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Dimeric rhodium(III), iridium(III) and ruthenium(II) thiosalicylate complexes

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Abstract

Reactions of the chloride-bridged dimers $[LMCl(\mu\text{-}Cl)]_2$ (M = Rh, Ir; L = Cp* = η^5-C_5Me_5; M = Ru, L = η^6-*p*-cymene) with two mole equivalents of thiosalicylic acid ($HSC_6H_4CO_2H$, H_2tsal) and excess base gives the dimeric rhodium(III), iridium(III) and ruthenium(II) thiosalicylate complexes $[LM(tsal)]_2$. Reaction of the complex $[Cp^*RhCl_2(PPh_3)]$ with one equivalent of H_2tsal and triethylamine in dichloromethane gives a mixture of the dimer $[Cp^*Rh(tsal)]_2$ and the phosphine complex $[Cp^*Rh(tsal)(PPh_3)]$; upon recrystallisation, pure dimer is obtained. A single-crystal X-ray diffraction study on the rhodium and ruthenium dimers reveals the expected thiolate-bridged $M_2(\mu\text{-}S)_2$ unit. Electrospray mass spectrometry (ESMS) is a useful technique in studying the chemistry of the thiosalicylate complexes, all complexes giving strong $[M + H]^+$ ions. With added thiosalicylic acid, cations of the type $[(LM)_2(Htsal)_3]^+$ were detected in the mass spectra.

Keywords: Rhodium; Ruthenium; Iridium; Thiosalicylate; Electrospray mass spectrometry; Crystal structures

1. Introduction

There is interest in the coordination chemistry of deprotonated thiosalicylic acid (H_2tsal, **1**), thiosalicylate, since the combination of hard carboxylate and soft thiolate donors makes it potentially able to form complexes with a wide range of metal centres. Recently, we and others have reported complexes of platinum(II), palladium(II) and nickel(II), [1–3] and gold(III) [4] in which the thiosalicylate ligand bonds as an S,O-chelated dianion. In addition, due to the bridging ability of thiolate ligands, the sulfur atom of platinum complexes containing a chelated thiosalicylate ligand is able to act as a donor ligand towards platinum(II) [2] and mercury(II) [5], forming thiolate-bridged compounds. In other complexes, thiosalicylate is able to adopt a variety of coordination modes, ranging from monodentate S-bonded [6], through to bridging [7,8]. As a result of this coordinative versatility, we wished to investigate the synthesis of other platinum-group metal complexes with thiosalicylate ligands, and here report our studies on π-hydrocarbon complexes of rhodium(III), iridium(III) and ruthenium(II).

Some ruthenium and rhodium thiosalicylate complexes have been prepared previously, but as far as we are aware, none have been characterised crystallographically. Rhodium(III) ions form a 1:2 complex with thiosalicylic acid [9] while the dinuclear rhodium(II) complex $Rh_2(Htsal)_4(H_2tsal)(H_2O)\cdot 2.5H_2O$ was prepared by reaction of $(NH_4)_3RhCl_6$ with H_2tsal [10]. Reaction of this complex with HCl gave a material of composition $Rh(H_2tsal)_3Cl_3$, and other dinuclear derivatives were also described. Other studies include the reaction of $[Ru(Hedta)(H_2O)]$ (H_4edta = ethylenediamine tetraacetic acid) with thiosalicylic acid [11] and a mixed thiosemicarbazone-thiosalicylate ruthenium complex [12]. The related compound thiosalicylamide has been used in the gravimetric and spectrophotometric determination of rhodium, iridium and ruthenium [13]. We are unaware of any thiosalicylate complexes of rhodium, iridium and ruthenium which also contain organometallic ligands.

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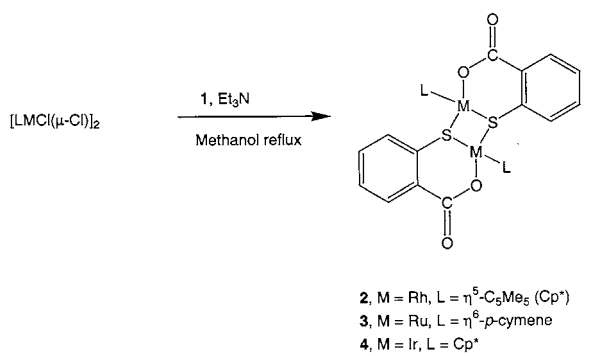
2. Results and discussion

