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Synthesis and molecular structure of an *exo*-bicyclic eleven-vertex *closo*-ruthenaborane $[(PPh_3)(C_6H_5COS)_2RuB_{10}H_8]\cdot(CH_2Cl_2)$

Hai-Jun Yao,[a] Chun-Hua Hu,[b] Jian-Min Dou,[b] Jing-De Wei,[a] Ruo-Shui Jin,[a]
Wen Li[b] and Pei-Ju Zheng[b]*

[a] Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

[b] Research Center of Analysis and Measurement, Fudan University, Shanghai 200433, P. R. China

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Abstract—The title compound has been separated in ca 13% yield from the reaction of *closo*-$[B_{10}H_{10}]^{2-}$, $[(PPh_3)_3RuCl_2]$ and C_6H_5COSH in CH_2Cl_2 solution, and characterized by elemental analysis, infrared spectroscopy, ^1H NMR and ^{31}P NMR spectroscopy and single-crystal X-ray diffraction analysis. The molecular structure is based on an eleven-vertex *closo*-type C_{2v} $\{RuB_{10}\}$ cluster-geometry with the ruthenium atom occupying the unique six-connected apical position. The metal center has three exopolyhedral ligands, one triphenylphosphine and two dative thiobenzoate sulfur atoms. The carbonyl oxygen atoms of two thiobenzoxy are additionally bonded to B2 and B3 atoms respectively, resulting in two exocyclic five-membered Ru—S—C—O—B rings. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: synthesis; molecular structure; metallaborane; ruthenaborane; exopolyhedral cyclic; *closo*-type $\{RuB_{10}\}$.

The exopolyhedral heterocyclic metallaborane and metallacarborane compounds with metal-to-cluster linkages have been the interesting subjects recently. Previous work in this area has been confined to four types of linkage. The *ortho*-cycloboronation processes that lead to the formation of the metal-to-boron *ortho*-P-phenyl linkage have been extensively studied in metallaborane chemistry [1–7]. Most of the known *exo*-cyclic metallaborane compounds which exhibited exopolyhedral metal-to-boron acetate linkage were generally obtained by the reactions in the presence of acetic acid [8–9], but the first example of metallacarborane compound with an acetate linkage on a *closo* ten-vertex $\{IrCB_8H_7\}$ system obtained in an obscure reaction process [4]. A series of compounds which exhibit a metal-to-boron dithioformate linkage have been obtained by the reactions between CS_2 and related metallaheteroborane or metallaborane species under reflux conditions [10–15]. The exopolyhedral heterocyclic platinaundecaborane [7-(PMe_2Ph)-2,7-(μ-S_2CNEt_2)-*nido*-7-$PtB_{10}H_{11}$] with an exopolyhedral metal-to-boron *N*,*N*-diethyldithio-carbamate linkage is obtained from the reaction of [7,7-(PMe_2Ph)-*nido*-7-$PtB_{10}H_{12}$] with $[AuBr_2(S_2CNEt_2)]$ [16]. All of these facts indicate that the cyclic exopolyhedral metal-to-cluster linkage in polyhedral metallaborane and metallacarborane compounds may be formed in a quite different way. We are interested in the synthesis of exopolyhedral cyclic metallaborane by the reaction of $MCl_2(PPh_3)_x$ (M = Ru, Ni and Pt; $x = 2$ or 3) with $B_{10}H_{10}^{2-}$ in the presence of carboxylic and thiocarboxylic acid in refluxing CH_2Cl_2 solution. We have reported a series of stable metallaboranes containing from one to three five-membered rings [17–20]. Here we report the synthesis and structure of an exopolyhedral cyclic *closo*-$\{RuB_{10}\}$ cluster compound with two five-membered Ru—S—C—O—B rings.

EXPERIMENTAL

The starting compounds $[(PPh_3)_3RuCl_2]$ [21], $[NEt_4]_2[B_{10}H_{10}]$ [22] and C_6H_5COSH [23] were prepared by previously published methods. Dichloromethane, n-pentane and petroleum ether (b.p. 60–

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* Author to whom correspondence should be addressed.

90°C) were purified by repeated distillation. Reactions were carried out under dry nitrogen in oxygen-free solvent, but subsequent manipulation and separation were carried out in air. Chromatography was carried out by preparative thin-layer using Kieselgel 60G (Merck) on plates of dimension 20 cm × 20 cm × ca 1mm, made in the laboratory as required.

