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The reactions of $CpRu(PPh_3)_2SR$ with the electrophiles HBF_4, $[MeSSMe_2]BF_4$ and MeSphth where $R = CMe_3$, $CHMe_2$, $4\text{-}C_6H_4Me$ and phth = phthalimide

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Abstract

Reaction of the ruthenium thiolato complexes $CpRu(PPh_3)_2SR$ (**1**), where $R = CMe_3$, $CHMe_2$, $4\text{-}C_6H_4Me$ with HBF_4 gave the corresponding thiol complex salts $[CpRu(PPh_3)_2(HSR)]BF_4$ (**2**) in very good yields. Treatment of the thiolato complexes with $[MeSSMe_2]BF_4$ gave the methyl thioether complex salt $[CpRu(PPh_3)_2SMe_2]BF_4$ (**3**). Reactions of **1** with MeSphth, where phth = phthalimide, gave $CpRu(PPh_3)_2(phth)$ (**4**) and the dimers $(\mu\text{-SMe})(\mu\text{-SR})[CpRu(phth)]_2$ (**5**) for $R = CMe_3$ and $CHMe_2$, however, for $R = 4\text{-}C_6H_4Me$ the same reaction gave $CpRu(PPh_3)(phth)(MeSS\text{-}4\text{-}C_6H_4Me)$ (**6**) and $(\mu\text{-SMe})(\mu\text{-S-}4\text{-}C_6H_4Me)[CpRu(S\text{-}4\text{-}C_6H_4Me)]_2$ (**7**). The crystal structure for **7** was determined: space group $P2_1/c$, $a = 8.805(2)$, $b = 13.668(3)$, $c = 26.026(6)$ Å, $\alpha = 90$, $\beta = 108.86(2)$, $\gamma = 90°$, $V = 2964.0(12)$ Å^3 and $Z = 4$.

Keywords: Ruthenium; Thiolate; Electrophiles; Dimers; Structure

1. Introduction

Organometallic thiolato complexes, M–SR, possess two sites which can react with electrophiles, namely the sulfur atom of the thiolato ligand and the metal center [1].

The reactivity of the thiolato ligand towards electrophiles is due to the availability of lone pairs of electrons on the sulfur atom [1]. Electrophilic attack at the metal center is observed only when the metal center is electron rich [2].

Protonation of thiolato complexes has been reported to give complexes containing thiol as a ligand, but in most cases the product thiol complexes were not isolated [1a–d]. The reactions between thiolato complexes and alkyl halides usually give complexes containing thioether ligands [2,3].

The sulfur transfer reagents, RSphth where phth = phthalimide are used in organic chemistry as a source of an electrophilic 'RS^+' group [4]. The applications of such reagents in organometallic chemistry have been demonstrated [5]. When the sulfur transfer reagents were used with thiolato complexes, complexes containing disulfide ligands were obtained [6]. In some cases, the formed disulfide ligand was substituted by another ligand present in solution [7]. Also, the reaction of $[MeSSMe_2]BF_4$ with metal thiolato complexes gave complexes having monodentate organic disulfide ligands [8].

We reported that the reaction of $CpRu(PPh_3)_2SR$ (**1**) with $NOBF_4$ gave $[CpRu(PPh_3)(NO)SR]BF_4$ in which the NO^+ attacked the Ru-center. However, the reaction of the carbonyl analogs $CpRu(PPh_3)(CO)SR$ with $NOBF_4$ gave dimeric salts of the type $(\mu\text{-RSSR})[CpRu(PPh_3)(CO)]_2[BF_4]_2$ in which NO oxidized the sulfur atom of the thiolato group [9]. In this paper, the reactions of **1** with the electrophiles HBF_4, $[MeSSMe_2]BF_4$ and phthSR are reported.

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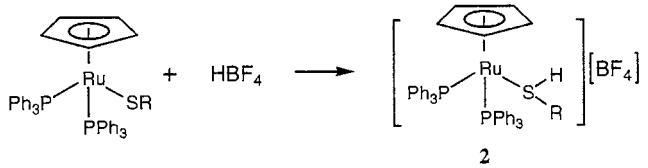
2. Results and discussion

Treatment of $CpRu(PPh_3)_2SR$ (**1**) with HBF_4 (85% in ether) gave the corresponding thiol complex salts, $[CpRu(PPh_3)_2(HSR)]BF_4$ (**2**) where R = CMe_3 (**a**), 4-C_6H_4Me (**b**), $CHMe_2$ (**c**), in very good yields (80–88%) (Eq. (1)).



