Structure and Reactions of the Thioether Half-sandwich Ruthenium(II) Complexes $[Ru(MeCN)_3([9]aneS_3)][CF_3SO_3]_2$ and $[Ru(MeCN)_2(PPh_3)([9]aneS_3)][CF_3SO_3]_2$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane)†

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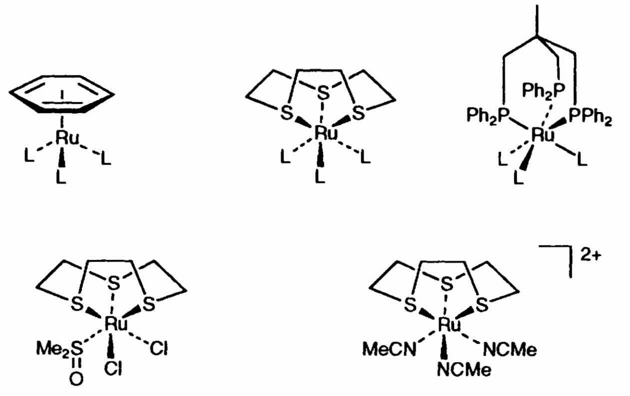
The complex $[Ru(MeCN)_3([9]aneS_3)][CF_3SO_3]_2$ **2** ($[9]aneS_3$ = 1,4,7-trithiacyclononane) was prepared by reaction of $[RuCl_2(dmso)([9]aneS_3)]$ **1** (dmso = dimethyl sulfoxide) with $Ag(CF_3SO_3)$ in acetonitrile. It has been employed as a starting material for the synthesis of the mixed-ligand sandwich complexes $[Ru\{HB(pz)_3\}([9]aneS_3)][CF_3SO_3]$ **3** (pz = pyrazol-1-yl) and $[Ru\{HC(pz)_3\}([9]aneS_3)][CF_3SO_3]_2$ **4** and the dinuclear half-sandwich complex $[\{Ru(\mu\text{-}S_2CNMe_2)([9]aneS_3)\}_2][CF_3SO_3]_2$ **5**. The complex $[Ru(MeCN)_2(PPh_3)([9]aneS_3)][CF_3SO_3]_2$ **6** may likewise be used for the preparation of thioether half-sandwich ruthenium(II) complexes such as $[Ru(S_2CNMe_2)(PPh_3)([9]aneS_3)][CF_3SO_3]$ **7** and $[Ru(C_7H_4NS_2)(PPh_3)([9]aneS_3)][CF_3SO_3]$ **8** ($C_7H_4NS_2$ = 2-sulfanylbenzothiazolate). The structures of **1**, **2** and **5**–**7** have been determined by X-ray crystallography.

The ability of the trithia macrocycle 1,4,7-trithiacyclononane ($[9]aneS_3$) to co-ordinate to transition metals in a facial manner as a six-electron donor is well documented.[1,2] However, despite the formal analogy of the co-ordination properties of this thioether to those of η^n-C_nH_n groups such as η^5-cyclopentadienyl or η^6-arene, relatively few studies of the synthetic potential of $[9]aneS_3$-κ^3S complexes have been reported. In recent publications Schröder and co-workers have described the preparation and properties of low-valent cations of the type $[M(alkene)_2([9]aneS_3\text{-}\kappa^3S)]^+$ (M = Rh or Ir)[3] and have presented the first examples[4] of half-sandwich complexes of $[9]aneS_3$ with ruthenium(II). Reaction of $[RuX_3(PRR'_2)_2]$ (X = Cl, PRR'_2 = PMe_2Ph, PEt_2Ph or $PEtPh_2$; X = Br, PRR'_2 = $PEtPh_2$) with $[9]aneS_3$ in EtOH or CH_2Cl_2 yields complexes of the type $[RuCl(PRR'_2)_2([9]aneS_3\text{-}\kappa^3S)]^+$. In contrast, presumably as a result of the bulkiness of the PPh_3 ligand, treatment of $[RuX_2(PPh_3)_3]$ (X = Cl or Br) with $[9]aneS_3$ affords $[RuX_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)]$, a useful starting material for the synthesis of chiral complexes of the type $[RuX(L)(PPh_3)([9]aneS_3\text{-}\kappa^3S)]^+$ by reaction with co-ordinating solvents or ligands [X = Cl; L = MeCN, PhCN, PMe_2Ph, $P(OMe)_2Ph$, CO, CS or C_5H_5N] in the presence of $TlPF_6$.[4] The reaction of $[RuCl_2(PPh_3)_3]$ with $[9]aneS_3$ was also studied by Hill and co-workers[5] who presented the crystal structure of the product $[RuCl_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)]$. This group has, furthermore, described the preparation of $Ru^{II}(PPh_3)([9]aneS_3)$ complexes containing carbonyl or thiocarbonyl ligands.[5,6]

In recent years we and others have reported the synthesis and structural characterisation of diastereoisomeric η^5-pentamethylcyclopentadienyl and η^6-arene complexes of Group 8 and 9 transition metals (η^5-C_5Me_5, M = Co^{III}, Rh^{III}, Ir^{III} or Ru^{II}; η^6-arene, M = Ru^{II} or Os^{II}), which bear amino acids or peptides as ligands.[7–9] Conventional starting materials for these and other organometallic half-sandwich complexes are mononuclear tris(acetonitrile) complexes such as $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ or chloro-bridged dinuclear complexes such as $[\{RuCl_2(\eta^6\text{-arene})\}_2]$.[10,11] We are currently interested in extending the class of amino acidato half-sandwich compounds to include non-organometallic face-capping ligands, of which $[9]aneS_3$ provides an example. We now report the preparation of the complex $[Ru(MeCN)_3([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **2** from $[RuCl_2(dmso)([9]aneS_3\text{-}\kappa^3S)]$ **1** (dmso = dimethyl sulfoxide) and demonstrate the potential of **1** as a starting material for the synthesis of further thioether half-sandwich complexes.



1 **2**

Scheme 1 Half-sandwich ruthenium(II) complexes with six-electron ligands

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 analyser. The complex $[RuCl_2(dmso)_4]$ was prepared according to the literature procedure,[12] $[RuCl_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)]$ in a manner similar to those recently described.[4,5] The synthesis of $[RuCl_2(dmso)([9]aneS_3\text{-}\kappa^3S)]$ **1** by reaction of $[RuCl_2(dmso)_4]$ with $[9]aneS_3$ in nitromethane

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

was mentioned briefly by Cooper and Rawle[1b] in their recent review of crown thioether chemistry, but to our knowledge preparative details and spectroscopic data have not been published. The compound [9]aneS$_3$ was obtained from Fluka and used as received.

Syntheses.—[RuCl$_2$(dmso)([9]aneS$_3$-κ^3S)] **1**. The compound [9]aneS$_3$ (0.540 g, 3 mmol) was added to a solution of [RuCl$_2$(dmso)$_4$] (1.455 g, 3 mmol) in CHCl$_3$ (25 cm^3) and the solution stirred for 2 h at reflux. The orange-yellow precipitate was filtered off, washed with CHCl$_3$ and dried in vacuum. Recrystallisation by slow evaporation of an aqueous solution afforded **1** in 91% yield (1.23 g) as a monohydrate (Found: C, 21.2; H, 4.4. Calc. for $C_8H_{18}Cl_2ORuS_4{\cdot}H_2O$: C, 21.4; H, 4.5%). FAB mass spectrum: *m*/*z* 432 (93, *M*$^+$) and 395 (60%, [*M* − Cl]$^+$). ^{1}H NMR (D$_2$O): δ 2.4–2.9 (12 H, m, CH$_2$ of [9]aneS$_3$), 3.11, 3.18 and 3.22 (6 H, 3s, CH$_3$). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 1095s (SO) and 423s (RuS).

