

Synthesis, structures and redox properties of platinum metal phosphathia complexes: crystal structures of *cis*-[RuCl₂(RSC₂H₄SR)]·0.75Et₂O and *cis*-[RhCl₂(RSC₂H₄SR)]PF₆·CH₂Cl₂ (R = Ph₂PCH₂CH₂)

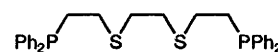
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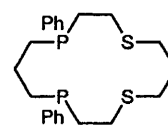
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Reaction of [RuCl₂(py)₄] (py = pyridine) with 1 molar equivalent of the new tetradentate acyclic phosphathia compound RSC₂H₄SR (Ph₂PCH₂CH₂SCH₂CH₂SCH₂CH₂PPh₂) or the macrocycle *meso*-Ph₂[14]aneP₂S₂ (4,8-diphenyl-1,11-dithia-4,18-diphosphacyclotetradecane) in refluxing toluene under a nitrogen atmosphere afforded the ruthenium(II) complexes [RuCl₂(RSC₂H₄SR)] and [RuCl₂(Ph₂[14]aneP₂S₂)] respectively as yellow solids. The crystal structure of [RuCl₂(RSC₂H₄SR)]·0.75Et₂O shows RSC₂H₄SR co-ordinated *via* all four donor atoms with the two P-donors occupying mutually *trans* co-ordination sites at Ru^{II}, and *cis*-dichlorides completing the overall octahedral stereochemistry, Ru–S 2.294(1), 2.292(1), Ru–P 2.339(2), 2.335(2), Ru–Cl 2.463(1), 2.463(1) Å. Phosphorus-31 NMR spectroscopic studies on the macrocyclic species [RuCl₂(Ph₂[14]aneP₂S₂)] are consistent with a *cis*-dichloro isomer in which one Cl is *trans* to P and the other *trans* to S. Cyclic voltammetry showed a reversible one-electron oxidation occurring at *E*₁ = +0.16 and +0.32 V *vs.* ferrocene–ferrocenium for [RuCl₂(RSC₂H₄SR)] and [RuCl₂(Ph₂[14]aneP₂S₂)] respectively. The complexes [MCl₂(RSC₂H₄SR)]PF₆ (M = Rh or Ir) have also been prepared. The structure of [RhCl₂(RSC₂H₄SR)]PF₆·CH₂Cl₂ shows discrete [RhCl₂(RSC₂H₄SR)]⁺ cations adopting a very similar arrangement to that in the ruthenium(II) analogue, with Rh–P 2.352(2), 2.342(2), Rh–S 2.303(2), 2.297(2), Rh–Cl 2.370(2), 2.359(2) Å. Rhodium-103 NMR spectroscopy reveals a triplet at δ +1405 (*J*_{RhP} 85 Hz).

Acyclic phosphine ligands are well known to form stable complexes with many metal ions,¹ whereas acyclic thioether complexes tend to be less stable, and often hydrolyse readily.² Macrocyclic thioethers, on the other hand, form complexes which are often significantly more robust with respect to demetallation.³ As part of a long-term project probing the differences in reactivity between phosphine ligands which involve cyclic *vs.* acyclic arrangements, we have been looking at ways of incorporating phosphine functions into macrocyclic environments and comparing the chemistry of these new macrocyclic compounds with that of related acyclic ligands which possess similar donor sets. We have recently reported the synthesis of the mixed phosphathia macrocycle Ph₂[14]aneP₂S₂ (4,8-diphenyl-1,11-dithia-4,8-diphosphacyclotetradecane), together with its complexes of Pd^{II}, Pt^{II} and Rh^{III}.⁴ Specifically, the acyclic phosphathia ligands which we have chosen to study in parallel incorporate the phosphine functions at the termini, with the thioether functions internal to the chain. We anticipated that, as phosphines are better σ donors compared to thioethers, this would assist in stabilisation of the mixed phosphine-thioether co-ordination, inhibiting decomplexation of the more weakly bound thioethers in solution. The copper(I) complex [Cu(RSC₂H₄SR)]⁺ (R = Ph₂PC₂H₄) shows tetrahedral ligation *via* a P₂S₂-donor set,⁵ while the gold(I) complexes [AuL]PF₆ (L = RSC₂H₄SR or RSC₃H₆SR) on the other hand adopt geometries intermediate between linear (P₂) and tetrahedral (P₂S₂), involving long-range, weak Au...S interactions of *ca.* 3 Å.⁶ This paper describes the synthesis, spectroscopic characterisation and redox properties of [RuCl₂(RSC₂H₄SR)], [MCl₂(RSC₂H₄SR)]PF₆ (M = Ir or Rh) and the macrocyclic species [RuCl₂(Ph₂[14]aneP₂S₂)]. We are not aware of any other examples of ruthenium complexes involving phosphine or phosphathia macrocycles. Single-crystal structure determinations on [RuCl₂(RSC₂H₄SR)]·0.75Et₂O and [RhCl₂(RSC₂H₄SR)]PF₆·CH₂Cl₂ are also reported.



RSC₂H₄SR



Ph₂[14]aneP₂S₂

Results and Discussion

Reaction of [RuCl₂(py)₄] (py = pyridine) with 1 molar equivalent of *meso*-Ph₂[14]aneP₂S₂ in refluxing toluene under a nitrogen atmosphere gave a yellow solution. Upon cooling a yellow solid was deposited which was filtered off and recrystallised from CH₂Cl₂–diethyl ether. The FAB mass spectrum (3-nitrobenzyl alcohol matrix) shows peaks at *m/z* = 557, 521 and 446, with the correct isotopic distributions for [RuCl₂(Ph₂[14]aneP₂S₂)]⁺, [RuCl₂(Ph₂[14]aneP₂S₂ – H)]⁺ and [RuCl₂(Ph₂[14]aneP₂S₂ + H)]⁺ respectively. The IR spectrum (CsI disc) shows two peaks at 309 and 283 cm^{–1} assigned to ν(Ru–Cl). Phosphorus-31 NMR spectroscopy (145.8 MHz, CH₂Cl₂–CDCl₃) shows a pair of doublets at δ +63.5 and +54.7 (²*J*_{PP} = 40 Hz), indicative of a *cis*-dichloro stereochemistry. These signals are shifted downfield of free *meso*-Ph₂[14]aneP₂S₂ by some 80–90 ppm, diagnostic of formation of a five-membered chelate ring at each P-donor and thus confirming that in addition to the phosphines the thioether functions are also co-ordinated in solution.⁷ These results, together with ¹H NMR, UV/VIS spectroscopic and microanalytical data, strongly support the formulation *cis*-[RuCl₂(Ph₂[14]aneP₂S₂)] for this product, in which one phosphine

donor occupies a site *trans* to S while the other lies *trans* to Cl[−], as illustrated in Fig. 1.

