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ARENE-RHODIUM(I) COMPLEXES WITH TRIMETHYLTETRAFLUOROBENZOBARRELENE. CRYSTAL STRUCTURE OF [Rh(Me_3TFB)(1,4-$C_6H_4Me_2$)]ClO_4

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Summary

The preparation of arene-rhodium(I) complexes of the general formula Rh(Me_3TFB)$PhBPh_3$ and [Rh(Me_3TFB)(arene)]ClO_4 (Me_3TFB = trimethyltetrafluorobenzobarrelene; arene = $C_6H_{6-n}Me_n$ (n = 0, 1, 2, 3, 4 or 6); $C_6H_{6-n}X_n$ (X = F, n = 2 or 6; X = Cl, n = 1 or 2) are described. For arenes of the type $C_6H_{6-n}X_n$ the dissociation of the coordinated arene (studied by NMR spectroscopy in deuteroacetone) is complete, but for arenes of the type $C_6H_{6-n}Me_n$ it decreases with increasing methyl substitution in the arene ligand.

The crystal structure of [Rh(Me_3TFB)(1,4-$C_6H_4Me_2$)]ClO_4 has been determined by X-ray diffraction. The compound crystallizes in the *Pbca* space group, with lattice periodicities of 17.7393(4), 15.7816(3) and 16.0071(3) Å. δR-analysis, for the 3953 total recorded reflections, support the refinement carried out to a final R-value of 0.062. The bonding of the arene to the rhodium is η^6, with the ring slightly puckered to give a distorted skew conformation.

Introduction

Arene complexes of Group VIII transition metals have been extensively studied [1,2] because of their chemical and catalytic activity. In particular, the preparations of several types of arene-rhodium(I) complexes have been described [3—10], and we recently reported the preparations of a series of com-

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pounds of the type [Rh(TFB)(arene)]ClO_4 in which the arene is labile in solution [11]. We now describe a family of related complexes in which the presence of the ligand trimethyltetrafluorobenzobarrelene (Me_3TFB, a diolefin containing a methyl group linked to one carbon of each double bond) lowers the lability of the arene—rhodium-bond.

Results and discussion

Preparation and properties of the complexes

Roe and Massey [12] reported the preparation of the ligand trimethyltetrafluorobenzobarrelene (Me_3TFB) (see Fig. 3) and of the binuclear complex [RhCl(Me_3TFB)]$_2$. Acetone suspensions of the latter react with silver perchlorate to give, as an intermediate, the solvate [Rh(Me_3TFB)(Me_2CO)$_x$]ClO_4, which reacts with acetone solutions of sodium tetraphenylborate to yield Rh(Me_3TFB)·$PhBPh_3$. This complex, which is non-conducting in acetone, has been identified by elemental analysis, IR [13] and NMR spectroscopy.

Other arene complexes of the general formula [Rh(Me_3TFB)(arene)]ClO_4 were made as indicated in eq. 1.

$$\tfrac{1}{2}\,[\mathrm{RhCl(Me_3TFB)}]_2 + \mathrm{AgClO_4} + \text{arene} \rightarrow [\mathrm{Rh(Me_3TFB)(arene)}]\mathrm{ClO_4} + \mathrm{AgCl} \qquad (1)$$

The complexes containing arenes of the type $C_6H_{6-n}Me_n$, C_6F_6 and C_6H_5Cl can be isolated reasonably pure. Analytical data, yields and conductivities are listed in Table 1. However, the complexes involving the types 1,3-$C_6H_4F_2$, 1,2-$C_6H_4F_2$ and 1,4-$C_6H_4Cl_2$ are hygroscopic, and could not be completely purified.

All the complexes are pale-yellow and behave as 1/1 electrolytes in acetone. In all cases the IR spectra show the presence of the uncoordinated perchlorate anion [14], and there are also strong bands characteristic of the coordinated trimethyltetrafluorobenzobarrelene group (at 1500, 1490, 1060, 970, 930 and 850 cm^{-1}) together with weak absorption bands arising from the coordinated arene.