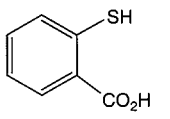
2.1. Synthesis and spectroscopic characterisation

Treatment of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ with two mole equivalents of thiosalicylic acid **1** in methanol, and triethylamine base gives the dimeric rhodium complex **2**. Which is precipitated by addition of water as red, air-stable crystals, which are soluble in dichloromethane and methanol but also have some water-solubility, giving an orange solution. In a similar fashion, reaction of the ruthenium complex $[(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)]_2$ with thiosalicylic acid and triethylamine in refluxing methanol gives the analogous complex **3**, which can be recovered in good yield as an orange microcrystalline solid by precipitation with water. The reaction with $[Cp^*IrCl(\mu\text{-}Cl)]_2$ proceeded similarly, though the complex $[Cp^*Ir(tsal)]_2$ (**4**) could only be recovered in low yield, as a bright yellow microcrystalline solid. The syntheses are summarised in Scheme 1. Complexes with M_2S_2 units formed by two bridging thiolates have been reported previously for ruthenium, e.g. from penicillamine [14] and other aliphatic thiols [15] and for rhodium [16] including complexes of the type $[Cp^*Rh(S\text{–}S)]_2$, where S–S is a bidentate dithiolate ligand such as benzene-1,2-dithiolate [17], toluene-3,4-dithiolate [18] or maleonitriledithiolate [19].

The ^{1}H-NMR spectrum of **3** showed the expected resonances due to the thiosalicylate ligand between δ 8.08 and 7.20, together with four doublet resonances for the cymene aromatic protons, with one pair [δ 4.73 and 4.71] appearing as a strong AB doublet pattern due to mutual coupling, and the other pair of doublets [δ 5.04 and 4.57] showing approximately equal intensity lines. There were also two doublet resonances due to the cymene isopropyl methyl resonances, at δ 1.10 and 0.81, but only one cymene methyl resonance at δ 1.79. The inequivalences of the cymene aromatic and isopropyl methyl groups arise because the ruthenium centre is unsymmetrical [20]. The rhodium complex **2** showed a single resonance for the methyl groups of the Cp* ligands, at δ 1.22 (^{1}H) and 8.3 (^{13}C), and the iridium complex **4** showed an analogous Me ^{1}H-NMR resonance at δ 1.25.



Scheme 1.



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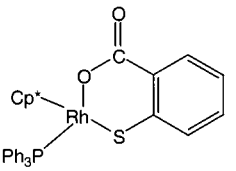

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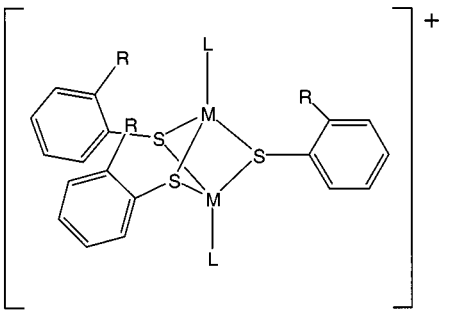
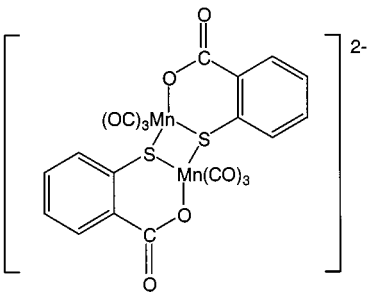


6, R = CO_2H
M = Rh, Ir, L = Cp*
M = Ru, L = *p*-cymene



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The dimeric structures appear to have appreciable stability towards cleavage of the thiolate bridges by neutral ligands, since the reaction of the ruthenium dimer **3** with a large excess of triphenylphosphine in refluxing methanol resulted only in recovery of unreacted **3**. Similarly no reaction was observed between **3** and excess CO after 5 days at room temperature, and no thiosalicylate transfer was observed between **3** and *cis*-$[PtCl_2(PPh_3)_2]$ after 3 weeks in methanol at room temperature. When the complex $[Cp^*RhCl_2(PPh_3)]$ is treated with one equivalent of thiosalicylic acid and Et_3N in dichloromethane at room temperature, a mixture of **2** and the mononuclear complex $[Cp^*Rh(tsal)(PPh_3)]$ (**5**) is obtained (as shown by ESMS), and on recrystallisation from dichloromethane–pentane, the dimer **2** was exclusively obtained. No further attempts were made to prepare mononuclear thiosalicylate complexes containing π-hydrocarbon ligands.

