Synthesis of Cationic Half-sandwich Rhodium(I) Complexes of 1,4,7-Trithiacyclononane ([9]aneS$_3$). The Single-crystal Structures of [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]PF$_6$, [Rh([9]aneS$_3$)-(C$_8$H$_{12}$)]BF$_4$ and [Rh([9]aneS$_3$)(C$_4$H$_6$)]PF$_6$·0.25OEt$_2$†

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Reaction of [Rh$_2$L$_2$L'$_2$Cl$_2$] {L, L' = C$_2$H$_4$, ½cod or ½nbd; L = C$_2$H$_4$, L' = PPr$^i_3$ or P(C$_6$H$_{11}$)$_3$; cod = cycloocta-1,5-diene, nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)} with 2 molar equivalents of 1,4,7-trithiacyclononane([9]aneS$_3$) in the presence of NaBF$_4$ or NH$_4$PF$_6$ at 293 K, or treatment of [Rh(C$_4$H$_6$)$_2$Cl] or [Rh(CO)Cl(PPh$_3$)$_2$] with 1 molar equivalent of [9]aneS$_3$ and NH$_4$PF$_6$ afforded [Rh([9]aneS$_3$)L(L')]X [L, L' = C$_2$H$_4$, ½cod, ½nbd or ½C$_4$H$_6$; L = C$_2$H$_4$, L' = PPr$^i_3$, P(C$_6$H$_{11}$)$_3$; L = CO, L' = PPh$_3$; X = BF$_4$ or PF$_6$] in moderate yields. The crystal structure of the complex [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]PF$_6$ has been determined: monoclinic, space group $P2_1/n$, a = 11.487(3), b = 9.459(3), c = 15.745(6) Å, β = 105.54(3)° and Z = 4. The cation adopts a trigonal-bipyramidal geometry, with one equatorial and one axial ethene ligand. The complex [Rh([9]aneS$_3$)(cod)]BF$_4$ crystallises in the triclinic space group $P\bar{1}$ with a = 11.491(13), b = 12.803(6), c = 13.377(15), α = 88.12(7), β = 70.30(8), γ = 74.68(7)° and Z = 4. The two molecules in each asymmetric unit also adopt distorted trigonal-bipyramidal stereochemistries, with the conformation in molecule 1 being related to that of molecule 2 by a 6° rotation of the macrocyclic ring about the central M–[9]aneS$_3$ axis. The complex [Rh([9]aneS$_3$)(C$_4$H$_6$)]PF$_6$ crystallises in the monoclinic space group $C2/c$ with a = 18.612(6), b = 8.679(5), c = 23.756(5), β = 96.844(18)° and Z = 8. The structure shows a quasi-square-pyramidal complex cation. Treatment of [Rh$_2$(CO)$_4$Cl$_2$] with [9]aneS$_3$ and NH$_4$PF$_6$ yielded the dimeric complex [Rh$_2$([9]aneS$_3$)$_2$(μ-CO)$_3$][PF$_6$]$_2$. Reaction of [Rh([9]aneS$_3$)(C$_2$H$_4$)L]$^+$ [L = C$_2$H$_4$ or P(C$_6$H$_{11}$)$_3$] with halogenated substrates afforded insoluble [Rh([9]aneS$_3$)X$_3$] (X = Cl or I), while no reaction was observed with C$_6$H$_6$ or SiEt$_3$H. Spectroscopic, structural and chemical evidence indicates that the [Rh([9]aneS$_3$)]$^+$ fragment has a high electrophilic character.

The chemistry of half-sandwich rhodium(I) and iridium(I) complexes containing tridentate facially binding ligands such as tris(pyrazolyl)borates, P$_3$O$_9$$^{3-}$ and the tripodal phosphines X(CH$_2$PPh$_2$)$_3$ (X = N, P or CMe) as protecting groups is of wide interest.[1–4] Such compounds are isoelectronic with the well known [Rh(C$_5$R$_5$)L$_2$] (R = H or Me; L = alkene, CO or PR$_3$),[5] the photochemistry of which has been the subject of several investigations.[6] Both the cyclopentadienyl complexes and their analogues have been shown to exhibit novel reactivity, particularly towards C–H bonds. For example, the unsaturated fragments [M(C$_5$Me$_5$)L] (M = Rh or Ir; L = C$_2$H$_4$, CO or PMe$_3$) generated by the low-temperature photolysis of [M(C$_5$Me$_5$)L$_2$] (L = C$_2$H$_4$ or CO) or [M(C$_5$Me$_5$)(PMe$_3$)H$_2$] oxidatively add across a range of alkane, alkene and arene C–H bonds,[6–8] while [Rh{HB(pz)$_3$}L$_2$] (pz = pyrazolyl; L = C$_2$H$_4$ or CO) undergo the same type of reaction under mild thermal conditions.[1] As part of our studies of the chemistry of the crown thioethers,[9] we argued that the small-ring macrocycle 1,4,7-trithiacyclononane ([9]aneS$_3$) could also act as a protecting group analogous to the cyclopentadienyl ligand, and that the complexes [Rh([9]aneS$_3$)L$_2$]$^+$ (L = C$_2$H$_4$, CO or PR$_3$) might exhibit novel chemistry. This paper describes the synthesis and structures of several such compounds, together with a preliminary study of their reactivity.

We and others have investigated the chemistry of rhodium(III) with thioether crowns.[10–12] In particular, we have shown that the octahedral hexathia cation [Rh([9]aneS$_3$)$_2$]$^{3+}$ can be reduced electrochemically to give an unusually stable mononuclear d^7 species [Rh([9]aneS$_3$)$_2$]$^{2+}$.[10,12] The second reduction product [Rh([9]aneS$_3$)$_2$]$^+$ is less stable, and is assumed to adopt either a tetragonal geometry by analogy with the isoelectronic complexes [Pd([9]aneS$_3$)$_2$]$^{2+}$ [13] and [Au([9]aneS$_3$)$_2$]$^{3+}$,[14] or a five-co-ordinate geometry as in [Pt([9]aneS$_3$)$_2$]$^{2+}$.[15] Neither [Rh([9]aneS$_3$)$_2$]$^{2+}$ nor [Rh([9]aneS$_3$)$_2$]$^+$ has been structurally characterised, and this led us towards the preparation of half-sandwich rhodium(I) complexes of [9]aneS$_3$ and to determine their geometry.

Relatively few rhodium(I) complexes of thioether ligands have been reported to date. The reaction of [Rh$_2$(CO)$_4$Cl$_2$] with 2,5-dithiahexane (dth) affords a polymeric species [{Rh(dth)(CO)Cl}$_n$][16] while an analogous reaction with Et$_2$S gives the monomeric *trans*-[Rh(SEt$_2$)$_2$(CO)Cl].[17] The synthesis of [Rh([14]aneS$_4$)]$^+$ ([14]aneS$_4$ = 1,4,8,11-tetrathiacyclotetradecane) was first described by Busch and co-workers[18] who reported this complex to be a strong nucleophile, forming adducts with O$_2$, SO$_2$, tcne (tetracyanoethene) and H$^+$, as well as undergoing oxidative-addition reactions with MeI and MeCOCl. A more recent structural determination has shown that [Rh([14]aneS$_4$)]$^+$ adopts a square-planar geometry, with weak intermolecular contacts in the solid state [Rh···Rh 3.313(1) Å].[19] The binuclear complex [Rh$_2$(cod)$_2$([20]aneS$_6$)]$^{2+}$ ([20]aneS$_6$ = 1,4,7,11,14,17-hexathiacycloicosane, cod = cycloocta-1,5-diene) exhibits a five-co-ordinate geometry in the solid state, with each Rh bound to three S-donors.[20]

A preliminary report on parts of this work has appeared,[21] while the synthesis and structures of analogous iridium(I) complexes of [9]aneS$_3$ are described in a companion paper.[22]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Results and Discussion

Reaction of [Rh$_2$L$_4$Cl$_2$] [L = C$_2$H$_4$, $\frac{1}{2}$cod or $\frac{1}{2}$nbd; nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)] with 2 molar equivalents of [9]aneS$_3$ in the presence of NaBF$_4$ or NH$_4$PF$_6$ at 293 K affords yellow solutions, from which bright yellow air-sensitive (L = C$_2$H$_4$) or air-stable microcrystalline solids can be isolated in moderate yield. Similarly, treatment of [Rh(C$_4$H$_6$)$_2$Cl] {generated *in situ* from [Rh$_2$(C$_2$H$_4$)$_4$Cl$_2$] and C$_4$H$_6$[23]} with 1 molar equivalent of [9]aneS$_3$ and NH$_4$PF$_6$ yields a pale yellow crystalline product. On the basis of microanalytical and IR spectroscopic data, these compounds were formulated as [Rh([9]aneS$_3$)L$_2$]X (X = BF$_4$ or PF$_6$). This assignment is supported further by FAB mass spectrometry. For example, the spectrum of [Rh([9]aneS$_3$)(cod)]$^+$ shows peaks at *m*/*z* = 391 and 282 corresponding to [^{103}Rh([9]aneS$_3$)(cod)]$^+$ and [^{103}Rh([9]aneS$_3$ − H)]$^+$ respectively. Both ^{1}H and ^{13}C NMR spectroscopy are consistent with the formation of rhodium(I) π complexes.

The attempted preparation of [Rh([9]aneS$_3$)(C$_8$H$_{14}$)$_2$]$^+$ (C$_8$H$_{14}$ = cyclooctene) by reaction of [Rh$_2$(C$_8$H$_{14}$)$_4$Cl$_2$] with [9]aneS$_3$ and NH$_4$PF$_6$ in tetrahydrofuran (thf) at 233 K yielded a yellow solid product, which rapidly decomposed on warming to 293 K and could not be characterised fully. Similarly, reaction of [Rh$_2$(C$_2$H$_4$)$_2$(C$_2$F$_4$)$_2$Cl$_2$][24] with [9]aneS$_3$ in the presence of NH$_4$PF$_6$ in thf at 293 K affords a pale tan solid, which decomposes to a red oil after 12 h at 293 K: IR spectroscopy of this product showed the presence of [9]aneS$_3$, C$_2$F$_4$ and PF$_6$$^-$, although no further characterisation was possible. Reaction of [Rh$_2$(C$_2$H$_4$)$_4$Cl$_2$] with [9]aneS$_3$ in the absence of a chloride abstractor gives [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]Cl only; interestingly, the analogous reaction using the tripodal phosphine ligand tdpme = MeC(CH$_2$PPh$_2$)$_3$ affords [Rh(tdpme)(C$_2$H$_4$)Cl].[25]

The ^{1}H NMR spectrum of [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]$^+$ shows a multiplet at δ 3.22–3.02 assigned to the methylene protons of [9]aneS$_3$, and a doublet at δ 2.76 [^2J(Rh-H) = 1.6 Hz] assigned to interchanging protons of C$_2$H$_4$. This spectrum is only slightly broadened at 188 K in (CD$_3$)$_2$CO showing that exchange of the inner and outer ethene proton environments in this complex is a highly facile process. This equilibration could occur either by intermolecular exchange of the ethene ligands, or by rotation of the ethene about the central Rh–C$_2$H$_4$ axis.[5] Given the inertness of [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]$^+$ towards nucleophilic ligand substitution (see below) the latter mechanism is more likely: this being the case, the estimated activation energy[26] of < 33 kJ mol^{-1} (T_c < 180 K) for this process is the lowest value yet to be reported for ethene rotation in a d^8 complex.[22] This suggests that Rh→C$_2$H$_4$ π-back bonding in [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]$^+$ is rather weak, consistent with the cationic charge on the complex.

