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Some new dinuclear rhodium compounds: preparations and structures

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Abstract

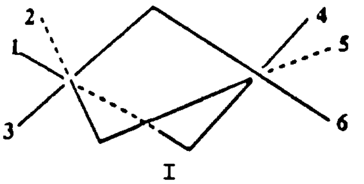
The following seven dinuclear rhodium compounds have been prepared, characterized spectroscopically and their crystal and molecular structures determined: 1,5,6-$Rh_2Cl_6(PEt_3)_3$ (**1**), 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ (**2**), 1,5,6-$Rh_2Cl_6(PPr^n{}_3)_3$ (**3**), 1,5,6-$Rh_2Br_6(PEt_3)_3$ (**4**), 1,5,6-$Rh_2Br_6(PPr^n{}_3)_3$ (**5**), 1,5,6-$Rh_2Br_6(PBu^n{}_3)_3$ (**6**), 1,3,6,8-$Rh_2Br_6(PBu^n{}_3)_4$ (**7**). In each case there are marked structural *trans* effects such that Rh–X_{br} bonds *trans* to PR_3 ligands are 0.12–0.17 Å (av. 0.15 Å) longer than those *trans* to an Rh–X bond. The fact that for the face-sharing bioctahedral (FSBO) molecules only one of the two possible isomers was formed and for the edge-sharing bioctahedral (ESBO) molecules only one of the nine possible isomers was formed is discussed and some principles that largely account for these observations are invoked. These principles are (i) that no μ-X ligand will have both of its Rh–X bonds *trans* to PR_3 and (ii) that in ESBO species phosphine ligands on two adjacent axial positions are sterically disfavored.

Introduction

Some halogen-bridged dinuclear complexes of Rh(III) of the general formula $Rh_2X_6(PR_3)_n$, where X = Cl, Br; $PR_3 = PEt_3$, PBu_3, $P(n\text{-}C_5H_{11})_3$, and $n = 3$ or 4, were reported as early as 1964 by Chatt *et al.* [1]. The first halogen-bridged bioctahedral dinuclear species of Rh(III) to be both synthesized and structurally characterized, $[Rh_2Cl_9]^{3-}$, was reported by Cotton and Ucko in 1972 [2]. The later structural characterization of $Rh_2Cl_6(PBu_3)_4$ [3] and $Rh_2Cl_6(PBu_3)_3$ [4] showed that the complexes reported by Chatt *et al.* comprise both edge-sharing bioctahedral (ESBO) or face-sharing bioctahedral (FSBO) types depending on the number of ligands in the complex. Several other chloro-bridged dinuclear complexes of Rh(III) were subsequently synthesized and structurally characterized [5], but there is only one report of a bromo-bridged dinuclear complex of Rh(III), namely $Rh_2Br_6(dppm)_2$, the synthesis and structural characterization of which were reported recently [6].

Several years ago we began in this laboratory a thorough NMR study of the interconversions of ESBO and FSBO species and found that we required further structural information in order to be certain about the interpretation of the NMR data. As a result we have accumulated structural data for five new FSBO complexes of the type 1,5,6-$Rh_2X_6(PR_3)_3$ and two new ESBO complexes of the type 1,3,6,8-$Rh_2X_6(PR_3)_4$, in which X = Cl or Br and PR_3 is one of several trialkyl phosphines. In this report we describe the preparations of these compounds and their crystal and molecular structures. We shall then compare the main features, such as bond lengths, for the entire set of compounds.

In the above paragraph we have employed numbering schemes for both ESBO and FSBO species. The scheme for ESBOs was only recently introduced [7] and the one for FSBOs is completely new. Both are defined in the diagrams I and II. In naming compounds, we



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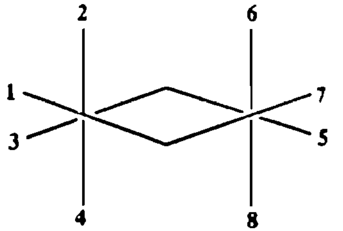

II

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give the position numbers of the neutral ligands, beginning with the lowest number possible (usually 1, but possibly, in the case of an ESBO, 2) and choosing the lowest numbers thereafter.

Experimental

Preparative procedures

General procedures

All operations were performed under an atmosphere of argon with carefully dried and distilled solvents using standard Schlenk line techniques. However, none of the products appears to be sensitive to air, either as a solid or in solution. The $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 operating at 81 MHz in 10-mm NMR tubes. Chemical shifts were referenced to an external standard of 85% phosphoric acid.

Starting materials

$RhCl_3 \cdot 3H_2O$ and $RhBr_3 \cdot 2H_2O$ were purchased from Aldrich or Sigma Chemical Co. PMe_3, PMe_2Ph, PEt_3, $PPr^n{}_3$ and $PBu^n{}_3$ (Strem Chemicals) were transferred into Schlenk tubes and kept under argon. These were stored in the refrigerator when not in use.

Preparation of 1,5,6-$Rh_2Cl_6(PEt_3)_3$ (1)

Rhodium trichloride (0.34 g, 1.4 mmol) was dissolved in 30 ml of methanol and evaporated to dryness twice to remove water. The solid was then dissolved in 25 ml of ethanol and triethylphosphine (0.27 ml, 2.1 mmol) was added. The resulting solution was heated for 30 min. The solvent was evaporated and the resulting red product washed with hexane followed by benzene, and then dried in vacuum. Yield 0.44 g (79%). Red crystals suitable for X-ray crystallographic analysis were obtained by the slow diffusion of hexane into a chloroform solution of $Rh_2Cl_6(PEt_3)_3$. $^{31}P\{^1H\}$ NMR: 1,5,6-$Rh_2Cl_6(PEt_3)_3$; δ 62.8 (d, 1P, $J = 115$), 47.0 (d, 2P, $J = 115$).

Preparation of 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ (2)

To a sample of **1** (*c.* 0.2 g) dissolved in dichloromethane and cooled to 0 °C one equivalent of PEt_3 was added by syringe. The solvent was then removed in vacuum at 0 °C, giving a microcrystalline solid. Crystals for X-ray work were obtained by dissolving this solid in chloroform and allowing hexane to diffuse slowly into the solution at room temperature. $^{31}P\{^1H\}$ NMR: δ 45.2 (d, 2P, $J = 115$), 10.8 (d, 2P, $J = 81$).

Preparation of 1,5,6-$Rh_2Cl_6(PPr^n{}_3)_3$ (3)

Rhodium trichloride (0.22 g, 0.84 mmol) was dissolved in 20 ml of methanol and the solution evaporated to dryness. This procedure was repeated. The solid was then dissolved in 20 ml of methanol, tri(n-propyl)phosphine (0.27 ml, 1.26 mmol) was added, and the resulting solution was heated for 15 min. The solvent was evaporated and the resulting brown product washed with hexane, followed by benzene, and then dried in vacuum. This solid was dissolved in dichloromethane and a small amount of black solid that did not dissolve was removed by filtration. On addition of hexane, a brown solid precipitated. Yield 0.29 g (66%). Red–brown crystals suitable for X-ray crystallographic analysis were obtained from an ethanol solution. $^{31}P\{^1H\}$ NMR: δ 52.8 (d, 1P, $J = 115$), 38.3 (d, 2P, $J = 116$).

Preparation of 1,5,6-$Rh_2Br_6(PEt_3)_3$ (4)

Rhodium tribromide (0.14 g, 0.37 mmol) was dried as previously described. The dry solid was dissolved in 10 ml of methanol, triethylphosphine (0.1 ml, 0.56 mmol) was added, and the resulting solution was heated for 20 min. The solvent was evaporated and the resulting brown product washed with hexane, followed by benzene, and then dried in vacuum. Yield 0.15 g (73%). Red–brown crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of hexane into a dichloromethane solution. $^{31}P\{^1H\}$ NMR: δ 65.5 (d, 1P, $J = 115$), 48.5 (d, 2P, $J = 115$).

Preparation of 1,5,6-$Rh_2Br_6(PPr^n{}_3)_3$ (5)

Rhodium tribromide (0.13 g, 0.34 mmol) was dried as previously described. The dry solid was dissolved in 15 ml of methanol, tri(n-propyl)phosphine (0.1 ml, 0.51 mmol) was added, and the resulting solution was heated for 5 min. The solvent was evaporated and the resulting brown product washed with hexane, followed by benzene, and then dried in vacuum. This solid was dissolved in dichloromethane and a small amount of black solid that did not dissolve was removed by filtration. On addition of hexane, a brown solid precipitated. Yield 0.14 g (64%). Red–brown crystals suitable for X-ray crystallographic analysis were obtained from an ethanol solution. $^{31}P\{^1H\}$ NMR: δ 55.3 (d, 1P, $J = 115$), 40.0 (d, 2P, $J = 115$).

Preparation of 1,5,6-$Rh_2Br_6(PBu_3)_3$ (6)

To 10 ml of ethanol in a Schlenk tube containing 1.0 mmol of $RhBr_3 \cdot 3H_2O$ (397 mg) under an atmosphere of argon 1.5 mmol of PBu_3 was added by syringe. After this mixture had been stirred at 60 °C for half an hour a red–brown solution was formed and this was filtered. The filtrate was set aside for the growth of single crystals and after one day crystals suitable for X-ray diffraction studies were found. Yield 60%. A band appeared at 550 nm in the UV–Vis spectrum. $^{31}P\{^1H\}$ NMR: δ 52.2 (d, 1P, $J = 116$), δ 37.5 (d, 2P, $J = 115$).

