13) | 6 303(12) | 3 359(6) | C(88) | 2 262(17) | 2 405(12) | 5 514(7) |
| C(35) | 3 598(10) | 5 237(10) | 3 719(5) | F(881) | 1 102(14) | 2 911(9) | 5 850(9) |
| C(36) | 2 556(10) | 4 507(8) | 3 537(5) | F(882) | 3 257(11) | 3 147(8) | 5 301(6) |
| C(41) | −863(8) | 3 460(7) | 3 551(4) | F(883) | 1 646(14) | 2 042(10) | 4 985(5) |

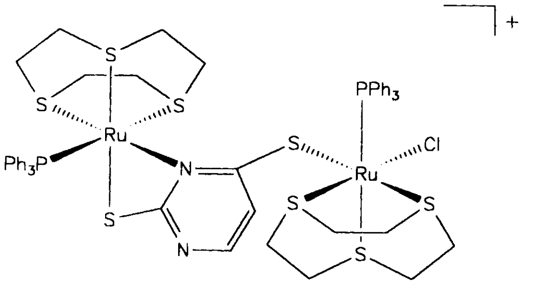
with dtuc$^{2-}$ in a 2:1 ratio in methanol does yield dinuclear complexes with the μ-1κ$^2$*N*,*S*:2κ$^2$*N*′,*S*′ co-ordination mode: **10a** (X = $CF_3SO_3$) and **10b** (X = Cl) were characterized by elemental analysis and FAB mass spectroscopy through their [*M* − X]$^+$ ions at respectively *m*/*z* 1379 and 1265. The possible co-ordination of Ru atoms by acetonitrile ligands can be ruled out by the absence of typical $^1$H NMR signals between δ 2.0 and 2.5. Further evidence for the postulated co-ordination mode is provided by the similarity of the $^{31}$P NMR shifts for the $PPh_3$ ligands at the different ruthenium centres, *e.g.* δ 35.60 and 36.28 for **10a**. The small difference in the positions of the resonances is caused by the asymmetry of the bridging dtuc$^{2-}$ dianion. Whereas **10a** can be isolated as the only product of the reaction between **2** and dtuc$^{2-}$, a minor product [{RuCl($PPh_3$)([9]ane$S_3$-κ$^3$*S*)}(μ-dtuc){Ru($PPh_3$)([9]ane$S_3$-κ$^3$*S*)}]Cl **11** is obtained together with **10b** in low yield. Of the three possible co-ordination modes, that of **C** was established by X-ray structural analysis, as depicted in Fig. 3. Refinement of the ring atoms N(11) and C(13) as expected for pattern **C** led in comparison to pattern **A** to a reduction in the reliability index *R*′, which was significant at the 0.005 level (Hamilton *R* test[23]). The equivalent isotropic thermal parameters for N(11) and C(13) and the endocyclic bond lengths to these atoms also provide confirmative evidence for the correctness of this interpretation. The alternative bridging mode **A** is hardly to be expected since it provides no steric hindrance to the formation of a second chelate ring, as observed in the μ-1κ$^2$*N*,*S*:2κ$^2$*N*′,*S*′ co-ordination pattern of the dtuc$^{2-}$ dianion in **10a** and **10b**. An



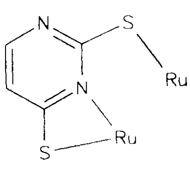
**9**



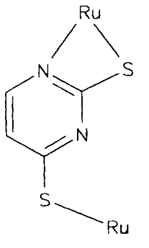
$X = CF_3SO_3$ **10a** $X = Cl$ **10b**



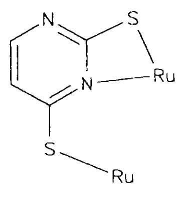
**11**



**A**



**B**



**C**

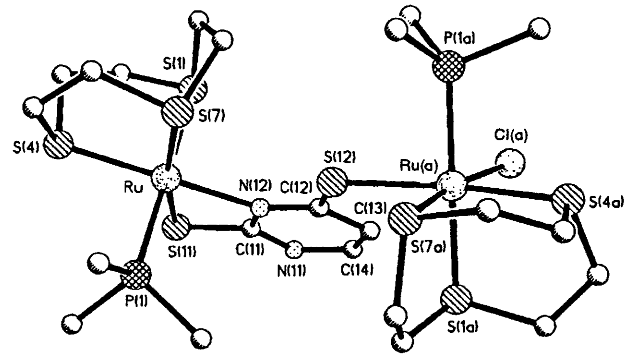
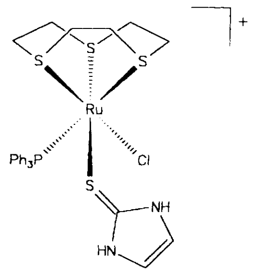
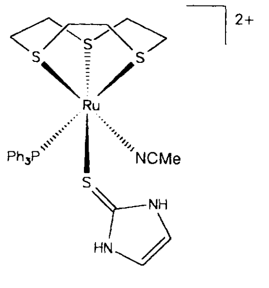
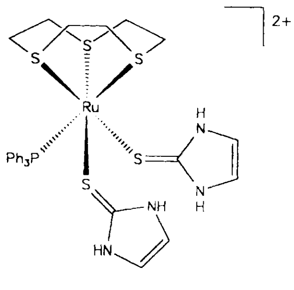