We have previously reported the single-crystal structure of [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]BF$_4$, which exhibits two independent molecules per asymmetric unit.[21] Unfortunately, the relatively poor crystal did not allow high-precision structural parameters to be obtained, and we therefore carried out a second structural determination on the PF$_6$$^-$ salt of this complex. In contrast to the BF$_4$$^-$ salt, the structure of [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]PF$_6$ contains only one molecule per asymmetric unit. The cation exhibits (Fig. 1, Table 1) an approximate trigonal-bipyramidal stereochemistry, with a shortened axial Rh–S(4) bond length [Rh–S(1) 2.446(2), Rh–S(4) 2.309(2), Rh–S(7) 2.411(2) Å]. These distances are longer than those observed for [Rh([9]aneS$_3$)$_2$]$^{3+}$ [Rh–S 2.332(1), 2.334(1) and 2.334(1)];[10] this is consistent with the reduced charge on the rhodium(I) complex and again implies only weak Rh–[9]aneS$_3$ π-back donation. Interestingly, the axial ethene ligand [C(1E)–C(2E)] shows significantly longer Rh–C and shorter C=C distances than does the equatorial ethene [C(3E)–C(4E)]: Rh–C(1E) 2.203(10), Rh–C(2E) 2.226(8), Rh–C(3E) 2.124(9), Rh–C(4E) 2.149(7), intra-C$_2$H$_4$ C(1E)–C(2E) 1.316(15), C(3E)–C(4E) 1.398(12), Rh–X(1) 2.114(8), Rh–X(2) 2.019(7) Å; S(1)–Rh–X(1) 98.3(3), S(4)–Rh–X(1) 174.6(3), S(7)–Rh–X(1) 93.4(3), S(1)–Rh–X(2) 129.5(3), S(4)–Rh–X(2) 85.0(3), S(7)–Rh–X(2) 142.9(3), X(1)–Rh–X(2) 91.5(3)°; where X(1) and X(2) are the midpoints of the C(1E)–C(2E) and C(3E)–C(4E) vectors respectively. The strong *trans* influence of a thioether donor [in this case S(4)] *trans* to an alkene ligand [C(1E)–C(2E)] leading to lengthening of the Rh–C bond has been noted previously.[20] For the related trigonal-bipyramidal complex [Rh(tdpme)(C$_2$H$_4$)Cl], C=C 1.49(4), Rh–C$_{eq}$ 2.19(2) and 2.20(2) Å. Significantly, this complex shows a non-fluxional ethene ligand at 308 K.[24]

Table 1 Bond lengths (Å), angles and torsion angles (°) for [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]PF$_6$

Rh–S(1)	2.446(2)	Rh–S(4)	2.309(2)
Rh–S(7)	2.411(2)	Rh–C(1E)	2.203(10)
Rh–C(2E)	2.226(8)	Rh–C(3E)	2.124(9)
Rh–C(4E)	2.149(7)	S(1)–C(2)	1.813(7)
S(1)–C(9)	1.831(8)	C(2)–C(3)	1.527(11)
C(3)–S(4)	1.821(7)	S(4)–C(5)	1.811(8)
C(5)–C(6)	1.514(9)	C(6)–S(7)	1.828(6)
S(7)–C(8)	1.812(6)	C(8)–C(9)	1.532(10)
S(1)–Rh–S(4)	87.1(1)	S(1)–Rh–S(7)	86.1(1)
S(4)–Rh–S(7)	87.1(1)	Rh–S(1)–C(2)	99.8(2)
Rh–S(1)–C(9)	105.0(2)	C(2)–S(1)–C(9)	101.9(3)
S(1)–C(2)–C(3)	114.8(5)	C(2)–C(3)–S(4)	111.8(5)
Rh–S(4)–C(3)	107.3(2)	Rh–S(4)–C(5)	102.8(2)
C(3)–S(4)–C(5)	101.2(4)	S(4)–C(5)–C(6)	113.2(5)
C(5)–C(6)–S(7)	111.6(4)	Rh–S(7)–C(6)	103.8(2)
Rh–S(7)–C(8)	102.1(3)	C(6)–S(7)–C(8)	101.5(3)
S(7)–C(8)–C(9)	115.4(4)	S(1)–C(9)–C(8)	112.1(4)

C(9)–S(1)–C(2)–C(3)	−63.8(6)
C(2)–S(1)–C(9)–C(8)	131.7(5)
S(1)–C(2)–C(3)–S(4)	−49.5(6)
C(2)–C(3)–S(4)–C(5)	134.5(5)
C(3)–S(4)–C(5)–C(6)	−63.8(5)
S(4)–C(5)–C(6)–S(7)	−51.9(6)
C(5)–C(6)–S(7)–C(8)	134.8(5)
C(6)–S(7)–C(8)–C(9)	−62.4(5)
S(7)–C(8)–C(9)–S(1)	−50.4(6)

The single-crystal structure of [Rh([9]aneS$_3$)(cod)]BF$_4$ contains (Fig. 2, Table 2) two crystallographically independent molecules per asymmetric unit. Both cations adopt distorted trigonal-bipyramidal geometries similar to that described for [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]PF$_6$ with S(1) and S(21) in the independent molecules occupying axial positions *trans* to C(16)=C(17) and C(35)=C(36) respectively. As for [Rh([9]aneS$_3$)(C$_2$H$_4$)$_2$]$^+$, the Rh–S bond lengths to axial S-donors, S(1) and S(21), are shortened relative those to the equatorial S-donors. For molecule 1 Rh(1)–S(1) 2.321(3), Rh(1)–S(4) 2.397(2), Rh(1)–S(7) 2.447(2), Rh(1)–X(1) 1.975(7) and Rh(1)–X(2) 2.099(10) Å; S(1)–Rh(1)–X(1) 88.44(2), S(4)–Rh(1)–X(1) 144.25(2), S(7)–Rh(1)–X(1) 128.66(2), S(1)–Rh(1)–X(2) 172.35(2), S(4)–Rh(1)–X(2) 96.42(2), S(7)–Rh(1)–X(2) 100.73(2) and X(1)–Rh(1)–X(2) 84.76(3)° where X(1) and X(2) are the midpoints of C(11)=C(12) and C(15)=C(16) respectively. For molecule 2 Rh(2)–S(21) 2.307(3), Rh(2)–S(24) 2.444(2), Rh(2)–S(27) 2.437(2), Rh(2)–X(3) 1.978(7) and Rh(2)–X(4) 2.107(11) Å; S(21)–Rh(2)–X(3) 89.15(3), S(21)–Rh(2)–X(4) 173.77(3), S(24)–Rh(2)–X(3) 135.89(3), S(24)–Rh(2)–X(4) 97.80(3), S(27)–Rh(2)–X(3) 137.43(3), S(27)–Rh(2)–X(4) 97.47(3) and X(3)–Rh(2)–X(4) 84.62(4)° where X(3) and X(4) are the midpoints of C(31)=C(32) and C(35)=C(36) respectively. The pattern of Rh–C and Rh–S distances is similar in the two molecules [for molecule 1 Rh(1)–C(11) 2.080(7), Rh(1)–C(12) 2.122(7), Rh(1)–C(15) 2.223(10), Rh(1)–C(16) 2.202(10), C(11)=C(12) 1.429(11) and C(15)=C(16) 1.397(11) Å: for molecule 2 Rh(2)–C(31) 2.116(7), Rh(2)–C(32) 2.080(6), Rh(2)–C(35) 2.190(11), Rh(2)–C(36) 2.224(12), C(31)=C(32)

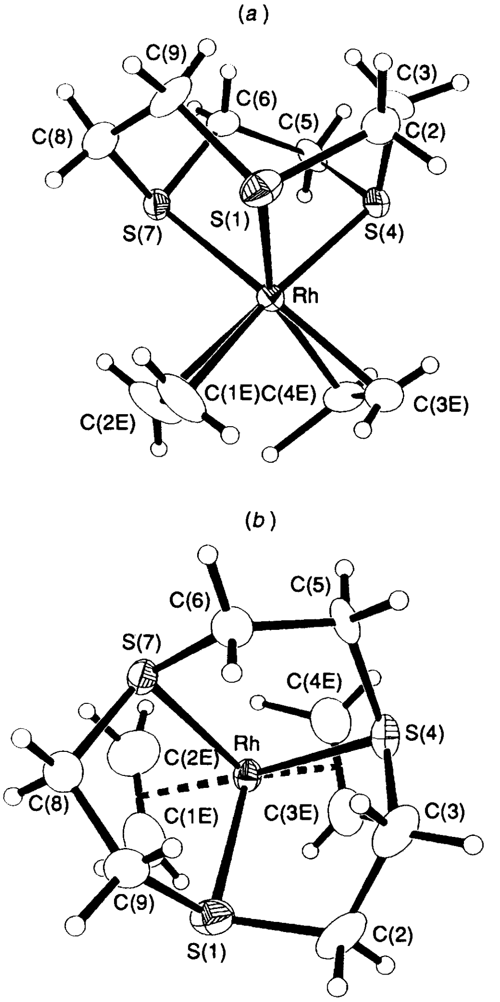

Fig. 1 Two views of the single-crystal structure of $[Rh([9]aneS_3)(C_2H_4)_2]^+$ with the numbering scheme adopted. Thermal ellipsoids enclose 50% probability surfaces

1.401(12) and C(35)=C(36) 1.315(14) Å]. Interconversion of the geometries exhibited by the two cations, molecules 1 and 2, involves rotation of the $[9]aneS_3$ macrocycle by 6° about the central Rh–$[9]aneS_3$ axis, the overall geometry of the cation in molecule 2 of $[Rh([9]aneS_3)(cod)]BF_4$ being similar to that exhibited by $[Rh_2([20]aneS_6)(cod)_2][PF_6]_2$ in the solid state.[20]

Taken together, the X-ray analyses of $[Rh([9]aneS_3)(C_2H_4)_2]PF_6$, $[Rh([9]aneS_3)(C_2H_4)_2]BF_4$,[21] $[Rh([9]aneS_3)(cod)]BF_4$, $[Ir([9]aneS_3)(C_2H_4)_2]PF_6$[22] and $[Ir([9]aneS_3)(cod)]PF_6$[22] all reveal five co-ordinate structures based around 18-electron metal(I) centres. The precise relative geometries observed for these cations may be strongly influenced by crystal-packing forces with rotation of the $[9]aneS_3$ ring about the metal–macrocycle axis being a relatively facile process (see above). Structural isomerism has been observed previously in rhodium(I) complexes of tripodal phosphines; thus, $[Rh\{RC(CH_2PPh)_3\}(nbd)]PF_6$ exhibits a square-pyramidal geometry in the solid state for R = Me, but a trigonal-bipyramidal geometry for R = H.[27]

The ^1H NMR spectrum of $[Rh([9]aneS_3)(C_4H_6)]PF_6$ in $(CD_3)_2CO$ at 293 K shows multiplet resonances at δ 5.60, 2.32 and 1.08 (each 2 H) corresponding to the butadiene H atoms, and a broad asymmetric resonance at δ 3.22–2.85 (12 H) from the $[9]aneS_3$ ligand. A variable-temperature ^1H NMR study showed that between 204 and 273 K the resonances due to $[9]aneS_3$ are resolved into two multiplets centred at δ 3.15 (4 H) and 2.91 (8 H), whilst above 306 K these resonances coalesce into a broad singlet at δ 3.01. The ^{13}C DEPT (distortionless enhancements by polarisation transfer) spectrum at 293 K exhibits peaks at δ 89.98 [d, ^1J(Rh–C) = 5.0] and 35.37 [d, ^1J(Rh–C) = 12.1 Hz] from the C_4H_6 ligand, and two broad singlets in the region expected for co-ordinated $[9]aneS_3$ at δ 36.24 and 34.69 with an integral ratio of approximately 1 : 2. At 319 K the last two resonances coalesce to a broad singlet at δ 35.9. The ^1H and ^{13}C resonances from the C_4H_6 ligand are unchanged between 204 and 327 K.

