

Tri- μ -chloro-bis[(η^5 -pentamethylcyclopentadienyl)rhodium(III)] tetrafluoroborateLihua Liu,^a Qian-Feng Zhang^{a*}
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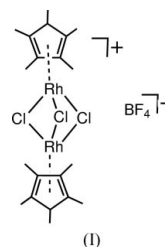
Key indicators

Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
 R factor = 0.042
 wR factor = 0.084
Data-to-parameter ratio = 20.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the cation of the title compound, $[\text{Rh}_2\text{Cl}_3(\text{C}_{10}\text{H}_{15})_2]\text{BF}_4$, two $\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)$ fragments are linked by three bridging Cl atoms. Each rhodium center has a pseudo-octahedral coordination geometry, with a C_5Me_5 group occupying three positions and three Cl atoms completing the coordination. The average $\text{Rh}-\text{Cl}$ bond length is 2.450 Å and the average $\text{Rh}-\text{Cl}-\text{Rh}$ bond angle is 81.6°.

Comment

Arene-rhodium complexes, such as $[\text{RhCl}(\text{arene})]_2$ and $[\text{RhCl}(\text{PR}_3)(\text{arene})]$, have been extensively used as homogeneous catalysts in organic synthesis and polymerization (Lavastre & Dixneuf, 1995; Pearson *et al.*, 1996). Following our interest in the synthesis and catalytic reactions of [(arene)Ru]-sulfur complexes (Zhang *et al.*, 2001), we have considered the analogous rhodium complexes. A dinuclear rhodium complex with pentamethylcyclopentadienyl ligands, $[\{\text{Rh}(\text{C}_{10}\text{H}_{15})\}_2(\mu\text{-Cl})_3]\text{BF}_4$, (I), has been synthesized and structurally characterized, and the results are presented here.



The molecular structure of (I) is depicted in Fig. 1. Two $\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)$ fragments of the cation are linked by three bridging Cl atoms; one of these (Cl3) has relatively long distances to the Rh atoms. The average $\text{Rh}-\text{Cl3}$ bond distance of 2.470 Å is *ca* 0.03 Å longer than the average $\text{Rh}-\text{Cl1/2}$ bond length of 2.441 Å; correspondingly, the angle $\text{Rh1}-\text{Cl3}-\text{Rh2}$ is slightly more acute than the angles $\text{Rh1}-\text{Cl1}-\text{Rh2}$ and $\text{Rh1}-\text{Cl2}-\text{Rh2}$ (Table 1). Each Rh atom exhibits a distorted octahedral coordination, with the ring of the C_5Me_5 ligand formally occupying three sites. The $\text{Rh}-\text{C}(\text{ring})$ distances span the range 2.116 (5)–2.146 (5) Å and compare well with those found in other pentamethylcyclopentadienylrhodium(III) complexes: 2.114 (4)–2.229 (4) Å in $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\eta^2\text{-}i\text{-}P, O\text{-Ph}_2\text{PCH}_2\text{CHMeCH}_2\text{OH})]\text{BF}_4$ (Valderrama *et al.*, 2001) and 2.113 (10)–2.239 (9) Å in $[(\eta\text{-C}_5\text{Me}_5)\text{RhCl}\{\eta^2\text{-}i\text{-}P, P'\text{-}(\text{Ph}_2\text{P})_2\text{NMe}\}]\text{BF}_4$ (Valderrama *et al.*, 2003). The average $\text{Cl}-\text{Rh}-\text{Cl}$ angle of 82.0° deviates by 8° from the ideal octahedral angle. The separation between the two Rh atoms is 3.202 (4) Å and thus these atoms are non-bonded. The geometry of the tetrahedral BF_4^- anion is normal.