The *cis*-dichloro stereochemistry proposed for [RuCl₂(Ph₂[14]aneP₂S₂)] contrasts with the structure which we reported previously for the rhodium(III) cationic species [RhCl₂(Ph₂[14]aneP₂S₂)]⁺ in which a *trans* dichloride arrangement is observed in the solid state by X-ray crystallography and in solution by ³¹P NMR spectroscopy.⁴ This difference is presumably principally a consequence of the slightly larger ionic radius for Ru^{II} *vs.* Rh^{III} (*ca.* 0.74 and 0.665 Å respectively),^{8,*} and illustrates a fine balance between the constraints of the cavity size available for Ph₂[14]aneP₂S₂ and the strain imparted particularly by the phenyl rings on the P-donors on a folded form of *meso*-Ph₂[14]aneP₂S₂. Indeed, we commented previously that the related tetrathioether macrocyclic species [RhCl₂([14]aneS₄)]⁺,⁹ [IrCl₂([14]aneS₄)]⁺¹⁰ and [RuCl₂([14]aneS₄)]⁺¹¹ ([14]aneS₄ = 1,4,8,11-tetrathia-cyclotetradecane) all adopt *cis* arrangements of the Cl[−] ligands with the macrocycle in a folded conformation.

We have also investigated the co-ordination chemistry of the related acyclic P₂S₂ donor RSC₂H₄SR (Ph₂PCH₂CH₂SCH₂CH₂SCH₂CH₂PPh₂) in which the P donors are located at the termini of the chain. We anticipated that placing the better σ donors at the termini would render the resultant complexes more stable with respect to demetallation. This open-chain compound was prepared by modification of a literature method.¹² Thus, PPh₂H was treated first with LiBuⁿ in dry, degassed tetrahydrofuran (thf) solution, followed by 1 molar equivalent of SCH₂CH₂. Addition of 0.5 molar equivalents of BrCH₂CH₂Br to the resulting yellow solution, followed by hydrolysis, extraction (diethyl ether) and recrystallisation from CH₂Cl₂–diethyl ether gave RSC₂H₄SR as a white solid (³¹P NMR δ = −16.3; FAB mass spectrum *m/z* = 519, [RSC₂H₄SR + H]⁺).

The compound RSC₂H₄SR, reacts with 1 molar equivalent of [RuCl₂(py)₄] in refluxing degassed toluene to afford an orange air-stable solid which was filtered off and recrystallised from CH₂Cl₂–diethyl ether. The FAB mass spectrum shows molecular ion peaks at *m/z* = 690, 655 and 627 with the correct isotopic distributions for [¹⁰²Ru³⁵Cl₂(RSC₂H₄SR)]⁺, [¹⁰²Ru³⁵Cl(RSC₂H₄SR)]⁺ and [¹⁰²Ru³⁵Cl(RSC₂H₄SR – C₂H₄)]⁺ respectively. These data, together with ¹H NMR, UV/VIS spectroscopic and microanalytical data, confirm the formulation [RuCl₂(RSC₂H₄SR)]. The ³¹P NMR spectrum (145.8 MHz, CDCl₃) shows a singlet at δ +42.7 confirming a single isomeric form in solution. Again, the large downfield shift relative to free RSC₂H₄SR is indicative of a five-membered chelate ring at each P-donor and hence strong evidence that the thioether functions are co-ordinated in solution.⁷ Upon co-ordination of linear tetradentate RSC₂H₄SR to a six-co-ordinate metal ion several isomeric forms are possible.¹³ Specifically, the equivalence of the phosphine suggests that the complex adopts either a *trans* or *cis*-α form. Unambiguous assignment of Ru–Cl stretches in the IR spectrum of [RuCl₂(RSC₂H₄SR)] was not possible.

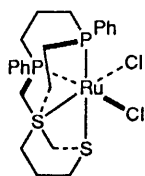


Fig. 1 Proposed structure of [RuCl₂(Ph₂[14]aneP₂S₂)]

* The ionic radius for Ru²⁺ is not given in ref. 8, however values for Ru³⁺ (0.68), Ru⁴⁺ (0.62) and Ru⁵⁺ (0.565 Å) are presented. Extrapolating these would give the ionic radius for Ru²⁺ as approximately 0.74 Å. Irrespective of this, since Ru³⁺ is larger than Rh³⁺, it is clear that Ru²⁺ will be even larger.

In order to confirm the stereochemistry around the Ru^{II} ion a single-crystal structure determination of [RuCl₂(RSC₂H₄SR)]·0.75Et₂O was undertaken. This shows (Fig. 2, Table 1) the Ru^{II} co-ordinated to all four donor atoms of the phosphathia ligand with *cis*-dichloride ligands completing a distorted octahedral stereochemistry. Consistent with the solution ³¹P NMR data, the P-donors occupy mutually *trans* co-ordination sites in the crystalline form and hence are equivalent, with the ligand in the *cis*-α form, Ru–P(1) 2.339(2), Ru–P(2) 2.335(2), Ru–S(1) 2.294(1), Ru–S(2) 2.292(1), Ru–Cl(1) 2.463(1) and Ru–Cl(2) 2.463(1) Å. Notably, the trend observed in the bond distances around the Ru^{II} (*i.e.* Ru–S < Ru–P < Ru–Cl) differs from that in *trans*-[RhCl₂(Ph₂[14]aneP₂S₂)]⁺ (*i.e.* Rh–P < Rh–S < Rh–Cl), presumably due to the *trans* influence of the Cl[−] ligands upon the metal–thioether bonding. The Cl[−] angles around the Ru lie in the range 85.6–94.2°; those involved in five-membered chelate rings are all less than 90°, reflecting the restricted bite size of the PCH₂CH₂S and SCH₂CH₂S linkages. It is noticeable that the particular co-ordination mode

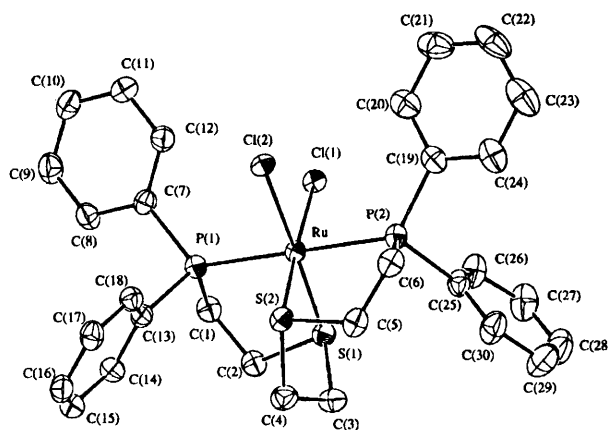


Fig. 2 View of the structure of *cis*-[RuCl₂(RSC₂H₄SR)] with the numbering scheme adopted; H atoms are omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) for *cis*-[RuCl₂(RSC₂H₄SR)]

