Mixed Phosphathia Macrocyclic Chemistry: Synthesis and Characterisation of $[M(Ph_2[14]aneP_2S_2)]^{2+}$ (M = Pd or Pt) and $[RhCl_2(Ph_2[14]aneP_2S_2)]^+$ (Ph_2[14]aneP_2S_2 = 8,12-Diphenyl-1,5-dithia-8,12-diphosphacyclotetradecane)[†]

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The new diphosphadithia macrocycle 8,12-diphenyl-1,5-dithia-8,12-diphosphacyclotetradecane $(Ph_2[14]aneP_2S_2)$ has been prepared and the *meso* isomer isolated as a white solid. Upon reaction with MCl₂ (M = Pd or Pt) in the presence of TIPF₆ in refluxing MeCN this isomer gave $[M(Ph_2[14]aneP_2S_2)][PF_6]_2$. The crystal structure of $[Pt(Ph_2[14]aneP_2S_2)][PF_6]_2$. MeNO₂ shows tetradentate P_2S_2 co-ordination at Pt" giving a distorted square-planar geometry with Pt-P 2.247(3), 2.252(3) Å and Pt-S 2.343(3), 2.341(4) Å. Phosphorus-31 and ¹⁹⁶Pt NMR spectroscopic data confirm retention of this P_2S_2 co-ordination in solution. Treatment of RhCl₃·3H₂O with $Ph_2[14]aneP_2S_2$ in refluxing aqueous EtOH followed by addition of an excess of NH₄PF₆ gave $[RhCl_2(Ph_2[14]aneP_2S_2)]PF_6$ as a yellow solid. The ³¹P NMR spectrum indicates that the complex exists as the *trans*-dichloro isomer exclusively, and a single-crystal X-ray structure determination confirms this. The crystal structure of $[RhCl_2(Ph_2[14]aneP_2S_2)]PF_6$ shows the macrocyclic donor atoms occupying the four equatorial co-ordination sites around the central Rh^{III} ion, Rh-P 2.286(1), 2.300(1) Å, Rh-S 2.374(1), 2.377(1) Å, with *trans*-dichloro ligands, Rh-Cl 2.347(1), 2.354(1) Å, giving a distorted octahedral geometry. Cyclic voltammetry shows that the complexes $[M(Ph_2[14]aneP_2S_2)][PF_6]_2$ (M = Pd or Pt) and *trans*- $[RhCl_2(Ph_2[14]aneP_2S_2)]PF_6$ each exhibit an irreversible reduction at E_{pc} values of -1.40, -1.93 and -1.06 V vs. ferrocene-ferrocenium respectively.

The co-ordination chemistry of phosphine ligands has been studied intensively and a vast number of mono- and bi-dentate phosphine complexes are known.¹ Interest in these has been stimulated largely by their catalytic properties which has led to several important industrial applications. In spite of this there have been relatively few systematic studies on macrocyclic phosphine chemistry.² This contrasts the now extensive chemistry of thioether and aza macrocycles, which are excellent ligands for both p- and d-block elements, forming highly stable species which are resistant to demetallation and often exhibit very unusual structural, electronic and redox properties.³

We have recently initiated a study aimed at establishing the effects upon the metal ion properties of placing phosphine functions together with S(thioether) or N(amine) donors in a macrocyclic environment. To this end, we are currently preparing a series of mixed phosphathia and phosphaaza macrocycles with a view to investigating their co-ordination to various metal ions.

Kyba *et al.*⁴ have reported the preparations of several P_2E_2 (E = O, NR or S) and P_3S donor macrocycles all of which incorporate *o*-phenylene units in the backbone. These were found to act only as bidentate phosphine ligands to metal ions unless the ligand incorporated a 1-E-2-phosphinobenzo moiety. Another *trans*- P_2S_2 macrocycle has recently been reported by Wild and co-workers.⁵ This was prepared in low yield *via* a Pt^{II}-template. The tetradentate P_2S_2 macrocycles chosen for our work involve a fully saturated backbone, thereby allowing greater conformational flexibility and a number of possible co-ordination modes. Some P_4E_2 (E = NR, O, S)⁶ and PS₂⁷ donor macrocycles having saturated backbones have been





reported although their co-ordination chemistry has not yet been fully studied.

We now wish to report the synthesis of the mixed P_2S_2 donor macrocycle $Ph_2[14]aneP_2S_2$ and the quadridentate platinum metal macrocyclic complexes $[M(Ph_2[14]aneP_2S_2)][PF_6]_2$ (M = Pd or Pt) and *trans*- $[RhCl_2(Ph_2[14]aneP_2S_2)]PF_6$. The single-crystal structures of $[Pt(Ph_2[14]aneP_2S_2)]PF_6]_2$. MeNO₂ and *trans*- $[RhCl_2(Ph_2[14]aneP_2S_2)]PF_6$ are also presented.

Results and Discussion

The macrocycle Ph₂[14]aneP₂S₂ was prepared according to



Scheme 1 (i) LiBu (2 equiv.)–thf; (ii) $(CH_2)_2S$ (2 equiv.) then MeOH–water; (iii) Br(CH₂)₃Br, Cs₂CO₃–dmf

Scheme 1 using a modification of the method reported by Blower and co-workers⁷ for the preparation of Ph[9]anePS₂.⁷ Thus, the disecondary phosphine PhHP(CH₂)₃PHPh was treated with 2 molar equivalents of LiBuⁿ and 2 molar equivalents of $(CH_2)_2S$ in tetrahydrofuran (thf) solution at -78 °C and hydrolysed with MeOH, to give the intermediate dithiol, HS(CH₂)₂PPh(CH₂)₃PPh(CH₂)₂SH. Cyclisation was then achieved by reaction of this dithiol with BrCH₂CH₂CH₂Br at 65 °C over 24 h under high-dilution conditions in dimethylformamide (dmf)-Cs₂CO₃. This gave Ph₂[14]aneP₂S₂ as a light yellow oil obtained as a mixture of two stereoisomers. Subsequent treatment of this oil with acetone gave *meso*-Ph₂[14]aneP₂S₂ as a white solid (³¹P NMR; δ -24.3, *m*/*z* = 421).

