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Supplementary Material Available: A listing of observed and calculated structure amplitudes (10 pages). Ordering information is given on any current masthead page.

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Dimeric (Pentamethylcyclopentadienyl)rhodium and -iridium Complexes. 4.[1–4] Crystal and Molecular Structure of $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ and of the Partially Halide-Exchanged Species $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$ Obtained by Recrystallization of the Bromo Complex from 1,2-Dichloroethane

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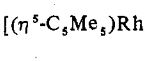
The complex di-μ-bromo-dibromobis(pentamethylcyclopentadienyl)dirhodium, $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$, has been investigated by means of single-crystal X-ray diffraction studies. The complex crystallizes from acetone in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 8.755$ (1) Å, $b = 8.943$ (2) Å, $c = 16.137$ (3) Å, $\alpha = 91.40$ (2)°, $\beta = 104.86$ (1)°, $\gamma = 93.58$ (1)°, $V = 1217.7$ (4) Å^3, ρ(obsd) = 2.26 (2) and ρ(calcd) = 2.17 g cm^{-3} for $Z = 2$ (dimers), and mol wt 795.88. Each molecule lies on a center of symmetry; the asymmetric unit consists of two independent half-molecules of the title compound. Diffraction data were collected with a Syntex $P2_1$ diffractometer and the structure was solved via Patterson, difference-Fourier, and least-squares refinement techniques yielding $R_F = 5.1\%$ and $R_{wF} = 2.7\%$ for all 3208 independent reflections with $4° < 2\theta < 45°$ (Mo Kα radiation). All atoms, including hydrogens, were located and refined. Rhodium···rhodium distances in the two independent molecules are 3.854 (1) and 3.841 (1) Å as compared to 3.7191 (6) Å in the chloro complex $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$. Rhodium–(terminal bromide) distances are 2.523 (1) and 2.532 (1) Å, while rhodium–(bridging bromide) linkages are 2.577 (1) and 2.587 (1) Å in molecule I and 2.566 (1) and 2.575 (1) Å in molecule II. The two Rh–Br–Rh bridge angles are 96.54 (3) and 96.70 (3)°. Recrystallization of $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ from 1,2-dichloroethane was found to result in halogen exchange, the crystal actually studied having the approximate net composition (as determined by an X-ray diffraction study) $[(\eta^5\text{-}C_5Me_5)RhCl_{0.67}Br_{0.33}]_2(\mu\text{-}Cl_{0.95}Br_{0.05})_2$. This species crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 8.430$ (1) Å, $b = 9.253$ (1) Å, $c = 15.760$ (2) Å, $\beta = 106.83$ (1)°, $V = 1176.7$ Å^3, ρ(obsd) = 1.831 (12) g cm^{-3}, and $Z = 2$. Diffraction data (two forms, complete to $2\theta = 45°$, using Mo Kα radiation) were collected with a Syntex $P2_1$ diffractometer, and the structure was refined to $R_F = 4.4\%$ and $R_{wF} = 5.1\%$ for those 1479 independent reflections with $|F_o| > 0$. The crystals are isomorphous with those of the pure complex $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$, and the structure elucidated shows only small differences relative to the chloro complex.

Introduction

We have previously reported the results of X-ray structural analyses of the species $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$,[2] $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$,[3] $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$,[4] and $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$.[4] We have now extended these studies to $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$, a complex previously reported by Gill and Maitlis.[5]

Experimental Section

Our first sample of $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ was prepared directly from the reaction of rhodium(III) bromide dihydrate (Chemical Procurement Laboratories) and hexamethyl(Dewar benzene) (Aldrich) in methanol (eq 1). The complex was recrystallized from 1,2-dichloroethane. [We note here that Gill and Maitlis recrystallized this species from chloroform/benzene[5] and that the recrystallization of $[(\eta^5\text{-}C_5Me_5)RhI]_2(\mu\text{-}I)_2$ from chloroform/methanol appears in the literature.[6]] Unfortunately (but, perhaps, interestingly), this "recrystallization" step results in halide exchange between the bromide and the 1,2-dichloroethane. A crystal structure of the resulting "$[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$" was performed and the details appear below.

2 

$$+ 2RhBr_3\cdot 2H_2O + 4MeOH \rightarrow$$

$$[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2 + 2MeCH(OMe)_2 + 2HBr + 4H_2O \quad (1)$$

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Our second sample of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhBr}]_2(\mu\text{-Br})_2$ was prepared from $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}]_2(\mu\text{-Cl})_2$[6] by metathesis with sodium bromide (eq 2). The chloro complex was dissolved in acetone and a 25-fold excess

$$[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}]_2(\mu\text{-Cl})_2 + 4\text{NaBr} \rightarrow [(\eta^5\text{-C}_5\text{Me}_5)\text{RhBr}]_2(\mu\text{-Br})_2 + 4\text{NaCl} \quad (2)$$

of NaBr was added; the solution was refluxed for 24 h, the acetone was removed, and the sodium bromide and chloride were removed by washing with water. This process was repeated three times and the product was recrystallized from acetone. This material is bona fide $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhBr}]_2(\mu\text{-Br})_2$, and a complete crystal structure analysis of this material has also been carried out.

Each of the materials is stable indefinitely in the solid state and does not decompose upon exposure to air or X-rays.

Collection and Reduction of X-ray Diffraction Data

All data collection and crystallographic calculations were performed using a Syntex $P2_1$ four-circle diffractometer in conjunction with the Syntex XTL system.[7] The latter consists of (a) a Data General NOVA 1200 computer with 24K of 16-bit word memory and with a parallel floating-point processor for 32- or 64-bit arithmetic, (b) a Diablo moving-head disk unit with 1.2 million 16-bit words, (c) a Versatec electrostatic printer/plotter, and (d) a locally modified version of the XTL interactive (conversational) crystallographic program package.

(1) $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhX}]_2(\mu\text{-X}')_2$. The crystal selected for the structural investigation was a red parallelepiped of approximate dimensions 0.24 × 0.18 × 0.18 mm. It was mounted on a thin glass fiber and fixed into a eucentric goniometer. The crystal was centered in a random orientation (with $[1\bar{4}6]$ ~2.4° from coincidence with the ϕ axis) on a Syntex $P2_1$ diffractometer. Measurement of unit cell parameters and data collection were carried out as described previously;[8] details are given in Table I.

(2) $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhBr}]_2(\mu\text{-Br})_2$. A beautiful red parallelepiped of dimensions 0.18 × 0.17 × 0.17 mm was mounted and aligned (with $[4\bar{3}9]$ offset by ~0.6° from the ϕ axis) on a Syntex $P2_1$ diffractometer. Axial photographs revealed C_i Laue symmetry; details of unit cell parameters and data collection appear in Table I.

Solution and Refinement of the Structures

Following correction for absorption and the merging of symmetry-equivalent reflections (see Table I), all data were corrected for Lorentz and polarization effects, the form of the Lp factor being that given in eq 3 and applied to the absorption-corrected intensities (I_{abscor})

$$Lp = \frac{0.5}{\sin 2\theta}\left[\left(\frac{1 + \cos^2 2\theta_{\text{M}} \cos^2 2\theta}{1 + \cos^2 2\theta_{\text{M}}}\right) + \left(\frac{1 + |\cos 2\theta_{\text{M}}| \cos^2 2\theta}{1 + |\cos 2\theta_{\text{M}}|}\right)\right] \quad (3)$$

as shown in eq 4. Equation 3 assumes that the equatorially mounted

$$|F_{\text{o}}|^2 = I_{\text{abscor}}/Lp \quad (4)$$

graphite monochromator is 50% mosaic and 50% perfect; $2\theta_{\text{M}}$, the monochromator angle, is 12.2° for Mo $K\bar{\alpha}$ radiation.

Data were converted to an (approximate) absolute scale by means of a Wilson plot.

For obtaining F_c values, we used the *analytical* scattering factors of Cromer and Mann[9a] for the appropriate *neutral* atoms; real and imaginary components of anomalous dispersion[9b] were applied to all nonhydrogen atoms. Discrepancy indices used below are defined in eq 5 and 6. The weights used in (6) are those obtained from counting

$$R_F = \left[\frac{\sum ||F_{\text{o}}| - |F_{\text{c}}||}{\sum |F_{\text{o}}|}\right] \times 100\ (\%) \quad (5)$$

$$R_{wF} = \left[\frac{\sum w(|F_{\text{o}}| - |F_{\text{c}}|)^2}{\sum w|F_{\text{o}}|^2}\right]^{1/2} \times 100\ (\%) \quad (6)$$

statistics, modified by an "ignorance factor" (p) (see eq 7). The final

$$w = \{[\sigma_{\text{c}}(F)]^2 + [pF_{\text{o}}]^2\}^{-1} \quad (7)$$

values for p (which may easily be changed under the XTL system) were 0.015 for the mixed-halide complex and 0.005 for the "pure-bromo" species.