Preparation of 1,3,6,8-$Rh_2Br_6(PBu_3)_4$ (7)

$RhBr_3 \cdot 3H_2O$ (1.0 mmol, 397 mg) was placed in a Schlenk tube and 10 ml of ethanol was added to it under an atmosphere of argon. Two mmol of PBu_3 (0.50 ml) were added to this solution and the mixture was stirred with heating for half an hour to get a clear red–brown solution. After filtering the solution, the filtrate was kept undisturbed for growing single crystals and red–brown prismatic crystals were found within one day. One of these crystals was used for X-ray diffraction studies. Yield *c.* 64%. The UV–Vis spectrum of this compound shows one band at 455 nm.

X-ray crystallography

In each case a crystal of suitable size and quality was mounted on the tip of a thin glass fiber with the use of epoxy cement. X-ray data were collected on an automated four-circle diffractometer, equipped with monochromated Mo Kα (or Cu Kα) radiation, following the procedures and practices routinely used in this laboratory [8, 9]. Axial lengths and Laue class were confirmed with oscillation photographs. Lorentz, polarization and empirical absorption corrections based on azimuthal scans of several reflections with setting angles (χ) near 90° were applied to the data [10]. Crystal parameters and basic information pertaining to data collection and structure refinement are summarized for all seven compounds in Table 1.

1,5,6-$Rh_2Cl_6(PEt_3)_3$ (1)

A red crystal was mounted on a quartz fiber with epoxy glue. Indexing gave a monoclinic cell and Laue symmetry 2/*m* was confirmed by an oscillation photograph. Systematic absences indicated that the space group was $P2_1/c$ (No. 14). The structure was partially solved when Rh, Cl and P atoms were found using direct methods (SHELXS 86). The rest of the non-hydrogen atoms were located by an alternating series of Fourier maps and least-squares refinement cycles. The model was refined to convergence with all Rh, Br, P and C atoms having anisotropic thermal parameters. Hydrogen atoms were not included in the refined model. Table 2 lists the final positional parameters.

1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ (2)

An orange–red crystal was mounted on a quartz fiber with epoxy glue. Preliminary examination of the crystal revealed that the crystal system was orthorhombic, the lattice primitive and the Laue group *mmm*. Systematic absences indicated that the space group was $P2_12_12_1$. The heavy atoms were found by direct methods and were consistent with the determined space group. The rest of the non-hydrogen atoms were located in an alternating series of Fourier maps and least-squares refinement cycles. The structure was finally refined with

TABLE 1. Crystallographic data

Compound	1	2	3	4	5	6	7
Formula	$Rh_2Cl_6P_3C_{18}H_{45}$	$Rh_2Cl_6P_4C_{24}H_{60}$	$Rh_2Cl_6P_3C_{27}H_{63}$	$Rh_2Br_6P_3C_{18}H_{45}$	$Rh_2Br_6P_3C_{27}H_{63}$	$Rh_2Br_6P_3C_{36}H_{81}$	$Rh_2Br_6P_4C_{48}H_{108}$
Formula weight	773.01	891.17	899.27	1039.75	1165.99	1292.23	1494.56
Space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
a (Å)	7.833(1)	18.882(3)	10.658(3)	11.601(5)	10.828(1)	12.779(2)	15.756(2)
b (Å)	22.621(3)	20.107(3)	27.145(4)	17.375(3)	16.797(4)	27.599(4)	20.829(3)
c (Å)	17.008(1)	10.430(3)	16.027(3)	15.647(2)	22.868(8)	17.237(3)	20.817(4)
β (°)	96.25(1)	90.00	105.55(2)	90.79(3)	94.17(2)	120.04(2)	103.20(1)
V (Å^3)	2996(1)	3960(1)	4467(1)	3154(1)	4148(2)	5262(3)	6651(3)
Z	4	4	4	4	4	4	4
D_{calc} (g cm^3)	1.71	1.50	1.34	2.19	1.89	1.631	1.492
μ (cm^{-1})	17.92	14.04	106.686	87.23	66.42	52.44	41.818
Radiation, λ (Å)	Mo Kα (0.71073)	Mo Kα	Cu Kα (1.54184)	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Temperature (°C)	20 ± 1	20 ± 1	20 ± 1	20 ± 1	20 ± 1	20 ± 1	20 ± 1
Transmission factors	0.99–0.88	0.99–0.70	0.99–0.75	0.99–0.35	0.99–0.51	0.99–0.73	0.99–0.66
R^a	0.0357	0.0486	0.0535	0.0460	0.0468	0.064	0.057
$R_w{}^b$	0.0052	0.0653	0.0860	0.0606	0.0628	0.081	0.072

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2\{|F_o|\}$.

TABLE 2. Positional and isotropic equivalent thermal parameters (Å^2) and their e.s.d.s for 1,5,6-$Rh_2Cl_6(PEt_3)_3$ (**1**)

Atom	x	y	z	B_{iso} (Å^2)[a]
Rh(1)	0.07824(6)	0.56853(2)	0.23636(3)	1.94(1)
Rh(2)	0.15003(6)	0.43026(2)	0.26429(3)	2.11(1)
Cl(1)	0.2469(2)	0.51246(7)	0.34304(9)	2.81(3)
Cl(2)	−0.1281(2)	0.49460(6)	0.24588(9)	2.52(3)
Cl(3)	0.2150(2)	0.49110(7)	0.15815(9)	2.79(3)
Cl(4)	0.3075(2)	0.63158(8)	0.2267(1)	3.70(4)
Cl(5)	0.0338(2)	0.35668(8)	0.1801(1)	3.50(4)
Cl(6)	0.0601(2)	0.37997(8)	0.3710(1)	3.45(4)
P(1)	−0.0623(2)	0.61181(7)	0.12692(9)	2.26(3)
P(2)	−0.0387(2)	0.62687(7)	0.3262(1)	2.57(3)
P(3)	0.4065(2)	0.38549(7)	0.2792(1)	2.61(3)
C(1)	0.2909(8)	0.4080(3)	0.8930(4)	3.4(1)
C(2)	0.321(1)	0.4680(4)	0.9359(4)	4.3(2)
C(3)	0.0250(8)	0.5906(3)	0.0359(4)	3.2(1)
C(4)	0.206(1)	0.6144(4)	0.0229(5)	4.6(2)
C(5)	0.054(1)	0.3064(3)	0.8731(4)	3.7(2)
C(6)	0.135(1)	0.2785(3)	0.9509(5)	5.0(2)
C(7)	0.971(1)	0.5949(3)	0.4249(4)	3.8(2)
C(8)	0.147(1)	0.4589(4)	0.5665(5)	4.5(2)
C(9)	0.2670(8)	0.3568(3)	0.6979(4)	3.4(1)
C(10)	0.347(1)	0.3204(4)	0.6324(5)	5.4(2)
C(11)	0.061(1)	0.6994(3)	0.3422(5)	4.5(2)
C(12)	0.205(1)	0.7051(5)	0.4088(6)	6.8(3)
C(13)	0.388(1)	0.3067(3)	0.3024(5)	4.2(2)
C(14)	0.570(1)	0.2767(4)	0.3180(7)	7.3(3)
C(15)	0.4740(9)	0.6088(4)	0.8074(4)	4.0(2)
C(16)	0.447(1)	0.3583(4)	0.1195(5)	5.0(2)
C(17)	0.4401(9)	0.5820(3)	0.6436(5)	3.7(2)
C(18)	0.485(1)	0.5920(4)	0.5587(5)	5.0(2)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}$.

TABLE 3. Positional and isotropic equivalent thermal parameters (Å^2) and their e.s.d.s for 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ (**2**)

Atom	x	y	z	B_{iso} (Å^2)[a]
Rh(1)	0.0002(4)	0.34014(6)	0.0933(1)	3.82(3)
Rh(2)	−0.0003(3)	0.18478(5)	−0.1044(1)	3.51(3)
Cl(1)	−0.001(1)	0.4533(2)	0.0459(6)	7.3(1)
Cl(2)	0.000(1)	0.3611(3)	0.3132(5)	6.6(1)
Cl(3)	−0.0001(9)	0.2232(2)	0.1251(4)	4.16(9)
Cl(4)	0.0022(8)	0.3100(2)	−0.1262(4)	5.0(1)
Cl(5)	0.1236(3)	0.1847(3)	−0.1073(7)	4.7(1)
Cl(6)	−0.1223(5)	0.1854(3)	−0.1091(6)	6.5(2)
P(1)	−0.1248(4)	0.3472(3)	0.0948(7)	5.3(2)
P(2)	0.1283(4)	0.3479(3)	0.1050(8)	6.5(2)
P(3)	0.001(1)	0.0758(2)	−0.0449(4)	4.2(1)
P(4)	−0.001(1)	0.1679(2)	−0.3204(5)	6.4(2)
C(1)	0.669(2)	0.729(2)	0.693(3)	10(1)*
C(2)	0.318(2)	0.229(2)	0.694(3)	11.3(9)*
C(3)	0.685(1)	0.651(1)	0.471(2)	5.4(6)*
C(4)	0.675(2)	0.585(2)	0.393(3)	8.9(9)*
C(5)	0.653(1)	0.589(1)	0.723(2)	3.6(4)*
C(6)	0.235(1)	0.920(1)	0.266(2)	6.2(7)*
C(7)	0.347(1)	0.572(1)	0.667(2)	4.1(4)*
C(8)	0.269(1)	0.557(1)	0.674(2)	5.8(6)*
C(9)	0.336(1)	0.640(1)	0.426(2)	4.5(5)*
C(10)	0.362(2)	0.580(1)	0.355(3)	7.4(7)*
C(11)	0.316(1)	0.717(1)	0.656(2)	5.2(6)*
C(12)	0.342(2)	0.737(2)	0.804(3)	7.7(9)*
C(13)	0.582(2)	−1.034(2)	0.462(3)	8.0(8)*
C(14)	0.625(2)	0.945(1)	0.598(2)	6.8(7)*
C(15)	0.439(1)	0.977(1)	0.360(2)	4.4(5)*
C(16)	0.433(2)	−0.949(2)	0.409(3)	8.8(9)*
C(17)	0.463(1)	0.936(1)	0.623(2)	5.4(6)*
C(18)	0.383(2)	0.923(1)	0.641(2)	7.0(7)*
C(19)	0.587(2)	0.362(2)	0.388(4)	12(1)*
C(20)	0.564(2)	0.372(2)	0.538(4)	13(1)*
C(21)	0.425(2)	0.395(1)	0.372(3)	7.4(7)*
C(22)	0.397(2)	0.390(2)	0.507(3)	8.6(9)*
C(23)	0.525(1)	0.254(1)	0.403(2)	6.3(6)*
C(24)	0.600(2)	0.230(2)	0.386(3)	11(1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}$.