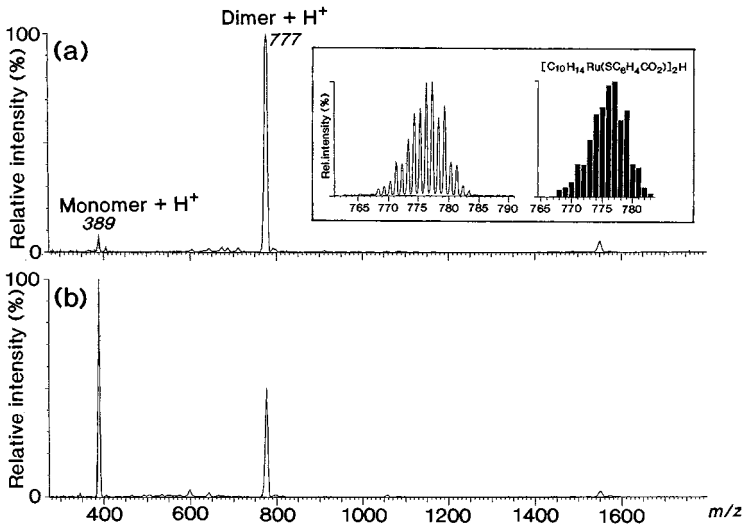

Fig. 1. Positive-ion electrospray mass spectra (in MeCN–H_2O) of the ruthenium thiosalicylate complex [(*p*-cymene)Ru(tsal)]$_2$ **3** ('dimer') at cone voltages of (a) 20 and (b) 80 V, showing the dimer to monomer fragmentation. The inset shows a comparison of experimental (left) and calculated (right) isotope patterns for the [dimer + H]$^+$ ion.

Complexes **2**–**4** give excellent ES mass spectra in positive-ion mode. At low cone voltages (20–50 V) the base peak is the $[M + H]^+$ ion (Ru, m/z 777; Rh, m/z 781; Ir, m/z 959), with excellent agreement observed between theoretical and calculated isotope distribution patterns for these ions. Weak ions due to $[2M + H]^+$, $[2M + Na]^+$, $[2M + K]^+$ etc. were also observed, particularly for the iridium complex where the spectrum was recorded in methanol. When the cone voltage is increased to ca. 80 V, the dimeric species undergo fragmentation to form the monomer, [Ru(tsal)(*p*-cymene) + H]$^+$, [Cp*Rh(tsal) + H]$^+$ and [Cp*Ir(tsal) + H]$^+$ which are the base peaks at m/z 389, 391, and 481, respectively. Fig. 1 shows the ES spectra for complex **3** at cone voltages of (a) 20 and (b) 80 V, showing the dimer to monomer fragmentation. At 100 V, the Rh complex also begins to undergo decarboxylation, as shown by the formation of a low intensity ion at m/z 347; platinum thiosalicylate complexes have been found to undergo the same behaviour at very high cone voltages [1]. The rhodium complex **2** is slightly soluble in water; after 2 weeks, the ES spectrum showed only $[\mathbf{2} + H]^+$.

Addition of thiosalicylic acid to dilute solutions of **2**–**4** in MeCN–H_2O followed by recording the positive-ion ES spectra resulted in complete disappearance of the $[M + H]^+$ ions, and formation of single new ions [Rh, m/z 935; Ru, m/z 931; Ir, m/z 1115] which are identified from the mass and isotope patterns as the tris(thiosalicylate) species $[M + H_2tsal + H]^+$ (M = **2**, **3** or **4**). These species probably contain three thiosalicylate ligands, each bridging the two metal centres by their thiolate sulfur atoms, with uncoordinated, protonated carboxylic acid groups, i.e. **6**. These species are stable up to moderate cone voltages such as 50 V, but at 70 V and higher, fragmentation occurs, giving the protonated bis-thiosalicylate species (**2**–**4**), together with some of the monomer, as observed for **2**–**4** also. Related ruthenium [(arene)Ru(μ-EPh)$_3$Ru(arene)]$^+$ (arene = *p*-cymene or C_6Me_6; E = S, Se or Te) [21] and rhodium and iridium [(Cp*M)(μ-SR)$_3$(MCp*)]$^+$ [22] cations have been reported previously.