Table I. Details of Data Collection for "$[(\eta^5\text{-C}_5\text{Me}_5)\text{RhX}]_2(\mu\text{-X}')_2$" and $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhBr}]_2(\mu\text{-Br})_2$

	$(\text{RhX})_2(\mu\text{-X}')_2$ complex	$(\text{RhBr})_2(\mu\text{-Br})_2$ complex
	(A) Crystal Parameters	
cryst system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	8.4298 (9)[a]	8.7548 (14)[b]
b, Å	9.2530 (10)[a]	8.9428 (15)[b]
c, Å	15.7602 (23)[a]	16.1374 (34)[b]
α, deg		91.402 (15)[b]
β, deg	106.828 (10)[a]	104.857 (14)[b]
γ, deg		93.581 (13)[b]
V, Å^3	1176.7 (2)	1217.7 (4)
Z	2 (dimers)	2 (dimers)
mol wt	c	795.88
ρ(obsd) g cm^{-3}	1.831 (12)[d]	2.26 (2)[d]
ρ(calcd), g cm^{-3}	c	2.170
temp, °C	24	25.5
	(B) Collection of Intensity Data	
radiation	Mo Kα ($\bar{\lambda}$ 0.710 730 Å)	
monochromator	highly oriented graphite; $2\theta_{\text{M}} = 12.2°$; equatorial mode	
reflections measd	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$
2θ range, deg	3.0–45.0	4.0–45.0
scan type	θ(crystal)–2θ(counter)	
scan speed, deg/min	2.0	2.0
scan range	$[2\theta(\text{K}\alpha_1) - 1.0]° \rightarrow [2\theta(\text{K}\alpha_2) + 1.0]°$	
bkgd measurement	at beginning and end of the 2θ scan; each for one-half of total scan time	at beginning and end of the 2θ scan; each for one-fourth of total scan time
standards	3 every 97 reflections; no significant deviations	
reflections collected	3438 total, leading to 1542 independent reflections	3450 total, leading to 3208 independent reflections
data averaging	$R(I) = 1.93\%$ for 1433 averaged pairs of reflections	
abs coeff	c	84.14 cm^{-1}
reflections used for empirical abs cor[e] (hkl, 2θ, $T_{\text{max}}/T_{\text{min}}$)	$0\bar{1}2$, 6.95°, 1.272 $1\bar{2}3$, 13.87°, 1.281 $0\bar{3}5$, 18.93°, 1.305 $1\bar{3}5$, 20.59°, 1.289 $1\bar{5}6$, 28.87°, 1.326 $2\bar{6}5$, 32.94°, 1.346 $1,\bar{6},11$, 41.96°, 1.257	$1\bar{1}2$, 8.90°, 1.304[f] $\bar{1}1\bar{2}$, 8.90°, 1.301 $2\bar{1}3$, 14.33°, 1.359 $\bar{2}1\bar{3}$, 14.33°, 1.328 $3\bar{2}5$, 23.19°, 1.323 $\bar{3}2\bar{5}$, 23.19°, 1.326 $4\bar{2}6$, 28.90°, 1.322 $\bar{4}2\bar{6}$, 28.90°, 1.369

[a] Based upon a least-squares fit to the setting angles of the unresolved Mo $K\bar{\alpha}$ peaks of 25 reflections with $2\theta = 21–29°$. [b] Based on 24 reflections with $2\theta = 24–30°$. [c] Not *precisely* determinable, since elemental composition subject to error (see text). [d] Not on the actual crystal for which diffraction data were collected. [e] For details of empirical absorption correction see M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, **16**, 2655 (1977). [f] The absorption curves of the Friedel pairs were averaged.

The "goodness of fit" (GOF) is defined in eq 8. Here NO is the

$$\text{GOF} = \left[\frac{\sum w(|F_{\text{o}}| - |F_{\text{c}}|)^2}{\text{NO} - \text{NV}}\right]^{1/2} \quad (8)$$

number of observations and NV is the number of variables.

(1) $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhX}]_2(\mu\text{-X}')_2$. The structural investigation of this material was begun under the mistaken impression that the material was the bromo complex (i.e., X = X' = Br). Solution of the structure was by the trivial means of using the known coordinates of atoms in the isomorphous chloro complex, $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}]_2(\mu\text{-Cl})_2$.[3] Four cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters led to convergence with unexpectedly high re-

Table II. Positional Parameters, with Esd's for Atoms in the $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$ Crystal[a]

atom	x	y	z
Rh	0.18828 (6)	0.03397 (6)	0.09412 (3)
X'(B)[b]	0.10746 (19)	0.01844 (20)	−0.06944 (11)
X(T)[c]	0.25356 (18)	−0.22498 (15)	0.11095 (11)
C(1)	0.2311 (12)	0.2593 (8)	0.1072 (6)
C(2)	0.1888 (9)	0.2012 (11)	0.1869 (7)
C(3)	0.3137 (9)	0.1017 (9)	0.2242 (5)
C(4)	0.4287 (8)	0.1000 (9)	0.1742 (5)
C(5)	0.3821 (10)	0.1872 (10)	0.1043 (5)
C(6)	0.1356 (19)	0.3713 (11)	0.0441 (10)
C(7)	0.0482 (13)	0.2460 (18)	0.2168 (13)
C(8)	0.3349 (17)	0.0168 (13)	0.3111 (6)
C(9)	0.5866 (11)	0.0079 (12)	0.1986 (8)
C(10)	0.4718 (16)	0.2175 (15)	0.0356 (7)

[a] The asymmetric unit consists of one half of a dimeric molecule centered on 0, 0, 0. The positions of atoms in the "other half" of the molecule can be generated by the transformation $(x^*, y^*, z^*) = (-x, -y, -z)$. [b] The bridging atom X'(B) was input as Cl, and its occupancy refined to 1.052 (8). To a first approximation this represents 95.1% Cl–4.9% Br. [c] Input as Cl; final occupancy 1.353 (8), consistent with 66.7% Cl–33.3% Br.

siduals of $R_F = 29.2\%$ and $R_{wF} = 35.6\%$. The use of anisotropic thermal parameters led to convergence and reduction in the discrepancy indices only to $R_F = 13.6\%$ and $R_{wF} = 16.7\%$. Clearly something was seriously wrong with our model! We noted the following points.

(a) The anisotropic thermal parameters for the halogen atoms (which were treated as bromine atoms) were very large, values for the bridging halogen being $B_{11} = 9.0$ Å^2, $B_{22} = 12.7$ Å^2, and $B_{33} = 8.3$ Å^2 as compared to 1.6–2.2 Å^2 for the diagonal elements of the anisotropic thermal parameters of the rhodium atom. Clearly there was disorder or substitution of the bromide ligands.

(b) The unit cell parameters were *very* closely similar to those of the chloro complex, $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$,[3] i.e., $a = 8.430$ (1) vs. 8.375 (1) Å, $b = 9.253$ (1) vs. 9.228 (2) Å, $c = 15.760$ (2) vs. 15.651 (2) Å, $\beta = 106.83$ (1) vs. 106.70 (1)°, and $V = 1176.7$ (2) vs. 1158.6 (3) Å^3.

(c) Measurement of the density of some crystals of our material (but *not* that from which the diffraction data were collected) yielded a value of 1.831 (12) g cm^{-3}—considerably lower than the calculated value of 2.246 g cm^{-3} for $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$, but higher than the value of 1.744 g cm^{-3} calculated for $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$.

(d) A careful analysis of our treatment of the originally synthesized $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ (eq 1) showed that the only material to which it had been exposed was 1,2-dichloroethane. Clearly the material under investigation was a bromide/chloride mixture.

We now returned to the refinement of the crystal structure. The first step was to change our model such that the "occupancies" of the bromine atoms were refined. Four cycles of full-matrix least-squares refinement led to convergence with $R_F = 4.5\%$ and $R_{wF} = 5.2\%$. The resulting occupancies for the halide ligands (treated as bromine atoms) were 0.475 (3) for "Br(B)" and 0.617 (3) for "Br(T)". There is thus more chloride than bromide at each site. We now changed our model so as to use the scattering factor of neutral chlorine for the halogen atoms. Continued full-matrix least-squares refinement led to final convergence with $R_F = 4.4\%$ and $R_{wF} = 5.1\%$ for those 1479 reflections with $|F_o| > 0$ and $R_F = 4.7\%$ and $R_{wF} = 5.2\%$ for all 1542 reflections. The "goodness of fit", GOF, was 1.92.

