Crystal Structures and Solution Dynamics of Mono- and Di-nuclear Rhodium Complexes of Heterodinucleating Macrocyclic Ligands containing the 2,6-Di(thiomethyl)pyridine Sub-unit†

Ian M. Helps, Karen E. Matthes, and David Parker*
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE
George Ferguson
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2WI, Canada

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Rhodium complexes of four macrocyclic ligands in which a polyether chain links a 2,6-di(thiomethyl)pyridine sub-unit are reported. The rhodium(I) carbonyl complex of 6,9,12-trioxa-3,15-dithia-21-azabicyclo[15.3.1]heneicosa-1(21),17,19-triene is dimeric with a weak metal–metal interaction [Rh–Rh 3.332 0(6) Å] and in the rhodium(III)–dichloro complex with 6,9,12,15,18-pentaoxa-3,21-dithia-27-azabicyclo[21.3.1]heptacosa-1(27),23,25-triene a water molecule is bound to the metal and is hydrogen bonded to two of the oxygens of the polyether chain. Dinuclear complexes with bridging and terminal carbonyl ligands are formed with 6-oxa-3,9-dithia-15-azabicyclo[9.3.1]pentadeca-1(15),11,13-triene and its dimer 6,20-dioxa-3,9,17,23-tetrathia-29,30-diazatricyclo[23.3.1.1^{11,15}]triaconta-1(29),11,13,15(30),25,27-hexaene respectively.

The structure and complexation behaviour of dinuclear macrocyclic and macropolycyclic ligands have been actively investigated in recent years.[1,2] In systems which incorporate relatively π-acidic ligands, the stabilisation of the lower oxidation states of certain transition metals has been demonstrated;[3] these being of particular interest to potential catalytic processes. With heterotopic ligands containing two distinctly different binding sites, the co-complexation of two different metals has been defined[4] and systems are being sought in which a neutral guest (*e.g.* H_2O, NH_3, urea) is bound in proximity to a reactive metal centre within a macrocyclic ligand.[5]

The synthesis of the macrocyclic ligands L^1—L^4 and their rhodium–carbonyl complexes are reported in which a polyether chain of varying length links the two sulphur atoms of the di(thiomethyl)pyridine sub-unit. The twenty-four-membered macrocycle L^4 is sufficiently large to permit co-complexation of a d^8 metal centre and Group 1A or 2A cation or a neutral small molecule. A preliminary account of some of this work has been given.[6]

Results and Discussion

Synthesis of the Ligands.—The simplest approach to sulphur-containing macrocyclic ligands invokes carbon–sulphur bond formation in the ring-forming reaction.[7] Condensation of 3-oxapentane-1,5-dithiol with 2,6-di(bromomethyl)pyridine affords the monomer L^1, dimer L^2, and the trimer L^5 in diminishing order of yield. Similarly, reaction of the disodium salt of 2,6-di(thiomethyl)pyridine with hexaethylene glycol (3,6,9,12,15-pentaoxaheptadecane-1,17-diol) ditosylate in boiling butan-1-ol afforded L^4 in moderate yield, while the 18-membered ring monocycle, L^3, was prepared analogously using 1,11-di-iodo-3,6,9-trioxaundecane.

Complex Formation.—Reaction of equimolar amounts of L^1 with $[Rh_2Cl_2(CO)_4]$ in methanol led to brisk evolution of CO and formation of a deep blue solution, from which an indigo solid was isolated following addition of ammonium hexafluorophosphate. A single carbonyl band was observed in the i.r. spectrum at 1 740 cm^{-1}, consistent with the presence of bridging carbonyl groups.[1,8] The ^{1}H n.m.r. spectrum (298 K, CD_3CN) revealed that the benzylic CH_2S protons were diastereotopic ($\Delta\delta$ = 0.04 p.p.m.) suggesting that the pyridine nitrogen and both of the sulphurs were simultaneously bound to rhodium, as in (**1**). The bridging carbonyl groups enforce a strong rhodium–rhodium interaction, as evidenced by the deep indigo colour of the complex. A description of the electronic structures of systems with metal–metal bonds between square-planar d^8 cations has been given.[9,10] It has been established, for example, that the principal spectroscopic feature of dinuclear rhodium isocyanide complexes is a prominent low-lying absorption band attributable to $^1A_{1g} \longrightarrow {}^1A_{2u}$. This transition involves axially directed donor and acceptor orbitals and the energy of the transition is a sensitive function of the metal–metal distance.

Reaction of L^2 with $[Rh_2Cl_2(CO)_4]$ followed by addition of hexafluorophosphate gave a brilliant red precipitate. The i.r. spectrum revealed two terminal CO bands at 2 044 and 1 993 cm^{-1}.[9,10] In the ^{1}H n.m.r. spectrum [$(CD_3)_2CO$, 240 K] two major species were observed in approximately a 2:1 ratio, and at 298 K these two species were exchanging rapidly on the n.m.r. time-scale. Such behaviour may be associated with the formation of two diastereoisomeric species, (**2**), in which the metal atoms lie either on opposite (*anti*) or the same sides (*syn*) of the mean ligand plane.[11] The two isomers differ in configuration at sulphur and may interconvert *via* an inversion at sulphur, with an associated change in the conformation of the oxyethylene chain.

