CATIONIC RHODIUM TETRAFLUOROBENZOBARRELENE COMPLEXES WITH DIOLEFIN OR ARENE LIGANDS, CRYSTAL STRUCTURES OF [Rh(TFB)(arene)] ClO₄, (arene = C₆Me₆, C₆H₃Me₃, C₆H₄Me₂)

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Summary

The preparation and properties of complexes of the general formulae [Rh-(TFB)(diolefin)]ClO₄, [Rh(TFB)(arene)]ClO₄ and [Rh(TFB)L₂]ClO₄, (TFB = tetrafluorobenzobarrelene, L = dimethylsulfoxide and tetrahydrothiophen) are described. The crystal structures of the arene complexes (arene = C₆Me₆, C₆H₃Me₃ and C₆H₄Me₂) have been solved by X-ray methods. The three compounds crystallize in quite similar lattices: $R3c$, $a = b = 27.122, 26.233, 25.731$ and $c = 17.079, 16.388, 16.256$ Å, respectively. δR-plots for about 2000 reflections show the agreement in the refinements carried out up to R-values of 5%, 5% and 4% respectively. The Rh atom is coordinated to the double bonds of the TFB and to the arene ring in all three compounds, but the deviation from planarity of the arene and its relative position with respect to the TFB moiety varies.

Introduction

During the last decade there has been a noteworthy development in the chemistry of cationic rhodium(I) complexes containing diolefin ligands [1]. In particular, Green and Kuc [2], and also Schrock and Osborn [3], have described complexes of the general formulae [Rh(diolefin)(diolefin′)]A and [Rh(diolefin)(arene)]A, (the diolefin being 1,5-cyclooctadiene (COD) or 2,5-norbornadiene (NBD). Green and Kuc suggested the need for an X-ray struc-

tural study to determine whether the coordination of the arene is of the η^4 or η^6 type. In a recent paper Muetterties et al. [4] have shown that the cation previously described as $[Rh(\eta^6\text{-}C_6Me_6)_2]^+$ is, in fact, $[Rh(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6H_2Me_4)]^+$. The stability which the tetrafluorobenzobarrelene ligand (TFB) confers on rhodium(I) complexes has been the subject of other studies [5,6].

In the present paper we describe the synthesis of cationic complexes of the types $[Rh(TFB)(diolefin)]ClO_4$ and $[Rh(TFB)(arene)]ClO_4$ and of the related complexes $[Rh(TFB)(DMSO)_2]ClO_4$ and $[Rh(TFB)(THT)_2]ClO_4$. In addition, the crystal structure of the complexes with arene = C_6Me_6, $C_6H_3Me_3$ and $C_6H_4Me_2$ (Rh6Me, Rh3Me and Rh2Me, hereafter) are described.

Results and discussion

The compounds $[Rh(TFB)(COD)]ClO_4$ and $[Rh(TFB)(NBD)]ClO_4$ were prepared according to eq. 1:

$$1/2[RhCl(diolefin)]_2 + AgClO_4 + TFB \rightarrow [Rh(diolefin)(TFB)]ClO_4 + AgCl \quad (1)$$
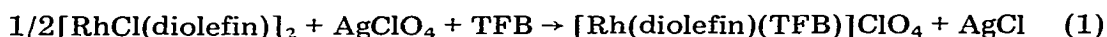
(diolefin = COD or NBD)

The analogous complexes with 2-methyl-1,3-butadiene (MeBD) or 2,3-dimethyl-1,3-butadiene (Me$_2$BD) were similarly obtained according to eq. 2:

$$1/2[RhCl(TFB)]_2 + AgClO_4 + diolefin \rightarrow [Rh(TFB)(diolefin)]ClO_4 + AgCl \quad (2)$$
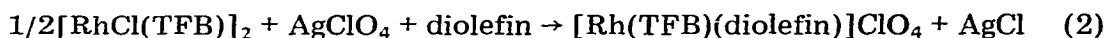
The molar conductivities of these complexes (120—140 ohm^{-1} cm^2 mol^{-1}) are those of 1 : 1 electrolyte. Their IR spectra show the absorptions due to the anion ClO_4^- [7] at 1115 and 620 cm^{-1}, along with strong bands characteristic of coordinated TFB (at 1500s, 1040s, 885m and 850s cm^{-1}). They decompose above 150°C and the MeBD and Me$_2$BD derivatives explode violently. The analytical results and other data for the novel complexes are listed in Table 1.

Complexes of the type $[Rh(TFB)(arene)]ClO_4$ (arene being C_6H_6, C_6H_5OH, C_6H_5Me, C_6H_5OMe, 1,3-$C_6H_4(OMe)_2$, 1,4-$C_6H_4Me_2$, 1,3,5-$C_6H_3Me_3$ or C_6Me_6) were prepared according to eq. 3:

$$1/2[RhCl(TFB)]_2 + AgClO_4 + arene \rightarrow [Rh(TFB)(arene)]ClO_4 + AgCl \quad (3)$$
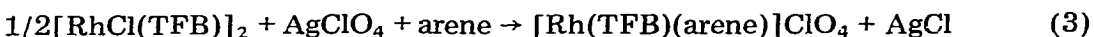
The analytical and other data for the arene complexes are listed in Table 1. They decompose between 160 and 270°C, and the 1,3,5-trimethylbenzene and 1,4-dimethylbenzene derivatives explode violently when heated slightly above their decomposition temperature. Their IR spectra reveal the presence of the ClO_4^- group (Td) and also show the vibrations due to the coordinated tetra-fluorobenzobarrelene along with several weak bands assignable to the coordinated arene.