The refined occupancies for the halide ligands (now input to the model as chlorine atoms) were 1.052 (8) for "Cl(B)" and 1.353 (8) for "Cl(T)". Assuming that the scattering curves for chlorine and bromine remain as the ratio of their atomic numbers over the range $3° < 2\theta < 45°$ and that x is the fraction of bromide at the terminal site, we may set up eq 9 to determine x. This yields a value of $x =$

$$x[Z(\mathrm{Br})] + (1 - x)[Z(\mathrm{Cl})] = 1.353[Z(\mathrm{Cl})] \qquad (9)$$

0.333. Applying this to the bridging position yields $x' = 0.049$. The formula of the material studied is thus found to be approximately $[(\eta^5\text{-}C_5Me_5)RhCl_{0.67}Br_{0.33}]_2(\mu\text{-}Cl_{0.95}Br_{0.05})_2$.

A final difference-Fourier synthesis had peaks of height 0.97 and 0.81 e Å^{-3} as its strongest features. There were indications of the positions of hydrogen atoms about some (but not all) of the methyl carbon atoms. This aspect of the structure was not further pursued.

The lack of variation of $\sum w(|F_o| - |F_c|)^2$ with $|F_o|$, $(\sin\theta)/\lambda$, identity or parity of Miller indices, or sequence number showed the weighting scheme to be satisfactory. Final positional and thermal parameters are collected in Tables II and III.

(2) $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$. The structure of this species was solved by means of a three-dimensional Patterson map, thereby resulting in the unambiguous location of the six independent "heavy" (rhodium and bromine) atoms; this also indicated that the crystallographic asymmetric unit consisted of two independent half-molecules of the complex—i.e., the triclinic cell contains two dimeric molecules centered on the inversion centers at (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$). Refinement of positional and isotropic thermal parameters for the heavy atoms led to $R_F = 19.3\%$ and $R_{wF} = 21.7\%$. A difference-Fourier synthesis now led to the location of all remaining nonhydrogen atoms. Continued full-matrix least-squares refinement (initially with isotropic thermal parameters, then with anisotropic thermal parameters for all nonhydrogen atoms) led to convergence with $R_F = 5.6\%$, $R_{wF} = 3.9\%$, and GOF = 1.72. A difference-Fourier synthesis now led to the location of all 30 hydrogen atoms. These were included in our model and their positional parameters were refined while their isotropic thermal parameters were fixed with $B = 8.0$ Å^2. Continued least-squares refinement led to final convergence with $R_F = 5.1\%$, $R_{wF} = 2.7\%$, and GOF = 1.56 for all 3208 reflections and $R_F = 3.6\%$, $R_{wF} = 2.6\%$, and GOF = 1.65 for those 2693 reflections with $|F_o| > 3\sigma(F_o)$. A final difference-Fourier synthesis showed no significant features save for peaks of height 1.37 and 0.83 e Å^{-3} in the vicinity of the terminal bromide ligands. The analysis was declared complete. The function $\sum w(|F_o| - |F_c|)^2$ showed no significant variation as a function of $|F_o|$, $(\sin\theta)/\lambda$, etc. The weighting scheme is thus satisfactory. Final positional and thermal parameters for the complex appear in Tables IV and V.

Discussion

(A) $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$. The composition of this species, as obtained by refinement of the occupancies of the halide ligands (vide supra), is $[(\eta^5\text{-}C_5Me_5)RhCl_{0.67}Br_{0.33}]_2(\mu\text{-}Cl_{0.95}Br_{0.05})_2$. Unlike the case of simple mineral structures,

Table III. Anisotropic Thermal Parameters,[a] with Esd's, for $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	3.11 (3)	2.64 (3)	2.94 (3)	0.03 (2)	−0.15 (2)	−0.32 (2)
X'(B)	3.58 (8)	5.11 (11)	3.32 (8)	−0.94 (6)	0.79 (6)	−1.05 (7)
X(T)	5.51 (8)	2.79 (7)	7.17 (10)	0.44 (6)	−1.05 (6)	0.00 (6)
C(1)	8.2 (6)	1.3 (3)	6.2 (5)	−0.4 (3)	−4.1 (5)	−0.4 (3)
C(2)	3.3 (3)	6.6 (5)	8.6 (6)	−1.2 (4)	1.2 (4)	−5.8 (5)
C(3)	4.8 (4)	4.5 (4)	3.3 (3)	−1.4 (3)	0.5 (3)	−0.7 (3)
C(4)	3.6 (3)	4.7 (4)	4.4 (4)	−0.3 (3)	−0.5 (3)	−1.0 (4)
C(5)	6.0 (4)	4.0 (4)	4.6 (4)	−1.8 (4)	0.0 (4)	−0.9 (4)
C(6)	21.1 (13)	2.3 (4)	16.9 (11)	0.8 (6)	−12.7 (10)	1.2 (6)
C(7)	5.7 (5)	19.1 (15)	25.9 (17)	−3.3 (7)	6.4 (8)	−19.2 (14)
C(8)	13.9 (9)	10.0 (8)	3.9 (4)	−4.9 (7)	1.4 (5)	0.6 (5)
C(9)	3.9 (4)	10.0 (7)	10.5 (8)	2.0 (4)	−0.7 (4)	−3.9 (6)
C(10)	14.1 (8)	13.3 (10)	5.9 (5)	−9.1 (8)	4.6 (6)	−3.8 (6)

[a] The anisotropic thermal parameters (units Å^2) enter the equation for the calculated structure factor in the form: $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$.

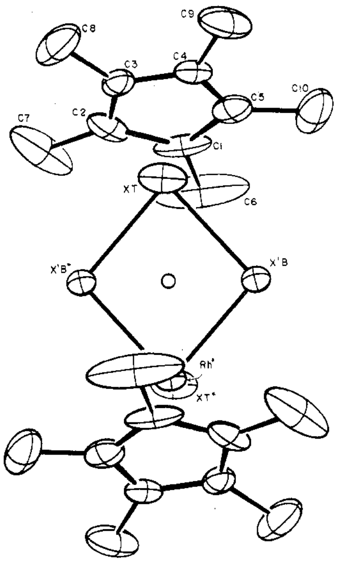

Figure 1. Labeling of atoms in $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$.

in which fractional occupancies usually arise as the result of ion substitution in an essentially ionic lattice, the present observed structure is composed of (up to) nine *discrete molecular species*, viz.

(i) $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$

(ii) $[(\eta^5\text{-}C_5Me_5)RhCl][(\eta^5\text{-}C_5Me_5)RhBr](\mu\text{-}Cl)_2$

(iii) $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Cl)_2$

(iv) $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)(\mu\text{-}Br)$

(v) $[(\eta^5\text{-}C_5Me_5)RhCl][(\eta^5\text{-}C_5Me_5)RhBr](\mu\text{-}Cl)(\mu\text{-}Br)$

(vi) $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Cl)(\mu\text{-}Br)$

(vii) $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Br)_2$

(viii) $[(\eta^5\text{-}C_5Me_5)RhCl][(\eta^5\text{-}C_5Me_5)RhBr](\mu\text{-}Br)_2$

(ix) $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$

Of these nine possible species, four have C_i symmetry (i, iii, vii, ix) and five have only C_1 symmetry (ii, iv, v, vi, viii) in their crystallographic site; these latter five structures will each be statistically disordered about the crystallographic center of symmetry. The net observed structure (see Figures 1–3) consists therefore of up to 14 overlapping molecular images of which four are dominant (i, ii and its centrosymmetrically related mate, and iii). The overall effects of this molecular disorder are surprisingly slight and are taken up in our model principally by the anisotropic thermal parameters—which are larger, for each atom, than those obtained in the structural study of the isomorphous homogeneous complex $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$.[3]

Interatomic distances and angles of the present $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$ and of pure $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$[3] are compared in Tables VI and VII. The principal differences are as follows.

