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Coordination chemistry of the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ metalloligand with π-hydrocarbon derivatives of d^6 ruthenium(II), osmium(II), rhodium(III) and iridium(III)

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Abstract

The reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards $[RuCl_2(\eta^6\text{-arene})]_2$ (arene = C_6H_6, C_6Me_6, p-$MeC_6H_4Pr^i$ = p-cymene), $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and $[MCl_2(\eta^5\text{-}C_5Me_5)]_2$ (M = Rh, Ir) have been probed using electrospray ionisation mass spectrometry. In all cases, dicationic products of the type $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ML]^{2+}$ (L = π-hydrocarbon ligand) are observed, and a number of complexes have been prepared on the synthetic scale, isolated as their BPh_4^- or PF_6^- salts, and fully characterised. A single-crystal X-ray structure determination on the Ru p-cymene derivative confirms the presence of a pseudo-five-coordinate Ru centre. This resists addition of small donor ligands such as CO and pyridine. The reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $RuClCp(PPh_3)_2$ (Cp = η^5-C_5H_5) gives $[Pt_2(\mu\text{-}S)_2(PPh_3)_4RuCp]^+$. In addition, the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the related carbonyl complex $[RuCl_2(CO)_3]_2$, monitored by electrospray mass spectrometry, gives $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)_3Cl]^+$.

Keywords: Mixed-metal complexes; Sulfide ligands; Electrospray mass spectrometry; Platinum complexes; Organometallic complexes

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1. Introduction

The sulfide-bridged dinuclear complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) contains highly nucleophilic sulfur atoms, and coordinates to a wide range of metal centres, ranging from main group and transition metals [1,2] to the actinide metal uranium [3]. One of our interests in this field of chemistry is to apply the technique of electrospray ionisation mass spectrometry (ESMS) to target subsequent chemical syntheses. ESMS ionisation is a soft ionisation technique, applied to the analysis of the solution phase, and, like all mass spectrometric techniques, requires only a minuscule amount of sample for analysis [4]. Using this methodology, we have probed the coordination chemistry (giving trimetallic sulfide-bridged aggregates) of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with a range of metals such as tin(IV) [5], gold(III) [5], mercury(II) [5], vanadium(V) [3], uranium(VI) [3] and nickel(II) [6]. We have also extended this technique to the analogous selenide complex $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ [7,8].

In this paper, we describe studies into the formation of sulfide-bridged aggregates of d^6 metals ruthenium(II), osmium(II), rhodium(III) and iridium(III), where the metal also bears a π-hydrocarbon ligand such as an η^6-arene or η^5-pentamethylcyclopentadienyl. Such "piano-stool" derivatives of the $\{Pt_2S_2\}$ core have not been described previously, and thus they extend the range of metal aggregates formed by the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ metalloligand. Furthermore, the reaction of $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ with $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ (and a variety of other metal–halide substrates) resulted in metal scrambling, giving compounds with $\{PtM_2(\mu\text{-}Se)_2\}$ cores [7], and so it is of interest to explore a range of derivatives of the $\{Pt_2S_2\}$ core to see if metal scrambling can also occur in this system.

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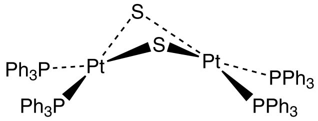
It is worth noting that a number of derivatives of **1** (and closely related analogues) with rhodium and iridium in the +I (as opposed to +III) oxidation state have been synthesised previously, including $[Pt_2(\mu\text{-}S)_2(PPh_3)_4RhL_2]^+$ (L_2 = cyclo-octa-1,5-diene; L = CO, C_2H_4, 2,6-$Me_2C_6H_3NC$) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ir(CO)(PPh_3)]^+$ [9,10]. The ruthenium(II) derivative $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(PPh_3)_2Cl]^+$, synthesised from $RuCl_2(PPh_3)_3$ and **1**, is also known [11], but this represents a rare example of a d^6 metal adduct of the d^8–d^8 $\{Pt_2S_2\}$ core, which forms numerous adducts with other d^8 and d^{10} metals [1]. A different approach by Hidai and coworkers [12] has produced complexes such as the sulfido-bridged $[(Ph_3P)_2Pt(RuC_5Me_5)_2(\mu\text{-}S)_2(\mu\text{-}SPr^i)_2]$. No osmium derivatives of the $\{Pt_2S_2\}$ core have been reported to date, although the related $\{Os_2PtS_2\}$ sulfido aggregate $[\{Os(N)(CH_2SiMe_3)_2\}_2(\mu\text{-}S)_2Pt(Ph_2PCH_2CH_2PPh_2)]$ (and a similar Ru complex) have been reported [13].