Reaction of MCl_2 (M = Pd or Pt) with 1 molar equivalent of meso-Ph₂[14]aneP₂S₂ in the presence of 2 molar equivalents of TlPF₆ in refluxing MeCN followed by addition of Et₂O yields pale yellow and white solids for M = Pd and Ptrespectively. FAB mass spectrometry shows peaks at m/z 671, 525 and m/z 760, 614 with the correct isotopic distributions corresponding to $[Pd(Ph_2[14]aneP_2S_2)]PF_6^+$, $[Pd(Ph_2[14]aneP_2S_2)]PF_6^+$, $[Pd(Ph_2[14]aneP_2S_2)]PF_6^+$. $[Pt(Ph_2[14]aneP_2S_2 - H)]^+$ respectively. Together with IR, UV/VIS and ¹H NMR spectroscopic and microanalytical data, these results confirm the formulations $[M(Ph_2[14]aneP_2S_2)]$ -[PF₆]₂ (M = Pd or Pt) for the products. The ³¹P-{¹H} NMR spectrum (145.8 MHz, CD₃CN, 298 K) of [Pd(Ph₂[14]aneP₂S₂)][PF₆]₂ shows a singlet at δ + 53.4 due to the macrocyclic P donors, as well as a septet at δ -146.6 due to the PF₆⁻ anions. For [Pt(Ph₂[14]aneP₂S₂)][PF₆]₂ ³¹P-{¹H} NMR spectroscopy gives δ +46.2 with ¹J_{PtP} = 2718 Hz, and $\delta - 145.8$ (PF₆⁻ anion). The ³¹P NMR resonances integrate as 1:1, confirming that only one macrocycle is ligated to each metal ion. Furthermore, in both systems a large downfield shift is observed upon co-ordination of Ph₂[14]aneP₂S₂. Such shifts are seen frequently where five-membered chelate rings occur, and hence are also consistent with P_2S_2 co-ordination to $M^{II.8}$ The ¹⁹⁵Pt NMR spectrum (77.42 MHz, CD₃CN, 300 K) of $[Pt(Ph_2[14]aneP_2S_2)][PF_6]_2$ (Fig. 1) shows a triplet at δ -5174 (${}^{1}J_{PtP} = 2718$ Hz). This chemical shift is intermediate between those seen for S_4 and P_4 donor sets around Pt^{II} .

To enable comparisons with other reported diphosphadithia macrocyclic systems a single-crystal structure determination was undertaken on $[Pt(Ph_2[14]aneP_2S_2)][PF_6]_2$ ·MeNO₂. Suitable crystals were grown by vapour diffusion of Et₂O into a solution of the complex in MeNO₂. The structure shows (Fig. 2) the macrocycle co-ordinated to the Pt^{II} ion in a tetradentate manner via two thioether and two phosphine donors, giving a distorted square-planar stereochemistry. Selected geometric parameters are listed in Table 1. The Ph groups are oriented on one side of the Pt^{II}P₂S₂ plane, with the methylene groups directed to the opposite side. The Pt^{II} ion is displaced above the least-squares P₂S₂ plane, towards the Ph rings, by 0.12 Å,







Fig. 2 View of the structure of $[Pt(Ph_2[14]aneP_2S_2)]^{2+}$ with numbering scheme adopted

indicating a rather poor size-match between the metal ion radius and the macrocyclic cavity. This contrasts with the structure of $[Pt([14]aneS_4)]^{2+}$ in which the Pt^{II} ion sits precisely in the least-squares S_4 co-ordination plane, Pt-S 2.271(3), 2.285(4), 2.301(3), 2.295(4) Å.¹⁰ The Pt-P bond lengths in $[Pt(Ph_2[14]aneP_2S_2)]^{2+}$ are *ca*. 0.05 Å shorter and the Pt-S bond lengths *ca*. 0.05 Å longer than in $[PtL^1]^{2+}$, in which the P donors are *trans* to each other $(Pt-P 2.300, 2.293, Pt-S 2.285, 2.294 Å).^4$ In our complexes the thioether donors are *trans* in the phosphine donor atoms and these data strongly suggest a greater *trans* influence for P over S. A similar effect has been observed in the M-donor-atom bond lengths in $[PtL^2]^{2+}$, Pt-P(trans P) 2.289, 2.283 Å, <math>Pt-P(trans S) 2.255 Å, $Pt-S(trans P) 2.317 Å.^4$

We have also investigated the reaction between *meso*-Ph₂[14]aneP₂S₂ and the low-spin d⁶ Rh^{III} metal ion. Reaction of RhCl₃·3H₂O with 1 molar equivalent of Ph₂[14]aneP₂S₂ in refluxing aqueous EtOH under N₂ affords a yellow solution and a brown precipitate. Addition of NH₄PF₆ to the filtered yellow solution gives the stable phosphathia macrocyclic complex [RhCl₂(Ph₂[14]aneP₂S₂)]PF₆ as an orange solid. The FAB mass spectrum of this species shows peaks with the correct isotopic distributions at *m*/*z* 593, 558 and 523, corresponding to [¹⁰³Rh³⁵Cl₂(Ph₂[14]aneP₂S₂)]⁺ and successive loss of

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30	2	3
50	J	J

Table 1 Selected bond lengths (Å), angles and torsion angles (°) for $[Pt(Ph_2[14]aneP_2S_2)]^{2+1}$

