Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.074$
$S = 1.017$
4093 reflections
428 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.211$ e Å^{-3}
$\Delta\rho_{min} = -0.207$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0020 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.005 (9)

Table 1. *Selected geometric parameters (Å, °)*

Cu—O1	1.918 (2)	Cl—O8	1.403 (3)
Cu—O2	1.924 (2)	Cl—O7	1.416 (3)
Cu—N3	2.010 (2)	Cl—O5	1.421 (4)
Cu—N2	2.023 (2)	Cl—O6	1.423 (5)
O1—Cu—O2	90.38 (8)	O1—Cu—N2	91.67 (9)
O1—Cu—N3	172.59 (10)	O2—Cu—N2	175.89 (10)
O2—Cu—N3	93.21 (8)	N3—Cu—N2	84.35 (9)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*1···O3	0.91 (3)	2.03 (4)	2.885 (4)	156 (4)
O2*W*—H2*W*2···N1	0.88 (3)	2.07 (3)	2.945 (4)	169 (3)
N3—H1N3···O7	0.87 (3)	2.42 (3)	3.203 (5)	150 (3)
N2—H1N2···O4^{i}	0.89 (2)	2.14 (2)	2.958 (3)	154 (3)
O2*W*—H1*W*2···O7^{ii}	0.90 (4)	2.05 (4)	2.927 (5)	165 (4)
N4—H1N4···O1*W*^{iii}	0.88 (3)	1.90 (3)	2.728 (3)	156 (3)
O1*W*—H2*W*1···O1^{iv}	0.87 (4)	1.84 (3)	2.652 (3)	156 (4)

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

The water H atoms and those attached to N atoms were localized in difference maps, while all other H atoms were placed in calculated positions riding on their attached C atoms.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1413). Services for accessing these data are described at the back of the journal.

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An *exo*-polyhedral bicyclic 11-vertex *closo*-ruthenaborane: $[(PPh_3)(CH_3COS)_2\text{-}RuB_{10}H_8]$

Yong Nie,[a] Chun-Hua Hu,[a] Jie Sun,[b] Ruo-Shui Jin[c] and Pei-Ju Zheng[a]

[a]*Research Center of Analysis and Measurement, Fudan University, Shanghai 200433, People's Republic of China,* [b]*Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China, and* [c]*Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China. E-mail: pjzheng@fudan.edu.cn*

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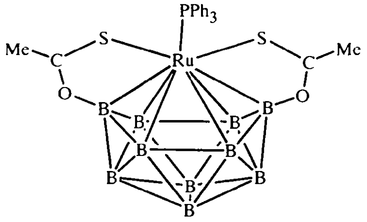
Abstract

The title compound, 1,2:1,3-bis(μ-thioacetato-*S*:*O*)-1-(triphenylphosphine-*P*)-1-ruthena-*closo*-undecaborane, $[Ru(C_4H_{14}B_{10}O_2S_2)(C_{18}H_{15}P)]$, contains an 11-vertex *closo*-type C_{2v} $\{RuB_{10}\}$ cluster and two symmetric *exo*-polyhedral five-membered Ru—S—C—O—B rings. The Ru—S bond lengths are 2.443 (2) and 2.445 (2) Å, and the Ru—B bond lengths are in the range 2.036 (9)–2.393 (9) Å.

Comment

There has been considerable interest in the incidence of cyclic *exo*-polyhedral metal-to-cluster linkages in polyhedral metalloborane compounds (Kennedy, 1984, 1986; Barton & Srivastava, 1995). However, such ruthenaboranes have not been fully explored. Only six complexes representative of two types of rings, to our knowledge, are known to date. It has been reported that the reaction of $[RuCl_2(PPh_3)_3]$ and $[B_{10}H_{10}]^{2-}$ with MeCOOH affords two novel ruthenaboranes with one and two five-membered Ru—O—C(Me)—O—B rings (Fontaine *et al.*, 1987). When the same reaction was carried out in the presence of PhCOOH or *o*-$PhNHC_6H_4$-COOH instead of MeCOOH, three 11-vertex *closo*-type ruthenaborane compounds, all with one or two five-membered Ru—O—C(Ar)—O—B rings (where Ar is

Ph or *o*-PhNHC$_6$H$_4$), were isolated (Yao, 1998; Yao *et al.*, 1995; Zheng, 1999). Yao *et al.* (1998) have also reported that the same reaction with PhCOSH results in a new compound, [(PPh$_3$)(PhCOS)$_2$RuB$_{10}$H$_8$], (II), with two novel five-membered Ru—S—C(Ph)—O—B cycles. However, no investigation of the influence of the cyclization on the cluster and/or the substituent effect on the *exo*-cyclization itself has been made. To emphasize such problems, we report here the title compound, (I), which was isolated from the same reaction with MeCOSH, and which has two five-membered Ru—S—C(Me)—O—B rings.