Attempts to use some $[Rh(TFB)(arene)]ClO_4$ complexes as homogeneous catalysts for the hydrogenation of benzene have been unsuccesful, because of formation of rhodium metal on exposure to hydrogen.

The NMR spectrum of $[Rh(TFB)(C_6Me_6)]ClO_4$ in deuteroacetone shows resonances at τ 7.5 (18 H, Me), 6.12—6.26 (4 H, CH=CH) and 4.7—4.8 (2 H, CH), which confirm that the complex is present as such in solution, but the NMR spectra of the other arene complexes with lower electron densities in the

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, YIELDS AND MELTING POINTS FOR THE COMPLEXES PREPARED

Complex	Found (calcd.) (%)		Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)	Dec. p. (°C)
	C	H			
[Rh(TFB)(NBD)]ClO$_4$	43.93 (43.84)	2.55 (2.71)	125	53	150—151 [b]
[Rh(TFB)(COD)]ClO$_4$	45.17 (44.77)	2.64 (3.38)	121	59	180—181 [b]
[Rh(TFB)(Me$_2$BD)]ClO$_4$	43.15 (42.33)	3.24 (3.16)	139	74	170—174 [b]
[Rh(TFB)(MeBD)]ClO$_4$	42.00 (41.11)	2.96 (2.84)	139	79	164—166 [b]
[Rh(TFB)(C$_6$H$_6$)]ClO$_4$	42.51 (42.63)	2.47 (2.39)	139	71	172—174 [b]
[Rh(TFB)(C$_6$H$_5$OH)]ClO$_4$	42.23 (41.36)	2.24 (2.31)	137	68	190—191 [b]
[Rh(TFB)(C$_6$H$_5$Me)]ClO$_4$	44.69 (43.22)	2.79 (2.71)	132	61	168—170 [b]
[Rh(TFB)(C$_6$H$_5$OMe)]ClO$_4$	42.78 (42.50)	2.34 (2.63)	138	48	175—178 [b]
[Rh(TFB){1,3-C$_6$H$_4$(OMe)$_2$}]ClO$_4$	41.50 (42.30)	2.42 (2.84)	130	63	185—187 [b]
[Rh(TFB){1,4-C$_6$H$_4$Me$_2$}]ClO$_4$	45.93 (45.00)	2.96 (3.36)	138	93	197—199 [b]
[Rh(TFB){1,3,5-C$_6$H$_3$Me$_3$}]ClO$_4$	46.35 (46.00)	3.18 (3.31)	137	83	210—212 [b]
[Rh(TFB)(C$_6$Me$_6$)]ClO$_4$	48.45 (48.79)	3.75 (4.00)	133	97	262—264 [b]
[Rh(TFB)(DMSO)$_2$]ClO$_4$	31.97 (32.83)	3.02 (3.10)	135	72	106—108 [a]
[Rh(TFB)(THT)$_2$]ClO$_4$	39.38 (39.71)	3.64 (3.67)	141	56	103—105 [a]

[a] Melts under decomposition. [b] Decomposes.

ring indicate the existence of an equilibrium according to eq. 4:

$$[Rh(TFB)(arene)]ClO_4 + (CD_3)_2CO \rightleftharpoons [Rh(TFB)\{(CD_3)_2CO\}_x]ClO_4 + arene \quad (4)$$

which, e.g. for arene = toluene, is characterized by the presence of the complexes [Rh(TFB)(toluene)]ClO$_4$ [τ 7.46 (3 H, Me), 5.5—5.7 (4 H, CH=CH), 4.7—4.9 (2 H, CH), 2.90 (5 H, aromatic)] and [Rh(TFB){(CD$_3$)$_2$CO}$_x$]ClO$_4$ [τ 5.9—6.15 (4 H, CH=CH). 4.15—4.25 (2 H, CH)]. In the presence of an excess of the arene the equilibrium is displaced towards the left. Moreover, if the coordinated arene has a reduced donor capacity (e.g. benzene) the spectrum of the corresponding complex indicates complete dissociation of the benzene and the presence of [Rh(TFB){(CD$_3$)$_2$CO}$_x$]ClO$_4$ as the only species *.

If solvents with a high donor capacity, such as dimethylsulfoxide, are used, even coordinated hexamethylbenzene, which showed greater resistance to the

* Related exchanges in acetone have been recently reported for [Ir(COD)(arene)]BF$_4$ complexes [8].

