Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Bis(η^4-cycloocta-1,5-diene)rhodium(I) trifluoromethanesulfonate

Lutz Dahlenburg,* Nils Osthoff and Frank W. Heinemann

Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstraße 1, D-91058 Erlangen, Germany

Correspondence e-mail:
dahlenburg@chemie.uni-erlangen.de

Received 5 February 2001
Accepted 15 February 2001
Online 28 February 2001

The crystal structure of the title compound, $[Rh(C_8H_{12})_2](CF_3SO_3)$, consists of $[(C_8H_{12})_2Rh]^+$ cations and $F_3CSO_3^-$ anions. The cycloocta-1,5-diene ligands are chelated to the central metal atom to create a coordination geometry about rhodium which is essentially square planar.

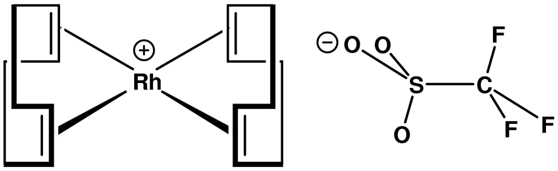
Key indicators

Single-crystal X-ray study
T = 203 K
Mean σ(C–C) = 0.019 Å
R factor = 0.058
wR factor = 0.154
Data-to-parameter ratio = 14.5

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

Comment

The title compound, (I), and related complexes containing BF_4^-, PF_6^-, SbF_6^- or ClO_4^- anions (Green *et al.*, 1970, 1971; Schenck *et al.*, 1985; Schrock & Osborn, 1971; Uson *et al.*, 1976) are frequently used as precursors of chiral chelate phosphine-substituted derivatives $[(C_8H_{12})RhL_2]X$ which have wide application as catalysts for asymmetric hydrogenation reactions (*e.g.* Burk *et al.*, 1993; Dahlenburg & Eckert, 1998; Dahlenburg & Kurth, 1999).



(I)

The structure of (I) consists of two discrete $[(C_8H_{12})_2Rh]^+$ cations lying on special positions 4*e* (site symmetry 2; molecule 1) and 4*b* (site symmetry $\overline{1}$; molecule 2) of the C-centered monoclinic unit cell, in addition to one $F_3CSO_3^-$ anion in a general position. The chelating cyclooctadiene ligands are π-bonded to the central metal in an essentially square-planar fashion, as anticipated. The range of interatomic distances spanned by the rhodium-to-carbon bonds, 2.240 (8)–2.263 (8) Å in molecule 1 and 2.205 (11)–2.269 (12) Å in molecule 2, compares well with that previously found for $[(C_8H_{12})_2Rh][(\mu\text{-Cl})_3\{Re(CO)_3\}_2]$ [Rh—C 2.198 (10)–2.254 (14) Å; Baenziger *et al.*, 1991], which appears to be the only other example of a crystallographically characterized $[(C_8H_{12})_2Rh]^+$ complex salt contained in the Cambridge Structural Database (Allen & Kennard, 1993). The trifluoromethanesulfonate counter-ion adopts the expected staggered conformation.

Experimental

$[(C_8H_{12})_2Rh](O_3SCF_3)$ was prepared according to published procedures (Burk *et al.*, 1993; Schenck *et al.*, 1985; Schrock & Osborn, 1971). Single crystals were grown from dichloromethane/pentane.

Crystal data

$[Rh(C_8H_{12})_2](CF_3SO_3)$
$M_r = 468.33$
Monoclinic, $C2/c$
$a = 14.072$ (2) Å
$b = 17.617$ (2) Å
$c = 14.840$ (2) Å
$\beta = 95.425$ (9)°
$V = 3662.5$ (8) Å^3
$Z = 8$

$D_x = 1.699$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.4$–11.8°
$\mu = 1.09$ mm^{-1}
$T = 203$ (2) K
Block, orange
0.23 × 0.18 × 0.18 mm

Data collection

Nonius CAD-4 MACH3 diffractometer
Non-profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.788$, $T_{\max} = 0.828$
7359 measured reflections
3300 independent reflections
2158 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.055$
$\theta_{\max} = 25.2°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.154$
$S = 1.02$
3300 reflections
228 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 12.5891P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.79$ e Å^{-3}
$\Delta\rho_{\min} = -1.02$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Labels '(*n*,*m*)' denote the midpoints of the olefin bonds between C atoms *n* and *m* in the C_8H_{12} ligands.

Rh1—C2	2.240 (8)	S1—O1	1.337 (9)
Rh1—C1	2.242 (8)	S1—O3	1.405 (6)
Rh1—C6	2.259 (8)	S1—O2	1.421 (9)
Rh1—C5	2.263 (8)	S1—C17	1.829 (13)
Rh1—(1,2)	2.137	F1—C17	1.215 (14)
Rh1—(5,6)	2.159	F2—C17	1.268 (14)
Rh2—C9	2.205 (11)	F3—C17	1.286 (14)
Rh2—C13	2.232 (9)	C1—C2	1.351 (12)
Rh2—C14	2.233 (7)	C5—C6	1.343 (12)
Rh2—C10	2.269 (12)	C9—C10	1.345 (19)
Rh2—(9,10)	2.134	C13—C14	1.330 (12)
Rh2—(13,14)	2.131		
(1,2)—Rh1—(1,2$^{\rm i}$)	94.82	C1—C2—C3	128.3 (9)
(1,2)—Rh1—(5,6$^{\rm i}$)	179.43	C6—C5—C4	129.9 (12)
(1,2)—Rh1—(5,6)	84.64	C5—C6—C7	122.7 (11)
(5,6)—Rh1—(5,6$^{\rm i}$)	95.89	C10—C9—C16	124.8 (11)
(9,10)—Rh2—(13,14)	84.46	C9—C10—C11	128.6 (12)
(9,10)—Rh2—(13,14$^{\rm ii}$)	95.54	C14—C13—C12	129.5 (13)
O1—S1—O3	113.6 (7)	C13—C14—C15	125.0 (10)
O1—S1—O2	119.5 (9)	F1—C17—F2	112.1 (17)
O3—S1—O2	109.1 (6)	F1—C17—F3	108.3 (13)
C2—C1—C8	126.3 (9)	F2—C17—F3	104.6 (12)