Ru–Cl(1)	2.463(1)	Ru–Cl(2)	2.463(1)
Ru–S(1)	2.294(1)	Ru–S(2)	2.292(1)
Ru–P(1)	2.339(2)	Ru–P(2)	2.335(2)
S(1)–C(2)	1.846(5)	S(1)–C(3)	1.822(5)
S(2)–C(4)	1.825(6)	S(2)–C(5)	1.845(6)
P(1)–C(1)	1.827(5)	P(1)–C(7)	1.831(5)
P(1)–C(13)	1.832(5)	P(2)–C(6)	1.838(5)
P(2)–C(19)	1.817(6)	P(2)–C(25)	1.825(5)
C(1)–C(2)	1.520(7)	C(3)–C(4)	1.523(7)
C(5)–C(6)	1.493(8)		
Cl(1)–Ru–Cl(2)	94.17(4)	Cl(1)–Ru–S(1)	88.54(4)
Cl(1)–Ru–S(2)	177.37(5)	Cl(1)–Ru–P(1)	86.51(4)
Cl(1)–Ru–P(2)	93.26(5)	Cl(2)–Ru–S(1)	177.13(5)
Cl(2)–Ru–S(2)	88.12(4)	Cl(2)–Ru–P(1)	93.59(5)
Cl(2)–Ru–P(2)	86.87(5)	S(1)–Ru–S(2)	89.19(5)
S(1)–Ru–P(1)	85.62(5)	S(1)–Ru–P(2)	93.92(5)
S(2)–Ru–P(1)	94.65(5)	S(2)–Ru–P(2)	85.57(5)
P(1)–Ru–P(2)	179.50(5)	Ru–S(1)–C(2)	108.3(2)
Ru–S(1)–C(3)	104.2(2)	C(2)–S(1)–C(3)	98.3(3)
Ru–S(2)–C(4)	103.6(2)	Ru–S(2)–C(5)	108.2(2)
C(4)–S(2)–C(5)	99.3(3)	Ru–P(1)–C(1)	104.2(2)
Ru–P(1)–C(7)	123.8(2)	Ru–P(1)–C(13)	117.3(2)
C(1)–P(1)–C(7)	101.9(2)	C(1)–P(1)–C(13)	104.9(2)
C(7)–P(1)–C(13)	102.4(2)	Ru–P(2)–C(6)	104.5(2)
Ru–P(2)–C(19)	123.7(2)	Ru–P(2)–C(25)	117.7(2)
C(6)–P(2)–C(25)	102.9(2)	C(6)–P(2)–C(25)	105.1(3)
C(19)–P(2)–C(25)	100.8(2)	P(1)–C(1)–C(2)	110.5(3)
S(1)–C(2)–C(1)	110.2(4)	S(1)–C(3)–C(4)	111.6(4)
S(2)–C(4)–C(3)	112.0(4)	S(2)–C(5)–C(6)	111.1(4)
P(2)–C(6)–C(5)	110.8(4)		

observed for $\text{RSC}_2\text{H}_4\text{SR}$ in this complex (*cis*- α) does not necessitate that two adjacent five-membered chelate rings lie parallel (*i.e.* there are no $\text{PCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S}$ linkages occupying meridional co-ordination sites as would occur in the *cis*- β forms). This avoids the additional ring strain that would otherwise occur. The structure determined for $[\text{RuCl}_2(\text{RSC}_2\text{H}_4\text{SR})]\cdot 0.75\text{Et}_2\text{O}$ contrasts with that reported for $[\text{RuCl}_2\{\text{RP}(\text{Ph})\text{C}_2\text{H}_4(\text{Ph})\text{PR}\}]\text{PF}_6$ [$\text{RP}(\text{Ph})\text{C}_2\text{H}_4(\text{Ph})\text{PR} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2(\text{Ph})\text{PCH}_2\text{CH}_2\text{PPh}_2$] in which a *trans*-dichloro stereochemistry is observed, with all three chelate rings occurring around the equatorial co-ordination sites.¹⁴ It is likely that the high barrier to inversion at P and the steric effect of the Ph groups bound to the internal phosphines in $\text{RP}(\text{Ph})\text{C}_2\text{H}_4(\text{Ph})\text{PR}$ play a significant role in determining the stereochemistries of its complexes.

The stereochemistries of $[\text{RuCl}_2(\text{RSC}_2\text{H}_4\text{SR})]$ and $[\text{RuCl}_2(\text{Ph}_2[14]\text{aneP}_2\text{S}_2)]$, although both involving *cis*-dichloro arrangements, are markedly different. This is mainly a consequence of the acyclic *vs.* macrocyclic configurations respectively. Clearly, unlike $\text{RSC}_2\text{H}_4\text{SR}$, it is not possible for $\text{Ph}_2[14]\text{aneP}_2\text{S}_2$ to co-ordinate to a metal ion to give a P-*trans*-P arrangement. Irrespective of this, $\text{Ph}_2[14]\text{aneP}_2\text{S}_2$ and $\text{RSC}_2\text{H}_4\text{SR}$ each co-ordinates *via* all four donor atoms to give stable complexes. Unfortunately to date we have been unable to grow crystals of $[\text{RuCl}_2(\text{Ph}_2[14]\text{aneP}_2\text{S}_2)]$ suitable for a crystal structure determination.

We have also investigated the redox properties of the ruthenium(II) complexes by cyclic voltammetry. In CH_2Cl_2 solution (0.1 mol dm^{-3} NBu_4BF_4 supporting electrolyte) *cis*- $[\text{RuCl}_2(\text{Ph}_2[14]\text{aneP}_2\text{S}_2)]$ shows a reversible one-electron oxidation at $E_{\frac{1}{2}} = +0.32$ V *vs.* ferrocene-ferrocenium (Fig. 3), assigned to a $\text{Ru}^{\text{II}}-\text{Ru}^{\text{III}}$ redox couple. This couple is observed at $E_{\frac{1}{2}} = +0.16$ V for *cis*- $[\text{RuCl}_2(\text{RSC}_2\text{H}_4\text{SR})]$. These potentials are comparable with those for other dichlororuthenium(II) complexes involving phosphine and thioether ligands, *e.g.* $[\text{RuCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^{0/+}$ ($E_{\frac{1}{2}} = +0.13$ V) and *trans*- $[\text{RuCl}_2(\text{MeSCH}_2\text{CH}_2\text{SMe})_2]^{0/+}$ ($E_{\frac{1}{2}} = +0.14$ V).¹⁵

The related low-spin d^6 complexes $[\text{MCl}_2(\text{RSC}_2\text{H}_4\text{SR})]\text{PF}_6$ ($\text{M} = \text{Rh}$ or Ir) are obtained either by chloride abstraction from $[\text{RhCl}_3(\text{RSC}_2\text{H}_4\text{SR})]$ (formed from $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ and $\text{RSC}_2\text{H}_4\text{SR}$ in EtOH -water), or by reaction of $[\{\text{IrCl}(\text{C}_8\text{H}_{14})_2\}_2]$ with 0.5 molar equivalents of $\text{RSC}_2\text{H}_4\text{SR}$ followed by oxidation by Cl_2 and anion metathesis. The FAB mass spectra show highest-mass peaks with the correct isotopic patterns for $[\text{RhCl}_2(\text{RSC}_2\text{H}_4\text{SR})]^+$ ($m/z = 691$) and $[\text{IrCl}_2-$

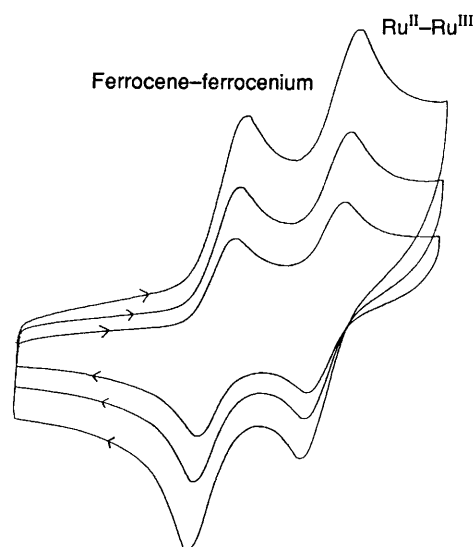


Fig. 3 Cyclic voltammogram of *cis*- $[\text{RuCl}_2(\text{Ph}_2[14]\text{aneP}_2\text{S}_2)]$ measured at 200, 100 and 50 mV s^{-1} in CH_2Cl_2 solution (0.1 mol dm^{-3} NBu_4BF_4 supporting electrolyte) and relative to equimolar ferrocene-ferrocenium

$(\text{RSC}_2\text{H}_4\text{SR} + \text{H})^+$ ($m/z = 781$), together with additional peaks corresponding to successive loss of Cl from these species. Proton NMR and IR spectroscopy and microanalytical data are also consistent with the formulation $[\text{MCl}_2(\text{RSC}_2\text{H}_4\text{SR})]\text{PF}_6$ for these products.

