Journal of Organometallic Chemistry, 288 (1985) 225–236
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

RHODIUM TETRAFLUOROBENZOBARRELENE OR TRIMETHYLTETRAFLUOROBENZOBARRELENE COMPLEXES WITH ARENE LIGANDS. CRYSTAL STRUCTURES OF [Rh(diolefin)(arene)]ClO_4, (diolefin = TFB, arene = 1,2,4-$C_6H_3Me_3$; diolefin = Me_3TFB, arene = 1,2,4-$C_6H_3Me_3$, C_6Me_6)

F.H. CANO, C. FOCES-FOCES,

Departamento de Rayos X. Instituto Rocasolano, C.S.I.C., Serrano 119, 28006 Madrid (Spain)

and L.A. ORO

Departamento de Química Inorgânica, Universidad de Zaragoza, 50009 Zaragoza (Spain)

(Received December 6th, 1984)

Summary

Crystal structures have been determined for [Rh(diolefin)(arene)]ClO_4 compounds, with (i) arene = 1,2,4-$C_6H_3Me_3$ diolefin TFB, (ii) arene = 1,2,4-$C_6H_3Me_3$, diolefin = Me_3TFB and (iii) arene = C_6Me_6 diolefin Me_3TFB. The lattice constants are (i) $a = b = 25.8460(8)$, $c = 16.4439(6)$ Å, $\gamma = 120°$, $\alpha = \beta = 90°$; (ii) $a = 15.1456(9)$, $b = 16.0826(12)$, $c = 19.1551(21)$ Å, $\alpha = \beta = \gamma = 90°$; and (iii) $a = 16.8808(6)$, $b = 17.7361(6)$, $c = 16.8647(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 98.241(2)°$. The R factors were 0.053, 0.042, and 0.035, respectively. The structures of nine complexes of this type are compared.

Introduction

In continuation of a study of the chemistry of cationic arenerhodium(I) complexes [1], we undertook the structural characterization of a series of such complexes involving trimethyltetrafluorobenzobarrelene (Me_3TFB) or tetrafluorobenzobarrelene (TFB) ligands [2–4]. Our aim was to reveal minor structural or stereochemical perturbations which, along with electronic considerations, might provide clues to the departure from planarity and relative disposition of the coordinated arene ligand. We report below the determination of the structures of three compounds of general formula $[Rh(arene)(diolefin)]^+$, namely those where the arene is 1,2,4-$C_6H_3Me_3$ (diolefin = TBF) or 1,2,4-$C_6H_3Me_3$ and C_6Me_6 (diolefin = Me_3TFB) (subsequently denoted by **3**, **3′**, and **5′**, respectively), and present a general comparison of the structures of these three compounds and those with arene = 1,3-$C_6H_4Me_2$, 1,3,5-

0022-328X/85/$03.30 © 1985 Elsevier Sequoia S.A.

$C_6H_3Me_3$, 1,2,4,5-$C_6H_2Me_4$ and C_6Me_6 with TFB, and 1,3-$C_6H_4Me_2$, 1,2,4,5-$C_6H_2Me_4$ with Me_3TFB (subsequently denoted by **1**, **2**, **4**, **5**, **1'**, **4'**, respectively) [2–4].

Experimental

The complexes were prepared as previously described [2–4]. The crystal data and procedures [5,6] are listed in Table 1. The correct choice of weights and the significance of the R_w value were tested by δR_w analysis [7].

Results

Figure 2 shows the structure of cation **5'** and the atom numbering scheme. The analogous numbering is used for the other cations, and it is the same as that used for