The reaction of equimolar amounts of L^3 with $[Rh_2Cl_2(CO)_4]$ in methanol was also accompanied by a brisk evolution of CO, and addition of hexafluorophosphate led to formation of a ruby-red crystalline solid. The i.r. carbonyl stretch occurred at 2 020 cm^{-1}, consistent with a terminal rhodium carbonyl, and the fast atom bombardment (f.a.b.) mass spectrum gave a peak at 460 corresponding to $[RhL^3(CO)]^+$. The ^{1}H n.m.r. spectrum (CD_2Cl_2, 298 K) revealed that the benzylic CH_2S protons were diastereotopic ($\Delta\delta$ = 0.28 p.p.m.) consistent with two equivalent stereogenic sulphur centres with a stable configuration. These solution data are consistent with formation of a mononuclear

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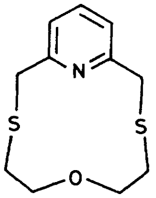
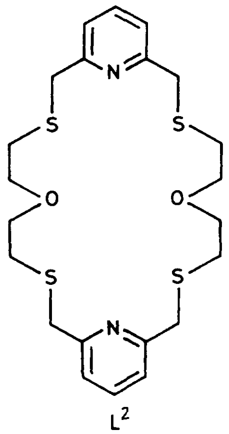
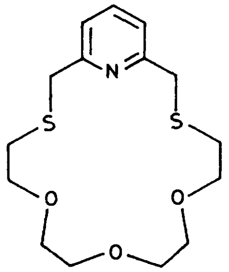
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



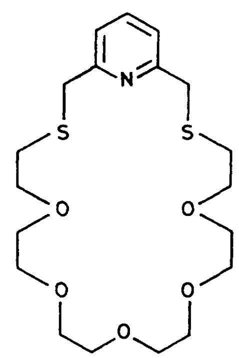
L^1



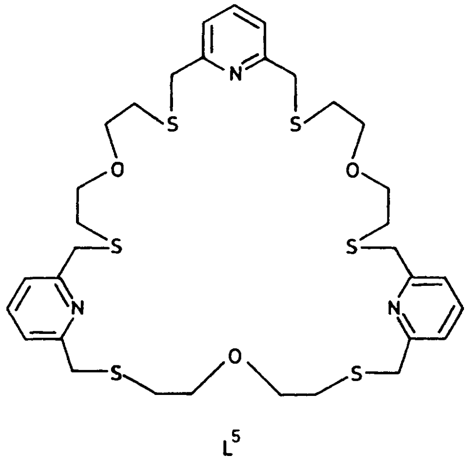
L^2



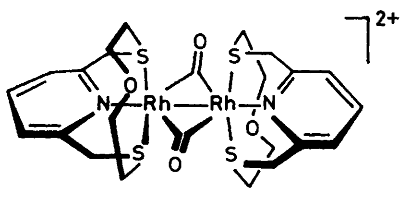
L^3



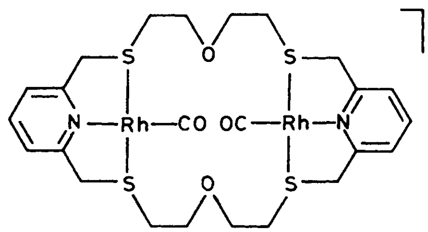
L^4



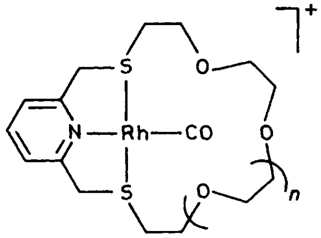
L^5



(1)



(2)



(3) n = 1

(4) n = 3

complex (3). The i.r. stretching frequency at 2 020 cm^{-1} and the ^{1}H n.m.r. spectrum were unchanged by the addition of $LiClO_4$ in either dichloromethane, tetrahydrofuran, or acetone, *i.e.* there was neither evidence for the binding of the lithium cation by the polyether chain nor by the oxygen of the terminal CO ligand.

The crystal-structure analysis of the complex cation (3) afforded a clear explanation for this observed behaviour. The red complex (3) is dimeric with a weak metal–metal interaction [Rh–Rh 3.332 0(6) Å], Figure 1. Dissociation occurs readily, particularly in co-ordinating solvents such as acetone or acetonitrile, to give yellow solutions. The rhodium–carbonyl vector is directed away from the polyether chain which is folded back towards the electron-poor pyridine ring. There may be a weak stabilising interaction between the oxygen lone pairs of the O_3 chain and the pyridine ring which favours the observed macrocycle conformation. Similar interactions between pyridinium cations or metal-bound bipyridines and polyether macrocycles have been defined in recent years.[12,13] It seems likely that the metal carbonyl or d_{z^2} orbital bound to the 2,6-di(thiomethyl)pyridine sub-unit reported in two other heterotopic macrocyclic ligands[4b,d] will also be directed away from the second binding site in these ligands, explaining the observed lack of interaction with the second metal.