(1) The net Rh–X(T) bond length of 2.456 (2) Å is some 0.059 Å longer than the Rh–Cl(T) bond length of 2.397 (1) Å and some 0.072 Å shorter than the average Rh–Br(T) bond length of 2.528 Å in pure $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ (vide infra). An independent assessment of x (the fraction of Br at X(T)) can be made by realizing that, to a first approximation, the position of X(T) represents the weighted mean of the expected positions of the constituent Cl(T) and Br(T) atoms in the crystal: see eq 10, whence $x = 0.28$—in reasonable agreement with the value of 0.33 found by refining the occupancy of X(T).

$$\delta[(\text{Rh–X(T)}) - (\text{Rh–Cl(T)})][Z(\text{Cl})](1 - x) = \delta[(\text{Rh–Br(T)}) - (\text{Rh–X(T)})][Z(\text{Br})]x \quad (10)$$

(2) The average Rh–X′(B) distance of 2.468 Å is intermediate between the average Rh–Cl(B) distance of 2.459 Å in $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$[3] and the average Rh–Br(B) distance of 2.576 Å in $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ (vide infra). Treatment of these data, as in eq 10, yields an independent measurement of x', the fractional occupancy of Br(B) at this

Table IV. Positional Parameters, with Esd's, for $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$

atom	x	y	z
	Molecule I[a]		
Rh(1)	0.10289 (6)	0.04395 (6)	−0.08969 (3)
Br(1B)	−0.18112 (8)	−0.00592 (8)	−0.07382 (4)
Br(1T)	0.11906 (10)	−0.23150 (8)	−0.12115 (5)
C(11)	0.0442 (8)	0.2489 (8)	−0.1558 (5)
C(12)	0.1728 (9)	0.2798 (7)	−0.0822 (5)
C(13)	0.3018 (8)	0.1946 (7)	−0.0925 (5)
C(14)	0.2515 (9)	0.1117 (7)	−0.1721 (4)
C(15)	0.0896 (9)	0.1389 (8)	−0.2100 (5)
C(16)	−0.1101 (12)	0.3206 (12)	−0.1734 (8)
C(17)	0.1784 (13)	0.3885 (11)	−0.0103 (7)
C(18)	0.4633 (11)	0.2048 (11)	−0.0336 (6)
C(19)	0.3510 (13)	0.0164 (11)	−0.2122 (6)
C(110)	−0.0075 (13)	0.0770 (12)	−0.2961 (6)
H(16A)	−0.099 (10)	0.413 (10)	−0.197 (6)
H(16B)	−0.145 (11)	0.314 (10)	−0.121 (6)
H(16C)	−0.190 (11)	0.260 (10)	−0.217 (6)
H(17A)	0.095 (11)	0.385 (10)	0.013 (6)
H(17B)	0.180 (10)	0.510 (10)	−0.033 (6)
H(17C)	0.247 (13)	0.410 (12)	0.022 (7)
H(18A)	0.470 (12)	0.220 (11)	0.018 (6)
H(18B)	0.504 (10)	0.310 (10)	−0.044 (6)
H(18C)	0.502 (11)	0.122 (10)	−0.035 (6)
H(19A)	0.273 (10)	−0.076 (10)	−0.243 (6)
H(19B)	0.418 (12)	−0.015 (11)	−0.172 (7)
H(19C)	0.373 (11)	0.067 (10)	−0.257 (6)
H(110A)	−0.015 (11)	−0.018 (10)	−0.313 (6)
H(110B)	−0.121 (11)	0.094 (10)	−0.306 (6)
H(110C)	0.031 (10)	0.143 (9)	−0.351 (6)
	Molecule II[b]		
Rh(2)	0.60268 (6)	0.45666 (6)	0.41119 (3)
Br(2B)	0.33980 (9)	0.55349 (9)	0.42445 (5)
Br(2T)	0.72297 (11)	0.72340 (9)	0.42009 (6)
C(21)	0.4907 (8)	0.3178 (7)	0.2988 (5)
C(22)	0.6283 (10)	0.4031 (7)	0.2862 (5)
C(23)	0.7637 (8)	0.3602 (8)	0.3488 (5)
C(24)	0.7114 (9)	0.2492 (8)	0.3993 (5)
C(25)	0.5442 (9)	0.2272 (7)	0.3689 (5)
C(26)	0.3260 (11)	0.3246 (13)	0.2457 (7)
C(27)	0.6309 (18)	0.5112 (12)	0.2161 (7)
C(28)	0.9358 (13)	0.4106 (13)	0.3610 (9)
C(29)	0.8085 (14)	0.1603 (12)	0.4706 (7)
C(210)	0.4379 (14)	0.1137 (10)	0.4023 (7)
H(26A)	0.251 (11)	0.288 (10)	0.278 (6)
H(26B)	0.307 (10)	0.241 (10)	0.191 (6)
H(26C)	0.324 (11)	0.402 (10)	0.199 (6)
H(27A)	0.505 (11)	0.522 (10)	0.188 (6)
H(27B)	0.664 (11)	0.602 (10)	0.224 (6)
H(27C)	0.645 (11)	0.467 (10)	0.167 (6)
H(28A)	0.912 (10)	0.505 (10)	0.297 (6)
H(28B)	0.975 (11)	0.352 (10)	0.326 (6)
H(28C)	0.957 (11)	0.505 (11)	0.370 (7)
H(29A)	0.763 (11)	0.153 (10)	0.519 (6)
H(29B)	0.893 (14)	0.204 (12)	0.452 (7)
H(29C)	0.911 (13)	0.233 (11)	0.499 (6)
H(210A)	0.450 (10)	0.006 (10)	0.383 (6)
H(210B)	0.330 (11)	0.132 (10)	0.378 (7)
H(210C)	0.504 (11)	0.105 (10)	0.461 (6)

[a] This dimeric molecule is centered at (0, 0, 0). Atoms in the other half of the molecule may be generated by the transformation $(-x, -y, -z)$. [b] This dimeric molecule is centered on $(^1/_2, {}^1/_2, {}^1/_2)$. Atoms in the other half may be generated by the transformation $(1 - x, 1 - y, 1 - z)$.

Table V. Anisotropic Thermal Parameters, with Esd's, for $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
			Molecule I			
Rh(1)	1.94 (3)	2.04 (3)	2.05 (3)	0.27 (2)	0.93 (2)	0.54 (2)
Br(1B)	1.95 (3)	3.62 (4)	2.27 (3)	0.06 (3)	0.67 (3)	0.68 (3)
Br(1T)	4.55 (5)	2.46 (3)	4.38 (4)	0.52 (3)	2.09 (3)	0.06 (3)
C(11)	2.5 (4)	2.8 (3)	3.9 (4)	1.1 (3)	1.5 (3)	2.2 (3)
C(12)	3.3 (4)	1.6 (3)	4.3 (4)	0.5 (3)	1.9 (3)	0.7 (3)
C(13)	2.6 (4)	2.8 (3)	2.2 (3)	−0.4 (3)	0.9 (3)	0.8 (3)
C(14)	3.0 (4)	2.5 (3)	2.7 (4)	0.1 (3)	1.8 (3)	0.8 (3)
C(15)	3.8 (4)	3.6 (4)	2.5 (4)	−0.7 (3)	1.1 (3)	1.7 (3)
C(16)	3.7 (5)	5.8 (6)	9.1 (8)	2.1 (4)	2.3 (5)	4.7 (6)
C(17)	6.8 (7)	3.0 (4)	5.9 (6)	0.2 (5)	3.6 (5)	0.0 (4)
C(18)	3.4 (5)	4.0 (5)	5.0 (5)	−0.3 (4)	0.1 (4)	1.0 (4)
C(19)	6.5 (6)	4.5 (5)	4.7 (6)	0.4 (4)	4.1 (5)	−0.3 (4)
C(110)	5.6 (6)	7.4 (6)	2.4 (4)	−2.3 (5)	−0.1 (4)	0.7 (4)
			Molecule II			
Rh(2)	2.00 (3)	2.34 (3)	2.01 (3)	−0.11 (2)	0.82 (2)	−0.02 (2)
Br(2B)	2.45 (4)	5.11 (4)	2.18 (4)	0.99 (3)	0.42 (3)	−0.09 (3)
Br(2T)	5.82 (5)	3.03 (4)	6.00 (5)	−1.30 (3)	3.33 (4)	−0.49 (3)
C(21)	2.6 (4)	2.6 (3)	2.7 (4)	0.2 (3)	0.3 (3)	−0.8 (3)
C(22)	5.2 (5)	2.4 (3)	2.1 (4)	−0.1 (3)	2.1 (3)	−0.3 (3)
C(23)	2.0 (4)	3.0 (4)	4.6 (4)	−0.5 (3)	1.6 (3)	−1.5 (3)
C(24)	4.2 (4)	2.8 (4)	2.4 (4)	1.9 (3)	0.4 (3)	−0.4 (3)
C(25)	3.0 (4)	2.2 (3)	3.1 (4)	0.3 (3)	1.6 (3)	−0.5 (3)
C(26)	3.8 (5)	7.2 (6)	4.0 (5)	1.0 (4)	−0.8 (4)	−1.7 (4)
C(27)	13.9 (10)	4.2 (5)	3.9 (6)	0.1 (6)	4.5 (6)	0.9 (4)
C(28)	5.0 (6)	5.9 (6)	11.9 (10)	−2.4 (5)	5.7 (6)	−3.9 (6)
C(29)	5.5 (6)	6.7 (6)	3.6 (5)	1.6 (5)	0.0 (4)	1.0 (4)
C(210)	8.1 (7)	2.9 (4)	6.6 (6)	−1.5 (5)	4.0 (6)	0.3 (4)

[a] See footnote to Table III.