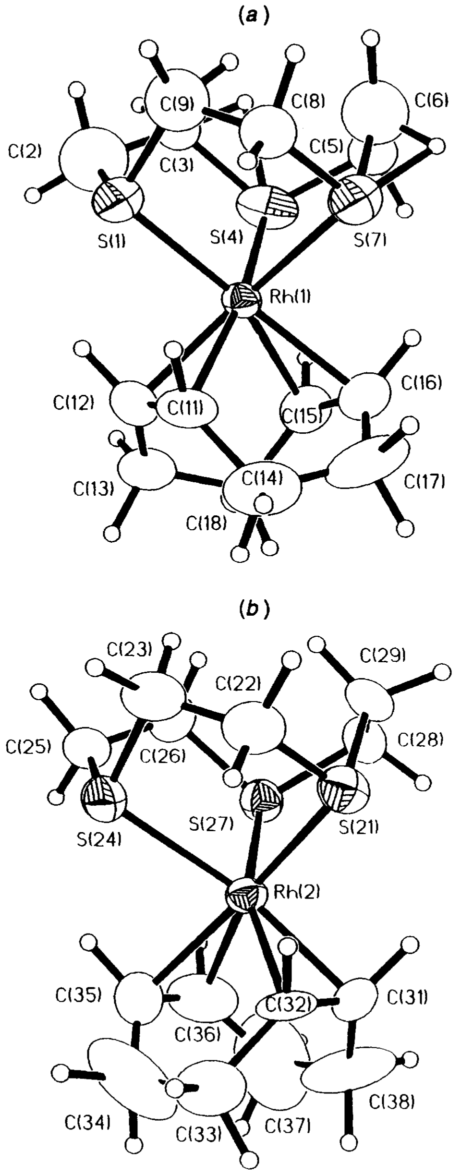

Fig. 2 View of the two independent molecules of $[Rh([9]aneS_3)(cod)]^+$ with the numbering scheme adopted: (*a*) molecule 1, (*b*) molecule 2. Thermal ellipsoids as in Fig. 1

The nature of the fluxional process operating for $[Rh([9]aneS_3)(C_4H_6)]^+$ is unclear, since any pseudo-rotation that would interchange two out of the three CH_2 environments of co-ordinated $[9]aneS_3$ is prevented by the rigidity of the macrocyclic ring. For the isoelectronic species $[Fe(CO)_3(C_4H_6)]$, carbonyl scrambling has been shown to occur by rotation of the $Fe(CO)_3$ fragment about the central Fe–diene axis, T_c for this process being measured as *ca.* 230 K.[28] This is also the most likely mechanism of the fluxionality in $[Rh([9]aneS_3)(C_4H_6)]^+$, with two of the macrocyclic CH_2 environments being coincidently NMR equivalent or near-equivalent. An investigation of the NMR behaviour of analogous rhodium complexes containing substituted dienes

Table 2 Bond lengths (Å), angles and torsion angles (°) for $[Rh([9]aneS_3)(cod)]BF_4$

Rh(1)–S(1)	2.321(3)	Rh(1)–S(4)	2.397(2)	Rh(2)–C(35)	2.190(11)	Rh(2)–C(36)	2.224(12)
Rh(1)–S(7)	2.447(2)	Rh(1)–C(11)	2.080(7)	S(21)–C(22)	1.798(9)	S(21)–C(29)	1.837(7)
Rh(1)–C(12)	2.122(7)	Rh(1)–C(15)	2.223(10)	C(22)–C(23)	1.542(10)	C(23)–S(24)	1.831(11)
Rh(1)–C(16)	2.202(10)	C(11)–C(12)	1.429(11)	S(24)–C(25)	1.850(8)	C(25)–C(26)	1.498(12)
C(11)–C(18)	1.486(14)	C(12)–C(13)	1.508(13)	C(26)–S(27)	1.824(7)	S(27)–C(28)	1.816(9)
C(13)–C(14)	1.496(12)	C(14)–C(15)	1.484(10)	C(28)–C(29)	1.514(13)	C(31)–C(32)	1.401(12)
C(15)–C(16)	1.397(11)	C(16)–C(17)	1.477(13)	C(31)–C(38)	1.536(17)	C(32)–C(33)	1.481(13)
C(17)–C(18)	1.515(12)	Rh(2)–S(21)	2.307(3)	C(33)–C(34)	1.446(14)	C(34)–C(35)	1.470(13)
Rh(2)–S(24)	2.444(2)	Rh(2)–S(27)	2.437(2)	C(35)–C(36)	1.315(14)	C(36)–C(37)	1.401(15)
Rh(2)–C(31)	2.116(7)	Rh(2)–C(32)	2.080(6)	C(37)–C(38)	1.410(16)		

S(1)–Rh(1)–S(4)	87.1(1)	S(1)–Rh(1)–S(7)	86.3(1)	C(14)–C(15)–C(16)	126.2(8)	Rh(1)–C(16)–C(15)	72.4(6)
S(4)–Rh(1)–S(7)	86.4(1)	S(1)–Rh(1)–C(11)	91.4(3)	Rh(1)–C(16)–C(17)	107.7(6)	C(15)–C(16)–C(17)	123.7(7)
S(4)–Rh(1)–C(11)	164.4(2)	S(7)–Rh(1)–C(11)	109.1(2)	C(16)–C(17)–C(18)	113.3(8)	C(11)–C(18)–C(17)	113.3(8)
S(1)–Rh(1)–C(12)	85.7(3)	S(4)–Rh(1)–C(12)	124.6(2)	S(21)–Rh(2)–S(24)	86.7(1)	S(21)–Rh(2)–S(27)	87.0(1)
S(7)–Rh(1)–C(12)	147.4(2)	C(11)–Rh(1)–C(12)	39.8(3)	S(24)–Rh(2)–S(27)	86.2(1)	S(21)–Rh(2)–C(31)	88.7(3)
S(1)–Rh(1)–C(15)	156.2(2)	S(4)–Rh(1)–C(15)	88.5(2)	S(24)–Rh(2)–C(31)	155.0(2)	S(27)–Rh(2)–C(31)	118.1(2)
S(7)–Rh(1)–C(15)	116.7(2)	C(11)–Rh(1)–C(15)	86.6(3)	S(21)–Rh(2)–C(32)	89.6(3)	S(24)–Rh(2)–C(32)	116.3(3)
C(12)–Rh(1)–C(15)	77.7(3)	S(1)–Rh(1)–C(16)	165.0(2)	S(27)–Rh(2)–C(32)	157.0(2)	C(31)–Rh(2)–C(32)	39.0(3)
S(4)–Rh(1)–C(16)	103.8(2)	S(7)–Rh(1)–C(16)	84.3(2)	S(21)–Rh(2)–C(35)	161.9(3)	S(24)–Rh(2)–C(35)	84.9(2)
C(11)–Rh(1)–C(16)	80.8(3)	C(12)–Rh(1)–C(16)	96.1(3)	S(27)–Rh(2)–C(35)	108.3(2)	C(31)–Rh(2)–C(35)	92.2(3)
C(15)–Rh(1)–C(16)	36.8(3)	Rh(1)–S(1)–C(2)	99.7(4)	C(32)–Rh(2)–C(35)	79.9(3)	S(21)–Rh(2)–C(36)	161.3(3)
Rh(1)–S(1)–C(2′)	105.2(4)	Rh(1)–S(1)–C(9)	105.8(3)	S(24)–Rh(2)–C(36)	110.2(2)	S(27)–Rh(2)–C(36)	86.4(2)
C(2)–S(1)–C(9)	104.9(5)	Rh(1)–S(1)–C(9′)	102.4(3)	C(31)–Rh(2)–C(36)	79.1(4)	C(32)–Rh(2)–C(36)	89.6(3)
C(2′)–S(1)–C(9′)	104.3(6)	S(1)–C(2)–C(3)	112.6(6)	C(35)–Rh(2)–C(36)	34.7(4)	Rh(2)–S(21)–C(22)	102.6(3)
S(1)–C(2′)–C(3′)	110.1(9)	C(2)–C(3)–S(4)	111.9(6)	Rh(2)–S(21)–C(29)	107.3(3)	C(22)–S(21)–C(29)	102.2(4)
C(2′)–C(3′)–S(4)	110.5(8)	Rh(1)–S(4)–C(3)	103.7(3)	S(21)–C(22)–C(23)	115.4(6)	C(22)–C(23)–S(24)	109.3(6)
Rh(1)–S(4)–C(3′)	98.7(4)	Rh(1)–S(4)–C(5)	101.5(3)	Rh(2)–S(24)–C(23)	104.7(2)	Rh(2)–S(24)–C(25)	100.6(3)
C(3)–S(4)–C(5)	105.8(4)	Rh(1)–S(4)–C(5′)	103.8(3)	C(23)–S(24)–C(25)	101.7(4)	S(24)–C(25)–C(26)	115.5(5)
C(3′)–S(4)–C(5′)	100.8(6)	S(4)–C(5)–C(6)	113.0(6)	C(25)–C(26)–S(27)	113.0(6)	Rh(2)–S(27)–C(26)	105.3(3)
S(4)–C(5′)–C(6′)	113.7(7)	C(5)–C(6)–S(7)	112.0(6)	Rh(2)–S(27)–C(28)	99.6(2)	C(26)–S(27)–C(28)	102.4(4)
C(5′)–C(6′)–S(7)	114.4(6)	Rh(1)–S(7)–C(6)	102.9(2)	S(27)–C(28)–C(29)	114.6(6)	S(21)–C(29)–C(28)	111.0(6)
Rh(1)–S(7)–C(8)	100.6(2)	C(6)–S(7)–C(8)	97.9(6)	Rh(2)–C(31)–C(32)	69.1(4)	Rh(2)–C(31)–C(38)	111.0(6)
Rh(1)–S(7)–C(8′)	103.0(3)	C(6′)–S(7)–C(8′)	98.2(6)	C(32)–C(31)–C(38)	120.2(9)	Rh(2)–C(32)–C(31)	71.9(4)
S(7)–C(8)–C(9)	111.5(6)	S(7)–C(8′)–C(9′)	112.2(9)	Rh(2)–C(32)–C(33)	115.4(5)	C(31)–C(32)–C(33)	124.4(9)
S(1)–C(9)–C(8)	111.7(8)	S(1)–C(9′)–C(8′)	111.7(7)	C(32)–C(33)–C(34)	114.0(7)	C(33)–C(34)–C(35)	118.2(10)
Rh(1)–C(11)–C(12)	71.7(4)	Rh(1)–C(11)–C(18)	114.6(5)	Rh(2)–C(35)–C(34)	110.0(7)	Rh(2)–C(35)–C(36)	74.1(7)
C(12)–C(11)–C(18)	124.5(9)	Rh(1)–C(12)–C(11)	68.6(4)	C(34)–C(35)–C(36)	121.4(8)	Rh(2)–C(36)–C(35)	71.3(7)
Rh(1)–C(12)–C(13)	113.3(5)	C(11)–C(12)–C(13)	125.3(9)	Rh(2)–C(36)–C(37)	112.3(8)	C(35)–C(36)–C(37)	130.2(9)
C(12)–C(13)–C(14)	112.8(6)	C(13)–C(14)–C(15)	111.3(8)	C(36)–C(37)–C(38)	116.8(12)	C(31)–C(38)–C(37)	117.7(8)
Rh(1)–C(15)–C(14)	114.7(6)	Rh(1)–C(15)–C(16)	70.8(6)				

C(9)–S(1)–C(2)–C(3)	56.9	C(9′)–S(1)–C(2′)–C(3′)	140.2	C(29)–S(21)–C(22)–C(23)	62.8
S(1)–C(2)–C(3)–S(4)	53.1	S(1)–C(2′)–C(3′)–S(4)	−58.8	S(21)–C(22)–C(23)–S(24)	51.5
C(2)–C(3)–S(4)–C(5)	−131.2	C(2′)–C(3′)–S(4)–C(5′)	−53.1	C(22)–C(23)–S(24)–C(25)	−131.6
C(3)–S(4)–C(5)–C(6)	61.1	C(3′)–S(4)–C(5′)–C(6′)	136.2	C(23)–S(24)–C(25)–C(26)	63.3
S(7)–C(6)–C(5)–S(4)	57.0	S(4)–C(5′)–C(6′)–S(7)	−52.6	S(27)–C(26)–C(25)–S(24)	51.0
C(8)–S(7)–C(6)–C(5)	−138.0	C(8′)–S(7)–C(6′)–C(5′)	−64.4	C(28)–S(27)–C(26)–C(25)	−132.5
C(9)–C(8)–S(7)–C(6)	58.6	C(9′)–C(8′)–S(7)–C(6′)	134.3	C(29)–C(28)–S(27)–C(26)	62.4
C(2)–S(1)–C(9)–C(8)	−139.9	C(8′)–C(9′)–S(1)–C(2′)	−60.1	C(22)–S(21)–C(29)–C(28)	−135.1
S(1)–C(9)–C(8)–S(7)	55.8	S(1)–C(9′)–C(8′)–S(7)	−54.2	S(21)–C(29)–C(28)–S(27)	50.7
C(18)–C(11)–C(12)–C(13)	−3.2	C(18)–C(11)–C(12)–C(13)	−3.2	C(38)–C(31)–C(32)–C(33)	5.8
C(11)–C(12)–C(13)–C(14)	−44.2	C(11)–C(12)–C(13)–C(14)	−44.2	C(31)–C(32)–C(33)–C(34)	−73.7
C(12)–C(13)–C(14)–C(15)	−31.7	C(12)–C(13)–C(14)–C(15)	−31.7	C(32)–C(33)–C(34)–C(35)	1.8
C(13)–C(14)–C(15)–C(16)	97.8	C(13)–C(14)–C(15)–C(16)	97.8	C(33)–C(34)–C(35)–C(36)	71.0
C(14)–C(15)–C(16)–C(17)	−7.2	C(14)–C(15)–C(16)–C(17)	−7.2	C(37)–C(36)–C(35)–C(34)	−0.4
C(18)–C(17)–C(16)–C(15)	−45.1	C(18)–C(17)–C(16)–C(15)	−45.1	C(38)–C(37)–C(36)–C(35)	−67.1
C(12)–C(11)–C(18)–C(17)	91.5	C(12)–C(11)–C(18)–C(17)	91.5	C(32)–C(31)–C(38)–C(37)	69.3
C(11)–C(18)–C(17)–C(16)	−29.2	C(11)–C(18)–C(17)–C(16)	−29.2	C(31)–C(38)–C(37)–C(36)	−5.8

and trithia macrocycles over a wider temperature range would be necessary to confirm this. Interestingly, $[Ir([9]aneS_3)(C_4H_6)]PF_6$ exhibits a static structure according to ^{13}C NMR spectroscopy at 293 K, with three distinct resonances for the $[9]aneS_3$ ligand being observed.[22]