The single-crystal structure of $[\text{RhCl}_2(\text{RSC}_2\text{H}_4\text{SR})]\text{PF}_6\cdot \text{CH}_2\text{Cl}_2$ shows (Fig. 4, Table 2) two independent half cations in which the Rh^{III} ions occupy sites of crystallographic two-fold symmetry, with one PF_6^- anion in a general position in the asymmetric unit. The stereochemistry at Rh^{III} is very similar to that observed for $[\text{RuCl}_2(\text{RSC}_2\text{H}_4\text{SR})]$ described above, with the cation showing a *cis*- α arrangement and similar trends in the metal-donor atom bond lengths and angles, $\text{Rh}(1)-\text{P}(1)$ 2.352(2), $\text{Rh}(1)-\text{S}(1)$ 2.303(2), $\text{Rh}(1)-\text{Cl}(1)$ 2.370(2) Å, $\text{Rh}(2)-\text{P}(2)$ 2.342(2), $\text{Rh}(2)-\text{S}(2)$ 2.297(2), and $\text{Rh}(2)-\text{Cl}(2)$

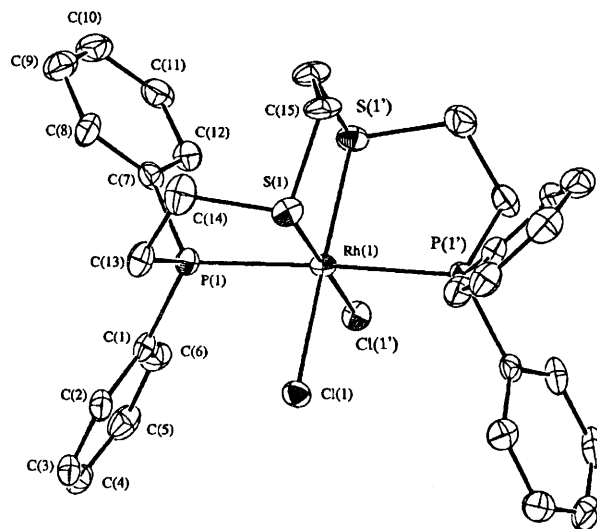


Fig. 4 View of the structure of one of the two independent *cis*- $[\text{RhCl}_2(\text{RSC}_2\text{H}_4\text{SR})]^+$ cations with the numbering scheme adopted. Primed atoms are related to unprimed ones by a two-fold operation. The other cation is essentially indistinguishable; H atoms are omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for *cis*- $[\text{RhCl}_2(\text{RSC}_2\text{H}_4\text{SR})]^+$

$\text{Rh}(1)-\text{Cl}(1)$	2.370(2)	$\text{Rh}(2)-\text{Cl}(2)$	2.359(2)
$\text{Rh}(1)-\text{S}(1)$	2.303(2)	$\text{Rh}(2)-\text{S}(2)$	2.297(2)
$\text{Rh}(1)-\text{P}(1)$	2.352(2)	$\text{Rh}(2)-\text{P}(2)$	2.342(2)
$\text{S}(1)-\text{C}(14)$	1.839(7)	$\text{S}(1)-\text{C}(15)$	1.821(6)
$\text{S}(2)-\text{C}(29)$	1.832(7)	$\text{S}(2)-\text{C}(30)$	1.811(6)
$\text{P}(1)-\text{C}(1)$	1.819(6)	$\text{P}(1)-\text{C}(7)$	1.817(6)
$\text{P}(1)-\text{C}(13)$	1.818(6)	$\text{P}(2)-\text{C}(16)$	1.820(6)
$\text{P}(2)-\text{C}(22)$	1.806(6)	$\text{P}(2)-\text{C}(28)$	1.802(6)
$\text{C}(13)-\text{C}(14)$	1.533(9)	$\text{C}(15)-\text{C}(15)$	1.50(1)
$\text{C}(28)-\text{C}(29)$	1.523(9)	$\text{C}(30)-\text{C}(30)$	1.52(1)
$\text{Cl}(1)-\text{Rh}(1)-\text{Cl}(1')$	92.74(8)	$\text{Cl}(2)-\text{Rh}(2)-\text{Cl}(2')$	93.67(8)
$\text{Cl}(1)-\text{Rh}(1)-\text{S}(1)$	177.53(6)	$\text{Cl}(2)-\text{Rh}(2)-\text{S}(2)$	88.11(5)
$\text{Cl}(1)-\text{Rh}(1)-\text{P}(1)$	92.45(6)	$\text{Cl}(2)-\text{Rh}(2)-\text{P}(2)$	85.98(6)
$\text{Cl}(1)-\text{Rh}(1)-\text{S}(1)$	88.98(5)	$\text{Cl}(2)-\text{Rh}(2)-\text{S}(2')$	177.50(6)
$\text{Cl}(1)-\text{Rh}(1)-\text{P}(1)$	85.51(6)	$\text{Cl}(2)-\text{Rh}(2)-\text{P}(2')$	92.29(6)
$\text{S}(1)-\text{Rh}(1)-\text{P}(1)$	85.91(6)	$\text{S}(2)-\text{Rh}(2)-\text{S}(2')$	90.15(9)
$\text{S}(1)-\text{Rh}(1)-\text{P}(1')$	96.19(6)	$\text{S}(2)-\text{Rh}(2)-\text{P}(2')$	95.70(6)
$\text{P}(1)-\text{Rh}(1)-\text{P}(1')$	177.06(9)	$\text{S}(2)-\text{Rh}(2)-\text{P}(2)$	86.09(6)
$\text{S}(1)-\text{Rh}(1)-\text{S}(1')$	89.36(8)	$\text{P}(2)-\text{Rh}(2)-\text{P}(2')$	177.47(9)
$\text{Rh}(1)-\text{S}(1)-\text{C}(14)$	106.9(2)	$\text{Rh}(1)-\text{S}(1)-\text{C}(15)$	103.0(2)
$\text{C}(14)-\text{S}(1)-\text{C}(15)$	99.4(3)	$\text{Rh}(2)-\text{S}(2)-\text{C}(29)$	106.3(2)
$\text{Rh}(2)-\text{S}(2)-\text{C}(30)$	102.8(2)	$\text{C}(29)-\text{S}(2)-\text{C}(30)$	100.8(3)
$\text{Rh}(1)-\text{P}(1)-\text{C}(1)$	117.8(2)	$\text{Rh}(1)-\text{P}(1)-\text{C}(7)$	117.1(2)
$\text{Rh}(1)-\text{P}(1)-\text{C}(13)$	103.1(2)	$\text{C}(1)-\text{P}(1)-\text{C}(7)$	104.9(3)
$\text{C}(1)-\text{P}(1)-\text{C}(13)$	106.0(3)	$\text{C}(7)-\text{P}(1)-\text{C}(13)$	106.9(3)
$\text{Rh}(2)-\text{P}(2)-\text{C}(16)$	115.0(2)	$\text{Rh}(2)-\text{P}(2)-\text{C}(22)$	118.7(2)
$\text{Rh}(2)-\text{P}(2)-\text{C}(28)$	103.1(2)	$\text{C}(16)-\text{P}(2)-\text{C}(22)$	105.2(3)
$\text{C}(16)-\text{P}(2)-\text{C}(28)$	106.8(3)	$\text{C}(22)-\text{P}(2)-\text{C}(28)$	107.3(3)