ESMS has also been used to investigate the possibility of formation of mixed-metal thiosalicylate complexes, by exchange reactions between **2** and **4**, and between **3** and **4**. However, such reactions appear to be slow in methanol solution at room temperature, with only traces of the mixed metal Rh–Ir and Ru–Ir species being observed on standing for 2 weeks. This suggests that the dimeric structure is retained in solution, since dissociation to a monomeric species would be expected to result in metal scrambling.

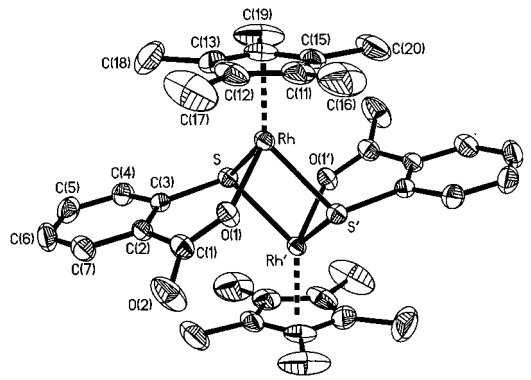

Fig. 2. Molecular structure of [Cp*Rh(tsal)]$_2$ (**2**) showing the atom numbering scheme. Thermal displacement ellipsoids are depicted at 50% probability, and hydrogen atoms have been omitted for clarity.

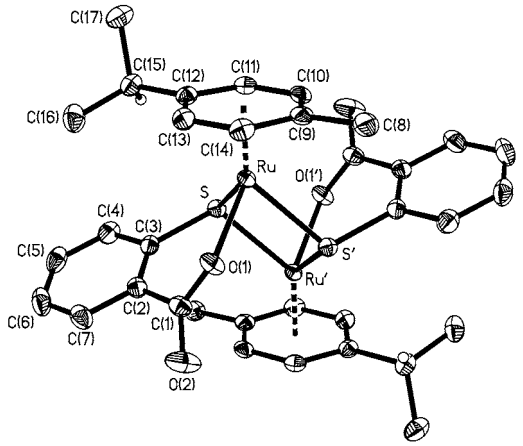

Fig. 3. Molecular structure of [(*p*-cymene)Ru(tsal)]$_2$ (**3**) showing the atom numbering scheme. Thermal displacement ellipsoids are shown at 50% probability, and all hydrogen atoms [except the isopropyl hydrogens H(15a) and H(15a)′] have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for [Cp*Rh(tsal)]$_2$ (**2**)

Rh–O(1)	2.084(2)	Rh–C(13)	2.144(4)
Rh–C(14)	2.155(4)	Rh–C(15)	2.158(4)
Rh–C(12)	2.173(4)	Rh–C(11)	2.186(4)
Rh–S	2.350(1)	Rh–S′	2.406(1)
S–C(3)	1.778(4)	S–Rh′	2.406(1)
O(1)–C(1)	1.278(4)	O(2)–C(1)	1.233(5)
C(1)–C(2)	1.511(5)	C(2)–C(3)	1.407(5)
C(2)–C(7)	1.411(5)	C(3)–C(4)	1.395(5)
C(4)–C(5)	1.380(5)	C(5)–C(6)	1.379(6)
C(6)–C(7)	1.370(6)		
O(1)–Rh–S	88.63(7)	O(1)–Rh–S′	77.97(7)
S–Rh–S′	82.68(3)	C(3)–S–Rh	103.82(12)
C(3)–S–Rh′	116.11(11)	Rh–S–Rh′	97.32(3)
C(1)–O(1)–Rh	133.1(2)	O(2)–C(1)–O(1)	121.3(4)
O(2)–C(1)–C(2)	117.2(3)	O(1)–C(1)–C(2)	121.5(3)
C(3)–C(2)–C(7)	117.8(3)	C(3)–C(2)–C(1)	125.4(3)
C(7)–C(2)–C(1)	116.7(3)	C(4)–C(3)–C(2)	119.7(3)
C(4)–C(3)–S	115.0(3)	C(2)–C(3)–S	125.3(3)
C(5)–C(4)–C(3)	120.9(4)	C(4)–C(5)–C(6)	119.9(4)
C(7)–C(6)–C(5)	120.2(4)	C(6)–C(7)–C(2)	121.5(4)