2

R= CMe_3; **2a**, 4-C_6H_4Me; **2b**, $CHMe_2$; **2c**

(1)

The IR spectra of **2a–c** showed a decrease in the SH stretching frequency compared to that of the free thiols. In the ^{1}H-NMR spectra of these complexes, the chemical shift of the S*H* proton was shifted downfield relative to that of the free thiol. The peak for this proton appeared as a triplet in **2a** and **2b** due to coupling with the two equivalent phosphorus atoms. In **2c**, this peak appeared as a multiplet due to coupling with the methine proton of the isopropyl group in addition to the two equivalent phosphorus atoms.

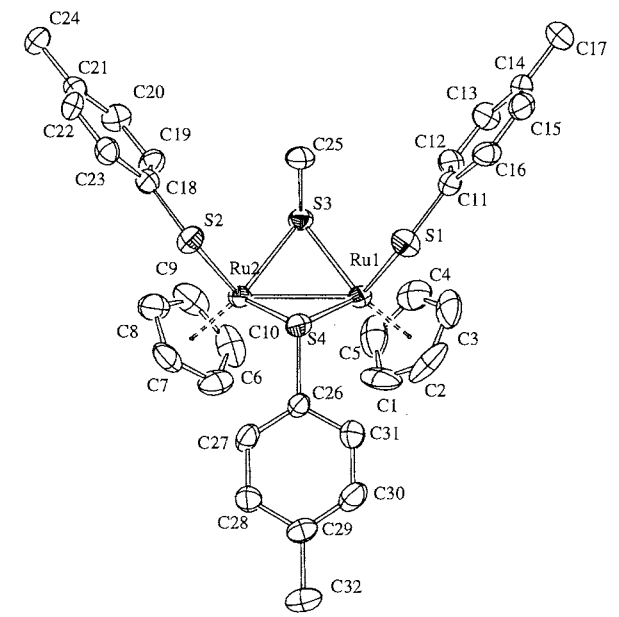
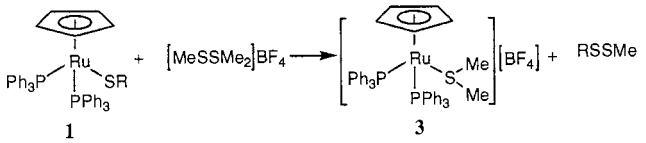


Fig. 1. An ORTEP diagram of (μ-SMe)(μ-S-4-C_6H_4Me)[CpRu(S-4-C_6H_4Me)]$_2$ (**5b**). Selected bond lengths (Å) and angles (°) are: Ru(1)–Ru(2) = 2.784(10) Ru(1)–S(1) = 2.398(3), Ru(1)–S(3) = 2.319(2), Ru(1)–S(4) = 2.325(2), Ru(2)–S(2) = 2.387(2), Ru(2)–S(3) = 2.332(2), Ru(2)–S(4) = 2.30(2), Ru(2)–Ru(1)–S(1) = 115.58(6), Ru(2)–Ru(1)–S(3) = 53.49(5), Ru(2)–S(3)–Ru(1) = 73.45(6), S(1)–Ru(1)–S(3) = 93.75(5), S(1)–Ru(1)–S(4) = 80.08(7), S(3)–Ru(1)–S(4) = 92.25(7), Ru(1)–Ru(2)–S(2) = 92.25(7), Ru(1)–Ru(2)–S(3) = 115.92(6), Ru(1)–Ru(2)–S(4) = 53.06(5), S(2)–Ru(2)–S(3) = 53.31(5), S(2)–Ru(2)–S(4) = 81.80(7), S(3)–Ru(2)–S(4) = 92.03(7), Ru(2)–S(4)–Ru(1) = 73.53(7), S(3)–Ru(1)–S(2) = 92.36(7).

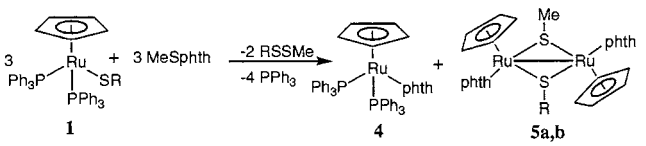
Treatment of **1** with $[MeSSMe_2]BF_4$ in THF at room temperature gave the air stable thioether complex, $[CpRu(PPh_3)_2(SMe_2)]BF_4$ (**3**) in good yields (Eq. (2)). The free alkylmethyl disulfide was detected in the ^{1}H-NMR spectra of the reaction mixture.