2.359(2) Å. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of $[\text{MCl}_2(\text{RSC}_2\text{H}_4\text{SR})]\text{PF}_6$ indicate that this stereochemistry and donor set is retained in solution, $\delta +41.1$, $^1J_{\text{RhP}} = 85$ Hz for $\text{M} = \text{Rh}$, $\delta +28.0$ for $\text{M} = \text{Ir}$. The ^{103}Rh NMR spectrum (11.4 MHz) of *cis*- $[\text{RhCl}_2(\text{RSC}_2\text{H}_4\text{SR})]\text{PF}_6$ shows a triplet at $\delta +1405$ ($^1J_{\text{RhP}} = 85$ Hz). This signal is intermediate between that observed for *trans*- $[\text{RhCl}_2(\text{MeSCH}_2\text{CH}_2\text{SMe})_2]^+$ (δ 2502–2585, mixture of invertomers)¹⁶ and *trans*- $[\text{RhCl}_2\{o\text{-C}_6\text{H}_4(\text{P-Me}_2)_2\}_2]\text{Cl}$ (δ 628, qnt, $^1J_{\text{RhP}} = 80$ Hz).¹⁷ It has already been noted that, for a given ligand set, changing from a *cis* to a *trans* arrangement results in a downfield shift, e.g. *cis*- $[\text{RhCl}_2(\text{AsMe}_3)_4]^+$ (δ 1455) and *trans*- $[\text{RhCl}_2(\text{AsMe}_3)_4]^+$ (δ 1946).¹⁸

The spectroscopic results obtained confirm that ligation of $\text{RSC}_2\text{H}_4\text{SR}$ to the octahedral metal centres Ru^{II} , Rh^{III} or Ir^{III} yields a single isomeric form. Although low-temperature NMR spectra were not recorded, ligand exchange would not be expected in these low-spin d^6 compounds. The spectroscopic data are consistent with the *cis*- α arrangement observed in the solid state for Ru^{II} and Rh^{III} being retained in solution. The compound *meso*- $\text{Ph}_2[14]\text{aneP}_2\text{S}_2$, on the other hand, co-ordinates to Rh^{III} to give exclusively the *trans*-dichloro isomer, whereas the larger Ru^{II} is not compatible with the hole size available, and spectroscopic data indicate formation of the *cis*-dichloro isomer. We are currently investigating the possibility of chloride abstraction from these *cis*-dichloro species to yield substitution-labile co-ordination sites for uptake of for example N_2 , O_2 or olefins.

Experimental

Infrared spectra were measured as KBr or CsI discs or as Nujol mulls using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm^{-1} , solution UV/VIS spectra in quartz cells (1 cm path length) using a Perkin-Elmer Lambda19 spectrophotometer, mass spectra by electron impact (EI) or fast-atom bombardment (FAB) using 3-nitrobenzyl alcohol as matrix on a VG Analytical 70-250-SE normal-geometry double-focusing spectrometer, ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra using a Bruker AM300 spectrometer operating at 300 and 75.7 MHz respectively, and ^{31}P and ^{103}Rh NMR spectra in 10 mm NMR tubes containing 10–15% deuterated solvent using a Bruker AM360 spectrometer operating at 145.8 and 11.4 MHz respectively and referenced to 85% H_3PO_4 (^{31}P , δ 0) and $\Xi = 3.16$ MHz (^{103}Rh , δ 0). Microanalyses were obtained from the Imperial College Microanalytical Laboratory. Cyclic voltammetric experiments were performed using an EG & G Princeton Applied Research model 362 scanning potentiostat with 0.1 mol dm^{-3} NBu_4BF_4 supporting electrolyte, using a double platinum electrode as working and auxiliary electrode and a Ag–AgCl reference electrode. All potentials are quoted *versus* ferrocene–ferrocenium. The compounds $[\text{RuCl}_2(\text{py})_4]$ ¹⁹ and PPh_2H ²⁰ were prepared by the literature methods and $\text{Ph}_2[14]\text{aneP}_2\text{S}_2$ was obtained as described previously.⁴

(a) Synthesis of $[\text{RuCl}_2(\text{Ph}_2[14]\text{aneP}_2\text{S}_2)]$

To a solution of $[\text{RuCl}_2(\text{py})_4]$ (56.0 mg, 0.11 mmol) in deoxygenated toluene was added $\text{Ph}_2[14]\text{aneP}_2\text{S}_2$ (47.1 mg, 0.11 mmol) under a flow of nitrogen. This reaction mixture was refluxed under a nitrogen atmosphere for 6 h before cooling. A yellow precipitate formed during the reaction and after cooling to -10°C overnight this solid was filtered off and washed with diethyl ether. The product was recrystallised from CH_2Cl_2 and diethyl ether and dried *in vacuo* (37 mg, 56%) (Found: C, 41.2; H, 4.9. $\text{C}_{30}\text{H}_{32}\text{Cl}_2\text{P}_2\text{RuS}_2\cdot\text{CH}_2\text{Cl}_2$ requires C, 40.8; H, 4.7%). FAB mass spectrum: $m/z = 557$, 521 and 446; calc. 557 for $[\text{Ru}^{102}\text{Ru}^{35}\text{Cl}(\text{Ph}_2[14]\text{aneP}_2\text{S}_2)]^+$, 522 for $[\text{Ru}^{102}\text{Ru}(\text{Ph}_2[14]\text{aneP}_2\text{S}_2)]^+$ and 445 for $[\text{Ru}^{102}\text{Ru}(\text{Ph}_2[14]\text{aneP}_2\text{S}_2)]^+$. NMR: ^1H (360 MHz, CDCl_3), δ 7.6–7.1 (m, 10 H, Ph) and 3.3–2.1 (m, 20 H, CH_2); $^{31}\text{P}\{-^1\text{H}\}$ (145.8 MHz, $\text{CH}_2\text{Cl}_2\text{-CDCl}_3$, 300 K), δ

+63.5 (d, $^2J_{\text{PP}}$ 40) and 54.7 (d, $^2J_{\text{PP}}$ 40 Hz). UV/VIS (CH_2Cl_2): λ_{max} 330 (ϵ 1575 $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and 400 (sh) nm. IR (CsI disc): 3051w, 2917m, 1530w, 1184m, 1432vs, 1261m, 1102vs, 915w, 840w, 805m, 746m, 696vs, 486m, 309m and 283w cm^{-1} .

