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Bis[μ-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzenethiolato]bis[(η^4-3,5-cyclooctadiene)rhodium(I)]

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In the structure of the title compound, $[Rh_2(C_7F_7S)_2(C_8H_{12})_2]$, important geometric parameters are $Rh\cdots Rh = 2.9595\ (3)$ Å, mean $Rh-S = 2.3949\ (8)$ Å, mean $S-C = 1.764\ (3)$ Å and mean $S-Rh-S = 87.37\ (3)°$. The S—Rh—S planes intersect at an angle of 117.4 (3)°.

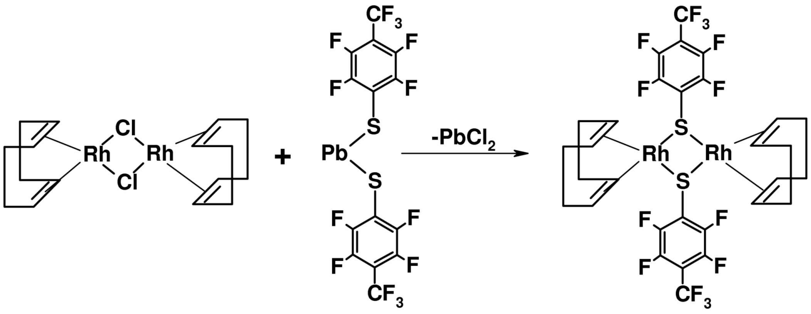
Key indicators

Single-crystal X-ray study
$T = 193$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.022
wR factor = 0.052
Data-to-parameter ratio = 10.2

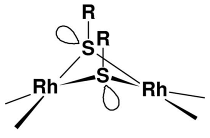
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

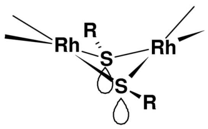
We have a long-standing interest in dinuclear transition metal complexes bearing fluorinated thiolates (Garcia *et al.*, 1993; Arroyo *et al.*, 2000; Villanueva *et al.*, 2004), since this type of compound is relevant, for example, to the development of chemical systems involving C—F bond activation (Richmond, 1999; Torrens, 2005) or to the study of fluorous biphasic catalytic processes (Barthel-Rosa & Gladysz, 1999). While working with this class of compounds, we have found that the metathetical reactions of $[(C_8H_{12})Rh(\mu\text{-OMe})_2Rh(C_8H_{12})]$ with $HSC_6F_4CF_3$-4, or $[(C_8H_{12})Rh(\mu\text{-Cl})_2Rh(C_8H_{12})]$ with $Pb(SC_6F_4CF_3\text{-4})_2$, give rise to the expected title dinuclear complex $[(C_8H_{12})Rh(\mu\text{-SC}_6F_4CF_3\text{-4})_2Rh(C_8H_{12})]$, (I).



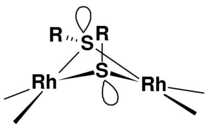
(I)



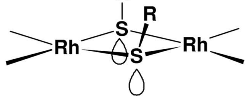
syn-endo



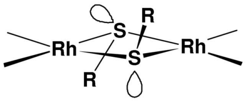
syn-exo



bent-anti



planar-syn



planar-anti

The single-crystal X-ray structure analysis of (I) (Fig. 1) shows it to adopt a *syn–endo* geometry. The coordination around each Rh atom is approximately square-planar (Table 1). The intermetallic distance of 2.9595 (3) Å is too