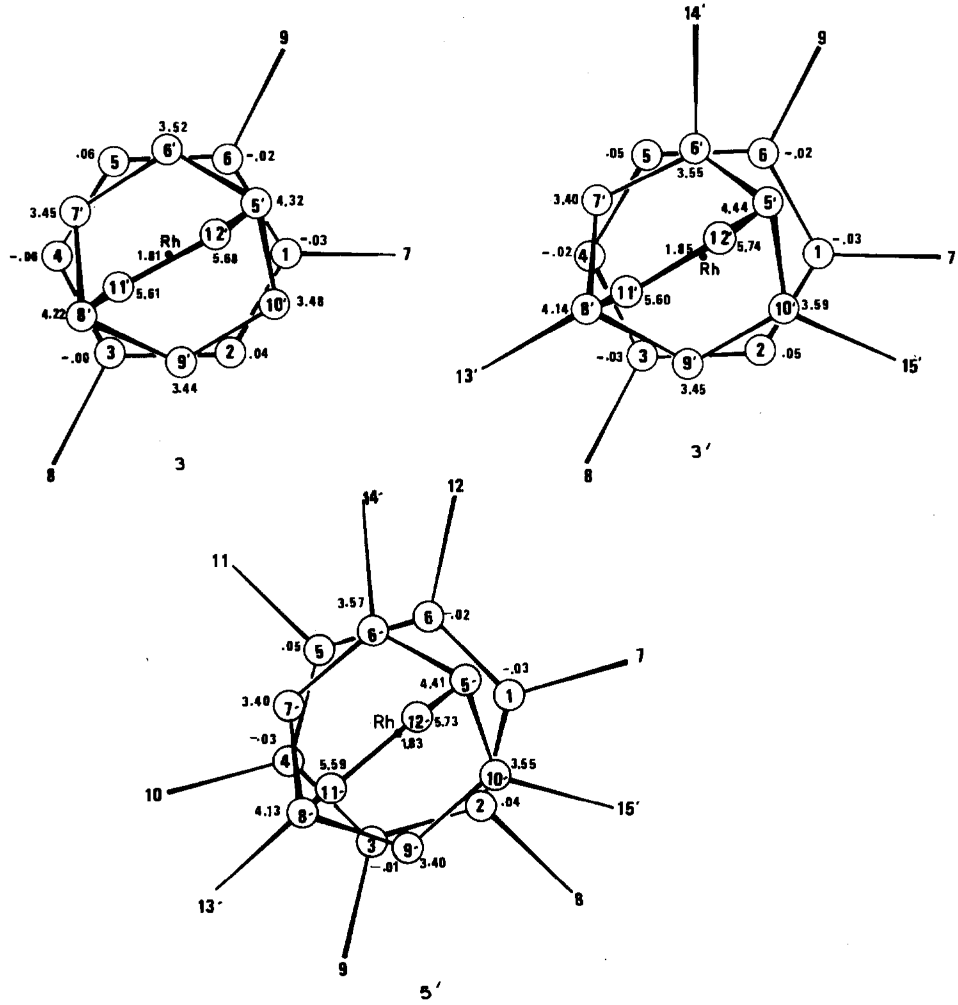

Fig. 1. Coordination around the metal, including deviations (Å) from the best least squares plane through the arene ring.

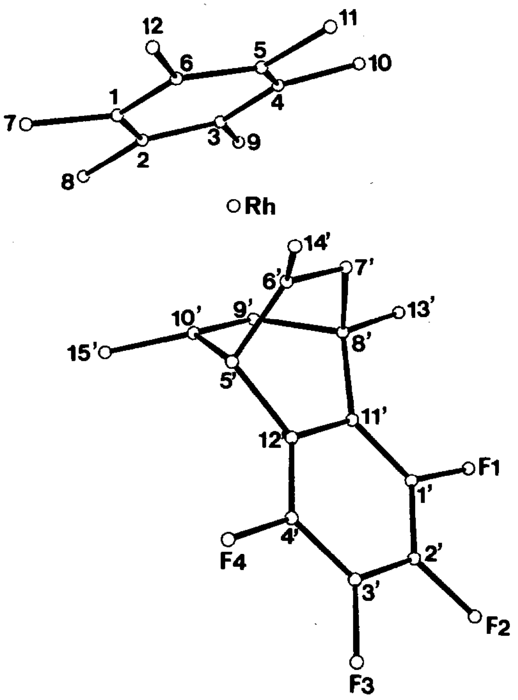

Fig. 2. ORTEP drawing showing the structure of the cation of $[Rh(Me_3TFB)(C_6Me_6)]ClO_4$, with the atom numbering.

the complexes previously reported [2–4]. The atomic coordinates are shown in Table 2, and the most relevant structural parameters in Tables 3 and 4. Figure 1 shows the coordination around the metal atom, together with the atom deviations from the best least squares plane through the arene ring. Lists of structure factors, hydrogen coordinates, and thermal factors can be obtained from the authors.

Discussion

The three complexes we describe here complete the pattern indicated by the six previously studied [2–4], and we make present comparison of the nine related structures. Unfortunately no crystals could be obtained for $[Rh(Me_3TFB)(1,3,5\text{-}C_6H_3Me_3)]\ ClO_4$ (2′).

(i) Crystal packing. The five compounds with the unmethylated TFB ligand crystallize with the same symmetry (*R3c* space group), similar values of the cell constants (25.731(1)–27.122(3), 16.256(1)–17.079(1) Å), and almost isomorphous atom positions. This isomorphism is lost upon methylation of the TFB ligand; the symmetry then falls to either orthorhombic or monoclinic, and the cell volume is reduced by 2 or 4, mainly due to the lowering of the 25 Å axes. Nevertheless the packing remains almost constant (16.9(2)–17.8(9) $Å^3$/non hydrogen atom) for the nine compounds and it seems that the Me groups in the TFB moiety strongly determines the form of the packing but not its density.

(ii) Relative positions of arene and TFB ligands. The idealized coordination

TABLE 1

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data			
Formula	$[Rh(TFB)(C_6H_3Me_3)]ClO_4$	$[Rh(Me_3TFB)(C_6H_3Me_3)]ClO_4$	$[Rh(Me_3TFB)(C_6Me_6)]ClO_4$
Crystal habit	Yellow, transparent, truncated prisms with distorted hexagonal basis		
Crystal size (mm)	0.14 × 0.13 × 0.11 × 0.32	0.14 × 0.27 × 0.30 × 0.27	0.34 × 0.27 × 0.29 × 0.27
Symmetry	$\bar{3}/m$.Rhombohedral,*R3c*	*mmm*.Orthorhombic,*Pbca*	$2/m$.Monoclinic,*C2/c*
Unit cell determination:			
Least squares fit to $\theta(Cu\text{-}K_\alpha) < 45°$	49 reflections	57 reflections	82 reflections
Unit cell dimensions (Å)	25.8460(8), 16.4439(6)	15.1456(9), 16.0826(12), 19.1551(21)	16.8808(6), 17.7361(6), 16.8647(4); 98.241(2)
Packing: V(Å^3), Z	9513.1(5), 18	4665.8(4), 8	4997.1(2), 8
$D(\text{g cm}^{-3})$, M, $F(000)$	1.72, 548.72, 4932	1.69, 590.80, 2384	1.68, 632.88, 2576
Experimental data			
Radiation and technique	Cu-K_α. PW1100 PHILIPS Diffractometer, bisecting geometry, Graphite monochromated		
Sample orientation	$00l$: $\chi \simeq -77°, \phi \simeq 278°$ $hh0$: $\chi \simeq -7°, \phi \simeq 39°$	$00l$: $\chi \simeq 88°, \phi \simeq 86°$ $hh0$: $\chi \simeq -1°, \phi \simeq 100°$	$00l$: $\chi \simeq 42°, \phi \simeq 79°$ $hh0$: $\chi \simeq 37°, \phi \simeq 319°$
Collection mode	$\omega/2\theta$. 1° × 1° detector. $\theta < 65°$. 1 min./rflex. 1.4° scan width. Sample stable.		
Total independent data	1828	3956	3963
Observed data: $I > 3\sigma_c(I)$	1607	3437	3685
Absorption: faces	$\pm(210\ 1\bar{3}0\ \bar{3}20\ 001)$	$\pm(103\ 20\bar{3}\ 1512\ \bar{1}152)$	$\pm(11\bar{1}\ \bar{1}01\ \bar{1}11),\bar{1}01\ 101$
$\mu(\text{cm}^{-1})$, Min.-Max. transmissions	84.61, 0.268–0.469	75.59, 0.155–0.419	72.26, 0.098–0.385
Solution and refinement			
Solution mode	Patterson. X-ray 70 System (5). UNIVAC 1108 Computer		
Refinement mode	Least Squares on F's. Observed reflections only. 3,5 and 6 blocks in final cycle respectively		
Final shift/error	0.13	0.08	0.15
Degrees of freedom	1243	3038	3231
Number of variables	352	399	454
Weighting scheme	Empirical as to give no trends $\langle w\Delta^2 \rangle$ vs. $\langle F_0 \rangle$ or $\langle \sin\theta/\lambda \rangle$		
Max. thermal values (Å^2)	$U_{33}(04) = 0.7(1)$	$U_{33}(04) = 0.29(1)$	$U_{22}(04) = 0.150(5)$
Final F peaks (e Å^{-3})	0.6	0.5	0.6
Final R, R_w	0.053, 0.061	0.042, 0.048	0.035, 0.036
Atomic factors	International Tables for X Ray Crystallography [6]. Neutral atoms with real part of anomalous dispersion applied to Rh and Cl atoms.		

