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A bis(benzenedithiolate)-bridged dinuclear Rh^{III} complex with capping triphenylphosphine ligands and an Rh_2S_2 core

Siphamandla W. Hadebe, Ross S. Robinson and Orde Q. Munro*

School of Chemistry, University of KwaZulu-Natal, Pietermaritzburg, Private Bag X01, Scottsville 3209, South Africa

Correspondence e-mail: munroo@ukzn.ac.za

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The title compound, bis(μ-benzene-1,2-dithiolato)bis[(2-mercaptobenzenethiolato)triphenylphosphine)rhodium(III)] dichloromethane tetrasolvate, $[Rh_2(C_6H_4S_2)_2(C_6H_5S_2)_2(C_{18}H_{15})_2]\cdot 4CH_2Cl_2$, isolated from the reaction of Wilkinson's catalyst $RhCl(PPh_3)_3$ and benzo[1,3,2]dithiaborole, is a neutral dinuclear species with two bridging benzenedithiolate ligands and two 2-mercaptobenzenethiolate ligands chelating each Rh^{III} ion. This compound is derived from decomposition of the borole derivative after its oxidative addition to Rh^{I}. The compound crystallizes as the dichloromethane tetrasolvate. The molecule is centrosymmetric. The Rh—S distances in the Rh_2S_2 core are inequivalent, measuring 2.383 (1) and 2.409 (1) Å.

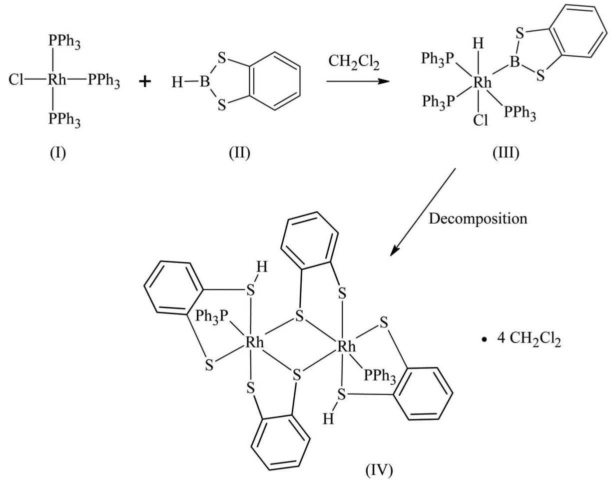
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.025
wR factor = 0.060
Data-to-parameter ratio = 14.8

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

Comment

Since Männig & Nöth (1985) discovered that $RhCl(PPh_3)_3$, (I), catalyzes the addition of benzo[1,3,2]dioxaborole (HBCat) to alkenes, several investigations have been reported that clarify the mechanisms of transition metal-catalyzed hydroborations (Evans *et al.*, 1992; Burgess *et al.*, 1991). Examples of crystal structures with Rh—B bonds involving BCat are now known, including $RhCl(BCat)_2(PPh_3)_2$ (Baker *et al.*, 1993), $RhHCl(BCat)(P^iPr_3)_2$ (Westcott *et al.*, 1991) and $RhCl_2(BCat)(PMe_3)_3$ (Souza *et al.*, 2005). However, the use of benzo[1,3,2]dithiaborole, (II), in Rh-catalyzed hydroborations has not been reported, despite our recent microwave-assisted hydroborations with the dioxaborole analogue (Hadebe & Robinson, 2006*a*,*b*).



Compound (II) oxidatively adds to Wilkinson's catalyst (I) to give (III). This key reaction step was evident from the

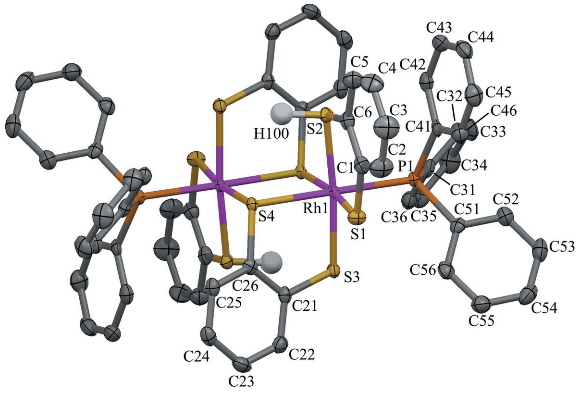


Figure 1
The molecular structure of (IV), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 80% probability level. All H atoms other than those of the SH groups, and the four dichloromethane solvent molecules, have been omitted for clarity. Unlabelled atoms are related to labelled atoms by (1 − *x*, 1 − *y*, 1 − *z*).