Synthesis of compound **1**

$[(PPh_3)_3RuCl_2]$ (0.38 g, 0.4 mmol), $[NEt_4]_2[B_{10}H_{10}]$ (0.15 g, 0.4 mmol) and C_6H_5COSH (0.11 g, 0.8 mmol) were stirred together in a refluxing CH_2Cl_2 (70 cm^3) solution under dry nitrogen for 112.5 h. The resulting bright-red solution was reduced (rotary evaporator, 30°C, water pump) to ca 5 cm^3, and chromatographed (t.l.c.) using CH_2Cl_2-light petroleum (b.p. 60–90°C) (5 : 3) as eluant to give an orange-red compound at $Rf = 0.81$, in ca 13% yield. The product was recrystallized from CH_2Cl_2/*n*-pentane to give air-stable orange-red crystals. Found : C, 48.71 ; H, 4.30 ; S, 7.31. $C_{33}H_{35}RuPB_{10}S_2O_2Cl_2$ requires C, 47.25 ; H, 4.21 ; S, 7.65%. FTIR(cm^{-1}) : 3050 (w), 2516 (vs), 2461 (s), 1786 (w), 1762 (m), 1733 (m), 1685 (vs), 1640 (vs), 1505 (vs), 1453 (s), 1419 (m), 1334 (m), 1303 (s), 1230 (vs), 1164 (m), 1095 (vs), 1025 (w), 974 (s), 763 (m), 731 (s), 680 (s), 554 (w). ^1H NMR ($CDCl_3$) : δ ppm 0.87 (q, 2H, BH), δ ppm 1.28 (t, 4H, BH), δ ppm 1.58 (s, 2H, BH), δ ppm 6.81–8.39 (25H, Ph) ; ^{31}P NMR ($CDCl_3$) δ 21.868 ppm.

Physical measurements

Elemental analyses were performed on a Carlo Erba 1106 elemental analyser.

IR spectra of the complex in the range 400–4000 cm^{-1} as KBr pellets was measured on a NICOLET 5SXC-FTIR spectrometer.

^1H NMR spectra was collected on a BRUCKER spectrometer and using TMS as the internal reference. ^{31}P NMR spectra was collected on a DRX400 spectrometer and using 85% H_3PO_4 as the external reference.

X-ray crystallography

A crystal with dimensions of 0.30 × 0.30 × 0.27 mm was mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined by a least-squares refinement of 25 reflections with $20.8° < 2\theta < 26.4°$ and the data were collected using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å) with $\omega/2\theta$ scan mode ($0° \leqslant 2\theta \leqslant 50°$) at 21 ± 1°C. The structure was determined by Direct methods (MULTAN-82). All non-hydrogen atoms were located successfully and all hydrogen atoms were treated as riding on their attached atoms. The refinement of positional and anisotropic thermal parameters was carried out by full-matrix least-squares method. All calculations were carried out on a Micro VAX-II computer with SDP-*Plus* software package. Experimental data are summarized in Table 1.

RESULTS AND DISCUSSION

In addition to the strong B—H stretch bonds [24,25] at 2516 and 2461 cm^{-1}, the infrared spectra of the compound also exhibits a strong absorption at 1095 cm^{-1} due to PPh_3 aromatic vibration involving some P—C stretching, which has a slight shift than the reported data of PPh_3 (1090 cm^{-1}) [26,27]. Three strong absorption bands at 1685, 1230, and 963 cm^{-1} which are assigned to ν(C—O), ν(C—phenyl) and ν(C—S) of thiobenzoxy ligands respectively, are in correspondence with the reported data (1690, 1210, 950 cm^{-1}) [28,29]. We can deduce that compound **1** contains both PPh_3 and thiobenzoxy as ligands.