**Fig. 3** Structure of the cation $[\{RuCl(PPh_3)([9]aneS_3\text{-}\kappa^3S)\}(\mu\text{-}dtuc)\{Ru(PPh_3)([9]aneS_3\text{-}\kappa^3S)\}]^+$ **11**



**12**





**13** **14**

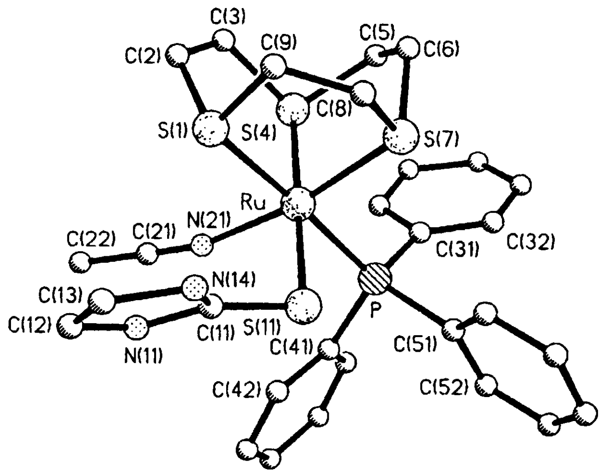


**Fig. 4** Structure of the cation $[Ru(H_2imt)(MeCN)(PPh_3)([9]aneS_3\text{-}\kappa^3S)]^{2+}$ **13**

indication of the extent of ring strain in the four-membered RuSCN ring may be gained from a comparison of the Ru–S(11)–C(11) and Ru(a)–S(12)–C(12) angles of 80.2(5) and 118.2(4)°.

Cooper and Rawle[24] have commented on the important role of charge neutralization in crown thioether co-ordination chemistry. As a result of their low σ-donor ability such thioethers are often incapable of displacing anions from metal co-ordination spheres. In pursuit of charge neutralization, complexes of crown thioethers have often been found to display a pronounced affinity for normally 'non-co-ordinating' anions such as $CF_3SO_3^-$, $BF_4^-$ and $ClO_4^-$. However, $[Ru(MeCN)_3([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **1** can be prepared by addition of $Ag(O_3SCF_3)$ to $[RuCl_2(Me_2SO)([9]aneS_3\text{-}\kappa^3S)]$ in acetonitrile,[1] indicating that the preference of $Ru^{II}$ for π-acceptor ligands such as MeCN is capable of overweighing the alternative of charge neutralization, which could be achieved by the incorporation of two $CF_3SO_3^-$ anions in the metal co-ordination sphere. It was, therefore, of interest to establish whether neutral S-donors such as 2-sulfanylimidazole ($H_2$imt) are capable of replacing one or two ligands in $[RuCl_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)]$ **3** or $[Ru(MeCN)_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **2**. In fact, only one chloride ligand can be substituted in the former complex to yield $[RuCl(H_2imt)(PPh_3)([9]aneS_3\text{-}\kappa^3S)]Cl$ **12**, even at molar ratios

$3:H_2imt$ of 1:2 and higher. In contrast, replacement of either one or two acetonitrile ligands can be achieved for **2**, as evidenced by the preparation of $[Ru(H_2imt)(MeCN)(PPh_3)([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **13** (Fig. 4) and $[Ru(H_2imt)_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **14** at appropriate molar ratios of the starting compounds. The restriction to monosubstitution for $[RuCl_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)]$ **3** is in accordance with the preparation of chiral complexes of the type $[RuCl(L)(PPh_3)([9]aneS_3\text{-}\kappa^3S)]^+$ [L = MeCN, PhCN, $PMe_2Ph$, $P(OMe)_2Ph$, CO, CS or $C_5H_5N$] reported by Schröder and co-workers.[7] The present results demonstrate that $[Ru(MeCN)_3([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **1** is an expedient starting material for the synthesis of dinuclear complexes with one to three bridging ligands. However, the limited steric demand of the facial $([9]aneS_3\text{-}\kappa^3S)Ru^{II}$ fragment tends to favour the formation of polymeric products for small bridging ligands such as $Cl^-$ or $SH^-$. This may be avoided by the employment of relatively bulky ligands such as the heterocyclic thioamides investigated in this work.

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