all Rh, Cl and P atoms having anisotropic thermal parameters. Hydrogen atoms are not included in the refined model. Table 3 lists the final positional and isotropic equivalent thermal displacement parameters.

1,5,6-$Rh_2Cl_6(PPr^n_3)_3$ (3)

Preliminary examination revealed that the crystal system was monoclinic, the lattice primitive, and the Laue group $2/m$, and systematic absences indicated that the space group was $P2_1/c$. The structure was partially solved when Rh, Cl and P atoms were found using direct methods (SHELXS 86). The rest of the non-hydrogen atoms were located by an alternating series of Fourier maps and least-squares refinement cycles. The model was refined to convergence with all Rh, Cl, P and C atoms having anisotropic thermal parameters. Hydrogen atoms were not included in the refined model. Table 4 lists the final positional parameters.

1,5,6-$Rh_2Br_6(PEt_3)_3$ (4)

A red–brown crystal was mounted on a quartz fiber with epoxy glue. Indexing gave a monoclinic cell and Laue symmetry $2/m$ was confirmed by an oscillation photograph. The space group was determined as $P2_1/c$ (No. 14) based on the systematic absences. All of the non-hydrogen atoms in the molecule were refined with anisotropic thermal parameters to low residuals. Final atomic positional and isotropic displacement parameters are listed in Table 5.

1,5,6-$Rh_2Br_6(PPr^n_3)_3$ (5)

Preliminary examination of the crystal revealed that the crystal system was monoclinic, the lattice primitive and the Laue group $2/m$. Systematic absences indicated that the space group was $P2_1/c$. The structure was partially solved when Rh, Br and P atoms were found using direct methods (SHELXS 86). The rest of the

TABLE 4. Positional and isotropic equivalent thermal parameters (Å^2) and their e.s.d.s for 1,5,6-$Rh_2Cl_6(PPr^n_3)_3$ (**3**)

Atom	x	y	z	B_{iso} (Å^2)
Rh(1)	0.07190(8)	0.35208(3)	0.36326(5)	5.08(2)
Rh(2)	−0.03830(7)	0.35799(3)	0.52997(5)	4.98(2)
Cl(1)	−0.1316(3)	0.3871(1)	0.3876(2)	6.28(7)
Cl(2)	0.0302(2)	0.2874(1)	0.4493(2)	5.37(6)
Cl(3)	0.1518(3)	0.3945(1)	0.5074(2)	5.95(7)
Cl(4)	0.1119(3)	0.4213(1)	0.2906(2)	7.40(8)
Cl(5)	0.0728(3)	0.3254(1)	0.6612(2)	6.59(8)
Cl(6)	−0.2272(3)	0.3167(1)	0.5326(2)	6.67(7)
P(1)	0.2678(3)	0.3169(1)	0.3676(2)	5.84(7)
P(2)	−0.0400(3)	0.3181(1)	0.2344(2)	6.18(8)
P(3)	−0.0885(3)	0.4226(1)	0.6016(2)	6.27(8)
C(1)	0.255(1)	0.2496(4)	0.3551(7)	6.4(3)
C(2)	0.389(1)	0.2758(5)	0.8601(9)	8.0(4)
C(3)	0.365(1)	0.3321(5)	0.8532(9)	8.9(4)
C(4)	0.388(1)	0.3278(6)	0.4710(8)	7.8(4)
C(5)	0.370(1)	0.2951(6)	0.5484(7)	8.0(4)
C(6)	0.469(2)	0.3110(9)	0.630(1)	15.2(7)
C(7)	0.348(1)	0.3386(5)	0.2854(7)	7.8(3)
C(8)	0.557(1)	0.6201(6)	0.6833(9)	14.1(4)
C(9)	0.491(2)	0.3984(7)	0.237(1)	15.3(5)
C(10)	0.115(1)	0.7412(5)	0.7523(8)	6.8(3)
C(11)	0.230(1)	0.7622(5)	0.2119(9)	7.5(4)
C(12)	0.257(1)	0.7128(6)	0.1794(9)	9.0(4)
C(13)	0.045(1)	0.3046(5)	0.1498(7)	7.2(3)
C(14)	0.070(1)	0.3517(5)	0.0978(8)	8.4(4)
C(15)	0.152(2)	0.3375(6)	0.0354(8)	11.1(4)
C(16)	0.172(1)	0.6388(5)	0.8191(7)	8.7(4)
C(17)	0.258(2)	0.6633(7)	0.9083(9)	10.7(5)
C(18)	0.347(2)	0.623(1)	0.958(1)	17.2(8)
C(19)	0.168(1)	0.5956(5)	0.3153(6)	7.2(3)
C(20)	0.212(1)	0.5496(6)	0.2699(8)	10.3(4)
C(21)	0.297(2)	0.5688(7)	0.2149(8)	14.8(5)
C(22)	0.048(1)	0.4633(4)	0.6520(8)	8.7(4)
C(23)	0.147(2)	0.4431(6)	0.733(1)	11.1(5)
C(24)	0.243(2)	0.4854(6)	0.770(1)	16.0(7)
C(25)	0.187(1)	0.5321(5)	0.4689(8)	8.2(4)
C(26)	0.330(1)	0.5502(5)	0.509(1)	9.8(4)
C(27)	0.401(2)	0.5078(8)	0.572(1)	13.5(6)

[a]Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}$.

TABLE 5. Positional and isotropic equivalent thermal parameters (Å^2) and their e.s.d.s for 1,5,6-$Rh_2Br_6(PEt_3)_3$ (**4**)

Atom	x	y	z	B_{iso} (Å^2)[a]
Rh(1)	0.39587(8)	0.24206(5)	0.97885(6)	1.73(2)
Rh(2)	0.68326(8)	0.25435(5)	0.94456(6)	1.81(2)
Br(1)	0.5428(1)	0.15579(7)	0.88906(9)	2.62(3)
Br(2)	0.5574(1)	0.23269(7)	1.08377(8)	2.35(2)
Br(3)	0.5244(1)	0.34501(7)	0.90663(9)	2.64(3)
Br(4)	0.2538(1)	0.23937(9)	0.86168(9)	3.36(3)
Br(5)	0.7975(1)	0.35779(8)	1.01120(9)	3.15(3)
Br(6)	0.8246(1)	0.15967(8)	0.9957(1)	3.32(3)
P(1)	0.3020(3)	0.3395(2)	1.0480(2)	2.37(7)
P(2)	0.3031(3)	0.1414(2)	1.0438(2)	2.14(7)
P(3)	0.7778(3)	0.2679(2)	0.8208(2)	2.13(6)
C(1)	0.288(2)	0.4301(8)	0.989(1)	4.2(4)
C(2)	0.187(2)	0.429(1)	0.916(1)	7.1(6)
C(3)	0.156(1)	0.3177(8)	1.085(1)	4.0(4)
C(4)	0.099(2)	0.3868(9)	1.134(1)	6.0(4)
C(5)	0.377(1)	0.3736(8)	1.148(1)	3.7(3)
C(6)	0.483(1)	0.4251(8)	1.135(1)	4.2(4)
C(7)	0.146(1)	0.1303(8)	1.0267(9)	3.0(3)
C(8)	0.097(1)	0.0568(8)	1.073(1)	3.9(4)
C(9)	0.363(1)	0.0485(7)	1.0063(9)	3.0(3)
C(10)	0.324(1)	0.0250(8)	0.9172(9)	3.9(4)
C(11)	0.321(1)	0.1413(8)	1.1634(8)	3.1(3)
C(12)	0.391(2)	0.078(1)	1.202(1)	5.9(5)
C(13)	0.933(1)	0.2805(8)	0.833(1)	3.2(3)
C(14)	0.993(1)	0.298(1)	0.745(1)	4.7(4)
C(15)	0.727(1)	0.3493(7)	0.7538(8)	2.9(3)
C(16)	0.756(2)	0.4299(8)	0.7911(9)	3.8(4)
C(17)	0.754(1)	0.1890(7)	0.7429(9)	3.1(3)
C(18)	0.811(2)	0.1119(8)	0.771(1)	4.5(4)

[a]Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}$.

non-hydrogen atoms were located by an alternating series of Fourier maps and least-squares refinement cycles. The model was refined to convergence with all Rh, Br and P atoms having anisotropic thermal parameters. Hydrogen atoms were not included in the refined model. Table 6 lists the final positional parameters.