The single-crystal structure of $[Rh([9]aneS_3)(C_4H_6)]PF_6$ shows (Fig. 3, Table 3) a quasi-square-pyramidal complex cation, with S(1) sitting above the open edge of the co-ordinated diene [Rh–S(1) 2.358(1), Rh–S(4) 2.337(1), Rh–S(7) 2.341(1), Rh–C(11) 2.110(5), Rh–C(12) 2.120(5), Rh–C(13) 2.127(5), Rh–C(14) 2.136(5), intra-C_4H_6 C(11)=C(12) 1.444(7), C(12)=C(13) 1.387(7), C(13)–C(14) 1.406(7), Rh–X(1) 1.989(5), Rh–X(2) 2.006(5), and Rh–X(3) 2.011(5) Å; S(1)–Rh–X(1) 123.39(15), S(1)–Rh–X(2) 146.17(15), S(1)–Rh–X(3) 121.69(15), S(4)–Rh–X(1) 147.24(15), S(4)–Rh–X(2) 113.80(15), S(4)–Rh–X(3) 97.73(15), S(7)–Rh–X(1) 98.11(15), S(7)–Rh–X(2) 116.18(15), and S(7)–Rh–X(3) 148.69(15)°; where X(1), X(2) and X(3) are the midpoints of C(11)=C(12), C(12)–C(13) and C(13)=C(14) respectively]. This geometry is similar to that adopted by $[Ir([9]aneS_3)(C_4H_6)]PF_6$[22] and other d^8 $[ML_3(C_4H_6)]$ species such as $[Fe(CO)_3(C_4H_6)]$ and $[Co(PMe_3)_3(C_4H_6)]^+$:[29] this orientation of a d^8 ML_3 fragment relative to a conjugated diene ligand has been shown to be electronically favoured.[30] However, the C–C distances within the butadiene ligand in $[Rh([9]aneS_3)(C_4H_6)]^+$ are significantly more distorted from those in free C_4H_6 than is generally

Table 3 Selected bond lengths (Å), angles and torsion angles (°) for $[Rh([9]aneS_3)(C_4H_6)]PF_6\cdot0.25OEt_2$

Rh–S(1)	2.358(1)	Rh–S(4)	2.337(1)
Rh–S(7)	2.341(1)	Rh–C(11)	2.110(5)
Rh–C(12)	2.120(5)	Rh–C(13)	2.127(5)
Rh–C(14)	2.136(5)	S(1)–C(2)	1.817(5)
S(1)–C(9)	1.824(6)	C(2)–C(3)	1.517(7)
C(3)–S(4)	1.818(5)	S(4)–C(5)	1.839(7)
C(5)–C(6)	1.485(9)	C(6)–S(7)	1.813(6)
S(7)–C(8)	1.830(7)	C(8)–C(9)	1.510(8)
C(11)–C(12)	1.444(7)	C(12)–C(13)	1.387(7)
C(13)–C(14)	1.406(7)		
S(1)–Rh–S(4)	88.7(1)	S(1)–Rh–S(7)	87.9(1)
S(4)–Rh–S(7)	88.6(1)	S(1)–Rh–C(11)	103.8(1)
S(4)–Rh–C(11)	167.2(1)	S(7)–Rh–C(11)	94.6(2)
S(1)–Rh–C(12)	142.8(1)	S(4)–Rh–C(12)	127.3(1)
S(7)–Rh–C(12)	100.7(2)	C(11)–Rh–C(12)	39.9(2)
S(1)–Rh–C(13)	140.7(1)	S(4)–Rh–C(13)	99.0(1)
S(7)–Rh–C(13)	130.4(1)	C(11)–Rh–C(13)	69.5(2)
C(12)–Rh–C(13)	38.1(2)	S(1)–Rh–C(14)	102.7(1)
S(4)–Rh–C(14)	95.6(2)	S(7)–Rh–C(14)	168.7(1)
C(11)–Rh–C(14)	79.1(2)	C(12)–Rh–C(14)	68.4(2)
C(13)–Rh–C(14)	38.5(2)	Rh–S(1)–C(2)	101.1(2)
Rh–S(1)–C(9)	105.3(2)	C(2)–S(1)–C(9)	101.8(3)
S(1)–C(2)–C(3)	115.9(4)	C(2)–C(3)–S(4)	113.0(4)
Rh–S(4)–C(3)	105.3(2)	Rh–S(4)–C(5)	100.6(2)
C(3)–S(4)–C(5)	101.3(3)	S(4)–C(5)–C(6)	114.5(4)
C(5)–C(6)–S(7)	112.5(4)	Rh–S(7)–C(6)	104.5(2)
Rh–S(7)–C(8)	101.4(2)	C(6)–S(7)–C(8)	101.8(3)
S(7)–C(8)–C(9)	114.6(4)	S(1)–C(9)–C(8)	111.8(4)
Rh–C(11)–C(12)	70.4(3)	Rh–C(12)–C(11)	69.6(3)
Rh–C(12)–C(13)	71.2(3)	C(11)–C(12)–C(13)	117.2(4)
Rh–C(13)–C(12)	70.7(3)	Rh–C(13)–C(14)	71.1(3)
C(12)–C(13)–C(14)	117.8(5)	Rh–C(14)–C(13)	70.4(3)

C(3)–C(2)–S(1)–C(9)	−67.8
S(4)–C(3)–C(2)–S(1)	−45.8
C(2)–C(3)–S(4)–C(5)	129.9
C(6)–C(5)–S(4)–C(3)	−65.1
S(4)–C(5)–C(6)–S(7)	−50.4
C(5)–C(6)–S(7)–C(8)	135.0
C(6)–S(7)–C(8)–C(9)	−63.9
C(8)–C(9)–S(1)–C(2)	132.5
S(1)–C(9)–C(8)–S(7)	−48.7
C(14)–C(13)–C(12)–C(11)	1.0

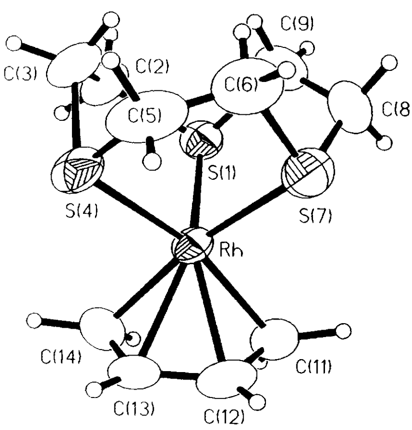

Fig. 3 View of the single-crystal structure of $[Rh([9]aneS_3)(C_4H_6)]^+$ with the numbering scheme adopted. Thermal ellipsoids as in Fig. 1.

observed for 1,3-diene complexes of d^8 metal ions {for $[Rh(C_4H_6)_2Cl]$ C=C 1.38(2), C–C 1.45(2) Å[31]}. Whilst equalisation of the C_4H_6 C–C bond lengths is expected on co-ordination to a metal centre,[30,32] the degree of distortion observed for $[M([9]aneS_3)(C_4H_6)]^+$ (M = Rh or Ir) is unusual for conjugated diene complexes of Group 8–9 metals, and is reminiscent of the metallacyclopent-3-ene structures observed for 1,3-diene complexes of Nb, Ta and Zr.[33] However, examination of the ^1J(C–H) coupling constants within the C_4H_6 ligands in $[M([9]aneS_3)(C_4H_6)]^+$ (M = Rh or Ir) [M = Rh, ^1J 158 (butadiene CH_2 groups), 170 Hz (CH)] suggests that these species do not exhibit the analogous configurations $[M^{III}([9]aneS_3)(\sigma,\eta^2,\sigma\text{-}C_4H_6)]^+$, but are probably best considered as metal(I) π complexes $[M^I([9]aneS_3)(\eta^4\text{-}C_4H_6)]^+$ with unusually electrophilic metal centres.[22]

Other methods of analyzing the bonding of diene fragments are based upon the distribution of bond lengths and dihedral angles θ in the diene fragment.[34] This approach defines two parameters Δd and Δl for a diene ligand labelled C(1), C(2), C(3) and C(4) (Fig. 4), equations (1) and (2). Using these guidelines,

$$\Delta d = \tfrac{1}{2}\{d[\mathrm{M{-}C(1)}] + d[\mathrm{M{-}C(4)}]\} - \tfrac{1}{2}\{d[\mathrm{M{-}C(2)}] + d[\mathrm{M{-}C(3)}]\} \quad (1)$$

$$\Delta l = \tfrac{1}{2}\{d[\mathrm{C(1){-}C(2)}] + d[\mathrm{C(3){-}C(4)}]\} - d[\mathrm{C(2){-}C(3)}] \quad (2)$$

it has been observed that for σ^2,η^2-metallacyclopent-3-ene species, Δd lies in the region −0.4 to 0 Å with Δl 0–0.2 Å. This compares with values of Δd = −0.1 to 0.1 Å and Δl −0.1 to 0 Å for η^4-butadiene complexes. In addition, the dihedral angle θ between the two planes defined by M–C(1)–C(4) and C(1)–C(2)–C(3)–C(4) is observed to fall in the region 75–90° for

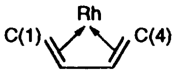

Fig. 4 Labelling of co-ordinated butadiene for bond length and angle analysis

a η^4-butadiene complex and is >90° for the corresponding σ^2,η^2-metallacyclopent-3-ene species.[34] Based on the single-crystal structure analysis the complex $[Rh([9]aneS_3)(C_4H_6)]^+$ has $\Delta d = 0.00$ Å, $\Delta l = 0.038$ Å, and $\theta = 86.7°$. Interestingly, Fryzuk *et al.*[35] have reported rather similar parameters for $[Ir(C_4H_6)\{N(SiMe_2CH_2PPh_2)_2\}]$ ($\Delta d = -0.01$ Å, $\Delta l = 0.017$ Å, and $\theta = 92.9°$). Based upon the above criteria, the complex $[Rh([9]aneS_3)(C_4H_6)]^+$ appears to be approaching the cross-over between η^4-butadiene and σ^2-η^2-metallacyclopent-3-ene assignments. We therefore propose the structure of $[Rh([9]aneS_3)(C_4H_6)]^+$ as involving predominantly η^4-butadiene co-ordination but with significant σ^2,η^2-metallacyclopent-3-ene contribution. The highly distorted intra-C_4H_6 C–C bond lengths observed in $[Rh([9]aneS_3)(C_4H_6)]^+$ probably arise from strong $C_4H_6 \rightarrow M$ σ donation, as in $[Ir([9]aneS_3)(C_4H_6)]^+$.

Treatment of $[Rh_2(C_2H_4)_4Cl_2]$ with 1 molar equivalent of PPh_3 in CH_2Cl_2 at 293 K, followed by addition of 2 molar equivalents of $[9]aneS_3$ in the presence of NH_4PF_6, affords a brick-red solid of stoichiometry $[Rh([9]aneS_3)(C_2H_4)(PPh_3)]PF_6$ (Found: C, 43.5; H, 4.3. Calc. for $C_{26}H_{31}F_6P_2RhS_3$: C, 43.5; H, 4.4%). However, mass spectrometry of this product shows, in addition to fragmentation products, peaks at m/z = 807, 573 and 339, assigned to the molecular ions $[^{103}Rh([9]aneS_3)(PPh_3)_2]^+$, $[^{103}Rh([9]aneS_3)(C_2H_4)(PPh_3)]^+$ and $[^{103}Rh([9]aneS_3)(C_2H_4)_2]^+$. In addition, ^1H NMR spectroscopy clearly shows the presence of $[Rh([9]aneS_3)(C_2H_4)_2]^+$ with the ^{31}P NMR spectrum exhibiting two separate doublet resonances of equal intensity at δ 46.17 [^1J(Rh–P) = 134] and 43.15 [^1J(Rh–P) = 169 Hz] in CD_3CN. Hence, this product was formulated as a statistical mixture of $[Rh([9]aneS_3)(PPh_3)_2]PF_6$, $[Rh([9]aneS_3)(C_2H_4)(PPh_3)]PF_6$ and $[Rh([9]aneS_3)(C_2H_4)_2]PF_6$. We were unable to separate these three complexes fully.