NMR studies

Solutions of the complexes of the type [Rh(Me_3TFB)($C_6H_{6-n}X_n$)]ClO_4 (X = F or Cl) in deuteroacetone all give the same ^{1}H NMR spectra as a result of the displacement of the coordinated arene and the subsequent formation of [Rh(Me_3TFB)$_2${$(CD_3)_2CO$}$_x$]$^+$ (τ 8.48 (6 H, Me), 7.39 (3 H, Me), 6.62 (2 H, CH=C) and 4.63 (1 H, CH)). This was confirmed by preparing the species as indicated in eq. 2.

$$\tfrac{1}{2}\,[\mathrm{RhCl(Me_3TFB)}]_2 + \mathrm{AgClO_4} + x\,\mathrm{(CD_3)_2CO} \rightarrow [\mathrm{Rh(Me_3TFB)}\{\mathrm{(CD_3)_2CO}\}_x]\mathrm{ClO_4} + \mathrm{AgCl} \qquad (2)$$

The NMR spectra of complexes of arenes of the type $C_6H_{6-n}Me_n$ (n = 0, 1, 2 or 3) reveal the presence of the rapidly established equilibrium 3, which is

$$[\mathrm{Rh(Me_3TFB)(C_6H_{6-n}Me_n)}]\mathrm{ClO_4} + x\,\mathrm{(CD_3)_2CO} \rightleftharpoons [\mathrm{Rh(Me_3TFB)}\{\mathrm{(CD_3)_2CO}\}_x]\mathrm{ClO_4} + \mathrm{C_6H_{6-n}Me_n} \qquad (3)$$

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, YIELDS AND NMR DATA FOR COMPLEXES OF THE TYPE $[Rh(Me_3TFB)(arene)]ClO_4$

Complex	Found (calcd.) (%)		Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)	Coordinated arene[a]	
	C	H			aromatic H	methyl
$[Rh(Me_3TFB)(C_6Me_6)]ClO_4$	51.37 (51.24)	4.83 (4.78)	131	51		7.52
$[Rh(Me_3TFB)(1,2,4,5\text{-}C_6H_2Me_4)]ClO_4$	50.00 (49.64)	4.42 (4.33)	138	85	3.50	7.47
$[Rh(Me_3TFB)(1,3,5\text{-}C_6H_3Me_3)]ClO_4$	49.54 (48.79)	4.10 (4.09)	133	93	3.13	7.49
$[Rh(Me_3TFB)(1,4\text{-}C_6H_4Me_2)]ClO_4$	48.68 (47.90)	3.73 (3.84)	140	98	2.97	7.41
$[Rh(Me_3TFB)(1,3\text{-}C_6H_4Me_2)]ClO_4$	48.43 (47.90)	4.15 (3.84)	129	89	3.02	7.43
$[Rh(Me_3TFB)(C_6H_5Me)]ClO_4$	47.74 (47.00)	3.66 (3.58)	139	90	2.93	7.39
$[Rh(Me_3TFB)(C_6H_6)]ClO_4$	45.96 (45.97)	3.34 (3.31)	127	74	2.81	
$[Rh(Me_3TFB)(C_6F_6)]ClO_4$	37.30 (38.41)	1.96 (1.81)	150	61	—	
$[Rh(Me_3TFB)(C_6H_5Cl)]ClO_4$	42.19 (43.04)	3.00 (2.94)	142	26	—	

[a] NMR (τ).

increasingly displaced towards the right with decreasing methyl substitution on the arene ring. The dissociation of the coordinated arene is less than that of the analogous tetrafluorobenzobarrelene complexes [11]. For the case of arene = toluene, the integrated signals show that the species $[Rh(Me_3TFB)\{(CD_3)_2CO\}_x]^+$ forms 50% of the mixture for a 0.2 M, 70% for a 0.05 M, 75% for a 0.025 M and 100% for a 0.005 M solution. For the analogous $[Rh(TFB)(C_6H_5Me)]ClO_4$, the $[Rh(TFB)\{(CD_3)_2CO\}_x]^+$ forms 54% of the mixture for a 0.2 M, 87% for 0.05 M and 100% for a 0.025 M.

The complexes with 1,2,4,5-tetramethylbenzene (durene) and hexamethylbenzene in deuteroacetone show no dissociation, while saturated deuteroacetone solutions of the related complexes $[Rh(C_6Me_6)(CO)_2]^+$ and $[Rh(C_6Me_5)(CO)P(p\text{-}MeC_6H_4)_3]^+$ [15] contain the corresponding solvated complex (73 and 58%, respectively), formed by displacement of the hexamethylbenzene.

In complexes of the type $[Rh(Me_3TFB)(C_6H_{6-n}Me_n)]ClO_4$ the chemical shift of the arene-methyl substituents moves downfield by ca. 0.3 ppm upon coordination. The resonances of protons directly bound to the arene ring are also modified upon coordination of the arene. The upfield displacement of the chemical shift of the vinyl protons * is directly related to the number of methyl groups present in the arene and increases with the donor capacity of the arene and the stability of the complexes [2]. Table 2 lists some relevant data for complexes of the type $[M(diolefin)(arene)]^+$ (M = Rh or Ir).