1,5,6-$Rh_2Br_6(PBu_3)_3$ (6)

Preliminary examination of an orange crystal and systematic absences led to the space group $P2_1/c$. Positions of all atoms heavier than carbon were found by direct methods (SHELXS 86), and the remaining non-hydrogen atoms were found in a series of alternating difference Fourier maps and least-squares cycles. The γ and δ carbon atoms in the butyl groups had large thermal motions and tended to give unusual C–C distances. These were refined with restrained C–C (1.54 Å) distances (along with constrained P–C (1.85 Å) distances). However, no actual disorder was seen. Hydrogen atoms were not included in the model. The final atomic positional and isotropic equivalent displacement parameters are listed in Table 7.

1,3,6,8-$Rh_2Br_6(PBu_3)_4$ (7)

A red–brown crystal was mounted on a glass fiber with epoxy cement. Preliminary examination showed that the unit cell was monoclinic and C-centered. Choice of the centrosymmetric monoclinic space group $C2/c$ revealed the correct positions of the rhodium, bromine and phosphorous atoms via Patterson maps. The rest of the structure was developed by alternating difference Fourier maps and least-squares cycles. The γ and δ carbon atoms of the PBu_3 group generally seemed to

TABLE 6. Positional and isotropic equivalent thermal parameters (Å) and their e.s.d.s for 1,5,6-$Rh_2Br_6(PPr^n{}_3)_3$ (**5**)

Atom	x	y	z	B_{iso} (Å^2)[a]
Rh(1)	0.0899(1)	0.86122(7)	0.12637(5)	3.46(2)
Rh(2)	−0.0824(1)	0.70023(7)	0.09890(5)	3.41(2)
Br(1)	−0.1290(1)	0.84128(9)	0.07133(7)	4.35(4)
Br(2)	0.0096(1)	0.76635(9)	0.19928(6)	4.11(3)
Br(3)	0.1284(1)	0.73307(9)	0.06643(7)	4.35(3)
Br(4)	0.1573(2)	0.9449(1)	0.04666(7)	5.43(4)
Br(5)	−0.0081(2)	0.5680(1)	0.12995(7)	5.25(4)
Br(6)	−0.2813(2)	0.6797(1)	0.14180(8)	5.58(4)
P(1)	0.2799(4)	0.8539(2)	0.1766(2)	4.12(9)
P(2)	0.0249(4)	0.9762(2)	0.1690(2)	4.13(9)
P(3)	−0.1605(4)	0.6482(2)	0.0136(2)	3.67(9)
C(1)	0.359(1)	0.7557(9)	0.1738(7)	5.2(4)*
C(2)	0.312(2)	0.689(1)	0.2102(9)	8.2(5)*
C(3)	0.406(2)	0.619(1)	0.209(1)	9.0(6)*
C(4)	0.399(2)	0.921(1)	0.1511(8)	6.1(4)*
C(5)	0.536(2)	0.388(1)	0.4026(9)	7.5(5)*
C(6)	0.451(2)	0.457(1)	0.424(1)	9.0(6)*
C(7)	0.273(1)	0.8744(9)	0.2566(7)	4.9(3)*
C(8)	0.405(2)	0.614(2)	0.788(1)	11.5(8)*
C(9)	0.393(2)	0.577(1)	0.846(1)	10.7(7)*
C(10)	0.142(2)	1.052(1)	0.1975(8)	6.3(4)*
C(11)	0.184(2)	0.394(1)	0.6525(9)	8.2(5)*
C(12)	0.280(2)	0.331(1)	0.685(1)	9.6(6)*
C(13)	0.087(1)	0.5306(8)	0.3795(6)	4.0(3)*
C(14)	0.138(2)	0.608(1)	0.3501(8)	5.9(4)*
C(15)	0.245(2)	0.643(1)	0.3913(8)	6.9(5)*
C(16)	0.053(1)	0.4575(9)	0.2639(7)	4.8(3)*
C(17)	0.186(1)	0.423(1)	0.2737(7)	5.5(4)*
C(18)	0.228(2)	0.399(1)	0.2127(9)	7.3(5)*
C(19)	−0.241(1)	0.5508(9)	0.0206(7)	4.6(3)*
C(20)	0.299(2)	0.482(1)	0.0376(8)	6.3(4)*
C(21)	0.364(2)	0.564(1)	0.0267(8)	6.2(4)*
C(22)	−0.039(1)	0.6235(8)	−0.0355(6)	4.1(3)*
C(23)	0.010(1)	0.308(1)	0.0766(7)	5.6(4)*
C(24)	0.100(2)	0.663(1)	0.8879(9)	7.6(5)*
C(25)	0.268(1)	0.2875(9)	0.0314(7)	5.0(4)*
C(26)	0.390(2)	0.272(1)	0.0029(8)	6.8(4)*
C(27)	0.477(2)	0.221(1)	0.049(1)	9.1(6)*

[a] Starred atoms were refined anisotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}$.

have large thermal motions and some of them were refined isotropically. Even so, three carbon atoms were disordered and were subsequently refined isotropically at two positions each with one half multiplicity. The hydrogen atoms were not included in the model. The final difference Fourier map showed no significant peaks. The atomic positional and isotropic equivalent displacement parameters are listed in Table 8.

TABLE 7. Positional and isotropic equivalent displacement parameters and their e.s.d.s for $Rh_2Br_6(PBu_3)_3$ (**6**)

Atom	x	y	z	B (Å^2)
Rh(1)	−0.0904(3)	0.1505(1)	−0.1707(2)	4.1(1)
Rh(2)	0.0059(3)	0.1447(1)	0.0474(2)	4.5(1)
Br(1)	−0.1236(4)	0.0761(1)	−0.2589(3)	5.4(2)
Br(2)	−0.1168(4)	0.1790(2)	0.1066(3)	6.1(2)
Br(3)	0.1872(4)	0.1886(2)	0.1591(3)	6.0(2)
Br(4)	−0.0492(4)	0.2189(1)	−0.0658(3)	5.1(2)
Br(5)	0.1082(4)	0.1150(1)	−0.0344(3)	4.8(2)
Br(6)	−0.1769(4)	0.1074(1)	−0.0802(3)	5.3(2)
P(1)	0.054(1)	0.0803(4)	0.1376(7)	5.2(5)
P(2)	−0.2722(9)	0.1861(4)	−0.2662(7)	4.8(4)
P(3)	0.013(1)	0.1798(4)	−0.2384(7)	5.0(5)
C(1)	0.179(3)	0.044(1)	0.147(3)	7(2)
C(2)	0.305(4)	0.067(2)	0.199(3)	8(2)
C(3)	0.390(4)	0.026(2)	0.205(4)	15(3)
C(4)	0.498(7)	0.040(3)	0.262(5)	20(5)
C(5)	−0.061(2)	0.0341(9)	0.104(2)	5.5(9)*
C(6)	−0.174(3)	0.049(1)	0.110(3)	8(2)
C(7)	−0.259(5)	0.005(2)	0.074(4)	13(3)
C(8)	−0.349(6)	0.013(3)	0.107(5)	21(3)*
C(9)	0.096(4)	0.096(1)	0.252(1)	6(2)
C(10)	0.114(3)	0.052(1)	0.312(2)	6(1)*
C(11)	0.127(4)	0.063(1)	0.404(2)	9(1)*
C(12)	0.137(5)	0.016(2)	0.453(3)	12(3)
C(13)	−0.360(3)	0.157(1)	−0.376(3)	6(2)
C(14)	−0.424(4)	0.115(2)	−0.369(3)	9(2)
C(15)	−0.487(8)	0.093(4)	−0.443(6)	24(4)*
C(16)	−0.478(7)	0.082(3)	−0.526(6)	21(3)*
C(17)	−0.259(3)	0.251(1)	−0.289(3)	7(2)
C(18)	−0.385(3)	0.275(1)	−0.351(3)	7(2)
C(19)	−0.380(3)	0.330(2)	−0.354(3)	7(2)
C(20)	−0.510(4)	0.351(2)	−0.426(3)	9(2)
C(21)	−0.387(3)	0.187(1)	−0.229(3)	6(2)
C(22)	−0.357(3)	0.222(2)	−0.152(3)	7(2)
C(23)	−0.487(6)	0.224(2)	−0.165(4)	17(2)*
C(24)	−0.478(6)	0.270(2)	−0.112(4)	17(2)*
C(25)	0.080(4)	0.240(1)	−0.195(3)	6(2)
C(26)	0.188(3)	0.241(2)	−0.098(3)	6(2)
C(27)	0.203(5)	0.294(2)	−0.065(3)	10(2)
C(28)	0.294(4)	0.294(2)	0.025(4)	11(2)
C(29)	0.142(3)	0.138(1)	−0.216(2)	5(2)
C(30)	0.218(4)	0.159(1)	−0.257(3)	6(2)
C(31)	0.319(4)	0.120(2)	−0.244(4)	14(3)
C(32)	0.259(7)	0.084(3)	−0.290(5)	19(3)*
C(33)	−0.070(3)	0.189(1)	−0.359(1)	6(2)
C(34)	−0.091(4)	0.144(1)	−0.418(2)	6(2)
C(35)	−0.131(5)	0.158(1)	−0.515(2)	13(4)
C(36)	−0.168(4)	0.112(2)	−0.573(3)	10(2)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