2. Results and discussion

2.1. Synthesis and spectroscopic characterisation

The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) reacts readily with the chloride-bridged dinuclear complexes $[RuCl_2(\eta^6\text{-arene})]_2$, $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$, $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ and $[IrCl_2(\eta^5\text{-}C_5Me_5)]_2$ in methanol to give the mixed-metal aggregates $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^6\text{-arene})]^{2+}$ (arene = *p*-cymene (**2**); C_6Me_6 (**3**); C_6H_6 (**4**)), $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Os(\eta^6\text{-}p\text{-cymene})]^{2+}$ (**5**) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4M(\eta^5\text{-}C_5Me_5)]^{2+}$ (M = Rh (**6**); M = Ir (**7**)). The reactions, which proceed with dissolution of the sparingly soluble platinum sulfide starting material, are very conveniently and directly monitored using ESMS. ESMS data for the reaction solutions are summarised in Table 1.

At low cone voltages (e.g. 20 V) a single M^{2+} ion is observed in each reaction mixture (e.g. **2**, *m/z* 869; **5**,



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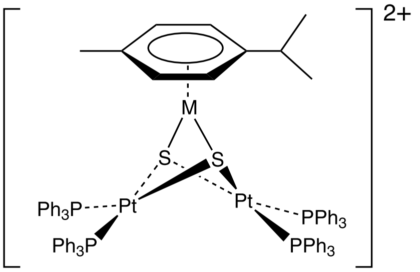
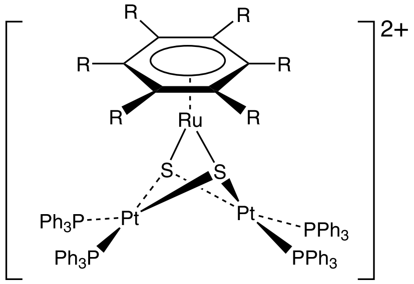
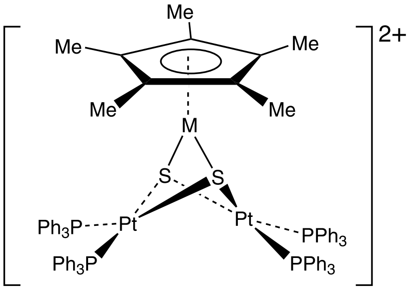


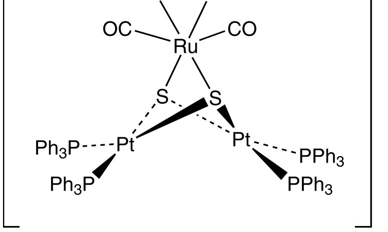
2, M = Ru
5, M = Os



3, R = Me
4, R = H



6, M = Rh
7, M = Ir



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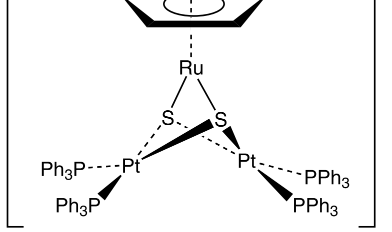

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Table 1
ESMS data for reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with various ruthenium(II), osmium(II), rhodium(III) and iridium(III) substrates in methanol [a]