Symmetry codes: (i) $2 - x, y, \frac{3}{2} - z$; (ii) $-x, 1 - y, -z$.

H atoms were included in geometrically idealized positions employing appropriate riding models with isotropic displacement parameters constrained to $1.2U_{\rm eq}$ of their carrier atoms. The high $U_{\rm eq}$ values observed for some of the C atoms of the cyclooctadiene ligands and the F and O atoms of the trifluoromethanesulfonate anion are associated with thermal motion of the rings and the respective CF_3 and SO_3 units of the anion. Several approaches to refining the structural model using split occupancies were attempted but the suspected disorder could not plausibly be resolved. As artificially short Csp^3—Csp^3 distances resulted for the bonds between C3 and C4 and, respectively, C11 and C12, these bond lengths were restrained to a more sensible target value of 1.50 (2) Å during the final cycles. The highest peaks and deepest holes in the final difference map were located at distances less than 1.3 Å from the heavy metal atom.

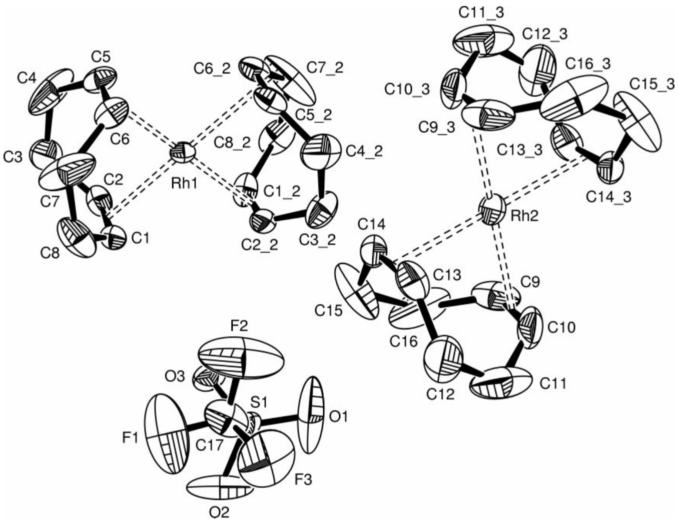


Figure 1
View of (I) (40% probability displacement ellipsoids); operators used for generating equivalent atoms _2 and _3 are $(2 - x, y, \frac{3}{2} - z)$ and $(-x, 1 - y, -z)$, respectively.

Data collection and cell refinement: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); data reduction: *XCAD*4 (Harms & Wocadlo, 1995); structure solution: *SIR*97 (Altomare *et al.*, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Support by the Deutsche Forschungsgemeinschaft (Bonn), the Fonds der Chemischen Industrie (Frankfurt/Main) and the Degussa–Hüls AG (Hanau) is gratefully acknowledged.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Burla, M. C., Polidori, G., Camalli, M. & Spagna, R. (1997). *SIR*97. Universities of Bari, Perugia and Rome, Italy.
Baenziger, N. C., Mottel, E. A. & Doyle, J. R. (1991). *Acta Cryst.* C**47**, 539–541.
Burk, M. J., Feaster, J. E., Nugent, W. A. & Harlow, J. (1993). *J. Am. Chem. Soc.* **115**, 10125–10138.
Dahlenburg, L. & Eckert, C. (1998). *J. Organomet. Chem.* **564**, 227–232.
Dahlenburg, L. & Kurth, V. (1999). *J. Organomet. Chem.* **585**, 315–325.
Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Green, M., Kuc, T. A. & Taylor, S. H. (1970). *J. Chem. Soc. Chem. Commun.* pp. 1553–1554.
Green, M., Kuc, T. A. & Taylor, S. H. (1971). *J. Chem. Soc. A*, pp. 2334–2337.
Harms, K. & Wocadlo, S. (1995). *XCAD*4. Universität Marburg, Germany.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Schenck, T. G., Downes, J. M., Milne, C. R. C., Mackenzie, P. B., Boucher, H., Whelan, J. & Bosnich, B. (1985). *Inorg. Chem.* **24**, 2334–2337.
Schrock, R. R. & Osborn, J. A. (1971). *J. Am. Chem. Soc.* **93**, 3089–3091.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Uson, R., Oro, L. A., Claver, C. & Garralda, M. A. (1976). *J. Organomet. Chem.* **105**, 356–37.

m118 Lutz Dahlenburg *et al.* • $[Rh(C_8H_{12})_2](CF_3SO_3)$ *Acta Cryst.* (2001). E**57**, m117–m118