Pt-P(1)	2.247(3)	C(4)-C(5)		1.547(18)	Pt-P(2)		2.252(3)	C(6)-C(7)		1.527(19)
Pt-S(1)	2.343(3)	C(8)–C(9)		1.523(20)	Pt-S(2)		2.341(4)	C(9)-C(10)		1.555(17)
P(1)-C(1)	1.824(14)	C(11)-C(12)		1.379(15)	P(1)-C(10)))	1.801(12)	C(11)-C(16)	1.373(17)
P(1)-C(11)	1.798(11)	C(12)-C(13)		1.395(19)	P(2)-C(7))	1.812(16)	C(13)-C(14))	1.387(23)
P(2)-C(8)	1.825(13)	C(14) - C(15)		1.383(21)	P(2)-C(1)	/)	1.787(11)	C(15)-C(16)	9	1.386(20)
S(1)-C(2)	1.826(14)	C(17) - C(18)		1.391(17)	S(1) - C(3)		1.824(14)	C(17) - C(22))	1.405(10)
S(2) = C(5)	1.827(12)	C(18)-C(19)		1.392(18)	S(2) = C(0)) \	1.850(14)	C(19) - C(20)	9	1.378(22)
C(1) = C(2)	1.527(18)	C(20)-C(21)		1.373(22)	C(3)-C(4)	1.323(22)	C(21) - C(22)	.)	1.575(19)
P(1) - Pt - P(2)	94.2(1)	S(1)-C(3)-C(4)		111.5(9)	P(1)-PtS	5(1)	88.3(1)	C(3)-C(4)-4	C(5)	116.8(11)
P(2)-Pt-S(1)	173.7(1)	S(2)-C(5)-C(4)		111.6(9)	P(1)-Pt-S	5(2)	173.2(1)	S(2)-C(6)-C	C(7)	112.9(10)
P(2) - Pt - S(2)	87.8(1)	P(2)-C(7)-C(6))	109.6(9)	S(1)-Pt-S	5(2)	89.0(1)	P(2)-C(8)-C(8)-C(8)-C(8)-C(8)-C(8)-C(8)-C(8	C(9)	113.5(9)
Pt-P(1)-C(1)	103.9(5)	C(8)-C(9)-C(1)	0)	115.1(11)	Pt-P(1)-C	C(10)	114.6(5)	P(1)-C(10)-	-C(9)	113.6(8)
C(1)-P(1)-C(10)	107.2(6)	P(1)-C(11)-C(1)	12)	118.0(9)	Pt-P(1)-C	$\mathcal{L}(\mathbf{H})$	113.7(4)	P(1)-C(11)-	-C(16)	122.7(8)
C(1)-P(1)-C(11)	108.2(6)	C(12)-C(11)-C	(16)	119.3(11)	C(10) - P(1)	I - C(II)	108.8(6)	C(11)-C(12))-C(13)	121.3(12)
Pt-P(2)-C(7)	104.6(4)	C(12)-C(13)-C	(14)	118.8(12)	Pt-P(2)-C	2(8)	116.8(4)	C(13)-C(14)	-C(15)	119.9(14)
C(7) - P(2) - C(8)	105.8(6)	C(14) - C(15) - C	(10)	120.2(14)	Pt-P(2)-C	L(1/)	114.0(4)	C(11)-C(10)	C(13)	120.4(11)
C(7)-P(2)-C(17) P(5(1), C(2))	107.3(6)	P(2) - U(1) - U(1)	18)	120.3(9)	$C(\delta) - P(2)$	-C(1)	107.3(3)	P(2) = C(17)	-C(22)	121.9(9) 121.4(12)
C(2) S(1) - C(2)	104.2(4)	C(18) - C(17) - C	(22)	117.0(11) 110.4(13)	Pt - S(1) - C	2(5) 2(5)	99.9(4)	C(10) = C(10)	C(19)	121.4(12) 110.7(13)
C(2) = S(1) = C(3) $P_{t_{1}}S(2) = C(6)$	103.3(0) 103.7(5)	C(10) - C(10	(20)	119.4(15) 121.5(12)	C(5) S(2)	-C(6)	104.0(6)	C(17) = C(20)	C(21)	179.7(13) 120.1(12)
P(1) = C(1) = C(2)	111 1(8)	C(20)-C(21)-C	(22)	121.3(12)	S(1) = C(2)	-C(0)	112 8(9)	C(1)-C(22	J-C(21)	120.1(12)
					S(1) C(2)		112.0())			
C(10) - P(1)	-C(1)-C(2)	-167.2	P(2)	C(8)C(9)C(10))	70.5	C(12)-C(11)-	C(16)-C(15)	-0.	.5
C(11)-P(1)	-C(1)-C(2)	75.6	C(1)	P(1) - C(10) - C(9)	<i>)</i>	172.0	C(14)-C(15	C(16) - C(11)	0.	7
C(3) = S(1) = C(3)	-C(2)-C(1)	78.3	C(1	1) - P(1) - C(10) - C	(9) -	-71.2	C(7) - P(2) - C(1)	(7)-C(18)	25.	.7
P(1) = C(1) = C(1)	-C(2)-S(1)	47.7	C(8)	P(1) = C(10) - P(1)	.) -	- 75.2	C(7)-P(2)-C(1)	(7)-C(22)	- 53.	.8
C(2) = S(1) = S(1)	C(3) - C(4)	-1/8.2		P(1) = C(11) = C(11)	-2) -	-81.0	C(8) - P(2) - C(1)	(7) - C(10)	- 20.	.8
S(1) - C(3) - C(3)	C(4) - C(5)	/3.2	C(1)	$\mathbf{P}(\mathbf{I}) = \mathbf{C}(\mathbf{I}) = \mathbf{C}(\mathbf{I})$	(0) (12)	91.1	P(2) = P(2) + C(1)	(12) - C(22)	39. 70	5
C(0) = S(2) = C(3) = C(4)	C(5) = C(4)	75.8		D = P(1) = C(11) = C	(12)	102.0	P(2)=C(17)=C	(10) - C(19)	/9	0
C(5) = C(4)	C(5) = S(2)			C(1) -	(10) = (13)	170.1	C(22) = C(17) = C(18)	C(10) - C(19)	-0.	8
C(8) - P(2)	C(0) - C(1)	171.6	C(1)	S-C(11)-C(12)-C	$\gamma(13)$	0.4	C(18) - C(19) - C(19	C(20) - C(21)	-4	9
C(17) - P(2)	-C(7)-C(6)	-73.8	COL	1) - C(12) - C(13) -	$\Gamma(14)$	0.4	C(19) - C(20) - C(20	C(21) - C(22)	3	2
S(2)-C(6)-	C(7) - P(2)	-49.1	ca	2 - C(13) - C(14) -	C(15)	2.1	P(2)-C(17)-C	(22)-C(21)	178	7
C(7) - P(2)-	-C(8)-C(9)	-166.8	Cú	3 - C(14) - C(15) -		1.9	C(18)-C(17)-	C(22) - C(21)	-0.	9
C(17) - P(2))-C(8)-C(9)	78.7	P(1)	-C(11)-C(16)-C	(15) -	179.2	C(20)-C(21)-	C(22)-C(17)	-0.	3
			(-)				-()			-

chlorine atoms from this species. This, together with IR and ¹H NMR spectroscopic and microanalytical data, confirms our assignment of the product as $[RhCl_2(Ph_2[14]ane-P_2S_2)]PF_6$.

In order to verify the stereochemistry around Rh^{III} we undertook a single-crystal X-ray analysis. Suitable crystals were obtained by slow evaporation from a solution of the complex in CH_2Cl_2 . The X-ray structure of $[RhCl_2(Ph_2 [14]aneP_2S_2)]PF_6$ shows (Fig. 3) the cation adopting a transdichloro octahedral geometry, with the macrocyclic ligand occupying the four equatorial co-ordination sites in an up, up, up, up or cccc configuration, i.e., as in the platinum(II) complex above, the methylene groups of the macrocycle all lie on one side of the RhP₂S₂ plane, with both phenyl substituents directed towards the opposite side of this plane. The Rh^{III} ion lies 0.08 Å above the least-squares P_2S_2 co-ordination plane towards the phenyl groups. The shorter Rh-P bond lengths (cf. Rh-S) are again consistent with the P-donors exhibiting a greater trans influence than the S-donors. There is a substantial steric interaction between the Ph groups and the adjacent Cl(2) atom, resulting in a tilting of Cl(2) from perpendicular [Cl-Rh-Cl 171.10(4)°]. The trans-dichloro stereochemistry observed for $[RhCl_2(Ph_2[14]aneP_2S_2)]^+$ markedly contrasts that seen for the analogous 14-membered tetrathia analogue [RhCl₂- $([14]aneS_4)]^+$ which exists exclusively as the *cis*-dichloro isomer, with the thioether crown in a folded configuration, Rh-S 2.2870(12), 2.3275(12) Å, Rh-Cl 2.3836(12) Å.¹¹ This difference is surprising given the similarity in the covalent radii of P and S (1.10 and 1.04 Å respectively), and hence the similarity in the macrocyclic cavity size. The difference is presumably largely a consequence of the steric influence of the Ph substituents on the phosphine donors, together with the fact that unlike thioethers there is a high energy barrier to