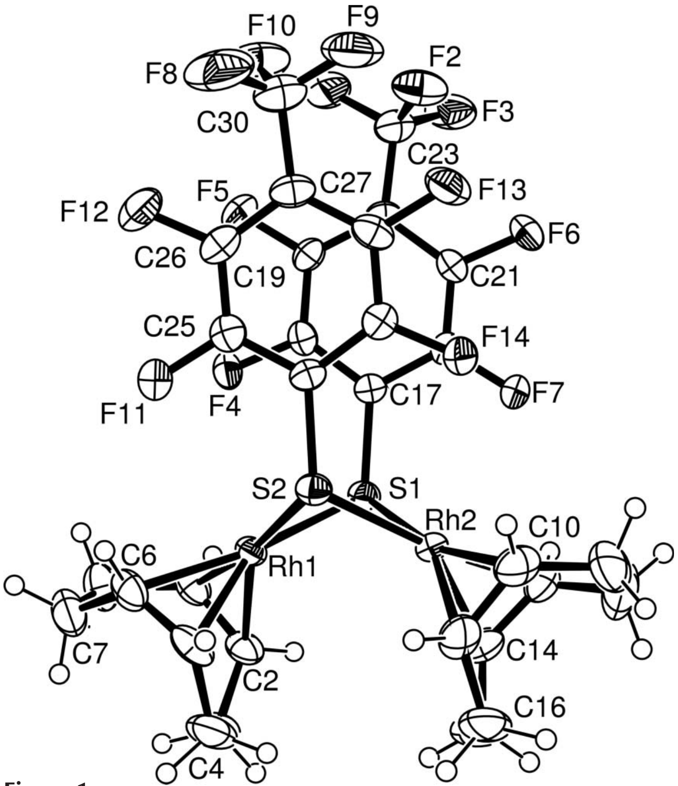


Figure 1
A view of the structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

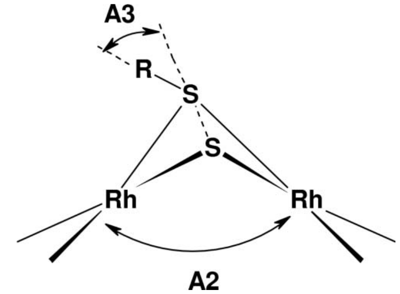


Figure 2
The definitions of the angles A_2 and A_3 used in Table 2.

large to indicate interaction between metal atoms (Cotton & Felthouse, 1981). The coordination planes through the Rh and S atoms are folded along the S$\cdots$S vector at a dihedral angle of 117.4 (3)°. The observed Rh$\cdots$Rh distance, as well as the dihedral angle, agree well with the values reported for other known examples (Table 2). The Rh—S [range 2.3917 (8)–2.3977 (8) Å] and S$\cdots$S [3.308 (3) Å] distances are in good agreement with those observed previously (Cruz-Garritz *et al.*, 1991, 1984; Bonnet *et al.*, 1977; Hill *et al.*, 1977). The S atoms have a tetrahedral geometry. The C—C distances in the aromatic ring fall in the normal range of 1.36–1.39 Å (Allen *et al.*, 1987), and the cyclooctadiene rings show shorter C—C distances for the metal-bound olefins (1.38–1.40 Å).

Possible structures for this class of compound include *syn–endo*, *syn–exo*, bent–*anti*, planar–*syn* and planar–*anti* (Aullón *et al.*, 1998). As mentioned above, the fluorinated benzene rings of the thiolate bridges are in a *syn–endo* configuration with respect to the four-membered $[RhS]_2$ core, and the mean planes of the benzene rings are approximately perpendicular to the S$\cdots$S vector. For comparison, several bis-thiolate complexes of the type $[Rh(dippe)(\mu\text{-}SR)]_2$, where dippe = ^{i}Pr$_2PCH_2CH_2$P^{i}Pr$_2$, R = H, Me, cyclohexyl, *o*-biphenyl or phenyl, or $(SR)_2$ = $SCH_2CH_2CH_2S$, have been synthesized and characterized by single-crystal X-ray diffraction (Oster & Jones, 2004). All $[Rh(dippe)(\mu\text{-}SR)]_2$ complexes except $[Rh(dippe)(\mu\text{-}SPh)]_2$ exhibit bent geometries (the exception is planar), while the orientation of the thiolate substituents changes with increasing steric bulk. Note that three of the complexes adopt the *syn–endo* geometry observed in (I).

^{1}H and ^{31}P NMR spectroscopies indicate that both ring inversion and sulfur inversion occur among the members of the series, which allows them to access several isomeric forms when they are in solution.

Experimental

Compound (I), $[Rh_2(\mu\text{-}SC_6F_4CF_3\text{-}4)_2(cod)_2]$, was prepared as follows. To a solution of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (cod is cyclooctadiene) (150 mg, 0.3 mmol) in acetone (25 ml) was added a solution of $Pb(SC_6F_4CF_3\text{-}4)_2$ (218 mg, 0.3 mmol) dissolved in acetone (25 ml). The reaction mixture rapidly turned red. A red precipitate formed, and this was filtered off and dried under vacuum to give $[Rh_2(\mu\text{-}SC_6F_4CF_3\text{-}4)_2(cod)_2]$. Single crystals of (I) were obtained by slow evaporation of an acetone solution under a stream of N_2 (yield 92%; m.p. 513–515 K). Analysis calculated for $C_{30}H_{24}F_{14}S_2Rh_2$: C 39.13, H 2.61, S 6.95%; found: C 39.10, H 2.65, S 7.04. IR (cm^{-1}): 1639 (*m*), 1474 (*s*), 1323 (*s*), 978 (*m*), 855 (*w*), 714 (*m*). ^{1}H NMR (d_6-acetone, δ, p.p.m.): 2.837 (*m*, CH$_2$), 2.871 (*m*, CH$_2$), 4.70 (*s*, CH). ^{19}F NMR (d_6-acetone, δ, p.p.m.): −57.41 (*s*, CF$_3$), −131.19 (*m*, F-2,6), −144.97 (*m*, F-3,5).