(b) Synthesis of $\text{RSC}_2\text{H}_4\text{SR}$

The compound PPh_2H (3.0 g, 16.1 mmol) was dissolved in dry, degassed thf (50 cm^3) and cooled to 0°C . *n*-Butyllithium in hexane (19.3 mmol) was added dropwise over ca. 30 min to give a deep red solution which was then cooled to -78°C (acetone slush). Ethylene sulfide SCH_2CH_2 (0.96 cm^3 , 16.1 mmol) dissolved in dry, degassed thf (20 cm^3) was then added over 2 h, followed by $\text{BrCH}_2\text{CH}_2\text{Br}$ (1.5 g, 8.06 mmol) dropwise to give a light yellow solution which was stirred under a nitrogen atmosphere overnight. After hydrolysing with water, the product was extracted with diethyl ether, dried (MgSO_4) and the solvent removed *in vacuo*. It was then recrystallised from $\text{CH}_2\text{Cl}_2\text{-EtOH}$ to yield a white solid (3.57 g, 52%) (Found: C, 68.9; H, 6.2. $\text{C}_{30}\text{H}_{32}\text{P}_2\text{S}_2$ requires C, 69.5; H, 6.2%). FAB mass spectrum: $m/z = 519$; calc. 518 for $\text{RSC}_2\text{H}_4\text{SR}$. NMR: ^1H (300 MHz, CDCl_3), δ 7.5–7.3 (m, 20 H, Ph), 2.65 (m, 4 H, CH_2P), 2.55 (m, 4 H, $\text{SCH}_2\text{CH}_2\text{P}$), and 2.30 (m, 4 H, $\text{SCH}_2\text{CH}_2\text{S}$); $^{13}\text{C}\{-^1\text{H}\}$ (75.5 MHz, CDCl_3), δ 137.89 (quaternary C of Ph), 132.80, 129.01, 128.75 (CH of Ph), 31.12 ($\text{SCH}_2\text{CH}_2\text{S}$), 28.75 ($\text{PCH}_2\text{CH}_2\text{S}$), 28.70 (d, PCH_2 , $^2J_{\text{PC}} = 37$ Hz); ^{31}P (145.8 MHz, $\text{CH}_2\text{Cl}_2\text{-D}_2\text{O}$), $\delta -16.3$. IR (CsI disc): 3066m, 3045w, 2941w, 2919m, 1583m, 1478vs, 1430vs, 1393w, 1326w, 1306w, 1280m, 1207m, 1178m, 1130w, 1097m, 1068m, 1025m, 998m, 907m, 843w, 757w, 737vs, 696vs, 531w, 504m, 479m, 438w and 395w cm^{-1} .

(c) Synthesis of *cis*- $[\text{RuCl}_2(\text{RSC}_2\text{H}_4\text{SR})]$

To a refluxing solution of $\text{RSC}_2\text{H}_4\text{SR}$ (50 mg, 0.097 mmol) in degassed toluene (35 cm^3) was added dropwise $[\text{RuCl}_2(\text{py})_4]$ (47 mg, 0.097 mmol) dissolved in $\text{CH}_2\text{Cl}_2\text{-MeCN-toluene}$ (1:1:2 v/v, 20 cm^3). After refluxing this orange solution for 12 h the solvent volume was reduced to ca. 5 cm^3 . Addition of diethyl ether afforded the product as a yellow solid which was recrystallised from $\text{CH}_2\text{Cl}_2\text{-diethyl ether}$ and dried *in vacuo* (57 mg, 82%) (Found: C, 48.2; H, 4.2. $\text{C}_{30}\text{H}_{32}\text{Cl}_2\text{P}_2\text{RuS}_2\cdot\text{CH}_2\text{Cl}_2$ requires C, 48.0; H, 3.8%). FAB mass spectrum: $m/z = 690$, 655 and 627; calc. 690 for $[\text{Ru}^{102}\text{Ru}^{35}\text{Cl}_2(\text{RSC}_2\text{H}_4\text{SR})]^+$, 655 for $[\text{Ru}^{102}\text{Ru}^{35}\text{Cl}(\text{RSC}_2\text{H}_4\text{SR})]^+$ and 627 for $[\text{Ru}^{102}\text{Ru}^{35}\text{Cl}(\text{RSC}_2\text{H}_4\text{SR} - \text{C}_2\text{H}_4)]^+$. NMR (CDCl_3): ^1H (300 MHz), δ 7.5–7.3 (m, 20 H, Ph) and 3.3–1.8 (m, 12 H, CH_2); ^{31}P (145.8 MHz), $\delta +42.7$. UV/VIS (CH_2Cl_2): λ_{max} 254 (ϵ 24 000), ca. 360 (sh) (ca. 600) and 450nm (380 $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$). IR (CsI disc): 3050w, 2961w, 2917w, 1570w, 1482m, 1431vs, 1407m, 1314w, 1260m, 1189m, 1096vs, 1028m, 899w, 812m, 742m, 702vs, 662w, 517m, 495m and 270w cm^{-1} .

(d) Single-crystal structure determination on *cis*- $[\text{RuCl}_2(\text{RSC}_2\text{H}_4\text{SR})]\cdot 0.75\text{Et}_2\text{O}$

Orange prismatic crystals were obtained by vapour diffusion of Et_2O into a solution of the complex in CH_2Cl_2 . The selected crystal (0.20 \times 0.10 \times 0.30 mm) was coated in silicone oil, mounted on a glass fibre and cooled under a stream of N_2 gas to prevent solvent loss.

Crystal data. $\text{C}_{33}\text{H}_{39.5}\text{Cl}_2\text{O}_{0.75}\text{P}_2\text{RuS}_2$ $M = 746.2$, monoclinic, space group $P2_1/n$, $a = 13.080(5)$, $b = 17.822(2)$, $c = 15.003(1)$ Å, $\beta = 102.87(2)^\circ$, $U = 3409(1)$ Å³ [from 20 values of 25 reflections measured at $\pm\omega$ ($39.4 \leq 2\theta \leq 39.9^\circ$), $\lambda = 0.71073$ Å], $Z = 4$, $D_c = 1.454$ g cm^{-3} , $T = 123$ K, $\mu = 0.857$ mm^{−1}, $F(000) = 1534$.

Data collection and processing. Rigaku AFC7R four-circle diffractometer equipped with an Oxford Cryostreams low-