TABLE 2

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

	Rh2Me	Rh3Me	Rh6Me
a) Crystal data			
Formulae	$[Rh(TFB)(C_6H_4Me_2)]^+ClO_4^-$	$[Rh(TFB)(C_6H_3Me_3)]^+ClO_4^-$ Yellow, Transparent, Prismatic	$[Rh(TFB)(C_6Me_6)]^+ClO_4^-$
Crystal habit	Hexagonal basis	Hexagonal basis	Rhombic basis
size (mm)	0.07 X 0.07 X 0.09 X 0.43	0.16 X 0.16 X 0.23 X 0.37	0.08 X 0.08 X 0.27
Symmetry	3/m Rhombohedral R3c. Acentric statistical test: N(Z) & E's		
Unit cell determination	$0(Cu) \leqslant 45^o$	$0(Cu) \leqslant 45^o$	$0(Mo) \leqslant 22^o$
Least-squares fit	73 reflections	55 reflections	56 reflections
Unit cell dimensions (Å)	25.7314(7), 16.2558(5)	26.2330(8), 16.3882(5)	27.1219(26), 17.0788(14)
Packing: V (Å^3), Z	9321.1(5), 18	9766.9(6), 18	10880.0(19), 18
D (g cm^{-3}), M, (F_{000})	1.714,534.7,4788	1.679,548.7,4932	1.623,590.8,5364
b) Experimental data			
Radiation and technique	CuK_α, 4-Circle PW1100 Philips diffractometer. Bisecting geometry		
Monochromator	Graphite oriented		
Orientation::	hh0: $\chi \sim -5^o$, $\varphi \sim 166^o$	hh0: $\chi \sim -6^o$, $\varphi \sim 160^o$	hh0: $\chi \sim -3^o$, $\varphi \sim 105^o$
	00l: $\chi \sim -85^o$, $\varphi \sim 2^o$	00l: $\chi \sim 81^o$, $\varphi \sim 153^o$	00l: $\chi \sim 81^o$, $\varphi \sim 180^o$

Collection mode (ω/2θ, 1° × 1° det. apertures)	0 ≤ 65°	0 ≤ 65°	0 ≤ 65°
	1.30°, 2 min/reflex.	1.30°, 1.25 min/reflex.	1.24°, 1.25 min/reflex.
Total, independent data and Rsym.	3765, 1764, 0.036	3928, 1847, 0.054	4347, 2048, 0.049
Obs. data: $2\sigma_c(I)$	1666	1553	1827
Stability	Two reflections every 90 min. No variation		
Absorption: faces	± (001, 2̄10, 1̄20, 110)	B (001, 210, 1̄30, 32̄0)	± (001, 320, 32̄0)
μ-Min. and max. transmission	85.89 cm⁻¹, 0.361—0.639	82.13 cm⁻¹, 0.469—0.634	74.15 cm⁻¹, 0.370—0.601

c) Solution and refinement

Solution mode		Patterson	
Refinement mode	X-Ray 70 system [20] UNIVAC 1100/80		
	Least-squares on F's. Observed reflections only. 3 blocks for the final L.S.		
	Mixed thermal mode with H		
Final shift/error	0.26	0.48	0.23
Parameters: no variables,	288	333	343
degrees pf freedom,	1378	1220	1484
ratio of freedom	5.8	4.7	5.3
ω-scheme	Empirical as to give trends in $(\omega\Delta^2)$ vs. $\langle F_0\rangle$ or $\langle\sin\theta/\lambda\rangle$		
ΔF	Gave all H-atoms		
Max. thermal values	Final ±0.54 $e\text{Å}^{-3}$	±0.38 $e\text{Å}^{-3}$	±0.50 $e\text{Å}^{-3}$
	$U_{33}F_2 = 0.41(3)$	$U_{33}C_2' = 0.62(8)$	$U_{33}O_1 = 0.56(6)$
R, R_w	0.037—0.046	0.039—0.047	0.046—0.047
Extinction	(220) omitted	None	Eleven omitted
Atomic factors	International Tables for X-ray Crystallography. Neutral atoms. [21]		
	Real part of anomalous dispersion applied for Rh and Cl		

TABLE 3

NORMAL PROBABILITY RESULTS

Type	Total points	Ex-cluded	Total R	Slope	Intercept	Correla-tion	DP. Ma:
f : δR-Rh6Me	2048	14	0.054	0.881(2)	—0.015(1)	0.997	±3
f : δR-Rh3Me	1847	8	0.048	0.910(1)	0.054(1)	0.999	±3
f : δR-Rh2Me	1764	69	0.039	1.324(2)	—0.017(2)	0.998	±3
h : Rh6Me vs. Rh3Me	92	3	0.066	23.1(4)	2.6(4)	0.987	50
h: Rh6Me vs. Rh2Me	89	35	0.112	61.3(17)	—4.1(8)	0.981	50
h : Rh3Me vs. Rh2Me	86	4	0.055	25.8(5)	—0.1(4)	0.987	50

exchange with acetone, is entirely replaced by dimethylsulfoxide. The complex thus formed, [Rh(TFB)(DMSO)$_2$]ClO$_4$, can also be prepared according to eq. 5:

$$1/2[RhCl(TFB)]_2 + AgClO_4 + 2 \text{ DMSO} \rightarrow [Rh(TFB)(DMSO)_2]ClO_4 + AgCl \quad (5)$$

In deuterochloroform this complex shows resonances at τ 7.2 (12 H, Me), 6.1—6.3 (4 H, CH=CH) and 4.25—4.45 (2 H, CH). The small variation of the methyl protons of DMSO relative to those in the free ligand point clearly to a coordination via the oxygen atom [9]. Such coordination of the dimethyl-sulfoxide by IR spectroscopy, as can be seen from the presence of a broad band due to ν(SO) at 940 cm^{-1} [10].