Substrate	Cone voltage (V)	Principal ions (*m*/*z*, %)
$[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$	20	$[\{Pt_2S_2\}Ru(\eta^6\text{-}p\text{-cymene})]^{2+}$ (869, 100)
	40	$[\{Pt_2S_2\}Ru(\eta^6\text{-}p\text{-cymene})\text{—}PPh_3]^{2+}$ (738, 13); $[\{Pt_2S_2\}Ru(\eta^6\text{-}p\text{-cymene})]^{2+}$ (869, 100)
	80	$[\{Pt_2S_2\}Ru(\eta^6\text{-}p\text{-cymene})\text{—}2PPh_3]^{2+}$ (607, 100); $[\{Pt_2S_2\}Ru(\eta^6\text{-}p\text{-cymene})\text{—}PPh_3]^{2+}$ (738, 62); $[\{Pt_2S_2\}+2H+Cl]^+$ (1538, 37); $[\{Pt_2S_2\}RuOMe]^+$ (1636, 32)
$[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$	20	$[\{Pt_2S_2\}Ru(\eta^6\text{-}C_6Me_6)]^{2+}$ (883, 100)
$[RuCl_2(\eta^6\text{-}C_6H_6)]_2$	20	$[\{Pt_2S_2\}Ru(\eta^6\text{-}C_6H_6)]^{2+}$ (841, 100)
$[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$	20	$[\{Pt_2S_2\}Ru(\eta^5\text{-}C_5H_5)]^+$ (1669, 100)
$[RuCl_2(CO)_3]_2$	5	$[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)_3Cl]^+$ (1724, 100)
	60	$[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)_2Cl]^+$ (1696, 100); $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)_3Cl]^+$ (1724, 40)
	80	$[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)Cl]^+$ (1668, 40); $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)_2Cl]^+$ (1696, 100); $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)_3Cl]^+$ (1724, 50)
$[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$	20	$[\{Pt_2S_2\}Os(\eta^6\text{-}p\text{-cymene})]^{2+}$ (913, 100)
$[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$	20	$[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)]^{2+}$ (871, 100)
	40	$[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)\text{—}PPh_3]^{2+}$ (739, 26); $[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)]^{2+}$ (871, 100)
	60	$[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)\text{—}2PPh_3]^{2+}$ (608, 49); $[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)\text{—}PPh_3]^{2+}$ (739, 100); $[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)]^{2+}$ (871, 25)
	80	$[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)\text{—}2PPh_3]^{2+}$ (608, 100); $[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)\text{—}PPh_3]^{2+}$ (739, 76); $[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)]^{2+}$ (871, 33); $[Pt_3S_2(PPh_3)_2Rh(C_5Me_5)Cl_2]^+$ (1482, 52); $[Pt_3S_2(PPh_3)_2Rh(C_5Me_5)Cl_2+MeOH]^+$ (1513, 20); $[\{Pt_2S_2\}Rh(C_5Me_4CH_2)]^+$ (1740, 28)
$[RhCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)]$	20	$[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)]^{2+}$ (871, 100)
$[IrCl_2(\eta^5\text{-}C_5Me_5)]_2$	20	$[\{Pt_2S_2\}Ir(\eta^5\text{-}C_5Me_5)]^{2+}$ (915, 100)
	60	$[Ir(C_5Me_5)(Ph_2PC_6H_4)]^+$ (589, 22); $[\{Pt_2S_2\}Ir(\eta^5\text{-}C_5Me_5)\text{—}2PPh_3]^{2+}$ (653, 43); $[\{Pt_2S_2\}Ir(\eta^5\text{-}C_5Me_5)\text{—}PPh_3]^{2+}$ (784, 100); $[\{Pt_2S_2\}Ir(\eta^5\text{-}C_5Me_5)]^{2+}$ (915, 39)
	80	$[PPh_3+H]^+$ (263, 100); $[Ir(C_5Me_5)(Ph_2PC_6H_4)]^+$ (589, 38); $[\{Pt_2S_2\}Ir(\eta^5\text{-}C_5Me_5)\text{—}2PPh_3]^{2+}$ (653, 58); $[\{Pt_2S_2\}Ir(\eta^5\text{-}C_5Me_5)\text{—}PPh_3]^{2+}$ (784, 48); $[\{Pt_2S_2\}Ir(\eta^5\text{-}C_5Me_5)]^{2+}$ (915, 42)

[a] $\{Pt_2S_2\} = [Pt_2(\mu\text{-}S)_2(PPh_3)_4]$.

m/*z* 913; **6**, *m*/*z* 871; **7**, *m*/*z* 915). The mononuclear phosphine complex $[RhCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)]$ also reacts rapidly with **1**, with loss of the PPh_3 ligand, also giving $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Rh(\eta^5\text{-}C_5Me_5)]^{2+}$ (**6**); however, the corresponding reaction using $[IrCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)]$ is much more sluggish, only giving $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ir(\eta^5\text{-}C_5Me_5)]^{2+}$ (**7**) after allowing the solution to stand for 4 days. This reflects the greater lability of rhodium when compared to iridium, and the strength of the Ir–PPh_3 bond. The loss of the PPh_3 ligand, giving a coordinatively unsaturated product, is noteworthy, and is discussed later in greater detail. Similarly, $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ reacted much more slowly than the Ru analogue; this was confirmed by a competition experiment, where 1 mol equivalent of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was added to a stirred solution containing 0.5 mol equivalents each of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (i.e. ratio of $\{Pt_2S_2\}$:Ru:Os = 1:1:1). After 4 h stirring, the ESMS spectrum of the resulting solution showed only the species **2** and **5** in an approximately 2:1 ratio, confirming greater reactivity in the ruthenium case. Continued stirring for several days resulted in no change in the product distribution, suggesting that this represents the initially formed product.

When either an excess of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ was added to a stirred methanol suspension of **1** or when the reaction was carried out in hot methanol, there was no evidence for the formation of any metal-scrambled product viz. $[Pt(\mu\text{-}S)_2\{Ru(cymene)\}_2(PPh_3)_2]^{2+}$. There was also no evidence for metal scrambling when $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ was the substrate; these results are in contrast to the analogous $\{Pt_2Se_2\}$ system, where metal scrambling was readily seen [7].