2.2. Crystal structure determinations

Single-crystal X-ray diffraction studies were carried out on the dimeric rhodium and ruthenium complexes **2** and **3**; the molecular structures are shown in Figs. 2 and 3, respectively. Selected bond lengths and angles for the structures are given in Table 1 (**2**) and Table 2 (**3**). Both complexes have a distorted octahedral ('bar-stool') metal coordination geometry, and overall pay a strong resemblance to the formally isoelectronic dimeric manganese(I) carbonyl complex **7**, in which the π-hydrocarbon ligand is replaced by three CO ligands [8], and to the related complexes [Cp*Rh(SC_6H_4S)]$_2$ [17] and [Cp*Rh{SC(CN)C(CN)S}]$_2$ [19]. The thiosalicylate ligand is coordinated such that it forms a six-membered ring, bonded through the thiolate sulfur and one of the carboxylate oxygens. The thiolate sulfurs then bridge to the other metal centres, forming the dimer containing a M–S–M–S four-membered ring core.

As with other complexes containing chelating thiosalicylate ligands [1] the metal-thiosalicylate ring system of **2** is folded, predominantly at the rhodium and the carboxylate, as seen from the obtuse Rh–O(1)–C(1) bond angle of 133.1(2)°, with the carboxylate group twisted by 31.4(5)° from the plane of the phenyl group. The thiolate sulfur is unequally coordinated to the two rhodium atoms, as seen in the different Rh–S bond lengths [Rh–S 2.350(1) compared to Rh–S′ 2.406(1) Å]. These bond lengths are comparable with those in the related complexes [Cp*Rh(S-S)]$_2$ [S–S = maleonitriledithiolate, 2.350(2) and 2.414(2) Å [19]; S–S = benzene-1,2-dithiolate, 2.356(1) and 2.401(1) Å [17]]. A similar asymmetric bridging coordination has been observed for platinum thiosalicylate complexes coordinated to platinum [2] or mercury [5]. The Rh–S–Rh′ bond angle of 97.32(3)° is comparable with that of the manganese analogue **7** [Mn-S-Mn' 96.56(4)°] [8], as are the S–M–S′ bond angles [82.68(3)° for S–Rh–S′ compared to 83.44(4)° for S–Mn–S′] and the O–M–S bond angles [88.63(7)° for the rhodium complex and 88.2(7)° for the manganese analogue]. The M–S bonds for both the rhodium and manganese complexes are, surprisingly, identical [Rh–S 2.350(1) and Mn–S 2.351(1) Å; Rh–S′ 2.406(1) and Mn–S′ 2.406(1) Å]. However, the M-O bonds for the two complexes differ slightly [Rh–O 2.084(2) versus Mn–O 2.031(2) Å]. The significant difference between these two complexes is that the Mn complex is charged, while the Rh complex is neutral.

Overall, the molecular geometry of the isoelectronic ruthenium complex **3** is very similar to the rhodium

Table 2
Selected bond lengths (Å) and angles (°) for [(*p*-cymene)Ru(tsal)]$_2$ (**3**)

Ru–O(1)	2.0930(12)	Ru–C(11)	2.1648(17)
Ru–C(10)	2.1760(17)	Ru–C(13)	2.2187(17)
Ru–C(14)	2.2274(17)	Ru–C(12)	2.2313(17)
Ru–C(9)	2.2637(17)	Ru–S	2.3848(4)
Ru–S′	2.4177(4)	S–C(3)	1.7831(18)
S–Ru′	2.4177(4)	O(1)–C(1)	1.288(2)
O(2)–C(1)	1.230(2)	C(1)–C(2)	1.513(3)
C(2)–C(3)	1.402(3)	C(2)–C(7)	1.404(3)
C(3)–C(4)	1.406(2)	C(4)–C(5)	1.387(3)
C(5)–C(6)	1.387(3)	C(6)–C(7)	1.390(3)
O(1)–Ru–S	87.80(4)	O(1)–Ru–S'	77.80(4)
S–Ru–S′	80.714(15)	C(3)–S–Ru	104.54(6)
C(3)–S–Ru′	112.48(6)	Ru–S–Ru′	99.286(15)
C(1)–O(1)–Ru	134.03(12)	O(2)–C(1)–O(1)	122.40(17)
O(2)–C(1)–C(2)	118.15(16)	O(1)–C(1)–C(2)	119.32(15)
C(3)–C(2)–C(1)	124.25(16)	C(3)–C(2)–C(7)	118.44(17)
C(7)–C(2)–C(1)	117.31(17)	C(2)–C(3)–C(4)	119.80(17)
C(2)–C(3)–S	123.70(14)	C(4)–C(3)–S	116.48(14)
C(5)–C(4)–C(3)	120.57(19)		

complex **2**, with comparable bond lengths. For example, the Ru–O(1) bond length [2.093(1) Å] is similar to the Rh–O(1) bond length [2.084(2) Å]. The ruthenium does not bond equidistantly to the π-hydrocarbon ligand, with the Ru–C bond lengths ranging from 2.165(2) Å for Ru–C(11) to 2.264(4) Å for Ru–C(9). Steric interactions with the thiosalicylate ligand are the likely cause of the longer Ru–C(9) bond. The ruthenium lies almost directly under the centre of the cymene ring.