interconversion of the stereochemistries at the phosphines. The ³¹P-{¹H} NMR spectrum of [RhCl₂(Ph₂[14]aneP₂S₂)]PF₆ measured at 300 K in MeCN solution shows, in addition to the septet at δ -146.0 from PF₆⁻, a sharp doublet centred at δ +50.6. Coupling to ¹⁰³Rh is well resolved giving ¹J_{RhP} = 96 Hz. The NMR spectroscopic data are consistent with the solid-state *trans*-dichloro stereochemistry being retained in solution.

The electronic spectrum of *trans*-[RhCl₂(Ph₂[14]aneP₂-S₂)]PF₆ (MeCN solution) approximates to local D_{4h} symmetry with an intense band at $\lambda_{max} = 261$ nm ($\varepsilon_{mol} = 23$ 430 dm³ mol⁻¹ cm⁻¹) assigned to the $\pi \longrightarrow \pi^*$ transition within the Ph groups. Additionally two much weaker bands are apparent at $\lambda_{max} = 299 (\varepsilon_{mol} ca. 7400, sh)$ and 410 nm (523 dm³ mol⁻¹ cm⁻¹), the latter corresponding to the ¹A_{1g} \longrightarrow ¹E_g transition.

Cyclic voltammetric measurements on [M(Ph₂[14]aneP₂-S₂)][PF₆]₂ in MeCN solution (0.1 mol dm⁻³ NBuⁿ₄BF₄ supporting electrolyte) show an irreversible reduction at $E_{pc} = -1.40$ and -1.93 V vs. ferrocene-ferrocenium respectively for M = Pd and Pt. These potentials are considerably more cathodic than for the corresponding tetrathia macrocyclic complexes [M([14]aneS₄)]²⁺ ($E_{pc} = -0.90$ and -1.45 V vs. ferrocene-ferrocenium respectively for M = Pd and Pt.]¹² The complex trans-[RhCl₂(Ph₂[14]aneP₂S₂)]PF₆ also exhibits an irreversible reduction at $E_{pc} = -1.06$ V vs. ferrocene-ferrocenium. The irreversibility may correspond to loss of Cl⁻ from a reduced rhodium(II) species. Similar behaviour has been observed for [RhCl₂L]⁺, L = [12]-, [14]- and [16]-aneS₄ ($E_{pc} = -1.10, -1.10$ and -0.83 V vs. ferrocene-ferrocenium respectively.¹¹

Conclusion

These results demonstrate that $meso-Ph_2[14]aneP_2S_2$ co-



Fig. 3 Top (a) and edge (b) views of the structure of *trans*- $[RhCl_2(Ph_2[14]aneP_2S_2)]^+$ with numbering scheme adopted (H atoms have been omitted for clarity)

ordinates readily to platinum metal centres in an endocyclic arrangement involving co-ordination through a P_2S_2 donor set, and without any additional rigidity such as *o*-phenylene moieties in the macrocyclic backbone being necessary. Also, the generation of a *trans*-dichloro stereochemistry for [RhCl₂(Ph₂-[14]aneP₂S₂)]⁺ indicates that the substitution of thioether donors for phosphines in [14]aneS₄ leads to different co-ordinating properties, and hence possibly different reactivities.

We are currently investigating the ability of $Ph_2[14]aneP_2S_2$ to stabilise other oxidation states such as Rh^{I} , Ir^{I} , Pd^{IV} and Pt^{IV} , as well as synthesis of other P, S and P, N macrocyclic ligands and separation of the stereoisomers.

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. Mass spectra were run by electron impact or fast-atom bombardment (FAB) using 3-noba (3-nitrobenzyl alcohol) as matrix on a VG Analytical 70-250-SE normal

J. CHEM. SOC. DALTON TRANS. 1994

geometry double focusing mass spectrometer. Solution UV/VIS spectra were recorded in 1 cm pathlength quartz cells using a Perkin-Elmer Lambda 19 spectrophotometer. Proton NMR spectra were recorded using a Bruker AM300 spectrometer. Phosphorus-31 NMR spectra were recorded using a Bruker AM360 spectrometer operating at 145.8 MHz and are referenced to 85% H₃PO₄ (δ 0). Platinum-195 NMR spectra were run using 10 mm diameter tubes containing 10-15% deuteriated solvent or a 5 mm insert tube of D_2O as a lock, on a Bruker AM360 spectrometer operating at 77.42 MHz and are referenced against a solution of Na_2PtCl_6 in H_2O (δ 0). Microanalyses were performed by the Imperial College microanalytical service. Cyclic voltammetric experiments were performed using an EG&G Princeton Applied Research Model 362 scanning potentiostat with 0.1 mol dm⁻³ NBuⁿ₄BF₄ supporting electrolyte, using a double platinum electrode as working and auxiliary electrode and a Ag-AgCl reference electrode. All potentials are quoted versus ferroceneferrocenium (for which $E_{\frac{1}{2}} = 0$ V).

All manipulations during the ligand preparation were performed using a dinitrogen atmosphere; thf was dried by distillation from sodium benzophenone under a N_2 atmosphere.

Synthesis.— $Ph_2[14]aneP_2S_2$. To a stirred solution of PhHP(CH₂)₃PHPh¹³ (4.0 g, 0.015 mol) in thf (70 cm³) was added dropwise LiBuⁿ (0.032 mol, 1.3 mol dm⁻³ in hexane) generating a red solution of the phosphide. This solution was cooled to -78 °C (acetone slush) and a solution of $(CH_2)_2S$ (1.85 g, 0.03 mol) in thf (15 cm³) was added dropwise over a period of 15 min. This mixture was allowed to warm to room temperature and was stirred for 30 min during which time the solution changed in colour from red to yellow. Methanol (40 cm³) was then added causing formation of a white precipitate which redissolved upon addition of further MeOH. The mixture was then washed with water (40 cm³) and the organic layer separated. The aqueous layer was washed with CH_2Cl_2 (2 × 15 cm³) and the combined organic layers dried over MgSO₄. The drying agent was filtered off and the solvent removed under vacuum giving a yellow oil, HS(CH₂)₂PPh(CH₂)₃PPh-(CH₂)₂SH, which was then washed with deoxygenated MeOH $(20 \text{ cm}^3).$