[Ru(MeCN)$_3$([9]aneS$_3$-κ^3S)][CF$_3$SO$_3$]$_2$ **2**. A solution of complex **1** (0.430 g, 1 mmol) in MeCN (30 cm^3) was refluxed under argon for 3 h in the presence of Ag(CF$_3$SO$_3$) (0.514 g, 2 mmol). After removal of AgCl by filtration the yellow filtrate was reduced in volume to 5 cm^3 and **2** precipitated by addition of toluene (50 cm^3). Pale yellow prismatic crystals of **2** were obtained in 90% yield (0.632 g) by recrystallisation from a MeCN solution covered with Et$_2$O (Found: C, 24.1; H, 2.9; N, 5.8. $C_{14}H_{21}F_6N_3O_6RuS_5$ requires C, 23.9; H, 3.0; N, 6.0%). FAB mass spectrum: *m*/*z* 1257 (63, [2*M* − CF$_3$SO$_3$]$^+$), 1134 (13, [2*M* − 3MeCN − CF$_3$SO$_3$]$^+$), 1051 (11, [2*M* − 5MeCN − CF$_3$SO$_3$]$^+$), 1010 (54, [2*M* − 6MeCN − CF$_3$SO$_3$]$^+$), 554 (41, [*M* − CF$_3$SO$_3$]$^+$), 513 (7, [*M* − MeCN − CF$_3$SO$_3$]$^+$), 472 (81, [*M* − 2MeCN − CF$_3$SO$_3$]$^+$) and 431 (39%, [*M* − 3MeCN − CF$_3$SO$_3$]$^+$). ^{1}H NMR (CD$_3$CN): δ 2.43 (9 H, s, CH$_3$), 2.69 and 2.82 (12 H, 2 m, CH$_2$ of [9]aneS$_3$). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 2324m and 2294m (CN).

[Ru{HB(pz)$_3$-κ^3N}([9]aneS$_3$-κ^3S)][CF$_3$SO$_3$] **3**. The salt Na[HB(pz)$_3$] (pz = pyrazol-1-yl) (47 mg, 0.2 mmol) was added to a solution of complex **2** (144 mg, 0.2 mmol) in MeOH (10 cm^3) and stirred for 3 h at reflux. The grey precipitate was filtered off and dried in vacuum to afford **3** in 56% yield (72 mg) (Found: C, 28.5; H, 3.3; N, 12.2. $C_{16}H_{22}BF_3N_6O_3RuS_4$ requires C, 29.9; H, 3.5; N, 13.1%). FAB mass spectrum: *m*/*z* 1128 (32, [2*M* − CF$_3$SO$_3$]$^+$) and 495 (31%, [*M* − CF$_3$SO$_3$]$^+$). ^{1}H NMR [(CD$_3$)$_2$SO]: δ 2.79 (6 H, m, CH$_2$ of [9]aneS$_3$), 3.06 (6 H, m, CH$_2$ of [9]aneS$_3$), 6.33 (3 H, dd, H^4 of pz), 7.63 (3 H, d, *J* = 2.31, H^3 of pz) and 7.97 (3 H, d, *J* = 1.85 Hz, H^5 of pz). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 2489m (BH).

[Ru{HC(pz)$_3$-κ^3N}([9]aneS$_3$-κ^3S)][CF$_3$SO$_3$]$_2$ **4**. The compound HC(pz)$_3$ (43 mg, 0.2 mmol) was added to a solution of complex **2** (144 mg, 0.2 mmol) in EtOH (10 cm^3) and stirred for 3 h at reflux. The yellow precipitate was filtered off and dried in vacuum to afford **4** in 76% yield (120 mg) (Found: C, 26.5; H, 2.1; N, 10.1. $C_{18}H_{22}F_6N_6O_6RuS_5$ requires C, 27.2; H, 2.8; N, 10.6%). FAB mass spectrum: *m*/*z* 1440 (66, [2*M* − CF$_3$SO$_3$]$^+$) and 645 (65%, [*M* − CF$_3$SO$_3$]$^+$). ^{1}H NMR [(CD$_3$)$_2$SO]: δ 2.92 (6 H, m, CH$_2$ of [9]aneS$_3$), 3.10 (6 H, m, CH$_2$ of [9]aneS$_3$), 6.71 (3 H, dd, H^4 of pz), 8.14 (3 H, d, *J* = 2.77, H^3 of pz), 8.54 (3 H, d, *J* = 2.31 Hz, H^5 of pz) and 9.76 (1 H, s, CH of pz).

[{Ru(μ-S$_2$CNMe$_2$)([9]aneS$_3$-κ^3S)}$_2$][CF$_3$SO$_3$]$_2$ **5**. A solution of complex **2** (144 mg, 0.2 mmol) in water (20 cm^3) was stirred for 3 d at room temperature together with Na[S$_2$CNMe$_2$]·2H$_2$O (36 mg, 0.2 mmol). A yellow precipitate was filtered off and the filtrate was reduced in volume to 3 cm^3 and left to give red crystals of **5**·2H$_2$O in 46% yield (52 mg) (Found: C, 20.0; H, 3.1; N, 1.8. $C_{20}H_{40}F_6N_2O_8Ru_2S_{12}$ requires C, 21.1; H, 3.5; N, 2.5%). FAB mass spectrum: *m*/*z* 952 (90, [*M* − CF$_3$SO$_3$]$^+$) and 552 (16%, [*M* − Ru(S$_2$CNMe$_2$)([9]aneS$_3$) − CF$_3$SO$_3$]$^+$). ^{1}H NMR (D$_2$O): δ 1.82 (2 H, m, CH$_2$ of [9]aneS$_3$), 2.0 (6 H, m, CH$_2$), 2.2 (2 H, m, CH$_2$), 2.65 (6 H, m, CH$_2$), 2.81 (6 H, m, CH$_2$), 3.01 (2 H, m, CH$_2$), 3.08 (6 H, s, CH$_3$ of S$_2$CNMe$_2$) and 3.29 (6 H, s, CH$_3$ of S$_2$CNMe$_2$).

[Ru(MeCN)$_2$(PPh$_3$)([9]aneS$_3$-κ^3S)][CF$_3$SO$_3$]$_2$ **6**. The complex [RuCl$_2$(PPh$_3$)([9]aneS$_3$)] (123 mg, 0.2 mmol) was dissolved in MeCN (10 cm^3) and the solution refluxed under argon for 2 h in the presence of Ag(CF$_3$SO$_3$) (102 mg, 0.4 mmol). The AgCl formed was filtered off and the filtrate reduced in volume to 5 cm^3. Complex **6** was precipitated by addition of diethyl ether (20 cm^3). Recrystallisation from chloroform afforded **6**·CHCl$_3$ (161 mg, 87% yield) (Found: C, 35.7; H, 3.4; N, 2.6. $C_{31}H_{34}Cl_3F_6N_2O_6PRuS_5$ requires C, 35.7; H, 3.3; N, 2.7%). FAB mass spectrum: *m*/*z* 775 (49, [*M* − CF$_3$SO$_3$]$^+$), 734 (11, [*M* − MeCN − CF$_3$SO$_3$]$^+$) and 693 (100%, [*M* − 2MeCN − CF$_3$SO$_3$]$^+$). NMR (CDCl$_3$): ^{1}H, δ 1.48 (2 H, m, CH$_2$ of [9]aneS$_3$), 2.19 (6 H, s, MeCN), 2.5 (2 H, m, CH$_2$ of [9]aneS$_3$), 2.92 (4 H, m, CH$_2$), 3.18 (4 H, m, CH$_2$) and 7.45 (15 H, m, C$_6$H$_5$); ^{31}P, δ 34.98 (s). IR (KBr disc): $\tilde{\nu}$/cm^{-1} 2328 and 2295m (CN).

[Ru(S$_2$CNMe$_2$)(PPh$_3$)([9]aneS$_3$-κ^3S)][CF$_3$SO$_3$] **7**. A solution of complex **6** (93 mg, 0.1 mmol) in MeOH (10 cm^3) was refluxed with Na[S$_2$CNMe$_2$]·2H$_2$O (18 mg, 0.1 mmol) for 2 h under argon. The solvent was removed and the resulting solid dissolved in CHCl$_3$ (3 cm^3). After filtration the solution was covered with hexane (6 cm^3) to afford yellow crystals of **7**·0.5CHCl$_3$ in 84% yield (73 mg) (Found: C, 39.1; H, 3.7; N, 1.4. $C_{28.5}H_{33.5}Cl_{1.5}F_3NO_3PRuS_6$ requires C, 39.2; H, 3.9; N, 1.6%). FAB mass spectrum: *m*/*z* 813 (24, *M*$^+$), 664 (87, [*M* − CF$_3$SO$_3$]$^+$) and 401 (12%, [*M* − PPh$_3$ − CF$_3$SO$_3$]$^+$). NMR (CDCl$_3$): ^{1}H, δ 1.32 (2 H, m, CH$_2$ or [9]aneS$_3$), 2.47 (2 H, m, CH$_2$), 2.7 (2 H, m, CH$_2$), 2.88 (4 H, m, CH$_2$), 2.98 (6 H, s, S$_2$CNMe$_2$), 3.02 (2 H, m, CH$_2$ of [9]aneS$_3$), 7.35 (9 H, m, C$_6$H$_5$) and 7.48 (6 H, m, C$_6$H$_5$); ^{31}P, δ 38.81 (s).