Sulfur-bonded rhodium complexes can be prepared by addition of tetrahy-drothiophen (THT) and AgClO$_4$ to [RhCl(TFB)]$_2$; the obtained [Rh(TFB)-(THT)$_2$]ClO$_4$ has been characterized by the usual techniques.

Crystal structure

The ClO$_4$ group has the same bond distribution in the three compounds: two long bonds (~1.41 Å), an intermediate one (~1.38 Å), and a much shorter one (see Table 4).

Figure 1 shows the Rh coordination as seen from the centre of the arene ring in the TFB moiety. The Rh—C (arene) lengths show different patterns: while Rh6Me shows three shorter [to C(1), C(2) and C(4)] along with three longer distances, Rh3Me and Rh2Me display only two shorter ones [to C(2) and C(5)] along with four longer distances, the latter being more evenly distributed for Rh2Me than for Rh3Me.

It seems useful to compare the present results with those described in the literature for Rh{P(OMe)$_3$}$_2$(PhBPh$_3$), Rh(diphos)(PhBPh$_3$) and [Rh(C$_6$H$_5$Me)-{P(OPh)$_3$}$_2$]ClO$_4$ [11—13]. The Rh distances to the best least-squares plane through the arene rings are shorter for the compounds (~1.82 Å) described here than for those with P ligands (~1.86 Å). In the phosphite derivatives the plane through Rh, P(1) and P(2) roughly bisects two opposite C—C bonds in the arene, with the four C atoms of these bonds nearer to the metal, the rings are thus adopting a conformation in between "skew" and "boat", whereas in the homologous diphosphine complex the two C atoms nearest to the metal are approximately *trans* with respect to both P atoms, and so the conformation appears inverted compared with that in the phosphite complexes.

For the three complexes described in this paper, whatever method is used for

TABLE 4

MOST RELEVANT BOND DISTANCES (Å) AND ANGLES (°)