The intermediate HS(CH₂)₂PPh(CH₂)₃PPh(CH₂)₂SH (3.56 g, 9.4 mmol) was dissolved in dmf (300 cm³) with $Br(CH_2)_3Br$ (1.90 g, 9.4 mmol) and this solution was added dropwise to a stirred suspension of Cs₂CO₃ (4.38 g, 0.013 mol) in dmf (1500 cm³) at 65 °C, over a period of 24 h. The reaction was stirred for a further 2 h and then allowed to cool to room temperature. The dmf was distilled off under vacuum leaving a light yellow oil. This oil was washed with deoxygenated water (30 cm³) to remove Cs₂CO₃. The resultant oil was redissolved in CH₂Cl₂ (15 cm³) and deoxygenated acetone added dropwise to give *meso*-Ph₂[14]aneP₂S₂ as a white precipitate which was filtered using Schlenk apparatus and dried in vacuo (0.20 g, 5%, unoptimised). FAB mass spectrum (3-noba matrix): m/z = 421; calc. for Ph₂[14]aneP₂S₂ 420. ³¹P-{¹H} NMR (CDCl₃, 298 K) $(145.8 \text{ MHz}), \delta - 24.3; {}^{1}\text{H} (360 \text{ MHz}), \delta 7.2-7.4 (m, Ph, 10 \text{ H}),$ 2.3-2.7 (m, PCH₂ and SCH₂, 16 H) and 1.8-2.0 (m, CH₂CH₂CH₂, 4 H).

 $[Pd(Ph_2[14]aneP_2S_2)][PF_6]_2$.Palladium(II) chloride (22 mg, 0.12 mmol), Ph_2[14]aneP_2S_2 (50 mg, 0.12 mmol) and TIPF_6 (87 mg, 0.25 mmol) were refluxed in MeCN (30 cm³) under a dinitrogen atmosphere for 3 h to give a yellow solution and white precipitate. The solution was then filtered to remove the TICl and the volume reduced to *ca*. 5 cm³ of MeCN. Diethyl ether was then added to give a yellow solid which was collected by filtration, recrystallised from acetone–MeOH and dried *in vacuo* (yield 71%) (Found: C, 31.6; H, 3.3. C_{22}H_{30}F_{12}P_4PdS_2 requires C, 32.40; H, 3.70%). FAB mass spectrum (3-noba matrix): m/z 671 and 525; calc. for $[^{106}Pd(Ph_2[14]aneP_2S_2)]^+$ 526. UV/VIS spectrum (MeCN solution): λ_{max} 271 nm (ε_{mot} 16 530 dm³ mol⁻¹

Table 2 Fractional atomic coordinates for [Pt(Ph₂[14]aneP₂S₂)][PF₆]₂·MeNO₂

Atom	x	у	Z	Atom	x	У	Ζ
Pt	4 783(1)	1 675(1)	1 928(1)	C(19)	2 067(11)	3 833(13)	711(9)
P(1)	4 378(2)	1 884(2)	3 008(2)	C(20)	2 109(11)	4 781(11)	426(7)
P(2)	4 949(2)	3 333(2)	1 743(2)	C(21)	2 992(13)	5 310(10)	571(1)
S(1)	4 801(2)	-64(2)	2 128(2)	C(22)	3 853(10)	4 898(8)	968(7)
S(2)	5 390(2)	1 387(2)	879(2)	P(3)	6 835(3)	6 750(3)	1 362(2)
C(1)	4 817(10)	734(11)	3 494(6)	F (1)	5 955(9)	7 455(8)	1 443(8)
C(2)	4 519(11)	$-192(9)^{2}$	3 024(7)	F(2)	7 086(10)	7 481(9)	791(8)
C(3)	6 145(10)	-300(10)	2 281(7)	F(3)	6 581(9)	5 997(9)	1 933(6)
C(4)	6 537(11)	-193(9)	1 589(8)	F(4)	6 116(9)	6 141(8)	764(6)
C(5)	6 617(9)	888(10)	1 303(7)	F(5)	7 697(8)	6 043(10)	1 257(7)
C(6)	5 666(10)	2 664(10)	585(7)	F(6)	7 582(11)	7 329(12)	1 939(8)
C(7)	5 901(10)	3 413(10)	1 206(8)	P(4)	9 033(2)	2 288(3)	658(2)
C(8)	5 398(9)	4 108(10)	2 537(7)	F (7)	8 947(8)	1 391(9)	1 178(6)
C(9)	4 821(10)	3 949(9)	3 134(7)	F(8)	9 187(9)	3 112(8)	89(6)
C(10)	5 002(10)	2 919(9)	3 527(7)	F(9)	9 441(12)	1 504(8)	173(8)
C(11)	3 053(8)	1 991(8)	2 964(6)	F(10)	7 948(7)	2 077(11)	243(6)
C(12)	2 418(9)	1 447(9)	2 442(7)	F(11)	10 121(7)	2 510(10)	1 070(7)
C(13)	1 382(10)	1 482(10)	2 382(8)	F(12)	8 581(15)	3 029(12)	1 119(9)
C(14)	992(10)	2 088(12)	2 851(9)	N(50)	2 438(14)	230(11)	512(8)
C(15)	1 630(12)	2 620(12)	3 383(8)	O(50)	3 220(14)	7(16)	339(10)
C(16)	2 658(9)	2 573(9)	3 434(6)	O(51)	2 182(17)	-18(12)	1 054(7)
C(17)	3 844(9)	3 915(8)	1 239(6)	C(50)	1 751(16)	794(12)	-16(10)
C(18)	2 940(9)	3 395(9)	1 097(7)				. ,

Table 3 Selected bond lengths (Å), angles and torsion angles (°) for *trans*- $[RhCl_2(Ph_2[14]aneP_2S_2)]^+$