The $\eta^5\text{-}C_5Me_5$–metal bonds in the Rh and Ir complexes **6** and **7** are inordinately robust when the cations are subjected to high cone voltages in the mass spectrometer, which typically induces collision-induced fragmentation. Loss of PPh_3 occurs, followed by aggregate rearrangement, to give (e.g. in the case of **6**) species such as $[Pt_3(\mu\text{-}S)_2(PPh_3)_2Rh(C_5Me_5)Cl_2]^+$ (*m*/*z* 1482), $[Pt_3(\mu\text{-}S)_2(PPh_3)_2Rh(C_5Me_5)Cl_2+MeOH]^+$ (*m*/*z* 1513), an ion at *m*/*z* 1740, which is possibly $[Pt_2(\mu\text{-}S)_2(PPh_3)_4\text{-}Rh(C_5Me_4CH_2)]^+$, formed by cyclometallation of one of the CH_3 groups, and $[Ir(C_5Me_5)(Ph_2PC_6H_4)]^+$ (*m*/*z* 589) (formed by cyclometallation of a PPh_3 ligand; such processes have been observed previously [14]). For the ruthenium–cymene complex, PPh_3 loss occurs at 40 V and above, with loss of one or two PPh_3 ligands, and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(OMe)]^+$ (*m*/*z* 1636) is formed by loss of the cymene ligand.

On the macroscopic scale, the complexes can be readily isolated by addition of a large anion, PF_6^- or BPh_4^-, to the reaction solutions, giving the solid products as powders. All are soluble in chlorinated hydrocarbon solvents, but are insoluble in water and alcohols. The identity of the isolated products was confirmed by ESMS and elemental analysis, and in most cases by NMR spectroscopy.

The reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) with the complex $[RuCl_2(CO)_3]_2$ (which is isoelectronic to the π-arene ruthenium complexes with three CO ligands in place of an η^6-hydrocarbon ligand) in methanol results initially in a pale yellow solution which fades rapidly to colourless, and ESMS showed predominantly the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)_3Cl]^+$ cation **8** at *m*/*z* 1724. This represents an additional example of a metal carbonyl derivative of the $\{Pt_2S_2\}$ system, of which relatively few examples have been reported previously [15]. It is noteworthy that the Ru centre in this species is coordinatively saturated, in contrast to the other derivatives described herein. Increasing the cone voltage allows the opportunity to investigate the loss of the CO ligands compared to an arene. At 60 V, the most intense peak is due to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)_2Cl]^+$ (*m*/*z* 1696) with $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)_3Cl]^+$ at ca. 40% relative intensity. When the cone voltage is further increased to 80 V, an additional peak at *m*/*z* 1668 is due to the monocarbonyl $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(CO)Cl]^+$.

The reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ was also investigated and provided a route to the monocationic cyclopentadienyl complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^5\text{-}C_5H_5)]^+$ (**9**) (together with a number of minor species observed in the ES mass spectrum) through displacement of the chloride and both of the triphenylphosphine ligands. The complex was isolated as the brown BPh_4^- salt, but attempts to purify the product by recrystallisation were not successful.

Reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the complexes $[RuCl_2(cod)]_n$ (cod = cyclo-octa-1,5-diene) or $[RuCl_2(\eta^5\text{-}C_5Me_5)]_2$ were unsuccessful, with the ES mass spectra showing several major ions, and no further studies were carried out in these systems.

2.2. X-ray crystal structure determination on $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^6\text{-}p\text{-}cymene)][BPh_4]_2$ ($\mathbf{2}[BPh_4]_2$)

An X-ray structure determination was carried out on complex $\mathbf{2}[BPh_4]_2$, in order to unequivocally determine the mode of binding of the $\{Pt_2S_2\}$ unit to the cymene–

Table 2

Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^6\text{-}p\text{-}cymene)][BPh_4]_2 \cdot \mathbf{2}Et_2O$

Bond lengths (Å)	
Pt(1)–P(2)	2.270(2)
Pt(1)–S(1)#1	2.334(2)
Pt(1)–Ru(2)	2.9668(10)
Ru(2)–C(1)#1	2.158(15)
Ru(2)–C(2)#1	2.165(14)
Ru(2)–C(3)	2.205(14)
Ru(2)–S(1)	2.318(2)
S(1)–Pt(1)#1	2.334(2)
Pt(1)–P(1)	2.298(2)
Pt(1)–S(1)	2.341(2)
Ru(2)–C(1)	2.158(15)
Ru(2)–C(2)	2.165(14)
Ru(2)–C(3)#1	2.205(14)
Ru(2)–S(1)#1	2.318(2)
Ru(2)–Pt(1)#1	2.9668(10)
Bond angles (°)	
P(2)–Pt(1)–P(1)	98.16(8)
P(1)–Pt(1)–S(1)#1	168.33(8)
P(1)–Pt(1)–S(1)	87.84(7)
Ru(2)–S(1)–Pt(1)#1	79.24(6)
Pt(1)#1–S(1)–Pt(1)	88.26(7)
P(2)–Pt(1)–S(1)#1	93.16(8)
P(2)–Pt(1)–S(1)	172.99(8)
S(1)#1–Pt(1)–S(1)	80.69(8)
Ru(2)–S(1)–Pt(1)	79.11(7)

Symmetry transformations used to generate equivalent atoms: #1, −*x*, *y*, −*z*+1/2.

