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Synthesis and crystal structures of π-tetramethylthiophene complexes of ruthenium(II)

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Abstract

The compound [$\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2$] reacts with a range of bases L to give the simple monomeric adducts [$\{Ru(\eta^5\text{-}C_4Me_4S)Cl_2L$] (L=$PPhMe_2$ **1**, $P(OMe)_3$ **2**, CO **3**, NC_5H_4 **4**, NC_5H_4CN **5**). Reaction of [$\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2$] with 2,2′-bipyridyl/$NH_4[PF_6]$ gives the cationic complex [$\{Ru(\eta^5\text{-}C_4Me_4S)Cl(bipy)][PF_6]$ **6** which reacts further with $PPhMe_2/Ag[PF_6]$ to give [$\{Ru(\eta^5\text{-}C_4Me_4S)(PPhMe_2)(bipy)][PF_6]_2$ **7**. In the presence of a tripodal ligand, such as $[HB(Pz)_3]^-$, all the chlorides are displaced from the ruthenium in a single synthetic step, giving [$\{Ru(\eta^5\text{-}C_4Me_4S)\{HB(Pz)_3\}][PF_6]$ **8**. Interestingly when [$\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2$] is placed in an aqueous solution in the absence of additional ligands the binuclear face-sharing bi-octadedral complex cation $[(\eta^5\text{-}C_4Me_4S)Ru(\mu\text{-}Cl)_3Ru(\eta^5\text{-}C_4Me_4S)]^+$ is formed, and can be trapped out as its hexafluorophosphate salt $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ **9**. Compounds **1**–**9** have been characterised fully by spectroscopic methods and crystal structure determinations of **1**, **7**, **8**, and **9** are reported. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The study of transition metal thiophene compounds is an area of great current interest. This is due in no small part to the importance of the hydrodesulfurisation reaction in the petroleum industry [1–5]. This reaction converts the organosulfur compounds which contaminate crude oil into alkanes, alkenes, and hydrogen sulfide, which can then be easily removed. Although there are a wide range of organosulfur compounds found in crude oil it is the thiophenes and benzothiophenes which are the most difficult to desulfurise. The industrial process is carried out heterogeneously over a $CoMo/Al_2O_3$ or CoW/Al_2O_3 catalyst. Increased activity of the catalyst has been observed when late transition metals are added as 'promoters' to the catalyst [1–4]. For these reasons thiophene and benzothiophene derivatives of elements such as ruthenium [6–9], rhodium [10–17], and platinum [18–20], and their catalytic reactions, have received considerable attention in recent years.

Almost 10 years ago Rauchfuss reported the preparation of [$\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2$] [21] which was employed as a synthon for two series of closely related complex ions $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-arene})]^{2+}$ and $[\{Ru(\eta^5\text{-}C_4Me_4S)(\eta^5\text{-thiophene})]^{2+}$ [22]. The organometallic chemistry of the π-thiophene rings in these systems has been extensively explored by Rauchfuss in a series of elegant papers [23–27], and related work on the ruthenium(0) derivatives has also been described [28–30]. In contrast the coordination chemistry of [$\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2$] remains relatively unexplored. The only significant coordination chemistry which has been reported for the binuclear compound is the formation of the simple bridge-cleaved adducts [$Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PR_3)$] and [$Ru(\eta^5\text{-}C_4Me_4S)Cl_2(NH_2C_6H_4Me)$] [22], and the preparation of *tris* substituted species $[Ru(\eta^5\text{-}C_4Me_4S)L_3]^{2+}$ (L=H_2O, NH_3, PH_3) [21]. A further reaction of note is that [$\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2$] reacts with $(Me_3Si)_2S$ to give the unusual polynuclear compound [$\{Ru(\eta^5\text{-}C_4Me_4S)(\mu\text{-}Cl)\}_3(\mu^3\text{-}S)$] [21]. Given the synthetic utility, and the increasing recognition of catalytic activity, demonstrated by the isoelectronic and isostructural series of compounds [$\{Ru(\eta^6\text{-arene})(\mu\text{-}Cl)Cl\}_2$] [31,32] there is clearly considerable scope for, and persuasive arguements in favour of, developing the coordination chemistry of [$\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2$]. With that goal in mind we now present a range of compounds, including key crystal

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structures, whose chemistry mimics that of the 'Ru(η^6-arene)' moiety, but which have not been fully described previously for the thiophene derivatives.

2. Experimental section

2.1. General and instrumental

Infrared spectra were recorded on a Nicolet-205 spectrometer between 4000 and 400 cm^{-1}, as their KBr discs and between 4000 and 250 cm^{-1} on a Perkin-Elmer 457 grating spectrometer, as nujol mulls on CsI discs. The ^{1}H NMR spectra were recorded on either a Varian VXR-400 or Bruker-spectrospin AC-300 instruments, (referenced internally against respective deuterated solvents: $CDCl_3$, δ 7.27; $(CD_3)_2CO$, δ 2.04; CD_2Cl_2, δ 5.32 ppm). Elemental analyses were carried out by the departmental service at University College London. Fast atom bombardment (FAB) mass spectra were recorded by the University of London Intercollegiate Research Service (ULIRS) at the London School of Pharmacy, while positive ion electrospray mass spectra were recorded at UCL (assignments based on the ^{102}Ru isotope). All manipulations were carried out under anaerobic conditions in a nitrogen atmosphere using conventional Schlenk-line techniques. Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc., and was purified before use by repeated dissolution in water and boiling to dryness. $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ was prepared according to literature methods [21]. Diethylether was distilled from sodium benzophenone ketyl; dichloromethane was distilled from CaH_2; H_2O was distilled over KOH and redistilled under nitrogen. All reaction solvents were degassed prior to use, by three repetitions of pump-freeze-thaw cycles. Pyridine was distilled off KOH, and 4-cyanopyridine was sublimed under vacuum prior to use. All other reagents were obtained from the usual commercial sources and were used as received.

2.2. Synthesis

2.2.1. $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPhMe_2)]$ **1**

$[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ (0.144 g, 0.23 mmol) was dissolved in dichloromethane (30 cm^3) to which an excess of $PPhMe_2$ (0.05 cm^3) was added and the reaction mixture stirred for 2 h. The solution was concentrated to ca. 10 cm^3 and hexane was added giving an orange–red precipitate. The solid was isolated by filtration and washed with hexane (50 cm^3) and diethylether (30 cm^3) and then dried in vacuo. Yield: 0.183 g, 0.41 mmol, 88%. Anal. (Found: C, 42.38; H, 5.11%. Calc. for $RuC_{16}H_{23}Cl_2PS$: C, 42.67; H, 5.10%). ^{1}H NMR [$CDCl_3$, −60°C]: δ 1.29 (s, 6H, TMT); δ 1.85 (d, 6H, $^2J_{PH}=11.5$ Hz. P–Me); δ 1.88 (s, 6H, TMT); δ 7.45 (m, 3H, *m*/*p*-Ph); δ 7.68 (m, 2H, *o*-Ph) ppm. Infrared (Nujol, CsI): $\nu_{(Ru-Cl)}$ 289(w) cm^{-1}. Mass spectrum (FAB): *m*/*z* 450, [M]$^+$; 415, [M-Cl]$^+$; 380, [M-Cl-Cl]$^+$, 277 [M-$PPhMe_2$-Cl].