The complex $[Rh(Me_3TFB)(C_6Me_6)]ClO_4$ does not undergo any change upon dissolution in dimethylsulfoxide (DMSO), whilst the analogous $[Rh(TFB)(C_6Me_6)]ClO_4$ reacts with DMSO to give $[Rh(TFB)(DMSO)_2]ClO_4$ [11]. These results reveal again the decreased lability of the arene ligand in trimethyltetrafluorobenzobarrelene derivatives, compared with that in the corresponding tetrafluorobenzobarrelene complexes.

The compound $Rh(Me_3TFB)PhBPh_3$ shows a complex NMR spectrum in the aromatic region, in accord with the presence of a coordinated phenyl group [13]. The coordinated trimethyltetrafluorobenzobarrelene gives resonances at τ 8.59 (6 H, Me), 7.94 (3 H, Me), 6.97 (2 H, CH=C) and 5.52 (1 H, CH). The relatively τ values for the resonances of protons of the methyl groups linked to doubly-bonded C atoms and also for the vinyl protons (see Table 2) suggest that the arene $PhBPh_3$ is not readily displaceable, and no species of the type $[Rh(Me_3TFB)\{(CD_3)_2CO\}_x]^+$ is observed in the corresponding NMR spectra. No reaction was observed when a dichloromethane solution of $Rh(Me_3TFB)PhBPh_3$ was refluxed with 2,2'-bipyridine or triphenylphosphine. However, this complex does react with these ligands in acetone solution at room temperature with formation of $[Rh(Me_3TFB)(bipy)]BPh_4$ and $[Rh(Me_3TFB)(PPh_3)_2]BPh_4$.

Crystal structure of $[Rh(Me_3TFB)(1,4\text{-}C_6H_4Me_2)]ClO_4$

The structure of the present compound resembles that of the unmethylated tetrafluorobenzobarrelene analogue [11], showing the same features in the ClO_4 group, the same decrease in the intracyclic arene angles where the methyl groups are attached though more symmetrical values are observed in the pres-

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[*] Similar behaviour is observed for methyl groups linked to doubly-bonded C atoms in the trimethyltetrafluorobenzobarrelene ligand. The chemical shift is in the range τ 8.4—8.1.

TABLE 2

CHEMICAL SHIFTS [a] OF VINYL PROTONS FOR [M(diolefin)(arene)]$^+$ COMPLEXES

Arene	Diolefin (M = Rh)				Diolefin (M = Ir)
	Me_3TFB [b]	TFB	NBD [c]	COD [c]	COD [d]
C_6Me_6	6.78	6.20	6.63	6.35	—
1,2,4,5-$C_6H_2Me_4$	6.50	—	—	—	5.81
1,3,5-$C_6H_3Me_3$	6.42	5.82	6.06	5.66	5.77
1,4-$C_6H_4Me_2$	6.27	5.72	—	—	—
1,3-$C_6H_4Me_2$	6.26	—	5.92	5.46	5.38
C_6H_5Me	6.13	5.60	5.80	5.41	—
C_6H_6	6.04	—	5.65	—	5.20

[a] τ. [b] Other NMR resonances: τ 8.4—8.1 (6 H, Me), 7.9—7.85 (3 H, Me), 5.3—5.1 (1 H, CH). [c] Ref. 4. [d] Ref. 2.

ent case and even showing the smallest values for the C(6′)—C(5′)—C(10′) and C(7′)—C(8′)—C(9′) angles (Table 3).

The Rh—C(olefin) distances in the present compound show a more symmetrical pattern, being similar and shorter to C(7′) and C(9′), and similar and larger to C(6′) and C(10′) (see Table 3), where the methyl groups are attached. The distribution of Rh—C(arene) distances shows a similar distribution to those in the unmethylated tetrafluorobenzobarrelene compound, with two values shorter than the others. But the four higher values show a broader spread in the present compound.

These distances, together with the values of the torsion angles within the ring (Table 4) and the deviations from the least squares plane of the ring atoms (Fig. 1), show that the puckering of the arene ring is best regarded as a distorted skew conformation, whilst the tetrafluorobenzobarrelene compound has the arene ring in a distorted boat conformation [11], the fit of a least squares plane through C(1), C(3), C(4), C(6) being much better than that in the present compound (see Fig. 2). We have calculated the angles formed between that plane and the other two flapping ones, through C(1), C(2), C(3) and through C(4), C(5), C(6), to give the deviations from the four atom plane of the carbon atoms C(2) and C(5), which lie closer to the Rh atom. These angles (Fig. 2) are 5.7 and 6.4°, respectively, for this compound compared with 4.0 and 7.0° for the tetrafluorobenzobarrelene derivative.