Table VI. Intramolecular Distances (Å) with Esd's, for Monoclinic $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$ Compared with Those for the Isomorphous Species $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$[a]

atoms	$[RhX]_2(\mu\text{-}X')_2$ complex	$[RhCl]_2(\mu\text{-}Cl)_2$ complex
Rh···Rh*	3.718 (1)	3.719 (1)
Rh-X'(B)	2.473 (2)	2.465 (1)
Rh-X'(B)*	2.458 (2)	2.452 (1)
Rh-X(T)	2.456 (2)	2.397 (1)
Rh-C(1)	2.116 (8)	2.116 (4)
Rh-C(2)	2.128 (10)	2.124 (4)
Rh-C(3)	2.111 (7)	2.121 (3)
Rh-C(4)	2.143 (7)	2.140 (3)
Rh-C(5)	2.134 (9)	2.137 (4)
Rh···C(6)	3.219 (10)	3.237 (7)
Rh···C(7)	3.210 (16)	3.224 (6)
Rh···C(8)	3.286 (10)	3.251 (6)
Rh···C(9)	3.293 (10)	3.284 (5)
Rh···C(10)	3.274 (13)	3.265 (5)
C(1)-C(2)	1.501 (14)	1.452 (7)
C(2)-C(3)	1.394 (12)	1.434 (6)
C(3)-C(4)	1.416 (10)	1.398 (5)
C(4)-C(5)	1.330 (12)	1.370 (5)
C(5)-C(1)	1.450 (13)	1.408 (6)
C(1)-C(6)	1.499 (16)	1.510 (8)
C(2)-C(7)	1.456 (16)	1.492 (7)
C(3)-C(8)	1.543 (13)	1.511 (7)
C(4)-C(9)	1.533 (13)	1.536 (7)
C(5)-C(10)	1.515 (15)	1.527 (6)

[a] See ref 3.

Table VII. Interatomic Angles (deg), with Esd's, for Monoclinic $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$ and $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$[a]

atoms	$[RhX]_2(\mu\text{-}X')_2$ complex	$[RhCl]_2(\mu\text{-}Cl)_2$ complex
Rh-X'(B)-Rh*	97.88 (6)	98.29 (3)
X'(B)-Rh-X'(B)*	82.12 (6)	81.71 (3)
X'(B)-Rh-X(T)	92.37 (6)	92.30 (4)
X'(B)*-Rh-X(T)	90.57 (6)	90.73 (4)
Rh*···Rh-X'(B)	40.91 (4)	40.73 (2)
Rh*···Rh-X'(B)*	41.21 (4)	40.98 (2)
C(5)-C(1)-C(2)	106.6 (8)	108.0 (3)
C(1)-C(2)-C(3)	104.8 (8)	105.7 (3)
C(2)-C(3)-C(4)	109.1 (7)	107.5 (4)
C(3)-C(4)-C(5)	111.7 (7)	110.7 (3)
C(4)-C(5)-C(1)	107.7 (8)	108.1 (4)
C(6)-C(1)-C(2)	126.2 (9)	126.1 (7)
C(6)-C(1)-C(5)	127.2 (9)	125.9 (7)
C(7)-C(2)-C(1)	125.5 (10)	127.2 (7)
C(7)-C(2)-C(3)	129.6 (10)	127.1 (7)
C(8)-C(3)-C(2)	126.1 (8)	126.6 (5)
C(8)-C(3)-C(4)	124.5 (8)	125.8 (5)
C(9)-C(4)-C(3)	123.4 (7)	122.1 (5)
C(9)-C(4)-C(5)	124.9 (8)	127.2 (5)
C(10)-C(5)-C(1)	124.2 (8)	126.5 (5)
C(10)-C(5)-C(4)	128.0 (9)	125.4 (4)

[a] See ref 3.

location, as 0.04—again, in good agreement with the previously determined value of 0.05.

(3) There is a considerably larger spread of carbon–carbon distances within the cyclopentadienyl ring of the mixed-halide species than there is in the pure chloro complex—i.e., 1.330 (12)–1.501 (14) Å as compared to 1.370 (5)–1.452 (7) Å. This, presumably, is a result of disorder in addition to the known problem of libration of the $(\eta^5\text{-}C_5Me_5)$ ring. All other interatomic distances (i.e., Rh···Rh contacts, Rh–C(cyclopentadienyl) distances, and Rh···C(Me) vectors) are remarkably similar from one species to the other.

The overall stoichiometry of the mixed-halide species (based upon refinement of halogen atom occupancies) is approximately $[(C_{10}H_{15}Br_{0.38}Cl_{1.62}Rh]_2$, corresponding to a "molecular weight" of ~651.86. This leads, in turn, to a calculated density of 1.840 g cm^{-3}—in good agreement with the experimentally determined density of 1.831 (12) g cm^{-3}. However, it should be emphasized that we were unable to measure the density of the crystal actually used for collection of diffraction data because it was contaminated with adhesive.

Two further points need mentioning here.

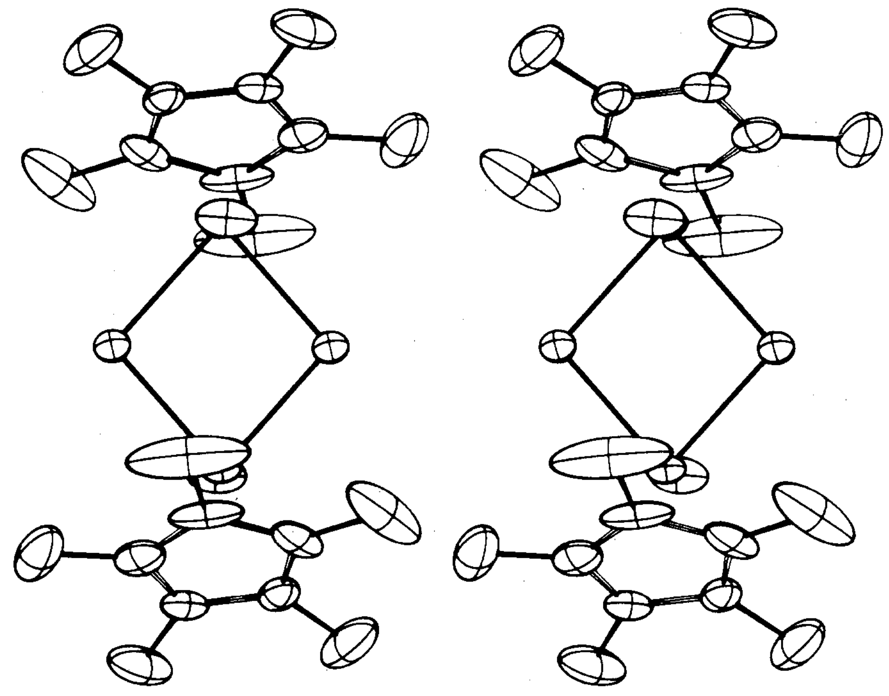

Figure 2. Stereoview of the net $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$ structure.