Crystal data

$[Rh_2(C_7F_7S)_2(C_8H_{12})_2]$
$M_r = 920.43$
Monoclinic, $P2_1/c$
$a = 12.5718$ (6) Å
$b = 19.5538$ (10) Å
$c = 13.3217$ (7) Å
$\beta = 110.5470$ (10)°
$V = 3066.5$ (3) Å^3
$Z = 4$

$D_x = 1.994$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4620 reflections
$\theta = 5.3$–$46.5°$
$\mu = 1.32$ mm^{-1}
$T = 193$ (2) K
Prism, red
$0.32 \times 0.32 \times 0.28$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan_ (*SADABS*; Blessing, 1995)
$T_{min} = 0.613$, $T_{max} = 0.691$
13638 measured reflections

4402 independent reflections
3998 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 23.3°$
$h = -11 \rightarrow 13$
$k = -19 \rightarrow 21$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.052$
$S = 1.04$
4402 reflections
433 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2 + 3.0986P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Rh1—C2	2.132 (3)	Rh2—C14	2.138 (3)
Rh1—C1	2.135 (3)	Rh2—C9	2.143 (3)
Rh1—C5	2.146 (3)	Rh2—C13	2.149 (3)
Rh1—C6	2.155 (3)	Rh2—S2	2.3917 (8)
Rh1—S1	2.3927 (8)	Rh2—S1	2.3976 (8)
Rh1—S2	2.3977 (8)	S1—C17	1.762 (3)
Rh2—C10	2.135 (3)	S2—C24	1.765 (3)
C2—Rh1—C1	37.90 (12)	C9—Rh2—S2	89.23 (10)
C5—Rh1—C6	37.86 (12)	S2—Rh2—S1	87.38 (3)
C1—Rh1—S1	91.37 (9)	C17—S1—Rh1	112.54 (10)
C2—Rh1—S2	149.71 (9)	C17—S1—Rh2	105.47 (9)
S1—Rh1—S2	87.36 (3)	Rh1—S1—Rh2	76.31 (2)
C10—Rh2—C9	38.06 (13)	C24—S2—Rh2	114.32 (10)
C14—Rh2—C13	37.58 (13)	C24—S2—Rh1	111.95 (9)
C10—Rh2—S2	95.16 (10)		

Table 2
Selected angles (°), distances (Å) and sums of angles (mean values) about the S atom in $[Rh(\mu\text{-}SR)(L_n)]_2$ (L_1 = cod, L_2 = dippe) complexes.

S*R*, L_n	Isomer	A_1†	A_2‡	A_3‡	Rh···Rh	S···S
SC_6F_5, L_1	*syn–endo*	311.7 294.3	118.4	87.4, 89.5	2.954	3.369§
SC_6HF_4, L_1	*syn–endo*	313.0 296.0	117.8	87.6, 89.8	2.956	3.330¶
SC_7F_7, L_1	*syn–endo*	294.3 302.6	117.4	86.0, 91.4	2.960	3.308††
SH, L_2	*syn–exo*	302.5	136.0	36.0	3.281	3.016‡‡
SCH_3, L_2	bent–*anti*	297.6_{endo} 327.7_{exo}	124.6	83.2_{endo} 16.9_{exo}	3.298	3.299‡‡
SC_6H_{11}, L_2	*syn–endo*	306.9	126.4	86.0	3.238	3.299‡‡
$S_2C_3H_6$, L_2	*syn–endo*	289.4	129.1	80.6	3.243	3.171‡‡
SC_6H_5, L_2	planar–*anti*	301.0	180.0	77.8	3.634	3.231‡‡

† A_1 is the sum of *X*—S—*X* angles at S. ‡ The angles are defined as shown in Fig. 2. § Cruz-Garritz *et al.*, (1984). ¶ Cruz-Garritz *et al.*, (1991). †† This work. ‡‡ Oster & Jones, (2004).

H atoms were positioned geometrically, with C—H distances in the range 0.99–1.00 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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