TABLE 2a

FINAL ATOMIC COORDINATES FOR $[Rh(TFB)C_6H_3Me_3]^+$ (3)

Atom	x	y	z
Rh	0.47262(3)	−0.01838(3)	0.25000(0)
Cl	0.39657(16)	0.02438(19)	0.52433(25)
O(1)	0.36220(109)	0.00806(191)	0.58984(172)
O(2)	0.44745(156)	0.02159(208)	0.52335(195)
O(3)	0.37056(152)	0.02697(178)	0.45362(136)
O(4)	0.42642(265)	0.08180(172)	0.53941(533)
C(1)	0.37756(74)	−0.09514(95)	0.28274(138)
C(2)	0.37815(63)	−0.07319(65)	0.20475(101)
C(3)	0.41831(78)	−0.07502(72)	0.14079(119)
C(4)	0.45486(80)	−0.09693(76)	0.16172(158)
C(5)	0.45835(139)	−0.11056(84)	0.24352(273)
C(6)	0.41788(142)	−0.11433(93)	0.30286(195)
C(7)	0.33781(178)	−0.10106(166)	0.34062(242)
C(8)	0.41269(100)	−0.05296(93)	0.05786(101)
C(9)	0.42404(200)	−0.13393(187)	0.38488(299)
C(1′)	0.64692(80)	0.20223(74)	0.23593(229)
F(1)	0.66530(74)	0.21224(59)	0.16032(173)
C(2′)	0.67377(108)	0.24491(82)	0.29376(312)
F(2)	0.72180(69)	0.29869(44)	0.27559(227)
C(3′)	0.66057(118)	0.23790(118)	0.36940(281)
F(3)	0.68969(69)	0.28153(59)	0.42399(156)
C(4′)	0.61294(78)	0.18419(93)	0.39878(213)
F(4)	0.59709(69)	0.17596(87)	0.47556(135)
C(5′)	0.53177(50)	0.07594(71)	0.36143(91)
C(6′)	0.54950(54)	0.03195(54)	0.32652(97)
C(7′)	0.56555(54)	0.04100(42)	0.24667(101)
C(8′)	0.56427(54)	0.09392(54)	0.20947(109)
C(9′)	0.49770(59)	0.07064(63)	0.22446(126)
C(10′)	0.48039(65)	0.06061(78)	0.30378(130)
C(11′)	0.59945(59)	0.14724(59)	0.26374(181)
C(12′)	0.58181(76)	0.13892(76)	0.34100(173)

symmetry for all the complexes is C_{2v} ($mm2$), with the arene least squares plane (π) and that through the Rh atom and through the midpoints of the olefinic double bonds (RhL_2-plane), quite orthogonal (86.0(1)–90.0(5)° as range). However in all the complexes except **5**, the olefinic bonds are close to C(2) and C(5) in projection (see Fig. 1). In **5** they almost eclipse the C(1)–C(2) and C(4)–C(5) arene bonds [2]. In order to describe the twist of the arene ring with respect to the TFB ligand we make use of the torsion values C_i (arene)...O...O′...L_j (olefin), where O and O′ are the centroids of the arene ring and the four atom olefinic set, and $i = 1$–6 and $j = 1$ or 2 and L_j are the midpoints of the olefinic double bonds. If we take the torsion angle to be zero when the double bonds eclipse in projection the C(1)–C(2) and C(4)–C(5) arene bonds, the values for this twist [8] range from −19.9(2) to −39.6(2)°, while for **5** the value is +5.4(3)°. It is noteworthly that to allow this disposition the Me substituents in the arene ring of complex **4′** have to be on 2, 3, 5, 6 instead of on 1, 3, 4, 6 in **4**; thus there is a relative twist of 60° between these positions. In this way, for all the complexes except **4′**, the diolefin avoids opposition

TABLE 2b

FINAL ATOMIC COORDINATES FOR $[Rh(Me_3TFB)(C_6H_3Me_3)]^+$ (3′)