2.2.2. $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(P(OCH_3)_3)]$ **2**

$[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ (0.070 g, 0.11 mmol) was dissolved in dichloromethane (30 cm^3) to which an excess of $P(OCH_3)_3$ (0.05 cm^3) was added and the reaction mixture stirred for 1 h. The solution was concentrated to ca. 10 cm^3 and hexane (40 cm^3) was added, giving an orange precipitate. The solid was isolated by filtration and washed with hexane (50 cm^3) and diethylether (30 cm^3) and then dried in vacuo. Yield: 0.080 g, 0.18 mmol, 82%. Anal. (Found: C, 29.92, H, 4.77%; Calc. for $RuC_{11}H_{21}O_3Cl_2PS$: C, 30.28, H, 4.86%). ^{1}H NMR [$CDCl_3$, −60°C]: δ 1.99 (s, 6H, TMT), δ 2.00 (s, 6H, TMT); δ 3.75 (d, $^3J_{PH}=11.0$ Hz., 9H, P–OCH_3) ppm. Infrared (KBr): $\nu_{(PO)}$, 1029(s); $\delta_{(OPO)}$, 536(w) cm^{-1}, (Nujol, CsI) $\nu_{(Ru-Cl)}$ 288(w) cm^{-1}. Mass spectrum (FAB): *m*/*z* 436, [M]$^+$; 401, [M-Cl]$^+$; 277, [M-$P(OMe)_3$-Cl]$^+$.

2.2.3. $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(CO)]$ **3**

$[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ (0.078 g, 0.13 mmol) was added to a CO saturated solution of dichloromethane (30 cm^3), which was refluxed for 1 h under a gentle stream of CO. The flask was then sealed under a CO atmosphere and the solution stirred at room temperature for a further 2 h, after which time a yellow solid precipitated. The solid was filtered off and washed with dichloromethane (20 cm^3) and diethylether (20 cm^3) and then dried in vacuo. Yield: 0.051 g, 0.15 mmol, 59%. Anal.: (Found: C, 31.16, H, 3.43%. Calc. for $RuC_9H_{12}Cl_2OS$: C, 31.77, H, 3.56%). Infrared (KBr): $\nu_{(CO)}$ 1982(s) cm^{-1}. Mass spectrum (positive ion electrospray): *m*/*z* 340, [M]$^+$; 305, [M-Cl]$^+$; 277, [M-CO-Cl]$^+$.

2.2.4. $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(NC_5H_5)]$ **4**

$[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ (0.070 g, 0.11 mmol) was dissolved in dichloromethane (30 cm^3) to which an excess of pyridine (0.10 cm^3) was added. The reaction mixture was stirred for 20 h then the solution concentrated to ca. 10 cm^3. This resulted in the slow formation of a yellow solid. Hexane (10 cm^3) was added in order to complete the precipitation. The solid was filtered off and washed with hexane (20 cm^3) and diethylether (40 cm^3) and dried in vacuo. Yield: 0.065 g, 0.17 mmol, 75%. Anal. (Found: C, 39.61, H, 4.27, N, 3.34%. Calc. for $RuC_{13}H_{17}Cl_2NS$: C, 39.90, H, 4.39, N, 3.58%). ^{1}H NMR [CD_2Cl_2]: δ 1.81 (br, 6H, TMT); δ 1.88 (br, 6H, TMT); δ 7.33 (dd, 2H) δ 7.76 (tt, 1H), δ 8.87 (br, 2H) ppm. (pyridine resonances). Infrared (Nujol, CsI) $\nu_{(Ru-Cl)}$ 284(w) cm^{-1}. Mass spectrum (positive ion electrospray): *m*/*z* 391, [M]$^+$; 356, [M-Cl]$^+$.

2.2.5. $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(NC_5H_4CN)]$ **5**

$[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ (0.071 g, 0.11 mmol) was dissolved in dichloromethane (30 cm^3) and an excess of 4-cyanopyridine (0.103 g, 0.36 mmol) added to the solution. The reaction mixture was stirred for 20 h, then filtered through celite to remove any undissolved material. The volume of solution was reduced in vacuo to ca. 10 cm^3, and a red solid precipitated. Addition of hexane (10 cm^3) to the concentrated solution ensured complete precipitation. The solid was filtered off and washed with hexane (20 cm^3) and diethylether (40 cm^3) and dried in vacuo. Yield: 0.074 g, 0.18 mmol, 78%. Anal. (Found: C, 40.27, H, 3.86, N, 6.48%. Calc. for $RuC_{14}H_{16}Cl_2N_2S$: C, 40.39, H, 3.88, N, 6.73%). ^{1}H NMR [CD_2Cl_2, 30°C]: δ 1.85 (br, 6H, TMT); δ 1.90 (br, 6H, TMT); δ 7.58 (m, 2H,), δ 9.20 (br, 2H,) ppm (cyanopyridine resonances). Infrared (KBr): $\nu_{(CN)}$, 2235(s) cm^{-1}, (Nujol, CsI) $\nu_{(Ru-Cl)}$ 288(w) cm^{-1}. Mass spectrum (positive ion electrospray): *m/z* 416, [M]$^+$; 381, [M-Cl]$^+$; 277 [M-Cl-py]$^+$.

2.2.6. [Ru(η^5-C_4Me_4S)(bipy)Cl][PF_6] **6**

[{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] (0.112 g, 0.18 mmol) was stirred in H_2O (20 cm^3) for ca. 10 min. 2,2′-Bipyridine (0.0583 g, 0.37 mmol) was then added to the aqueous solution which became a dark orange/red colour. The mixture was stirred for 10 min then filtered through celite. The celite was washed with H_2O (10 cm^3) and the filtrate and washings combined. Addition of an excess of aqueous $NH_4[PF_6]$ resulted in the formation of a yellow precipitate on cooling in an ice bath. The solid was isolated by filtration, washed with hexane (30 cm^3) and then dried in vacuo. Yield: 0.149 g, 0.26 mmol, 72%. Anal. (Found: C, 37.62, H, 3.26, N, 4.78, Cl, 6.44%. Calc. for $RuC_{18}H_{20}N_2SClPF_6$: C, 37.40, H, 3.50, N, 4.85, Cl, 6.13%). ^{1}H NMR [$(CD_3)_2CO$]: δ 2.10 (br s, 12H, TMT); δ 7.81 (ddd, 2H) δ 8.28 (ddd, 2H) δ 8.63 (br dd, 2H), δ 9.25 (br, 2H) ppm (2,2′-bipyridine resonances). Infrared (Nujol, CsI): $\nu_{(PF_6)}$, 839(s), $\nu_{(Ru-Cl)}$ 294(w) cm^{-1}. Mass spectrum (FAB): *m/z* 433, [M-PF_6]$^+$; 398, [M-PF_6-Cl]$^+$.