[Ru(C$_7$H$_4$NS$_2$)(PPh$_3$)([9]aneS$_3$-κ^3S)][CF$_3$SO$_3$] **8**. 2-Sulfanylbenzothiazole (C$_7$H$_5$NS$_2$) (25 mg, 0.15 mmol) was dissolved in MeOH (15 cm^3) by addition of 1 mol dm^3 KOH (0.15 cm^3). The resulting solution was refluxed with complex **6** (139 mg, 0.15 mmol) for 3 h. After subsequent filtration and reduction in volume to 5 cm^3 the solution was left at room temperature to give yellow crystals of **8** in 81% yield (105 mg) (Found: C, 43.7; H, 3.5; N, 1.3. $C_{32}H_{31}F_3NO_3PRuS_6$ requires C, 44.7; H, 3.6; N, 1.6%). FAB mass spectrum: *m*/*z* 859 (3, *M*$^+$) and 710 (100%, *M* − CF$_3$SO$_3$]$^+$). NMR (CDCl$_3$): ^{1}H, δ 0.65 (1 H, m, CH$_2$ of [9]aneS$_3$), 1.98 (1 H, m, CH$_2$), 2.38 (1 H, m, CH$_2$), 2.57 (2 H, m, CH$_2$), 2.72 (3 H, m, CH$_2$), 2.89 (1 H, m, CH$_2$), 3.34 (1 H, m, CH$_2$), 3.45 (1 H, m, CH$_2$), 6.78 (2 H, d, C$_7$H$_4$NS$_2$), 7.09 (2 H, m, C$_7$H$_4$NS$_2$), 7.19 (9 H, m, C$_6$H$_5$) and 7.42 (6 H, m, C$_6$H$_5$); ^{31}P, δ 39.15 (s).

X-Ray Crystallography.—Crystal and refinement data for complexes **1**·H$_2$O, **2**, **5**·2H$_2$O, **6**·CHCl$_3$ and **7**·0.5CHCl$_3$ are provided in Table 1). Diffracted intensities were collected on a Siemens P4 four-circle diffractometer in the ω-scan mode with graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å) at 295 K. 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.[13] With the exception of the phenyl carbon atoms in **7** all non-hydrogen atoms were refined anisotropically. The asymmetric units of **2** and **7** each contain two independent molecules, in the latter case together with one solvent chloroform. Both the [CF$_3$SO$_3$]$^-$ anion, S(77)/C(77), and the solvent chloroform in the crystal lattice of **6** display rotational disorder, the respective axes being S(77)–C(77) and Cl(91)–C(99). Site-occupation factors of 0.6 were introduced for F(771)–F(773), O(771)–O(773) and the chloroform atoms Cl(92) and Cl(93). The remaining disordered atoms F(774)–F(776), O(774)–O(776), Cl(94) and Cl(95) were assigned complementary site-occupation factors of 0.4. The hydrogen atoms in **1** were located in difference syntheses and refined freely with *d*(C–H) = 0.96 Å. This was also the case for

Table 1 Crystal and refinement data for complexes **1**, **2** and **5**–**7**

	1	**2**	**5**	**6**	**7**
Formula	$C_8H_{18}Cl_2ORuS_4 \cdot H_2O$	$C_{14}H_{21}F_6N_3O_6RuS_5$	$C_{20}H_{36}F_6N_2O_6Ru_2S_{12} \cdot 2H_2O$	$C_{30}H_{33}F_6N_2O_6PRuS_5 \cdot CHCl_3$	$C_{28}H_{33}F_3NO_3PRuS_6 \cdot 0.5CHCl_3$
M	448.5	702.7	1137.4	1043.3	872.7
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/n$
a/Å	7.641(5)	13.804(3)	18.079(2)	11.527(5)	14.477(4)
b/Å	11.116(4)	18.523(3)	10.107(1)	12.529(5)	23.887(4)
c/Å	18.258(7)	21.043(6)	22.103(2)	16.670(4)	20.844(2)
α/°	90	90	90	87.46(3)	90
β/°	91.69(4)	94.23(2)	102.87(1)	72.09(3)	92.80(2)
γ/°	90	90	90	69.57(3)	90
U/Å^3	1550(1)	5366(2)	3937.4(7)	2141(1)	7200(2)
Z	4	8	4	2	8
D_c/g cm^{-3}	1.922	1.740	1.919	1.618	1.610
F(000)	904	2816	2288	1052	3544
Crystal size/mm	0.35 × 0.36 × 0.50	0.42 × 0.48 × 0.50	0.24 × 0.31 × 0.38	0.37 × 0.48 × 0.50	0.42 × 0.43 × 0.44
μ(Mo-Kα)/mm^{-1}	1.85	1.02	1.44	0.89	0.96
Scan width/°	1.80	1.20	1.40	1.20	1.20
$2\theta_{max}$/°	55	50	55	50	50
hkl Range	0–9, 0–14, −23 to 3	0–16, 0–22, −25 to 24	0–23, −13 to 0, −28 to 28	−13 to 0, −14 to 13, −19 to 18	0–17, 0–28, −24 to 24
Transmission (maximum, minimum)	0.17, 0.13	0.36, 0.31	0.37, 0.31	0.55, 0.51	0.33, 0.26
Reflections collected	4004	10 160	4909	7912	13 480
Independent reflections	3554	9404	4501	7510	12 598
R_{int}	0.021	0.045	0.014	0.036	0.046
$I/\sigma(I)$ criterion	1.5	2.0	1.5	2.0	2.0
Observed reflections	2966	6107	3568	5568	6444
No. of parameters	230	704	282	684	649
R	0.032	0.048	0.031	0.040	0.048
R'	0.035	0.046	0.032	0.041	0.047
g in weighting scheme	0.0003	0.0002	0.0003	0.0002	0.0002
ΔF synthesis (maximum, minimum, e Å^{-3})	0.48 −1.13	0.70, −0.61	0.45, −0.40	0.47, −0.47	1.33, −0.71

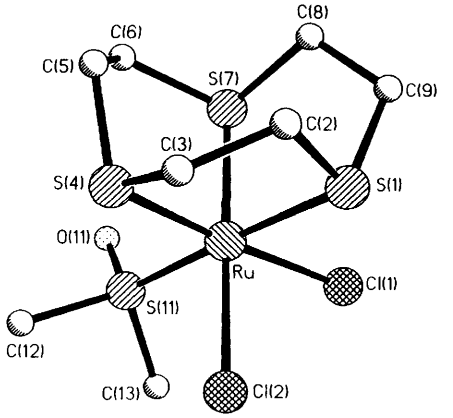


Fig. 1 Molecular structure of $[RuCl_2(dmso)([9]aneS_3)]$ **1**

the phenyl protons in **6** and the $[9]aneS_3$ methylene protons in **5**, **6** and the first independent cation of **2**. The remaining phenyl, methylene and methyl protons in **2** and **5**–**7** were included at geometrically calculated positions with joint isotopic 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. 14. Fractional atomic coordinates for the refined crystal structures are listed in Table 2, selected bond lengths and angles in Tables 3 and 4.