Rh-Cl(1) Rh-S(1) Rh-P(1) S(1)-C(2) S(2)-C(5) P(1)-C(1)	2.347(1) 2.377(1) 2.300(1) 1.812(5) 1.809(5) 1.849(5)	P(1)-C(11) P(2)-C(8) C(1)-C(2) C(4)-C(5) C(8)-C(9)	1.819(5) 1.830(4) 1.539(7) 1.519(8) 1.533(6)	Rh-Cl(2) Rh-S(2) Rh-P(2) S(1)-C(3) S(2)-C(6) P(1)-C(10)	2.354(1) 2.374(1) 2.286(1) 1.829(6) 1.828(5) 1.819(4)	P(2)-C(7) P(2)-C(17) C(3)-C(4) C(6)-C(7) C(9)-C(10)	1.849(4) 1.820(4) 1.529(8) 1.512(7) 1.536(7)
Cl(1)-Rh-Cl(2) Cl(1)-Rh-S(2) Cl(1)-Rh-P(2) Cl(2)-Rh-S(2) Cl(2)-Rh-P(2) S(1)-Rh-P(1) S(2)-Rh-P(1) P(1)-Rh-P(2) Rh-S(1)-C(3) Rh-S(2)-C(5) Cl(5) Cl(6) Cl(171.10(4) 88.04(4) 88.18(4) 85.45(4) 97.30(4) 85.61(4) 174.79(4) 92.26(4) 108.3(2) 108.3(2) 104.0(2)	Rh-P(1)-C(10) C(1)-P(1)-C(10) C(10)-P(1)-C(11) Rh-P(2)-C(8) C(7)-P(2)-C(8) C(8)-P(2)-C(17) P(1)-C(1)-C(2) S(1)-C(3)-C(4) S(2)-C(5)-C(4) P(2)-C(7)-C(6) C(8) C(9) C(10)	111.1(1) 109.0(2) 105.4(2) 111.6(2) 107.3(2) 103.4(2) 114.0(3) 111.9(4) 111.7(4) 113.5(3)	Cl(1)-Rh-S(1)Cl(1)-Rh-P(1)Cl(2)-Rh-S(1)Cl(2)-Rh-P(1)S(1)-Rh-S(2)S(1)-Rh-P(2)S(2)-Rh-P(2)Rh(1)-S(1)-C(2)C(2)-S(1)-C(3)Rh-S(2)-C(6)Bh B(1) C(1)	88.22(4) 87.33(4) 86.52(4) 99.40(4) 96.65(4) 175.89(4) 85.20(4) 101.2(2) 100.8(2) 100.7(1) 106.3(2)	$\begin{array}{l} Rh-P(1)-C(11)\\ C(1)-P(1)-C(11)\\ Rh-P(2)-C(1)\\ Rh-P(2)-C(17)\\ C(7)-P(2)-C(17)\\ S(1)-C(2)-C(1)\\ C(3)-C(4)-C(5)\\ S(2)-C(6)-C(7)\\ P(2)-C(8)-C(9)\\ P(1)-C(10)-C(9) \end{array}$	121.6(1) 102.8(2) 106.8(2) 122.9(2) 103.7(2) 109.5(3) 115.0(5) 109.0(3) 113.8(3) 114.9(3)
$\begin{array}{c} S(1)-C(2)-C(1)\\ P(1)-C(10)-C(1)\\ P(1)-C(11)-C(1)\\ P(2)-C(17)-C(1)\\ C(1)-P(1)-C(1)\\ C(1)-P(1)-C(1)\\ C(2)-S(1)-C(3)\\ C(2)-C(1)-P(1)\\ C(5)-S(2)-C(6)\\ C(6)-C(7)-P(2)\\ C(7)-P(2)-C(1)\\ C(8)-P(2)-C(1)\\ C(9)-C(8)-P(2)\\ C(10)-P(1)-C(1)\\ C(1)-P(1)-C(1)\\ C(1$	$\begin{array}{cccc}4\\ 9)-C(8) &7\\ 16)-C(15) & 17\\ 18)-C(19) & 17\\ 0)-C(9) & 17\\ 1)-C(16) & 11\\ -C(4) & -16\\ -C(11) & 14\\ -C(7) & -16\\ -C(17) & -14\\ 7)-C(18) & 13\\ 7)-C(18) & -10\\ -C(17) & 7\\ 10)-C(12) & 17\\ \end{array}$	$\begin{array}{cccc} c(i) & c(i) & c(i) \\ \hline 5.3(4) & C(1) \\ 0.1(5) & C(1) \\ 9.7(4) & C(1) \\ 8.5(4) & C(1) \\ 8.5(4) & C(1) \\ 0.5(4) & C(1) \\ 3.1(4) & S(1) \\ 4.2(4) & P(1) \\ 4.1(3) & P(2) \\ 8.0(3) & P(2) \\ 8.4(4) & C(1) \\ 9.7(4) & C(1) \\ 3.6(4) & C(2) \\ 8.1(4) \end{array}$	$\begin{array}{l} 1)-C(12)-C(13)-C(1)\\ 2)-C(11)-C(16)-C(1)\\ 3)-C(12)-C(11)-C(1)\\ 3)-C(12)-C(11)-C(1)\\ 3)-C(12)-C(13)-C(2)-C(2)\\ 9)-C(18)-C(17)-C(2)-C(2)\\ 9)-C(18)-C(17)-C(2)-C(13)\\ -C(3)-C(4)-C(5)\\ +C(11)-C(12)-C(13)\\ +C(3)-C(9)-C(10)\\ +C(17)-C(22)-C(21)\\ +C(17)-C(22)-C(21)\\ +C(11)-C(11)-C(12)\\ +C(1)-C(11)-C(12)\\ +C(1)-C(11)-C(13)\\ +C(1)-C(10)\\ +C(1)-C$	$\begin{array}{r} (1) & (1) & (1) \\ (4) & -1.7(10) \\ (5) & -2.0(8) \\ (6) & 3.0(8) \\ (0) & -1.1(8) \\ (1) & -0.6(7) \\ (2) & 1.3(7) \\ & 64.1(5) \\ (2) & 1.3(7) \\ & 64.1(5) \\ (3) & -178.6(5) \\ & 69.8(5) \\ (3) & -177.9(4) \\ & -67.7(4) \\ & 162.8(4) \\ & -104.4(4) \end{array}$	$\begin{array}{c} C(4)-C(5)-S(2)\\ C(6)-C(7)-P(2)-C(3)\\ C(7)-P(2)-C(3)\\ C(7)-P(2)-C(3)\\ C(7)-P(2)-C(3)\\ C(8)-P(2)-C(3)\\ C(9)-C(10)-P\\ C(10)-P(1)-C\\ C(10)-P(1)-C\\ C(11)-C(16)-4\\ C(12)-C(13)-4\\ C(13)-C(14)-4\\ C(17)-C(22)-4\\ C(18)-C(19)-4\\ C(19)-C(20)-4\\ \end{array}$	$\begin{array}{cccc} 2)-C(6) & 164\\ 2)-C(8) & 103\\ 8)-C(9) & -177\\ 17)-C(22) & -44\\ 17)-C(22) & 67\\ (1)-C(11) & -73\\ (11)-C(16) & -3\\ C(15)-C(14) & -0\\ C(15)-C(14) & -0\\ C(15)-C(16) & 1\\ C(21)-C(20) & -0\\ C(20)-C(21) & 0\\ C(21)-C(22) & 0\\ \end{array}$.8(4) .0(3) .2(3) .4(4) .5(4) .5(4) .6(5) .4(8) (1) .8(10) .3(8) .2(9) .5(8)

cm⁻¹). NMR (300 K): ¹H (360 MHz, CDCl₃), δ 7.5–7.8 (m, Ph, 10 H), 3.5 (m), 3.1-3.3 (m), 2.8-3.0 (m) (all PCH₂) and SCH₂, 16 H) and 2.4 (br, CH₂CH₂CH₂, 4 H); ³¹P-{¹H} (145.8 MHz, MeCN), δ + 53.4 (s, macrocyclic P, 2 P) and -146.6 (spt, PF_6^- , 2 P). IR spectrum (KBr disc): 3040w, 2980w, 2962w, 2840w, 1437m, 1420m, 1261m, 975m, 910w, 839vs br, 746m, 717m, 704w, 558vs, 490m, 473m and 396m cm⁻¹

