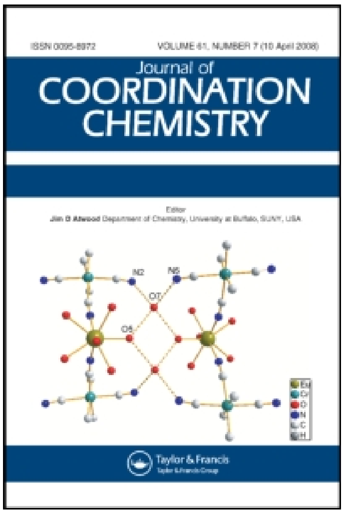

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Two iso-closo 11-vertex ruthenaborane clusters with exo-polyhedral cyclization of para-iodobenzoate

Qingliang Guo[a]; Jianmin Dou[a]; Libin Wu[a]; Dacheng Li[a]; Daqiwang[a]
[a] School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, People's Republic of China

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Two iso-closo 11-vertex ruthenaborane clusters with exo-polyhedral cyclization of para-iodobenzoate

QINGLIANG GUO, JIANMIN DOU*, LIBIN WU,
DACHENG LI and DAQIWANG

School of Chemistry and Chemical Engineering, Liaocheng University,
Liaocheng, 252059, People's Republic of China

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The reaction of $[RuCl_2(PPh_3)_3]$ and *closo*-$[B_{10}H_{10}]^{2-}$ with *p*-IPhCOOH in CH_2Cl_2 solution affords two *para*-iodobenzoate *exo*-cyclized 11-vertex *closo*-ruthenaborane clusters $[(PPh_3)(p\text{-}IPhCO_2)_2RuB_{10}H_8]$ (**1**) and $[(PPh_3)_2ClRu(PPh_3)(p\text{-}IPhCO_2)RuB_{10}H_9]\cdot CH_2Cl_2$ (**2**) that have been characterized by elemental analysis, FT-IR, ^{1}H and ^{13}C NMR spectra and single-crystal X-ray diffraction analysis. Both clusters are based on a *closo*-type C_{2v} 1 : 2 : 4 : 2 : 2 RuB_{10} stack with the metal occupying the unique six-connected apical position. In **1**, the metal center has three *exo*-polyhedral ligands: one triphenylphosphine and two native oxygen atoms of *para*-iodobenzoates. The other oxygen atoms of two *para*-iodobenzoates are additionally bonded to B(2) and B(3) atoms respectively, resulting in two *exo*-cyclic five-membered Ru–O–C–O–B rings and engendering a symmetrical conformation. For **2**, the metal center also has three *exo*-polyhedral ligands, one triphenylphosphine and one *para*-iodobenzoate to form one *exo*-cyclic five-membered Ru–O–C–O–B ring. There is an additional *exo*-polyhedral ruthenium atom bonding to the $\{RuB_{10}\}$ center via a {Ru–Ru} linkage and two $\{RuH_\mu B\}$ bridges resulting in one *closo* distorted *exo*-polyhedral Ru(1)–Ru(2)–B(2)–B(4) tetrahedron.

Keywords: Ruthenaborane cluster; Crystal structure; *para*-Iodobenzoate; Metallaborane

1. Introduction

In recent years, boron cluster chemistry has developed into a far-reaching area that includes neutral boranes and their anions, metallaboranes, carboranes and metallacarboranes, main group heteroboranes and their derivatives. These compounds offer interesting potential and actual applications, including boron neutron capture therapy (BNCT), solvent extraction, nonlinear optics, liquid crystals, ion-selective electrodes, catalysts and host-guest chemistry [1–5]. Five- or six-membered ring(s) of *exo*-polyhedral cyclization of metal ligand(s) to boron cage can strengthen the metal-to-boron bonding in some borane clusters [6]. Cyclized groups include P-phenyl [7], carboxylate or thiocarboxylate [8], dithioformate [9] and diethyldithio-carbamate [10]. We are interested in structures of *exo*-cyclic ruthenaborane clusters containing