The co-ordination geometry about the equivalent rhodium atoms (Figure 1) is a distorted square pyramid. The major distortion arises from the intrinsically small bite angles of the

Table 1. Selected molecular dimensions for $[RhL^3(CO)]_2[PF_6]_2$; distances in Å, angles in °, with estimated standard deviations (e.s.d.s) in parentheses

Rh-Rh′	3.332 0(6)	Rh-S(20)	2.298(2)
Rh-N(1)	2.060(4)	Rh-C(22)	1.833(6)
Rh-S(8)	2.295(2)		
S(8)-Rh-S(20)	169.77(6)	Rh′-Rh-N(1)	91.8(1)
S(8)-Rh-C(22)	94.2(2)	Rh′-Rh-S(8)	92.72(4)
S(20)-Rh-C(22)	95.0(2)	N(1)-Rh-S(8)	85.1(1)
Rh-S(20)-C(19)	107.8(2)	N(1)-Rh-S(20)	85.7(1)
Rh-S(20)-C(21)	99.3(2)	N(1)-Rh-C(22)	179.2(2)

Refers to the equivalent position *y*, *x*, 1 − *z*.

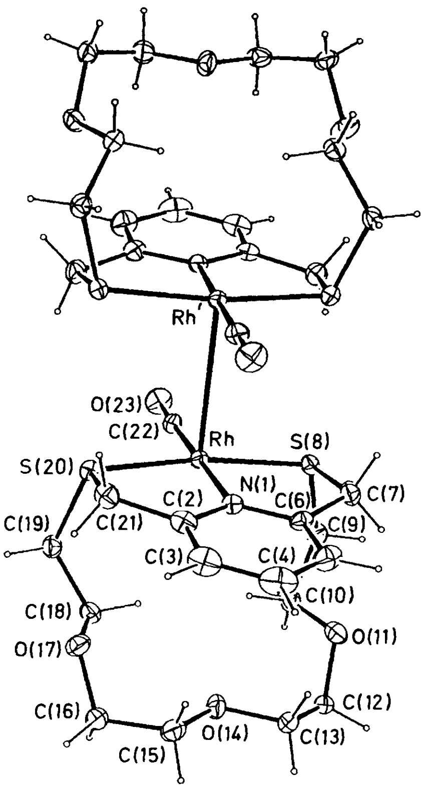
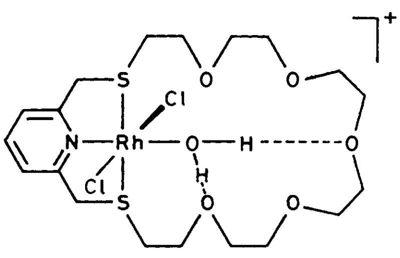


Figure 1. Perspective (ORTEP) view of the dication (**3**) showing the crystallographic numbering scheme. Ellipsoids are at the 20% level

two adjacent five-membered-ring chelates, giving a bond angle of 169.77(6)° for S(8)-Rh-S(20). Other bond lengths and bond angles are close to the expected values (Table 1).

Reaction of L^4 with $[Rh_2Cl_2(CO)_4]$ in methanol followed by addition of hexafluorophosphate gave a red microcrystalline solid, (**4**). Transformation to an orange-yellow solid occurred readily upon exposure of the complex to moisture, and the complex dissolved readily in acetone or dichloromethane to give yellow solutions. It is likely that the metal-metal interaction in the solid state is very weak. The terminal carbonyl stretching frequency occurred at 2 020 cm^{-1} and the f.a.b. mass spectrum revealed peaks centred at *m/e* 548 and 520 corresponding to $[L^4\text{-}RhCO]^+$ and $[L^4\text{-}Rh]^+$. The complex gave an exchange-broadened ^1H n.m.r. spectrum at room temperature (CD_2Cl_2, 298 K) in which the benzylic CH_2S signal resonated as a broad singlet ($\omega_{\frac{1}{2}}$ = 16 Hz). On cooling the solution to 260 K, this signal sharpened and resolved into a simple AB multiplet (δ_{H^a} = 4.91, δ_{H^b} = 5.03 p.p.m.). Careful analysis of this dynamic behaviour over the range 260—315 K gave $\Delta G_c^{\ddagger}$ = 64 ± 0.4 kJ mol^{-1} (T_c = 303 K). The exchange process is associated with inversion at sulphur and may be related to a 'ring skip' of the conformationally mobile polyether chain over the Rh-CO vector.



(**5**)

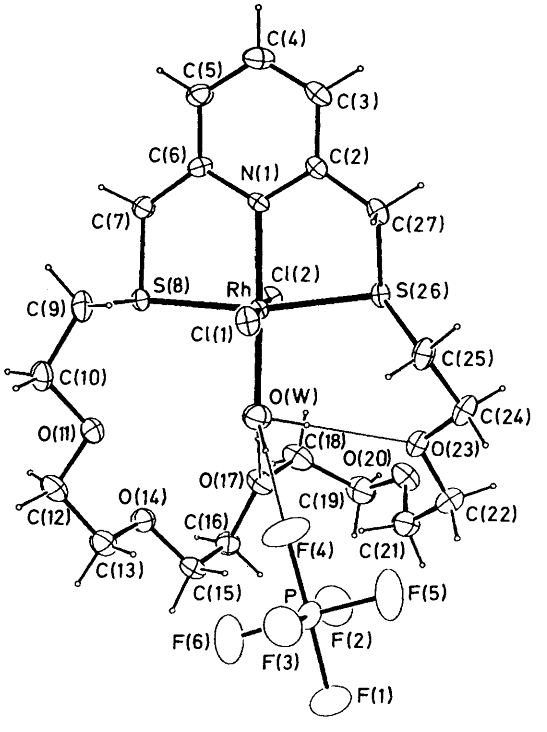


Figure 2. A view of compound (**5**) showing the crystallographic numbering scheme. Ellipsoids are at the 20% level