 $[Pt(Ph_2[14]aneP_2S_2)][PF_6]_2$. Method as above, using PtCl₂ (34 mg, 0.13 mmol), Ph₂[14]aneP₂S₂ (54 mg, 0.13 mmol) and TIPF₆ (91 mg, 0.26 mmol). The product was isolated

as a white solid (yield 50%) (Found: C, 26.9; H, 3.20%. C₂₂H₃₀F₁₂P₄PtS₂·2CH₂Cl₂ requires C, 26.8; H, 3.20%). FAB mass spectrum (3-noba matrix): m/z 760 and 614; calc. for [¹⁹⁵Pt(Ph₂[14]aneP₂S₂)PF₆]⁺ 760, [¹⁹⁵Pt(Ph₂[14]aneP₂-S₂)]⁺ 615. UV/VIS spectrum (MeCN solution): λ_{max} 260 nm (sh) (ε_{mol} ca. 3190 dm³ mol⁻¹ cm⁻¹). NMR (300 K): ¹H (360 MHz, CDCl₃), δ 7.5–7.8 (m, Ph, 10 H), 3.7 (m), 3.2 (m), 3.0–2.7 (m) (PCH₂, SCH₂, 12 H) and 2.4 (br, $CH_2CH_2CH_2$, 4 H); (iii) (1014), 5012, 12 ii) and 21 (iii, 512) (2012), 12 ii) ${}^{31}P_{+}{1H}$ (145.8 MHz, CD₃CN), δ + 46.2 (macrocyclic P, 2 P, ${}^{1}J_{PtP} = 2718$ Hz) and -145.8 (spt, PF₆⁻, 2 P); ${}^{195}Pt$ (77.4 MHz, MeCN), $\delta - 5174$ (t, ${}^{1}J_{PtP} = 2718$ Hz). IR spectrum (KBr disc):

Table 4	Fractional	atomic co	ordinates !	for trans-	[RhCl ₂	(Ph	,[14]a	neP,S,)]PF	6
I abic 4	ractional	atonne co	orumates	ior nums-	Truci2	(1 1)	7 14 ai	$1 c r_2 o_2 / 1 r_1$	6

Atom	x	у	Z	Atom	x	у	z
Rh	0.264 55(2)	0.148 02(3)	0.958 56(2)	C(3)	0.2186(4)	0.086 7(5)	0.785 7(3)
Cl(1)	0.107 55(8)	0.040 53(10)	0.942 97(6)	C(4)	0.313 4(5)	0.005 8(5)	0.793 1(3)
Cl(2)	0.431 02(8)	0.241 55(9)	0.958 69(6)	C(5)	0.309 1(4)	-0.075 0(4)	0.853 8(3)
S(1)	0.238 19(10)	0.209 4(1)	0.841 42(6)	C(6)	0.314 9(4)	-0.1112(4)	0.9982(3)
S(2)	0.365 08(8)	-0.01442(9)	0.933 61(6)	C(7)	0.3261(4)	-0.0580(4)	1.069 5(3)
P(1)	0.155 25(8)	0.294 78(9)	0.986 33(6)	C(8)	0.1452(3)	0.085 3(4)	1.110 6(2)
P(2)	0.276 83(8)	0.087 43(9)	1.071 50(6)	C(9)	0.090 5(4)	0.199 8(4)	1.112 9(2)
P(3)	0.843 9(1)	0.144 9(1)	0.718 65(8)	C(10)	0.049 9(3)	0.249 9(4)	1.043 0(3)
F(1)	0.881 2(3)	0.271 9(3)	0.724 7(2)	C(11)	0.209 9(4)	0.421 9(4)	1.025 6(3)
F(2)	0.808 0(3)	0.017 9(3)	0.714 8(2)	C(12)	0.296 0(4)	0.473 7(4)	0.993 4(3)
F(3)	0.865 5(8)	0.138 2(5)	0.802 6(3)	C(13)	0.341 8(5)	0.569 2(5)	1.022 0(4)
F(3a)	0.767(2)	0.149(2)	0.777(1)	C(14)	0.299 8(6)	0.615 0(5)	1.082 0(4)
F(4)	0.727 3(4)	0.185 4(7)	0.731 9(7)	C(15)	0.214 4(5)	0.568 0(4)	1.112 0(3)
F(4a)	0.745(2)	0.166(2)	0.663(1)	C(16)	0.167 7(4)	0.470 2(4)	1.084 5(3)
F(5)	0.828 6(9)	0.166 2(8)	0.640 3(3)	C(17)	0.363 6(3)	0.153 3(4)	1.138 2(2)
F(5a)	0.908(2)	0.108(1)	0.651(1)	C(18)	0.405 2(4)	0.260 7(4)	1.129 8(3)
F(6)	0.967 5(5)	0.119 0(6)	0.712 1(5)	C(19)	0.469 1(4)	0.306 7(5)	1.184 1(3)
F(6a)	0.930(2)	0.090(2)	0.762(2)	C(20)	0.489 7(4)	0.248 5(6)	1.245 3(3)
C(1)	0.092 5(4)	0.345 1(4)	0.903 1(3)	C(21)	0.447 6(4)	0.144 4(5)	1.253 3(3)
C(2)	0.101 9(4)	0.263 0(5)	0.842 1(3)	C(22)	0.385 5(4)	0.096 3(5)	1.200 9(3)