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*Corresponding author. Tel.: 86 0635 8239069. Fax: 86 0635 8239121. Email: jmdou@lctu.edu.cn

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exo-polyhedral carboxylate. In this article, we report the X-ray crystal structures and spectroscopic properties of two new *exo*-cyclic ruthenaborane clusters $[(PPh_3)(p\text{-}IPhCO_2)_2RuB_{10}H_8]$ (**1**) and $[(PPh_3)_2ClRu(PPh_3)(p\text{-}IPhCO_2)RuB_{10}H_9]\cdot CH_2Cl_2$ (**2**) containing one or two *para*-benzoate ligand(s).

2. Experimental

2.1. *Materials and instrumentation*

The starting compounds $[RuCl_2(PPh_3)_3]$ and $(Et_4N)_2[B_{10}H_{10}]$ were prepared as described [11, 12]. Dichloromethane was dried with CaH_2 and distilled prior to use. Light petroleum refers to that fraction of boiling point 60–90°C. The reagents and solvents were A.R. grade, purchased commercially and used without further purification. The reaction was carried out under an atmosphere of dry nitrogen in oxygen-free solvents, but subsequent manipulations and separations were generally carried out in air. Chromatography was carried out by preparative thin-layer using silica gel G (type HG/T2354-92) on plates of dimensions 200 × 200 × 1mm, made in the laboratory as required. Elemental analyses (C and H) were performed with a Perkin-Elemer 2400 II Elemental Analyzer. FT-IR spectra were recorded in the range 400–4000cm^{-1} with a Nicolet-460 FT-IR spectrophotometer as KBr pellets. NMR spectra were measured on a Varian Mercury 400 (400 MHz) nuclear magnetic resonance system.

2.2. *Synthesis of clusters*

$[RuCl_2(PPh_3)_3]$ (384 mg, 0.4 mmol), $(Et_4N)_2[B_{10}H_{10}]$ (150 mg, 0.4 mmol) and *p*-IPhCOOH (198 mg, 8 mmol) were stirred together in refluxing CH_2Cl_2 (70 mL) solution under N_2 for 120 h. The volume of brown-red solution was reduced (rotary evaporator, 38°C, water pump) to ca 10 mL, and chromatographed (TLC) using CH_2Cl_2–light petroleum (b.p. 60–90°C) (silica G, CH_2Cl_2–light petroleum 4 : 1) to give **1** (orange, $Rf = 0.96$; yield, 149.3 mg, 38.3% (based on B)) and **2** (dark-red, $Rf = 0.93$; yield, 112.6 mg, 19.1% (based on B)). Single crystals of the clusters were recrystallized from dichloromethane/*n*-pentane solution. Cluster **1**: m.p.: 264–265°C. Anal. Calcd for $C_{32}H_{31}B_{10}I_2O_4PRu$: C, 39.48; H, 3.21. Found: C, 39.44; H, 3.28. FI-IR (KBr, cm^{-1}): 3050 (ν(Ar–H), m), 2515 (ν(B–H), m), 1582 (ν(C = O), s), 1552 (ν(Ar CC), m), 1480 (ν(Ar CC), w), 1434 (ν(Ar CC), m), 1350 (ν(C–O), s), 1099 (ν(P–C), m), 1056 (ν(C–I), m), 876 (δ(Ar–H), w), 749 (δ(Ar–H), m), 694 (δ(Ar–H), m), 560 (δ(P–C), w), 522 (δ(P–C), m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.87 (2H, BH), 1.27 (4H, BH), 1.56 (2H, BH), 7.08–7.35 (m, 15H, Ph), 7.69–7.83 (8H, C_6H_4); ^{13}C NMR (100.63 MHz, $CDCl_3$) δ: 103.89 (2C, C–I), 126.00–133.78 (24C, Ph), 138.89 (4C, C_6H_4), 175.16 (2C, C=O). Cluster $\mathbf{2}\cdot CH_2Cl_2$: m.p.: 229–230°C. Anal. Calcd for $C_{62}H_{60}B_{10}Cl_3IO_2P_3Ru_2$: C, 50.54; H, 4.10. Found: C, 50.56; H, 4.06; FI-IR (KBr, cm^{-1}): 3045 (ν(Ar–H), m), 2516 (ν(B–H), m), 1634 (ν(Ar CC), m), 1592 (ν(C=O), s), 1553 (ν(Ar CC), m), 1481 (ν(Ar CC), w), 1434 (ν(Ar CC), m), 1384 (ν(C–O), m), 1092 (ν(P–C), m), 1060 (ν(C–I), w), 843 (δ(Ar–H), w), 746 (δ(Ar–H), m), 694 (δ(Ar–H), m), 520 (δ(P–C), s). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.90