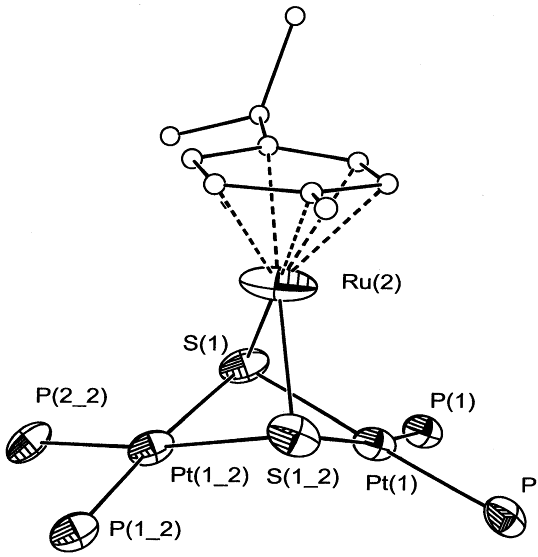

Fig. 1. Molecular structure of the cation $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^6\text{-}p\text{-}cymene)]^{2+}$ (**2**) showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level. The phenyl rings of the triphenylphosphine ligands and the $[BPh_4]^-$ counterions have been omitted for clarity, and the carbon atoms of the (disordered) *p*-cymene ligand are shown as small open circles.

ruthenium moiety. Single crystals of the complex, which were dark green-yellow dichroic in appearance, were obtained by vapour diffusion of diethyl ether into a dichloromethane solution. Selected bond lengths and angles for the structure are summarised in Table 2.

The cation lies on a twofold axis passing through the Ru atom and the midpoints of the S···S and Pt···Pt vectors. This leads to a twofold disorder of the cymene ligand. This was readily modelled, though parameters involving the Ru-arene fragment will not be accurate, so only the main structural features merit discussion. The molecular structure, shown in Fig. 1, shows one component of the disordered structure, with a triangular $\{RuPt_2\}$ core capped on both sides by symmetrical μ^3-sulfido ligands. The overall structure is similar to that of many other adducts of the $\{Pt_2S_2\}$ core [1]. The d^8 platinum centres exhibit the usual slightly distorted square-planar coordination environments, while the ruthenium is coordinated by the η^6-*p*-cymene ligand (considered to occupy three coordination sites), as well as the two sulfido ligands.

The Pt···Pt and S···S distances are 3.255 and 3.026 Å, respectively, and the dihedral angle between the two PtS_2 planes is 132.0°. These values are extremely similar to those of related adducts of the $\{Pt_2S_2\}$ core, e.g. involving rhodium(I) [1,10]. The Pt···Ru distances of 2.9668(10) Å are relatively short when compared with other derivatives of second row transition metals [1]. The S–Ru–S "bite" angle of the $\{Pt_2S_2\}$ metalloligand [S(1)#1–Ru(2)–S(1)] is 81.50(10)°, is around the average for other adducts, e.g. those with square-planar metal centres such as $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Rh(CO)_2]^+$ (79.9(1)°) [10].

The pseudo-five-coordination and thus coordinative unsaturation at the ruthenium centre is particularly noteworthy. Other five-coordinate (η^6-arene)Ru(dithiolate) complexes are well-known, such as the carborane derivative (η^6-*p*-cymene)$Ru(S_2C_2B_{10}H_{10})$, which readily adds a wide range of neutral (phosphine, phosphite, isocyanide, amine, CO) and anionic (cyanide and thiocyanate) donor ligands to give six-coordinate derivatives [16]. Monomer–dimer equilibria have also been reported for (η^6-*p*-cymene)$Ru(S_2C_6H_4)$ [17] and (η^5-C_5Me_5)$Rh(S_2C_6H_4)$ [18], although monomeric structures are found in the X-ray structure determinations of the latter complex and of (η^6-C_6Me_6)$Ru(S_2C_6H_4)$ [17]. The ferrocenyl-thiolate and -selenolate complexes (η^5-C_5Me_5)$Ir(EC_5H_4)_2Fe$ (E = S, Se) also exist as dimers in the solid state [19]. In the case of complex **2**, the steric bulk of the $\{Pt_2S_2\}$ moiety clearly leaves no room for dimerisation or coordination of an ancillary ligand. Hence, a chloride ligand from the $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ or $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ starting materials is not incorporated into the product, which would give a six-coordinate monocationic product of the type $[\{Pt_2S_2\}MCl(\pi\text{-hydrocarbon})]^+$. This contrasts with results in the $[RuCl_2(CO)_3]_2$ system, as described above.