A deviation from planarity of the coordinated ring is observed for this as well as for other arene—rhodium(I) complexes whose structures have recently been determined [8,11,16,17]. The rhodium—olefin (or rhodium—phosphorus) bond generally strengthens the Rh—C bonds *trans* to it, so that the arene shows a slight tendency to depart from planarity in accord with the strong tendency of the rhodium(I) to achieve a square-planar coordination. Nonetheless, we think that the arene is always six-bonded to the rhodium atom, even though a certain localization in the molecular orbitals of the arene *trans* to the ancillary ligand takes place.

The previously mentioned increased lability of the rhodium—arene bond in tetrafluorobenzobarrelene derivatives compared with that in the analogous tri-

TABLE 3

BOND DISTANCES (Å) AND ANGLES (°)

Rh—C(1)	2.333(10)	C(1')—C(2')	1.365(12)
Rh—C(2)	2.258(8)	C(1')—F(1)	1.347(10)
Rh—C(3)	2.344(9)	C(1')—C(11')	1.384(11)
Rh—C(4)	2.293(10)	C(2')—C(3')	1.373(15)
Rh—C(5)	2.245(10)	C(2')—F(2)	1.338(11)
Rh—C(6)	2.365(9)	C(3')—C(4')	1.384(13)
Rh—C(6')	2.156(7)	C(3')—F(3)	1.342(11)
Rh—C(7')	2.117(7)	C(4')—C(12')	1.376(12)
Rh—C(9')	2.115(7)	C(4')—F(4)	1.361(11)
Rh—C(10')	2.154(8)	C(5')—C(6')	1.547(11)
C(1)—C(2)	1.422(14)	C(5')—C(10')	1.521(11)
C(2)—C(3)	1.400(14)	C(5')—C(12')	1.506(11)
C(3)—C(4)	1.399(14)	C(6')—C(7')	1.390(12)
C(4)—C(5)	1.411(14)	C(7')—C(8')	1.535(11)
C(5)—C(6)	1.397(14)	C(8')—C(9')	1.552(11)
C(6)—C(1)	1.406(14)	C(8')—C(11')	1.525(10)
C(3)—C(7)	1.511(19)	C(9')—C(10')	1.388(11)
C(6)—C(8)	1.508(17)	C(11')—C(12')	1.387(11)
Cl—O(1)	1.392(10)	C(8')—C(13')	1.526(12)
Cl—O(2)	1.399(8)	C(6')—C(14')	1.476(12)
Cl—O(3)	1.385(12)	C(10')—C(15')	1.494(14)
Cl—O(4)	1.365(13)		
C(6)—C(1)—C(2)	119.1(9)	C(6')—C(7')—C(8')	116.3(7)
C(1)—C(2)—C(3)	122.7(8)	C(7')—C(8')—C(11')	108.3(6)
C(2)—C(3)—C(4)	117.1(8)	C(7')—C(8')—C(9')	96.3(6)
C(3)—C(4)—C(5)	120.4(9)	C(9')—C(8')—C(11')	106.8(6)
C(4)—C(5)—C(6)	122.1(9)	C(8')—C(9')—C(10')	115.4(7)
C(5)—C(6)—C(1)	117.9(9)	C(5')—C(10')—C(9')	111.8(7)
C(2)—C(3)—C(7)	121.5(10)	C(1')—C(11')—C(8')	128.6(7)
C(4)—C(3)—C(7)	121.3(10)	C(8')—C(11')—C(12')	113.0(6)
C(1)—C(6)—C(8)	121.1(9)	C(1')—C(11')—C(12')	118.3(7)
C(5)—C(6)—C(8)	121.0(9)	C(5')—C(12')—C(11')	115.0(7)
C(11')—C(1')—F(1)	122.0(7)	C(4')—C(12')—C(11')	120.1(7)
C(2')—C(1')—F(1)	116.7(7)	C(4')—C(12')—C(5')	124.9(7)
C(2')—C(1')—C(11')	121.3(8)	C(11')—C(8')—C(13')	117.4(7)
C(1')—C(2')—F(2)	120.4(8)	C(7')—C(8')—C(13')	112.6(7)
C(1')—C(2')—C(3')	120.4(9)	C(9')—C(8')—C(13')	113.3(7)
C(3')—C(2')—F(2)	119.2(8)	C(5')—C(6')—C(14')	121.3(7)
C(2')—C(3')—F(3)	119.8(9)	C(7')—C(6')—C(14')	124.9(7)
C(2')—C(3')—C(4')	119.0(9)	C(9')—C(10')—C(15')	124.2(8)
C(4')—C(3')—F(3)	121.2(9)	C(5')—C(10')—C(15')	120.3(7)
C(3')—C(4')—F(4)	118.0(8)	O(1)—Cl—O(2)	108.9(6)
C(3')—C(4')—C(12')	120.8(8)	O(1)—Cl—O(3)	108.9(6)
C(12')—C(4')—F(4)	121.2(8)	O(1)—Cl—O(4)	105.9(8)
C(10')—C(5')—C(12')	109.0(6)	O(2)—Cl—O(3)	109.7(6)
C(6')—C(5')—C(12')	109.4(6)	O(2)—Cl—O(4)	111.1(8)
C(6')—C(5')—C(10')	99.0(6)	O(3)—Cl—O(4)	108.6(8)
C(5')—C(6')—C(7')	110.7(6)		