(2H, BH), 0.92 (1H, BH), 0.96 (1H, BH), 1.26 (2H, BH), 1.28 (1H, BH) 1.38 (1H, BH), 1.62 (2H, BH), 7.23–7.34 (m, 45H, Ph), 7.53–7.72 (4H, C_6H_4); ^{13}C NMR (100.63 MHz, $CDCl_3$) δ: 102.35 (1C, C–I), 127.06–134.15 (57C, Ph), 138.04 (2C, C_6H_4), 167.74 (1C, C=O).

2.3. *Crystal structure determination*

Crystallographic data for clusters **1** and **2** were measured on a Bruker SMART 1000 CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) and 298(2) K, respectively. Both structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using SHELXTL program packages [13]. Details of the crystal parameters, data collection and refinement are summarized in table 1.

3. Results and discussion

3.1. *Description of the crystal structure*

3.1.1. Cluster 1. The molecular structure of **1**, together with the atomic numbering scheme, are presented in figure 1. The selected bond lengths and angles are listed

Table 1. Crystallographic data for clusters **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{32}H_{31}B_{10}I_2O_4PRu$	$C_{62}H_{60}B_{10}Cl_3IO_2P_3Ru_2$
Formula weight	973.51	1473.5
Color and shape	Orange block	Dark-red block
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	26.1891(14)	12.638(11)
b (Å)	15.3671(9)	14.086(12)
c (Å)	19.2472(11)	19.897(16)
α (°)	90	82.122(11)
β (°)	93.9000(10)	72.172(10)
γ (°)	90	86.091(12)
V (Å^3)	7728.1(8)	3339(5)
Z	8	2
T (K)	293(2)	298(2)
μ (mm^{-1})	2.080	1.147
Reflections collected	20012	16498
Independent reflections	6795	11361
Crystal size (mm^3)	0.48 × 0.41 × 0.35	0.45 × 0.39 × 0.33
θ range (°)	1.84–25.00	2.13–25.10
$h/k/l$ (max, min)	−31, 31/−18, 17/−22, 18	−12, 15/−15, 16/−23, 23
R_{int}	0.0210	0.0518
GoF	1.001	1.012
Absorption correction	Semi-expirical from equivalents	Semi-expirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
R_1 and wR_2 [$I > 2\sigma(I)$]	0.0298, 0.0771	0.0791, 0.1922
R_1 and wR_2 (all data)	0.0336, 0.0792	0.1297, 0.2400
Largest diff. peak and hole (e Å^{-3})	1.351, −0.913	1.918, −1.948