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

Results and Discussion

Treatment of $[RuCl_2(dmso)([9]aneS_3\text{-}\kappa^3S)]$ **1** with 2 equivalents of $Ag(CF_3SO_3)$ in refluxing acetonitrile provides the tris(acetonitrile) complex $[Ru(MeCN)_3([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **2** which, in analogy[10,15] to $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)_3]^+$ and $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$, proves to be an expedient starting material for the synthesis of half-sandwich ruthenium(II) complexes. Complexes **1** and **2** were characterised by FAB mass and ^1H NMR spectroscopy and X-ray structural analysis (Figs. 1 and 2). The presence of three dmso methyl singlets of differing integral values in the proton NMR spectrum of **1** indicates that D_2O/Cl^- exchange occurs. As may be discerned from Table 4, angle deviations from an idealised octahedron are relatively small, with average S–Ru–S angles to the facial ligand $[9]aneS_3$ of 88.7(4)° in **1** and **2** (for both independent cations). The influence of crystal-packing effects on the N–Ru–N angles in the independent cations of **2** is apparent from their relatively wide range of values between 84.9(1) and 91.3(1)°. The tris(acetonitrile) cations **2** exhibit C_3 symmetry in solution with multiplets at δ 2.69 and 2.82 for the CH_2 protons in the ^1H NMR spectrum. Sequential loss of MeCN ligands is observed in the fragmentation pattern of **2** in its FAB mass spectrum.

In their recent review Cooper and Rawle[1b] commented on the important role of charge neutralisation 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 neutralisation, complexes of crown thioethers have been found to display a pronounced affinity for normally 'non-co-ordinating' anions such as $CF_3SO_3^-$, BF_4^- and ClO_4^-. For instance, thioether copper(II) complexes form more stable complexes with perchlorate ions than do aquacopper(II) ions.[16] Abstraction of the chloride ligands in **1** may be achieved by addition of $Ag(CF_3SO_3)$ in acetonitrile leading to the formation of the tris(acetonitrile) dication **2**. The preference of Ru^{II} for π-acceptor ligands such as MeCN obviously overweighs the alternative of charge neutralisation, which could be achieved by the incorporation of two $CF_3SO_3^-$ anions in the metal co-ordination sphere. The Ru–S bonds in the two independent cations of **2** are on average [2.292(7) Å] 0.016 Å longer than the Ru–S(4) and Ru–S(7) bonds in **1** [2.278(2) and 2.273(2) Å], which are *trans* to the Ru–Cl bonds. Spectroscopic and magnetic studies have indicated that thioethers exhibit appreciable π acidity.[1] This suggests that competitive π acceptance of the acetonitrile ligands may play a role in the weakening of the Ru–S bonds in **2**. A more pronounced *trans* influence is observed for the Ru–S(1) ($[9]aneS_3$) and Ru–S(11) (dmso) distances in **1**, which are respectively 2.326(2) and 2.287(2) Å.

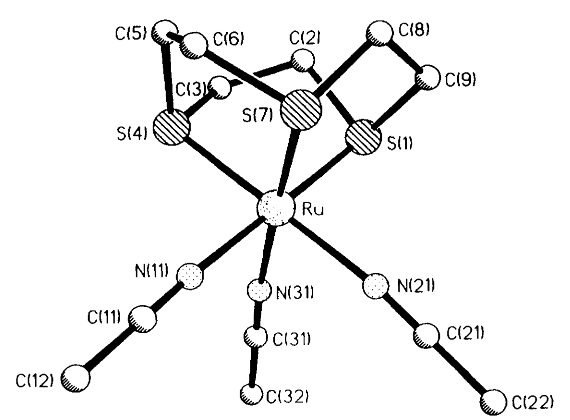
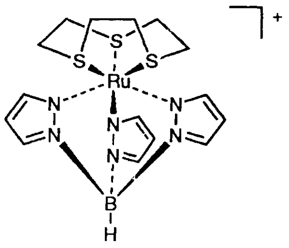


Fig. 2 Molecular structure of the first cation $[Ru(MeCN)_3([9]aneS_3)]^{2+}$ of **2**



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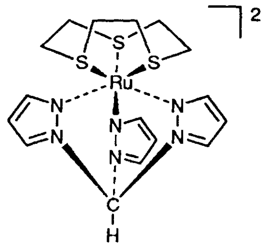

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We investigated the synthetic potential of complex **2** by studying its reactions with the potentially tridentate ligands $HB(pz)_3^-$, $HC(pz)_3$ and $S_2CNMe_2^-$. Refluxing an alcohol solution of **2** with $Na[HB(pz)_3]$ (in MeOH) or $HC(pz)_3$ (in EtOH) leads to precipitation of the novel mixed-sandwich complexes $[Ru\{HB(pz)_3\text{-}\kappa^3N\}([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]$ **3** and $[Ru\{HC(pz)_3\text{-}\kappa^3N\}([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **4**, which may be regarded as analogues of $[Ru(\eta^5\text{-}C_5H_5)\{HB(pz)_3\text{-}\kappa^3N\}]$ and $[Ru(\eta^6\text{-}C_6H_6)\{HB(pz)_3\text{-}\kappa^3N\}]PF_6$.[17,18] Complexes **3** and **4** were characterised by FAB mass and proton NMR spectroscopy; both display C_{3v} symmetry in solution. In each case three sets of peaks are observed for the aromatic protons of the three equivalent pyrazolyl groups. Whereas overlapping doublets of doublets at δ 6.33 (**3**) and 6.71 (**4**) may immediately be assigned to the central H^4 pyrazolyl protons, distinction of the H^3 (the proton closest to the metal) and H^5 signals is more difficult. During an investigation of the ^1H NMR spectrum of free $[HB(pz)_3]^-$, Trofimenko[19] observed that the resonance with the largest coupling constant was consistently more sensitive to changes in metal binding. This led him to conclude that this signal belonged to H^3, the proton closest to the pyrazolyl nitrogen involved in the metal co-ordination sphere. Using this argument, Mann and co-workers[17] assigned the doublet at δ 7.63 for $[Ru(\eta^5\text{-}C_5H_5)\{HB(pz)_3\text{-}\kappa^3N\}]$ to H^3 and that at δ 8.12 to H^5. An analogous assignment is possible for the hydrotris(1-pyrazolyl)borate protons of **3** in $(CD_3)_2SO$, with the resonance at δ 7.63 belonging to H^3, that at δ 7.97 to H^5. The infrared spectrum of **3** exhibits a band at 2489 cm^{-1}, which is attributable to the B–H stretching mode. It appears at