methyltetrafluorobenzobarrelene complexes is not reflected in the distances of the rhodium atom from the best least squares plane through the arene ring[*] (1.83 Å for [Rh(Me$_3$TFB)(1,4-C$_6$H$_4$Me$_2$)]ClO$_4$ and 1.82 Å for [Rh(TFB)(1,4-

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[*] A related situation was recently reported for Ni(C$_6$F$_5$)$_2$(arene) complexes [18].

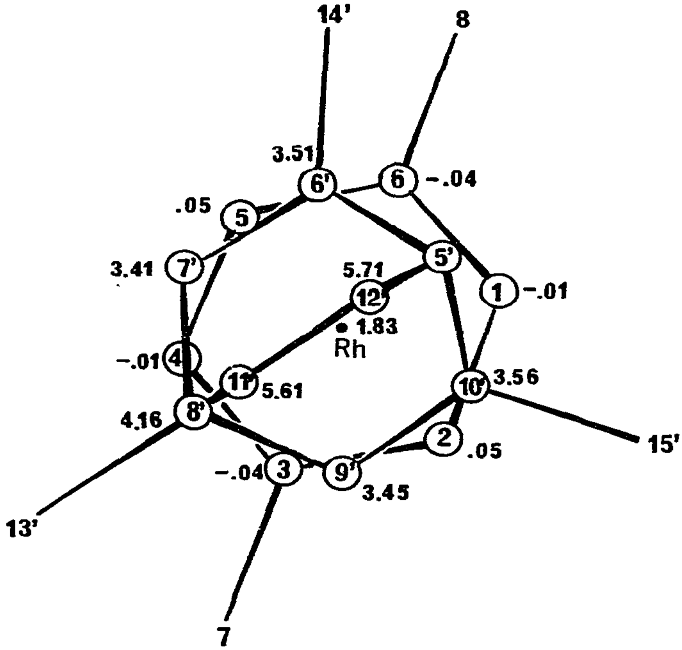

Fig. 1. Rh-coordination as seen perpendicular to the arene ring, including deviations (Å) from the mean six-membered plane of the arene ring. Olefinic carbons of the coordinated TFB ligand are also included.

$C_6H_4Me_2)]ClO_4)$ [11]. The relative disposition of the diolefin with respect to the *p*-xylene is identical in both cases, with a twist of −35.4° from the bond to bond coincidence (Fig. 1) in projection, compared with −32.9° in the tetrafluorobenzobarrelene compound. So the diolefin is not situated *trans* to the carbon atoms attached to the methyl groups which have a relatively lower π-electron density.

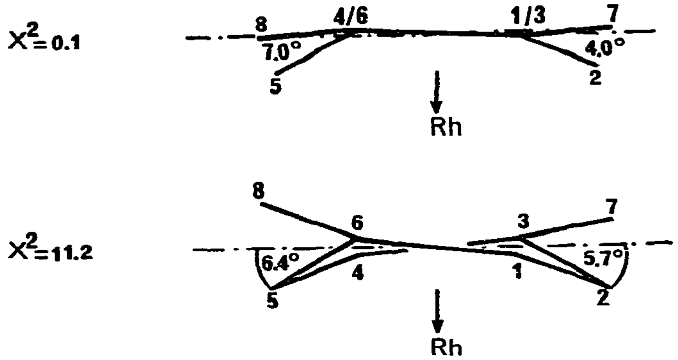

Fig. 2. The puckering of the arene rings in the trimethyltetrafluorobenzobarrelene (below) and tetrafluorobenzobarrelene (above) compounds, to show the different conformations and the angular deviations of the atoms of the cation.