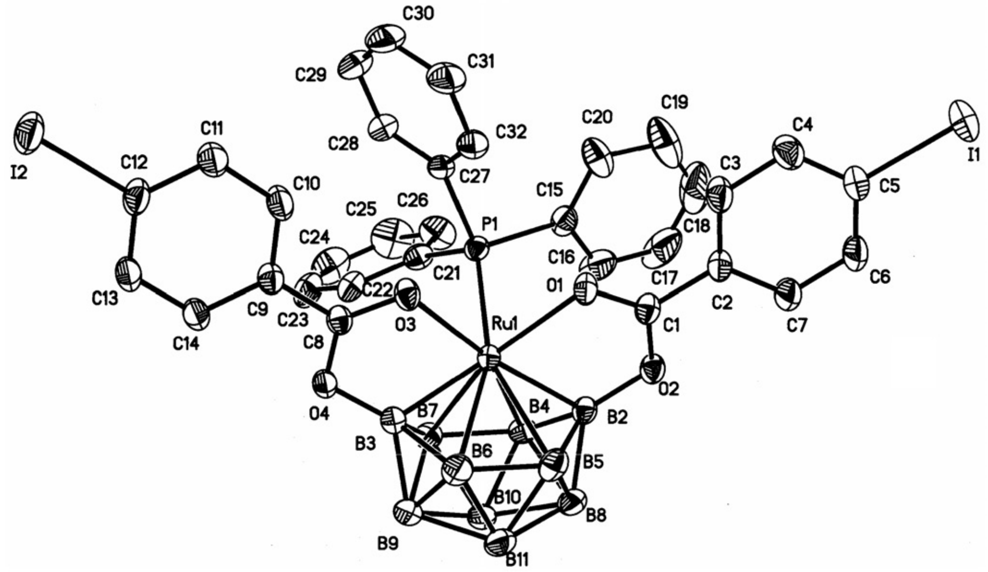

Figure 1. Molecular structure of **1** with 30% probability ellipsoids (H atoms have been omitted for clarity).

Table 2. Selected bond lengths (Å) and angles (°) of **1**.

Ru(1)–B(2)	2.019(3)	Ru(1)–O(3)	2.224(2)	O(3)–C(8)	1.237(3)
Ru(1)–B(3)	2.022(4)	Ru(1)–P(1)	2.4768(8)	O(4)–C(8)	1.316(4)
Ru(1)–B(4)	2.291(3)	B(2)–O(2)	1.437(4)	C(8)–C(9)	1.469(4)
Ru(1)–B(5)	2.369(4)	B(3)–O(4)	1.442(4)	C(9)–C(10)	1.370(5)
Ru(1)–B(6)	2.368(4)	C(1)–O(1)	1.241(4)	I(1)–C(5)	2.092(3)
Ru(1)–B(7)	2.300(3)	C(1)–O(2)	1.320(3)	I(2)–C(12)	2.091(3)
Ru(1)–O(1)	2.221(2)	C(1)–C(2)	1.469(4)		
O(1)–Ru(1)–P(1)	81.50(6)	B(5)–Ru(1)–B(6)	41.80(14)		
O(1)–Ru(1)–O(3)	88.86(7)	B(2)–Ru(1)–O(1)	72.72(11)		
O(3)–Ru(1)–P(1)	83.91(6)	C(1)–O(1)–Ru(1)	113.96(19)		
B(2)–Ru(1)–P(1)	109.54(10)	O(1)–C(1)–O(2)	120.6 (3)		
B(3)–Ru(1)–P(1)	114.85(4)	C(1)–O(2)–B(2)	112.5(2)		
B(2)–Ru(1)–B(3)	117.46(15)	O(2)–B(2)–Ru(1)	116.7(2)		
B(2)–Ru(1)–B(5)	46.43(14)	B(3)–Ru(1)–O(3)	72.37(12)		
B(5)–Ru(1)–B(7)	87.79(14)	C(8)–O(3)–Ru(1)	114.46(19)		
B(3)–Ru(1)–B(7)	46.14(14)	O(3)–C(8)–O(4)	120.5(3)		
B(3)–Ru(1)–B(6)	46.47(14)	C(8)–O(4)–B(3)	112.5(2)		
B(4)–Ru(1)–B(6)	88.03(14)	O(4)–B(3)–Ru(1)	117.0(2)		
B(2)–Ru(1)–B(4)	46.64 (13)	C(4)–C(5)–I(1)	119.2(3)		
B(4)–Ru(1)–B(5)	72.06(13)	C(6)–C(5)–I(1)	120.0(3)		
B(6)–Ru(1)–B(7)	71.90(15)	C(11)–C(12)–I(2)	119.8(3)		
B(4)–Ru(1)–B(7)	44.96(13)	C(13)–C(12)–I(2)	119.3(2)		