The green colour of the ruthenium (**2**–**4**) and rhodium (**6**) complexes is also indicative of a pseudo-five-coordinate metal centre, for example, (η^6-*p*-cymene)$Ru(S_2C_2B_{10}H_{10})$ which is blue [16] and (η^6-C_6H_6)$Ru(SR)_2$ (R = 2,6-xylyl) which is greenish-blue [17]. In contrast, six-coordinated analogues such as (η^6-arene)Ru(dithiolate)L (L = neutral donor ligand) [16] and (η^5-C_5R_5)Rh(dithiolate)(PMe_3) (R = H, Me) [20] typically have a reddish colour.

In order to probe the propensity, if any, of the metal centre to bind a sixth ligand, ligand addition reactions were investigated by the change in colour (monitored by UV–vis spectroscopy) on addition of a neutral donor ligand to solutions of either $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^6\text{-}p\text{-cymene})][BPh_4]_2$ or $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ir(\eta^5\text{-}C_5Me_5)][BPh_4]_2$. The ligands investigated were carbon monoxide, pyridine and triphenylphosphine. No change in the absorption maxima was observed for either of the complexes with any of the ligands. This lack of reactivity indicates a profound stability of the coordinatively unsaturated state in these systems.

3. Conclusions

The $\{Pt_2S_2\}$ core is shown in this work to support a range of π-hydrocarbon-substituted d^6 metal centres, with the resulting cationic adducts of the type $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ML]^{2+}$ appearing to have a distinct reluctance to capture an additional ligand to give a six-coordinate metal. As in previous studies, we have initially used the technique of electrospray mass spectrometry to probe the coordination chemistry and identify suitable targets for synthetic study. The availability of d^6 adducts of the $\{Pt_2S_2\}$ core offers potential for the investigation of properties of these systems; both d^6 and d^8 metal centres are typically catalytically active, and their close proximity in the adducts described herein may result in interesting bimetallic catalysis. In addition, these adducts may have interesting electrochemical properties, by oxidation–reduction of the heterometal as well as the $\{Pt_2S_2\}$ core, and studies are planned in this area.

4. Experimental

4.1. General methods and materials

Reactions were carried out in LR grade methanol. Reactions were initially run under an inert atmosphere, though this was found not to be essential. Products were recrystallised from dichloromethane and diethyl ether which were dried and distilled (from calcium hydride and sodium benzophenone ketyl, respectively) under a nitrogen atmosphere prior to use. ^{1}H-, ^{31}P-{^{1}H}- and ^{13}C-{^{1}H}-NMR spectra were recorded in $CDCl_3$ solution on a Bruker AC300P spectrometer at 300.13, 121.51 and 75.47 MHz, respectively. Electrospray mass spectra were recorded in methanol solution on a VG Platform II instrument, using a capillary voltage of 3.5 kV and cone voltages in the range 5–80 V. Assignment of ions was achieved by comparison of experimental and calculated isotopic envelopes; the latter were obtained using the ISOTOPE simulation program [21]. UV–vis spectra were recorded in dichloromethane solution in quartz cells, using a Perkin–Elmer Lambda 11 spectrophotometer. Melting points were recorded on a Reichert Thermopan apparatus and are uncorrected. Microanalytical data were obtained from the Campbell Microanalytical Laboratory, University of Otago, New Zealand, or the Microanalytical Laboratory, Department of Chemistry, National University of Singapore.

The complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) [22], $[RuClCp(PPh_3)_2]$ [23], $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ [24], $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ [25], $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ [26], $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ [27], $[IrCl_2(\eta^5\text{-}C_5Me_5)]_2$ [27], $[RhCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)]$ [27], $[IrCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)]$ [27], $[RuCl_2(cod)]_n$ [28] and $[RuCl_2(\eta^5\text{-}C_5Me_5)]_2$ [28] were prepared by minor modifications of the literature procedures. The complex $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ was prepared from hydrated $RuCl_3$ (Aldrich) and technical grade α-terpinene (Aldrich), as described by Spicer and coworkers [29]; $[RuCl_2(CO)_3]_2$ (Aldrich), $Na[BPh_4]$ (BDH) and $[NH_4][PF_6]$ (Aldrich) were used as supplied.