In order to avoid the formation of $[Rh([9]aneS_3)(PR_3)_2]^+$, the reaction was repeated using phosphines with Tolman angles (θ) greater than that of PPh_3 ($\theta = 145°$[36]). Reaction as above using 1 molar equivalent of $P(C_6H_{11})_3$ ($\theta = 170°$) or PPr^i_3 ($\theta = 160°$) yields air- and thermally-sensitive pale yellow solids that analyse as $[Rh([9]aneS_3)(C_2H_4)(PR_3)]PF_6$. In this case, however, parent molecular ions corresponding to $[^{103}Rh([9]aneS_3)(C_2H_4)(PR_3)]^+$ only are observed by mass spectroscopy (m/z = 591 for R = C_6H_{11}, 471 for R = Pr^i), implying the presence of the desired species $[Rh([9]aneS_3)(C_2H_4)(PR_3)]PF_6$ only in these products. Interestingly, the ^1H NMR spectrum at 293 K of $[Rh([9]aneS_3)(C_2H_4)\{P(C_6H_{11})_3\}]PF_6$ shows, in addition to multiplets from the $[9]aneS_3$ and $P(C_6H_{11})_3$ ligands, two multiplets arising from a static C_2H_4 ligand at δ 2.52 (2 H) and 2.18 (2 H), in contrast to the behaviour of $[Rh([9]aneS_3)(C_2H_4)_2]^+$. The non-fluxionality of the ethene ligand in $[Rh([9]aneS_3)(C_2H_4)\{P(C_6H_{11})_3\}]^+$ probably arises from the steric demands of the $[9]aneS_3$ ($\theta \approx 220°$[37]) and $P(C_6H_{11})_3$ ligands, rather than any differences in electronic character between this complex and its bis(ethene) congener, although an X-ray structural determination would be needed to confirm this. An NMR investigation of $[Rh([9]aneS_3)(C_2H_4)(PPr^i_3)]^+$ and a high-temperature ^1H NMR study of $[Rh([9]aneS_3)(C_2H_4)\{P(C_6H_{11})_3\}]^+$ were not possible because of the low thermal stabilities of these complexes in solution. Attempts to prepare $[Rh([9]aneS_3)(C_2H_4)(PMe_3)]^+$ by the above methodology at 233 K gave only red oils and decomposition products which were not characterised further.

Reaction of $[Rh(CO)Cl(PPh_3)_2]$ with 1 molar equivalent of $[9]aneS_3$ and NH_4PF_6 affords a yellow microcrystalline solid in moderate yield. Infrared (ν_{CO} 1960 cm^{-1} in $MeNO_2$) and mass spectrometric and microanalytical data on this product were consistent with the formulation $[Rh([9]aneS_3)(CO)(PPh_3)]PF_6$: this was confirmed by a structure determination, which showed a trigonal-bipyramidal cation containing equatorial CO and axial PPh_3 ligands. The details of this structural analysis have been reported separately.[38]

Treatment of $[Rh([9]aneS_3)(C_2H_4)_2]PF_6$ with CO, PPh_3 or cod in acetone or thf at 293 K for 30 min yields only the unreacted bis(ethene) starting material, with no incorporation of the attacking nucleophile; reaction at higher temperatures results in decomposition of the complex, with no peaks due to co-ordinated CO, PPh_3 or cod being observed in the resultant product mixture by IR spectroscopy. This inertness to thermal ligand substitution implies that the solid-state 18-electron configuration of $[Rh([9]aneS_3)(C_2H_4)_2]^+$ is maintained in solution, and that formation of a transient co-ordinatively unsaturated rhodium centre *via* loss of an ethene ligand or S-donor {*cf.* $\eta^5 \rightarrow \eta^3$ slippage of the C_5R_5 ligand in $[M(C_5R_5)L_2]$ (M = Rh or Ir, R = H or Me, L = C_2H_4 or CO)[6]} is not a favourable process.[5] Likewise, no reaction was observed between $[Rh([9]aneS_3)(C_2H_4)_2]PF_6$ and the electrophiles C_2F_4, CS_2, H^+ and tcne at 293 K; in the latter case, green charge-transfer salts of composition $[Rh([9]aneS_3)(C_2H_4)_2]PF_6 \cdot x$tcne ($x$ < 1) were obtained. In contrast, reaction of $[Rh([9]aneS_3)(cod)]^+$ with tcne in refluxing MeCN afforded a pale yellow soluble product which is assigned as $[Rh([9]aneS_3)(tcne)(MeCN)]X$ (X = BF_4 or PF_6). The IR spectrum of this product showed ν_{CN} stretching vibrations at 2320m, 2295m, 2245w, 2220s and 2150w cm^{-1}, consistent with an *N*-bound tcne ligand,[39] in addition to absorptions for $[9]aneS_3$. The FAB mass spectrum exhibited peaks at m/z = 452, 411, 385 and 323 corresponding to the molecular ions $[^{103}Rh([9]aneS_3)(tcne)(MeCN)]^+$, $[^{103}Rh([9]aneS_3)(tcne)]^+$, $[^{103}Rh([9]aneS_3)(tcne - CN)]^+$ and $[^{103}Rh([9]aneS_3 - H)(MeCN)]^+$ respectively. The NMR characterisation was hampered by the insolubility of the complex in solvents other than CD_3CN, although a ^1H NMR spectrum in that solvent showed $[9]aneS_3$ multiplets at δ 3.64 (6 H) and 1.79 (6 H). A definitive structural assignment for $[^{103}Rh([9]aneS_3)(tcne)(MeCN)]^+$ could not therefore be made, although a di- or polymeric structure in the solid state with bridging tcne ligands is most likely. Treatment of $[Rh([9]aneS_3)(cod)]^+$ with tcne in refluxing acetone, CH_2Cl_2 or thf yielded charge-transfer salts as above.

Reaction of $[Rh_2(CO)_4Cl_2]$ with 2 molar equivalents of $[9]aneS_3$ and NH_4PF_6 in acetone at 293 K affords initially a yellow solution, which becomes dark green on further stirring for 15 min. Both yellow and green products can be isolated as microcrystalline solids. However, all samples of the yellow complex were shown by IR spectroscopy to be contaminated by the green species, and solid-state samples of the yellow product convert quantitatively into the green complex on standing at 293 K *in vacuo* for 2 d. In addition to absorbances due to the $[9]aneS_3$ ligand and PF_6^- counter ion, the initial yellow product exhibits two intense ν_{CO} stretching vibrations at 2080 and 2012 cm^{-1} in $MeNO_2$. The FAB mass spectrum shows peaks at m/z = 339, 311 and 283 assigned to the molecular ions $[^{103}Rh([9]aneS_3)(CO)_2]^+$, $[^{103}Rh([9]aneS_3)(CO)]^+$ and $[^{103}Rh([9]aneS_3)]^+$ respectively. In contrast, the IR spectrum of the final green complex in $MeNO_2$ shows a single ν_{CO} stretching vibration at 1855 cm^{-1}, while FAB mass spectroscopy shows additional peaks at m/z = 795, 650, 622 and 593 attributable to the molecular ions $[^{103}Rh_2([9]aneS_3)_2(CO)_3(PF_6)]^+$, $[^{103}Rh_2([9]aneS_3)_2(CO)_3]^+$, $[^{103}Rh_2([9]aneS_3)_2(CO)_2]^+$ and $[^{103}Rh_2([9]aneS_3)([9]aneS_3 - H)(CO)]^+$. The ^{13}C NMR spectrum of the final product in CD_3NO_2 exhibits a triplet resonance at δ 202.51 [^1J(Rh–C) = 26.9 Hz] consistent with a bridging μ-CO species, and a singlet at δ 32.71 from the

SCH$_2$ groups of [9]aneS$_3$. The ^{1}H NMR spectrum shows only a multiplet for [9]aneS$_3$ at δ 3.22.

On the basis of these data, the yellow and green complexes are tentatively formulated as $[Rh([9]aneS_3)(CO)_2]^+$ and $[Rh_2([9]aneS_3)_2(\mu\text{-}CO)_3]^{2+}$ respectively, although further work is required to confirm these assignments. It is noteworthy that heating $[Rh_2([9]aneS_3)_2(\mu\text{-}CO)_3][PF_6]_2$ in refluxing acetone under N_2 for 30 min results in its quantitative further transformation to a dark blue mixture of [9]aneS$_3$-, CO- and PF_6^--containing species (by IR spectroscopy), suggesting that further loss of CO from this complex may be a facile process under thermal conditions. The analogous compounds $[RhL(CO)_2]$ and $[Rh_2L_2(\mu\text{-}CO)_3]$ [L = tris(pyrazolyl)-borate or -gallate] have been well characterised,[40] and exhibit in the IR spectra very similar CO stretching frequencies to those above, *e.g.* for $[Rh_2\{HB(pz)_3\}_2(\mu\text{-}CO)_3]$ ν_{CO} 1845 cm^{-1}. In contrast, the doubly carbonyl-bridged complex $[Rh_2(C_5Me_5)_2(\mu\text{-}CO)_2]$ shows a ν_{CO} stretching vibration at 1732 cm^{-1}.[41]

Treatment of $[Rh_2(C_2H_4)_2(CO)_2Cl_2]$[42] with [9]aneS$_3$ and NH_4PF_6 also gives $[Rh_2([9]aneS_3)_2(\mu\text{-}CO)_3][PF_6]_2$ as the only isolable product, albeit in lower yield (30%). Reaction of $[Rh_2(CO)_4Cl_2]$ with 2 molar equivalents of [9]aneS$_3$ in the absence of a chloride-abstracting agent rapidly leads to an insoluble blue solid, which exhibits five ν_{CO} stretching vibrations at 2055s, 1995s, 1835s, 1778s and 1750m cm^{-1}, in addition to bands due to co-ordinated [9]aneS$_3$. Further characterisation of this product was hampered by its insolubility; the formation of polymeric products on reaction of $[Rh_2(CO)_4Cl_2]$ with 2,5-dithiahexane has been noted.[16]

Treatment of $[Rh([9]aneS_3)(C_2H_4)L]^+$ [L = C_2H_4 or $P(C_6H_{11})_3$] with stoichiometric amounts of MeCOCl, $SiMe_3Cl$, I_2 or MeI in acetone or thf at 293 K, or by stirring in CH_2Cl_2 or $CHCl_3$ at 293 K, affords insoluble yellow (for Cl-containing substrates) or orange (for I_2 or MeI) precipitates as the only isolable products. On the basis of IR spectroscopic and microanalytical data these products are formulated as $[Rh([9]aneS_3)X_3]$ (X = Cl or I). The IR spectrum of $[Rh([9]aneS_3)Cl_3]$ contains bands at 340 and 295 cm^{-1} which might be assigned to Rh–Cl stretching vibrations; the insolubility of $[Rh([9]aneS_3)X_3]$ prevented further characterisation.

No reaction was observed between $[Rh([9]aneS_3)(cod)]^+$ and MeI, MeCOCl or CH_2Cl_2 either at 293 K or under reflux. The complex $[Rh([9]aneS_3)(CO)(PPh_3)]^+$ did not react with CH_2Cl_2 under reflux, but rapidly formed $[Rh([9]aneS_3)I_3]$ with MeI in refluxing thf. No reaction was observed between $[Rh([9]aneS_3)(C_2H_4)_2]^+$ and benzene or $SiEt_3H$ at 293 K, the bis(ethene) complex being recovered from the solution. When heated under reflux, deep red solutions were formed from which rust-red solids could be isolated. The products exhibited IR and FAB mass spectra similar to those obtained by the thermal decomposition of $[Rh([9]aneS_3)(C_2H_4)_2]^+$ (see below). No evidence for the incorporation of benzene or $SiEt_3H$ into the metal-based products was obtained.

Refluxing solutions of $[Rh([9]aneS_3)(C_2H_4)_2]^+$ in acetone or thf under N_2 for 30 min gave a red solution from which red-brown solids can be isolated. The same product could be obtained by the thermal decomposition of solid $[Rh([9]aneS_3)(C_2H_4)_2][PF_6]_2$ at 298 K *in vacuo* for 2 weeks. Interestingly, the FAB mass spectra of these materials give a clue to a potential decomposition route for $[Rh([9]aneS_3(C_2H_4)_2]^+$. The spectrum shows major peaks at m/z = 477, 449, 421, 393, 365 and 337 which correspond to the molecular ions $[^{103}Rh([9]aneS_3)(C_2H_4)_n - 2H]^+$ (n = 2–7). The thermal decomposition of $[Rh([9]aneS_3)(C_2H_4)_2]^+$ was also followed by NMR spectroscopy. After 30 min in $(CD_3)_2CO$ the ^{1}H NMR spectrum of the reaction solution exhibited new resonances at δ 5.64, 5.38 and 1.62 in addition to resonances assigned to co-ordinated [9]aneS$_3$ (δ 3.1) and π-bound C_2H_4 (δ 2.76). After a further 30 min, the resonances at δ 5.64, 5.38, 3.10 and 2.76 are still present whilst additional resonances between δ 4.5 and 1.5 are observable. No resonances assignable to RhH species were observed. A ^{13}C DEPT NMR spectrum obtained on a sample that had reacted for 2 h showed an intense peak at δ 34.62 assigned to co-ordinated [9]aneS$_3$, together with weaker resonances at δ 52.3, 46.4, 41.4, 37.1 and 32.0. These preliminary results suggest that $[Rh([9]aneS_3)(C_2H_4)_2]^+$ may decompose *via* the coupling of ethene ligands to give a mixture of products. Further experiments are required to determine the mechanism of this reaction and to characterise fully the products formed.