1 **3**

(2)

The reaction of **1** with MeSphth gave the substitution product, $CpRu(PPh_3)_2$(phth) (**4**) and the dimers (μ-SMe)(μ-SR)[CpRu(phth)]$_2$ (**5a**,**b**) according to Eq. (3). The IR spectra of **5a**,**b** showed a carbonyl band in the range 1658–1663 cm^{-1} indicative of the presence of a coordinated phthalimido ligand [10a]. Their ^{1}H-NMR spectra showed a multiplet in the aromatic region integrating for eight protons due to two phthalimido ligands. It also showed a singlet Cp-peak integrating for ten protons, while the aliphatic protons appeared as peaks in the expected region in the appropriate multiplicity and relative intensities. The free disulfide ligands, RSSMe, were detected in the ^{1}H-NMR spectra of the reaction mixtures.

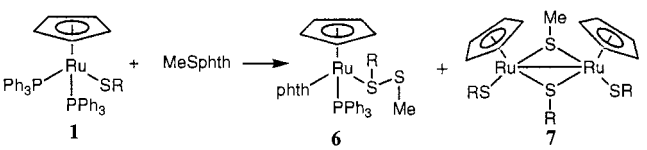


1 **4** **5a,b**

R= CMe_3 (**a**), $CHMe_2$ (**b**)

(3)

The reaction of $CpRu(PPh_3)_2$S-4-C_6H_4Me with MeSphth gave the disulfide complex **6** and the dimer **7** (Eq. (4)) together with other unidentified compounds. The IR spectrum of **6** showed a carbonyl band at 1652 cm^{-1}.



1 **6** **7**

R= 4-C_6H_4Me

(4)

The structure of **7** was determined and is shown in Fig. 1 [9]. The crstallographic data are presented in Table 1. Molecule **7** is symmetric but its mirror plane is not crystallographically required. The compound has a Ru–Ru bond length of 2.784(1) Å which is longer than the corresponding bond lengths observed in the Ru(II) trimer [10b] $[CpRuS(C_3H_7)]_3$ (average = 2.714 Å) and in [Cp*Ru(SPh)$_3$RuCp*]C1 (2.630(1) Å) (Cp* = C_5Me_5) [11]. The Ru–S_b (bridge) bond lengths (average 2.326 Å) are longer than the Ru–S_b bonds in the Ru(II)–trimer (average 2.306 Å). The terminal Ru–S

Table 1
Crystallographic data for (μ-SMe)((μ-S-4-C_6H_4Me)[CpRu(S-4-C_6H_4Me) (**7**)

Chemical formula	$C_{32}H_{34}Ru_2S_4$
Molecular weight	748.97
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.805(2)
b (Å)	13.668(3)
c (Å)	26.026(6)
α (°)	90
β (°)	108.86(2)
γ (°)	90
V (Å^3)	2964.0(12)
Z	4
D_{calc} (g cm^{-3})	1.678
F(000)	1512
Crystal size (mm)	$0.50 \times 0.13 \times 0.11$
Reflections measured	5588
Unique reflections	5223
[a]R_1 ($I > 2\sigma(I)/a11$)	0.0501/0.1056
[b]wR_2 ($I/2\sigma(I)/a11$)	0.1038/0.1213

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w[(F_o^2 - F_c^2)]^2]/\Sigma[w(F_o^2)^2\}^{1/2}$.

bond lengths (2.398(3), 2.391(3) Å) are similar to those observed in complexes of the type $CpRu(PPh_3)(CO)E$, where $E = SSCHMe_2$ (2.393(3) Å) [12], $SSSC_3H_7$ (2.370(2) Å) [12], $SS(O)CHMe_2$ (2.379(2) Å) [13], $SS(O)CH_2Ph$ (2.377(3) Å) [14] and $SS(O)_2$-4-C_6H_4Me (2.383(2) Å) [13].