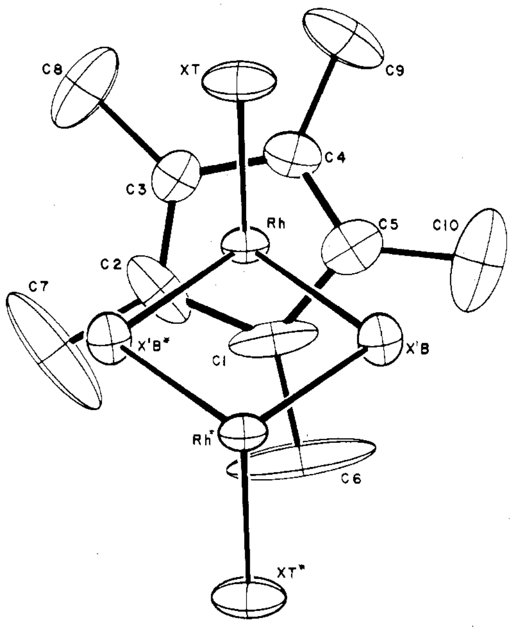

Figure 3. A portion of the $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$ structure, projected onto the carbocyclic ring.

(a) The prolonged exposure of organometallic halides to dissimilarly halogenated solvents should be avoided. It *may* be safe to recrystallize organometallic bromides and iodides from chlorocarbon solvents provided that the procedure is carried out rapidly. However, prolonged exposure (as is frequently necessary for obtaining crystals suitable for an X-ray diffraction study) may lead to halogen exchange and should be avoided.

(b) The exchange process for $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ with dichloroethane appears to be slow (our material was in solution for 3–4 days) and operates so as to yield a product in which chloride ion appears preferentially at the bridging position. This suggests either (i) that the mechanism does not involve facile scrambling of bridging and terminal halide ligands or (ii) that the bridging chloride species are more stable than the bridging bromide species.

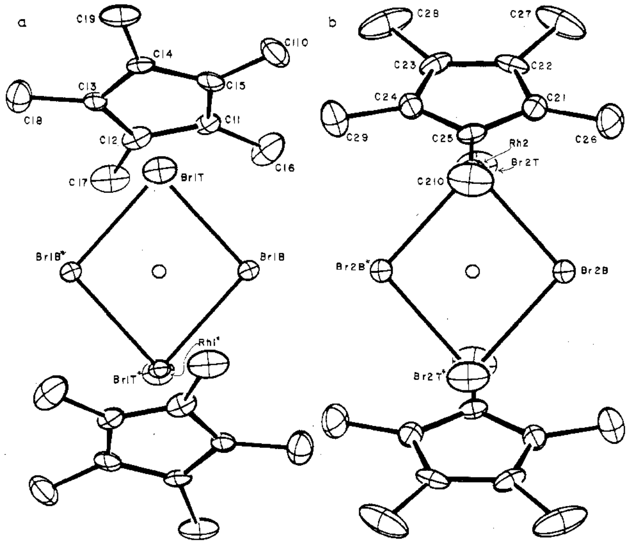

Figure 4. Labeling of atoms in the two $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ molecules: (a) molecule I; (b) molecule II.

(B) $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$. Interatomic distances and angles are collected in Tables VIII and IX. Important least-squares planes are given in Table X. Illustrations of the two crystallographically independent molecules are presented in Figures 4–6.

The two independent molecules, termed molecule I and molecule II, have closely similar molecular parameters but differ in the rotomeric conformation of the C_5Me_5 ring about the Rh···ring axis. The two intramolecular rhodium···rhodium distances are Rh(1)···Rh(1)* = 3.854 (1) Å and Rh(2)···Rh(2)* = 3.841 (1) Å, the average value of 3.848 Å being expanded by 0.129 Å relative to the intermetallic distance of 3.719 (1) Å in pure $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$. The rhodium–(terminal bromide) bonds, Rh(1)–Br(1T) = 2.523 (1) Å and Rh(2)–Br(2T) = 2.532 (1) Å [average 2.528 Å], are approximately 0.048 Å shorter than the rhodium–(bridging bromide) linkages [Rh(1)–Br(1B) = 2.577 (1) Å, Rh(1)–Br(1B)* = 2.587 (1) Å, Rh(2)–Br(2B) = 2.566 (1) Å, Rh-

Table VIII. Intramolecular Distances (Å), with Esd's, for Triclinic $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$

molecule I		molecule II	
atoms	dist	atoms	dist
(A) Distances within the Rh_2Br_4Core			
Rh(1)· · ·Rh(1)*	3.854 (1)	Rh(2)· · ·Rh(2)*	3.841 (1)
Rh(1)–Br(1T)	2.523 (1)	Rh(2)–Br(2T)	2.532 (1)
Rh(1)–Br(1B)	2.577 (1)	Rh(2)–Br(2B)	2.566 (1)
Rh(1)–Br(1B)*	2.587 (1)	Rh(2)–Br(2B)*	2.575 (1)
(B) Rhodium–Carbon Distances			
Rh(1)–C(11)	2.167 (7)	Rh(2)–C(21)	2.149 (7)
Rh(1)–C(12)	2.151 (6)	Rh(2)–C(22)	2.132 (7)
Rh(1)–C(13)	2.144 (7)	Rh(2)–C(23)	2.141 (8)
Rh(1)–C(14)	2.157 (7)	Rh(2)–C(24)	2.164 (7)
Rh(1)–C(15)	2.117 (7)	Rh(2)–C(25)	2.135 (7)
Rh–C(av)	2.147	Rh–C(av)	2.144
(C) Rhodium–C(Methyl) Contacts			
Rh(1)· · ·C(16)	3.297 (11)	Rh(2)· · ·C(26)	3.250 (10)
Rh(1)· · ·C(17)	3.270 (10)	Rh(2)· · ·C(27)	3.266 (11)
Rh(1)· · ·C(18)	3.278 (10)	Rh(2)· · ·C(28)	3.268 (12)
Rh(1)· · ·C(19)	3.307 (11)	Rh(2)· · ·C(29)	3.321 (11)
Rh(1)· · ·C(110)	3.247 (9)	Rh(2)· · ·C(210)	3.291 (10)
Rh· · ·C(av)	3.280	Rh–C(av)	3.279
(D) Distances within Carbocyclic Rings			
C(11)–C(12)	1.419 (11)	C(21)–C(22)	1.446 (11)
C(12)–C(13)	1.442 (10)	C(22)–C(23)	1.426 (11)
C(13)–C(14)	1.420 (9)	C(23)–C(24)	1.425 (10)
C(14)–C(15)	1.431 (11)	C(24)–C(25)	1.419 (11)
C(15)–C(11)	1.441 (10)	C(25)–C(21)	1.406 (10)
C–C(Cp) (av)	1.431	C–C(Cp) (av)	1.424
(E) Carbon–Methyl Distances			
C(11)–C(16)	1.496 (13)	C(21)–C(26)	1.482 (13)
C(12)–C(17)	1.485 (13)	C(22)–C(27)	1.510 (13)
C(13)–C(18)	1.483 (12)	C(23)–C(28)	1.508 (14)
C(14)–C(19)	1.504 (13)	C(24)–C(29)	1.520 (13)
C(15)–C(110)	1.502 (12)	C(25)–C(210)	1.534 (13)
C–Me(av)	1.494	C–Me(av)	1.511
(F) Carbon–Hydrogen Distances			
C(16)–H(16A)	0.93 (10)	C(26)–H(26A)	0.98 (10)
C(16)–H(16B)	0.97 (10)	C(26)–H(26B)	1.11 (9)
C(16)–H(16C)	0.98 (10)	C(26)–H(26C)	1.03 (10)
C(17)–H(17A)	0.90 (10)	C(27)–H(27A)	1.09 (11)
C(17)–H(17B)	1.15 (9)	C(27)–H(27B)	0.84 (10)
C(17)–H(17C)	0.70 (12)	C(27)–H(27C)	0.91 (10)
C(18)–H(18A)	0.82 (10)	C(28)–H(28A)	1.33 (10)
C(18)–H(18B)	1.02 (10)	C(28)–H(28B)	0.91 (10)
C(18)–H(18C)	0.84 (10)	C(28)–H(28C)	0.86 (10)
C(19)–H(19A)	1.07 (9)	C(29)–H(29A)	0.97 (10)
C(19)–H(19B)	0.82 (11)	C(29)–H(29B)	0.94 (13)
C(19)–H(19C)	0.92 (9)	C(29)–H(29C)	1.07 (11)
C(110)–H(110A)	0.88 (9)	C(210)–H(210A)	1.02 (10)
C(110)–H(110B)	0.98 (10)	C(210)–H(210B)	0.95 (10)
C(110)–H(110C)	1.19 (9)	C(210)–H(210C)	0.98 (10)
C–H(av)	0.95	C–H(av)	1.00