A drawing of the molecular structure of compound **1** is shown in Fig. 1. The selected bond lengths and bond angles are listed in Table 2 and Table 3 respectively. Both X-ray diffraction analysis and ^1H NMR spectrum have showed that the cluster has an eleven-vertex cluster structure of idealized C_{2v} symmetry. The borane-to-metal bonding mode is boat-hexaphto. The ruthenium center has three exopolyhedral ligands, one triphenylphosphine and two dative S atoms of thiobenzoxy groups. The exopolyhedral ruthenium-bound ligand phosphorus atom is almost in the reflection plane which bisects the two B4—B5 and B6—B7 vectors. The two thiobenzoxy groups behave as bridging ligands between the ruthenium center and two prow boron atoms, in which their two sulfur atoms coordinate to Ru1 and two carbonyl oxygen atoms are bound to B2 and B3 respectively. This results in two nearly symmetric exopolyhedral five-membered Ru—S—C—O—B rings. From Table 2, the interatomic distance of Ru—B and B—B within the $\{RuB_{10}\}$ cage are similar to those observed in reported 11-vertex *closo*-ruthenaundecaborane clusters as shown in literatures 8 and 30–32. The average values of interatomic distances of C7—O1 and C14—O2 is 1.311 Å, which are between those of C—O single-bond (1.43 Å) and C=O double-bond (1.22 Å). This fact indicates that the carbon–oxygen bonds of two thiocarboxyl groups have some double-bond character and is supported by the infrared spectroscopic observation as shown above.

The idealized C_{2v} closed eleven-vertex metallaborane structural type is to be of interest because of its contravention of the simple Wade-Williams cluster-geometry and electron-counting rules. According to the Wade-Williams' electron-counting rules, there are two possible electron structures for this C_{2V} $\{RuB_{10}\}$ cage. The first would be that the $[Ru(1\text{-}1)PPh_3(SCPh)_2]$ moiety contributes three orbitals and two electrons to cluster bonding, so that the closed structure has two electron less than that required for

Table 1. Crystallographic data

Chemical formula	$RuCl_2S_2PO_2C_{33}B_{10}H_{35}$
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 12.610(2)$ Å, $\alpha = 110.89(1)$ $b = 12.860(2)$ Å, $\beta = 103.52(1)$ $c = 14.365(2)$ Å, $\gamma = 106.84(1)$
Volume	1930(1) $Å^3$
Z	2
D_{calc}	1.444 g/cm^3
μ	7.1 cm^{-1}
No. of measured reflections	7059
No. of unique reflections	6461
No. of observed $[I > 3\sigma(I)]$ reflections	5057
Index ranges	$-15 \leqslant h \leqslant 15$, $-15 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 17$
Absorption correction	Empirical
Weight scheme	Unit weights
Parameters refined	460
Final R indices $[I > 3\sigma(I)]$	$R = 0.039$, $Rw = 0.054$
Goodness-of-fit (S)	1.91
Largest shift/esd	0.02
Highest peak in the last difference fourier	0.51 e/$Å^3$

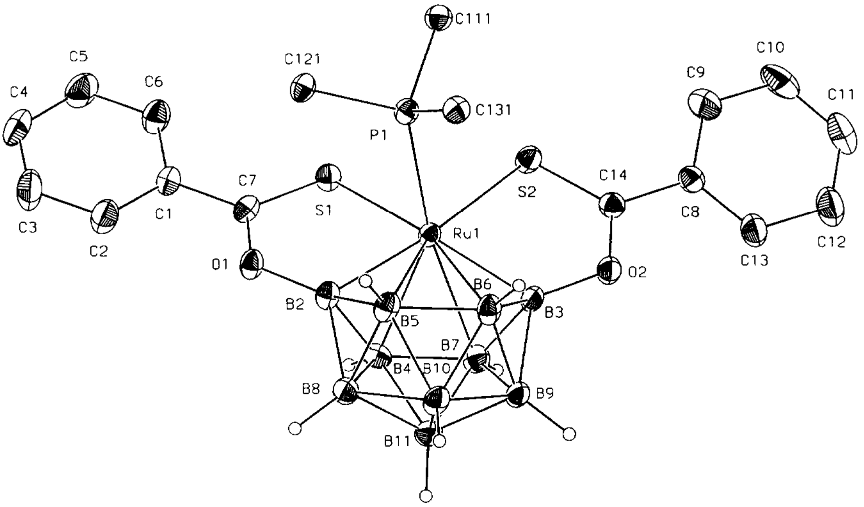

Fig. 1. ORTEP drawing of the title compound (30% probability ellipsoids). Some C and H atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) for compound **1**