Received 18 February 2004

Accepted 26 March 2004

Online 31 March 2004

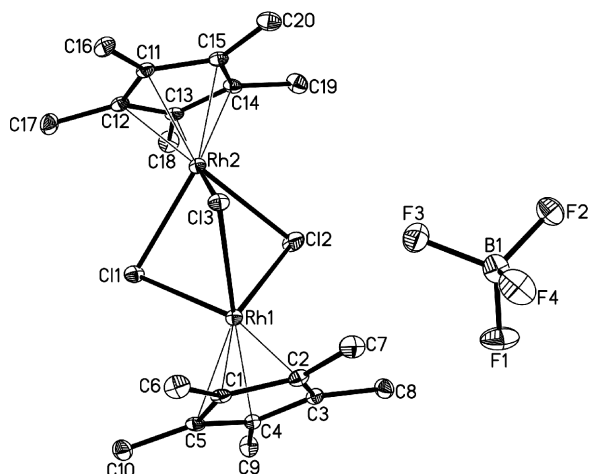


Figure 1
The structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

Experimental

Treatment of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2(\mu\text{-Cl})_2]$ (80 mg, 0.26 mmol) with dilute HBF_4 (1 M in Et_2O , 1.5 ml) in acetone (20 ml) at room temperature afforded a yellow solution. This was stirred under reflux for 2 h, and then the solvent was pumped off and the residue was extracted with CH_2Cl_2 (10 ml). Recrystallization from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ gave orange block crystals. $^1\text{H NMR}$ (CDCl_3 , p.p.m.): δ 1.75 (t, 30H, $J = 2.6$ Hz, C_5Me_5). MS (FAB): m/z 583 ($[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}]_2(\mu\text{-Cl})_3^+$ + 1). Analysis calculated for $\text{C}_{20}\text{H}_{30}\text{BCl}_3\text{F}_4\text{Rh}_2$: C 35.85, H 4.48%; found: C 35.73, H 4.42%.

Crystal data

$[\text{Rh}_2\text{Cl}_3(\text{C}_{10}\text{H}_{15})_2]\text{BF}_4$
 $M_r = 669.42$
 Triclinic, $P\bar{1}$
 $a = 8.1768$ (16) Å
 $b = 11.858$ (2) Å
 $c = 14.007$ (3) Å
 $\alpha = 67.534$ (3)°
 $\beta = 82.032$ (3)°
 $\gamma = 89.421$ (4)°
 $V = 1241.6$ (4) Å³

$Z = 2$
 $D_x = 1.791$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1788 reflections
 $\theta = 2.5\text{--}27.9^\circ$
 $\mu = 1.69$ mm⁻¹
 $T = 296$ (2) K
 Block, orange
 $0.35 \times 0.30 \times 0.28$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997a)
 $T_{\min} = 0.542$, $T_{\max} = 0.629$
 7407 measured reflections

5533 independent reflections
 3807 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -10 \rightarrow 10$
 $k = -10 \rightarrow 15$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.084$
 $S = 0.96$
 5533 reflections
 271 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2)]$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.92$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.97$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Rh1—C2	2.116 (5)	Rh2—C13	2.106 (5)
Rh1—C4	2.119 (5)	Rh2—C15	2.117 (5)
Rh1—C1	2.123 (5)	Rh2—C12	2.123 (5)
Rh1—C3	2.132 (5)	Rh2—C14	2.123 (5)
Rh1—C5	2.146 (5)	Rh2—C11	2.125 (5)
Rh1—Cl1	2.4358 (13)	Rh2—Cl2	2.4403 (13)
Rh1—Cl2	2.4396 (15)	Rh2—Cl1	2.4468 (14)
Rh1—Cl3	2.4697 (13)	Rh2—Cl3	2.4705 (13)
Cl1—Rh1—Cl2	82.30 (5)	Cl1—Rh2—Cl3	81.83 (4)
Cl1—Rh1—Cl3	82.07 (4)	Rh1—Cl1—Rh2	81.94 (4)
Cl2—Rh1—Cl3	81.70 (5)	Rh1—Cl2—Rh2	82.00 (4)
Cl2—Rh2—Cl1	82.06 (5)	Rh1—Cl3—Rh2	80.79 (4)
Cl2—Rh2—Cl3	81.67 (5)		

All H atoms were found in a difference map, but were then placed in calculated positions ($\text{C-H} = 0.96$ Å) and included in the refinement using the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXTL (Sheldrick, 1997b); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Financial support from Natural Science Foundation of China (grant No. 90301005) and the Hong Kong Research Grants Council is gratefully acknowledged.

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