The ligand L^4 forms an isolable potassium complex, in the ^{13}C n.m.r. spectrum of which the carbon atoms of the polyether chain are shifted between 0.45 and 0.75 p.p.m. relative to the free ligand. The complex gave a f.a.b. mass spectrum with a peak centred at *m/e* 456 corresponding to $[L^4\text{-}K]^+$. When potassium perchlorate (or $LiClO_4$ and $NaClO_4$) was added to a solution of the rhodium complex (**4**) in dichloromethane, the i.r. stretching frequency of the bound carbonyl at 2 020 cm^{-1} was unperturbed, notwithstanding the ability of the free ligand to form a potassium complex.

When L^4 was boiled in methanol with $RhCl_3 \cdot 3H_2O$ an orange solution formed from which a complex (**5**) was isolated following addition of hexafluorophosphate. The f.a.b. mass spectrum revealed peaks at *m/e* 608, 573, 555, and 520 corresponding to fragmentation of $[L^4\text{-}RhCl_2(H_2O)]^+$ to yield $[L^4\text{-}RhCl(H_2O)]^+$, $[L^4\text{-}RhCl]^+$, and $[L^4\text{-}Rh]^+$ respectively. An identical complex [i.r. fingerprint, f.a.b. mass spectrum, and

Table 2. Selected molecular dimensions for [$RhL^4Cl_2(OH_2)$][PF_6]; distances in Å, angles in °, with e.s.d.s in parentheses

Rh–Cl(1)	2.332(1)	Rh–N(1)	2.025(4)
Rh–Cl(2)	2.330(1)	O(W) ··· O(17)	2.986(6)
Rh–S(8)	2.329(1)	O(W) ··· O(23)	3.128(6)
Rh–S(26)	2.327(1)	O(W) ··· F(4)	3.133(6)
Rh–O(W)	2.070(4)		
Cl(1)–Rh–Cl(2)	179.50(5)	S(8)–Rh–N(1)	85.9(1)
Cl(1)–Rh–S(8)	96.48(5)	S(8)–Rh–O(W)	92.9(1)
Cl(1)–Rh–S(26)	91.48(5)	S(8)–Rh–S(26)	166.76(5)
Cl(1)–Rh–O(W)	89.4(1)	Cl(2)–Rh–S(8)	84.02(5)
O(W)–Rh–N(1)	178.2(2)	Cl(2)–Rh–S(26)	88.04(5)
S(26)–Rh–N(1)	83.6(1)	Cl(2)–Rh–O(W)	90.5(1)
S(26)–Rh–O(W)	97.7(1)		

^1H n.m.r. spectrum] was formed by aerial oxidation of (**4**) in chloride-saturated methanol. The ^1H n.m.r. spectrum of (**5**) (CD_2Cl_2, 298 K) revealed diastereotopic benzylic CH_2S protons ($\Delta\delta = 0.22$ p.p.m.) consistent with stereogenic sulphur centres with a stable configuration, *i.e.* the polyether chain was not conformationally mobile at 298 K, as had been the case with (**4**). The crystal structure of (**5**) (Figure 2) showed that the rhodium was octahedrally co-ordinated with two *trans*-related chloride ligands and a water molecule tightly bound *trans* to the short nitrogen–rhodium bond. As in the structure of (**3**), the main distortion from a more regular geometry (Table 2) arises from the intrinsically small bite angles of the two five-membered-ring chelates, so that the angle S(8)–Rh–S(26) is 166.76(5)°. The co-ordinated water molecule is strongly bound to the rhodium(III) centre [Rh–O(W) 2.070(4) Å], increasing the acidity of the bound water molecule. The water molecule is directed towards the polyether chain and is hydrogen bonded to two of the oxygen atoms of the chain [O(W) ··· O(17) 2.986(2), O(W) ··· O(23) 3.128(6) Å] and to a fluorine of the proximate hexafluorophosphate anion [O(W) ··· F(4) 3.133(6) Å]. Electron-density difference maps at $R = 0.025$ clearly showed that the water hydrogens are disordered over these three sites, and form three hydrogen bonds. The site occupancies, as deduced from peak intensity measurements, are 0.72, 0.80, and 0.48 for the hydrogen bonds to O(17), O(23), and F(4) respectively. This secondary binding is a consequence of the enhanced polarisation of the OH bonds of the complexed water, and it stabilises the overall complex. The secondary binding also inhibits the mobility of the polyether chain, so that the sulphur centres are not inverting configuration at 298 K.

There are several examples of rhodium aqua complexes with short rhodium–oxygen distances {for example in the *trans*-diaqua-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)-rhodium] cation, Rh–OH_2 2.107(8) Å; 2.117(1) Å in *trans*-μ$_3$-oxo-tris[bis(acetato)aquarhodium(III)] perchlorate, and in aqua(ethylenediaminetriacetatoacetic acid)rhodium(III), Rh–OH_2 2.096(2) Å},[14] but none is as short as in (**3**). There is only one other example in which a water molecule may be deemed to be bound by simultaneous primary and secondary co-ordination.[15] In that case, a water molecule was tightly bound to a rhodium(I) complex of a trioxo–phosphine complex in which Rh–O(W) 2.107(6) Å, and the water was additionally hydrogen bonded to the polyether chain.