in table 2. The core cluster of **1** is seen to have an 11-vertex $\{RuB_{10}\}$ *iso*-*closo* geometry with the characteristic 11-vertex *iso*-*closo* $\{MB_{10}\}$ metallaborane 1 : 2 : 4 : 2 : 2 stack. This conformation is a closed deltahedron corresponding to that reasonably supposed for *closo*-$[B_{11}H_{11}]^{2-}$ and established for its derivative $[B_{11}H_{10}(SMe_2)]^-$ [14]. In gross geometric terms it is derived from the complete capping of the characteristic C_{2v} open 10-vertex nido-decaboranyl cluster shape with the metal atom to produce an MB_{10} 1 : 2 : 4 : 2 : 2 stack also of idealized C_{2v} symmetry, the effective borane ligand exhibits an

η^6 boat coordination to the metal center [8, 15–18], which is compared to the η^6 chair in the 10-vertex species in previously reported complexes [19–21]. The average bond length of Ru(1)–B(4), Ru(1)–B(5), Ru(1)–B(6) and Ru(1)–B(7) bonds is 2.332 Å which is consistent with the corresponding Ru-B distance in $[(PPh_3)(p\text{-}MeC_6H_4CO_2)_2RuB_{10}H_8]$ (average 2.342 Å) [8d] and $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$ (average 2.373 Å) [15b]. The Ru(1)–B(2) and Ru(1)–B(3) distances, which average 2.021 Å, are also essentially the same as the corresponding distances found in cyclized ruthenaborane clusters $[(PPh_3)(p\text{-}MeC_6H_4CO_2)_2RuB_{10}H_8]$ (average 2.019 Å) [8d] and $[(PPh_3)_2(PhCO_2)RuB_{10}H_8Cl] \cdot C_5H_{12}$ (average 2.030 Å) [8c], but all these are slightly shorter than those in the non-cyclized clusters $[\eta^6\text{-}\{1,4\text{-}(Me)(^iPr)C_6H_4\}RuB_{10}H_{10}]$ (average 2.098 Å) [18] and $[\{(\eta6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)\}RuB_{10}H_8(OEt)_2]$ (average 2.106 Å) [22].

The ruthenium center has three *exo*-polyhedral ligands, one PPh_3 and two *para*-iodobenzoate groups which behave as bridging ligands between the ruthenium center and two prow boron atoms, in which their two carbonyl oxygen atoms coordinate to Ru(1) and the other two carbonyl oxygen atoms are bounded to B(2) and B(3). This results in two nearly symmetric *exo*-polyhedral five-membered Ru–O–C–O–B rings, the same as those observed in reported 11-vertex *closo*-ruthenaborane clusters [8a–f]. The distance of Ru(1)–P(1), 2.4768(8) Å, falls in the normal range. The average bond lengths of Ru–O (2.223 Å) and B–O (1.440 Å) are comparable to these in the analogous cluster $[(PPh_3)(p\text{-}MeC_6H_4CO_2)_2RuB_{10}H_8]$ (2.220 and 1.437 Å) [8d] and the average B–O distance (1.440 Å) is again shorter than that in alkoxy substituted ruthenaborane clusters $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$ (1.365 Å) [15b] $[(PPh_3)_2RuB_{10}H_8(O^iPr)_2]$ (1.366 Å) [16]. Moreover, the C(1)–O(1) and C(8)–O(3) distances are 1.241(4) and 1.237(3) Å, respectively, which are in accord with the normal value (ca 1.22 Å) of a double bond, while the C(1)–O(2) and C(8)–O(4) distances (1.320(3) and 1.316(4) Å, respectively) are between the values of single (ca 1.43 Å) and double bonds, suggesting a partial but unequal electron delocalization over the O–C–O system.