2.2.7. [Ru(η^5-C_4Me_4S)(bipy)($PPhMe_2$)][PF_6]$_2$ **7**

The compound [Ru(η^5-C_4Me_4S)(bipy)Cl][PF_6] (0.040 g, 0.07 mmol) was stirred in H_2O (20 cm^3) to which was added Ag[PF_6] (0.019 g, 0.07 mmol). The mixture was stirred for 30 min and then filtered through celite, to remove the AgCl precipitate that had formed. The celite was washed with H_2O (10 cm^3) and the filtrate and the washings combined. An excess of $PPhMe_2$ (0.05 cm^3) was added to the clear yellow solution and resulted in the formation of an orange suspension. On cooling in an ice bath a yellow solid precipitated which was isolated by filtration, washed with hexane (50 cm^3), and dried in vacuo. Yield: 0.0150 g; 0.02 mmol; 26%. Anal. (Found: C, 37.94, H, 3.61, N, 3.26%. Calc. for $RuC_{26}H_{31}N_2SP_3F_{12}$: C, 37.82, H, 3.79, N, 3.39%). ^{1}H NMR [CD_2Cl_2]: δ 1.85 (d, 6H, $^2J_{PH}=9.9$, P–Me); δ 2.04 (br s, 6H, TMT); δ 2.06 (br s, 6H, TMT); δ 6.58 (m, 2H), δ 7.05 (m, 2H), δ 7.29 (m, 1H) (phenyl resonances); δ 8.93 (d, 2H); δ 8.11 (dd, 2H); δ 7.93 (d, 2H), δ 7.85 (dd, 2H) ppm (2,2′-bypyridyl resonances). Infrared (KBr): $\nu_{(PF_6)}$, 837 cm^{-1}. Mass spectrum (positive ion electrospray): *m/z* 681, [M-PF_6]$^+$; 649, [M-PF_6-S]$^+$; 541 [M-PF_6-TMT]$^+$.

2.2.8. [Ru(η^5-C_4Me_4S)(κ^3-$HBPz_3$)][PF_6] **8**

[{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] (0.055 g, 0.09 mmol) was stirred in H_2O (10 cm^3) to which Na[$HBPz_3$] (0.046 g, 0.19 mmol) was added. The mixture was stirred for 4 h at 20°C, then filtered through celite. The celite was washed with water and the filtrate and washings combined. The volume of the solution was reduced to ca. 10 cm^3 and this was treated with an excess of aqueous $NH_4[PF_6]$. This resulted in the immediate formation of a yellow precipitate which was filtered off and washed with H_2O (20 cm^3), $CHCl_3$ (20 cm^3) and diethylether (30 cm^3), and then dried in vacuo. Yield: 0.060 g, 0.10 mmol, 57%. Anal.: (Found: C, 33.61, H, 3.51, N, 13.91%. Calc. for $RuC_{17}H_{21}N_6F_6PBS$: C, 34.07, H, 3.71, N, 14.05%). ^{1}H NMR [$(CD_3)_2CO$]: δ 2.40 (s, 6H, TMT), δ 2.45 (s, 6H, TMT); δ 6.41 (dd, 3H), δ 7.98 (d, 3H), δ 8.14 (d, 3H) (pyrazolyl resonances). Infrared (KBr): $\nu_{(BH)}$, 2502(m); $\nu_{(PF)}$, 835(s) cm^{-1}. Mass spectrum (FAB): *m/z* 455 [M-PF_6]$^+$.

2.2.9. [Ru_2(η^5-C_4Me_4S)$_2$(μ-Cl)$_3$][PF_6] **9**

[{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] (0.051 g, 0.08 mmol) was dissolved in H_2O (20 cm^3) containing an excess of $NH_4[PF_6]$. The solution was stirred for 72 h at room temperature during which time a red solid was deposited. This was isolated by filtration and washed with cold water (10 cm^3) and diethylether (50 cm^3), and then dried in vacuo. Yield: 0.043 g, 0.06 mmol, 71%. Anal.: (Found: C, 26.25, H, 3.00, Cl, 14.65%. Calc. for $Ru_2C_{16}H_{24}Cl_3S_2PF_6$: C, 26.18, H, 3.30, Cl, 14.49%). NMR: ^{1}H [$(CD_3)_2CO$]: δ 2.10 (s, 12H, TMT), δ 2.15 (s, 12H, TMT) ppm. Infrared (KBr): $\nu_{(PF_6)}$ 841(vs) cm^{-1}. Mass spectrum (FAB): *m/z* 591 [M-PF_6]$^+$.

2.3. X-ray crystallography

Crystal and refinement data for compounds **1**, **7**.CH_2Cl_2, **8** and **9** are provided in Table 1. For compounds **1**, **7**, and **8** the data were measured at 293 K on an automated four-circle diffractometer (Nicolet R3mV) equipped with graphite monochromated Mo Kα radiation operating at 293 K. The $\omega-2\theta$ method was used to to measure reflections in the range $5<2\theta<50°$. Three standard reflections were measured at regular intervals and indicated that none of the crystals decayed during the experiments. The data were corrected for Lorentz and polarisation effects and for absorption, based on additional azimuthal scan data. For **9** crystallographic measurements were recorded at 196 K with a Nonius Kappa CCD diffractometer equipped with

Table 1
Crystal and refinement data for compounds **1**, **7**–**9**

	1	**7**·CH_2Cl_2	**8**	**9**
Formula	$C_{16}H_{23}Cl_2PRuS$	$C_{27}H_{33}Cl_2F_{12}N_2P_3RuS$	$C_{17}H_{22}BF_6N_6PRuS$	$C_{16}H_{24}Cl_3F_6Ru_2S_2$
M	450.3	910.5	599.3	733.9
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	Cc	$P2_12_12_1$	$P2_1/c$	P-1
a/Å	9.380(2)	12.843(3)	11.483(2)	10.1369(4)
b/Å	15.614(3)	12.873(3)	15.130(3)	11.4708(3)
c/Å	13.107(3)	22.869(5)	13.442(3)	12.7140(5)
α/°	90	90	90	114.681(2)
β/°	100.06(3)	90	92.83(3)	110.547(2)
γ/°	90	90	90	95.433(2)
U/Å^3	1890(1)	3781(2)	2332(1)	1206.2(1)
Z	4	4	4	2
D_c/g cm^{-3}	1.583	1.600	1.707	2.021
F(000)	912	1824	1200	720
μ(Mo Kα) mm^{-1}	1.30	0.82	0.90	1.87
$2\theta_{max}$/°	50	50	50	52
hkl range	0–12, 0–20, −17–16	0–15, 0–15, 0–27	0–13, 0–18, −16–15	0–12, −13–13, −16–15
Reflections collected	2298	3707	4287	10513
Independant	2298	3707	4074	4426
Data/parameters	2295/189	3697/434	4074/298	4414/272
Goodness of fit on F^2	1.051	1.065	1.043	1.095
R [$I>2\sigma(I)$]	$R1=0.0220$	0.0665	0.0391	0.0254
	$wR2=0.0555$	0.1449	0.1000	0.0620
R (all data)	$R1=0.0235$	0.1332	0.0530	0.0290
	$wR2=0.0607$	0.2137	0.1204	0.0869
ΔF synthesis	0.65	1.023	0.745	0.476
(max, min e Å^{-3})	−0.48	−0.754	−0.471	−0.808

graphite monochromated Mo Kα radiation using φ rotations with 2° frames and a detector to crystal distance of 25 mm. Integration was carried out by the program DENZO-SMN [33]. Data were corrected for Lorentz and polarization effects, and for the effects of absorption using the program SCALEPACK [33].