Given that L^4 also forms well defined chloro complexes with palladium and platinum, ligands such as this offer considerable potential for the co-complexation of a neutral guest (H_2O, NH_3, or other amines) in proximity to a co-ordinatively unsaturated d^8 metal centre. In particular, systems in which an η^2-donor is bound by the metal may display an enhanced sensitivity to nucleophilic attack by the proximate neutral guest.

Experimental

Reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Commercial solvents were distilled from an appropriate drying agent prior to use according to standard procedures. Proton and carbon-13 n.m.r. spectra were recorded on a Bruker AC 250 spectrometer operating at 250.1 and 62.9 MHz respectively. Chemical shifts are given in p.p.m. relative to $SiMe_4$ (0 p.p.m.). Infrared spectra were recorded as KBr discs or as a mull in Nujol with a Perkin-Elmer 577 spectrometer, or a Mattson-Sirius 100 F.T. spectrometer. Mass spectra were recorded on a VG 7070 E spectrometer with a f.a.b., c.i., e.i., or d.c.i. ionization mode (f.a.b. = fast atom bombardment, c.i. = chemical ionization, e.i. = electron impact, d.c.i. = desorption chemical ionization), as stated. The ligands 6-oxa-3,9-dithia-15-azabicyclo[9.3.1]-pentadeca-1(15),11,13-triene (L^1) and 6,9,12(trioxa-3,15-dithia-21-azabicyclo[15.3.1]heneicosa-1(21),17,19-triene (L^3) were prepared according to the method of Vogtle.[7]

Synthesis of Ligands L^1—L^5.—*6-Oxa-*3,9-*dithia-*15-*aza-bicyclo*[9.3.1]*pentadeca-*1(15),11,13-*triene* (L^1), 6,20-*dioxa-*3,9,17,23-*tetrathia-*29,30-*diazatricyclo*[23.3.1.1^{11,15}]*triaconta-*1(29),11,13,15(30),25,27-*hexaene* (L^2), *and* L^5. A solution of 3-oxapentane-1,5-dithiol (2.76 g, 20 mmol) in butan-1-ol (50 cm^3) was stirred with potassium hydroxide (2.24 g, 40 mmol) for 1 h, and a solution of 2,6-di(bromomethyl)pyridine (5.3 g, 20 mmol) in butan-1-ol (75 cm^3) was added over a period of 2 h. The resulting mixture was heated at 80 °C for 18 h. After cooling, solid was removed by filtration and the filtrate was evaporated under reduced pressure to yield a colourless residue which was chromatographed on neutral alumina [dichloromethane–toluene (1:1)] permitting the separation of L^1, L^2, and L^5. Yields: L^1, 1.1 g (23%); L^2, 210 mg (5%); L^5, 25 mg. R_F(1% MeOH–CH_2Cl_2–Al_2O_3): L^1, 0.75; L^2, 0.51; L^5, 0.44.

L^1. M.p. 133—134 °C (lit.,[7] 133—135 °C); δ_H($CDCl_3$) 7.73 (1 H, t, *J* 7.8), 7.32 (2 H, d), 3.85 (4 H, s, benzylic CH_2), 3.32 (4 H, t, *J* 8.04 Hz, CH_2O), and 2.60 (4 H, t, CH_2S); δ_C($CDCl_3$) 157.6, 138.3, 121.9, 67.0 (CH_2O), 36.9 and 27.5 (CH_2S); *m/e* (c.i., isobutane) 242 ($M^+ + 1$) and 241 (M^+).

L^2. M.p. 106—108 °C (Found: C, 54.4; H, 6.20; N, 5.40. $C_{22}H_{30}N_2O_2S_4$ requires C, 54.5; H, 6.20; N, 5.75%); δ_H($CDCl_3$) 7.63 (2 H, t, *J* 7.68), 7.24 (4 H, d), 3.81 (8 H, s, benzylic CH_2S), 3.54 (8 H, t, *J* 6.97 Hz, CH_2O), and 2.67 (8 H, t, CH_2S); δ_C($CDCl_3$) 158.4, 137.4, 121.1, 70.0 (CH_2O), 37.8 and 30.5 (CH_2S); *m/e* (c.i., isobutane) 485 ($M^+ + 1$) and 484.

L^5. Oil (Found: C, 54.7; H, 6.35; N, 5.90. $C_{33}H_{45}N_3O_3S_6$ requires C, 54.5; H, 6.20; N, 5.75%); δ_H($CDCl_3$) 7.61 (3 H, t, *J* 7.82), 7.26 (6 H, d), 3.63 (12 H, s), 3.56 (12 H, t, *J* 6.75 Hz), and 2.67 (12 H, t, CH_2S); *m/e* (d.c.i., isobutane) 725 ($M^+ + 1$), 724 (M^+), 379, 242, and 138.