TABLE 4

SELECTED TORSION ANGLES (°)

6—1—2—3	−5.0(14)
1—2—3—4	7.8(13)
2—3—4—5	−2.4(13)
3—4—5—6	−5.8(14)
4—5—6—1	8.6(14)
5—6—1—2	−3.3(13)
11′—8′—5′—12′	0.3(5)
11′—8′—5′—10′	−124.2(5)
11′—8′—5′—6′	125.4(5)
7′—8′—5′—12′	−125.3(5)
7′—8′—5′—10′	110.2(5)
7′—8′—5′—6′	−0.2(4)
9′—8′—5′—12′	124.1(5)
9′—8′—5′—10′	−0.4(5)
9′—8′—5′—6′	−110.7(5)
5′—6′—7′—8′	−0.3(9)
6′—7′—8′—9′	58.7(8)
7′—8′—9′—10′	−58.4(8)
8′—9′—10′—5′	−0.7(9)
9′—10′—5′—6′	61.8(8)
10′—5′—6′—7′	−61.5(7)
5′—6′—7′—8′	−0.3(9)
6′—7′—8′—11′	−51.4(9)
7′—8′—11′—12′	50.8(8)
8′—11′—12′—5′	0.5(9)
11′—12′—5′—6′	−53.6(9)
12′—5′—6′—7′	52.4(8)
5′—10′—9′—8′	−0.7(9)
10′—9′—8′—11′	52,9(8)
9′—8′—11′—12′	−52.0(8)
8′—11′—12′—5′	0.5(9)
11′—12′—5′—10′	53.6(9)
12′—5′—10′—9′	−52,3(8)

Experimental

The C, H and N analyses were carried out on a Perkin—Elmer 240 microanalyser. The IR spectra were recorded on a Perkin—Elmer 599 spectrophotometer (over the range 4000—200 cm^{-1}) using Nujol mulls between polyethylene sheets. The conductivities were measured in ca. 5×10^{-4} M acetone solutions with a Philips 9501/01 conductimeter. The ^1H NMR spectra were recorded on a Varian XL-100, using 0.2—0.005 M solutions (TMS as a reference). The percentage of arene displacement was determined by integration of methyl proton resonances for free and complexed arenes.

The ligand trimethyltetrafluorobenzobarrelene (Me_3TFB) and the binuclear complex $[RhCl(Me_3TFB)]_2$ were prepared as described in the literature [12].

Synthesis of $Rh(Me_3TFB)PhBPh_3$

81.32 mg (0.1 mmol) of $[RhCl(Me_3TFB)]_2$ and 41.5 mg (0.2 mmol) of $AgClO_4$ in acetone were stirred for 30 min at room temperature and filtered through kieselguhr. Treatment of the yellow filtrate with an excess of $NaBPh_4$

(102.7 mg, 0.3 mmol) in acetone gave an immediate white precipitate. The suspension was evaporated to dryness and extracted with a minimum of dichloromethane. The pale-yellow complex crystallized upon addition of ether to the dichloromethane extract. Yield: 80%. Analysis. Found: C, 67.71; H, 4.74. $C_{39}H_{32}BF_4Rh$, calcd.: C, 67.85; H, 4.67%.

Synthesis of complexes of the type [Rh(Me_3TFB)(arene)] ClO_4

A suspension of 81.32 mg (0.1 mmol) of $[RhCl(Me_3TFB)]_2$ in 15 ml of acetone was treated with 41.5 mg (0.2 mmol) of $AgClO_4$ and the appropriate arene ligand C_6Me_6 (32.46 mg, 0.2 mmol); 1,2,4,5-$C_6H_2Me_4$ (26.85 mg, 0.2 mmol); 1,3,5-$C_6H_3Me_3$ (1 ml); 1,4-$C_6H_4Me_2$ (1 ml); 1,3-$C_6H_4Me_2$ (1 ml); C_6H_5Me (1 ml) or C_6H_6 (1 ml). After 30 min stirring at room temperature and filtration through kieselguhr (to remove AgCl) the pale-yellow filtrate was concentrated and ether was added to precipitate the complexes, which were recrystallized from dichloromethane/ether.