The electrophiles HBF_4 and $[MeSSMe_2]BF_4$ attack the sulfur atoms of **1** to give the thiol (**2**) and thioether (**3**) complex salts, respectively; the later being formed by ligand substitutions of the disulfides MeSSR by the Me_2S present in solution. The electrophilic MeS^+ species of MeSphth can attack the sulfur lone pairs of **1** as shown by the presence of MeSSR. However presence of the MeS^- ligand attached to the ruthenium atoms of **5** and **7** shows that it can also attack the metal atom.

3. Experimental

All experiments were performed under nitrogen using vacuum line and Schlenk techniques. THF and hexanes were refluxed over Na–benzophenone and distilled under nitrogen just prior to use. Methylene chloride was refluxed over phosphorus pentoxide and distilled under nitrogen. Deuterated solvents (Isotec) were used as received. The ruthenium thiolates $CpRu(PPh_3)_2SR$ [15] and methylthiophthalimide [16] were all prepared according to published procedures. The salt $[MeSSMe_2]BF_4$ (Aldrich) was used as received.

Nuclear magnetic resonance spectra (^{1}H-NMR) were recorded on a Varian XL-300 or a JEOL-270 spectrometer. Samples were prepared under nitrogen. Chemical shifts are in ppm relative to TMS (^{1}H) or 85% H_3PO_4 (^{31}P) at 0 ppm. Infrared spectra were recorded on an Analect AQS-20 FT-IR spectrophotometer. Low resolution mass spectra were measured on a KRATOS MS25RFA mass spectrometer. High resolution mass spectra were measured on a ZAB 2F HS mass spectrometer at the McGill University Biomedical Mass Spectrometry Unit. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and were uncorrected.

3.1. General procedure for the formation of $[CpRu(PPh_3)_2(HSR)]BF_4$

In a 100 ml Schlenk flask, $CpRu(PPh_3)_2SR$ (0.25 mmol) was dissolved in THF (20.0 ml) and $HBF_4 \cdot Et_2O$ (0.052 ml, 0.30 mmol) was added. The reaction mixture was stirred for 30 min. The yellow precipitate that formed was isolated by the removal of the mother liquor with a syringe. The precipitate was washed with hexanes (3×5.0 ml) and recrystallized from methylene chloride–hexanes to give the analytically pure products.

3.1.1. $[CpRu(PPh_3)_2(HSCMe_3)]BF_4$ (**2a**)

Orange crystals (0.19 g, 88%). m.p.: 144–146°C. IR (KBr): $\nu_{(SH)}$ 2505(w) cm^{-1}. ^{1}H-NMR (CD_2C1_2): δ 1.39 (s, 9H, C(CH_3), 2.60 (t, 1H, S*H*), 4.69 (s, 5H, Cp), 6.95 (m, 12H, PPh_3), 7.40 (m, 18H, PPh_3). Anal. Calc. for $C_{45}H_{45}BF_4P_2RuS$: C, 62.28; H, 5.23; S, 3.69. Found: C, 61.86; H, 5.20; S, 3.34%.

3.1.2. $[CpRu(PPh_3)_2(HSCHMe_2)]BF_4$ (**2b**)

Orange crystals (0.18 g, 81%). m.p.: 185–187°C. IR (KBr): $\nu_{(SH)}$ 2512(w) cm^{-1}. ^{1}H-NMR (CD_2C1_2): δ 1.32 (d, 6H, CH(CH_3)$_2$), 2.72 (septet, 1H, C*H*(CH_3)$_2$), 2.93 (m, 1H, S*H*), 4.62 (s, 5H, Cp), 6.95 (m, 12H, PPh_3), 7.22 (m, 18H, PPh_3). Anal. Calc. for $C_{44}H_{43}BF_4P_2RuS$: C, 61.90; H, 5.08; S 3.76. Found: C, 61.71; H, 5.34; S, 4.12%.

3.1.3. $[CpRu(PPh_3)_2(HS\text{-}4\text{-}C_6H_4Me)]BF_4$ (**2c**)

Yellow air sensitive crystals, that decomposed during elemental analysis (0.20 g, 80%). m.p.: 138–140°C. IR (KBr): $\nu_{(SH)}$ 2514(w) cm^{-1}. ^{1}H-NMR (CD_2C1_2): δ 2.38 (s, 3H, 4-$C_6H_4CH_3$), 4.44 (s, 5H, Cp), 4.93 (t, 1H, S*H*), 6.92 (m, 16H, PPh_3, $C_6H_4CH_3$), 7.21 (m, 18H, PPh_3). Anal. Calc. for $C_{48}H_{43}BF_4P_2RuS$: C, 63.92; H, 4.80; S, 3.55. Found: C, 56.40; H, 4.25; S, 3.55%.