Table 3 Fractional atomic coordinates for *cis*-[RuCl₂(RSC₂H₄SR)]·0.75Et₂O

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ru	0.516 38(3)	0.042 58(2)	0.751 89(3)	C(14)	0.798 1(4)	−0.121 5(3)	0.846 4(4)
Cl(1)	0.510 81(9)	0.143 19(7)	0.863 22(8)	C(15)	0.852 2(4)	−0.176 0(3)	0.808 9(4)
Cl(2)	0.581 51(10)	0.125 18(7)	0.645 11(8)	C(16)	0.865 5(4)	−0.168 8(3)	0.721 6(4)
S(1)	0.458 6(1)	−0.039 40(7)	0.847 82(9)	C(17)	0.824 5(4)	−0.106 6(3)	0.670 4(4)
S(2)	0.515 3(1)	−0.053 69(7)	0.650 41(9)	C(18)	0.771 7(4)	−0.051 7(3)	0.706 6(4)
P(1)	0.684 5(1)	0.015 88(8)	0.838 13(9)	C(19)	0.300 6(4)	0.163 2(3)	0.634 7(4)
P(2)	0.347 9(1)	0.068 96(8)	0.666 89(9)	C(20)	0.362 3(5)	0.225 7(3)	0.661 3(4)
O	0.850 9(7)	0.173 2(6)	0.513 8(5)	C(21)	0.323 3(6)	0.297 5(4)	0.632 0(5)
C(1)	0.662 2(4)	−0.019 3(3)	0.946 6(3)	C(22)	0.226 2(6)	0.305 2(4)	0.574 7(5)
C(2)	0.574 0(4)	−0.076 7(3)	0.929 9(3)	C(23)	0.163 5(6)	0.242 4(4)	0.547 9(4)
C(3)	0.424 0(4)	−0.123 7(3)	0.779 0(4)	C(24)	0.200 6(5)	0.172 2(4)	0.578 8(4)
C(4)	0.499 1(4)	−0.137 2(3)	0.716 2(4)	C(25)	0.237 2(4)	0.030 5(3)	0.707 4(4)
C(5)	0.387 1(4)	−0.053 7(3)	0.568 5(4)	C(26)	0.222 3(4)	0.057 9(4)	0.790 1(4)
C(6)	0.341 9(4)	0.023 5(3)	0.555 9(3)	C(27)	0.136 7(5)	0.033 9(4)	0.823 8(4)
C(7)	0.785 5(4)	0.087 2(3)	0.876 5(3)	C(28)	0.066 1(5)	−0.017 8(4)	0.775 4(5)
C(8)	0.879 7(4)	0.067 2(3)	0.936 1(4)	C(29)	0.082 7(5)	−0.046 6(4)	0.694 6(5)
C(9)	0.953 8(4)	0.121 0(3)	0.970 6(4)	C(30)	0.167 0(5)	−0.021 8(4)	0.659 4(4)
C(10)	0.936 8(4)	0.195 7(3)	0.944 8(4)	C(31)	0.941 5(8)	0.163 8(8)	0.672 9(7)
C(11)	0.845 5(4)	0.215 9(3)	0.883 4(4)	C(32)	0.878(1)	0.127(1)	0.601 8(10)
C(12)	0.769 0(4)	0.161 8(3)	0.849 1(4)	C(33)	0.771(1)	0.236 4(8)	0.476(1)
C(13)	0.758 0(4)	−0.058 7(3)	0.796 2(4)	C(34)	0.779(1)	0.241 5(9)	0.391(1)

temperature attachment, using graphite-monochromated Mo-K α X-radiation, ω scans with ω -scan width = $(1.68 + 0.35 \tan \theta)^\circ$, 8040 data collected, 7710 unique ($R_{\text{int}} = 0.016$) ($2\theta_{\text{max}} 54^\circ$, h 0–22, k −18 to 18, l −18 to 17) giving 6511 reflections with $F \geq 5\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed. The data were corrected for Lorentz and polarisation effects. No absorption correction was applied since preliminary ψ scans revealed no significant absorption.

Structure solution and refinement. The structure was solved by direct methods²¹ and developed by using iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms in an ordered [RuCl₂(RSC₂H₄SR)] molecule.²² During refinement a partially occupied (75%) Et₂O solvent molecule was found to be present. All non-H atoms were refined anisotropically, while H atoms were located in the difference map and their coordinates fixed. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. At final convergence R , $R' = 0.043$, 0.068 respectively, $S = 5.59$ for 380 refined parameters. The final ΔF synthesis showed no peaks above 1.31 or below $-0.88 \text{ e } \text{\AA}^{-3}$ and the maximum $\Delta/\sigma = 0.01$. Fractional atomic coordinates are listed in Table 3.

(e) Synthesis of *cis*-[RhCl₂(RSC₂H₄SR)]PF₆

The phosphine (0.0986 g, 0.190 mmol) was dissolved in degassed ethanol (15 cm³) and heated to reflux; RhCl₃·3H₂O (50 mg, 0.19 mmol) was dissolved in water–ethanol (1:2 v/v, 15 cm³) and added dropwise over 1 h. Reflux was continued for 1.5 h before the resulting orange solution was allowed to cool. A small amount of yellow ethanol-insoluble solid was filtered off. The solvent was then removed *in vacuo* and the product redissolved in CH₂Cl₂ and filtered once again. The product, thought to be RhCl₂(RSC₂H₄SR), was precipitated as a pale orange solid by the addition of diethyl ether (116 mg, 84%). This was dissolved in MeCN–CH₂Cl₂ (1:1 v/v, 30 cm³) and refluxed for 1 h with TIPF₆ (56 mg, 0.16 mmol). The resulting yellow-orange solution was filtered through Celite to remove the white TiCl₄ precipitated. The product was precipitated from CH₂Cl₂–diethyl ether as a yellow powder and dried *in vacuo* (76 mg, 48%) (Found: C, 39.5; H, 3.9. C₃₀H₃₂Cl₂F₆P₃RhS₂·CH₂Cl₂ requires C, 40.4; H, 3.7%). FAB mass spectrum: $m/z = 691$, 656 and 621; calc. 691 for [¹⁰³Rh³⁵Cl₂(RSC₂H₄SR)]⁺, 656 for

[¹⁰³Rh³⁵Cl(RSC₂H₄SR)]⁺ and 621 for [¹⁰³Rh(RSC₂H₄SR)]⁺. NMR: ¹H (300 MHz, CDCl₃), δ 7.9–7.3 (m, 20 H, Ph) and 3.5–2.6 (m, 12 H, CH₂); ³¹P (145.8 MHz, CH₂Cl₂–D₂O), δ +41.1 (d, 2 P, ¹J_{RhP} = 85, RSC₂H₄SR) and −146.3 (spt, 1 P, PF₆[−]); ¹⁰³Rh (11.4 MHz, MeCN–CD₃CN, 300 K), δ +1405 (t, 85 Hz). UV/VIS (MeCN): λ_{max} 226 (sh) (ϵ ca. 33 000), 286 (sh) (ca. 18 500), 316 (23 000) and 421 (sh) nm (ca. 550 dm³ mol^{−1} cm^{−1}). IR (CsI disc): 3060w, 2963w, 1570w, 1482m, 1433vs, 1406m, 1337w, 1314w, 1262w, 1191w, 1097m, 1027m, 998w, 840vs, 745m, 709m, 694m, 558vs, 520m, 368w and 336w cm^{−1}.

(f) Single-crystal structure determination on *cis*-[RhCl₂(RSC₂H₄SR)]PF₆·CH₂Cl₂

Orange rhomb-shaped crystals were obtained by vapour diffusion of Et₂O into a solution of the complex in CH₂Cl₂. The selected crystal (0.60 × 0.44 × 0.26 mm) was coated in silicone oil, mounted on a glass fibre and cooled under a stream of N₂.

Crystal data. C₃₁H₃₄Cl₄P₂RhS₂·PF₆[−], $M = 922.4$, monoclinic, space group $C2/c$, $a = 25.183(5)$, $b = 15.622(5)$, $c = 22.520(5)$ Å, $\beta = 123.90(1)^\circ$, $U = 7352(3)$ Å³ [from 20 values of 23 reflections measured at $\pm\omega$ ($39.0 \leq 2\theta \leq 39.9^\circ$, $\lambda = 0.710 73$ Å)], $Z = 8$, $D_c = 1.666 \text{ g cm}^{-3}$, $T = 123 \text{ K}$, $\mu = 1.052 \text{ mm}^{-1}$, $F(000) = 3712$.

Data collection and processing. As for [RuCl₂(RSC₂H₄SR)] except ω scan width = $(1.78 + 0.35 \tan \theta)^\circ$, 6157 data collected, 6004 unique ($R_{\text{int}} = 0.051$) ($2\theta_{\text{max}} 48^\circ$, h 0–32, k 0–20, l −29 to 29) giving 4248 reflections with $F \geq 5\sigma(F)$ for use in all calculations.