3.1.2. Cluster 2. The structure of cluster **2** is shown in figure 2. Selected bond lengths and angles of **2** are listed in table 3. As shown in figure 2, there is also an 11-vertex $\{RuB_{10}\}$ geometry in **2**. In gross geometric terms it also produces an MB_{10} 1 : 2 : 4 : 2 : 2 stack of idealized C_{2v} symmetry with the borane ligand exhibiting an η^6 boat coordination to the metal center, as for **1**. The distances of Ru(1)–B(2) and Ru(1)–B(3) are 2.031(9) and 2.015(10) Å, respectively, and the average distance of Ru(1)–B(4), Ru(1)–B(5), Ru(1)–B(6) and Ru(1)–B(7) bonds is 2.309 Å, consistent with those observed in similar 11-vertex *closo*-ruthenaborane clusters [8a–f]. There are also three *exo*-polyhedral atoms attached to Ru(1), one P atom of triphenylphosphine, one *para*-iodobenzoate as a bridging ligand between the Ru(1) and the prow B(3), with one carbonyl oxygen bound to Ru(1) and another carbonyl oxygen atom attached to B(2) and B(3). This results in one *exo*-polyhedral five-membered Ru–O–C–O–B ring, as observed in $[(PPh_3)_2(PhCO_2)RuB_{10}H_8Cl \cdot C_5H_{12}$ [8c]. The Ru(1)–O(1) and B(3)–O(2) distances are 2.221(6) and 1.446(11) Å, respectively, and the Ru(1)–P(1) bond length is 2.439(3) Å. All of these and the other bond lengths are consistent with the corresponding distances found in cluster **1**.

In addition, there is an *exo*-polyhedral ruthenium, numbered Ru(2), encompassed in a $\{RuCl(PPh_3)_2\}$ unit bonded to the center $\{RuB_{10}\}$ cluster via one Ru–Ru linkage and two Ru–B bonds, forming a *closo* distorted *exo*-polyhedral Ru(1)–Ru(2)–B(2)–B(4)

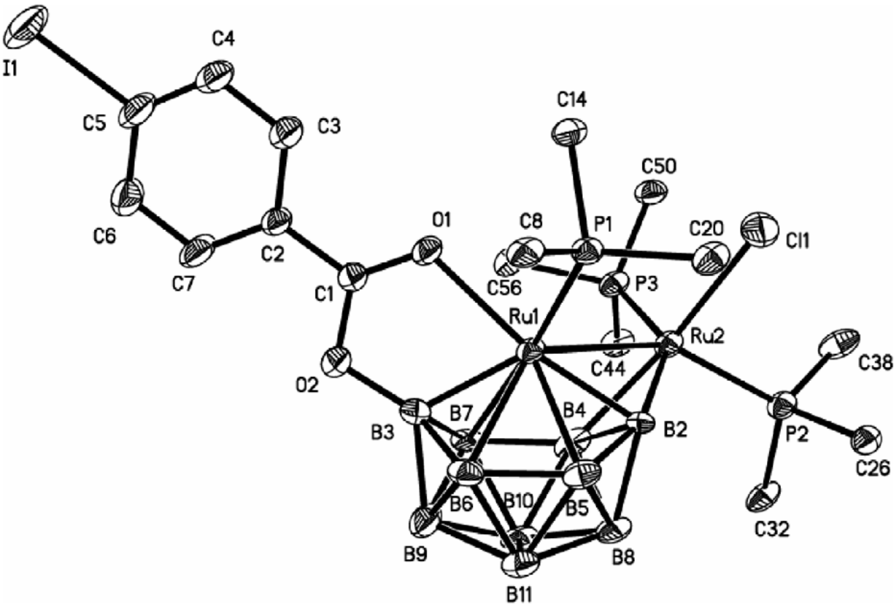

Figure 2. Molecular structure of **2** with 30% probability ellipsoids (H atoms, phenyl group atoms other than the iso carbons and the solvated CH_2Cl_2 molecule have been omitted for clarity).