The primary difference between the geometries of the Rh and Ru complexes is the inclination angle of the thiosalicylate ligand. With the plane of the π-hydrocarbon ligand as a reference, the angle of inclination of the thiosalicylate phenyl ring can be determined. The inclination angle for the Rh complex is 12.2(3)°, whereas for the Ru complex it is much larger, at 23.1(1)°. This also shows in the twisting of the carboxylate group from the plane of the phenyl group, 41.7(3)° for the ruthenium and 31.4(5)° for the rhodium complex. Steric interactions between the π-hydrocarbon and thiosalicylate ligands may be the cause of these differences, although the intramolecular contacts between the atoms of either the Cp* or *p*-cymene and thiosalicylate ligands are quite long [closest contacts: Rh complex 3.362(7) Å for C(20)···C(2′) and Ru complex 3.435(4) Å for C(10)···C(3′)]. The *p*-cymene ligand of **3** may provide less steric hindrance, as it only has two substituents (Me and Pr^i) (in contrast to the fully substituted Cp* ligand), allowing the thiosalicylate to fit into a pocket of reduced steric interaction.

Overall the conformation of the $tsal^{2-}$ ligand in these complexes fits the pattern established for the nickel(II), palladium(II) and platinum(II) complexes [2] which showed that the ligand adapts readily to steric constraints by folding about the S···O atoms by varying the M–O–C angle, and by twisting of the carboxylate group from the plane of the rest of the ligand.

3. Experimental

3.1. General experimental procedures

Electrospray mass spectra were recorded on a VG Platform II instrument with nitrogen as the nebulising and drying gas, and identification of ions was aided by comparison of experimental and theoretical [23] isotope distribution patterns. NMR spectra were recorded on a Bruker AC300P instrument (^{1}H, 300.133 MHz, ^{13}C 75.47 MHz) in $CDCl_3$, and IR spectra were recorded on a Perkin–Elmer 1600 series instrument as KBr disks. Melting points (m.p.s) were recorded using a Reichert–Jung hotstage apparatus, and are uncorrected.

The complexes $[Cp^*RhCl(\mu\text{-}Cl)]_2$ [24], [(*p*-cymene)$RuCl(\mu\text{-}Cl)]_2$ [25], $[Cp^*RhCl_2(PPh_3)]$ [24] and $[Cp^*IrCl(\mu\text{-}Cl)]_2$ [26] were prepared according to the literature procedures. Triphenylphosphine (Pressure Chemical Co.), and thiosalicylic acid (Sigma) were used as supplied. Reactions were carried out in LR grade methanol without further purification, and without exclusion of air. Petroleum spirits refers to the fraction of boiling point 60–80°C, and was used as supplied, while dichloromethane was distilled from calcium hydride prior to use.

3.2. Synthesis of $[Cp^*Rh(tsal)]_2$ (2)

A mixture of the complex $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (300 mg, 0.484 mmol) and thiosalicylic acid (150 mg, 0.974 mmol) in methanol (7 ml) with triethylamine (10 drops, excess) was refluxed for 10 min., giving a clear red–orange solution. Water (70 ml) was added, giving red–orange microcrystals. The mixture was allowed to stand at room temperature (r.t.) for 3 days, and the product filtered, washed with water (5 ml) and diethyl ether (5 ml) and dried in vacuo to give **2** as a red–orange microcrystalline solid (220 mg, 58%). Crystals of suitable quality for an X-ray diffraction study were grown by vapour diffusion of pentane into a dichloromethane solution of the complex at 4°C. M.p.(dec.) >280°C. Found: C, 51.5; H, 4.6. $C_{34}H_{38}O_4S_2Rh_2$ requires C, 52.3; H, 4.9%. ESMS (positive-ion, $MeCN–H_2O$, cone voltage 20 V) $[M+H]^+$ m/z 781 (100%); cone voltage 80 V, $[Cp^*Rh(tsal)+H]^+$ m/z 391 (100%), $[M+H]^+$ m/z 781 (70%). NMR: ^{1}H, δ 8.3–7.1 (m, 8H, Ph), 1.22 (s, 30H, Me); ^{13}C-{^{1}H}, δ 170.1 (s, CO_2), 138.8 (s, C of Ph), 134.6 (s, CH of Ph), 134.4 (s, C of Ph), 133.6 (s, CH of Ph), 128.6 (s, CH of Ph), 127.8 (s, CH of Ph), 95.5 [d, C of Cp*, ^1J(RhC) 7.0], 8.3 (s, Me of Cp*).