Cyclic voltammetry of $[Rh([9]aneS_3)L(L')]PF_6$ (L, L′ = C_2H_4, $\frac{1}{2}$cod, $\frac{1}{2}$nbd, or $\frac{1}{2}C_4H_6$: L = CO, L′ = PPh) in MeCN–0.1 mol dm^{-3} $NBu^n{}_4PF_6$ at 293 K shows in each case a broad single irreversible oxidation at E_{pa} = +0.29 (L = $\frac{1}{2}$cod) to +1.10 V (L = $\frac{1}{2}C_4H_6$) *vs.* ferrocene–ferrocenium at 400 mV s^{-1}, with no well defined return waves. These processes remain irreversible at scan rates of 100–1000 mV s^{-1} at 293 and 253 K. Coulometric determinations of these oxidative processes in MeCN–0.1 mol dm^{-3} $NBu^n{}_4PF_6$ at 293 K at a platinum-basket electrode give variable results between 1.5 and 2 electrons, while controlled-potential electrolysis of bulk samples of these compounds yields pale yellow ESR-silent solutions. These results show that any rhodium(II) species formed from $[Rh([9]aneS_3)L(L')]^+$ precursors decompose rapidly, possibly by disproportionation or dimerisation to form diamagnetic dirhodium(II) products {*cf.* $[Rh([9]aneS_3)_2]^{2+}$ [10]}.

Experimental

Infrared spectra were run as KBr discs unless otherwise stated, on a Perkin-Elmer 598 spectrometer over the range 200–4000 cm^{-1}, electronic spectra of solutions in 1 cm quartz cells using a Perkin-Elmer Lambda 9 spectrophotometer and fast atom bombardment mass spectra on a Kratos MS 50TC spectrometer using a 3-nitrobenzyl alcohol matrix. Microanalyses were carried out by the University of Edinburgh Chemistry Department microanalytical service. Proton and ^{13}C NMR spectra were obtained using Bruker WP80, WP200 and WH360 spectrometers, ^{31}P NMR spectra on JEOL FX90Q or Bruker WP200 spectrometers. Electrochemical measurements were performed using a Bruker E310 Universal Modular Polarograph; for all readings a three-electrode system in acetonitrile containing 0.1 mol dm^{-3} $NBu^n{}_4PF_6$ as supporting electrolyte was employed. Cyclic voltammetric measurements were obtained with a double platinum electrode and a Ag–AgCl reference electrode. Potentials are quoted *versus* ferrocene–ferrocenium, at a scan rate of 400 mV s^{-1}. All operations were performed under N_2 using standard Schlenk techniques. The complexes $[Rh_2(C_2H_4)_4Cl_2]$, $[Rh_2(C_8H_{14})_4Cl_2]$, $[Rh_2(cod)_2Cl_2]$, $[Rh_2(nbd)_2Cl_2]$, $[Rh_2(CO)_4Cl_2]$ and $[Rh(CO)Cl(PPh_3)_2]$ were synthesised according to literature methods.[43]

Syntheses—$[Rh([9]aneS_3)(C_2H_4)_2]BF_4$. $[Rh_2(C_2H_4)_4Cl_2]$ (0.032 g, 0.8 × 10^{-4} mol) was stirred with [9]aneS$_3$ (0.030 g, 1.6 × 10^{-4} mol) and $NaBF_4$ (0.018 g, 1.6 × 10^{-4} mol) in acetone (6 cm^3) at 293 K for 15 min. The resultant yellow solution was filtered and the crude solid crystallised by addition of Et_2O. Recrystallisation from CH_2Cl_2–hexane at 243 K yielded a bright yellow solid. Yield 0.025 g, 35% (Found: C, 27.3; H, 4.6. Calc. for $C_{10}H_{20}BF_4RhS_3$: C, 28.1; H, 4.7%). FAB mass spectrum: m/z 339, $[^{103}Rh([9]aneS_3)(C_2H_4)_2]^+$ (calc. 339); 311, $[^{103}Rh([9]aneS_3)(C_2H_4)]^+$ (calc. 311); and 283, $[^{103}Rh([9]aneS_3)]^+$ (calc. 283), with correct isotopic distributions. NMR $[(CD_3)_2CO$, 233 K]: ^{1}H (360.13 MHz), δ 3.22–3.02 (m, 12 H, [9]aneS$_3$) and 2.76 (d, 8 H, J = 1.6, C_2H_4); ^{13}C DEPT (50.32 MHz), δ 51.41 (d, J = 9.6 Hz, C_2H_4) and 33.78 (s, [9]aneS$_3$). Electronic spectrum (MeCN): λ_{max} = 380 (ε_{max} 590), 298 (2360), and 234 nm (9295 dm^3 mol^{-1} cm^{-1}). IR: 3040w, 2940m, 2900m, 1515w, 1440s, 1410s, 1380w, 1300m, 1255w, 1165m, 1060vs, 1030m, 990w, 970w, 940w, 905m, 815s, 770w, 660w, 620w, 570w, 525s, 480m, 450w and 410w cm^{-1}.

$[Rh([9]aneS_3)(C_2H_4)\{P(C_6H_{11})_3\}]PF_6$. The complex $[Rh_2(C_2H_4)_4Cl_2]$ (0.032 g, 0.8×10^{-4} mol) and $P(C_6H_{11})_3$ (0.046 g, 1.6×10^{-4} mol) were stirred in CH_2Cl_2 (6 cm^3) at 293 K until all the solid had dissolved. To the resultant yellow-orange solution was added $[9]aneS_3$ (0.030 g, 1.6×10^{-4} mol) and NH_4PF_6 (0.027 g, 1.6×10^{-4} mol) and the mixture stirred for 10 min. The pale yellow solution was filtered, reduced in volume to *ca.* 1 cm^3 and the pale yellow solid product crystallised by addition of hexane. Yield 0.073 g, 59% (Found: C, 42.2; H, 6.8. Calc. for $C_{28}H_{49}BF_4PRhS_3$: C, 42.4; H, 6.7%). FAB mass spectrum: *m*/*z* 591, $[^{103}Rh([9]aneS_3)(C_2H_4)\{P(C_6H_{11})_3\}]^+$ (calc. 591); and 562, $[^{103}Rh([9]aneS_3 - H)\{P(C_6H_{11})_3\}]^+$ (calc. 562). NMR $[(CD_3)_2CO$, 293 K]: ^1H (200.13 MHz), δ 3.08–2.95 (m, 12 H, $[9]aneS_3$), 2.52 (m, 2 H), 2.18 (m, 2 H, C_2H_4) and 2.04–1.28 [m, 33 H, $P(C_6H_{11})_3$]. ^{13}C DEPT (50.32 MHz), δ 35.02 [d, *J* = 19.2, CH of $P(C_6H_{11})_3$], 34.43 (s, $[9]aneS_3$), 29.15 [d, ^1J(Rh–C) = 12 Hz, C_2H_4], 28.85, 26.66, and 25.28 [s, CH_2 of $P(C_6H_{11})_3$]; $^{31}P-\{^1H\}$ (81.02 MHz), δ 36.75 [d, ^1J(Rh–P) = 130.4 Hz]. Electronic spectrum (MeCN): λ_{max} = 365 (sh), 260 (sh), and 239 nm (ε_{max} = 14 860 dm^3 mol^{-1} cm^{-1}). IR: 3070w, 3020w, 2920s, 2840s, 2650w, 1490w, 1445s, 1410s, 1380w, 1345w, 1330w, 1295m, 1270m, 1225w, 1200m, 1160m, 1115m, 1070w, 1045w, 1020w, 1000m, 940m, 915w, 895w, 875w, 840vs, 780w, 730m, 700w, 665w, 560s, 515m, 495w, 450w, 435w, 420w and 400w cm^{-1}.

$[Rh([9]aneS_3)(C_2H_4)(PPr^i_3)]PF_6$. Method as above, using PPr^i_3 (1.6 cm^3 of a 0.1 mol dm^{-3} solution in thf). Yield 0.030 g, 29% (Found: C, 33.4; H, 6.1. Calc. for $C_{17}H_{37}BF_4PRhS_3$: C, 33.1; H, 6.1%). FAB mass spectrum: *m*/*z* 471, $[^{103}Rh([9]aneS_3)(C_2H_4)(PPr^i_3)]^+$ (calc. 471); and 443, $[^{103}Rh([9]aneS_3)(PPr^i_3)]^+$ (calc. 443). IR: 2970s, 2930m, 2880w, 2720w, 1450s, 1410s, 1390m, 1370w, 1290w, 1250m, 1175w, 1145m, 1090s, 1055w, 1035m, 950s, 840vs, 740m, 720w, 655m, 640w, 605w, 560s, 530m, 490w, 470w and 405w cm^{-1}.

$[Rh([9]aneS_3)(cod)]PF_6$. The complex $[Rh_2(cod)_2Cl_2]$ (0.041 g, 0.8×10^{-4} mol), $[9]aneS_3$ (0.03 g, 1.6×10^{-4} mol) and NH_4PF_6 (0.027 g, 1.6×10^{-4} mol) were stirred in CH_2Cl_2 (6 cm^3) at 293 K for 15 min. After filtration and reduction of the solution volume to *ca.* 1 cm^3 the yellow product was crystallised by addition of hexane. Yield 0.062 g, 70% (Found: C, 31.4; H, 4.5. Calc. for $C_{14}H_{24}F_6PRhS_3$: C, 31.4; H, 4.5%). FAB mass spectrum: *m*/*z* = 391, $[^{103}Rh([9]aneS_3)(cod)]^+$ (calc. 391); and 282, $[^{103}Rh([9]aneS_3 - H)]^+$ (calc. 282). NMR (CD_3NO_2, 293 K): ^1H (360.13 MHz), δ 4.10 (br, 4 H, cod CH), 3.01–2.79 (m, 12 H, $[9]aneS_3$), 2.52 (m, 4 H), and 2.20 (m, 4 H, cod CH_2); ^{13}C DEPT (50.32 MHz), δ 78.33 [d, ^1J(Rh–C) = 11 Hz, cod CH], 33.84 (s, $[9]aneS_3$), and 30.80 (s, cod CH_2). Electronic spectrum (MeCN): λ_{max} = 390 (sh), 304 (ε_{max} = 2460), 245 (14 780), and 220 nm (25 870 dm^3 mol^{-1} cm^{-1}). IR: 2980w, 2920m, 2860m, 2810m, 1470w, 1440s, 1410s, 1380w, 1325m, 1300m, 1285w, 1260w, 1245m, 1215m, 1170s, 1120w, 1090w, 1010w, 980w, 935w, 900m, 890w, 875m, 840vs, 780w, 685w, 660w, 620w, 560s, 505w, 480m, 445w and 385w cm^{-1}.

$[Rh([9]aneS_3)(nbd)]PF_6$. The complex $[Rh_2(nbd)_2Cl_2]$ (0.037 g, 0.8×10^{-4} mol) was stirred with $[9]aneS_3$ (0.030 g, 1.6×10^{-4} mol) and NH_4PF_6 (0.027 g, 1.6×10^{-4} mol) in CH_2Cl_2 (6 cm^3) at 293 K for 30 min, giving a bright yellow solution, which was then filtered and reduced in volume to *ca.* 1 cm^3. Addition of an excess of hexane afforded a yellow microcrystalline product. Yield 0.045 g, 52% (Found: C, 30.1; H, 3.9. Calc. for $C_{13}H_{20}F_6PRhS_3$: C, 30.0; H, 3.9%). FAB mass spectrum: *m*/*z* = 375, $[^{103}Rh([9]aneS_3)(C_7H_8)]^+$ (calc. 375); and 282, $[^{103}Rh([9]aneS_3 - H)]^+$ (calc. 282). NMR $[(CD_3)_2CO$, 293 K]: ^1H (200.13 MHz), δ 3.58 (dd, 4 H, *J* = 2.1, 4.7, nbd sp^2-CH), 3.49 (tt, 2 H, *J* = 1.6, 4.7, nbd sp^3-CH), 2.87–2.66 (m, 12 H, $[9]aneS_3$), and 1.17 (t, 2 H, *J* = 1.6, nbd CH_2); ^{13}C DEPT (50.32 MHz), δ 59.32 (d, *J* = 4.8, nbd CH_2), 46.10 (s, nbd sp^3-CH), 41.45 (d, *J* = 8.4 Hz, nbd sp^2-CH),[44] and 33.71 (s, $[9]aneS_3$). Electronic spectrum (MeCN): λ_{max} = 388 (sh), 309 (ε_{max} = 2360), and 222 nm (20 600 dm^3 mol^{-1} cm^{-1}). IR: 3060w, 2990w, 2960m, 2910m, 2840w, 1450m, 1435w, 1410s, 1385w, 1340w, 1305s, 1285w, 1260w, 1245w, 1225w, 1170m, 1140w, 1110w, 1035m, 995w, 940w, 920w, 905m, 890w, 840vs, 790m, 770w, 740w, 685w, 660w, 560s, 490w, 440w and 360m cm^{-1}.