Structure solution and refinement. Structure solution as for [RuCl₂(RSC₂H₄SR)] located all non-H atoms in the two independent half [RhCl₂(RSC₂H₄SR)]⁺ cations, one complete PF₆[−] anion and CH₂Cl₂ solvent molecule in the asymmetric unit.²² Since there were no identifiable faces on the crystal, at isotropic convergence the data were corrected for absorption using DIFABS²³ (maximum and minimum transmission factors = 1.174 and 0.868 respectively). All non-H atoms were refined anisotropically, while H atoms were placed in fixed, calculated positions. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. At final convergence R , $R' = 0.045$, 0.043 respectively, $S = 3.55$ for 425 refined parameters.

Table 4 Fractional atomic coordinates for *cis*-[RhCl₂(RSC₂H₄SR)]PF₆·CH₂Cl₂

Atom	x	y	z	Atom	x	y	z
Rh(1)	0	−0.777 23(4)	−0.25	C(8)	−0.058 0(3)	−0.658 7(3)	−0.469 1(3)
Rh(2)	0	−0.280 72(4)	−0.25	C(9)	−0.031 8(4)	−0.613 7(4)	−0.500 1(4)
Cl(1)	−0.074 93(7)	−0.881 90(9)	−0.265 69(9)	C(10)	0.030 8(4)	−0.628 3(4)	−0.478 0(4)
Cl(2)	−0.039 32(8)	−0.384 02(10)	−0.341 65(9)	C(11)	0.067 6(3)	−0.686 4(4)	−0.423 7(4)
Cl(3)	0.206 8(1)	0.188 1(3)	−0.288 1(2)	C(12)	0.042 6(3)	−0.729 3(4)	−0.390 7(3)
Cl(4)	0.253 3(1)	0.244 2(2)	−0.142 9(2)	C(13)	−0.132 1(3)	−0.736 1(4)	−0.405 8(3)
S(1)	−0.072 08(8)	−0.672 39(10)	−0.268 55(9)	C(14)	−0.122 9(3)	−0.652 6(4)	−0.365 5(4)
S(2)	−0.040 07(8)	−0.176 89(10)	−0.336 89(9)	C(15)	−0.023 8(3)	−0.575 3(4)	−0.240 1(4)
P(1)	−0.054 28(8)	−0.781 1(1)	−0.375 28(8)	C(16)	−0.112 9(3)	−0.214 2(4)	−0.213 9(3)
P(2)	−0.102 20(8)	−0.284 0(1)	−0.271 11(9)	C(17)	−0.158 4(3)	−0.150 2(4)	−0.240 9(4)
P(3)	0.291 82(9)	−0.022 1(1)	−0.048 3(1)	C(18)	−0.163 1(4)	−0.096 9(4)	−0.194 3(5)
F(1)	0.316 9(2)	0.033 2(4)	−0.085 7(3)	C(19)	−0.124 7(4)	−0.110 1(5)	−0.122 1(5)
F(2)	0.299 3(3)	−0.104 0(4)	−0.084 0(4)	C(20)	−0.080 1(4)	−0.174 9(5)	−0.095 0(4)
F(3)	0.267 4(2)	−0.082 6(4)	−0.012 2(3)	C(21)	−0.072 4(3)	−0.225 4(4)	−0.139 8(3)
F(4)	0.282 7(2)	0.059 7(4)	−0.014 5(3)	C(22)	−0.135 1(3)	−0.386 0(4)	−0.269 3(3)
F(5)	0.220 1(2)	−0.011 5(3)	−0.115 2(2)	C(23)	−0.115 1(3)	−0.424 6(4)	−0.204 3(4)
F(6)	0.363 1(2)	−0.029 0(3)	−0.017 8(3)	C(24)	−0.138 6(4)	−0.503 2(4)	−0.200 6(4)
C(1)	−0.070 0(3)	−0.885 3(4)	−0.418 0(3)	C(25)	−0.183 4(3)	−0.544 5(4)	−0.262 9(4)
C(2)	−0.130 2(3)	−0.923 6(4)	−0.451 5(3)	C(26)	−0.204 7(3)	−0.507 4(4)	−0.328 0(4)
C(3)	−0.141 6(3)	−1.002 3(4)	−0.484 2(4)	C(27)	−0.179 7(3)	−0.429 7(4)	−0.331 3(4)
C(4)	−0.093 3(4)	−1.045 2(4)	−0.483 7(4)	C(28)	−0.152 6(3)	−0.242 6(4)	−0.360 8(3)
C(5)	−0.032 8(3)	−1.008 4(4)	−0.448 9(4)	C(29)	−0.123 5(3)	−0.160 2(5)	−0.366 6(4)
C(6)	−0.021 5(3)	−0.929 2(4)	−0.417 1(4)	C(30)	−0.003 4(3)	−0.080 1(4)	−0.285 8(3)
C(7)	−0.021 5(3)	−0.717 0(4)	−0.415 0(3)	C(31)	0.234 4(5)	0.156 6(7)	−0.202 9(6)

The final ΔF synthesis showed no peaks above 1.43 or below $-1.02 \text{ e } \text{\AA}^{-3}$ and the maximum $\Delta/\sigma = 0.01$. Fractional atomic coordinates are listed in Table 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles for both crystal structures have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

(g) Synthesis of [IrCl₂(RSC₂H₄SR)]PF₆

The complex $[\{\text{IrCl}(\text{C}_8\text{H}_{14})_2\}_2]$ (98 mg, 0.145 mmol) and RSC₂H₄SR (150 mg, 0.289 mmol) were added to degassed methanol (40 cm³) giving a yellow solution, which was refluxed overnight under N₂. On cooling to 0 °C a solution of Cl₂ in CCl₄ was added ($\approx 5 \text{ cm}^3$), causing the colour to fade. After stirring for 10 min the solvent was removed *in vacuo*. The resulting solid was refluxed in water (80 cm³), NH₄PF₆ (100 mg) was added in MeCN and reflux was continued overnight. Removal of the solvent *in vacuo* and precipitation from CH₂Cl₂ by addition of Et₂O gave a pale yellow solid (147 mg, 45%). (Found: C, 38.8; H, 3.5. C₃₀H₃₂Cl₂F₆IrP₃S₂ requires C, 38.9; H, 3.5%). FAB mass spectrum: $m/z = 781$, 747 and 683; calc. 780 for $[\text{Ir}^{35}\text{Cl}_2(\text{RSC}_2\text{H}_4\text{SR})]^+$, 745 for $[\text{Ir}^{35}\text{Cl}(\text{RSC}_2\text{H}_4\text{SR})]^+$ and 682 for $[\text{Ir}^{35}\text{Cl}(\text{RSC}_2\text{H}_4\text{SR} - \text{C}_2\text{H}_4)]^+$. NMR: ¹H (300 MHz, CDCl₃); δ 7.8–7.1 (m, 20 H, Ph) and 3.4–2.2 (m, 12 H, CH₂); ³¹P (145.8 MHz, CH₂Cl₂-CDCl₃) δ +28.0 (2P, RSC₂H₄SR) and −146.3 (spt, 1P, PF₆[−]). IR (CsI disc): 3053w, 2963w, 2920w, 1570w, 1482m, 1432vs, 1405w, 1311w, 1272w, 1162w, 1099m, 1027w, 998w, 840vs, 744m, 695m, 558vs, 537m, 526m, 494w and 375w cm^{−1}.

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