3.2. $[CpRu(PPh_3)_2SMe_2]BF_4$ (**3**)

In a 100 ml Schlenk flask, $CpRu(PPh_3)_2SR$ (0.25 mmol) was dissolved in THF (10.0 ml). The salt $[MeSSMe_2]BF_4$ (0.055 g, 0.28 mmol) was added and the

resulting mixture was stirred for 3 h. The yellow precipitate was isolated by removal of the mother liquor with a syringe. The precipitate was washed with hexanes (3×5.0 ml) and recrystallized from methylene chloride–hexanes to give yellow crystals. Yields 85% (R = CMe_3); 70% (R = 4-C_6H_4Me); 80% (R = $CHMe_2$). m.p.: 181–183°C. ^{1}H-NMR (CD_2C1_2): δ 2.26 (s, 6H, CH_3), 4.47 (s, 5H, Cp), 7.03 (m, 12H, PPh_3), 7.38 (m, 18H, PPh_3). Anal. Calc. for $C_{43}H_{41}BF_4P_2RuS$: C, 61.50; H, 4.92; S, 3.82. Found: C, 61.17; H, 4.91; S, 3.99%.

3.2.1. $CpRu(PPh_3)_2(phth)$ (4)

In a 100-ml Schlenk flask **1a** or **1b** (0.65 mmol) was dissolved in THF (30.0 ml). MeSphth (0.13 g, 0.65 mmol) was added as a solid. The resulting mixture was stirred at room temperature (r.t.) for 2 days. The volume was concentrated to 3.0 ml under vacuum and the concentrate placed on an alumina column (2×30 cm). Elution with hexanes removed PPh_3. Elution with THF in hexanes (1:2) gave a yellow fraction, which was collected and reduced to 15.0 ml and cooled to 0°C overnight. Yellow crystals of **4** are formed. Yields 78% (R = CMe_3); 84% (R = $CHMe_2$). m.p.: 126–127°C. IR (KBr): $\nu_{(CO)}$ 1651(s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 4.32 (s, 5H, Cp), 7.15 (m, 34H, PPh_3, C_6H_4). Anal. Calc. for $C_{49}H_{39}NO_2P_2Ru$: C, 70.32; H, 4.70; N, 1.67; Found: C, 69.52; H, 5.16; N, 1.63%. A red fraction was collected by eluting the column with THF in hexanes (2:1). Recrystallization of the crude solid from methylene chloride–hexanes gave red crystals of **5a** where R = CMe_3 or **5b** where R = $CHMe_2$ (see below).

3.2.2. (μ-SMe)(μ-$SCMe_3$)[CpRu(phth)]$_2$ (5a)

Yield (0.70 g, 43%). m.p.: 162–164°C. IR (KBr): $\nu_{(CO)} = 1658$(s) cm^{-1}. ^{1}H-NMR ($CDC1_3$): δ 1.90 (s, 9H, C(CH_3), 3.44 (s, 3H, SCH_3), 5.22 (s, 10H, Cp), 7.41 (m, 4H, C_6H_4), 7.47 (m, 4H, C_6H_4). Anal. Calc. for $C_{31}H_{30}N_2O_4Ru_2S_2$: C, 48.92; H, 3.97; N, 3.86; S, 8.68. Found: C, 49.00; H, 4.12; N, 3.51; S, 8.16%.

3.2.3. (μ-SMe)(μ-$SCHMe_2$)[CpRu(phth)]$_2$ (5b)

Yield (0.05 g, 31%). m.p.: 171–173°C. IR (KBr): $\nu_{(CO)} = 1663$(s) cm^{-1}. ^{1}H-NMR (CD_2C1_2): δ 1.98 (d, 6H, CH(CH_3)$_2$), 3.25 (septet, 1H, CH(CH_3)$_2$), 3.39 (s, 3H, SCH_3), 5.17 (s, 10H, Cp), 7.48 (m, 8H, C_6H_4). Anal. Calc. for $C_{30}H_{28}N_2O_4Ru_2S_2$: C, 48.23; H, 3.78; N, 3.75; S, 8.58. Found: C, 48.09; H, 3.73; N, 3.33; S, 6.98%.