6,9,12,15,18-*Pentaoxa-*3,21-*dithia-*27-*azabicyclo*[21.3.1]-*heptacosa-*1(27),23,25-*triene*, L^4. To a solution of hexaethylene glycol ditosylate (3.9 g, 6.6 mmol) in butan-1-ol (250 cm^3) was added the disodium salt of 2,6-di(thiomethyl)pyridine (1.4 g, 6.6 mmol). The mixture was boiled for 6 h, filtered, and solvent was removed under reduced pressure to yield a residue which was extracted with chloroform (3 × 30 cm^3). The extracts were evaporated to yield a residue which was chromatographed on neutral alumina [toluene–methanol (100:3)] to yield a colourless oil (1 210 mg, 29%) (Found: C, 54.5; H, 7.30; N, 3.70. $C_{19}H_{31}NO_5S_2$ requires C, 54.7; H, 7.45; N, 3.35%); δ_H($CDCl_3$) 7.64 (1 H, t, *J* 7.3), 7.28 (2 H, d), 3.85 (4 H, s, CH_2S), 3.64 (20 H, m, CH_2O), and 2.70 (4 H, t, CH_2S, *J* 6.7 Hz); δ_C($CDCl_3$) 158.5, 137.4, 121.2, 70.6, 70.5, 70.3, 37.9, and 30.5; *m*/*e* (c.i., isobutane) 418 ($M^+ + 1$) and 417 (M^+).

Synthesis of Complexes.—$[RhL^3(CO)]_2[PF_6]_2$. A solution of freshly sublimed $[Rh_2Cl_2(CO)_4]$ (39.3 mg, 0.1 mmol) in methanol (1 cm^3) was added to a solution of L^3 (66.5 mg, 0.2 mmol) in methanol (2 cm^3). Brisk evolution of CO ensued, and after 0.2 h a solution of ammonium hexafluorophosphate in methanol (0.5 mol dm^{-3}, 2 cm^3) was added slowly over 5 min. A red microcrystalline solid was deposited which was filtered off, washed with cold methanol (2 × 2 cm^3), and dried under a stream of nitrogen, 97 mg (80%); $\delta_H(CD_2Cl_2)$ 7.92 (1 H, t, *J* 8.0), 7.53 (2 H, d), 5.07 (2 H, d, *J* 17.0), 4.79 (2 H, d), 4.18 (4 H, m), 3.53 (4 H, t, *J* 7.8 Hz), 3.38 (4 H, m), and 3.15 (4 H, m); i.r. (CH_2Cl_2) 2 020 cm^{-1}; *m*/*e* (f.a.b., glycerol) 460 [L^3–Rh(CO)$^+$].

The following organorhodium complexes were prepared analogously.

$[RhL^4(CO)][PF_6]$ (Found: C, 34.3; H, 4.20; N, 2.30. $C_{20}H_{31}F_6NO_6PRhS_2$ requires C, 34.6; H, 4.45; N, 2.00%); i.r. (CH_2Cl_2) 2 020 cm^{-1}; *m*/*e* (f.a.b., glycerol) 548 [L^4–Rh(CO)$^+$] and 520 [L^4–Rh$^+$]; $\delta_H^{298}(CD_2Cl_2)$ 7.92 (1 H, t, *J* 7.77 Hz), 7.60 (2 H, d), 4.97 (4 H, br), 4.01—3.55 (20 H, m), and 3.12 (4 H, br s, CH_2S). The signal at 4.97 sharpened on cooling; δ_H^{260} 5.03 (2 H, d, *J* 18.3 Hz) and 4.91 (2 H, d).

$[RhL^1(CO)]_2[PF_6]_2$ (Found: C, 28.3; H, 2.95; N, 2.65. $C_{12}H_{15}F_6NO_2PRhS_2$ requires C, 27.9; H, 2.90; N, 2.70%); i.r. (Nujol) 1 740 cm^{-1}; $\delta_H(CD_3CN)$ 7.96 (1 H, t, *J* 7.63), 7.63 (2 H, d), 4.72 (4 H, dd, *J* 18.3 Hz), 3.84 (2 H, m), and 3.50—3.28 (6 H, m).

$[Rh_2L^2(CO)_2][PF_6]_2$ (Found: C, 28.4; H, 3.05; N, 2.70. $C_{24}H_{30}F_{12}N_2O_4P_2Rh_2S_4$ requires C, 27.9; H, 2.90; N, 2.70%); i.r. 1 993 and 2 044 cm^{-1}; $\delta_H[(CD_3)_2CO]$ 8.08 (2 H, t, *J* 7.5 Hz), 7.72 (4 H, d), 5.07 (8 H, br s, CH_2S), 4.16 (8 H, br s, CH_2O), and 3.43 (8 H, br s, CH_2S).