3.3. Synthesis of [(p-cymene)Ru(tsal)]$_2$ (3)

[(*p*-cymene)$RuCl(\mu\text{-}Cl)]_2$ (600 mg, 0.99 mmol) and thiosalicylic acid (305 mg, 1.98 mmol) were suspended in methanol (20 ml) and triethylamine (2 ml) added. The resulting deep red solution was refluxed for 30 min. Water (70 ml) was added and the mixture cooled to r.t., resulting in the deposition of orange microcrystals. After standing for 2 days, the product was filtered, washed with water (10 ml), petroleum spirits (10 ml) and dried under vacuum, to give 627 mg of **2** (82% yield). M.p.(dec.) >260°C. The product is soluble in dichloromethane and chloroform, sparingly soluble in diethyl ether, but insoluble in water. ESMS (positive-ion, $MeCN–H_2O$, cone voltage 20 V), [Ru(tsal)(cymene) + H]$^+$ m/z 389 (8%), $[M+H]^+$ m/z 777 (100%), $[2M+H]^+$ m/z 1552 (5%). Cone voltage 80 V, [Ru(tsal)(cymene) + H]$^+$ m/z 389 (100%), $[M+H]^+$ m/z 777 (50%), $[2M+H]^+$ m/z 1552 (2%). NMR: ^{1}H, δ 8.08 [d, 1H, Ph of tsal, J(HH) 7.7], 7.62 [d, 1H, Ph of tsal, J(HH) 7.7], 7.31 [t, 1H, Ph of tsal, J(HH) 7.5],

Table 3
Crystal data and structure refinement for [Cp*Rh(tsal)]$_2$ (**2**) and [(*p*-cymene)Ru(tsal)]$_2$ (**3**)

	2	**3**
Empirical formula	$C_{34}H_{38}O_4Rh_2S_2$	$C_{34}H_{36}O_4Ru_2S_2$
Formula weight	780.60	774.89
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
[3]Unit cell dimensions		
a (Å)	11.3821(2)	9.6046(1)
b (Å)	10.2707(2)	12.8655(2)
c (Å)	13.4726(2)	12.4167(1)
β (°)	99.658(1)	105.819(1)
Volume (Å^3)	1552.65(5)	1476.20(3)
Z	4	2
Density (calculated) (g cm^{-3})	1.670	1.743
Crystal size (mm)	$0.28\times0.20\times0.07$	$0.40\times0.18\times0.07$
θ Range for data collection (°)	2.17–28.21	2.20–28.21
Reflections collected	9585	9217
Independent reflections	3443 [R_{int} 0.0288]	3301 [R_{int} 0.0161]
Absorption coefficient (mm^{-1})	1.235	1.204
Maximum transmission	0.9186	0.9205
Minimum transmission	0.7238	0.6445
F(000)	772	784
Data/restraints/parameters	3443/0/195	3301/0/194
Goodness-of-fit on F^2	1.087	1.029
Final R indices [$I>2\sigma(I)$]		
R_1	0.0340	0.0186
wR_2	0.0738	0.0471
R indices (all data)		
R_1	0.0508	0.0221
wR_2	0.0811 [a]	0.0482 [b]
Largest difference peak (e Å^{-3})	0.605	0.365
Largest difference hole (e Å^{-3})	−0.601	−0.380

[a] $w=1/[\sigma^2(F_o^2)+(0.0299P)^2+2.3859P]$ where $P=(F_o^2+2F_c^2)/3$.
[b] $w=1/[\sigma^2(F_o^2)+(0.0245P)^2+0.7557P]$ where $P=(F_o^2+2F_c^2)/3$.