3.2.4. $CpRu(PPh_3)(phth)(MeSS–4-C_6H_4Me)$ (6)

In a 100 ml Schlenk flask, $CpRu(PPh_3)_2$S-4-C_6H_4Me (0.50 g, 0.62 mmol) was dissolved in THF (30.0 ml) and MeSphth (0.14 g, 0.68 mmol) was added. The resulting mixture was stirred at r.t. for 6 days. The volume was concentrated to 3.0 ml under vacuum and placed on an alumina column (2×30 cm). Elution with hexanes removed PPh_3. The ^{1}H-NMR spectrum of the residue from the orange band demonstrated the presence of two compounds. Elution with THF in hexanes (1:2) gave an orange fraction, which was collected and stripped to dryness. Elution with THF in hexanes (2:1) gave a red fraction whose ^{1}H-NMR spectrum revealed the presence of several unidentified compounds; this band was discarded. The orange product was redissolved in THF and was chromatographed on another alumina column (1×20 cm). Elution with THF in hexanes (1:5) gave a yellow band, which was collected and reduced to 10 ml. Storage at 0°C overnight gave **6** as a yellow solid (23.0 mg, 15%). m.p.: 97–99°C. IR (KBr): $\nu_{(CO)} = 1652$(s) cm^{-1}. ^{1}H-NMR (C_6D_6): δ 2.02 (s, 3H, 4-$C_6H_4CH_3$), 2.15 (s, 3H, CH_3), 4.33 (s, 5H, Cp), 6.94 (d, 2H, $C_6H_4CH_3$), 6.95 (d, 2H, $C_6H_4CH_3$), 6.97 (m, 8H, PPh_3, C_6H_4), 7.45 (m, 11H, PPh_3, C_6H_4). Mass spectrum (FAB in NBA): m/e 744 ($M^{\bullet+}$), 598 ($M^{\bullet+}$ − phth), 428 ($M^{\bullet+}$ − (phth + $MeSSC_6H_4Me$)), 166 ($M^{\bullet+}$ − (phth + $MeSSC_6H_4Me$ + PPh_3)). High resolution mass spectrum (FAB, Glycerol) for $C_{39}H_{34}O_2NS_2P$ ^{102}Ru: 746.0892100 (Calc.: 746.0890342). Elution with THF in hexanes (1:2) gave a red fraction, which was collected and stripped to dryness. Recrystallization from methylene chloride–hexanes gave red crystals of **7** (see below).

3.2.5. (μ-SMe)(μ-S-4-C_6H_4Me)[$CpRu$(S-4-C_6H_4Me)]$_2$ (7)

Yield (30.0 mg. 10%). m.p.: 160–162°C. ^{1}H-NMR (CD_2C1_2): δ 1.79 (s, 3H, $C_6H_4CH_3$), 2.22 (s, 6H, $C_6H_4CH_3$), 2.33 (s, 3H, CH_3), 5.05 (s, 10H, Cp), 6.85 (d, 2H, $C_6H_4CH_3$), 7.10 (d, 2H, $C_6H_4CH_3$), 7.30 (m, 8H, $C_6H_4CH_3$). Mass spectrum (FAB in NBA): m/e 750 ($M^{\bullet+}$), 627 ($M^{\bullet+}$ − SC_6H_4Me), 504 ($M^{\bullet+}$ − 2(SC_6H_4Me)),489 ($M^{\bullet+}$ − (2(SC_6H_4Me) + Me)), 289 ($M^{\bullet+}$(CpRu + 2(SC_6H_4Me) + SMe)). High resolution mass spectrum (FAB, Glycerol) for $C_{32}H_{34}O_2NS_4$ $^{102}Ru_2$: 750.9707100 (Calc.: 750.9708586).

3.3. Crystallographic analysis

Data for the rod shaped crystals of **7** were measured on an Rigaku AFC65 diffractometer using Mo–K_α radiation and ω scan mode. The structure was solved by the Patterson method and expanded using d4map synthesis. Refinement was on F^2 using SHELXL 96. The assignment of the space group was confirmed by the program PLATON, this was also used in the verification of possible voids and missed symmetry. All non-hydrogen atoms were refined anisotropically, hydrogen atoms are isotropic and were introduced at calculated positions. Final agreement factors and other details are given in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with Cambridge Crystallographic Data Center, CCDC no. 132 173 for **7**. Copies of the information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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