Results and discussion

Preparation

All of the reported compounds are easy to prepare, simply by combining the rhodium halide with the phosphine in the appropriate mole ratio. While in many

TABLE 8. Positional and isotropic equivalent displacement parameters and their e.s.d.s for $Rh_2Br_6(PBu_3)_4$ (**8**)

Atom	x	y	z	B (Å^2)
Rh(1)	0.000	0.18213(8)	0.250	3.43(4)
Rh(2)	0.000	0.37039(8)	0.250	3.40(4)
Br(1)	−0.0984(1)	0.27254(7)	0.26740(8)	4.01(4)
Br(2)	0.1054(1)	0.10000(8)	0.2337(1)	5.89(5)
Br(3)	0.0759(1)	0.37358(8)	0.36865(9)	4.67(4)
P(1)	−0.0635(3)	0.1738(2)	0.1347(2)	4.8(1)
P(2)	0.1037(3)	0.4437(2)	0.2376(2)	4.1(1)
C(1)	−0.073(1)	0.0888(8)	0.1059(9)	6.3(5)
C(2)	−0.118(1)	0.0847(8)	0.0301(9)	7.2(6)
C(3)	−0.126(2)	0.0098(9)	0.016(1)	8.8(7)
C(4)	−0.165(2)	0.005(1)	−0.059(1)	10.5(8)
C(5)	−0.005(1)	0.2123(8)	0.0771(8)	5.6(5)
C(6)	0.084(1)	0.1803(9)	0.077(1)	8.2(6)
C(7)	0.129(1)	0.220(1)	0.029(1)	12.1(8)
C(8)	0.094(3)	0.199(2)	−0.034(2)	11(2)*
C(8)′	0.171(5)	0.184(3)	−0.003(3)	17(2)*
C(9)	−0.173(1)	0.2106(8)	0.1041(9)	5.9(5)
C(10)	−0.247(1)	0.1774(9)	0.128(1)	7.5(6)
C(11)	−0.330(2)	0.217(1)	0.095(1)	11.1(8)*
C(12)	−0.396(3)	0.182(2)	0.093(2)	22(2)*
C(13)	0.110(1)	0.5134(7)	0.2918(8)	5.6(5)
C(14)	0.134(1)	0.5787(7)	0.2630(8)	5.7(5)
C(15)	0.140(2)	0.6304(8)	0.324(1)	8.7(7)
C(16)	0.183(3)	0.693(2)	0.308(2)	10(1)*
C(16)′	0.142(2)	0.701(2)	0.292(2)	5.8(9)*
C(17)	0.097(1)	0.4740(8)	0.1538(8)	5.8(5)
C(18)	0.128(1)	0.423(1)	0.1090(8)	7.4(6)
C(19)	0.111(2)	0.457(2)	0.039(2)	16(1)*
C(20)	0.125(3)	0.420(2)	−0.003(2)	25(2)*
C(21)	0.2143(9)	0.4056(7)	0.2606(9)	5.5(5)
C(22)	0.285(1)	0.4523(9)	0.255(1)	7.1(6)
C(23)	0.374(1)	0.417(1)	0.259(1)	9.8(8)
C(24)	0.406(4)	0.378(3)	0.305(3)	16(2)*
C(24)′	0.376(3)	0.373(2)	0.205(2)	7(1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

cases the rhodium halide was dried prior to dissolving it in ethanol this precaution does not actually seem to be necessary. In the case of **2**, the preparation began with 1,5,6-$Rh_2Cl_6(PEt_3)_3$, which reacted rapidly with an additional mole of phosphine. As we shall show in a later report, the following equilibrium is very labile and product control in these preparations is effected simply by adjusting the ratio of phosphine to RhX_3 in solution.

$$Rh_2Cl_6(PR_3)_3 + PR_3 \rightleftharpoons Rh_2Cl_6(PR_3)_4$$

Structures

Tables 9–15 give the principal molecular dimensions for the seven compounds and Figs. 1–7 show the structures. Table 16 lists several key bond lengths, averaged over equivalent bonds for all the known structures. It is to be noted that for both the ESBO and FSBO compounds, several isomers are possible, but only one is seen. We shall show in a future report that these same isomers persist, exclusively, in solution.

TABLE 9. Selected bond distances (Å) and angles (°) for 1,5,6-$Rh_2Cl_6(PEt_3)_3$ (**1**)

Rh(1)–Cl(1)	2.475(2)	Rh(2)–Cl(1)	2.368(2)
Rh(1)–Cl(2)	2.344(2)	Rh(2)–Cl(2)	2.610(1)
Rh(1)–Cl(3)	2.509(2)	Rh(2)–Cl(3)	2.369(2)
Rh(1)–Cl(4)	2.313(2)	Rh(2)–Cl(5)	2.316(2)
Rh(1)–P(1)	2.278(2)	Rh(2)–Cl(6)	2.316(2)
Rh(1)–P(2)	2.285(2)	Rh(2)–P(3)	2.240(2)
Cl(1)–Rh(1)–Cl(2)	84.31(5)	Cl(1)–Rh(2)–Cl(2)	80.91(5)
Cl(1)–Rh(1)–Cl(3)	78.83(5)	Cl(1)–Rh(2)–Cl(3)	83.84(5)
Cl(1)–Rh(1)–Cl(4)	90.65(6)	Cl(1)–Rh(2)–Cl(5)	173.83(6)
Cl(2)–Rh(1)–Cl(3)	82.87(5)	Cl(1)–Rh(2)–Cl(6)	92.78(6)
Cl(2)–Rh(1)–Cl(4)	172.54(6)	Cl(2)–Rh(2)–Cl(3)	80.24(5)
Cl(3)–Rh(1)–Cl(4)	90.76(6)	Cl(2)–Rh(2)–Cl(5)	93.43(6)
Cl(1)–Rh(1)–P(1)	172.44(6)	Cl(2)–Rh(2)–Cl(6)	92.68(6)
Cl(1)–Rh(1)–P(2)	91.53(6)	Cl(3)–Rh(2)–Cl(5)	92.82(6)
Cl(2)–Rh(1)–P(1)	95.03(5)	Cl(3)–Rh(2)–Cl(6)	172.53(6)
Cl(2)–Rh(1)–P(2)	92.07(6)	Cl(5)–Rh(2)–Cl(6)	89.93(6)
Cl(3)–Rh(1)–P(1)	93.61(6)	Cl(1)–Rh(2)–P(3)	93.59(6)
Cl(3)–Rh(1)–P(2)	169.48(6)	Cl(2)–Rh(2)–P(3)	172.95(6)
Cl(4)–Rh(1)–P(1)	89.24(6)	Cl(3)–Rh(2)–P(3)	94.86(6)
Cl(4)–Rh(1)–P(2)	93.58(6)	Cl(5)–Rh(2)–P(3)	91.85(6)
P(1)–Rh(1)–P(2)	96.02(6)	Cl(6)–Rh(2)–P(3)	91.99(6)
Rh(1)–Cl(1)–Rh(2)	82.82(5)	Rh(1)–Cl(2)–Rh(2)	80.40(4)
Rh(1)–Cl(3)–Rh(2)	82.07(5)		

TABLE 10. Selected bond distances (Å) and angles (°) for 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ (**2**)

Rh(1)–Cl(1)	2.328(5)	Rh(2)–Cl(3)	2.515(4)
Rh(1)–Cl(2)	2.332(5)	Rh(2)–Cl(4)	2.528(4)
Rh(1)–Cl(3)	2.375(4)	Rh(2)–Cl(5)	2.339(8)
Rh(1)–Cl(4)	2.368(4)	Rh(2)–Cl(6)	2.30(1)
Rh(1)–P(1)	2.36(1)	Rh(2)–P(3)	2.277(4)
Rh(1)–P(2)	2.42(1)	Rh(2)–P(4)	2.278(5)
Cl(1)–Rh(1)–Cl(2)	91.9(2)	Cl(3)–Rh(2)–Cl(4)	77.3(1)
Cl(1)–Rh(1)–Cl(3)	175.7(2)	Cl(3)–Rh(2)–Cl(5)	90.6(5)
Cl(1)–Rh(1)–Cl(4)	92.6(2)	Cl(3)–Rh(2)–Cl(6)	91.1(5)
Cl(1)–Rh(1)–P(1)	86.2(5)	Cl(3)–Rh(2)–P(3)	92.1(1)
Cl(1)–Rh(1)–Cl(2)	87.5(5)	Cl(3)–Rh(2)–P(4)	170.7(2)
Cl(2)–Rh(1)–Cl(3)	92.3(2)	Cl(4)–Rh(2)–Cl(5)	88.9(4)
Cl(2)–Rh(1)–Cl(4)	175.55(2)	Cl(4)–Rh(2)–Cl(6)	90.6(4)
Cl(2)–Rh(1)–P(1)	89.0(6)	Cl(4)–Rh(2)–P(3)	169.2(2)
Cl(2)–Rh(1)–P(2)	86.5(6)	Cl(4)–Rh(2)–P(4)	93.4(2)
Cl(3)–Rh(1)–Cl(4)	83.2(1)	Cl(5)–Rh(2)–Cl(6)	178.0(2)
Cl(3)–Rh(1)–P(1)	93.2(5)	Cl(5)–Rh(2)–P(3)	89.6(6)
Cl(3)–Rh(1)–P(2)	93.4(5)	Cl(5)–Rh(2)–P(4)	89.6(6)
Cl(4)–Rh(1)–P(1)	92.1(4)	Cl(6)–Rh(2)–P(3)	91.2(6)
Cl(4)–Rh(1)–P(2)	92.9(4)	Cl(6)–Rh(2)–P(4)	88.5(6)
P(1)–Rh(1)–P(2)	172.2(2)	P(3)–Rh(2)–P(4)	97.2(2)
Rh(1)–Cl(1)–Rh(2)	99.8(1)	Rh(1)–Cl(2)–Rh(2)	99.7(1)