3020w, 2925w, 2860w, 1436m, 1420m, 1108m, 975m, 832vs br, 745m, 718m, 699m, 669w, 557vs, 505m, 493m, 475w, 453w cm⁻¹. trans-[RhCl₂(Ph₂[14]aneP₂S₂)]PF₆. To a degassed solution of RhCl₃·3H₂O (0.03 g, 0.12 mmol) in EtOH (40 cm³) and H₂O (1 cm^3) was added Ph₂[14]aneP₂S₂ (0.49 g, 0.12 mmol). Refluxing under a N₂ atmosphere for 1 h gave a yellow-brown solution. After cooling the solution was filtered yielding a brown solid. The yellow filtrate was treated with an excess of NH_4PF_6 , the solvent removed and the product redissolved in CH_2Cl_2 (10 cm³). This yellow solution was washed with H_2O (2 × 5 cm³) to remove excess NH_4PF_6 and Et_2O added yielding a yellow precipitate (0.02 g, 23%) (Found: C, 34.6; H, 4.45. $C_{22}H_{30}Cl_2F_6P_3RhS_2\cdot H_2O$ requires C, 34.9; H, 4.27%). FAB mass spectrum (3-noba matrix): m/z 593, 558, 523; calc. for $[^{103}\text{Rh}^{35}\text{Cl}_2(\text{Ph}_2[14]\text{aneP}_2\text{S}_2)]^+$ 593, $[^{103}\text{Rh}^{35}\text{Cl}(\text{Ph}_2[14]\text{-aneP}_2\text{S}_2)]^+$ 523. NMR (CD₃CN): ¹H (300 MHz), δ 7.1-7.6 (m, Ph, 10 H), 2.4-3.4 (m, PCH₂ and SCH₂, 16 H) and 1.8-2.1 (m, CH₂CH₂CH₂, 4 H); ³¹P-{¹H} (145.8 MHz), δ 50.6 (d, ¹J_{RhP} = 96 Hz) and -146 (spt, PF₆⁻). IR spectrum (KBr disc): 3020w, 2923w, 2870w, 1432m, 1420w, 1358w, 1261w, 1101m, 971w, 840vs br, 747m, 696m, 558vs, 508m and 448m cm⁻¹.

Crystallography.—Structure determination on [Pt(Ph₂[14]-aneP₂S₂)][PF₆]₂·MeNO₂. Colourless crystals of the complex were obtained by vapour diffusion of diethyl ether into a solution of the complex in MeNO₂. The selected crystal (0.78 \times 0.30 \times 0.05 mm) was sealed in a glass capillary to prevent solvent loss.

Crystal data. $C_{22}H_{30}F_{12}P_4PtS_2$ ·MeNO₂, M = 966.7, monoclinic, space group $P2_1/n$, a = 13.649(5), b = 13.299(2), c = 18.983(7) Å, $\beta = 101.89(3)^\circ$, U = 3372 Å³ [from 2 θ values of 30 reflections measured at $\pm \omega$ (15 $\leq 2\theta \leq 26^\circ$, $\lambda =$ 0.710 73 Å)], Z = 4, $D_c = 1.90$ g cm⁻³, T = 293 K, $\mu = 4.60$ mm⁻¹, F(000) = 1888.

Data collection and processing. Nicolet R3mV four-circle diffractometer, graphite-monochromated Mo-K $_{\alpha}$ X-radiation, T = 293 K, ω -2 θ scans, 6502 data collected, 5943 unique $(R_{int} = 0.052) (2\theta_{max} 50^\circ, h \ 0 \longrightarrow 17, k \ 0 \longrightarrow 16, l - 23 \longrightarrow 23)$ giving 4109 reflections with $F \ge 6\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed. The data were corrected for Lorentz and polarisation effects and empirically for absorption (max. and min. transmission factors = 0.98 and 0.36 respectively).

Structure solution and refinement. The structure was solved by direct methods and developed by using interative cycles of least-squares refinement and Fourier difference syntheses¹⁴ which

located all non-H atoms. The $[Pt(Ph_2[14]aneP_2S_2)]^{2+}$ cation, PF_6^- anions and MeNO₂ solvent molecule were all found to be ordered. All non-H atoms were refined anisotropically, while Hatoms were included in fixed, calculated positions (C-H = 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08 \text{ Å}^2$). The weighting scheme $w^{-1} = \sigma^2(F) + 0.001 \ 29F^2$ gave satisfactory agreement analyses. At final convergence R, R' = 0.0541, 0.0554 respectively, S = 1.45 for 406 refined parameters. The final ΔF synthesis showed two peaks above 1.5 e Å⁻³ both of which lie close to the metal ion. Selected bond lengths, angles and torsion angles are given in Table 1. Fractional atomic coordinates are listed in Table 2.

Structure determination on $[RhCl_2(Ph_2[14]aneP_2S_2)]PF_6$. Orange crystals of the complex were obtained by slow evaporation from a solution of the complex in CH_2Cl_2 . The selected crystal (0.20 × 0.08 × 0.45 mm) was mounted on a glass fibre.

Crystal data. $C_{22}H_{30}Cl_2F_6P_3RhS_2$, M = 739.3, monoclinic, space group $P2_1/c$, a = 12.431(2), b = 11.990(2), c = 19.206(1)Å, $\beta = 92.437(9)^\circ$, U = 2860 Å³ [from 20 values of 25 reflections measured at $\pm \omega$ (37.0 $\leq 20 \leq 39.9^\circ$, $\lambda = 0.710$ 73 Å)], Z = 4, $D_c = 1.72$ g cm⁻³, T = 294 K, μ (Mo-K α) = 1.133 mm⁻¹, F(000) = 1488.

Data collection and processing. Rigaku AFC7R four-circle diffractometer, graphite-monochromated Mo-K α X-radiation, T = 294 K, $\omega - 2\theta$ scans, 6841 data collected, 6545 unique $(R_{int} = 0.121), (2\theta_{max} 54^\circ, h \ 0 \longrightarrow 16, k \ 0 \longrightarrow 15, l - 25 \longrightarrow 25)$ giving 4691 reflections with $F \ge 5\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed. The data were corrected for Lorentz and polarisation effects and as there were no measurable faces on the crystal the data were corrected empirically for absorption using ψ -scans (max. and min. transmission factors 0.999 and 0.856 respectively).

Structure solution and refinement. The structure was solved using heavy-atom Patterson methods.¹⁵ Iterative cycles of leastsquares refinement and Fourier difference synthesis revealed the positions of all non-H atoms for the one cation and PF₆⁻ anion in the asymmetric unit.¹⁶ The structure was refined by fullmatrix least squares, with anisotropic thermal parameters for all non-H atoms: H atoms were included but not refined. The PF₆⁻ anion was found to be disordered in one plane. This disorder was modelled by using partial F atom occupancies such that the P atom had a total of six F atoms around it, giving alternative F atom positions for F(3)–F(6). The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. At final convergence, R, R' = 0.038, 0.043 respectively, S = 2.01 for 362 refined parameters. The final ΔF synthesis showed no peaks

above 0.78 or below $-1.25 \text{ e} \text{ Å}^{-3}$. Selected bond lengths, angles and torsion angles are given in Table 3. Fractional atomic coordinates are listed in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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