Table 2 Fractional atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Compound **1**							
Ru	1 735(1)	2 312(1)	1 293(1)	C(6)	2 613(5)	−517(3)	1 682(2)
Cl(1)	3 604(1)	3 938(1)	1 773(1)	C(8)	3 247(5)	1 192(4)	2 813(2)
Cl(2)	−433(1)	3 741(1)	810(1)	C(9)	1 347(5)	1 316(4)	2 997(2)
S(1)	219(1)	2 374(1)	2 379(1)	S(11)	3 158(1)	2 337(1)	209(1)
S(4)	−16(1)	755(1)	925(1)	O(11)	2 496(4)	1 567(3)	−397(2)
S(7)	3 604(1)	969(1)	1 836(1)	C(12)	3 344(6)	3 820(4)	−145(2)
C(2)	−1 776(5)	1 555(3)	2 144(2)	C(13)	5 430(6)	2 013(5)	322(3)
C(3)	−1 449(5)	440(3)	1 692(2)	O(99)	2 136(5)	−3 547(3)	911(2)
C(5)	1 440(5)	−532(3)	995(2)				
Compound **2**							
Ru	1 485(1)	2 952(1)	3 428(1)	C(22′)	6 050(6)	4 964(5)	1 406(6)
S(1)	2 781(1)	2 171(1)	3 456(1)	C(31′)	2 323(5)	5 164(4)	727(3)
S(4)	972(1)	2 488(1)	2 448(1)	C(32′)	1 896(6)	4 606(5)	321(4)
S(7)	2 392(1)	3 775(1)	2 926(1)	S(66)	746(1)	−43(1)	3 582(1)
N(11)	342(4)	3 674(3)	3 397(2)	S(77)	5 763(2)	8 194(1)	3 954(1)
N(21)	1 936(4)	3 361(3)	4 322(3)	S(88)	−563(2)	1 663(1)	859(1)
N(31)	660(4)	2 243(3)	3 926(3)	S(99)	3 983(2)	9 675(2)	1 667(2)
C(2)	2 684(6)	1 705(4)	2 682(4)	F(661)	2 007(4)	−927(3)	3 181(3)
C(3)	1 641(6)	1 644(4)	2 424(4)	F(662)	752(4)	−1 434(3)	3 469(4)
C(5)	1 594(6)	3 028(4)	1 864(3)	F(663)	1 816(5)	−1 023(3)	4 156(3)
C(6)	1 841(6)	3 759(4)	2 105(4)	F(771)	7 065(5)	8 033(3)	4 887(3)
C(8)	3 571(5)	3 341(5)	2 846(4)	F(772)	5 793(4)	7 443(4)	4 985(3)
C(9)	3 781(6)	2 793(5)	3 355(4)	F(773)	5 745(7)	8 622(5)	5 122(3)
C(11)	−253(5)	4 090(4)	3 402(3)	F(881)	−1 237(5)	1 601(4)	−309(3)
C(12)	−1 028(6)	4 633(4)	3 415(4)	F(882)	−1 540(6)	671(4)	243(4)
C(21)	2 095(5)	3 542(4)	4 820(4)	F(883)	−122(5)	813(4)	−58(3)
C(22)	2 291(7)	3 771(6)	5 483(4)	F(991)	4 671(6)	10 384(6)	752(3)
C(31)	231(5)	1 921(4)	4 252(3)	F(992)	3 644(7)	9 620(5)	435(4)
C(32)	−336(6)	1 507(4)	4 690(4)	F(993)	5 058(7)	9 286(6)	763(4)
Ru′	3 298(1)	6 336(1)	1 688(1)	O(661)	1 517(4)	463(3)	3 707(3)
S(1′)	2 997(1)	5 576(1)	2 508(1)	O(662)	288(4)	−5(4)	2 956(3)
S(4′)	1 851(1)	6 902(1)	1 815(1)	O(663)	102(5)	−114(4)	4 078(3)
S(7′)	4 026(1)	7 113(1)	2 430(1)	O(771)	4 717(3)	8 188(3)	3 907(3)
N(11′)	3 496(4)	7 009(3)	920(3)	O(772)	6 197(5)	7 571(3)	3 660(3)
N(31′)	2 650(4)	5 605(3)	1 046(3)	O(773)	6 203(5)	8 875(3)	3 808(3)
N(21′)	4 598(4)	5 806(3)	1 567(3)	O(881)	147(5)	2 164(3)	667(3)
C(2′)	1 688(5)	5 680(4)	2 549(4)	O(882)	−1 465(4)	1 968(3)	1 020(3)
C(3′)	1 321(5)	6 439(4)	2 467(3)	O(883)	−151(5)	1 146(3)	1 301(3)
C(5′)	2 224(5)	7 743(4)	2 188(4)	O(991)	4 870(4)	9 811(4)	2 038(3)
C(6′)	3 049(5)	7 681(4)	2 685(3)	O(992)	3 281(5)	10 236(4)	1 685(4)
C(8′)	4 265(5)	6 533(4)	3 114(3)	O(993)	3 699(8)	8 951(4)	1 676(6)
C(9′)	3 457(5)	6 036(4)	3 237(3)	C(66)	1 346(5)	−890(4)	3 600(4)
C(11′)	3 503(6)	7 357(5)	481(4)	C(77)	6 087(6)	8 083(5)	4 784(5)
C(12′)	3 498(8)	7 814(6)	−91(4)	C(88)	−887(7)	1 158(5)	156(5)
C(21′)	5 222(6)	5 452(4)	1 490(4)	C(99)	4 353(8)	9 718(6)	880(6)
Compound **5**							
Ru	582(1)	312(1)	1 934(1)	C(11)	899(2)	−1 676(3)	2 918(1)
S(1)	400(1)	243(1)	866(1)	C(12)	994(3)	−3 972(3)	3 200(2)
S(4)	1 835(1)	775(1)	1 990(1)	C(13)	999(3)	−2 233(4)	4 002(2)
S(7)	332(1)	2 565(1)	1 846(1)	S(99)	2 027(1)	5 021(1)	283(1)
C(2)	1 326(2)	644(4)	694(1)	O(991)	1 900(2)	3 734(3)	501(2)
C(3)	1 976(2)	299(5)	1 224(2)	O(992)	2 794(2)	5 502(3)	460(2)
C(5)	1 903(2)	2 588(4)	1 939(2)	O(993)	1 675(3)	5 278(3)	−352(1)
C(6)	1 265(2)	3 283(4)	2 153(2)	F(991)	784(2)	5 807(4)	585(2)
C(8)	193(2)	2 945(4)	1 012(2)	F(992)	1 564(2)	7 350(3)	554(2)
C(9)	−115(2)	1 762(4)	620(2)	F(993)	1 795(3)	5 998(4)	1 305(1)
S(11)	886(1)	−1 978(1)	2 59(1)	C(99)	1 519(3)	6 097(4)	703(2)
S(12)	759(1)	29(1)	3 043(1)	O(88)	8 381(2)	2 825(3)	1 278(2)
N(11)	996(2)	−2 564(3)	3 359(1)				
Compound **6**							
Ru	2 657(1)	2 945(1)	2 192(1)	C(54)	4 475(5)	−1 689(5)	3 449(3)
P	2 372(1)	2 203(1)	3 538(1)	C(55)	4 705(5)	−989(5)	3 931(4)
S(1)	2 831(1)	3 612(1)	828(1)	C(56)	4 092(5)	178(4)	3 964(3)
S(4)	1 177(1)	4 749(1)	2 730(1)	S(77)	2 500(2)	8 348(1)	1 073(1)
S(7)	4 287(1)	3 613(1)	2 206(1)	O(771)	2 994(11)	7 193(6)	1 174(10)
N(11)	4 055(3)	1 410(3)	1 623(2)	O(772)	1 592(9)	9 158(13)	1 741(7)
N(21)	1 281(3)	2 377(3)	2 011(2)	O(773)	3 490(12)	8 677(13)	512(7)
C(2)	1 339(5)	4 846(4)	1 033(3)	O(774)	1 900(23)	7 887(21)	1 821(8)
C(3)	1 021(6)	5 580(4)	1 805(4)	O(775)	2 427(20)	9 481(8)	1 197(12)
C(5)	2 101(5)	5 384(5)	3 138(4)	O(776)	3 811(12)	7 688(28)	649(14)