4.2. Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^6\text{-}p\text{-cymene})][BPh_4]_2$ (**2**$[BPh_4]_2$)

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) (200 mg, 0.133 mmol) and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (41 mg, 0.067 mmol) in methanol (20 ml) was stirred for 48 h to give a dark greenish-brown solution. The solution was filtered and a solution of $Na[BPh_4]$ (91 mg, 0.266 mmol) in methanol (5 ml) added, giving a greenish-brown precipitate. This was filtered off, washed with distilled water (5 ml), methanol (5 ml) and diethyl ether (5 ml), and dried under vacuum to give a greenish powder (210 mg, 66%). m.p.: 149–154 °C. Found: C, 66.1; H, 4.9; P, 5.2; S, 2.7. $C_{130}H_{114}B_2P_4Pt_2RuS_2$ requires C, 65.7; H, 4.8; P, 5.2; S, 2.7%. ^{31}P-{^{1}H}-NMR: δ 15.2 (s, $^1J(PtP) = 3323$). ^{1}H-NMR: δ 7.22–7.37 (m, 100H, PPh_3 and $[BPh_4]^-$), 5.72–5.85 (m, 4H, *p*-cymene), 2.09 (q, 1H, CH of Pr^i), 1.26 (s, 3H, CH_3), 0.81 (d, 6H, CH_3 of Pr^i, $J(HH) = 7$). Recrystallisation by vapour diffusion of diethyl ether into a dichloromethane solution of the complex gave dark green crystals suitable for an X-ray diffraction study.

4.3. Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^6\text{-}p\text{-}C_6Me_6)][BPh_4]_2$ (**3**$[BPh_4]_2$)

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) (200 mg, 0.133 mmol) and $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ (44 mg, 0.066 mmol) in methanol (20 ml) was stirred for 48 h to give a dark greenish-brown solution. The solution was filtered and a solution of $Na[BPh_4]$ (89 mg, 0.260 mmol) in methanol (5 ml) added, giving a greenish-brown precipitate. This was filtered off and washed with distilled water (5 ml), methanol (5 ml) and diethyl ether (5 ml), and dried under vacuum to give **3**$[BPh_4]_2$ as a greenish powder (140 mg, 44%). m.p.: 146–149 °C. ^{31}P-{^{1}H}-NMR: δ 12.6 (s, $^1J(PtP) = 3077$). ^{1}H-NMR: δ 7.49–6.91 (m, 100H, PPh_3 and $[BPh_4]^-$), 1.74 (18H, CH_3). A sample for elemental analysis was recrystallised by vapour diffusion of diethyl ether into a dichloromethane solution of the complex. Found: C, 64.5; H, 5.0. $C_{132}H_{118}B_2P_4Pt_2S_2Ru$ requires C, 65.9; H, 4.9%.

4.4. Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^6\text{-}p\text{-}C_6H_6)][BPh_4]_2$ (**4**$[BPh_4]_2$)

Following the method for **3**, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) (200 mg, 0.133 mmol) and $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ (33 mg, 0.066 mmol) in methanol (20 ml) gave a deep blue-green solution. Addition of $Na[BPh_4]$ (150 mg, 0.439 mmol) gave a grey precipitate, which was filtered off, washed and dried under vacuum to give 130 mg (42%) of **4**$[BPh_4]_2$. m.p.: 160–167 °C. Found: C, 64.1; H, 4.3. $C_{126}H_{106}B_2P_4Pt_2S_2Ru$ requires C, 65.2; H, 4.6%.

4.5. Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Rh(\eta^5\text{-}C_5Me_5)][PF_6]_2$ (**6**$[PF_6]_2$)

A suspension of **1** (82 mg, 0.055 mmol) and $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ (16.9 mg, 0.027 mmol) in methanol (20 ml) was stirred under argon for 24 h to give a green solution. The solution was filtered, the filter washed with methanol (2 × 5 ml) and the filtrate and washings combined. Excess solid $[NH_4][PF_6]$ was added and after stirring for 1 h a green solid precipitated. Distilled water (10 ml) was added to complete precipitation. The green solid was filtered off, washed with water (2 × 10 ml), ethanol (5 ml) and diethyl ether (10 ml), and dried under vacuum to give **6**$[PF_6]_2$ as a green powder (87 mg, 79%). Found: C, 48.5; H, 3.7; P, 9.1; S, 3.1. $C_{82}H_{75}F_{12}P_6Pt_2RhS_2$ requires C, 48.5; H, 3.7; P, 9.2; S, 3.2%. ^{31}P-{^{1}H}-NMR, δ 13.3 (s, $^1J(PtP) = 3304$), −144.2 (septet, $^1J(PF) = 713$). ^{1}H-NMR: δ 7.18–7.38 (m, 60H, PPh_3), 1.60 (s, 15H, CH_3).