For an $M_2X_6L_3$ compound having the ligands L distributed so that they are not all on one metal atom, there are two possible isomers, 1,4,5 and 1,5,6. All compounds reported here are of the 1,5,6 type. For an $M_2X_6L_4$ compound with two ligands L on each metal

TABLE 11. Selected bond distances (Å) and angles (°) for 1,5,6-$Rh_2Cl_6(PPr^n{}_3)_3$ (**3**)

Rh(1)–Cl(1)	2.493(3)	Rh(2)–Cl(1)	2.367(3)
Rh(1)–Cl(2)	2.348(3)	Rh(2)–Cl(2)	2.527(3)
Rh(1)–Cl(3)	2.516(3)	Rh(2)–Cl(3)	2.369(3)
Rh(1)–Cl(4)	2.311(3)	Rh(2)–Cl(5)	2.296(3)
Rh(1)–P(1)	2.281(3)	Rh(2)–Cl(6)	2.314(3)
Rh(1)–P(2)	2.285(3)	Rh(2)–P(3)	2.238(3)
Cl(1)–Rh(1)–Cl(2)	83.3(1)	Cl(1)–Rh(2)–Cl(2)	82.22(9)
Cl(1)–Rh(1)–Cl(3)	77.08(9)	Cl(1)–Rh(2)–Cl(3)	82.4(1)
Cl(1)–Rh(1)–Cl(4)	93.1(1)	Cl(1)–Rh(2)–Cl(5)	172.6(1)
Cl(1)–Rh(1)–P(1)	169.0(1)	Cl(1)–Rh(2)–Cl(6)	92.1(1)
Cl(1)–Rh(1)–P(2)	91.7(1)	Cl(1)–Rh(2)–P(3)	97.8(1)
Cl(2)–Rh(1)–Cl(3)	82.76(9)	Cl(2)–Rh(2)–Cl(3)	82.1(1)
Cl(2)–Rh(1)–Cl(4)	173.9(1)	Cl(2)–Rh(2)–Cl(5)	91.6(1)
Cl(2)–Rh(1)–P(1)	89.1(1)	Cl(2)–Rh(2)–Cl(6)	90.8(1)
Cl(2)–Rh(1)–P(2)	95.3(1)	Cl(2)–Rh(2)–P(3)	176.8(1)
Cl(3)–Rh(1)–Cl(4)	91.6(1)	Cl(3)–Rh(2)–Cl(5)	92.8(1)
Cl(3)–Rh(1)–P(1)	94.7(1)	Cl(3)–Rh(2)–Cl(6)	171.6(1)
Cl(3)–Rh(1)–P(2)	168.8(1)	Cl(3)–Rh(2)–P(3)	94.7(1)
Cl(4)–Rh(1)–P(1)	93.7(1)	Cl(5)–Rh(2)–Cl(6)	92.0(1)
Cl(4)–Rh(1)–P(2)	89.7(1)	Cl(5)–Rh(2)–P(3)	88.1(1)
P(1)–Rh(1)–P(2)	96.3(1)	Cl(6)–Rh(2)–P(3)	92.3(1)
Rh(1)–Cl(1)–Rh(2)	82.25(9)	Rh(1)–Cl(2)–Rh(2)	81.89(9)
Rh(1)–Cl(3)–Rh(2)	81.72(8)		

TABLE 12. Selected bond distances (Å) and angles (°) for 1,5,6-$Rh_2Br_6(PEt_3)_3$ (**4**)

Rh(1)–Br(1)	2.682(2)	Rh(2)–Br(1)	2.510(2)
Rh(1)–Br(2)	2.480(2)	Rh(2)–Br(2)	2.665(2)
Rh(1)–Br(3)	2.597(2)	Rh(2)–Br(3)	2.490(2)
Rh(1)–Br(4)	2.449(2)	Rh(2)–Br(5)	2.457(2)
Rh(1)–P(1)	2.293(3)	Rh(2)–Br(6)	2.449(2)
Rh(1)–P(2)	2.298(3)	Rh(2)–P(3)	2.251(3)
Br(1)–Rh(1)–Br(2)	80.22(5)	Br(1)–Rh(2)–Br(2)	79.99(5)
Br(1)–Rh(1)–Br(3)	77.53(5)	Br(1)–Rh(2)–Br(3)	82.78(5)
Br(1)–Rh(1)–Br(4)	91.33(5)	Br(1)–Rh(2)–Br(5)	171.72(6)
Br(1)–Rh(1)–P(1)	165.8(1)	Br(1)–Rh(2)–Br(6)	94.76(5)
Br(1)–Rh(1)–P(2)	96.40(9)	Br(1)–Rh(2)–P(3)	95.5(1)
Br(2)–Rh(1)–Br(3)	84.26(5)	Br(2)–Rh(2)–Br(3)	82.66(5)
Br(2)–Rh(1)–Br(4)	171.54(7)	Br(2)–Rh(2)–Br(5)	93.14(5)
Br(2)–Rh(1)–P(1)	95.5(1)	Br(2)–Rh(2)–Br(6)	90.57(5)
Br(2)–Rh(1)–P(2)	90.7(1)	Br(2)–Rh(2)–P(3)	175.3(1)
Br(3)–Rh(1)–Br(4)	94.12(5)	Br(3)–Rh(2)–Br(5)	91.81(5)
Br(3)–Rh(1)–P(1)	88.61(9)	Br(3)–Rh(2)–Br(6)	173.10(6)
Br(3)–Rh(1)–P(2)	172.7(1)	Br(3)–Rh(2)–P(3)	95.5(1)
Br(4)–Rh(1)–P(1)	92.8(1)	Br(5)–Rh(2)–Br(6)	89.89(6)
Br(4)–Rh(1)–P(2)	90.1(1)	Br(5)–Rh(2)–P(3)	91.3(1)
P(1)–Rh(1)–P(2)	97.2(1)	Br(6)–Rh(2)–P(3)	91.1(1)
Rh(1)–Br(1)–Rh(2)	81.47(5)	Rh(1)–Br(2)–Rh(2)	82.37(5)
Rh(1)–Br(3)–Rh(2)	83.57(5)		

TABLE 13. Selected bond distances (Å) and angles (°) for 1,5,6-$Rh_2Br_6(PPr^n{}_3)_3$ (**5**)

Rh(1)–Br(1)	2.622(2)	Rh(2)–Br(1)	2.494(2)
Rh(1)–Br(2)	2.507(2)	Rh(2)–Br(2)	2.676(2)
Rh(1)–Br(3)	2.602(2)	Rh(2)–Br(3)	2.512(2)
Rh(1)–Br(4)	2.455(2)	Rh(2)–Br(5)	2.450(2)
Rh(1)–P(1)	2.286(4)	Rh(2)–Br(6)	2.455(2)
Rh(1)–P(2)	2.296(4)	Rh(2)–P(3)	2.246(4)
Br(1)–Rh(1)–Br(2)	83.87(6)	Br(1)–Rh(2)–Br(2)	83.01(6)
Br(1)–Rh(1)–Br(3)	79.36(6)	Br(1)–Rh(2)–Br(3)	83.57(6)
Br(1)–Rh(1)–Br(4)	91.38(6)	Br(1)–Rh(2)–Br(5)	172.23(7)
Br(1)–Rh(1)–P(1)	169.5(1)	Br(1)–Rh(2)–Br(6)	93.85(7)
Br(1)–Rh(1)–P(2)	91.0(1)	Br(1)–Rh(2)–P(3)	95.4(1)
Br(2)–Rh(1)–Br(3)	84.32(6)	Br(2)–Rh(2)–Br(3)	82.71(6)
Br(2)–Rh(1)–Br(4)	173.77(7)	Br(2)–Rh(2)–Br(5)	91.95(6)
Br(2)–Rh(1)–P(1)	88.5(1)	Br(2)–Rh(2)–Br(6)	89.89(6)
Br(2)–Rh(1)–P(2)	96.9(1)	Br(2)–Rh(2)–P(3)	178.4(1)
Br(3)–Rh(1)–Br(4)	90.86(7)	Br(3)–Rh(2)–Br(5)	89.94(7)
Br(3)–Rh(1)–P(1)	92.7(1)	Br(3)–Rh(2)–Br(6)	172.40(7)
Br(3)–Rh(1)–P(2)	170.1(1)	Br(3)–Rh(2)–P(3)	97.0(1)
Br(4)–Rh(1)–P(1)	95.7(1)	Br(5)–Rh(2)–Br(6)	92.04(7)
Br(4)–Rh(1)–P(2)	87.1(1)	Br(5)–Rh(2)–P(3)	89.6(1)
P(1)–Rh(1)–P(2)	97.1(1)	Br(6)–Rh(2)–P(3)	90.3(1)
Rh(1)–Br(1)–Rh(2)	80.84(6)	Rh(1)–Br(2)–Rh(2)	79.55(6)
Rh(1)–Br(3)–Rh(2)	80.92(6)		

atom, there are nine isomers, but only the 1,3,6,8 isomer has been found in this work and in previous work.