Distance	Rh2Me	Rh3Me	Rh6Me	Angle	Rh2Me	Rh3Me	Rh6Me
Rh—C(1)	2.303(10)	2.323(9)	2.260(8)	C(6)—C(1)—C(2)	121.4(14)	120.6(12)	118.8(10)
Rh—C(2)	2.253(9)	2.258(11)	2.282(9)	C(1)—C(2)—C(3)	121.5(12)	120.8(12)	120.8(10)
Rh—C(3)	2.324(9)	2.351(13)	2.334(11)	C(2)—C(3)—C(4)	118.0(11)	118.0(12)	118.4(11)
Rh—C(4)	2.311(12)	2.347(12)	2.283(14)	C(3)—C(4)—C(5)	120.0(12)	119.3(12)	120.7(12)
Rh—C(5)	2.232(13)	2.289(12)	2.324(14)	C(4)—C(5)—C(6)	121.8(14)	121.2(12)	120.0(12)
Rh—C(6)	2.337(12)	2.316(11)	2.331(10)	C(5)—C(6)—C(1)	116.8(15)	119.6(12)	120.8(11)
Rh—C(6')	2.118(11)	2.144(12)	2.125(10)	C(11')—C(1')—F(1)	120.0(18)	118.5(17)	120.9(20)
Rh—C(7')	2.125(9)	2.127(19)	2.123(10)	C(2')—C(1')—F(1)	120.9(19)	125.4(22)	123.7(22)
Rh—C(9')	2.125(9)	2.087(13)	2.128(15)	C(2')—C(1')—C(11')	119.1(18)	114.9(21)	115.4(21)
Rh—C(10')	2.153(12)	2.121(15)	2.142(19)	C(1')—C(2')—F(2)	118.4(19)	113.0(29)	117.3(25)
C(1)—C(2)	1.414(21)	1.407(19)	1.431(14)	C(1')—C(2')—C(3')	122.8(20)	121.0(33)	122.1(27)
C(2)—C(3)	1.406(18)	1.427(21)	1.413(20)	C(3')—C(2')—F(2)	118.8(19)	120.7(34)	119.9(27)
C(3)—C(4)	1.387(21)	1.427(22)	1.448(20)	C(2')—C(3')—F(3)	122.0(19)	119.1(28)	123.4(24)
C(4)—C(5)	1.413(21)	1.429(19)	1.404(18)	C(2')—C(3')—C(4')	118.1(19)	126.0(28)	124.4(24)
C(5)—C(6)	1.432(26)	1.396(19)	1.400(23)	C(4')—C(3')—F(3)	119.9(18)	112.7(20)	111.7(19)
C(6)—C(1)	1.369(29)	1.389(21)	1.430(19)	C(3')—C(4')—F(4)	118.0(16)	124.6(19)	121.4(20)
C(1')—C(2')	1.362(34)	1.462(47)	1.438(39)	C(3')—C(4')—C(12')	121.0(16)	113.0(18)	114.0(19)
C(1')—F(1)	1.325(33)	1.350(27)	1.349(31)	C(12')—C(4')—F(4)	121.0(15)	122.0(17)	124.6(19)
C(1')—C(11')	1.400(15)	1.397(17)	1.403(21)	C(10')—C(5')—C(12')	106.4(9)	108.0(12)	107.8(13)
C(2')—C(3')	1.336(42)	1.193(64)	1.219(49)	C(6')—C(5')—C(12')	109.9(9)	108.4(12)	111.0(12)
C(2')—F(2)	1.343(16)	1.339(27)	1.325(27)	C(6')—C(5')—C(10')	98.5(9)	96.4(11)	97.0(12)
C(3')—C(4')	1.391(17)	1.434(23)	1.486(26)	C(5')—C(6')—C(7')	111.6(10)	113.7(11)	111.3(11)
C(3')—F(3)	1.317(25)	1.385(30)	1.399(27)	C(6')—C(7')—C(8')	114.8(10)	113.5(11)	114.6(12)
C(4')—C(12')	1.371(21)	1.429(26)	1.373(26)	C(7')—C(8')—C(11')	109.0(10)	111.4(12)	108.3(12)
C(4')—F(4)	1.367(25)	1.331(26)	1.307(30)	C(7')—C(8')—C(9')	98.1(9)	96.3(11)	97.1(11)
C(5')—C(6')	1.527(18)	1.554(22)	1.546(24)	C(9')—C(8')—C(11')	109.0(10)	106.1(12)	108.0(12)
C(5')—C(10')	1.519(16)	1.537(21)	1.526(21)	C(8')—C(9')—C(10')	111.9(9)	115.3(14)	113.4(13)
C(5')—C(12')	1.524(11)	1.523(15)	1.496(17)	C(5')—C(10')—C(9')	114.1(10)	113.4(13)	114.2(14)
C(6')—C(7')	1.409(18)	1.399(19)	1.423(18)	C(1')—C(11')—C(8')	127.1(13)	127.5(16)	123.4(16)
C(7')—C(8')	1.503(18)	1.520(20)	1.503(23)	C(8')—C(11')—C(12')	113.8(11)	111.8(15)	114.7(13)
C(8')—C(9')	1.495(16)	1.607(20)	1.524(21)	C(1')—C(11')—C(12')	119.0(13)	120.5(16)	121.8(16)
C(8')—C(11')	1.529(16)	1.513(20)	1.541(18)	C(5')—C(12')—C(11')	113.9(10)	116.3(15)	113.5(13)
C(9')—C(10')	1.423(14)	1.332(26)	1.381(21)	C(4')—C(12')—C(11')	119.9(13)	120.8(16)	121.7(16)
C(11')—C(12')	1.367(20)	1.394(30)	1.370(24)	C(4')—C(12')—C(5')	126.1(12)	122.8(15)	124.8(15)
C1—O(1)	1.406(23)	1.315(18)	1.298(37)	O(1)—C1—O(2)	101.0(19)	109.4(12)	112.1(17)
C1—O(2)	1.352(41)	1.374(24)	1.408(26)	O(1)—C1—O(3)	105.7(19)	109.8(15)	105.7(26)
C1—O(3)	1.385(26)	1.426(22)	1.407(28)	O(1)—C1—O(4)	104.1(16)	113.5(12)	118.8(26)
C1—O(4)	1.417(15)	1.414(13)	1.388(22)	O(2)—C1—O(3)	114.7(19)	105.3(18)	103.8(18)
				O(2)—C1—O(4)	118.3(16)	116.1(10)	113.4(15)
				O(3)—C1—O(4)	111.0(16)	102.1(11)	100.9(15)
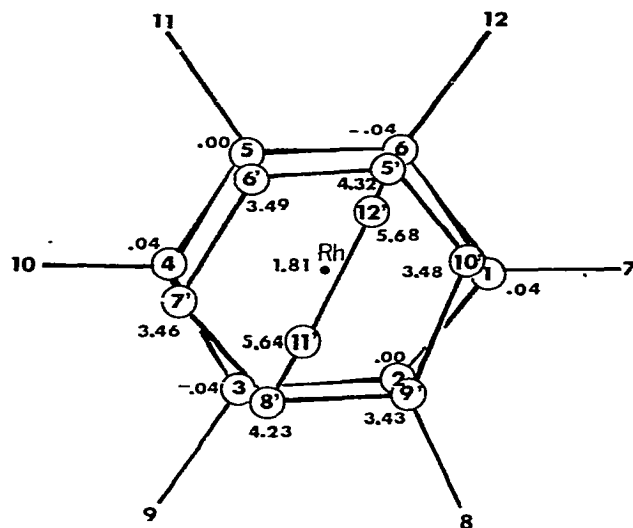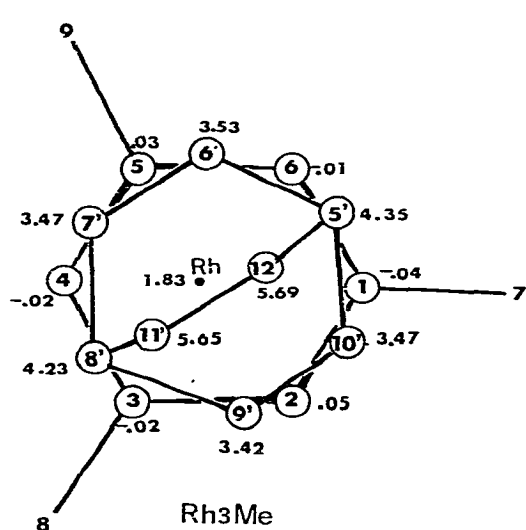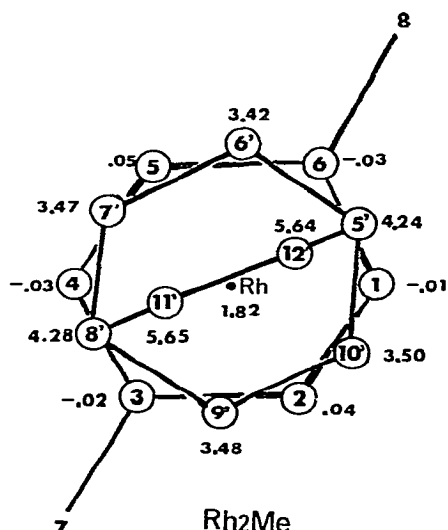
Fig. 1. Coordination around the Rh atom, including deviations (Å) from the mean six-membered plane of the arene ring. Olefinic carbons of the coordinated TFB ligand are also included.