Structures were solved by direct methods (SHELXS-86) [34] developed using alternating cycles of least-squares refinement and difference Fourier synthesis (SHELX-93) [35]. All non-hydrogen atoms were refined anisotropically whilst the hydrogen atoms were fixed in idealised positions and allowed to ride on the atom to which they were attached. During the latter stages of the refinement of **7** the presence of a solvent of crystallisation became apparent. This was successfully modelled as dichloromethane. Selected geometrical parameters are reported in Tables 2–5.

Table 2
Selected bond lengths (Å) and angles (°) for [Ru(η^5-C_4Me_4S)Cl_2($PPhMe_2$)] **1**

Lengths			
Ru(1)–C(1)	2.158(4)	Ru(1)–S(1)	2.4422(12)
Ru(1)–C(2)	2.221(4)	Ru(1)–P(1)	2.3303(10)
Ru(1)–C(3)	2.228(4)	Ru(1)–Cl(1)	2.4414(11)
Ru(1)–C(4)	2.169(4)	Ru(1)–Cl(2)	2.4419(11)
S(1)–C(1)	1.799(4)	C(1)–C(2)	1.427(7)
C(2)–C(3)	1.444(7)	C(3)–C(4)	1.425(7)
S(1)–C(4)	1.790(5)	P(1)–C(9)	1.835(4)
P(1)–C(10)	1.854(4)	P(1)–C(11)	1.842(4)
Angles			
Cl(1)–Ru(1)–Cl(2)	90.82(4)	Cl(1)–Ru(1)–P(1)	86.84(4)
Cl(2)–Ru(1)–P(1)	83.17(4)	C(1)–S(1)–C(4)	90.3(2)
S(1)–C(1)–C(2)	110.9(3)	C(1)–C(2)–C(3)	112.9(4)
C(2)–C(3)–C(4)	112.5(4)	C(3)–C(4)–S(1)	111.5(4)

Table 3
Selected bond lengths (Å) and angles (°) for [Ru(η^5-C_4Me_4S)(bipy)($PPhMe_2$)][PF_6]$_2$·CH_2Cl_2 **7**

Lengths			
Ru(1)–C(1)	2.27(2)	Ru(1)–S(1)	2.397(5)
Ru(1)–C(2)	2.26(2)	Ru(1)–P(1)	2.364(4)
Ru(1)–C(3)	2.28(2)	Ru(1)–N(1)	2.089(14)
Ru(1)–C(4)	2.20(2)	Ru(1)–N(2)	2.091(14)
S(1)–C(1)	1.77(2)	C(1)–C(2)	1.40(2)
C(2)–C(3)	1.49(2)	C(3)–C(4)	1.44(3)
S(1)–C(4)	1.76(2)	P(1)–C(21)	1.82(2)
P(1)–C(31)	1.82(2)	P(1)–C(41)	1.83(2)
Angles			
N(1)–Ru(1)–N(2)	77.4(5)	N(1)–Ru(1)–P(1)	87.4(4)
N(2)–Ru(1)–P(1)	89.7(4)	C(1)–S(1)–C(4)	91.8(8)
S(1)–C(1)–C(2)	112.3(13)	C(1)–C(2)–C(3)	113(2)
C(2)–C(3)–C(4)	110(2)	C(3)–C(4)–S(1)	112.6(10)
Ru(1)–N(1)–C(11)	125.7(14)	Ru(1)–N(1)–C(15)	115.5(12)
Ru(1)–N(2)–C(20)	124.5(12)	Ru(1)–N(2)–C(16)	117.7(11)

Table 4
Selected bond lengths (Å) and angles (°) for $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$ **8**

Lengths			
Ru(1)–C(1)	2.184(4)	Ru(1)–S(1)	2.4006(12)
Ru(1)–C(3)	2.240(4)	Ru(1)–N(12)	2.151(4)
Ru(1)–C(5)	2.245(4)	Ru(1)–N(22)	2.159(4)
Ru(1)–C(7)	2.204(4)	Ru(1)–N(32)	2.125(3)
S(1)–C(1)	1.795(5)	C(1)–C(3)	1.419(6)
C(3)–C(5)	1.464(7)	C(5)–C(7)	1.415(7)
S(1)–C(7)	1.800(5)		
Angles			
N(12)–Ru(1)–N(22)	82.94(14)	N(12)–Ru(1)–N(32)	84.51(14)
N(22)–Ru(1)–N(32)	85.21(14)	C(1)–S(1)–C(7)	90.2(2)
S(1)–C(1)–C(3)	112.4(3)	C(1)–C(3)–C(5)	112.0(4)
C(3)–C(5)–C(7)	112.9(4)	C(5)–C(7)–S(1)	111.9(4)
Ru(1)–N(12)–N(11)	120.0(3)	Ru(1)–N(22)–N(21)	120.3(3)
Ru(1)–N(32)–N(31)	120.3(3)	N(11)–B(1)–N(21)	108.0(4)
N(11)–B(1)–N(31)	107.9(4)	N(21)–B(1)–N(31)	108.1(4)

3. Results and discussion

Only a few compounds of the type $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2L]$ have been reported previously. Notable among these are the $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PR_3)]$ [21] (R= Me, Bu, Ph, *p*-tolyl) series of compounds. While the trialkylphosphine derivatives have unremarkable NMR spectra the variable temperature spectra of the triarylphosphine compounds are interesting. In particular at low temperature the TMT ligand exhibits four methyl resonances consistent with hindered rotation about the Ru–P bond due to significant steric interaction with the substituents on the thiophene ring such that each methyl is rendered unique [21]. We were interested to probe whether mixed alkyl/aryl phosphine ligands also gave rise to significant interactions and to that end prepared the compound $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPhMe_2)]$ **1** by the reaction of $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ with $PPhMe_2$ in dichloromethane. In the room temperature ^1H NMR spectrum the methyl signals on the thiophene ligands appear as two widely spaced broad singlets, δ 1.30 and 1.88 ppm. On lowering the temperature of the NMR probe to −60°C the signals sharpen, δ 1.28 and 1.87 ppm, but no splitting occurs, indicating that even at this temperature the rotation of both the phosphine and thiophene ligands is rapid. As no $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PR_3)]$ compound had been previously characterised by X-ray diffraction we decided to undertake such a study on **1**, Fig. 1. If we assume the thiophene ligand to coordinate as a tridentate diolefin–thioether ligand then we can see that this ligand occupies three facial sites on an octahedral ruthenium(II) ion. The only previously reported X-ray structure of a simple $[Ru(\eta^5\text{-}C_4Me_4S)L_3]$ compound was that of $[Ru(\eta^5\text{-}C_4Me_4S)(H_2O)_3][OTf]_2$, which was severely disordered [22]. The thiophene ligand in **1** is approximately planar. However the sulfur atom is displaced 0.27 Å out of the plane formed by the atoms C(1), C(2), C(3), and C(4) on the side away from the metal. This slight folding of the ligand is also apparent in the angle of 12.5° formed between the planes [C(1)S(1)C(4)] and [C(1) C(2)C(3)C(4)]. Further distortions from planarity are observed for the methyl substituents on the thiophene which are displaced somewhat from the metal, with deviations ranging from 6.1 to 7.5°. Although inspection of the C–C bond lengths implies some localisation of the olefinic bonds the differences are not statistically significant in this structure. The Ru–C bond lengths form two pairs with those to the carbons adjacent to sulfur significantly shorter, average 2.163(4) Å, than those to the