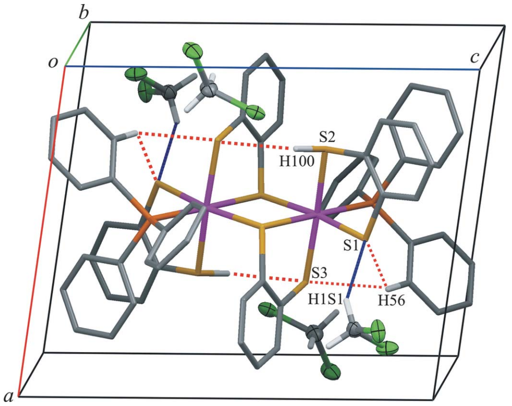


Figure 2
The unit-cell contents of (IV). Displacement ellipsoids for solvent non-H atoms are at the 50% probability level. All other atoms are shown only as the intersections and end-points of bonds represented as cylinders (including solvent H atoms). H atoms involved in intramolecular (red dashed lines) and intermolecular (blue lines) hydrogen bonds are shown and labelled. Unlabelled atoms are related to labelled atoms by (1 − *x*, 1 − *y*, 1 − *z*).

dramatic colour change of the solution (brick red to dark green). Crystallization of (III) was, however, thwarted by its decomposition (mechanism unknown) to the dinuclear Rh^{III} complex, (IV) (18 electrons per Rh centre), the structure of which we present here.

The centrosymmetric compound, (IV), belongs to an interesting class of cluster compounds containing an Rh_2S_2 core bridged by two benzene-1,2-bis(thiolate) groups (Fig. 1). The Rh—S bond distances of (IV) within the Rh_2S_2 core (Table 1) are significantly different, at 2.3829 (5) (Rh—S4) and 2.4093 (5) Å (Rh—S4^{i}) [symmetry code: (i) 1 − *x*, 1 − *y*, 1 − *z*]. Similar asymmetry for the in-plane Rh—S distances exists for the dinuclear complex [(Cp*)Rh-(1,2-$C_6H_4S_2$)$_2$-Rh(Cp*)] (Xi *et al.*, 1997). This most likely reflects the fact that the *trans* ligands differ for each bridging sulfide atom. Indeed, the shorter Rh—S distance is observed for the sulfide donor *trans* to P (a good π-acceptor ligand), while the longer Rh—S distance occurs for the sulfide donor *trans* to a good σ-donor (*i.e.* the sulfide donor of the chelating mercaptobenzenethiolate ligand). The internuclear Rh···Rh distance is 3.6056 (5) Å, slightly longer than the Rh···Rh distance of 3.531 (1) Å reported for [(Cp*)Rh-(1,2-$C_6H_4S_2$)$_2$-Rh(Cp*)] (Xi *et al.*, 1997), a finding consistent with slight expansion of the Rh_2S_2 core of (IV) driven by the greater σ-donor power of the *trans* ligands relative to Cp* (where Cp* = pentamethylcyclopentadienate).

The unit-cell contents of (IV) are shown in Fig. 2. Four dichloromethane solvent molecules are present. The most significant intermolecular interaction is the C—H···S hydrogen bond that exists between one of the solvent molecules and atom S1 of the mercaptobenzenethiolate ligand. The geometries of this interaction and of the three intramolecular hydrogen bonds for (IV) are listed in Table 2.

Experimental

A solution of benzo[1,3,2]dithiaborole in CH_2Cl_2 (0.4 ml, 0.16 mmol) was injected into a flame-dried nitrogen-purged septum-capped test tube. To this solution was added $RhCl(PPh_3)_3$ (4.72 mg, 5.1 μmol), which had been dissolved in dichloromethane (3.5 ml) n a separate flame-dried nitrogen-flushed test tube. The resulting mixture was shaken vigorously and allowed to stand for *ca* 2 weeks. Evaporation of the solvent through the septum afforded a dark-green powder containing, as the minor component, brick-red crystals of (IV) (m.p. 418.5–422.6 K).