the analysis of the non-planarity of the arene rings [14—15], the following pattern emerges: the *trans* region of the rings relative to the olefin bonds are closer to the Rh atoms, and Rh6Me has almost a regular "skew" conformation with four carbons roughly "*trans*" with respect to the olefins bonds; the Rh2Me complex forms an "inverted boat", distorted towards an envelope, with two carbon atoms (C(2) and C(5)) *trans* relative to the olefin bonds; in the

TABLE 5

SELECTED TORSION ANGLES (°), THROUGH CARBON ATOMS

	Rh2Me	Rh3Me	Rh6Me
6—1—2—3	4.5(21)	9.0(19)	—3.4(16)
1—2—3—4	—4.7(18)	—7.5(19)	—3.2(17)
2—3—4—5	—1.4(17)	1.1(19)	6.8(18)
3—4—5—6	7.9(21)	3.9(18)	—3.6(19)
4—5—6—1	—8.1(23)	—2.6(19)	—3.3(19)
5—6—1—2	1.9(23)	—3.8(19)	6.8(17)
11'—8'—5'—12'	—0.1(9)	—0.4(11)	1.6(11)
11'—8'—5'—10'	122.4(9)	124.2(12)	125.1(14)
11'—8'—5'—6'	—126.2(9)	—127.1(11)	—125.4(11)
7'—8'—5'—12'	125.6(9)	126.9(11)	126.8(12)
7'—8'—5'—10'	—112.0(8)	108.5(9)	—109.7(11)
7'—8'—5'—6'	—0.6(6)	0.2(7)	—0.2(7)
9'—8'—5'—12'	—124.4(9)	—123.2(12)	—123.8(12)
9'—8'—5'—10'	—2.0(7)	1.4(8)	—0.3(11)
9'—8'—5'—6'	109.5(7)	110.1(8)	109.2(8)
5'—6'—7'—8'	—1.0(14)	0.3(16)	—0.4(16)
6'—7'—8'—9'	—61.0(12)	—58.0(13)	—60.4(14)
7'—8'—9'—10'	62.5(11)	58.9(16)	61.4(15)
8'—9'—10'—5'	—3.6(13)	2.8(19)	—0.6(19)
9'—10'—5'—6'	—58.1(11)	—62.0(15)	—60.7(16)
10'—5'—6'—7'	59.8(12)	61.6(14)	60.4(14)
5'—6'—7'—8'	—1.0(14)	0.3(16)	—0.4(16)
6'—7'—8'—11'	52.4(13)	51.9(16)	51.2(16)
7'—8'—11'—12'	—51.9(14)	—51.5(18)	—54.0(17)
8'—11'—12'—5'	—0.1(15)	—0.7(21)	3.0(19)
11'—12'—5'—6'	52.4(13)	50.7(18)	50.2(17)
12'—5'—6'—7'	—51.2(13)	—49.8(15)	—51.8(15)
5'—10'—9'—8'	—3.6(13)	2.8(19)	—0.6(19)
10'—9'—8'—11'	—50.9(12)	—55.5(17)	—50.4(17)
9'—8'—11'—12'	54.2(13)	52.1(17)	50.1(17)
8'—11'—12'—5'	—0.1(15)	—0.7(21)	3.0(19)
11'—12'—5'—10'	—53.3(13)	—52.7(81)	—54.8(17)
12'—5'—10'—9'	55.7(12)	49.7(17)	54.1(18)

Rh3Me the last conformation is distorted mainly at the C(6)—C(1) bond, towards a "skew" conformation.

Furthermore, in complexes where an alternative is possible, i.e. [Rh(TFB)-(1,4-$C_6H_4Me_2$)]ClO_4 and [Rh(C_6H_5Me){P(OPh)$_3$}$_2$]ClO_4 [13], the C atoms attached to the methyl group are further from the rhodium atom.

The different relative positions of the arene relative to the TFB moiety are noteworthy: the average twist between these entities is 5.5° (Rh6Me), —24.4° (Rh3Me) and —32.9° (Rh2Me) respectively, as measured from the bond—bond coincidence in the projection (see Fig. 1).

In the TFB moiety the three rings have a typical "boat" conformation, but again Rh6Me is different from the other two in having the less distorted "boat" facing the Rh atom, the other two compounds having the conformation distorted at the 9'—10' torsion angle (see Table 5). The relative twist of the rings along C(5')⋯C(8') is negligible (0.4°, 0.4° and —0.9°) for the three compounds.