Atom	*x*	*y*	*z*
Rh	0.02917(1)	0.18084(1)	0.17250(1)
C(1)	0.09157(34)	0.05371(28)	0.13333(27)
C(2)	0.01808(37)	0.03945(28)	0.17795(32)
C(3)	0.01680(35)	0.06696(28)	0.24864(28)
C(4)	0.08733(42)	0.11735(31)	0.27022(27)
C(5)	0.15525(34)	0.13889(29)	0.22472(27)
C(6)	0.16128(32)	0.10461(30)	0.15663(27)
C(7)	0.09476(50)	0.01186(42)	0.06485(33)
C(8)	−0.05868(54)	0.04425(43)	0.29511(42)
C(9)	0.24121(39)	0.12094(45)	0.11266(37)
C(1′)	−0.18166(31)	0.43854(27)	0.17647(27)
C(2′)	−0.20710(37)	0.49706(29)	0.12727(30)
C(3′)	−0.17111(38)	0.49645(30)	0.06209(29)
C(4′)	−0.10865(33)	0.43724(28)	0.04510(25)
C(5′)	−0.01928(28)	0.30784(26)	0.07958(21)
C(6′)	0.05159(27)	0.30691(25)	0.13615(23)
C(7′)	0.01422(28)	0.30668(25)	0.20351(21)
C(8′)	−0.08647(28)	0.30765(25)	0.20558(21)
C(9′)	−0.10152(28)	0.22655(23)	0.16416(23)
C(10′)	−0.06544(28)	0.22567(25)	0.09703(23)
C(11′)	−0.11949(28)	0.37899(23)	0.15989(22)
C(12′)	−0.08277(28)	0.37837(25)	0.09278(22)
C(13′)	−0.12137(38)	0.30256(28)	0.27960(26)
C(14′)	−0.09448(37)	0.16972(32)	0.03874(28)
C(15′)	0.14474(31)	0.33286(31)	0.11956(29)
F(1)	−0.22072(21)	0.44351(17)	0.23923(16)
F(2)	−0.26921(26)	0.55369(21)	0.14422(22)
F(3)	−0.19821(29)	0.55270(22)	0.01471(21)
F(4)	−0.07445(23)	0.43793(21)	−0.01997(15)
Cl	0.13669(10)	0.19869(10)	−0.09990(7)
O(1)	0.19409(93)	0.19250(80)	−0.04553(47)
O(2)	0.18123(43)	0.21541(50)	−0.16210(33)
O(3)	0.06762(65)	0.25468(69)	−0.09083(45)
O(4)	0.09993(95)	0.12001(65)	−0.10578(80)

to the substituted C atoms, which have a relatively lower π-electron density.

Complexes **1** to **5** have the arene least squares plane (π) and the diolefin least squares plane (π′, through C(6′), C(7′), C(9′), C(10′)) more nearly parallel than those in **1′** to **5′**, (1.4(4)–2.5(5)° compared with 4.7(3)–6.1(2)°). The distances O-π′ and O′-π are equal and constant within each of the two groups (**1** to **5** and **1′** to **5′**), but they have lower values in the first group 3.466(8)–3.471(2) (except for 3.484(5) for **2** compared with 3.480(3)–3.521(2) Å). In projection the Rh atom lies at the centre of the arene plane and at that of the four olefinic atoms, since RhO ≈ Rhπ and RhO′ ≈ Rhπ′, but, again, in the first group of complexes these distances are smaller (1.809(2)–1.816(4), but 1.840(4) for **2**, vs. 1.829(3)–1.855(1) Å) and (1.652(4)–1.661(6), 1.645(5) for **2** vs. 1.655(4)–1.670(2) Å, less marked than in the previous range). Thus within each group, the ππ′ distance is constant and the Rh atom is nearer to the diolefin plane π′ than to the arene plane (π).

TABLE 2c

FINAL ATOMIC COORDINATES FOR [Rh(Me$_3$TFB)(C$_6$Me$_6$]$^+$ (*5′*)

Atom	*x*	*y*	*z*
Rh	0.27150(1)	0.10243(1)	0.22755(1)
C(1)	0.28925(21)	0.02812(19)	0.11512(19)
C(2)	0.21358(21)	0.06545(17)	0.10360(19)
C(3)	0.15575(20)	0.05199(19)	0.15691(21)
C(4)	0.17738(21)	0.00606(20)	0.22448(21)
C(5)	0.25651(21)	−0.02429(17)	0.24125(20)
C(6)	0.31163(21)	−0.01660(17)	0.18371(21)
C(7)	0.34550(33)	0.03381(31)	0.05305(28)
C(8)	0.19033(32)	0.11410(26)	0.03015(25)
C(9)	0.07469(27)	0.08811(32)	0.14087(38)
C(10)	0.11781(27)	−0.01148(28)	0.28096(28)
C(11)	0.27990(32)	−0.07076(25)	0.31530(27)
C(12)	0.39044(27)	−0.05663(26)	0.19797(33)
C(1′)	0.28438(23)	0.33250(20)	0.42433(20)
F(1′)	0.21505(15)	0.33723(13)	0.45546(14)
C(2′)	0.34377(28)	0.38269(19)	0.45355(21)
F(2)	0.33125(19)	0.43243(13)	0.51101(14)
C(3′)	0.41615(27)	0.38165(20)	0.42606(22)
F(3)	0.47378(17)	0.43082(14)	0.45476(16)
C(4′)	0.42935(22)	0.32976(20)	0.36862(22)
F(4)	0.50106(14)	0.32963(14)	0.34209(16)
C(5′)	0.38081(20)	0.21469(19)	0.28297(20)
C(6′)	0.36239(20)	0.14049(17)	0.32260(19)
C(7′)	0.28574(20)	0.14196(17)	0.34698(17)
C(8′)	0.24066(20)	0.21683(17)	0.33058(19)
C(9′)	0.23847(20)	0.21737(17)	0.23887(19)
C(10′)	0.31362(20)	0.21609(17)	0.21304(19)
C(11′)	0.29631(21)	0.27993(17)	0.36705(19)
C(12′)	0.37144(21)	0.27864(17)	0.33985(20)
C(13′)	0.15641(22)	0.21498(23)	0.35308(25)
C(14′)	0.42951(25)	0.08974(23)	0.35651(26)
C(15′)	0.32871(28)	0.24226(23)	0.13167(22)
Cl	0.45363(5)	0.18992(5)	−0.07252(5)
O(1)	0.37219(25)	0.19946(23)	−0.05889(28)
O(2)	0.47213(29)	0.11170(23)	−0.06535(30)
O(3)	0.45596(31)	0.21317(30)	−0.15243(27)
O(4)	0.50440(42)	0.23382(42)	−0.01934(40)