Table 2 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Compound **6**							
C(6)	3 475(6)	5 120(5)	2 595(4)	F(771)	1 962(9)	7 377(10)	−13(9)
C(8)	5 012(5)	3 740(6)	1 088(3)	F(772)	390(8)	8 440(19)	830(8)
C(9)	4 071(6)	4 268(6)	614(4)	F(773)	1 430(23)	9 223(16)	−67(14)
C(11)	4 813(4)	582(4)	1 290(3)	F(774)	1 149(36)	7 494(18)	427(21)
C(12)	5 770(5)	−505(4)	867(4)	F(775)	426(12)	9 192(11)	594(13)
C(21)	566(5)	2 116(4)	1 817(3)	F(776)	2 198(11)	8 506(13)	−379(5)
C(22)	−386(7)	1 796(6)	1 560(6)	C(77)	1 558(6)	8 363(5)	402(4)
C(31)	710(4)	2 291(4)	4 144(3)	S(88)	7 373(1)	4 950(1)	2 103(1)
C(32)	−364(4)	3 017(4)	3 956(3)	O(881)	8 534(3)	4 615(3)	2 331(3)
C(33)	−1 600(5)	3 072(5)	4 430(4)	O(882)	7 407(5)	4 278(5)	1 430(4)
C(34)	−1 771(6)	2 412(5)	5 095(4)	O(883)	6 193(4)	5 280(4)	2 797(3)
C(35)	−719(6)	1 674(6)	5 283(4)	F(881)	8 343(4)	6 129(5)	938(3)
C(36)	519(5)	1 605(5)	4 804(3)	F(882)	7 350(4)	7 020(3)	2 145(3)
C(41)	2 877(4)	2 845(3)	4 274(3)	F(883)	6 258(4)	6 726(4)	1 399(3)
C(42)	4 170(5)	2 752(4)	4 058(3)	C(88)	7 318(6)	6 297(6)	1 629(4)
C(43)	4 581(7)	3 271(5)	4 578(5)	C(99)	8 589(9)	9 519(7)	2 842(4)
C(44)	3 713(8)	3 859(5)	5 324(5)	Cl(91)	7 393(2)	10 138(2)	2 321(1)
C(45)	2 452(7)	3 946(5)	5 544(4)	Cl(92)	8 356(5)	8 323(4)	3 351(3)
C(46)	2 020(5)	3 454(4)	5 028(3)	Cl(93)	7 887(10)	10 518(7)	3 729(5)
C(51)	3 246(4)	665(3)	3 517(3)	Cl(94)	8 765(16)	8 292(10)	3 067(9)
C(52)	3 014(5)	−61(4)	3 034(3)	Cl(95)	8 595(10)	10 443(6)	3 610(6)
C(53)	3 630(6)	−1 217(4)	3 002(3)				
Compound **7**							
Ru	5 782(1)	362(1)	1 532(1)	S(11′)	10 733(2)	2 023(1)	6 325(1)
S(1)	5 886(2)	1 318(1)	1 280(1)	S(12′)	10 513(2)	1 449(1)	5 126(1)
S(4)	6 973(2)	515(1)	2 304(1)	N(11′)	12 169(5)	1 859(3)	5 558(4)
S(7)	6 920(2)	207(1)	804(1)	C(11′)	11 263(6)	1 793(3)	5 652(4)
C(2)	6 455(6)	1 602(4)	2 000(4)	C(12′)	12 763(6)	2 132(4)	6 048(6)
C(3)	7 254(6)	1 260(3)	2 259(5)	C(13′)	12 567(7)	1 677(5)	4 964(6)
C(5)	7 986(6)	201(4)	1 955(5)	P′	9 342(1)	865(1)	6 372(1)
C(6)	8 028(6)	285(4)	1 252(4)	C(31′)	8 316(5)	428(3)	6 206(4)
C(8)	6 882(7)	848(4)	330(5)	C(32′)	7 641(6)	338(3)	6 654(4)
C(9)	6 804(7)	1 370(4)	712(5)	C(33′)	6 878(7)	18(4)	6 490(5)
S(11)	4 466(2)	311(1)	773(1)	C(34′)	6 740(7)	−191(4)	5 872(5)
S(12)	4 434(2)	630(1)	2 092(1)	C(35′)	7 387(6)	−104(4)	5 421(5)
N(11)	2 880(5)	582(3)	1 341(3)	C(36′)	8 164(6)	211(3)	5 580(4)
C(11)	3 790(6)	520(3)	1 390(4)	C(41′)	10 322(5)	381(3)	6 243(4)
C(12)	2 356(6)	731(4)	1 896(4)	C(42′)	10 220(6)	−160(4)	6 041(4)
C(13)	2 350(7)	444(5)	754(5)	C(43′)	10 985(6)	−512(4)	6 003(4)
P	5 582(2)	−559(1)	1 883(1)	C(44′)	11 842(7)	−314(4)	6 169(4)
C(31)	5 434(5)	−660(3)	2 754(4)	C(45′)	11 963(7)	226(4)	6 374(4)
C(32)	5 200(6)	−1 196(4)	2 981(5)	C(46′)	11 203(6)	576(4)	6 420(4)
C(33)	5 129(6)	−1 273(4)	3 639(5)	C(51′)	9 454(5)	882(3)	7 256(4)
C(34)	5 270(7)	−844(4)	4 055(5)	C(52′)	9 523(5)	382(4)	7 590(4)
C(35)	5 470(6)	−318(4)	3 846(5)	C(53′)	9 635(6)	368(4)	8 262(4)
C(36)	5 545(5)	−231(3)	3 182(4)	C(54′)	9 664(6)	865(4)	8 585(5)
C(41)	6 566(5)	−1 027(3)	1 716(4)	C(55′)	9 607(6)	1 374(4)	8 272(4)
C(42)	7 091(6)	−1 296(3)	2 212(4)	C(56′)	9 485(6)	1 376(4)	7 596(4)
C(43)	7 858(6)	−1 618(4)	2 050(5)	S(88)	5 334(2)	1 561(1)	3 835(2)
C(44)	8 089(6)	−1 678(4)	1 431(5)	F(881)	4 392(5)	2 032(3)	2 886(3)
C(45)	7 599(6)	−1 398(4)	952(5)	F(882)	3 918(5)	2 243(3)	3 798(3)
C(46)	6 818(6)	−1 084(3)	1 096(4)	F(883)	3 633(5)	1 446(3)	3 383(4)
C(51)	4 573(6)	−964(3)	1 572(4)	O(881)	5 051(7)	1 356(5)	4 435(4)
C(52)	4 617(6)	−1 415(4)	1 160(4)	O(882)	5 609(6)	1 142(3)	3 410(4)
C(53)	3 827(7)	−1 719(4)	974(5)	O(883)	5 892(6)	2 043(4)	3 869(6)
C(54)	3 001(7)	−1 561(4)	1 195(5)	C(88)	4 284(8)	1 840(5)	3 451(6)
C(55)	2 930(7)	−1 124(4)	1 595(5)	S(77)	9 967(2)	1 470(1)	840(2)
C(56)	3 703(6)	−813(4)	1 795(4)	O(771)	9 184(6)	1 593(4)	1 223(4)
Ru′	9 290(1)	1 717(1)	5 808(1)	O(772)	10 870(6)	1 638(4)	1 129(5)
S(1′)	9 345(2)	2 576(1)	5 250(1)	O(773)	9 926(8)	944(4)	529(6)
S(4′)	8 035(2)	1 472(1)	5 118(1)	F(771)	9 872(5)	2 479(3)	406(4)
S(7′)	8 222(2)	2 134(1)	6 459(1)	F(772)	10 505(6)	1 899(4)	−214(3)
C(2′)	8 739(6)	2 396(4)	4 501(4)	F(773)	9 055(6)	1 893(4)	−125(4)
C(3′)	7 860(6)	2 073(4)	4 568(4)	C(77)	9 827(9)	1 968(6)	189(6)
C(5′)	7 027(5)	1 550(4)	5 580(5)	Cl(91)	−670(4)	2 324(2)	2 759(2)
C(6′)	7 084(6)	2 033(4)	6 041(5)	Cl(92)	1 274(4)	2 329(2)	2 666(3)
C(8′)	8 409(7)	2 877(4)	6 320(5)	Cl(93)	304(6)	1 338(3)	2 992(3)
C(9′)	8 526(7)	3 038(4)	5 626(5)	C(99)	283(9)	1 923(5)	2 549(7)

Table 3 Selected bond lengths (Å) for complexes **1**, **2** and **5**–**7** with e.s.d.s in parentheses

Compound **1**			
Ru–Cl(1)	2.448(2)	Ru–Cl(2)	2.441(2)
Ru–S(1)	2.326(2)	Ru–S(4)	2.278(2)
Ru–S(7)	2.273(2)	Ru–S(11)	2.287(2)
S(11)–O(11)	1.476(3)	S(11)–C(12)	1.778(4)
S(11)–C(13)	1.780(5)		
Compound **2**			
Ru–S(1)	2.298(2)	Ru–S(4)	2.296(2)
Ru–S(7)	2.281(2)	Ru–N(11)	2.066(6)
Ru–N(21)	2.082(5)	Ru–N(31)	2.072(5)
Ru′–S(1′)	2.289(2)	Ru′–S(4′)	2.289(2)
Ru′–S(7′)	2.299(2)	Ru′–N(11′)	2.075(6)
Ru′–N(31′)	2.069(6)	Ru′–N(21′)	2.078(6)
Compound **5**			
Ru–S(1)	2.311(1)	Ru–S(4)	2.290(1)
Ru–S(7)	2.322(1)	Ru–S(11)	2.405(1)
Ru–S(12)	2.416(1)	Ru–S(12a)	2.452(1)
S(11)–C(11)	1.701(3)	S(12)–C(11)	1.773(5)
Compound **6**			
Ru–S(1)	2.362(2)	Ru–S(4)	2.317(1)
Ru–S(7)	2.314(2)	Ru–P	2.362(2)
Ru–N(11)	2.062(3)	Ru–N(21)	2.054(5)
Compound **7**			
Ru–S(1)	2.350(2)	Ru–S(4)	2.329(2)
Ru–S(7)	2.323(3)	Ru–S(11)	2.420(2)
Ru–S(12)	2.409(2)	Ru–P	2.340(2)
S(11)–C(11)	1.727(9)	S(12)–C(11)	1.716(9)
Ru′–S(1′)	2.363(2)	Ru′–S(4′)	2.337(2)
Ru′–S(7′)	2.331(3)	Ru′–S(11′)	2.417(2)
Ru′–S(12′)	2.410(3)	Ru′–P′	2.349(2)
S(11′)–C(11′)	1.722(9)	S(12′)–C(11′)	1.716(8)