Table 5
Selected bond lengths (Å) and angles (°) for $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ **9**

Lengths			
Ru(1)–Cl(1)	2.4792(7)	Ru(2)–Cl(1)	2.4160(7)
Ru(1)–Cl(2)	2.4615(7)	Ru(2)–Cl(2)	2.4600(7)
Ru(1)–Cl(3)	2.4167(7)	Ru(2)–Cl(3)	2.4752(7)
Ru(1)–S(1)	2.3375(7)	Ru(2)–S(2)	2.3353(7)
Ru(1)–C(1)	2.117(3)	Ru(2)–C(9)	2.114(3)
Ru(1)–C(2)	2.170(3)	Ru(2)–C(10)	2.153(3)
Ru(1)–C(3)	2.155(3)	Ru(2)–C(11)	2.172(3)
Ru(1)–C(4)	2.116(3)	Ru(2)–C(12)	2.133(3)
S(1)–C(1)	1.770(3)	S(2)–C(9)	1.773(3)
C(1)–C(2)	1.420(4)	C(9)–C(10)	1.414(4)
C(2)–C(3)	1.437(4)	C(10)–C(11)	1.441(4)
C(3)–C(4)	1.418(4)	C(11)–C(12)	1.420(4)
C(4)–S(1)	1.766(3)	C(12)–S(2)	1.764(3)
Angles			
Cl(1)–Ru(1)–Cl(2)	80.73(2)	Cl(1)–Ru(2)–Cl(2)	82.03(2)
Cl(2)–Ru(1)–Cl(3)	80.93(2)	Cl(2)–Ru(2)–Cl(3)	79.81(2)
Cl(1)–Ru(1)–Cl(3)	80.29(2)	Cl(1)–Ru(2)–Cl(3)	80.39(2)
Ru(1)–Cl(1)–Ru(2)	83.39(2)	Ru(1)–Cl(2)–Ru(2)	82.86(2)
Ru(1)–Cl(3)–Ru(2)	83.46(2)	C(9)–S(2)–C(12)	91.30(14)
C(1)–S(1)–C(4)	90.96(14)	S(2)–C(9)–C(10)	111.0(2)
S(1)–C(1)–C(2)	111.6(2)	C(9)–C(10)–C(11)	113.3(3)
C(1)–C(2)–C(3)	112.2(2)	C(10)–C(11)–C(12)	111.9(3)
C(2)–C(3)–C(4)	112.7(2)	C(11)–C(12)–S(2)	111.8(2)
C(3)–C(4)–S(1)	111.6(2)		

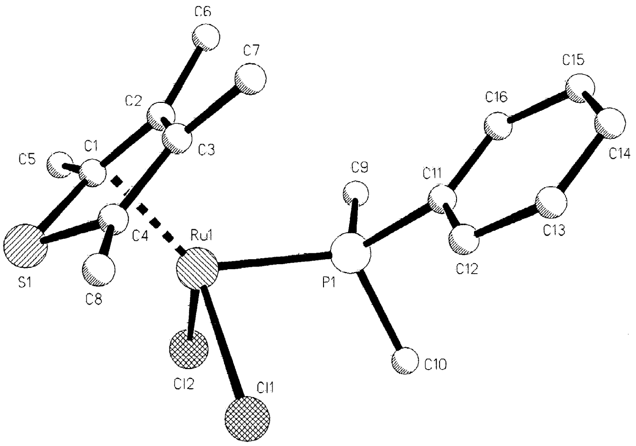

Fig. 1. The crystal structure of $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPhMe_2)]$ **1**, showing the atom labelling scheme.

other two carbon atoms, average 2.224(4) Å. The Ru–S bond, 2.442(1) Å, is considerably longer than those observed in [Ru(η^5-C_4Me_4S)(H_2O)$_3$][OTf]$_2$, 2.307(6) Å [22], or [Ru(η^5-C_4Me_4S)$_2$][BF_4]$_2$, average 2.355(2) Å [21], but rather more comparable to those observed in the polynuclear compound [{Ru(η^5-C_4Me_4S)(μ-Cl)}$_3$(μ^3-S)], 2.414(4)–2.432(4) Å [21]. The structure can be compared to that of the related isoelectronic Ru(arene) derivative [Ru(η^6-*p*-cymene)Cl_2($PPhMe_2$)] [36], and indeed with around ten other crystal structures of [Ru(η^6-arene)Cl_2(PR_3)] compounds [37–43] documented on the Cambridge Crystallographic database. Interestingly, while the Ru–P bond length in this compound, 2.330(1) Å, does not differ greatly from the average, 2.357 Å (range 2.291–2.379 Å), found for [Ru(η^6-arene)Cl_2(PR_3)] compounds the Ru–Cl bonds for **1**, 2.441(1) Å, are considerably longer than those observed in the Ru(arene) analogues, average 2.406 Å (range 2.381–2.425 Å).

The reaction of [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] with $P(OCH_3)_3$ gives an analogous compound to **1**, namely [Ru(η^5-C_4Me_4S)Cl_2($P(OCH_3)_3$)] **2**. Given the small cone angle for this phosphite ligand one would anticipate that the ^{1}H NMR spectrum would be essentially invariant with temperature and indeed the spectrum remains unchanged in the range −60 to 0°C, with only two tetramethylthiophene methyl resonances observed throughout, δ 1.98 and 2.00 ppm. At 20°C the two singlets are unresolved, appearing as a symmetrical singlet, but we attribute that to accidental coincidence of the chemical shifts, which vary slightly with temperature in any case, rather than some dynamic process. A dichloromethane solution of [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] reacts with carbon monoxide to give a yellow insoluble precipitate of [Ru(η^5-C_4Me_4S)Cl_2(CO)] **3**. The positive ion electrospray mass spectrum of this compound exhibits a parent ion peak, at *m*/*z* 340, and shows fragmentation peaks due to the loss of chloride and CO (see Section 2). The infrared spectrum of **3** contains a $\nu_{(CO)}$ band at 1982 cm^{-1}, compared to one of 2054 cm^{-1} reported for [Ru(η^5-C_4Me_4S)$(OTf)_2$(CO)] [22]. The reaction of [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] with pyridine gives [Ru(η^5-C_4Me_4S)Cl_2(NC_5H_5)] **4** which has been routinely characterised (see Section 2). The ^{1}H NMR spectrum recorded at 20°C in CD_2Cl_2 exhibits two rather broad thiophene methyl resonances, at δ 1.81 and 1.88 ppm, as well as the usual three signals for the pyridine ligand. On cooling to 0°C the methyl signals become degenerate, and further cooling results in the precipitation of the compound from solution and no useful spectra could be obtained. In contrast if one prepares the 4-cyanopyridine analogue [Ru(η^5-C_4Me_4S)Cl_2(NC_5H_4CN)] **5** NMR measurements can be made over a wide temperature range. At 30°C in CD_2Cl_2 the NMR spectrum consist of a pair of broad methyl resonances, at δ 1.85 and 1.90 ppm, and two broad signals, at δ 7.57 and 9.21 ppm, due to the protons on the pyridyl ring. On cooling to −80°C the spectrum changes dramatically, such that the pyridyl resonances are sharp and give rise to the eight-line pattern expected for an AA′BB′ spin system, chemical shifts δ 7.54, 7.64, 8.80 and 9.24 ppm. At the same time the thiophene methyls appear as four singlets, δ 1.50, 1.97, 2.01 and 2.02 ppm. Clearly for **5** at low temperature in solution we have frozen out a structure in which each methyl is unique. Whether this arises due to restricted rotation about the Ru–N bond, or restricted rotation of the tetramethylthiophene ligand, or both, is unclear. However, as Rauchfuss pointed out in his discussion of the NMR spectrum of [Ru(η^5-C_4Me_4S)Cl_2(PPh_3)] inhibiting rotation about one Ru–ligand bond can be sufficient to render each methyl unique if the ‘rotamer’ stabilised at low temperature has the unique ligand, in our case 4-cyanopyridine, placed such that its projection bisects a S–C bond [21].