While we cannot claim to explain rigorously why only one isomer of each type of compound occurs, it can be said that the observed isomers are the preferred ones on the basis of some simple principles. In the FSBO case, the only principle needed is the assumption that no μ-X ligand should have *both* of its bonds weakened by the *trans* effect of the phosphine ligand (to be discussed below). The 1,5,6 disposition meets this requirement, whereas the alternate 1,4,5 disposition does not.

For the ESBO case we invoke a second principle, namely, that for steric reasons two phosphine ligands should not occupy adjacent axial positions on the two rhodium atoms. Figure 8 shows all of the nine possible isomers for an $M_2X_6L_4$ ESBO. If we call the two principles we have just mentioned I and II, respectively, we can draw up the following list of how many times each of the isomers violates them.

Isomer	Principle I	Principle II
1	0	2
2	2	0
3	0	0
4	1	1
5	0	1
6	1	0
7	0	0
8	1	0
9	0	1

Thus we see that only isomers 3 and 7 are free of violations. Of course, isomer 3 is the one seen, while isomer 7 has not been observed, to our knowledge, for any metal. Clearly, while our two principles go a long way towards accounting for the observations, they are not entirely sufficient.

We turn now to the basis for the first principle, namely, the existence of a marked structural *trans* effect

TABLE 14. Selected bond distances (Å) and angles (°) for $Rh_2Br_6(PBu_3)_3$ (**6**)

Rh(1)–Br(1)	2.462(5)	Rh(1)–P(2)	2.290(9)	Rh(2)–Br(4)	2.670(5)
Rh(1)–Br(4)	2.482(5)	Rh(1)–P(3)	2.300(15)	Rh(2)–Br(5)	2.493(7)
Rh(1)–Br(5)	2.636(4)	Rh(2)–Br(2)	2.449(7)	Rh(2)–Br(6)	2.491(4)
Rh(1)–Br(6)	2.607(7)	Rh(2)–Br(3)	2.465(4)	Rh(2)–P(1)	2.235(11)
Br(1)–Rh(1)–Br(4)	173.0(2)	Br(5)–Rh(1)–P(3)	92.5(3)	Br(3)–Rh(2)–Br(6)	172.6(2)
Br(1)–Rh(1)–Br(5)	91.8(2)	Br(6)–Rh(1)–P(2)	92.5(4)	Br(3)–Rh(2)–P(1)	91.3(3)
Br(1)–Rh(1)–Br(6)	89.8(2)	Br(6)–Rh(1)–P(3)	170.5(3)	Br(4)–Rh(2)–Br(5)	81.9(2)
Br(1)–Rh(1)–P(2)	96.6(3)	P(2)–Rh(1)–P(3)	96.7(4)	Br(4)–Rh(2)–Br(6)	83.3(1)
Br(1)–Rh(1)–P(3)	86.9(3)	Br(2)–Rh(2)–Br(3)	91.8(2)	Br(4)–Rh(2)–P(1)	177.0(4)
Br(4)–Rh(1)–Br(5)	82.8(1)	Br(2)–Rh(2)–Br(4)	91.0(2)	Br(5)–Rh(2)–Br(6)	83.7(2)
Br(4)–Rh(1)–Br(6)	84.8(2)	Br(2)–Rh(2)–Br(5)	171.6(2)	Br(5)–Rh(2)–P(1)	95.2(4)
Br(4)–Rh(1)–P(2)	88.0(3)	Br(2)–Rh(2)–Br(6)	90.8(2)	Br(6)–Rh(2)–P(1)	95.5(3)
Br(4)–Rh(1)–P(3)	97.8(3)	Br(2)–Rh(2)–P(1)	91.7(4)	Rh(1)–Br(4)–Rh(2)	80.2(1)
Br(5)–Rh(1)–Br(6)	78.7(2)	Br(3)–Rh(2)–Br(4)	89.7(2)	Rh(1)–Br(5)–Rh(2)	80.7(2)
Br(5)–Rh(1)–P(2)	167.8(4)	Br(3)–Rh(2)–Br(5)	92.8(2)	Rh(1)–Br(6)–Rh(2)	81.3(2)

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 15. Selected bond distances (Å) and angles (°) for $Rh_2Br_6(PBu_3)_4$ (**7**)

Rh(1)–Br(1)	2.518(2)	Rh(1)–P(1)	2.386(5)	Rh(2)–Br(3)	2.487(2)
Rh(1)–Br(2)	2.461(2)	Rh(2)–Br(1)	2.635(2)	Rh(2)–P(2)	2.294(4)
Br(1)–Rh(1)–Br(1)	83.16(7)	Br(2)–Rh(1)–P(1)	87.2(1)	Br(3)–Rh(2)–Br(3)	176.94(9)
Br(1)–Rh(1)–Br(2)	175.50(7)	P(1)–Rh(1)–P(1)	171.7(2)	Br(3)–Rh(2)–P(2)	84.3(1)
Br(1)–Rh(1)–Br(2)	92.45(6)	Br(1)–Rh(2)–Br(1)	78.69(7)	Br(3)–Rh(2)–P(2)	93.7(1)
Br(1)–Rh(1)–P(1)	93.9(1)	Br(1)–Rh(2)–Br(3)	92.80(6)	P(2)–Rh(2)–P(2)	96.5(2)
Br(1)–Rh(1)–P(1)	92.3(1)	Br(1)–Rh(2)–Br(3)	89.57(6)	Rh(1)–Br(1)–Rh(2)	99.07(6)
Br(2)–Rh(1)–Br(2)	91.95(8)	Br(1)–Rh(2)–P(2)	170.7(1)		
Br(2)–Rh(1)–P(1)	87.0(1)	Br(1)–Rh(2)–P(2)	92.5(1)		

Numbers in parentheses are e.s.d.s in the least significant digits.

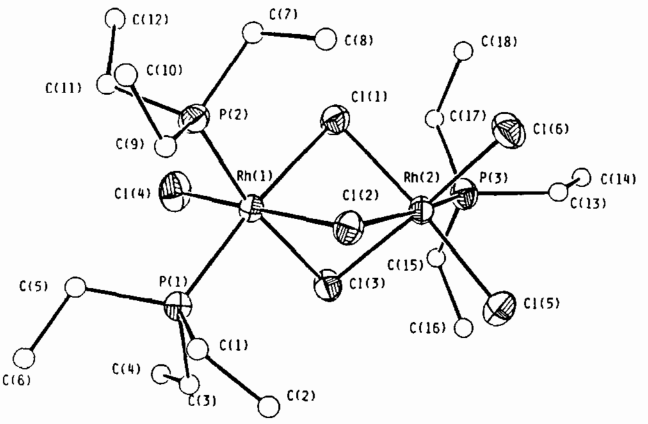

Fig. 1. An ORTEP drawing for 1,5,6-$Rh_2Cl_6(PEt_3)_3$ (**1**).

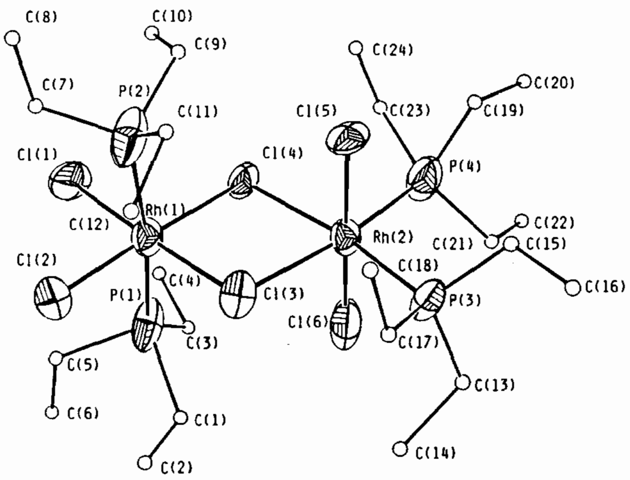

Fig. 2. An ORTEP drawing for 1,3,6,8-$Rh_2Cl_6(PEt_3)_4$ (**2**).

caused by the phosphine ligands. The data collected in Table 16 clearly show that this is of considerable, and consistent, magnitude. In the ESBO structures, the Rh–P bonds for phosphines *trans* to each other are about 0.11 Å longer than those *trans* to X ligands. For all eight molecules, the lengths of the $M–X_{br,L}$ and the $M–X_{br,X}$ bonds differ by 0.12–0.17 Å, the average difference being 0.15 Å. As we will see in later papers dealing with NMR studies of the reactivity of these and related types of compounds, these structural *trans* effects have distinct and important consequences in the stereospecificity of their reactions.

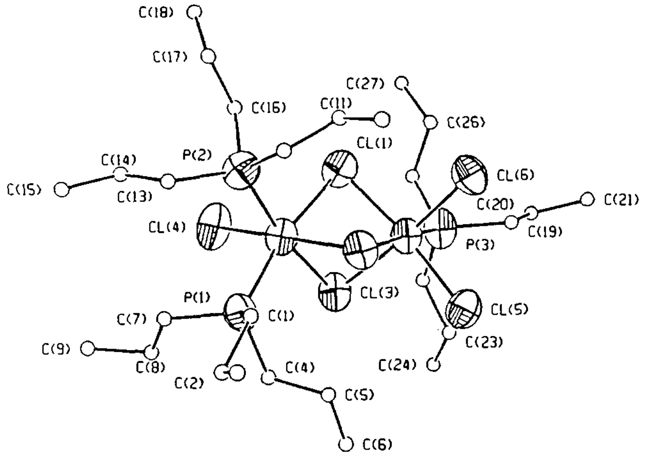

Fig. 3. An ORTEP drawing for 1,5,6-$Rh_2Cl_6(PPr^n_3)_3$ (3).