Table 4 Selected bond angles (°) with e.s.d.s in parentheses

Compound **1**			
Cl(1)–Ru–Cl(2)	91.8(1)	Cl(1)–Ru–S(1)	88.5(1)
Cl(2)–Ru–S(1)	86.5(1)	Cl(1)–Ru–S(4)	176.2(1)
Cl(2)–Ru–S(4)	90.1(1)	S(1)–Ru–S(4)	88.3(1)
Cl(1)–Ru–S(7)	88.7(1)	Cl(2)–Ru–S(7)	174.8(1)
S(1)–Ru–S(7)	88.3(1)	S(4)–Ru–S(7)	89.2(1)
Cl(1)–Ru–S(11)	90.8(1)	Cl(2)–Ru–S(11)	90.8(1)
S(1)–Ru–S(11)	177.2(1)	S(4)–Ru–S(11)	92.5(1)
S(7)–Ru–S(11)	94.4(1)		
Compound **2** (first independent cation)			
S(1)–Ru–S(4)	88.6(1)	S(1)–Ru–S(7)	88.8(1)
S(4)–Ru–S(7)	88.7(1)	S(1)–Ru–N(11)	178.6(2)
S(4)–Ru–N(11)	91.7(1)	S(7)–Ru–N(11)	89.8(2)
S(1)–Ru–N(21)	91.4(2)	S(4)–Ru–N(21)	179.1(2)
S(7)–Ru–N(21)	92.2(2)	N(11)–Ru–N(21)	88.2(2)
S(1)–Ru–N(31)	92.5(1)	S(4)–Ru–N(31)	94.2(1)
S(7)–Ru–N(31)	176.8(2)	N(11)–Ru–N(31)	88.8(2)
N(21)–Ru–N(31)	84.9(2)		
Compound **5**			
S(1)–Ru–S(4)	88.6(1)	S(1)–Ru–S(7)	87.9(1)
S(4)–Ru–S(7)	88.6(1)	S(1)–Ru–S(11)	99.0(1)
S(4)–Ru–S(11)	90.5(1)	S(7)–Ru–S(11)	173.1(1)
S(1)–Ru–S(12)	171.5(1)	S(4)–Ru–S(12)	93.7(1)
S(7)–Ru–S(12)	100.4(1)	S(11)–Ru–S(12)	72.8(1)
S(1)–Ru–S(12a)	95.8(1)	S(4)–Ru–S(12a)	173.4(1)
S(7)–Ru–S(12a)	86.6(1)	S(11)–Ru–S(12a)	93.7(1)
S(12)–Ru–S(12a)	82.7(1)	Ru–S(11)–C(11)	89.1(1)
Ru–S(12)–C(11)	87.0(1)	Ru–S(12)–Ru(a)	95.7(1)
Ru(a)–S(12)–C(11)	107.0(1)	S(11)–C(11)–S(12)	110.9(2)
Compound **6**			
P–Ru–S(1)	175.3(1)	P–Ru–S(4)	93.3(1)
P–Ru–S(7)	97.1(1)	S(1)–Ru–S(4)	87.7(1)
S(1)–Ru–S(7)	87.7(1)	S(4)–Ru–S(7)	87.5(1)
P–Ru–N(11)	91.4(1)	S(1)–Ru–N(11)	87.8(1)
S(4)–Ru–N(11)	174.8(1)	S(7)–Ru–N(11)	89.6(1)
P–Ru–N(21)	90.2(1)	S(1)–Ru–N(21)	85.1(1)
S(4)–Ru–N(21)	94.0(1)	S(7)–Ru–N(21)	172.4(1)
N(11)–Ru–N(21)	88.2(2)		
Compound **7** (first independent cation)			
S(1)–Ru–S(4)	87.0(1)	S(1)–Ru–S(7)	87.3(1)
S(4)–Ru–S(7)	87.3(1)	S(1)–Ru–S(11)	87.7(1)
S(4)–Ru–S(11)	172.9(1)	S(7)–Ru–S(11)	97.2(1)
S(1)–Ru–S(12)	85.0(1)	S(4)–Ru–S(12)	102.3(1)
S(7)–Ru–S(12)	167.3(1)	S(11)–Ru–S(12)	72.5(1)
S(1)–Ru–P	173.5(1)	S(4)–Ru–P	91.8(1)
S(7)–Ru–P	99.0(1)	S(11)–Ru–P	93.0(1)
S(12)–Ru–P	89.1(1)	Ru–S(11)–C(11)	87.5(3)
Ru–S(12)–C(11)	88.1(3)	S(11)–C(11)–S(12)	112.0(5)

about 40 cm^{-1} higher than the corresponding band for the free anion, in good agreement with data observed for other pyrazolylborate complexes.[17,20]

In the dinuclear carbonylruthenium(II) complex $[\{Ru(S_2CNEt_2)_2(CO)\}_2]$ two of the diethyldithiocarbamate ligands exhibit respectively a bridging $1\kappa^2S,S'{:}2\kappa S$ and $1\kappa S{:}2\kappa^2S,S'$ co-ordination mode, leading to the formation of a central $(RuS)_2$ four-membered ring.[21] The complex displays approximately C_2 symmetry with each of the ruthenium atoms being co-ordinated by a further bidentate S_2CNEt_2 ligand. Two tridentate diethyldithiocarbamate ligands with a bridging function are also observed in $[Ru_2(S_2CNEt_2)_5]Cl$ and $[Ru_3Cl_2(S_2CNEt_2)_4(CO)_3]$.[22,23] In contrast to $[\{Ru(S_2CNEt_2)_2(CO)\}_2]$ each of the tridentate S_2CNEt_2 ligands forms a four-membered chelate ring to one and the same ruthenium atom in these latter complexes. The observed co-ordination modes are $1\kappa^2S,S'{:}2\kappa S$ for the bridging S_2CNEt_2 ligands in $[Ru_2(S_2CNEt_2)_5]Cl$ and respectively $1\kappa^2S,S'{:}2\kappa S$ and $1\kappa^2S,S'{:}3\kappa S$ for the analogous tridentate ligands in $[Ru_3Cl_2(S_2CNEt_2)_4(CO)_3]$. Reaction of $[\{RhCl(\eta^5\text{-}C_5Me_5)\}_2]$ with 2 equivalents of $Na[S_2CNMe_2]\cdot 2H_2O$ in acetonitrile leads to the formation of the monomeric complex $[RhCl(\eta^5\text{-}C_5Me_5)(S_2CNMe_2\text{-}\kappa^2S)]$.[24] In the presence of an excess of $[S_2CNMe_2]^-$, $[Rh(\eta^5\text{-}C_5Me_5)(S_2CNMe_2\text{-}\kappa S)(S_2CNMe_2\text{-}\kappa^2S)]$ may be isolated which contains one mono- and one bidentate dimethyldithiocarbamate ligand. The formation of dinuclear complexes containing bridging tridentate S_2CNMe_2 ligands is precluded by the steric demands of the C_5Me_5 ligands. Attempts to synthesise the related $(\eta^6\text{-}C_6H_6)Ru^{II}$ complexes under similar conditions were unsuccessful. Greenish brown paramagnetic solids were obtained which contained no benzene ring[23] and were presumably 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).[22,25] However reaction of $[\{RuCl_2(\eta^6\text{-}C_6H_6)\}_2]$ with the less nucleophilic phosphinodithioato anions $[S_2PR_2]^-$ (R = Me or Ph) did allow the synthesis of monomeric complexes $[Ru(S_2PR_2\text{-}\kappa^2S)(S_2PR_2\text{-}\kappa S)(\eta^6\text{-}C_6H_6)]$.[24]