$[RhL^4Cl_2(H_2O)][PF_6]$. To a solution of rhodium trichloride trihydrate (41.1 mg, 0.16 mmol) in aqueous methanol (2 cm^3) was added a solution of L^4 (72.4 mg, 0.17 mmol) in methanol (2 cm^3). The mixture was heated under reflux for 18 h, yielding an orange solution to which a solution of ammonium hexafluorophosphate in methanol (0.5 mol dm^{-3}, 3 cm^3) was added. An orange microcrystalline solid was precipitated which was washed with methanol and dried under a stream of nitrogen; 68 mg (56%); $\delta_H(CD_2Cl_2)$ 7.93 (1 H, t, *J* 7.9), 7.60 (2 H, d), 4.92 (2 H, d, *J* 16.2 Hz), 4.70 (2 H, d), 3.66 (22 H, m), and 2.87 (2 H, m); *m*/*e* (f.a.b., glycerol) 608 [L^4–$RhCl_2(H_2O)^+$], 573 [L^4–$RhCl(H_2O)^+$], 555 (L^4–$RhCl^+$), and 520 (L^4–Rh^+). The same complex was also formed by aerial oxidation of a methanol solution of $[RhL^4(CO)][PF_6]$ in the presence of chloride (as KCl).

Crystal Data for $[RhL^3(CO)]_2[PF_6]_2$.—$C_{32}H_{46}F_{12}N_2O_8P_2Rh_2S_4$, *M* = 1 210.72, tetragonal, *a* = 11.800(2), *c* = 31.822(8) Å, *U* = 4 430.9 Å^3, *Z* = 4, D_c = 1.81 g cm^{-3}, *F*(000) = 2 432, $\mu(Mo\text{-}K_\alpha)$ = 10.8 cm^{-1}. Space group determined from the systematic absences as $P4_12_12$. Crystal dimensions 0.11 × 0.18 × 0.40 mm.

Data collection and processing. CAD 4 diffractometer, ω—2θ mode with ω scan width = 0.6 + 0.350 tanθ, ω scan speed 0.2° min^{-1}, graphite-monochromated Mo-K_α radiation; 2 958 reflections measured of which 2 844 were unique. Data were collected to a maximum 2θ of 49°. The range of indices was *h*, 0 to 13; *l*, −14 to 14; and *k*, 0 to 30. After correction for Lorentz, polarisation, and absorption effects, 1 737 were used with $I > 5\sigma(I)$.

Structure analysis and refinement. The co-ordinates of the rhodium atom were located from a three-dimensional Patterson synthesis and the remaining non-hydrogen atoms were found by the heavy-atom method. Refinement was by full-matrix, least-squares calculations with all non-hydrogen atoms allowed anisotropic motion, and with hydrogen atoms 'riding' at calculated positions from the relevant atoms. The final cycle of refinement has 280 variable parameters and converged with *R* = 0.027, *R'* = 0.033. All calculations were performed on a PDP 11/73 computer using the SDP-plus suite of programs.[16] Final atomic co-ordinates are given in Table 3.

Crystal Data for $[RhL^4Cl_2(H_2O)][PF_6]$.—$C_{19}H_{33}Cl_2F_6NO_6PRhS_2$; *M* = 754.38, monoclinic, *a* = 10.767(2), *b* = 23.479(4), *c* = 11.577(2) Å, β = 95.04°, *U* = 2 915.4 Å^3, *Z* = 4, D_c = 1.72 g cm^{-3}, *F*(000) = 1 528, $\mu(Mo\text{-}K_\alpha)$ = 10.3 cm^{-1}. Space group determined uniquely from the systematic absences as $P2_1/n$. Crystal dimensions 0.06 × 0.20 × 0.30 mm.

Data collection and processing. CAD 4 diffractometer, ω—2θ scan-mode, ω scan width = 0.6 + 0.35 tanθ, ω scan speed = 1.3° min^{-1}, graphite-monochromated Mo-K_α radiation; 5 002 reflections measured of which 4 637 were unique. Data were collected to a maximum 2θ of 54°. The range of indices was *h*, 0 to 15; *k*, 0 to 15; and *l*, 0 to 40. After correction for Lorentz, polarisation, and absorption effects, 2 103 were used with $I > 9\sigma(I)$.

Structure analysis and refinement. The structure was solved using the Patterson heavy-atom method which revealed the positions of the rhodium and phosphorus atoms. The remaining

Table 3. Atomic co-ordinates for $[RhL^3(CO)]_2[PF_6]_2$, with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	0.326 32(4)	0.145 53(4)	0.522 22(1)	C(16)	0.758 9(6)	−0.012 5(6)	0.493 4(3)
N(1)	0.373 7(4)	0.081 6(4)	0.464 6(1)	O(17)	0.695 2(4)	0.089 6(3)	0.499 0(2)
C(2)	0.462 1(5)	0.128 7(6)	0.443 8(2)	C(18)	0.630 3(5)	0.094 4(6)	0.536 0(2)
C(3)	0.502 3(6)	0.081 2(7)	0.407 4(2)	C(19)	0.594 6(6)	0.214 1(5)	0.543 6(2)
C(4)	0.450 5(7)	−0.015 1(8)	0.392 4(2)	S(20)	0.475 0(1)	0.269 4(1)	0.514 03(5)
C(5)	0.358 8(6)	−0.060 2(6)	0.412 1(2)	C(21)	0.511 1(6)	0.238 9(6)	0.460 0(2)
C(6)	0.321 8(5)	−0.009 7(5)	0.448 7(2)	C(22)	0.283 3(5)	0.200 5(5)	0.573 7(2)
C(7)	0.217 5(5)	−0.051 9(6)	0.469 9(2)	O(23)	0.254 5(4)	0.234 3(4)	0.604 6(1)
S(8)	0.195 9(1)	0.001 3(1)	0.522 52(5)	P	0.480 0(2)	0.549 7(2)	0.376 11(6)
C(9)	0.248 6(5)	−0.110 2(5)	0.556 3(2)	F(1)	0.367 6(4)	0.480 0(5)	0.376 7(2)
C(10)	0.368 3(5)	−0.151 2(5)	0.549 6(2)	F(2)	0.411 6(5)	0.657 2(4)	0.385 0(2)
O(11)	0.371 3(4)	−0.224 9(4)	0.515 2(2)	F(3)	0.490 5(6)	0.533 4(6)	0.424 2(1)
C(12)	0.472 0(5)	−0.289 0(5)	0.510 7(3)	F(4)	0.547 1(5)	0.436 7(5)	0.367 2(2)
C(13)	0.551 7(5)	−0.238 8(5)	0.479 7(2)	F(5)	0.468 7(5)	0.563 5(6)	0.327 7(1)
O(14)	0.609 4(4)	−0.145 3(4)	0.497 3(2)	F(6)	0.590 9(4)	0.619 6(6)	0.375 1(2)
C(15)	0.695 2(6)	−0.103 3(6)	0.471 1(2)				