TABLE 5

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

(a) *Crystal data*	
Formula	$[Rh(Me_3TFB)(C_6H_4Me_2)]^+ \cdot ClO_4^-$
Crystal habit	Yellow, Transparent, Prismatic, Trapezium basis
size (mm)	0.11 × 0.14 × 0.38
Symmetry	*mmm*, Orthorhombic *Pbca*
Unit cell determination	θ(Cu) $\leqslant 45^\circ$
least-squares fit	66 reflections
Unit cell dimensions (Å)	17.7393(4), 15.7816(3), 16.0071(3)
Packing: V (Å^3), Z	4481.3(1), 8
D (g cm^{-3}), M, (F(000))	1.710, 576.8, 2320
(b) *Experimental data*	
Radiation and technique	Mo-K_α. 4-Circle PW 1100 Philips Diffractometer. Bisecting geometry
Monochromator	Graphite oriented
Orientation	$0k0$: $\chi \sim -8^\circ$, $\phi \sim 321^\circ$; hhh: $\chi \sim 36^\circ$, $\phi \sim 353^\circ$
Collection mode	$\theta \leqslant 25^\circ$
($\omega/2\theta$, $1^\circ \times 1^\circ$ det. apertures)	1.30°, 1 min/reflex.
Total, independent data	3953
Observed data: $2\sigma_c(1)$	2584
Stability	Two reflections every 90 min. No variation.
Absorption: faces	± 100, $\pm(001, 0\bar{1}0, 01\bar{1})$
μ-Min. and max transmission	9.29 cm^{-1}, 0.853—0.913
(c) *Solution and refinement*	[21] X-ray 70 system, Univac 1100/80
Solution mode	Patterson
Refinement mode	Least-square on F's. Observed reflections only. 4 blocks for the final least square
Final shift/error	0.26
Parameters: no. variables,	386
degrees of freedom,	2198
ratio of freedom	6.7
w-scheme	Empirical as to give no trends in $\langle w\Delta^2 \rangle$ vs. $\langle F_0 \rangle$ or $\langle \sin \theta / \lambda \rangle$
ΔF final	± 0.53 eÅ^{-3}
Max. thermal values	$U_{11}O_4 = 0.27(2)$ Å^2
R, R_w	0.062, 0.054
Atomic factors	[22] International Tables for X-ray Crystallography. Neutral atoms. Real part of anomalous dispersion applied for Rh and Cl.

TABLE 6

NORMAL PROBABILITY RESULTS

Type	$\lvert F_O \rvert$ vs. $\lvert F_c \rvert$ full normal	d(Me_3TFB) vs. d(TFB) half normal
Total points	3953	108
Excluded	15	12
Total *R*	0.10	0.01
Slope	0.958(1)	1.169(10)
Intercept	0.010(1)	—0.015(8)
Correlation	0.999	0.996
DP Max	±4.4	±4.3

A similar procedure was used for the preparation of complexes from arenes of the type $C_6H_{6-n}X_n$ (X = F or Cl), C_6F_6 (3 ml); 1,3-$C_6H_4F_2$ (2 ml); 1,2-$C_6H_4F_2$ (2 ml); 1,4-$C_6H_4Cl_2$ (29.40 mg, 0.2 mmol) or C_6H_5Cl (1 ml), but the synthesis was carried out under argon. The products are much more soluble than those

TABLE 7

FINAL ATOMIC COORDINATES FOR [Rh(Me_3TFB)(1,4-$C_6H_4Me_2$)]ClO_4

	x	*y*	*z*
Rh	0.16326(3)	0.01496(4)	0.16150(4)
C(1)	0.11302(56)	0.07789(64)	0.04192(58)
C(2)	0.15514(58)	0.00422(58)	0.02111(48)
C(3)	0.23226(55)	—0.00363(59)	0.03798(50)
C(4)	0.26554(55)	0.06018(68)	0.08610(57)
C(5)	0.22271(57)	0.13045(59)	0.11294(59)
C(6)	0.14838(55)	0.14324(60)	0.08696(54)
C(7)	0.27670(108)	—0.08013(102)	0.00982(85)
C(8)	0.10722(90)	0.22427(83)	0.10725(100)
C(1′)	0.17686(46)	—0.17891(51)	0.42710(50)
F(1)	0.24502(31)	—0.21641(31)	0.42976(29)
C(2′)	0.12644(60)	—0.20174(57)	0.48746(52)
F(2)	0.14523(34)	—0.25899(38)	0.54546(33)
C(3′)	0.05604(61)	—0.16569(63)	0.48986(52)
F(3)	0.00695(37)	—0.18889(44)	0.54941(35)
C(4′)	0.03700(51)	—0.10610(57)	0.43007(54)
F(4)	—0.03312(29)	—0.07131(37)	0.43343(35)
C(5′)	0.06923(43)	—0.02657(51)	0.29569(46)
C(6′)	0.13170(44)	0.04144(45)	0.28895(46)
C(7′)	0.20254(49)	0.00387(48)	0.28589(42)
C(8′)	0.20434(42)	—0.09327(50)	0.29009(46)
C(9′)	0.15491(45)	—0.10875(48)	0.21153(45)
C(10′)	0.08346(44)	—0.07307(49)	0.21394(48)
C(11′)	0.15789(44)	—0.12136(45)	0.36533(42)
C(12′)	0.08670(42)	—0.08510(49)	0.36744(46)
C(13′)	0.28392(54)	—0.12897(65)	0.28193(59)
C(14′)	0.11721(62)	0.13062(62)	0.31169(73)
C(15′)	0.01877(63)	—0.10185(71)	0.16130(86)
Cl	0.39552(13)	0.14521(16)	0.28987(18)
O(1)	0.44347(52)	0.21258(58)	0.27185(69)
O(2)	0.32125(43)	0.17501(61)	0.29172(82)
O(3)	0.40152(55)	0.07973(67)	0.23261(81)
O(4)	0.41711(98)	0.11588(87)	0.36645(78)