4.6. Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ir(\eta^5\text{-}C_5Me_5)][PF_6]_2$ ($7[PF_6]_2$)

A suspension of **1** (82 mg, 0.055 mmol) and $[IrCl_2(\eta^5\text{-}C_5Me_5)]_2$ (21.7 mg, 0.027 mmol) in methanol (20 ml) was stirred under argon to give an orange suspension which turned clear red after ca. 3 h. After stirring for an additional 24 h the red solution was filtered, the filter washed with methanol (2 × 5 ml) and the filtrate and washings combined. Excess solid $[NH_4][PF_6]$ was added and after stirring for 1 h a red solid precipitated. Distilled water (10 ml) was added to complete precipitation. The solid was filtered off, washed successively with water (2 × 10 ml), ethanol (5 ml) and diethyl ether (10 ml), and dried under vacuum to give $\mathbf{7}[PF_6]_2$ as a red powder (97 mg, 84%). Found: C, 46.5; H, 3.5; P, 8.8; S, 3.0. $C_{82}H_{75}F_{12}IrP_6Pt_2S_2$ requires C, 46.4; H, 3.6; P, 8.8; S, 3.0%. $^{31}P\text{-}\{^1H\}$-NMR: δ 11.7 (s, $^1J(PtP) = 3380$), -144.2 (septet, $^1J(PF) = 710$). ^1H-NMR: δ 7.14–7.38 (m, 60H, PPh_3), 1.60 (s, 15H, Me).

4.7. Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ir(\eta^5\text{-}C_5Me_5)][BPh_4]_2$ ($7[BPh_4]_2$)

A mixture of **1** (300 mg, 0.200 mmol) and $[IrCl_2(\eta^5\text{-}C_5Me_5)]_2$ (80 mg, 0.100 mmol) in methanol (30 ml) was stirred for 20 h, giving a red solution. After filtration, $Na[BPh_4]$ (150 mg, 0.439 mmol) was added to the filtrate, giving a pink-red precipitate which was filtered off, washed with water (10 ml), methanol (2 × 5 ml) and diethyl ether (5 ml), and dried to give $\mathbf{7}[BPh_4]_2$ (249 mg, 51%) as a pink powder. A sample for elemental analysis was recrystallised by vapour diffusion of diethyl ether into a dichloromethane solution of the complex, giving bright red plates. m.p. (dec.): > 160 °C, melting: 211–214 °C. Found: C, 63.2; H, 4.5. $C_{130}H_{115}B_2P_4Pt_2S_2Ir$ requires C, 63.2; H, 4.7%.

4.8. Competitive reaction of 1 with $[RuCl_2(\eta^6\text{-}p\text{-}cymene)]_2$ and $[OsCl_2(\eta^6\text{-}p\text{-}cymene)]_2$

$[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (20.8 mg) and $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (26.2 mg) were dissolved in methanol (20 ml). Complex **1** (100 mg) was added, and after 4 h stirring, ESMS of the resulting brown solution showed $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(p\text{-cymene})]^{2+}$ (m/z 869) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Os(p\text{-cymene})]^{2+}$ (m/z 914) in a ca. 100:40 ratio. The product distribution did not change on stirring for 6 days.

4.9. X-ray structure determination of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^6\text{-}p\text{-cymene})][BPh_4]_2\cdot 2Et_2O$

Crystals of the complex were obtained by vapour diffusion of diethyl ether into a dichloromethane solution of the complex at room temperature.

Unit cell parameters and intensity data were collected using a Siemens SMART CCD diffractometer, using standard collection procedures, with monochromatic Mo–K_α X-rays (0.71073 Å). Corrections for absorption and other effects were carried out with SADABS [30]. All other calculations used the SHELX97 programs [31]. The structure was solved by Patterson methods and developed with refinement based on F^2. For the cations and anions the non-hydrogen atoms were assigned anisotropic temperature factors, and hydrogen atoms were included in calculated positions except for those on the disordered cymene ligand. For the disordered solvent the atoms were refined isotropically with bond distances constrained and hydrogen atoms were not included. Some isolated residual electron density remained, suggesting other very disordered solvent molecules in the lattice, but these were not modelled.

4.9.1. Crystal data for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ru(\eta^6\text{-}p\text{-cymene})][BPh_4]_2\cdot 2Et_2O$

$C_{138}H_{134}B_2O_2P_4S_2RuPt_2$, M_r 2525.32, monoclinic, $C2/c$, $a = 34.372(3)$ Å, $b = 15.381(2)$ Å, $c = 27.747(3)$ Å, $\beta = 127.811(3)^\circ$, $V = 11589(2)$ Å^3, $D_{calc} = 1.447$ g cm^{-3}, $Z = 4$, $F(0\,0\,0) = 5120$, μ(Mo–K_α) 2.682 mm^{-1}, T_{max} 0.4211, T_{min} 0.3202, crystal size 0.55 × 0.44 × 0.39 mm^3, T 168 K.

A total of 41 739 reflections, 11 714 unique (R_{int} 0.0401) was collected $2^\circ < \theta < 26.5^\circ$. Final R_1 0.0559 [data with $I > 2\sigma(I)$], wR_2 0.1861 (all data), GoF 1.066, final Δe 4.1/-3.5 e Å^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 209259. 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 www: http://www.ccdc.cam.ac.uk).

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