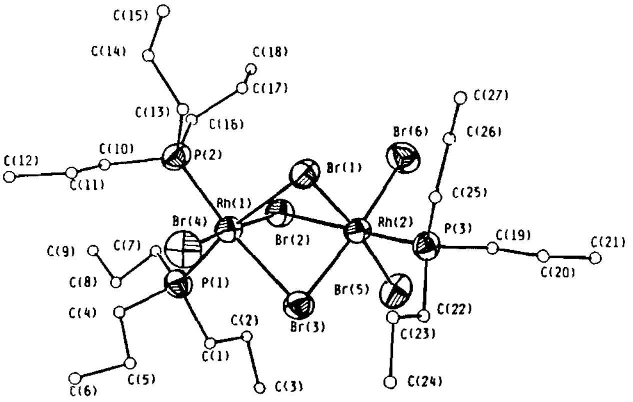

Fig. 5. An ORTEP drawing for 1,5,6-$Rh_2Br_6(PPr^n_3)_3$ (5)

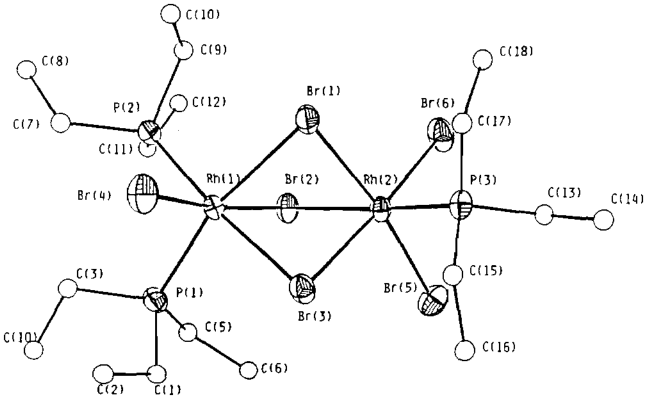

Fig. 4. An ORTEP drawing for 1,5,6-$Rh_2Br_6(PEt_3)_3$ (4).

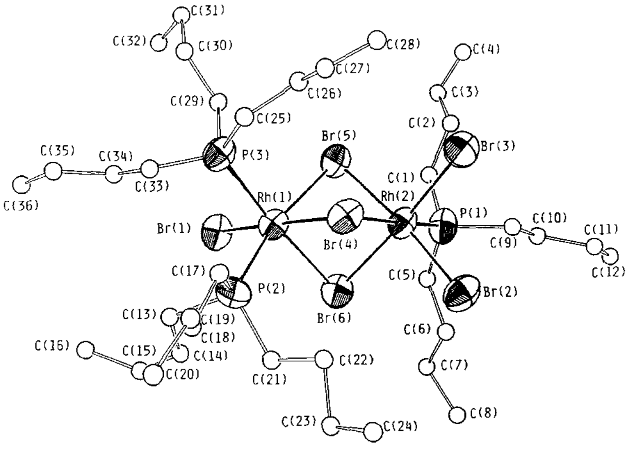

Fig. 6. An ORTEP drawing for 1,5,6-$Rh_2Br_6(PBu_3)_3$ (6).

TABLE 16. Selected bond distances (Å) in ESBO and FSBO structures[a,b]

Compound	Type of bond (Å)				
	M-M	M-X_t	M-$X_{br,L}$	M-$X_{br,x}$	M-L
ESBOs, 1,3,6,8-$Rh_2X_6(PR)_3$					
$Rh_2Cl_6(PEt_3)_4$	3.743(2)	2.32[1]	2.522[6]	2.372[2]	2.39[2] 2.278[5]
$Rh_2Br_6(PBu_3)_4$	3.921(2)	2.47[1]	2.635(2)	2.518(2)	2.386(5) 2.294(4)
FSBOs, 1,5,6-$Rh_2X_6(PR_3)_3$					
$Rh_2Cl_6(PEt_3)_3$	3.19(1)	2.315[2]	2.531[2]	2.360[2]	2.268[2]
$Rh_2Cl_6(PPr^n_3)_3$	3.197(3)	2.307[3]	2.512[3]	2.361[3]	2.268[3]
$Rh_2Cl_6(PBu^n_3)_3$	3.187(4)	2.296[10]	2.513[10]	2.362[10]	2.254[11]
$Rh_2Br_6(PEt_3)_3$	3.319(3)	2.452[2]	2.648[2]	2.493[2]	2.281[3]
$Rh_2Br_6(PPr^n_3)_3$	3.319(2)	2.453[2]	2.633[2]	2.504[2]	2.276[4]
$Rh_2Br_6(PBu^n_3)_3$	3.32(2)	2.459[7]	2.638[7]	2.489[7]	2.275[7]

[a]Averaged over all those of each type in the molecule for the FSBO structures. [b]All data from the present study except those for $Rh_2Cl_6(PBu_3)_3$ which are from ref. 4.

Supplementary data

More detailed lists of bond distances and angles and tables of anisotropic thermal displacement parameters may be obtained from author F. A. Cotton.

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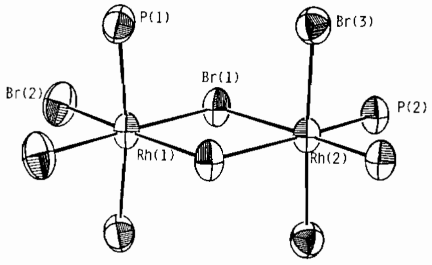
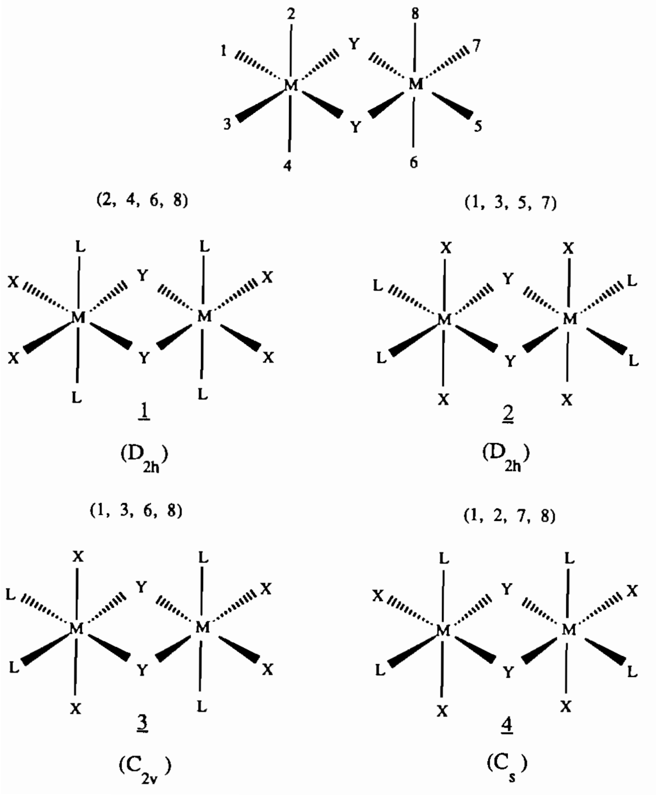


Fig. 7. An ORTEP drawing for 1,3,6,8-$Rh_2Br_6(PBu_3)_4$ (7).



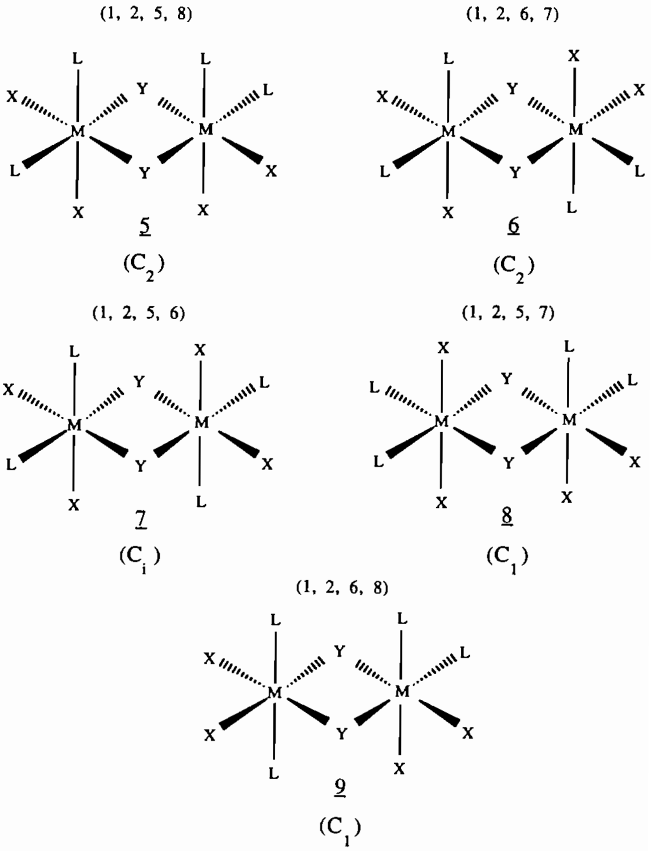


Fig. 8. The nine possible isomers for an $M_2X_6L_4$ ESBO.

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