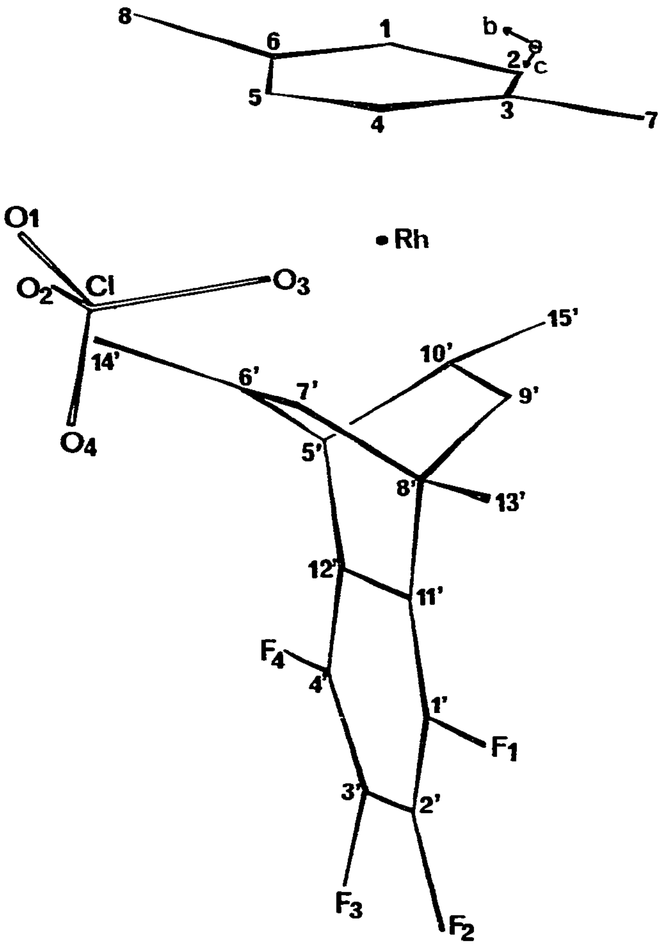

Fig. 3. A view of the complex showing the atom numbering.

prepared from arenes of the type $C_6H_{6-n}Me_n$ and were isolated from mixtures of dichloromethane/ether/hexane.

Synthesis of $[Rh(Me_3TFB)L_2]BPh_4$ $(L_2 = bipy, L = PPh_3)$

$Rh(Me_3TFB)PhBPh_3$ and a slight excess of the appropriate ligand (bipy or PPh_3) in acetone were stirred for 30 min at room temperature. The solution was concentrated and the complexes were precipitated with pentane and recrystallized from dichloromethane-pentane. L_2 = bipy. Yield: 85%. Analysis. Found: C, 69.58; H, 4.97; N, 3.38. $C_{49}H_{40}BF_4N_2Rh$, calcd.: C, 69.52; H, 4.76; N, 3.31%. L = PPh_3. Yield: 69%. Analysis. Found: C, 73.82; H, 5.34. $C_{75}H_{62}BF_4P_2Rh$ calcd.: C, 74.14; H, 5.14%.

X-Ray analysis

Crystal structure parameters are given in Table 5. The final observed and calculated spectra were tested by δR-plots [19], giving the values shown in Table

6. The table also shows the results of comparing distances up to 3.5 Å with those in the unmethylated tetrafluorobenzobarrelene compound [20]. The atomic numbering is shown in Fig. 3, and the molecular geometry in Tables 3 and 4. A list of structure factors, and thermal parameters can be obtained from the authors on request. Atomic coordinates are given in Table 7.

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