The reaction of complex **2** with 2 equivalents of $Na[S_2CNMe_2]\cdot 2H_2O$ in water yields the dinuclear complex $[\{Ru(\mu\text{-}S_2CNMe_2)([9]aneS_3\text{-}\kappa^3S\}_2][CF_3SO_3]_2$ **5**, the cation structure of which is depicted in Fig. 3. The preparation of this complex underlines two important advantages of $[Ru(MeCN)_3([9]aneS_3\text{-}\kappa^3S)]^{2+}$ in comparison to $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ as a starting material for the synthesis of half-sandwich ruthenium(II) complexes, namely the increased stability and reduced steric demands of the $([9]aneS_3\text{-}\kappa^3S)Ru^{II}$ fragment in comparison to $(\eta^6\text{-}C_6H_6)Ru^{II}$. The closest contact between the $[9]aneS_3$ ligands in **5** is provided by the S(7) ··· S(7a) interaction at a distance of 3.369(2) Å, which is markedly shorter than the sum of the van der Waals radii for these atoms (3.60 Å[26]). This weak secondary bond [C(8)–S(7)–S(7a) 149.5(2), Ru–S(7)–S(7a) 91.6(1), C(6)–S(7)–S(7a) 99.1(2)°] will stabilise the observed geometry, which displays

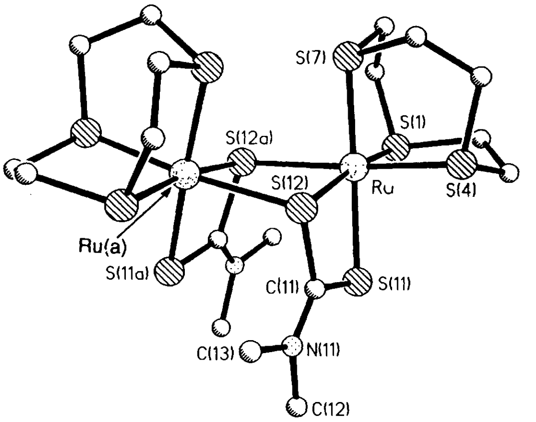
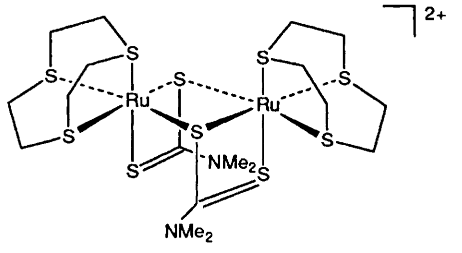


Fig. 3 Molecular structure of the cation $[\{Ru(\mu\text{-}S_2CNMe_2)([9]aneS_3\text{-}\kappa^3S)\}_2]^{2+}$ **5**



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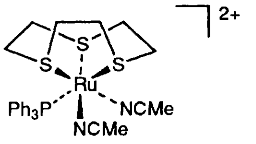

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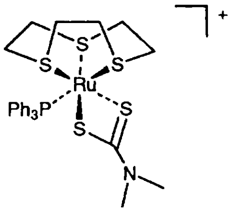

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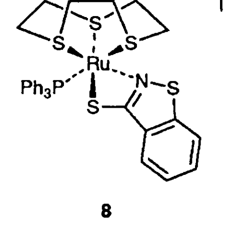

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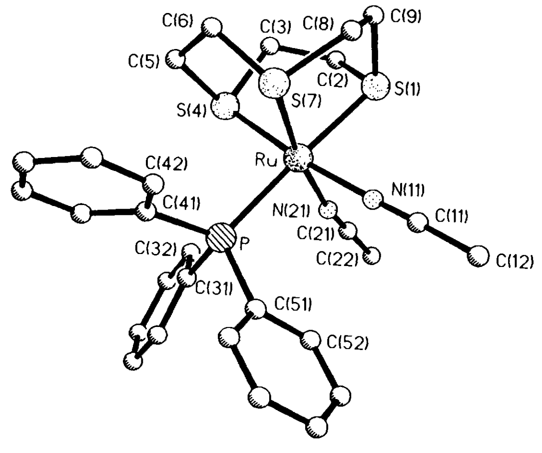

Fig. 4 Molecular structure of the cation $[Ru(MeCN)_2(PPh_3)[9]aneS_3\text{-}\kappa^3S)]^{2+}$ in complex **6**

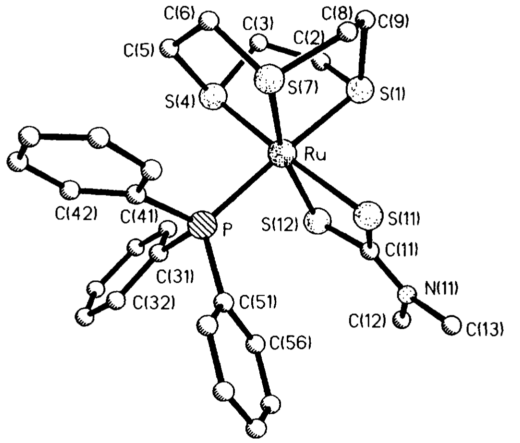

Fig. 5 Molecular structure of the first cation $[Ru(S_2CNMe_2)(PPh_3)([9]aneS_3\text{-}\kappa^3S)]^+$ of complex **7**

crystallographic C_2 symmetry. A *trans* influence is once again apparent in the dimensions of the distorted-octahedral co-ordination spheres of the ruthenium atoms. For instance, the Ru–S(4) bond, which is in *trans* position to the long bridging Ru–S(12a) bond [2.452(1) Å], is significantly shorter [2.290(1) Å] than the Ru–S (thioether) bonds [2.311(1) and 2.322(1) Å] sited *trans* to the Ru–S (S_2CNMe_2) bonds of the four-membered chelate ring [2.416(1) and 2.405(1) Å]. The C(11)–S(12) bond [1.773(5) Å] is markedly longer than C(11)–S(11) [1.701(3) Å] and the analogous C–S bonds of the dimethyldithiocarbamate ligands in **7** [1.716(8)–1.727(9) Å], a fact which indicates the presence of a pronounced degree of strain in the bridging four-membered ring systems of **5**. The central $(RuS)_2$ ring is non-planar (atom deviations ±0.143 Å) and exhibits a Ru$\cdots$Ru distance of 3.609(1) Å.

As mentioned in the Introduction, Schröder and co-workers[4] reported the preparation of chiral complexes of the type $[RuX(L)(PPh_3)([9]aneS_3\text{-}\kappa^3S)]^+$ (X = Cl or Br) by reaction of $[RuX_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)]$ with $TlPF_6$ in the presence of co-ordinating solvents (*e.g.* MeCN) or ligands L. We have now prepared the bis(acetonitrile) complex $[Ru(MeCN)_2(PPh_3)([9]aneS_3)][CF_3SO_3]_2$ **6** by reaction of $[RuCl_2(PPh_3)([9]aneS_3\text{-}\kappa^3S)]$ with $Ag(CF_3SO_3)$ in acetonitrile and present its molecular structure (Fig. 4). The Ru–S(1) bond *trans* to the triphenylphosphine ligand is markedly longer [2.362(2) Å] than the Ru–S (thioether) bonds *trans* to acetonitrile ligands [2.317(1) and 2.314(2) Å], an observation which is in accordance with the greater π acidity of PPh_3 in comparison to MeCN. The bulkiness of PPh_3 also leads to a small but significant reduction in the average S–Ru–S angle from 88.7(4)° in **2** to 87.6(2)° in **6**. Both acetonitrile ligands in **6** may readily be replaced by chelating ligands containing S or N donor atoms, as exemplified by the reaction with $Na[S_2CNMe_2]{\cdot}2H_2O$ or 2-sulfanylbenzothiazolate leading to the formation of the respective monomeric complexes $[Ru(S_2CNMe_2)(PPh_3)([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]$ **7** and $[Ru(C_7H_4NS_2)(PPh_3)[9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]$ **8**. The molecular structure of one of the independent cations of **7** is depicted in Fig. 5.

The present results indicate that $[Ru(MeCN)_3([9]aneS_3\text{-}\kappa^3S)][CF_3SO_3]_2$ **2** should be an expedient starting material for the synthesis of a wide range of half-sandwich ruthenium(II) complexes and may well be expected to possess a synthetic potential similar to that of (arene)ruthenium(II) complexes.[10,27] Two important advantages of $[Ru(MeCN)_3([9]aneS_3\text{-}\kappa^3S)]^{2+}$ in comparison to $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ or $[\{RuCl_2(\eta^6\text{-}C_6H_6)\}_2]$, namely the increased stability and reduced steric demands of the facial $([9]aneS_3\text{-}\kappa^3S)Ru^{II}$ fragment, are exemplified by the synthesis of $[\{Ru(\mu\text{-}S_2CNMe_2)([9]aneS_3\text{-}\kappa^3S)\}_2][CF_3SO_3]_2$ **5**.

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