In addition to simple bridge cleavage reactions it is possible to prepare compounds in which one or more of the chloride ligands have been displaced from the metal centre. Rauchfuss used silver reagents to remove the halides from [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$], in the preparation of [Ru(η^5-C_4Me_4S)$_2$][BF_4]$_2$ [21] and [Ru(η^5-C_4Me_4S)$(OTf)_2$]$_n$ [22], however, we report here that for some ligands at least the use of the expensive silver reagent is unnecessary.

Aqueous solutions of [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] react rapidly with 2,2′-bipyridine. When the reaction time is in excess of 30 min addition of $NH_4[PF_6]$ to the reaction mixture gives the well-known [Ru(bipy)$_3$][PF_6]$_2$ as the only isolated product. However, if the reaction time is limited to a maximum of 15 min, and the work up is performed rapidly then the complex [Ru(η^5-C_4Me_4S)Cl(bipy)][PF_6] **6** is obtained in good yield. Although the solid is stable, solutions of **6** rapidly decompose. The proton resonances for the thiophene methyl groups are not resolved for this compound and appear as a broad singlet at ambient temperature. However, the four anticipated resonances for the aromatic protons of the 2,2′-bipyridine ligand are clearly seen and integration of the spectrum confirms the ligand stoichiometry. The highest peak in the FAB mass spectrum corresponds to the [Ru(η^5-C_4Me_4S)Cl(bipy)]$^+$ ion and the sequential loss of chloride from this is observed (see Section 2). Compound **6** will react further with $PPhMe_2$/Ag[PF_6] to give [Ru(η^5-C_4Me_4S)(bipy)($PPhMe_2$)][PF_6]$_2$ **7**, albeit in only modest yield. The spectroscopic characterisation of **7** was routine, with integration of the ^{1}H NMR spectrum being consistent with a 1:1:1 ratio of the ligands C_4Me_4S, bipy, and $PPhMe_2$. Confirmation of the identity of **7** was obtained by X-ray structure determination, Fig. 2. Unfortunately the crystal used in this study was significantly poorer than that employed for the other three structure determinations reported herein (only ca. 60% of the measured reflections were observed at the $2\sigma(I)$ level). Hence, the lower precision in the reported geometrical parameters, precludes a detailed discussion of the structure. Nevertheless, the

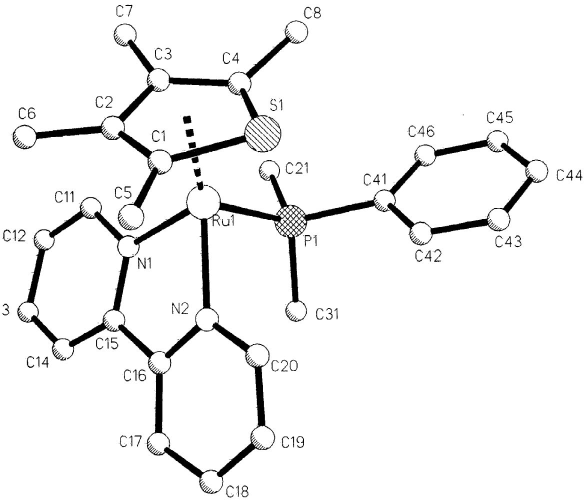

Fig. 2. The crystal structure of the cation in $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_4Me_4S})(\mathrm{bipy})(\mathrm{PPhMe_2})][\mathrm{PF_6}]_2$ **7**, showing the atom labelling scheme.

diffraction experiment clearly demonstrates the octahedral coordination at the metal. We also note that the thiophene ring is closer to planarity than was observed to be the case for **1**, and interestingly while the Ru–P distance, 2.364(4) Å, is somewhat longer than that observed for **1** the Ru–S distance, 2.397(5) Å, is markedly shorter, by some 0.045 Å. Finally it should be noted that while ‘Ru(arene)’ analogues of **6** and **7** have been described [44] none of these have been crystallographically characterised.

By studying the reaction of $[\{\mathrm{Ru}(\eta^5\text{-}\mathrm{C_4Me_4S})\mathrm{Cl}(\mu\text{-}\mathrm{Cl})\}_2]$ with $\mathrm{Na[HB(Pz)_3]}$ we have established that all the chlorides can be removed from the metal, while the thiophene ligand is retained, in a single synthetic step. Initially we attempted this reaction in a variety of organic solvents, however yields were invariably low. Indeed the optimum solvent for this, and a number of other reactions, would, rather surprisingly, appear to be water. Aqueous solutions of $\mathrm{Na[HB(Pz)_3]}$ react smoothly with $[\{\mathrm{Ru}(\eta^5\text{-}\mathrm{C_4Me_4S})\mathrm{Cl}(\mu\text{-}\mathrm{Cl})\}_2]$ to give a yellow solution from which $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_4Me_4S})(\kappa^3\text{-}\mathrm{HBPz_3})][\mathrm{PF_6}]$ **8** can be precipitated by the addition of $\mathrm{NH_4[PF_6]}$. The infrared spectrum of this material exhibits typical $\nu_{(\mathrm{BH})}$ and $\nu_{(\mathrm{PF})}$ bands, at 2052 and 835 $\mathrm{cm^{-1}}$, respectively. The ^{1}H NMR spectrum consists of the three pyrazolyl resonances, δ 8.14, 7.98, and 6.41 ppm, two methyl resonances from the thiophene ligand, δ 2.45 and 2.40 ppm, and a rather broad signal at ca. 4.2 ppm, due to the proton on boron. Complete confirmation of the structure of **8** is obtained by a single crystal structure determination, Fig. 3. The basic geometry is as described previously with pseudo-octahedral coordination at ruthenium, though it should be noted that the angles subtended at ruthenium are somewhat smaller than in the two previous compounds, 83–85°, as a consequence of the chelate bite of the hydrido*tris*(pyrazolyl)borate ligand. While the thiophene ligand can be described as approximately planar there are nevertheless deviations from planarity similar to those described for **1**. In general, however, these deviations are somewhat smaller than before. For example, the sulfur is displaced by 0.15 Å from the plane of the metallated carbons on the side away from the metal and the folding of the thiophene ligand is 7.1°, cf. 12.5° for **1**. The Ru–C bonds again form a long and a short pair, however the average Ru–C distance in **8**, 2.218(4) Å, is significantly longer than that for **1**, 2.194(4) Å, reflecting the superior sigma donor power of the $\mathrm{N_3}$ ligand set in **8**, which is also reflected in the shorter Ru–S distance, 2.401(1) Å. The Ru–N distances can be usefully compared to those observed for the analogous Ru(arene) compound, $[\mathrm{Ru}(p\text{-cymene})\{\mathrm{HB(Pz)_3}\}][\mathrm{PF_6}]$ [45]. As with $[\mathrm{Ru}(p\text{-cymene})\{\mathrm{HB(Pz)_3}\}][\mathrm{PF_6}]$ the Ru–N distances are unequal, with two longer, 2.151(4) and 2.159(4) Å, and one shorter, 2.125(3) Å, bond. Each of these bonds is approximately 0.03 Å longer in **8** reflecting the greater *trans* influence of the thiophene ligand and which is consistent with the fact that $[\{\mathrm{Ru}(\eta^5\text{-}\mathrm{C_4Me_4S})\mathrm{Cl}(\mu\text{-}\mathrm{Cl})\}_2]$ is prepared from $[\{\mathrm{Ru}(\eta^6\text{-}p\text{-cymene})\mathrm{Cl}(\mu\text{-}\mathrm{Cl})\}_2]$ via an arene displacement reaction.