All these parameters seem to reflect that the Rh coordination geometry is to some extent determined by the ancillary ligands.

(iii) Bond lengths and angles. The pattern of the Rh–C(arene) distances is clear: all the compounds except **5**, have C(2) and C(5) nearer to the Rh atom than the remaining arene atoms, and both eclipse the olefinic bonds of the TFB. In **5**, C(3) and C(6) are further away than the rest of the arene; the olefinic bonds in this case eclipse the C(1)–C(2) and C(4)–C(5) bonds. Thus the eclipsed part, that is, the region *trans* to the olefinic bonds, seems to move out of the arene plane towards the metal. The ranges are: long Rh–C distances, 2.293(10)–2.374(5) Å; short Rh–C distances 2.224(25)–2.324(14) Å. From this point, the arene atom set can be separated into a four atom set nearer to the metal, in **5**, and the other two atoms

TABLE 3a

BOND DISTANCES (Å) WITH THE esd WHITHIN PARENTHESES. (C ATOMS ARE DENOTED SIMPLY BY NUMBERS)

Bond	**3**	**3′**	**5′**	Bond	**3**	**3′**	**5′**
Rh–1	2.321(16)	2.374(5)	2.363(3)	1′–2′	1.355(48)	1.387(7)	1.378(5)
Rh–2	2.250(14)	2.283(5)	2.274(3)	1′–F(1)	1.310(45)	1.342(6)	1.352(5)
Rh–3	2.299(18)	2.349(5)	2.317(3)	1′–11′	1.411(23)	1.380(6)	1.378(5)
Rh–4	2.347(23)	2.307(5)	2.329(4)	2′–3′	1.279(68)	1.362(8)	1.368(7)
Rh–5	2.224(25)	2.259(5)	2.277(3)	2′–F(2)	1.355(24)	1.349(7)	1.349(4)
Rh–6	2.324(22)	2.366(5)	2.368(3)	3′–4′	1.403(33)	1.381(7)	1.377(5)
Rh–6′	2.154(13)	2.171(4)	2.162(3)	3′–F(3)	1.340(41)	1.346(7)	1.344(5)
Rh–7′	2.107(11)	2.121(4)	2.114(3)	4′–12′	1.406(35)	1.373(6)	1.370(5)
Rh–9′	2.097(17)	2.118(4)	2.129(3)	4′–F(4)	1.312(41)	1.350(6)	1.349(5)
Rh–10′	2.140(22)	2.159(4)	2.163(3)	5′–6′	1.534(26)	1.525(6)	1.528(5)
1–2	1.399(25)	1.422(8)	1.427(5)	5′–10′	1.514(23)	1.532(6)	1.515(4)
2–3	1.495(28)	1.425(8)	1.439(5)	5′–12′	1.526(20)	1.508(6)	1.508(5)
3–4	1.366(34)	1.403(8)	1.406(5)	6′–7′	1.362(23)	1.409(6)	1.413(5)
4–5	1.405(51)	1.392(8)	1.430(5)	7′–8′	1.514(21)	1.526(6)	1.536(5)
5–6	1.398(54)	1.419(7)	1.444(5)	8′–9′	1.532(20)	1.544(6)	1.542(5)
6–1	1.399(47)	1.409(7)	1.409(5)	8′–11′	1.506(24)	1.527(6)	1.532(5)
1–7	1.352(50)	1.475(8)	1.514(7)	9′–10′	1.361(29)	1.397(6)	1.399(5)
3–8/2–8	1.513(28)	1.494(10)	1.515(5)	11′–12′	1.331(40)	1.401(6)	1.409(5)
6–9/3–9	1.477(60)	1.498(8)	1.500(5)	6′–14′	–	1.505(6)	1.495(5)
4–10	–	–	1.513(6)	8′–13′	–	1.515(7)	1.524(5)
5–11	–	–	1.501(6)	10′–15′	–	1.500(7)	1.505(5)
6–12	–	–	1.497(6)	Cl–O(1)	1.324(28)	1.360(12)	1.436(5)
Cl–O(2)	1.353(50)	1.395(7)	1.423(4)	Cl–O(3)	1.361(32)	1.391(11)	1.415(5)
Cl–O(4)	1.309(41)	1.387(12)	1.387(7)				