The Rh—C (olefin) distances are very similar in the Rh6Me complex, not so

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similar in Rh2Me, and irregularly distributed in Rh3Me. The two olefinic * bonds show a similar elongation in Rh2Me, different elongations in Rh6Me, and very different elongations in Rh3Me (see Table 4), i.e. the coordination around the Rh atom is most symmetric in Rh6Me and least symmetric in Rh3Me.

The reasons for the different conformation and relative ring positions are not clear. It seems very doubtful that they could be due simply to packing forces in the solid, and it is more likely that electronic factors are responsible. Work on this problem is in progress.

Experimental

C, H and N analyses were carried out on a Perkin-Elmer 240 microanalyzer. Conductivities were measured in approx. 5×10^{-4} M acetone solutions with a Philips 9501/01 conductimeter. IR spectra were recorded (over the range 4000—200 cm^{-1}) on a Perking-Elmer 577 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian XL-100 and a Perkin-Elmer R-12B instrument, with TMS as reference.

All the complexes are yellow, they were prepared under argon at room temperature, but reasonably stable as solids. The dimeric starting complexes were obtained as described elsewhere [5,17].

Synthesis of complexes of the type [Rh(TFB)(diolefin)]ClO$_4$

To an acetone solution of [RhCl(COD)]$_2$ [17] (30 mg, 0.66 mmol) were added AgClO$_4$ (25.3 mg, 0.12 mmol) and TFB (27.6 mg, 0.12 mmol). After 30 min stirring the precipitated AgCl was removed by filtration through kieselguhr and the filtrate was concentrated to 3 ml. Addition of diethyl ether caused precipitation of [Rh(TFB)(COD)]ClO$_4$, which was filtered off.

[Rh(TFB)(NBD)]ClO$_4$ was prepared analogous by treating [RhCl(NBD)]$_2$ [17] (40 mg, 0.09 mmol) with AgClO$_4$ (36.1 mg, 0.18 mmol) and TFB (39.4 mg, 0.18 mmol).

[Rh(TFB)(MeBD)]ClO$_4$ and [Rh(TFB)(Me$_2$BD)]ClO$_4$ were prepared analogously by treating [RhCl(TFB)]$_2$ [5] (30 mg, 0.04 mmol) with AgClO$_4$ (17.1 mg, 0.08 mmol) and 1 ml of the corresponding diene (MeBD or Me$_2$BD). (The MeBD complex was precipitated by successive addition of 0.5 ml each of the diolefine and ether).

Synthesis of complexes of the type [Rh(TFB)(arene)]ClO$_4$

A suspension of [RhCl(TFB)]$_2$ in 10 ml of acetone was treated with AgClO$_4$ (17.1 mg, 0.08 mmol) and the corresponding arene (C$_6$Me$_6$ (13.34 g, 0.08 mmol); C$_6$H$_3$Me$_3$ (0.5 ml); C$_6$H$_4$Me$_2$ (1 ml); C$_6$H$_4$(OMe)$_2$ (0.1 ml); C$_6$H$_5$Me (1 ml); C$_6$H$_5$OMe (0.5 ml); C$_6$H$_5$OH (37.8 mg, 0.41 mmol); C$_6$H$_6$ (1 ml). After work-up as above, the complexes were precipitated with diethyl ether and recrystallized from dichloromethan/hexane.

Synthesis of [Rh(TFB)(DMSO)$_2$]ClO$_4$

Similar treatment of [RhCl(TFB)]$_2$ (40 mg, 0.05 mmol) in 10 ml of acetone

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* Olefinic C—C distances for free TFB: 1.307 and 1.302 Å [16].

with $AgClO_4$ (22.8 mg, 0.11 mmol) and DMSO (0.1 ml) gave the required complex, which was recrystallized from dichloromethane/ether.

Synthesis of [Rh(TFB)(THT)$_2$]ClO$_4$

Similarly, reaction of [RhCl(TFB)]$_2$ (30 mg, 0.04 mmol) in acetone with $AgClO_4$ (17.1 mg, 0.08 mmol) and THT (19.97 mg, 0.23 mmol) gave the required complex, which was precipitated by addition of ethanol/ether.