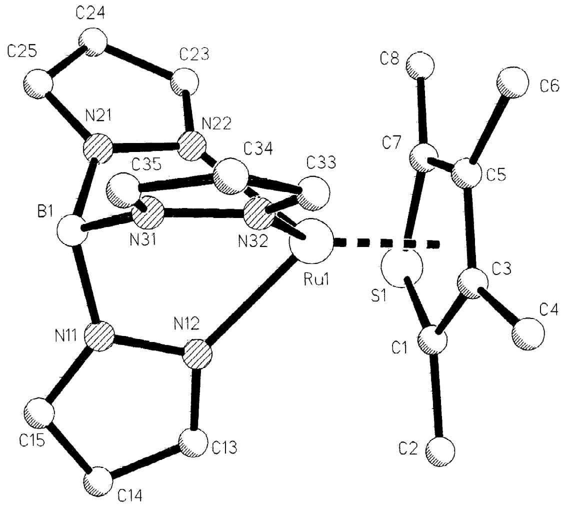

Fig. 3. The crystal structure of the cation in $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_4Me_4S})(\kappa^3\text{-}\mathrm{HBPz_3})][\mathrm{PF_6}]$ **8**, showing the atom labelling scheme.

It will have been noticed that many of the reactions described above have been performed in aqueous solution. Rauchfuss originally examined the behaviour of $[\{\mathrm{Ru}(\eta^5\text{-}\mathrm{C_4Me_4S})\mathrm{Cl}(\mu\text{-}\mathrm{Cl})\}_2]$ in aqueous solution by ^{1}H NMR spectroscopy [21]. He reported that in $\mathrm{D_2O}$ two species were present in an approximate ratio of 10:1. The minor species was identified as the ion $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_4Me_4S})(\mathrm{D_2O})_3]^{2+}$ which could be synthesised independantly, isolated as its triflate salt, and characterised by X-ray diffraction [22]. At the time of the original report the major component was not identified. Given our success in synthesising new compounds in aqueous solution we thought it important to re-examine this reaction. When $[\{\mathrm{Ru}(\eta^5\text{-}\mathrm{C_4Me_4S})\mathrm{Cl}(\mu\text{-}\mathrm{Cl})\}_2]$ is placed in an aqueous solution containing an excess of $\mathrm{NH_4[PF_6]}$ a red solid deposits from solution over a period of 72 h. The ^{1}H NMR spectrum of that compound exhibits only one set of tetramethylthiophene signals, δ 2.15 and 2.10 ppm. A simple test with $HNO_3/AgNO_3$ reveals that the compound still contains chloride ions. The mass spectrum exhibits a peak at m/z 591 which displays the predicted isotope pattern for two ruthenium and three chlorine atoms. This data together with the elemental analysis (see Section 2) suggest that the compound be formulated as $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ **9**, which was subsequently confirmed by X-ray diffraction, Fig. 4. The complex cation has a face-sharing bi-octahedral structure with the two ruthenium(II) ions bridged unsymmetrically by three chloride ions. There are four long Ru–Cl distances, 2.4600(7)–2.4792 Å, and two short, 2.4168(7) and 2.4160(7) Å. The short bonds are approximately *trans* to the Ru–S bonds, S(1)–Ru(1)–Cl(3) 167.58(3)°, S(2)–Ru(2)–Cl(1) 167.24(3)°, and reflect the *trans* influence of the ligating sulfur atoms, which form shorter bonds to the metal, 2.3375(7) and 2.3353(7) Å, than seen in the other compounds we have investigated. Nevertheless, the sulfur atoms are still displaced, 0.18 Å S(1) and 0.17 Å S(2), from the plane of the four metallated carbon atoms of the thiophene ligand on the side away from the metal. Despite the wide range of Ru–Cl distances the mean value, 2.4514(7) Å, is not very different from the mean value observed for the analogous $[Ru_2(\eta^6\text{-arene})_2(\mu\text{-}Cl)_3]^+$ cations reported in the literature, 2.430 Å [46–50]. The angles Cl–Ru–Cl subtended at ruthenium are $80(\pm 1)°$, while the angles at the bridging chlorides are $83(\pm 1)°$. These values are unremarkable and fall within the normal range for compounds in which three halide ions bridge two metal centres in the absence of any metal–metal bond. Although it might seem unlikely that **9** be formed in aqueous solution, its preparation closely mimics that of $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}Cl)_3][PF_6]$, which can be obtained in low yield by stirring $[\{Ru(\eta^6\text{-}C_6H_6)Cl(\mu\text{-}Cl)\}_2]$ in an aqueous solution of $NH_4[PF_6]$ [51], or in higher yield by using a methanolic solution [52].

Clearly, while most reports of the chemistry of π-thiophene complexes of ruthenium(II) has focused on the reactivity of the metallated ligand, we have demonstrated that there is considerable scope for developing the coordination chemistry of the Ru(η^5-thiophene) moiety, perhaps into such areas as bio-organometallic chemistry and water soluble catalysts.

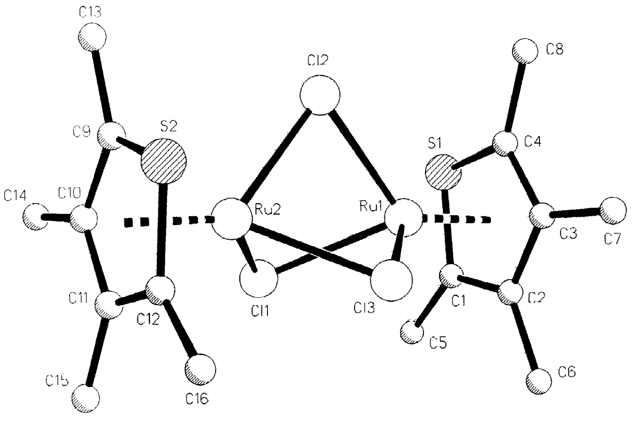

Fig. 4. The crystal structure of the cation in $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ **9**, showing the atom labelling scheme.

Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers CCDC 112384–112387.