away from it, i.e. (C(1), C(2), C(4), C(5) as distinct from C(3) and C(6)), and in the other complexes there is a four atom set away from the metal and a two atom set nearer to it, i.e. (C(1), C(3), C(4), C(6) as distinct from C(2) and C(5)). The range of distances to the least squares plane through the four atom set is 1.834(1)–1.837(4) for **1**, **3** and **4**, 1.860(1) for **2**, 1.853(1)–1.877(1) for **1′**, **3′**, **4′** and **5′** and 1.794(1) Å, much lower, for **5**. The average $\langle \text{Rh–C}_{4\ \text{set}} \rangle$ for the **1**,**3**,**4** range is 2.319(6)–2.332(5) Å, 2.334(6) Å for **2**, 2.328(5)–2.349(3) Å for **1′** to **5′** and 2.387(7) Å for **5**. The complementary case, $\langle \text{Rh–C}_{2\ \text{set}} \rangle$, shows the reverse distribution of values, 2.237(7)–2.243(9) Å, 2.274(9) Å, 2.252(7)–2.289(7) Å and 2.333(10), Å, respectively. Finally the values for the θ angle [9] (C(2)–C(5) $\cdots$ RhL_2 except for **5**, for which it is C(3)–C(6) $\cdots$ RhL_2) range from 0.2(2) to 10.1(4)°; for **5** it is 84.8(5)°. We thus see the two limiting conformations of the arene for η^6-arene-ML_2 complexes [9], the boat for **5** and the inverted boat for the other complexes.

The two Rh–L distances are a little different in each of the compounds, the ranges for shorter and longer values being 2.001(7)–2.029(2) and 2.017(8)–2.053(2) Å, respectively. This is reflected in the R–C(olefin) distances, which range from 2.097(17) to 2.138(12) Å for the shorter ones and from 2.139(10) to 2.171(4) Å for the longer ones. The L–Rh–L angle is fairly constant (68.8(4)–70.5(3)°). The lengths of the olefinic bonds also differ by as much as 0.067(32) Å, with upper values and lower values of 1.362(23)–1.423(14) and 1.332(26)–1.409(18) Å. The C–C distances in the arene ring (1.366(34)–1.495(28) Å) show no apparent systematic variations

TABLE 3b

BOND ANGLES (°) WITH THE esd. WITHIN PARENTHESES. (C ATOMS ARE DENOTED SIMPLY BY NUMBERS)

Angle	3	3′	5′	Angle	3	3′	5′
6–1–2	120.1(22)	119.3(5)	120.2(3)	6′–5′–12′	107.5(14)	109.7(4)	108.8(3)
1–2–3	119.9(17)	122.1(5)	120.8(3)	6′–5′–10′	96.9(13)	99.1(3)	100.3(3)
2–3–4	118.1(18)	116.7(5)	118.8(3)	5′–6′–7′	114.3(13)	111.6(4)	111.3(3)
3–4–5	119.3(23)	121.5(5)	120.3(3)	6′–7′–8′	113.7(13)	115.2(4)	114.5(3)
4–5–6	123.1(30)	121.8(5)	120.3(3)	7′–8′–11′	108.1(13)	108.7(3)	107.5(3)
5–6–1	118.3(28)	118.0(5)	118.3(3)	7′–8′–9′	96.2(12)	97.2(3)	97.2(3)
6–1–7	116.9(28)	121.5(5)	119.0(3)	9′–8′–11′	108.0(14)	107.0(3)	108.9(3)
2–1–7	123.0(26)	119.1(5)	120.9(3)	8′–9′–10′	115.3(16)	115.1(4)	114.8(3)
2–3–8/1–2–8	115.0(17)	120.1(5)	119.8(3)	5′–10′–9′	112.9(16)	111.8(4)	111.7(3)
4–3–8/3–2–8	126.9(19)	123.2(5)	119.1(3)	1′–11′–8′	123.6(19)	127.8(4)	129.3(3)
5–6–9/2–3–9	117.1(33)	120.1(5)	120.0(3)	8′–11′–12′	114.6(18)	113.0(4)	112.7(3)
1–6–9/4–3–9	124.4(31)	122.0(5)	121.2(4)	1′–11′–12′	121.8(21)	119.2(4)	117.9(3)
3–4–10	–	–	120.7(3)	5′–12′–11′	114.9(19)	114.4(4)	113.6(3)
5–4–10	–	–	119.0(3)	4′–12′–11′	120.2(21)	119.5(4)	120.2(3)
4–5–11	–	–	119.9(3)	4′–12′–5′	124.5(20)	126.1(4)	126.0(3)
6–5–11	–	–	119.5(3)	5′–6′–14′	–	120.5(4)	119.7(3)
5–6–12	–	–	119.4(3)	7′–6′–14′	–	124.8(4)	125.1(3)
1–6–12	–	–	121.8(3)	7′–8′–13′	–	111.9(4)	113.1(3)
11′–1′–F(1)	123.6(23)	123.2(4)	122.4(3)	9′–8′–13′	–	113.6(4)	111.2(3)
2′–1′–F(1)	121.2(26)	116.5(4)	116.6(3)	5′–10′–15′	–	119.3(4)	120.6(3)
2′–1′–11′	115.2(25)	120.3(5)	121.1(3)	9′–10′–15′	–	125.2(4)	124.0(3)
1′–2′–F(2)	120.9(29)	119.2(5)	119.9(3)	10′–5′–12′	107.8(15)	108.7(4)	110.4(3)
1′–2′–3′	125.1(33)	120.5(5)	120.6(4)	O(1)–Cl–O(2)	120.5(33)	111.0(6)	107.7(3)
3′–2′–F(2)	113.7(31)	120.3(5)	119.5(4)	O(1)–Cl–O(3)	116.2(21)	115.6(7)	106.0(3)
2′–3′–F(3)	122.3(33)	119.4(5)	120.3(4)	O(1)–Cl–O(4)	97.4(41)	104.6(8)	110.3(4)
4′–3′–F(3)	116.6(29)	120.9(5)	120.3(4)	O(2)–Cl–O(3)	120.6(22)	110.2(5)	109.2(3)
3′–4′–12′	116.4(26)	121.0(5)	120.8(4)	O(2)–Cl–O(4)	91.5(37)	107.5(6)	112.6(4)
12′–4′–F(4)	120.9(24)	120.7(4)	120.7(3)	O(3)–Cl–O(4)	97.6(41)	104.7(7)	110.7(4)
3′–4′–F(4)	122.7(27)	118.3(4)	118.5(3)	11′–8′–13′	–	117.6(4)	117.1(3)
2′–3′–4′	121.0(33)	119.7(5)	119.3(4)				

outside the experimental uncertainty, but we can make a brief comment on the values of the endocyclic angles (116.7(5)–123.1(30)°). The Me-substitution does not always lower the endocyclic value. Except for **5**, **5′** and **4′**, the angles at C(3) and C(6) have the lowest values, and those at C(2) and C(5) have the highest. Complex **4′** has a different distribution from **4**, and **5** and **5′** and show different distributions of the values of the angles.