$[Rh([9]aneS_3)(C_4H_6)]PF_6$. Butadiene was bubbled through a solution of $[Rh_2(C_2H_4)_4Cl_2]$ (0.032 g, 0.8×10^{-4} mol) in CH_2Cl_2 at 293 K for 10 min, affording a yellow solution. The macrocycle $[9]aneS_3$ (0.03 g, 1.6×10^{-4} mol) and NH_4PF_6 (0.027 g, 1.6×10^{-4} mol) were then added, and the mixture was stirred for 30 min. The solution was filtered and the solvent removed under vacuum. The crude product was recrystallised from MeCN–Et_2O, giving pale yellow microcrystals. Yield 0.038 g, 47% (Found: C, 25.2; H, 3.8. Calc. for $C_{10}H_{18}F_6PRhS_3$: C, 24.9; H, 3.8%). FAB mass spectrum: *m*/*z* = 337, $[^{103}Rh([9]aneS_3)(C_4H_6)]^+$ (calc. 337); and 282, $[^{103}Rh([9]aneS_3 - H)]^+$ (calc. 282). NMR $[(CD_3)_2CO$, 293 K]: ^1H (360.13 MHz), δ 5.60 (m, 2 H, CH of C_4H_6), 3.22–2.85 (br, 12 H, $[9]aneS_3$), 2.32 (m, 2 H), and 1.08 (m, 2 H, CH_2 of C_4H_6); ^{13}C DEPT (90.56 MHz), δ 89.98 [d, ^1J(Rh–C) = 5.0, CH of C_4H_6], 36.24 (br, $[9]aneS_3$), 35.37 [d, ^1J(Rh–C) = 12.1 Hz, CH_2 of C_4H_6], and 34.69 (br, $[9]aneS_3$). Electronic spectrum (MeCN): λ_{max} = 352 (sh), 283 (ε_{max} = 3360), and 229 nm (18 900 dm^3 mol^{-1} cm^{-1}). IR: 3040w, 3000m, 2960m, 2920w, 2840w, 1470s, 1445s, 1430m, 1410s, 1385w, 1370m, 1285m, 1265w, 1240m, 1195m, 1175w, 1130w, 1115w, 1050m, 1005m, 990w, 960m, 935s, 910s, 870m, 840vs, 740w, 680m, 655m, 620w, 560s, 495m, 480m, 450w, 415w and 400m cm^{-1}.

$[Rh([9]aneS_3)(CO)(PPh_3)]PF_6$. The complex $[Rh(CO)Cl(PPh_3)_2]$ (0.115 g, 1.6×10^{-4} mol), $[9]aneS_3$ (0.030 g, 1.6×10^{-4} mol) and NH_4PF_6 (0.027 g, 1.6×10^{-4} mol) were stirred in CH_2Cl_2 (6 cm^3) at 293 K for 15 min, yielding a yellow solution. The solution was filtered and reduced in volume to *ca.* 1 cm^3. Addition of an excess of hexane gave a yellow crystalline product which was analysed without further purification. Yield 0.065 g, 55% (Found: C, 41.4; H, 3.7. Calc. for $C_{25}H_{27}F_6OP_2RhS_3$: C, 41.8; H, 3.8%). FAB mass spectrum: *m*/*z* = 573, $[^{103}Rh([9]aneS_3)(CO)(PPh_3)]^+$ (calc. 573); 545, $[^{103}Rh([9]aneS_3)(PPh_3)]^+$ (calc. 545); and 468, $[^{103}Rh([9]aneS_3)(PPh_2)]^+$ (calc. 468). NMR (CD_3CN, 293 K): ^1H (200.13 MHz), δ 7.80–7.45 (m, 15 H, PPh_3) and 2.57–2.40 (m, 12 H, $[9]aneS_3$); $^{13}C-\{^1H\}$ (50.32 MHz), δ 133.51 (d, *J* = 11.4), 131.75 (d, *J* = 51.0), 131.06 (d, *J* = 2.5), 128.43 (d, *J* = 10.7, PPh_3), and 33.44 (s, $[9]aneS_3$); $^{31}P-\{^1H\}$ (81.02 MHz), δ 43.80 (d, *J* = 129 Hz). Electronic spectrum (MeCN): λ_{max} = 370 (sh), 278 (sh), and 251 nm (ε_{max} = 21 980 dm^3 mol^{-1} cm^{-1}). IR ($MeNO_2$ solution): 1960; (KBr disc) 3070w, 3040m, 3000w, 2950w, 2920w, 2840w, 1955vs, 1905w, 1580w, 1570w, 1480m, 1450m, 1435s, 1410s, 1335w, 1315w, 1300m, 1270w, 1175m, 1150w, 1115w, 1090s, 1075w, 1025w, 1000m, 985w, 970w, 940w, 905w, 870w, 840vs, 765s, 755m, 745m, 710s, 695s, 660w, 620w, 560s, 545s, 535s, 510s, 485w, 470w, 445w and 430m cm^{-1}.

$[Rh([9]aneS_3)(tcne)(MeCN)]PF_6$. The complex $[Rh([9]aneS_3)(cod)]BF_4$ (0.040 g, 8.4×10^{-5} mol) and tcne (0.011 g, 8.4×10^{-5} mol) were allowed to react in refluxing MeCN (6 cm^3) at 293 K for 2 h. The resultant yellow solution was filtered, reduced in volume to *ca.* 1 cm^3 and the pale yellow solid product crystallised from Et_2O. Yield 0.035 g, 78% (Found: C, 31.7; H, 2.9; N, 12.4. Calc. for $C_{14}H_{15}BF_4N_5RhS_3$: C, 31.2; H, 2.8; N, 13.0%). FAB mass spectrum: *m*/*z* = 452, $[^{103}Rh([9]aneS_3)(tcne)(MeCN)]^+$ (calc. 452); 411, $[^{103}Rh([9]aneS_3)(tcne)]^+$ (calc. 411); 385, $[^{103}Rh([9]aneS_3)(tcne - CN)]^+$ (calc. 385); 323, $[^{103}Rh([9]aneS_3 - H)(MeCN)]^+$ (calc. 323); and 283, $[^{103}Rh([9]aneS_3)]^+$ (calc. 283). NMR (CD_3CN, 293 K): ^1H (200.13 MHz), δ 3.64 (m, 6 H, $[9]aneS_3$), 1.96 (s, 3 H, MeCN), and 1.79 (m, 6 H, $[9]aneS_3$); $^{13}C-\{^1H\}$ (50.32 MHz), δ 37.27 (s), 34.06 (s), 33.53 (s, $[9]aneS_3$). Electronic spectrum (MeCN): λ_{max} = 330 (sh), 299 (ε_{max} = 14 345), and 255 nm (26 900 dm^3 mol^{-1} cm^{-1}). IR: 2980m, 2930m, 2860w, 2320m, 2295m, 2245w, 2220s, 2150w, 1440s, 1410s, 1380w, 1300m, 1285m, 1260w, 1245w, 1210s, 1190w, 1170w, 1140m, 1125m, 1060vs, 945m,

Table 4 Experimental data * for the single-crystal structure determinations of $[Rh([9]aneS_3)L_2]^+$

L	C_2H_4	$\frac{1}{2}$cod	$\frac{1}{2}C_4H_6$
Molecular formula	$C_{10}H_{20}F_6PRhS_3$	$C_{14}H_{24}BF_4RhS_3$	$C_{10}H_{18}F_6PRhS_3{\cdot}0.25C_4H_{10}O$
M_r	484.32	478.20	500.56
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$
a/Å	11.487(3)	11.491(13)	18.612(6)
b/Å	9.459(3)	12.803(6)	8.679(5)
c/Å	15.745(6)	13.377(15)	23.756(5)
α		88.12(7)	
β	105.54(3)	70.30(8)	96.844(18)
γ		74.68(7)	
U/Å^3	1648	1784	3810
Z	4	4	8
D_c/g cm^{-3}	1.952	1.781	1.746
Crystal appearance	Orange lath	Orange plates	Pale yellow lath
Crystal dimensions/mm	0.97 × 0.35 × 0.12	0.62 × 0.62 × 0.39	0.82 × 0.43 × 0.23
μ(M–Kα)/mm^{-1}	1.561 (Mo)	11.48 (Cu)	1.326 (Mo)
F(000)	968	968	2004
T/K	150	298	277
hkl ranges	−12 to 11, −9 to 10, 0–16	−9 to 10, −11 to 11, 0–12	−20 to 19, 0–9, 0–25
Data measured	3353	2838	2684
Data used	1964 [$F > 4\sigma(F)$]	2608 [$F > 6\sigma(F)$]	2329 [$F > 4\sigma(F)$]
Absorption corrections			
ψ scans	No	Yes	Yes
Maximum, minimum	—	0.088 9, 0.018 2	0.158 5, 0.095 4
DIFABS[45]	No	Yes	No
Maximum, minimum	—	1.631, 0.994	—
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0020F^2$	$\sigma^2(F) + 0.007\,496F^2$	$\sigma^2(F) + 0.00050F^2$
Final R, R'	0.048 3, 0.084 9	0.057 7, 0.084 3	0.046 7, 0.067 1
Final S	1.79	1.038	2.676
No. of parameters	216	452	281
Maximum, minimum residues in final ΔF synthesis/e Å^{-3}	1.35, −0.82	1.05, −0.55	0.82, −1.08

* Details in common: Stoë Stadi-4 four-circle diffractometer; ω–2θ scan mode; radiation: graphite monochromated Mo–Kα (λ 0.710 73 Å) or Cu–Kα (λ = 1.541 84 Å); $2\theta_{max}$ 45 (Mo), 90° (Cu).

910s, 850w, 830s, 770w, 660w, 625w, 560w, 525s, 490m and 330m cm^{-1}.

$[Rh_2([9]aneS_3)_2(CO)_3][PF_6]_2$. The complex $[Rh_2(CO)_4Cl_2]$ (0.032 g, 0.8 × 10^{-4} mol) was stirred with $[9]aneS_3$ (0.03 g, 1.6 × 10^{-4} mol) and NH_4PF_6 (0.027 g, 1.6 × 10^{-4} mol) in acetone (6 cm^3) at 293 K for 30 min, giving a dark green solution which was then filtered and reduced in volume to *ca.* 1 cm^3. Addition of an excess of Et_2O afforded a green microcrystalline product which was recrystallised from $MeNO_2$–Et_2O. Yield 0.060 g, 79% (Found: C, 17.3; H, 3.0. Calc. for $C_{15}H_{24}F_{12}O_3P_2Rh_2S_6$: C, 19.2; H, 2.6%). FAB mass spectrum: m/z = 795, $[^{103}Rh_2([9]aneS_3)_2(CO)_3(PF_6)]^+$ (calc. 795); 650, $[^{103}Rh_2([9]aneS_3)_2(CO)_3]^+$ (calc. 650); 622, $[^{103}Rh_2([9]aneS_3)_2(CO)_2]^+$ (calc. 622); 593, $[^{103}Rh_2([9]aneS_3)([9]aneS_3 - H)(CO)]^+$ (calc. 593); 339, $[^{103}Rh([9]aneS_3)(CO)_2]^+$ (calc. 339); and 283, $[^{103}Rh([9]aneS_3)]^+$ (calc. 283). NMR (CD_3NO_2, 293 K): ^1H (80.13 MHz), δ 3.22 (m, $[9]aneS_3$); ^{13}C-{^1H} (50.32 MHz), δ 202.51 [t, ^1J(Rh–C) = 26.9 Hz, CO] and 32.71 (s, $[9]aneS_3$). Electronic spectrum (MeCN): λ_{max} = 894 (ε_{max} = 75.1), 532 (sh), 388 (sh), 346 (sh), and 310 nm (14 390 dm^3 mol^{-1} cm^{-1}). IR: ($MeNO_2$ solution) 1855; (KBr disc) 2990m, 2960m, 2920m, 1915w, 1850vs, 1775w, 1445s, 1410s, 1360w, 1295m, 1270w, 1250w, 1180m, 1135w, 1070w, 1040w, 1015w, 990w, 935m, 840vs, 740m, 680s, 625m, 560s, 540m, 480w and 440w cm^{-1}.