Acknowledgements

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References

[1] H. Topsoe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysis, Springer-Verlag, Berlin, 1996.
[2] J. Scherzer, A.J. Gruia, Hydrocracking Science and Technology, Dekker, New York, 1996.
[3] J.W. Benson, G.L. Schrader, R.J. Angelici, J. Mol. Catal. 96 (1995) 283.
[4] A.N. Startsev, Catal. Rev.-Sci. Eng. 37 (1995) 353.
[5] J.G. Reynolds, Chem. Ind. (1991) 570.
[6] K. Matsubara, R. Okamura, M. Tanaka, H. Suzuki, J. Am. Chem. Soc. 120 (1998) 1108.
[7] X. Zhang, C.A. Dullaghan, E.J. Watson, G.B. Carpenter, D.A. Sweigart, Organometallics 17 (1998) 2067.
[8] C. Bianchini, A. Meli, S. Moneti, F. Vizza, Organometallics 17 (1998) 2636.
[9] C. Bianchini, D. Masi, A. Meli, M. Peruzzini, F. Vizza, F. Zanobini, Organometallics 17 (1998) 2495.
[10] A.W. Myers, W.D. Jones, Organometallics 15 (1996) 2905.
[11] M. Paneque, S. Taboada, E. Carmona, Organometallics 15 (1996) 2678.
[12] C. Bianchini, M.V. Jimenez, C. Mealli, A. Meli, S. Moneti, V. Patinec, F. Vizza, Angew. Chem., Int. Ed. Engl. 35 (1996) 1706.
[13] C. Bianchini, D. Fabbri, S. Gladiali, A. Meli, W. Pohl, F. Vizza, Organometallics 15 (1996) 4604.
[14] C. Bianchini, J.A. Casares, A. Meli, V. Sernau, F. Vizza, R.A. Sanchez Delgado, Polyhedron 16 (1997) 3099.
[15] C. Bianchini, A. Meli, V. Patinec, V. Sernau, F. Vizza, J. Am. Chem. Soc. 119 (1997) 4945.
[16] V. Herrera, A. Fuentes, M. Rosales, R.A. Sanchez Delgado, C. Bianchini, A. Meli, F. Vizza, Organometallics 16 (1997) 2465.
[17] C. Bianchini, M.V. Jimenez, A. Meli, S. Moneti, V. Patinec, F. Vizza, Organometallics 16 (1997) 5696.

[18] J.J. Garcia, A. Arevalo, S. Capella, A. Chehata, M. Hernandez, V. Montiel, G. Picazo, F. Del Rio, R.A. Toscano, H. Adams, P.M. Maitlis, Polyhedron 16 (1997) 3185.
[19] J.J. Garcia, A. Arevalo, V. Montiel, F. Del Rio, B. Quiroz, H. Adams, P.M. Maitlis, Organometallics 16 (1997) 3216.
[20] A. Iretskii, J.J. Garcia, G. Picazo, P.M. Maitlis, Catal. Lett. 51 (1998) 129.
[21] J.R. Lockemeyer, T.B. Rauchfuss, A.L. Rheingold, S.R. Wilson, J. Am. Chem. Soc. 111 (1989) 8828.
[22] E.A. Ganja, T.B. Rauchfuss, C.L. Stern, Organometallics 10 (1991) 270.
[23] S. Luo, T.B. Rauchfuss, Z. Gan, J. Am. Chem. Soc. 115 (1993) 4943.
[24] H. Krautscheid, Q. Feng, T.B. Rauchfuss, Organometallics 12 (1993) 3273.
[25] Q. Feng, T.B. Rauchfuss, S.R. Wilson, Organometallics 14 (1995) 2923.
[26] Q. Feng, H. Krautscheid, T.B. Rauchfuss, A.E. Skaugset, A. Venturelli, Organometallics 14 (1995) 297.
[27] K.K. Dailey, T.B. Rauchfuss, Organometallics 16 (1997) 858.
[28] S. Luo, T.B. Rauchfuss, S.R. Wilson, Organometallics 11 (1992) 3497.
[29] S. Luo, T.B. Rauchfuss, S.R. Wilson, J. Am. Chem. Soc. 114 (1992) 8515.
[30] S. Luo, T.B. Rauchfuss, A.L. Rheingold, J. Organomet. Chem. 472 (1994) 295.
[31] M.A. Bennett, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, 1st ed., Vol. 4, Pergamon Press, 1982, p. 796, Chapter 32.3.
[32] M.A. Bennett, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, 2nd ed., Vol. 7, Elsevier Science, 1995, p. 556, Chapter 9.
[33] Z. Otwinowski, W. Minor, in: C.W. Carter, R.M. Sweet (Eds.), Methods in Enzymology, Academic Press, New York, 1996.
[34] G.M. Sheldrick, SHELXS-86, Acta Crystallogr., Sect. A 46 (1990) 467.
[35] G.M. Sheldrick, SHELXL-93, University of Gottingen, 1993.
[36] M.A. Bennett, G.B. Robertson, A.K. Smith, J. Organomet. Chem. 43 (1972) C41.
[37] R.D. Brost, G.C. Bruce, S.R. Stobart, J. Chem. Soc., Chem. Commun. (1986) 1580.
[38] A.W. Coleman, Hongming Zhang, S.G. Bott, J.L. Atwood, P.H. Dixneuf, J. Coord. Chem. 16 (1987) 9.
[39] P. Salvadori, P. Pertici, F. Marchetti, R. Lazzaroni, G. Vitulli, M.A. Bennett, J. Organomet. Chem. 370 (1989) 155.
[40] J. Browning, G.W. Bushnell, K.R. Dixon, R.W. Hilts, J. Organomet. Chem. 452 (1993) 205.
[41] P. Pertici, E. Pitzalis, F. Marchetti, C. Rosini, P. Salvadori, M.A. Bennett, J. Organomet. Chem. 466 (1994) 221.
[42] A. Hafner, A. Muhlebach, P.A. van der Schaaf, Angew. Chem., Int. Ed. Engl. 36 (1997) 2121.
[43] M.R.J. Elsegood, D.A. Tocher, Polyhedron 14 (1995) 3147.
[44] D.R. Robertson, I.W. Robertson, T.A. Stephenson, J. Organomet. Chem. 202 (1980) 309.
[45] S. Bhambri, D.A. Tocher, Polyhedron 15 (1996) 2763.
[46] D.A. Tocher, M.D. Walkinshaw, Acta Crystallogr. B38 (1982) 3083.
[47] F.B. McCormick, W.B. Gleason, Acta Crystallogr., Sect. C 49 (1993) 1493.
[48] Yu.T. Struchkov, A.S. Batsanov, Metalloorg. Khim. 1 (1988) 1143.
[49] R. Goerissen, U. Koelle, T.P. Spaniol, Polyhedron 11 (1992) 2317.
[50] F. Grepioni, D. Braga, P.J. Dyson, B.F.G. Johnson, F.M. Sanderson, M.J. Calhorda, L.F. Veiros, Organometallics 14 (1995) 121.
[51] M.A. Bennett, T.W. Matheson, J. Chem. Soc. Dalton Trans (1974) 233.
[52] D.R. Robertson, T.A. Stephenson, T. Arthur, J. Organomet. Chem. 162 (1978) 121.