7.23 [t, 1H, Ph of tsal, J(HH) 7.7], 5.04 [d, 1H, CH of cymene aromatic ring, J(HH) 5.9], 4.73 [d, AB pattern, 1H, CH of cymene aromatic ring, J(HH) 5.8], 4.71 [d, AB pattern, 1H, CH of cymene aromatic ring, J(HH) 5.8], 2.51 [hept., 1H, C**H**Me$_2$ of cymene, J(HH) 6.9], 1.79 [s, 3H, Me of cymene], 1.10 [d, 3H, CHMe$_A$ of cymene, J(HH) 6.9], 0.81 [d, 3H, CHMe$_B$ of cymene, J(HH) 6.9].

Crystals suitable for a single-crystal X-ray diffraction study were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex at 4°C. Found: C, 52.6; H, 4.65; N, 0.0. $C_{34}H_{36}O_4Ru_2S_2$ requires C, 52.7; H, 4.7; N, 0.0%

3.4. Synthesis of [Cp*Ir(tsal)]$_2$ (4)

A mixture of [Cp*IrCl(μ-Cl)]$_2$ (300 mg, 0.377 mmol) and thiosalicylic acid (116 mg, 0.753 mmol) in methanol (10 ml) with triethylamine (10 drops, excess) was refluxed for 30 min, to give a cloudy yellow solution. Water (60 ml) was added, giving a clear yellow solution, which on standing at r.t. for 1 week deposited yellow microcrystals. These were filtered, washed with water (10 ml) and petroleum spirits (10 ml) and dried in vacuo. Yield 53 mg (15%). Found: C, 42.5; H, 3.9; N, 0.0. $C_{34}H_{39}Ir_2O_4S_2$ requires C, 42.6; H, 4.0; N, 0.0%. M.p.(dec.) >290°C. ESMS (MeOH, cone voltage 50 V), $[M+H]^+$ (m/z 959, 100%), $[M+Na]^+$ (m/z 981, 27%), $[M+K]^+$ (m/z 997, 16%), $[2M+Na]^+$ (m/z 1941, 20%), $[2M+K]^+$ (m/z 1957, 7%). ^{1}H-NMR, δ 8.3–7.1 (m, 4H, Ph), 1.25 (s, 15H, Me of Cp*).

3.5. Reaction of [Cp*RhCl$_2$(PPh$_3$)] with thiosalicylic acid

To the rhodium complex (50 mg, 0.088 mmol) and thiosalicylic acid (13.5 mg, 0.088 mmol) in dichloromethane (5 ml) was added triethylamine (5 drops) and the mixture stirred at r.t. for 10 min to give a red–orange solution. Petroleum spirits (60 ml) was added, to give an orange precipitate, which was filtered and dried, yield 35 mg. ESMS showed a mixture of [Cp*Rh(tsal)]$_2$ (**2**) and [Cp*Rh(tsal)(PPh$_3$)] (**5**). Recrystallisation from dichloromethane–pentane gave red crystals of **2**.

3.6. Attempted reaction of 3 with PPh$_3$

The ruthenium dimer **3** (100 mg) and triphenylphosphine (300 mg) in methanol (20 ml) was refluxed for 30 min to give an orange solution. Addition of water (60 ml) gave a light orange precipitate, which was allowed to stand overnight, filtered, and the solid washed with water (10 ml) and diethyl ether (2×20 ml) to remove PPh$_3$. The orange microcrystals (92 mg) were identified as unreacted **2** by ESMS.

3.7. Exchange reactions

Approximately equimolar amounts (ca. 0.1 mg) of complexes **2** and **4**, and in a separate experiment, **3** and **4**, were dissolved in methanol (1 ml), and the ES spectrum recorded. The solutions were allowed to stand at r.t. for 2 weeks and the extent of exchange determined from the ES spectrum.

3.8. X-ray crystal structure determinations

Data for both structures were collected on a Siemens SMART CCD diffractometer, using Mo–K$_\alpha$ radiation ($\lambda=0.71073$ Å) at 203(2) K, and an absorption correction applied [27]. Both structures were solved by Patter-

son methods and refined routinely against F^2 with non-hydrogen atoms anisotropic and hydrogen atoms included in calculated positions. Table 3 summarises the data collection, solution and final refinement details for both structures. The SHELX-97 suite of programs were used [28].

4. Supplematary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC 150413 for compound **2**, and CCDC no. 150414 for compound **3**. Copies of this information may 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 http://www.ccdc.cam.ac.uk).

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