Table IX. Selected Interatomic Angles (deg), with Esd's, for Triclinic $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$

molecule I		molecule II	
atoms	angle	atoms	angle
(A) Angles within the Rh(μ-Br)$_2$Rh Bridges			
Rh(1)–Br(1B)–Rh(1)*	96.54 (3)	Rh(2)–Br(2B)–Rh(2)*	96.70 (3)
Br(1B)–Rh(1)–Br(1B)*	83.46 (3)	Br(2B)–Rh(2)–Br(2B)*	83.30 (3)
Rh(1)*· · ·Rh(1)–Br(1B)	41.83 (2)	Rh(2)*· · ·Rh(2)–Br(2B)	41.73 (2)
Rh(1)*· · ·Rh(1)–Br(1B)*	41.63 (2)	Rh(2)*· · ·Rh(2)–Br(2B)*	41.56 (2)
(B) Angles Involving the Terminal Bromide Ligands			
Br(1B)–Rh(1)–Br(1T)	90.75 (3)	Br(2B)–Rh(2)–Br(2T)	90.26 (3)
Br(1B)*–Rh(1)–Br(1T)	91.30 (3)	Br(2B)*–Rh(2)–Br(2T)	92.32 (3)
(C) Internal Angles of the η^5-C_5Me_5 Ligand			
C(15)–C(11)–C(12)	108.1 (6)	C(25)–C(21)–C(22)	107.0 (6)
C(11)–C(12)–C(13)	107.8 (6)	C(21)–C(22)–C(23)	107.9 (6)
C(12)–C(13)–C(14)	108.1 (6)	C(22)–C(23)–C(24)	108.0 (7)
C(13)–C(14)–C(15)	108.1 (6)	C(23)–C(24)–C(25)	107.6 (6)
C(14)–C(15)–C(11)	107.7 (6)	C(24)–C(25)–C(21)	109.6 (6)
(D) External Angles of the η^5-C_5Me_5 Ligand			
C(15)–C(11)–C(16)	126.7 (7)	C(25)–C(21)–C(26)	127.5 (7)
C(12)–C(11)–C(16)	125.3 (7)	C(22)–C(21)–C(26)	125.6 (7)
C(11)–C(12)–C(17)	126.3 (7)	C(21)–C(22)–C(27)	126.4 (8)
C(13)–C(12)–C(17)	125.8 (7)	C(23)–C(22)–C(27)	125.6 (8)
C(12)–C(13)–C(18)	125.2 (7)	C(22)–C(23)–C(28)	129.1 (8)
C(14)–C(13)–C(18)	126.4 (7)	C(24)–C(23)–C(28)	122.9 (8)
C(13)–C(14)–C(19)	126.6 (7)	C(23)–C(24)–C(29)	129.3 (7)
C(15)–C(14)–C(19)	125.2 (7)	C(25)–C(24)–C(29)	123.1 (7)
C(14)–C(15)–C(110)	125.4 (7)	C(24)–C(25)–C(210)	125.7 (7)
C(11)–C(15)–C(110)	126.6 (7)	C(21)–C(25)–C(210)	124.6 (7)

(2)–Br(2B)* = 2.575 (1) Å; average 2.576 Å]. The average Rh–Br(T) bond length is 0.131 Å longer than the corresponding Rh–Cl(T) bond length of 2.397 (1) Å, while the average Rh–Br(B) linkage is 0.117 Å longer than the average Rh–Cl(B) bond length of 2.459 Å. The two independent Rh–Br(B)–Rh bridge angles are Rh(1)–Br(1B)–Rh(1)* = 96.54 (3)° and Rh(2)–Br(2B)–Rh(2)* = 96.70 (3)°; the average value of 96.62° is 1.67° less obtuse than the Rh(1)–Cl(B)–Rh(1)* angle of 98.29 (3)° in $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$.

The coordination geometry about the rhodium(III) centers is of the so-called "three-legged piano stool" variety, in which angles between the simple ligands are each close to 90°—viz., ∠Br(1B)–Rh(1)–Br(1T) = 90.75 (3)°, ∠Br(1B)–Rh(1)–Br(1B)* = 83.46 (3)°, ∠Br(1B)*–Rh(1)–Br(1T) = 91.30 (3)°, ∠Br(2B)–Rh(2)–Br(2T) = 90.26 (3)°, ∠Br(2B)–Rh(2)–Br(2B)* = 83.30 (3)°, ∠Br(2B)*–Rh(2)–Br(2T) = 92.32 (3)°. The rotational orientations of the $RhBr_3$ groups relative to the η^5-C_5Me_5 ligands are shown in Figure 6.

The individual rhodium–carbon linkages range from 2.117 (7) to 2.167 (7) Å [average 2.147 Å] in molecule I and from 2.132 (7) to 2.164 (7) Å [average 2.144 Å] in molecule II. There is significant librational motion of the (η^5-C_5Me_5) ligands about their fivefold axes (see Figure 6); however, the degree of libration is substantially lower than that found in the mixed-halide species $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X')_2$ (cf. Figure 3) or in the species $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$ (see Figure 2 of ref 3) and $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$ (see Figure 4 of ref 4). In keeping with this observation, the carbon–carbon bond lengths within the carbocyclic systems of the present $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ molecules are all close to the expected value of ~1.43 Å[10] and have excellent internal consistency. Thus, carbocyclic C–C distances within molecule I range from 1.419 (11) to 1.442 (10) Å [average 1.431 Å] and within molecule II range from 1.406 (10) to 1.446 (11) Å [average 1.424 Å]. The internal C–C–C angles are also regular, with spreads of 107.7 (6)–108.1 (6) and 107.0 (6)–109.6 (6)°, respectively, for the two independent systems. The average value of 108.0° is that expected for a planar pentagonal figure.

C(ring)–Me distances are, likewise, internally consistent, with ranges of 1.483 (12)–1.504 (13) Å [average 1.494 Å] and 1.482 (13)–1.534 (13) Å [average 1.511 Å] in the two systems; these results should be compared to the accepted $C(sp^2)$–$C(sp^3)$ single-bond distance of 1.510 ± 0.005 Å.[11]

All 30 hydrogen atoms within the two crystallographically-independent η^5-C_5Me_5 ligands were located and their positional parameters refined. The overall spread of the resulting C–H distances is from 0.70 (12) to 1.33 (10) Å; however, 18 of the 30 derived C–H distances lie in the range 0.85–1.05 Å (i.e., less than 1.0σ from the expected "X-ray value" of ~0.95 Å)[12] and 27 of the 30 C–H distances lie in