Crystal data

$[Rh_2(C_6H_4S_2)_2(C_6H_5S_2)_2(C_{18}H_{15}P)_2]\cdot 4CH_2Cl_2$
$M_r = 1632.93$
Triclinic, $P\overline{1}$
$a = 10.8719$ (5) Å
$b = 11.0495$ (5) Å
$c = 14.2621$ (5) Å
$\alpha = 104.781$ (4)°
$\beta = 97.789$ (4)°
$\gamma = 96.089$ (4)°
$V = 1623.53$ (12) Å^3
$Z = 1$
$D_x = 1.67$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 1.19$ mm^{-1}
$T = 100$ (2) K
Rhomb, red
0.22 × 0.12 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur2 CCD area-detector diffractometer
ω scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2005; Clark & Reid, 1995)
$T_{min} = 0.808$, $T_{max} = 0.880$
15977 measured reflections
5650 independent reflections
5476 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.06$
$S = 1.08$
5650 reflections
383 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 2.3569P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

P1—Rh1	2.3542 (5)	Rh1—S4	2.3829 (5)
Rh1—S1	2.3483 (5)	Rh1—S4^{i}	2.4093 (5)
Rh1—S3	2.3512 (6)	S2—H100	1.31 (3)
Rh1—S2	2.3614 (6)		
S1—Rh1—S3	89.708 (19)	S2—Rh1—S4	88.307 (19)
S1—Rh1—P1	87.264 (19)	S1—Rh1—S4^{i}	172.623 (19)
S3—Rh1—P1	94.227 (19)	S3—Rh1—S4^{i}	86.131 (19)
S1—Rh1—S2	87.451 (19)	P1—Rh1—S4^{i}	99.105 (19)
S3—Rh1—S2	173.370 (19)	S2—Rh1—S4^{i}	96.034 (19)
P1—Rh1—S2	91.621 (19)	S4—Rh1—S4^{i}	82.405 (19)
S1—Rh1—S4	91.223 (19)	Rh1—S2—H100	102.1 (12)
S3—Rh1—S4	85.765 (18)	Rh1—S4—Rh1^{i}	97.595 (19)
P1—Rh1—S4	178.486 (19)		
C26—C21—S3—Rh1	17.52 (19)	Rh1—S4—C26—C21	−21.29 (18)
C22—C21—S3—Rh1	−164.84 (16)	Rh1—S4—C26—C25	160.60 (15)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
S2—H100⋯S3^{i}	1.31 (3)	2.78 (3)	3.5137 (8)	113.8 (18)
C1*S*—H1S1⋯S1	0.99	2.86	3.660 (3)	139
C56—H56⋯S1	0.95	2.77	3.396 (2)	125
C56—H56⋯S3	0.95	2.70	3.395 (2)	131

Symmetry code: (i) $-x+1, -y+1, -z+1$.

The H atom attached to atom S2 was located in a difference Fourier map and refined isotropically without constraints. The remaining H atoms were positioned geometrically and refined using a riding model, with C—H = 0.97 Å and $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$ for methylene H, and with C—H = 0.93 Å and $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$ for aromatic H.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Baker, R. T., Calabrese, J. C., Westcott, S. A., Nguyen, P. & Marder, T. B. (1993). *J. Am. Chem. Soc.* **115**, 4367–4368.

Burgess, K., Kook, A. M. & van der Donk, W. A. (1991). *J. Org. Chem.* **56**, 2949–2951.

Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.

Evans, D. A., Fu, G. C. & Anderson, A. B. (1992). *J. Am. Chem. Soc.* **114**, 6679–6685.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Hadebe, S. W. & Robinson, R. S. (2006*a*). *Tetrahedron Lett.* **47**, 1299–1302.

Hadebe, S. W. & Robinson, R. S. (2006*b*). *Eur. J. Org. Chem.* **21**, 4898–4904.

Männig, D. & Nöth, H. (1985). *Angew. Chem. Int. Ed. Engl.* **24**, 878–897.

Oxford Diffraction (2005). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.27p5 beta. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Souza, F. E. S., Nguyen, P., Marder, T. B., Scott, A. J. & Clegg, W. (2005). *Inorg. Chim. Acta*, **358**, 1501–1509.

Westcott, S. A., Talyor, N. J., Marder, T. B., Baker, R. T., Jones, N. J. & Calabrese, J. C. (1991). *J. Chem. Soc. Chem. Commun.* pp. 304–305.

Xi, R., Abe, M., Suzuki, T., Nishioka, T. & Isobe, K. (1997). *J. Organomet. Chem.* **549**, 117–125.

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