Ru1—S1	2.455(1)	Ru1—S2	2.460(1)	Ru1—P1	2.4823(8)
Ru1—B2	2.052(6)	Ru1—B3	2.067(5)	Ru1—B4	2.337(4)
Ru1—B5	2.313(6)	Ru1—B6	2.385(6)	Ru1—B7	2.397(4)
O1—B2	1.430(6)	O2—B3	1.428(6)	B2—B4	1.747(6)
B2—B5	1.717(8)	B2—B8	1.684(6)	B3—B6	1.730(8)
B3—B7	1.762(7)	B3—B9	1.725(7)	B4—B7	1.693(9)
B4—B8	1.843(8)	B4—B11	1.801(8)	B5—B6	1.767(9)
B5—B8	1.822(6)	B5—B10	1.798(6)	B6—B9	1.831(5)
B6—B10	1.780(6)	B7—B9	1.838(9)	B7—B11	1.779(8)
B8—B10	1.775(8)	B8—B11	1.775(7)	B9—B10	1.748(9)
B10—B11	1.754(7)				

Table 3. Selected bond angles (°) for compound **1**

S1—Ru1—S2	88.73(4)	S1—Ru1—P1	82.25(4)	S1—Ru1—B2	74.9(2)
S1—Ru1—B3	148.6(2)	S1—Ru1—B4	83.3(1)	S1—Ru1—B5	117.1(1)
S1—Ru1—B6	161.2(1)	S1—Ru1—B7	111.1(1)	S2—Ru1—P1	85.92(3)
S2—Ru1—B2	161.2(2)	S2—Ru1—B3	74.1(2)	S2—Ru1—B4	123.7(1)
S2—Ru1—B5	152.7(1)	S2—Ru1—B6	110.1(1)	S2—Ru1—B7	92.5(1)
P1—Ru1—B2	100.7(1)	P1—Ru1—B3	121.4(1)	P1—Ru1—B4	146.6(1)
P1—Ru1—B5	89.00(9)	P1—Ru1—B6	97.74(9)	P1—Ru1—B7	166.6(1)
B2—Ru1—B3	115.7(2)	B2—Ru1—B4	46.3(2)	B2—Ru1—B5	45.8(3)
B2—Ru1—B6	86.7(3)	B2—Ru1—B7	85.0(2)		

a formal *closo* electron count, and it would be regarded as "electron hyper-deficient" [33,34]. This situation is based on the assumption that the metal center is electronically saturated. If the metal center is allowed to be electronically unsaturated, the second possible electron structure would be that the [Ru(II) $PPh_3(SCPh)_2$] moiety contributes three obitals and four electrons to cluster bonding, so that the cluster has sufficient electrons for a formal *closo* electron count, in this case the compound would have a formally unsaturated 16-electron Ru(II) center. However, there is also a possible electron structure called *isocloso* structure with the metal center having a four-orbital four-electron contribution [30,35]. All of these views are short of sufficient experimental evidences.

Although the reaction mechanism is complex, overall reaction is stoicheiometric and can easily be expressed by a simple equation [eqn (2)],

$$[(PPh_3)_3RuCl_2]+[B_{10}H_{10}]^{2-}+2C_6H_5COSH \rightarrow [(PPh_3)(C_6H_5COS)_2RuB_{10}H_8] + 2H_2 + 2Cl^- + 2PPh_3 \quad (2)$$

Two interesting facts show that the reaction mechanism is not simple. The first one is that the ruthenium(II) vertex is coordinated by the sulfur atoms of two thiobenzoxy. This gives an evidence that the elimination of two molecules of hydrogen must involve a series of process, not a simple reaction between the terminal-hydrogen of $[B_{10}H_{10}]^{2-}$ anion and the -SH group of thiobenzoic acid. The second fact is that the carbon-oxygen bond of thiobenzoxy in compound **1** keeps its carbonyl character. It implies that the carbonyl group of thiobenzoic acid plays the role as a Lewis base. As we know that $B_{10}H_{12}L_2$ can react with a strong Lewis base R_3N to give the *closo*-$B_{10}H_{10}^{2-}$:

$$B_{10}H_{12}L_2+2R_3N = 2R_3NH^+ + B_{10}H_{10}^{2-} + 2L$$

It is reasonable that the presence of a weak Lewis base species, such as the carbonyl group of carboxy or thiocaboxy ligands, would be favorable for the reverse process which leads to the opening of the $B_{10}H_{10}^{2-}$ cage. Because of the great complexity, the mechanism of this type of reaction needs to be further studied in the future.

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