(iv) The arene conformation. Although the above mentioned features are consistent with the two typical conformations described, the atomic separations from the best least squares plane through the ring [10] and the pattern of torsion angles on it [11] show significant departures from these of the two model forms. When the last criterion is used, all the rings except for **5**, approximate to boat conformations [11] at $\Sigma = 300°$ and $\delta = 180°$, but only **4** and **3′** are close to it (see Fig. 3). The rings of **1**, **2**

TABLE 3c

SELECTED TORSION ANGLES (°). (C ATOMS DENOTED SIMPLY BY NUMBERS)

Angle	**3**	**3′**	**5′**
6–1–2–3	5.2(30)	−7.4(8)	−6.5(5)
1–2–3–4	−1.8(27)	7.1(8)	5.1(5)
2–3–4–5	−7.1(33)	−0.3(8)	2.3(5)
3–4–5–6	13.2(44)	−6.3(8)	−8.3(5)
4–5–6–1	−9.8(48)	6.0(8)	6.8(5)
5–6–1–2	0.4(40)	0.7(7)	0.5(5)
11′–8′–5′–12′	1.8(14)	0.2(3)	−0.8(2)
11′–8′–5′–10′	126.4(15)	−123.8(3)	−126.0(2)
11′–8′–5′–6′	−123.8(12)	125.5(3)	122.4(2)
7′–8′–5′–12′	126.5(14)	−125.4(3)	−124.1(2)
7′–8′–5′–10′	−108.9(12)	110.6(3)	110.7(2)
7′–8′–5′–6′	0.9(8)	−0.1(3)	−0.9(2)
9′–8′–5′–12′	−124.5(14)	123.6(3)	125.1(2)
9′–8′–5′–10′	0.5(12)	−0.4(3)	−0.1(2)
9′–8′–5′–6′	110.3(9)	−111.1(3)	−111.7(2)
5′–6′–7′–8′	1.7(18)	−0.2(5)	−1.6(4)
6′–7′–8′–9′	−60.2(15)	59.0(4)	59.9(3)
7′–8′–9′–10′	60.0(18)	−58.6(4)	−59.4(3)
8′–9′–10′–5′	1.1(22)	−0.7(5)	−0.2(4)
9′–10′–5′–6′	−60.4(18)	61.6(4)	61.4(3)
10′–5′–6′–7′	60.1(16)	−61.1(4)	−60.4(3)
5′–6′–7′–8′	1.7(18)	−0.2(5)	−1.6(4)
6′–7′–8′–11′	51.4(17)	−51.7(5)	−52.5(4)
7′–8′–11′–12′	−54.8(22)	51.3(5)	54.0(4)
8′–11′–12′–5′	3.5(26)	0.3(5)	−1.5(4)
11′–12′–5′–6′	48.9(23)	−53.4(5)	−54.2(4)
12′–5′–6′–7′	−51.5(18)	52.6(5)	55.4(4)
5′–10′–9′–8′	1.1(22)	−0.7(5)	−0.2(4)
10′–9′–8′–11′	−51.9(20)	53.5(5)	51.9(4)
9′–8′–11′–12′	48.6(22)	−52.7(5)	−54.0(4)
8′–11′–12′–5′	3.5(26)	0.3(5)	−1.5(4)
11′–12′–5′–10′	−55.0(23)	54.0(5)	54.9(4)
12′–5′–10′–9′	50.9(21)	−52.9(5)	−53.3(4)

and **5′** are more of the monoplanar type [11]. That of **3** is better described as diplanar [11], while **1′** and **4′** are skews, as is **5**, although this is a skew of a different type, as it is near the boat conformation with $\Sigma = 180°$ and $\delta = 180°$ (See Fig. 3 and Table 4). In all cases except **5**, there is a difference in Σ, of about 40°, between the phases (Σ) of the group of arenes in complexes with unmethylated TFB ligands and those with methylated ones. All arene rings have a quasi-symmetry which agrees well with that given by other symmetry criteria [12], as indicated in Table 4.

The actual conformation exhibited by a compound and the relative position of the arene with respect to the TFB moiety, seems to be a compromise between the tendency to square planar coordination of Rh(1), the variations in the Rh–C(olefin) distances, and the effects of substitution in the arene ring and the corresponding π-electron redistribution in it.