$[Rh([9]aneS_3)Cl_3]$. Reaction of $RhCl_3{\cdot}3H_2O$ (0.044 g, 1.6 × 10^{-4} mol) with $[9]aneS_3$ (0.030 g, 1.6 × 10^{-4} mol) in refluxing ethanol (15 cm^3) for 3 h afforded a pale yellow precipitate, which was collected and washed with ethanol. Yield 0.042 g, 64% (Found: C, 18.6; H, 3.2. Calc. for $C_6H_{12}Cl_3RhS_3$: C, 18.5; H, 3.1%). IR: 2980m, 2920m, 2880w, 1440s, 1400s, 1365w, 1295w, 1280m, 1260m, 1170w, 1120m, 1010w, 940m, 905s, 830s, 675w, 660m, 560w, 430w, 340s and 295s cm^{-1}.

$[Rh([9]aneS_3)I_3]$. The complex $[Rh([9]aneS_3)(C_2H_4)_2]PF_6$ (0.060 g, 1.2 × 10^{-4} mol) was stirred with an excess of MeI (four drops) in acetone at 293 K for 15 min. The resultant orange precipitate was filtered off and washed with acetone and Et_2O. Yield 0.041 g, 51% (Found: C, 10.9; H, 1.8. Calc. for $C_6H_{12}I_3RhS_3$: C, 10.9; H, 1.8%). IR: 2940m, 2880m, 2840w, 1435s, 1400s, 1360w, 1290w, 1260m, 1235w, 1160m, 1120m, 1090w, 1020w, 930m, 900s, 820s, 675w, 590w and 480w cm^{-1}.

Crystal-structure Determinations.—Experimental data for single-crystal structure determinations are given in Table 4.

$[Rh([9]aneS_3)(C_2H_4)_2]PF_6$. A sample of $[Rh([9]aneS_3)(C_2H_4)_2]PF_6$ was prepared as above, using NH_4PF_6 as the counter ion metathesis agent. Crystals suitable for X-ray analysis was obtained by slow diffusion of Et_2O into an acetone solution of the complex. The chosen crystal was coated in oil, mounted on a glass fibre and cooled to 150 K in the cold stream of an Oxford Cryosystems low-temperature device.[46] The structure were solved by direct methods and developed by iterative rounds of least-squares refinement and Fourier-difference synthesis.[47] Anisotropic thermal parameters were refined for all non-H atoms, and macrocyclic H atoms were included in fixed, calculated positions. Ethene H atoms were located from a Fourier-difference map and allowed to refine freely with a common U_{iso} of 0.047(5) Å^2. Bond lengths, angles and torsion angles are listed in Table 1, and atomic coordinates in Table 5.

$[Rh([9]aneS_3)(cod)]BF_4$. A sample of the BF_4^- salt of $[Rh([9]aneS_3)(cod)]^+$ was synthesised as above, using $NaBF_4$ as chloride-abstracting agent. Crystals suitable for X-ray diffraction study were obtained by diffusion of Et_2O vapour into a solution of the complex in MeCN. The rhodium positions were deduced from a Patterson synthesis,[48] while successive

Table 5 Atomic coordinates (× 10^4)

Atom	x	y	z	Atom	x	y	z
$[Rh([9]aneS_3)(C_2H_4)_2]PF_6$							
Rh	667.9(4)	2 513.4(4)	8 607.5(3)	C(2E)	2 350(8)	3 447(10)	9 471(5)
S(1)	426.2(15)	34.1(16)	8 968.8(11)	C(3E)	−549(7)	3 813(8)	9 061(5)
C(2)	−1 099(6)	−274(7)	8 293(5)	C(4E)	−9(7)	4 641(7)	8 537(5)
C(3)	−1 368(6)	325(7)	7 360(5)	P	6 042.7(15)	1 842.1(17)	9 142.6(10)
S(4)	−902.5(15)	2 164.8(19)	7 357.8(11)	F(1)	6 840(8)	3 016(10)	9 666(5)
C(5)	−144(6)	2 150(8)	6 487(4)	F(2)	5 044(7)	2 957(9)	8 795(5)
C(6)	972(5)	1 226(6)	6 693(4)	F(3)	5 494(5)	1 577(5)	9 953(3)
S(7)	1 994.6(12)	1 654.4(15)	7 767.4(10)	F(4)	6 597(4)	2 138(5)	8 323(3)
C(8)	2 384(16)	−90(6)	8 233(4)	F(5)	7 006(7)	676(10)	9 489(4)
C(9)	1 326(6)	−961(6)	8 373(5)	F(6)	5 201(8)	689(7)	8 600(4)
C(1E)	1 870(10)	2 617(10)	9 956(7)				
$[Rh([9]aneS_3)(cod)]BF_4$							
Rh(1)	10 412(1)	1 936(1)	3 076(1)	S(24)	6 950(2)	4 863(2)	2 185(2)
S(1)	8 749(2)	1 650(2)	2 604(2)	C(25)	8 274(7)	5 120(7)	1 042(6)
C(2)	8 405(7)	538(8)	3 436(10)	C(26)	7 890(7)	6 033(6)	389(6)
C(2′)	8 816(10)	217(7)	2 805(10)	S(27)	6 922(2)	7 287(2)	1 187(2)
C(3)	9 581(7)	−387(6)	3 291(8)	C(28)	5 609(7)	7 712(7)	670(6)
C(3′)	9 280(9)	−141(9)	3 726(10)	C(29)	4 789(7)	6 928(7)	819(5)
S(4)	10 869(2)	63(2)	3 475(2)	C(31)	4 353(8)	7 916(7)	4 040(7)
C(5)	12 296(8)	−534(7)	2 336(6)	C(32)	4 428(7)	6 882(7)	4 435(6)
C(5′)	11 753(12)	−661(7)	2 170(7)	C(33)	4 947(8)	6 497(7)	5 296(7)
C(6)	12 162(11)	−172(7)	1 295(6)	C(34)	6 328(10)	6 260(9)	4 973(8)
C(6′)	12 591(9)	−70(7)	1 410(7)	C(35)	7 041(8)	6 449(7)	3 874(7)
S(7)	11 785(2)	1 306(2)	1 246(2)	C(36)	6 980(8)	7 436(8)	3 549(7)
C(8)	10 585(7)	1 477(9)	606(6)	C(37)	6 295(10)	8 444(10)	4 100(11)
C(8′)	10 677(7)	1 005(11)	664(7)	C(38)	4 945(11)	8 699(8)	4 424(8)
C(9)	9 489(7)	1 035(9)	1 244(7)	B(1)	15 756(9)	948(8)	1 803(7)
C(9′)	9 336(7)	1 718(12)	1 159(7)	F(11)	16 936(8)	272(8)	1 491(8)
C(11)	9 661(7)	3 610(6)	3 150(7)	F(12)	15 590(9)	1 309(10)	2 809(8)
C(12)	8 989(7)	3 211(7)	4 124(6)	F(13)	14 970(10)	536(10)	1 472(9)
C(13)	9 184(8)	3 314(8)	5 172(7)	F(14)	15 578(12)	1 947(9)	1 484(11)
C(14)	10 571(7)	3 067(7)	5 062(7)	F(15)	14 878(12)	387(12)	2 037(11)
C(15)	11 381(7)	2 240(7)	4 179(6)	F(16)	15 284(13)	1 582(13)	1 340(12)
C(16)	12 071(7)	2 444(7)	3 147(6)	F(17)	15 224(13)	844(12)	2 819(12)
C(17)	11 975(9)	3 542(8)	2 747(7)	F(18)	16 805(13)	806(12)	1 178(12)
C(18)	10 606(9)	4 243(7)	3 042(8)	B(2)	1 089(9)	6 855(8)	1 329(7)
Rh(2)	5 787(1)	6 717(1)	2 916(1)	F(21)	153(6)	6 529(6)	1 133(6)
S(21)	4 263(2)	6 560(2)	2 208(2)	F(22)	2 170(6)	5 975(5)	1 071(5)
C(22)	4 546(7)	5 114(7)	2 060(7)	F(23)	776(8)	7 115(6)	2 404(5)
C(23)	5 959(8)	4 472(7)	1 519(7)	F(24)	1 353(8)	7 685(6)	801(6)
$[Rh([9]aneS_3)(C_4H_6)]PF_6{\cdot}0.25OEt_2$							
Rh	4 056(1)	2 319(1)	746(1)	F(2)	3 928(6)	1 825(13)	3 326(6)
S(1)	2 797(1)	1 877(1)	653(1)	F(3)	3 060(6)	321(8)	3 071(3)
C(2)	2 743(8)	−32(5)	338(2)	F(4)	2 472(5)	774(10)	3 829(4)
C(3)	3 325(3)	1 163(6)	573(3)	F(5)	2 822(8)	2 686(10)	3 269(6)
S(4)	4 228(1)	−331(1)	650(1)	F(6)	3 744(5)	272(16)	3 983(6)
C(5)	4 557(3)	−855(7)	1 385(3)	F(7)	3 397(5)	2 749(8)	4 122(4)
C(6)	4 157(3)	−120(7)	1 819(3)	F(8)	3 908(10)	2 058(17)	3 384(8)
S(7)	4 069(1)	1 947(2)	1 724(1)	F(9)	3 112(10)	−18(13)	3 153(8)
C(8)	3 116(4)	2 254(7)	1 812(3)	F(10)	2 604(7)	845(18)	3 920(6)
C(9)	2 586(3)	1 481(7)	1 370(2)	F(11)	2 708(8)	2 499(14)	3 250(7)
C(11)	4 146(3)	4 738(6)	806(2)	F(12)	3 592(9)	−37(13)	3 927(7)
C(12)	4 843(3)	4 081(6)	735(2)	O(1S)	0	1 539(9)	2 500
C(13)	4 879(3)	3 126(6)	271(2)	C(1S)	568(4)	567(10)	2 349(4)
C(14)	4 241(3)	2 891(6)	−99(2)	C(2S)	1 257	1 129	2 416
P	3 229(1)	1 351(2)	3 611(1)	C(1S′)	568(4)	567(10)	2 349(4)
F(1)	3 323(7)	2 169(10)	4 130(5)	C(3S)	1 060	1 365	2 139

cycles of least-squares refinement and Fourier-difference synthesis[49] located all other non-H atoms. During refinement the C atoms of one $[9]aneS_3$ ring (molecule 1) were found to be disordered over two possible orientations; this was modelled using the fixed parameters S–C 1.83, C–C 1.52 Å, and S–C–C = 109.5°. Inspection of the final thermal parameters and bond lengths suggested that the CH_2 groups of one cod ligand (molecule 2) were also disordered, although this could not be successfully modelled. At isotropic convergence an empirical absorption correction was applied[45] (maximum 1.631, minimum 0.994). Anisotropic thermal parameters were refined for all Rh, S, F and wholly occupied C atoms, and H atoms were included in fixed, calculated positions. A secondary extinction parameter refined to 0.0161(8). Bond lengths, angles and torsion angles are listed in Table 2, and atomic coordinates in Table 5.

$[Rh([9]aneS_3)(C_4H_6)]PF_6{\cdot}0.25OEt_2$. Suitable crystals were obtained by slow diffusion of Et_2O into a solution of the complex in acetone. The crystal was mounted on a glass fibre and cooled to 277 K in the cold stream of an Oxford Cryosystems low-temperature device.[46] The Rh atom was located from a Patterson synthesis,[48] and the structure developed by iterative cycles of least-squares refinement and Fourier-difference synthesis.[49] During refinement the PF_6^- counter ion was found to be disordered; this was modelled using twelve half-occupied F atoms. Anisotropic thermal parameters were refined for all Rh, S, P, F, O and non-solvent C atoms. Macrocyclic and solvent H atoms were included in fixed calculated positions; butadiene H-atom positions were refined with a fixed C–H bond length of 1.08 Å and constraints such that all C–C–H, and both H–C–H, angles were equal. Bond lengths, angles and torsion angles are listed in Table 3, and atomic coordinates in Table 5.

Structure-factor data were inlaid[47,49] or taken from ref. 50. Illustrations were prepared using SHELXTL/PC[47] and molecular geometry calculations performed using CALC.[51]

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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