Table 4. Atomic co-ordinates for $[RhL^4Cl_2(OH_2)][PF_6]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	0.317 15(3)	0.002 17(2)	−0.266 16(3)	C(2)	0.377 7(5)	−0.089 7(2)	−0.422 5(4)
Cl(1)	0.117 7(1)	−0.036 98(7)	−0.292 7(1)	C(3)	0.428 6(5)	−0.140 8(3)	−0.456 1(5)
Cl(2)	0.516 2(1)	0.041 63(6)	−0.241 3(1)	C(4)	0.487 4(6)	−0.175 0(3)	−0.373 6(6)
S(8)	0.360 9(1)	−0.027 90(6)	−0.075 2(1)	C(5)	0.498 0(6)	−0.158 4(3)	−0.259 2(5)
S(26)	0.316 6(1)	0.021 75(6)	−0.463 2(1)	C(6)	0.450 2(5)	−0.106 7(2)	−0.228 0(5)
P	−0.117 1(2)	0.167 19(7)	−0.272 3(1)	C(7)	0.468 5(5)	−0.084 1(3)	−0.107 9(5)
F(1)	−0.189 8(4)	0.225 8(2)	−0.274 0(4)	C(9)	0.230 8(6)	−0.066 5(3)	−0.020 1(5)
F(2)	0.005 0(4)	0.203 3(2)	−0.281 3(4)	C(10)	0.179 1(5)	−0.029 2(3)	0.068 7(5)
F(3)	−0.239 5(4)	0.132 1(2)	−0.263 6(4)	C(12)	0.150 9(6)	0.065 1(3)	0.117 8(5)
F(4)	−0.041 5(4)	0.110 9(2)	−0.266 7(5)	C(13)	0.133 5(6)	0.122 8(3)	0.074 1(6)
F(5)	−0.132 8(5)	0.164 0(2)	−0.407 3(4)	C(15)	0.228 9(6)	0.197 8(3)	−0.019 5(5)
F(6)	−0.103 8(5)	0.172 7(2)	−0.136 6(4)	C(16)	0.349 2(6)	0.213 8(2)	−0.055 2(5)
O(W)	0.240 2(4)	0.078 2(2)	−0.216 6(4)	C(18)	0.501 8(6)	0.196 8(3)	−0.186 1(6)
O(11)	0.164 3(3)	0.027 3(2)	0.024 8(3)	C(19)	0.481 4(7)	0.242 0(3)	−0.277 5(7)
O(14)	0.246 0(3)	0.143 7(2)	0.033 9(3)	C(21)	0.281 8(7)	0.230 1(3)	−0.377 5(6)
O(17)	0.390 8(4)	0.179 9(2)	−0.137 3(3)	C(22)	0.214 5(6)	0.200 1(3)	−0.476 0(6)
O(20)	0.409 2(4)	0.221 1(2)	−0.378 0(4)	C(24)	0.175 3(6)	0.110 3(3)	−0.556 5(5)
O(23)	0.220 2(4)	0.140 2(2)	−0.456 7(3)	C(25)	0.166 9(6)	0.047 8(3)	−0.526 4(5)
N(1)	0.389 2(4)	−0.073 5(2)	−0.311 2(3)	C(27)	0.302 9(5)	−0.052 8(2)	−0.507 2(4)

atoms were located in succeeding difference Fourier syntheses. Refinement was by full-matrix, least-squares calculations with all non-hydrogen atoms allowed anisotropic motion, and with hydrogen atoms riding at calculated positions from the atoms to which they were bonded. The final cycle of refinement had 343 variables and converged with $R = 0.024$, $R' = 0.032$. The highest peak in the final difference Fourier map had a height of 0.40 e Å^{-3}, and the top ten peaks in this final difference map were located around the highly anisotropic fluorine atoms of the $[PF_6]^-$ counter ion. Electron density difference maps at $R = 0.025$ showed that the two water hydrogens are disordered over three sites (occupancies from peak densities are 0.72, 0.80, and 0.48) and form three hydrogen bonds to O(17), O(23), and a fluorine atom in the $[PF_6]^-$ counter ion.

Final atomic co-ordinates are given in Table 4.

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

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