TABLE 4

CONFORMATIONAL PARAMETERS FOR THE ARENE RINGS OF THE Rh COMPLEXES

Compound	$q3\times10^3$	$q2\times10^3$	$\phi2$	θ	$Q\times10^3$ [a]	*Tm*	q	Σ	δ [b]	Conformations[12] [c]
1	15(12)	77(12)	−117(10)	79(9)	78(12)	1.7(9)	7.3(13)	296(4)	153(4)	Monoplanar-boat (m through C(2), C(5))
2	−22(11)	72(11)	−131(10)	107(9)	75(11)	−2.5(8)	6.8(11)	323(4)	223(4)	Monoplanar-boat (m through C(2), C(5))
3	32(21)	96(20)	−141(13)	72(11)	101(21)	3.9(18)	9.3(25)	343(6)	130(6)	Diplanar-monoplanar (2 through C(1)-C(2))
4	−2(9)	86(9)	−119(7)	91(6)	86(9)	−0.2(7)	8.3(9)	297(2)	183(2)	Boat (*mm*2 through C(5), C(2))
5	0(12)	73(13)	−29(9)	90(9)	73(13)	−0.0(7)	6.8(11)	118(4)	180(4)	Skew' (222 through C2, C5)
1′	3(9)	87(9)	−99(6)	88(6)	87(9)	0.4(6)	3.4(8)	261(2)	174(2)	Skew-monoplanar (222 through C1, C4)
2′	No crystal available									
3′	−6(5)	81(5)	−121(4)	94(4)	81(5)	−0.5(3)	7.8(5)	304(2)	188(2)	Boat (mm2 through C2, C5)
4′	3(10)	50(10)	−99(10)	87(11)	50(10)	0.3(6)	4.7(9)	259(4)	172(4)	Skew-monoplanar (222 through C1, C4)
5′	8(3)	85(3)	−130(2)	85(2)	86(3)	0.9(2)	7.9(3)	321(2)	167(2)	Boat (mm2 through C2, C5)

[a] $q3$, $q2$, Q (Å) and $\phi2$, θ (°) are the parameters of criterion on atomic displacements [10], starting at C(1), then C(2) and so on. Theoretical values for a boat and a skew conformation are: Q, O, n.60°, 90°, Q and Q, O, 30° + n.60°, 90°, Q (n being any integer). [b] *Tm*, q, Σ, δ (°) are the parameters of the criterion [11] on torsion angles starting at C(1)–C(2), then C(2)–C(3) and so on. Phases $\phi2$ and Σ are related by the expression $\Sigma + 2\phi2 = 60°$ (mod 360°). [c] See Fig. 2.

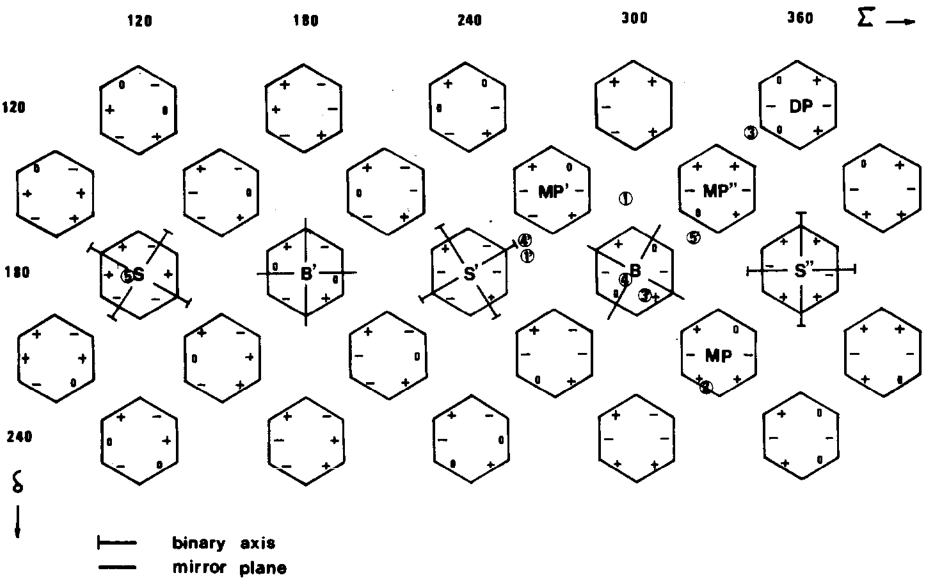

Fig. 3. Distribution of conformations according to criteria of ref. 11. The circled numbers denote the compound, the capital letters specify the conformation, the signs denote the torsion angles, and the lines show the symmetry.

Acknowledgements

The authors thank Prof. S. Garcia-Blanco, Head of the Department of Crystallography of C.S.I.C. (Spain) for the facilities and support provided during this work.

References

1 R. Usón, P. Lahuerta, J. Reyes, L.A. Oro, C. Foces-Foces, F.H. Cano and S. García-Blanco, Inorg. Chim. Acta, 42 (1980) 75.
2 R. Usón, L.A. Oro, C. Foces-Foces, F.H. Cano, A. Vegas and M. Valderrama, J. Organomet. Chem., 215 (1981) 241.
3 R. Usón, L.A. Oro, C. Foces-Foces, F.H. Cano. S. Garcia-Blanco and M. Valderrama, J. Organomet. Chem., 229 (1982) 293.
4 L.A. Oro, C. Foces-Foces, F.H. Cano and S. García-Blanco, J. Organomet. Chem., 236 (1982) 385.
5 J.M. Stewart, F.A. Kundell and J.C. Baldwin, The X-Ray System. Computer Science Center, Univ. of Maryland. College Park, Maryland, 1970.
6 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.
7 S.C. Abrahams and E.T. Kere, Acta Cryst. A, 27 (1971) 157.
8 F.H. Cano, C. Foces-Foces and S. Garcia-Blanco, J. Cryst. Mol. Struc., 9 (1979) 107.
9 E.L. Muetterties, J.R. Bleeke, E.J. Wucherer and T.A. Albright, Chem. Rev., 82 (1982) 499.
10 D. Cremer and J.A. Pople, J. Am. Chem. Soc., 97 (1975) 1354.
11 F.H. Cano, C. Foces-Foces and S. García-Blanco, Tetrahedron, 33 (1977) 797.
12 W.L. Duax, C.M. Weeks and D.C. Rohrer, Top. Stereochem., 9 (1976) 271.