X-ray analysis

Crystal and experimental data and refinement parameters for the three compounds are given in Table 2. In spite of the similar composition, cell dimensions and space group, the isomorphism was not exact enough for one structure to be solved from another. δR plots [18] were used as a test for the refinements, and Table 3 lists the results. In the same table the half normal analysis [18] between coordinates confirm the lack of isomorphism. In Fig. 2 we show the half normal analysis in terms of the contact distances up to 4 Å [19] which
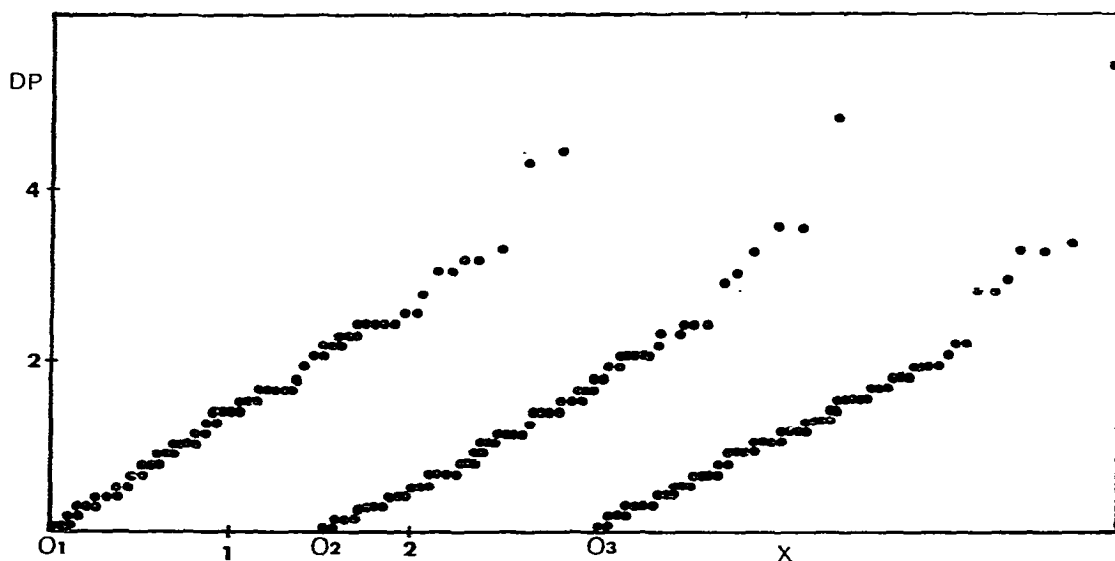
O$_1$, O$_2$ & O$_3$ are the shifted origins

	Rh2Me vs. Rh3Me	Rh2Me vs. Rh6Me	Rh3Me vs. Rh6Me
N$_t$	116	116	116
R$_t$	0.016	0.014	0.012
N$_{ex}$	10	7	6
DP$_{max}$	2.5	2.5	2.5
e	0.997	0.997	0.999
x^2	0.003	0.003	0.001

DP=1.552(10)X+0.020(9) DP=1.349(10)X−0.054(9) DP=1.183(5)X+0.021(4)

Fig. 2. Half normal probability plot of the distances less than 4 Å based on the results from the three compounds, with the parameters of the fit.
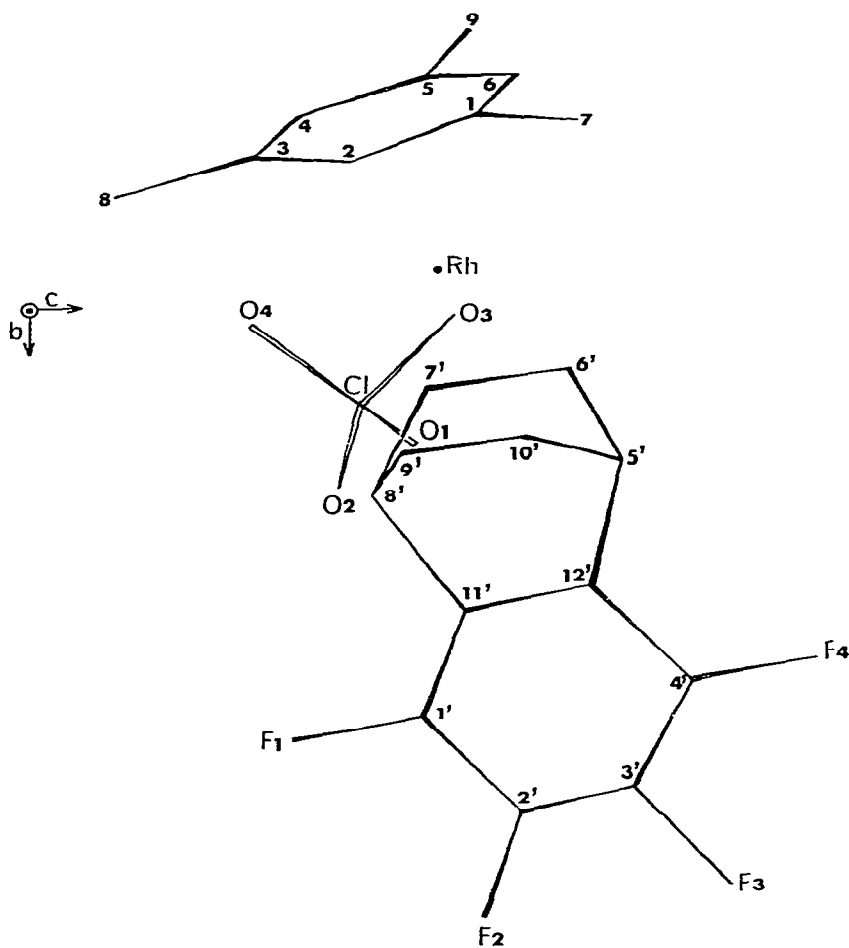
Fig. 3. A view of the Rh3Me complex showing the atomic numbering for all three compounds.

reveal the main differences among the compounds. Figure 3 displays the atomic numbering for one of the compounds (Rh3Me), the others being the same. In Table 4 are the most relevant bond distances and angles. The geometry of the rings can be seen through the torsion angles (Table 5) and the results of some least squares calculations (Fig. 1). A list of the structure factors, atomic coordinates and the thermal parameters can be obtained from the authors.

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