(I)

In the title compound (Fig. 1), the 11-atom *closo*-type framework has near C_{2v} symmetry, with the {(PPh$_3$)Ru} moiety lying above the boat-type face of six B atoms, rather similar to that of (II). The Ru—B2 and Ru—B3 bond lengths of 2.036 (9) and 2.062 (8) Å, respectively, are close to, but slightly shorter than, the corresponding distances of 2.052 (6) and 2.067 (5) Å for (II), and all these values are again shorter than those of 2.092 (7) and 2.103 (7) Å, respectively, in the non-cyclized compound [1-(pcym)-*isocloso*-1-RuB$_{10}$H$_{10}$] (where pcym is *p*-cymene or 1-Me-4-^{i}PrC$_6$H$_4$; Bown *et al.*, 1990). This indicates that *exo*-cyclization in such ruthenaboranes strengthens the Ru—B bonding slightly at the cyclized sites compared with non-cyclized compounds. The same situation could also be observed in the related acetato- and benzoato-linked compounds mentioned above.

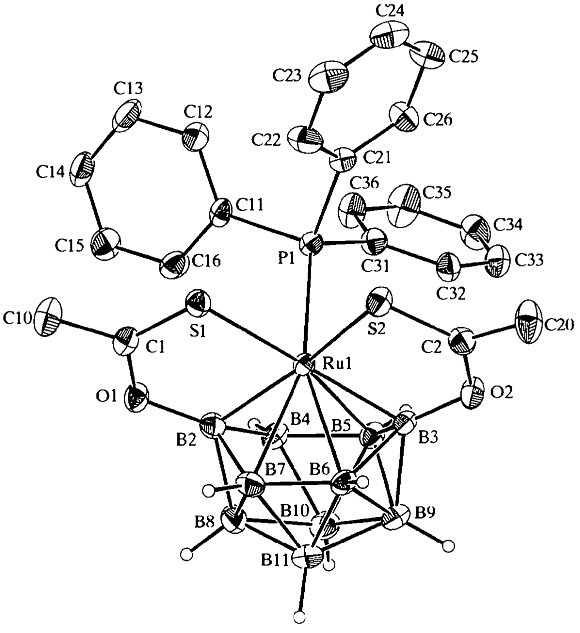


Fig. 1. *ZORTEP* drawing (Zsolnai & Huttner, 1994) of (I) showing 30% probability displacement ellipsoids.

As expected, the mean C—O bond length [1.298 (9) Å *cf.* 1.311 Å in (II)] is between those of a single (*ca* 1.43 Å) and a double bond (*ca* 1.22 Å). Meanwhile, the C—S bond distances [1.641 (8) and 1.641 (8) Å *cf.* 1.673 (5) and 1.657 (5) Å in (II)] are significantly shorter than the usual single-bond length (*ca* 1.8 Å), suggesting a partial electron delocalization in the O—C—S system (Dou *et al.*, 1997; Yao *et al.*, 1998). Additionally, the Ru—S distances of 2.443 (2) and 2.445 (2) Å are somewhat shorter than those of 2.455 (1) and 2.460 (1) Å for (II). All these subtle differences between (I) and (II) can be attributed to the fact that the methyl group of the thioacetate in the present work acts as a relatively stronger electron-donating group with a smaller steric effect when compared with the phenyl group in compound (II).

Experimental

The synthesis of the title compound was effected by the reaction of [RuCl$_2$(PPh$_3$)$_3$] (0.38 g, 0.4 mmol) and [NEt$_4$]$_2$B$_{10}$H$_{10}$ (0.16 g, 0.4 mmol) with MeCOSH (0.06 ml, 0.8 mmol) in refluxing dichloromethane for 120 h under an atmosphere of dry nitrogen. The resulting solution was reduced in volume and chromatographed using dichloromethane/light petroleum (b.p. 333–363 K) (5:3) as the eluting medium to give the red title compound at R_f = 0.67. Crystals suitable for X-ray study were grown from an *n*-pentane/dichloromethane (2:1) solution.