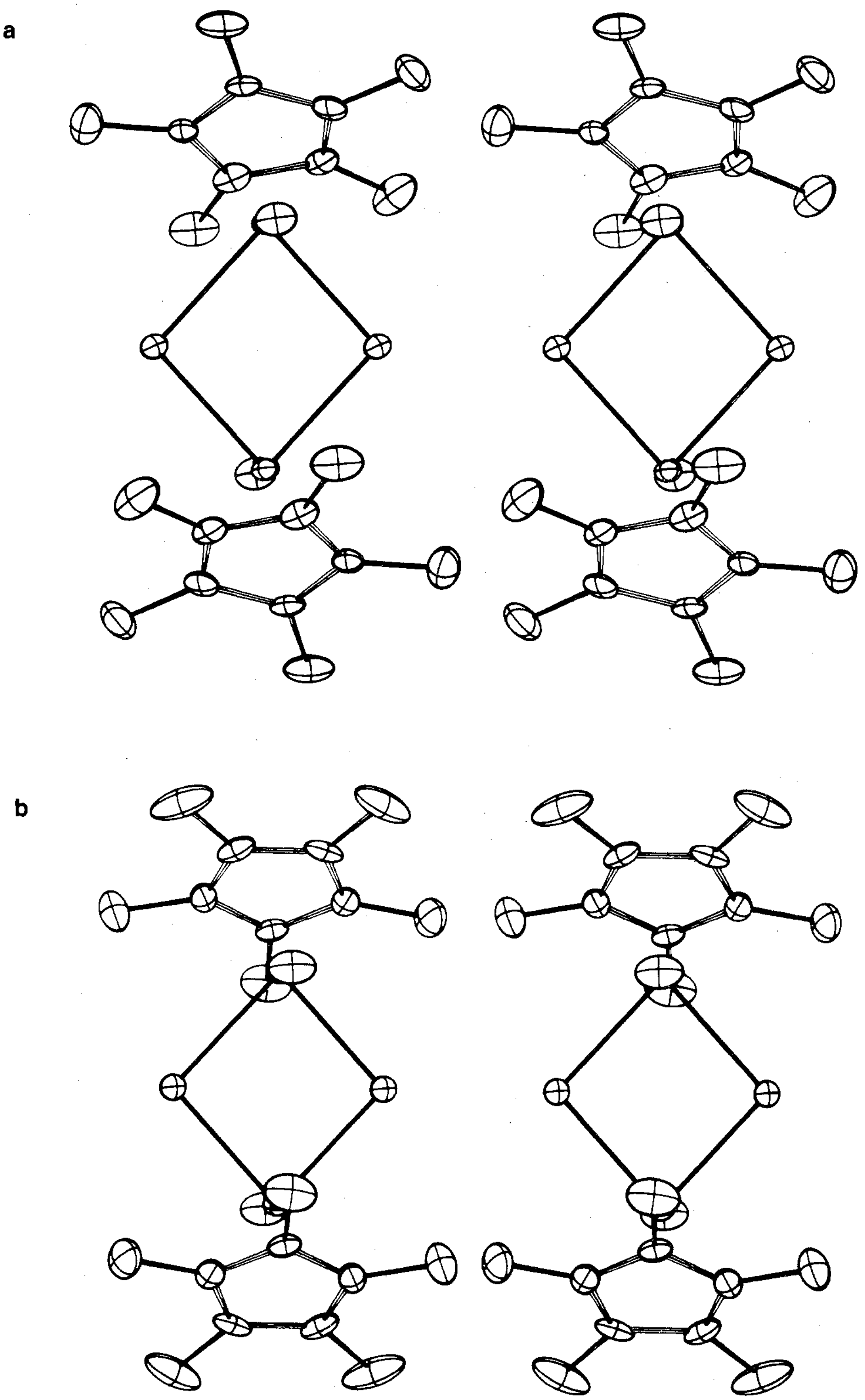

Figure 5. Stereoviews of the two $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ molecules: (a) molecule I; (b) molecule II. Note the different rotational orientations of the C_5Me_5 ligands about their Rh···ring axes.

the range 0.75–1.15 Å (i.e., less than 2.0σ from the expected value). Furthermore, it should be noted that it is not possible to *calculate* the positions of these hydrogen atoms because the rotational orientation of a CH_3 group about its C(ring)–C(Me) axis is indeterminate.

Each of the rhodium atoms lies −1.769 (1) Å from its appropriate η^5-cyclopentadienyl system (see Table X). In each of the two independent $\eta^5\text{-}C_5Me_5$ ligands, the carbon atoms of the methyl groups are displaced from the least-squares plane through the carbocyclic ring such that they bend *away* from the rhodium atoms. Individual atomic displacements in molecule I are +0.103 (11) Å for C(16), +0.045 (11) Å for C(17), +0.087 (10) Å for C(18), +0.135 (10) Å for C(19), and +0.032 (11) Å for C(110); corresponding values for molecule II are +0.056 (11) Å for C(26), +0.068 (11) Å for C(27), +0.043 (13) Å for C(28), +0.095 (11) Å for C(29), and +0.047 (10) Å for C(210).

Finally, we note that the dihedral angle between the cyclopentadienyl plane and the $Rh(\mu\text{-}Br)_2Rh$ plane is 127.26° in molecule I and 126.87° in molecule II.

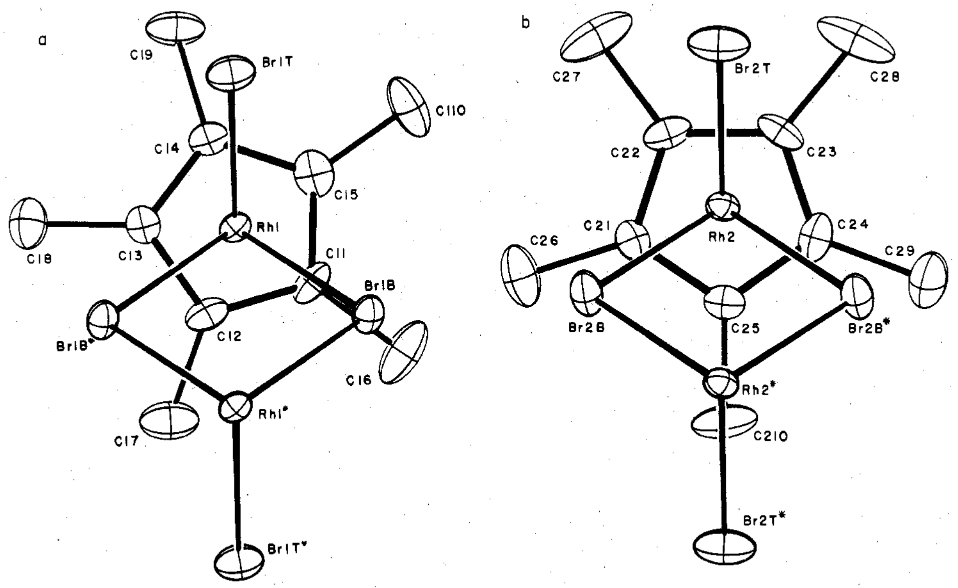

Figure 6. Projections of portions of the two $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ molecules onto their cyclopentadienyl rings: (a) molecule I; (b) molecule II.

Table X. Least-Squares Planes and Atomic Deviations Therefrom, for $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$

atom	dev, Å	atom	dev, Å
I. Rh(μ-Br)$_2$Rh Plane–Molecule I			
$0.1586x - 0.9722y - 0.1721z = 0.0000^a$			
Rh(1)^b	0.000	Br(1B)^b	0.000
Rh(1)*^{b}	0.000	Br(1B)*^{b}	0.000
Br(1T)	2.522 (1)		
II. C(11)–C(15) Plane–Molecule I			
$0.4186x + 0.7748y - 0.4737z = 3.3030^a$			
C(11)^b	0.022 (7)	C(16)	0.103 (11)
C(12)^b	−0.009 (7)	C(17)	0.045 (11)
C(13)^b	−0.007 (7)	C(18)	0.087 (10)
C(14)^b	0.020 (7)	C(19)	0.135 (10)
C(15)^b	−0.026 (7)	C(110)	0.032 (11)
Rh(1)	−1.769 (1)		
III. Rh(μ-Br)$_2$Rh Plane–Molecule II			
$-0.3402x - 0.9355y - 0.0951z = -5.3002^a$			
Rh(2)^b	0.000	Br(2B)^b	0.000
Rh(2)*^{b}	0.000	Br(2B)*^{b}	0.000
Br(2T)	−2.530 (1)		
IV. C(21)–C(25) Plane–Molecule II			
$0.3340x - 0.6984y - 0.6330z = -3.8372^a$			
C(21)^b	0.008 (7)	C(26)	0.056 (11)
C(22)^b	−0.002 (7)	C(27)	0.068 (11)
C(23)^b	−0.005 (8)	C(28)	0.043 (13)
C(24)^b	0.010 (7)	C(29)	0.095 (11)
C(25)^b	−0.011 (7)	C(210)	0.047 (10)
Rh(2)	−1.769 (1)		
Dihedral Angles			
I–II	127.26°	III–IV	126.87°

[a] Cartesian coordinates. [b] These atoms included in the calculation of the plane.

Conclusions

The product obtained from recrystallization of $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ from 1,2-dichloroethane is shown to be a mixture of chloro and bromo derivatives with an approximate composition of $[(\eta^5\text{-}C_5Me_5)RhCl_{0.67}Br_{0.33}]_2(\mu\text{-}Cl_{0.95}Br_{0.05})_2$. This formulation is consistent with (a) the results of refining the occupancies of both bridging and terminal halide ligands, (b) consideration of the terminal Rh–X and the bridging Rh–X′ "bond distances", and (c) the observed density of the material.

Crystals of $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ are not isomorphous with those of $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$; nevertheless, substitution of ca. 19% of the chloride ligands in $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$ by bromide ligands causes no gross change in the crystal structure.

The crystal structure of pure $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$ has also been examined, and an analysis of Rh···Rh contacts, Rh–Br(T) bond lengths, and Rh–Br(B) distances (coupled with comparison with the pure chloro complex) indicates that there is no rhodium···rhodium bonding. We are currently attempting to crystallize samples of $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}H)(\mu\text{-}Br)$ in order to assess the influence of a bridging hydride ligand on the remaining Rh(μ-Br)Rh bridge.

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Registry No. $[(\eta^5\text{-}C_5Me_5)RhBr]_2(\mu\text{-}Br)_2$, 36484-11-4; $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$, 12354-85-7.

Supplementary Material Available: Two listings of structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

References and Notes

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