Crystal data

[Ru(C$_4$H$_{14}$B$_{10}$O$_2$S$_2$)-(C$_{18}$H$_{15}$P)]
M_r = 629.71
Monoclinic
$P2_1/n$
a = 8.441 (4) Å
b = 21.879 (7) Å
c = 15.561 (4) Å
β = 95.72 (3)°
V = 2859.5 (18) Å^3
Z = 4
D_x = 1.463 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 17 reflections
θ = 7.3–12.6°
μ = 0.772 mm^{-1}
T = 294 (2) K
Square prism
0.42 × 0.36 × 0.32 mm
Red

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.738, $T_{\max}$ = 0.790

3710 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.032
$\theta_{\max}$ = 25°
h = 0 → 10
k = 0 → 26
l = −18 → 18

5371 measured reflections
5010 independent reflections

3 standard reflections
every 200 reflections
intensity decay: 0.372%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.167$
$S = 1.138$
5010 reflections
343 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 17.9297P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.626$ e Å^{-3}
$\Delta\rho_{\min} = -0.870$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ru1—B2	2.036 (9)	Ru1—P1	2.487 (2)
Ru1—B3	2.062 (8)	S1—C1	1.641 (8)
Ru1—B4	2.329 (8)	S2—C2	1.641 (8)
Ru1—B5	2.341 (8)	O1—C1	1.296 (9)
Ru1—B7	2.393 (9)	O1—B2	1.447 (10)
Ru1—B6	2.393 (8)	O2—C2	1.301 (9)
Ru1—S2	2.443 (2)	O2—B3	1.437 (10)
Ru1—S1	2.445 (2)		
B2—Ru1—S2	151.7 (3)	B6—Ru1—S1	114.8 (2)
B3—Ru1—S2	74.7 (2)	S2—Ru1—S1	84.87 (7)
B4—Ru1—S2	159.7 (2)	B2—Ru1—P1	109.7 (3)
B5—Ru1—S2	115.2 (2)	B3—Ru1—P1	112.7 (2)
B7—Ru1—S2	114.6 (2)	B4—Ru1—P1	93.1 (2)
B6—Ru1—S2	85.8 (2)	B5—Ru1—P1	94.6 (2)
B2—Ru1—S1	74.8 (2)	B7—Ru1—P1	155.6 (2)
B3—Ru1—S1	152.6 (2)	B6—Ru1—P1	159.4 (2)
B4—Ru1—S1	115.3 (2)	S2—Ru1—P1	86.82 (7)
B5—Ru1—S1	159.8 (2)	S1—Ru1—P1	83.63 (7)
B7—Ru1—S1	86.7 (2)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994). Software used to prepare material for publication: *SHELXL*97.

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A three-ring *exo*-polyhedral-cyclized nickelaundecaborane cluster: $[(CH_3COS)_3NiB_{10}H_7(PPh_3)]$

Jian-Min Dou,[a,c] Chun-Hua Hu,[a] Hai-Jun Yao,[b] Ruo-Shui Jin[b] and Pei-Ju Zheng[a]

[a]*Research Center of Analysis and Measurement, Fudan University, Shanghai 200433, People's Republic of China,* [b]*Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China, and* [c]*Department of Chemistry, Liaocheng Teacher's University, Shandong Province 252000, People's Republic of China. E-mail: pjzheng@fudan.edu.cn*

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Abstract

The title compound 3,7:7,8:7,11-tris(μ-thioacetate-*S*:*O*)-10-(triphenylphosphine-*P*)-8,9-μH-7-nickela-*nido*-undecaborane, $[Ni(C_{24}H_{31}B_{10}O_3PS_3)]$, has a *nido*-type $\{NiB_{10}\}$ cage fused to three five-membered Ni—S—C—O—B rings.

Comment

The chemistry of metallaborane clusters is still attracting a great deal of interest and a large variety of novel structural motifs is continually revealed (Greenwood, 1983, 1991; Kennedy, 1986, 1997). We have synthesized