Table 3. Selected bond lengths (Å) and angles (°) of **2**.

Ru(1)–B(2)	2.031(9)	Ru(1)–P(1)	2.439(3)	B(3)–O(2)	1.446(11)
Ru(1)–B(3)	2.015(10)	Ru(1)–Ru(2)	2.999(2)	B(2)–B(4)	1.725(14)
Ru(1)–B(4)	2.236(9)	Ru(2)–B(2)	2.238(10)	C(1)–O(1)	1.218(10)
Ru(1)–B(5)	2.264(11)	Ru(2)–B(4)	2.278(13)	C(1)–O(2)	1.327(11)
Ru(1)–B(6)	2.361(11)	Ru(2)–P(2)	2.348(3)	C(1)–C(2)	1.451(11)
Ru(1)–B(7)	2.375(9)	Ru(2)–P(3)	2.318(3)	I(1)–C(5)	2.104(9)
Ru(1)–O(1)	2.221(6)	Ru(2)–Cl(1)	2.388(3)		
B(2)–Ru(1)–B(3)	118.4(4)	P(2)–Ru(2)–P(3)	99.68(10)		
O(1)–Ru(1)–Ru(2)	120.24(17)	P(2)–Ru(2)–B(2)	105.6(3)		
O(1)–Ru(1)–P(1)	80.93(17)	P(3)–Ru(2)–B(2)	144.9(2)		
Ru(2)–Ru(1)–P(1)	102.11(6)	P(2)–Ru(2)–B(4)	109.9(2)		
B(2)–Ru(1)–P(1)	96.5(3)	B(2)–Ru(2)–B(4)	44.9(4)		
B(3)–Ru(1)–P(1)	127.5(3)	B(4)–Ru(2)–P(3)	103.6(3)		
B(6)–Ru(1)–P(1)	103.7(3)	Ru(1)–Ru(2)–B(2)	42.8(2)		
B(3)–Ru(1)–B(5)	86.4(4)	Ru(1)–Ru(2)–P(3)	107.58(7)		
B(4)–Ru(1)–B(5)	71.8(4)	B(4)–Ru(2)–Ru(1)	47.8(2)		
B(2)–Ru(1)–B(4)	47.4(4)	P(2)–Ru(2)–Ru(1)	147.90(7)		
B(2)–Ru(1)–B(7)	87.8(4)	Ru(2)–B(2)–B(4)	68.8(5)		
B(6)–Ru(1)–B(7)	71.8(4)	Ru(2)–B(2)–Ru(1)	89.1(3)		
B(3)–Ru(1)–B(6)	45.7(4)	Ru(2)–B(4)–B(2)	66.3(5)		
B(5)–Ru(1)–B(6)	43.8(4)	Ru(2)–B(4)–Ru(1)	83.3(4)		
B(4)–Ru(1)–B(7)	42.9(4)	B(2)–B(4)–Ru(1)	60.1(4)		
B(4)–Ru(1)–B(6)	87.3(4)	B(4)–B(2)–Ru(1)	72.5(4)		
B(5)–Ru(1)–B(7)	88.2(4)	B(3)–B(7)–Ru(1)	56.0(4)		
B(2)–Ru(1)–O(1)	167.6(3)	C(4)–C(5)–I(1)	119.3(8)		
C(1)–O(1)–Ru(1)	116.6(6)	C(6)–C(5)–I(1)	117.9(8)		
O(1)–C(1)–O(2)	120.4(8)	Cl(1)–Ru(2)–Ru(1)	107.03(8)		
C(1)–O(2)–B(3)	111.4(7)	Cl(1)–Ru(2)–B(2)	110.2(3)		
O(2)–B(3)–Ru(1)	119.7(7)	Cl(1)–Ru(2)–B(4)	152.2(2)		
B(3)–Ru(1)–Ru(2)	130.3(3)	Cl(1)–Ru(2)–P(2)	86.71(10)		
B(6)–Ru(1)–Ru(2)	131.3(2)	Cl(1)–Ru(2)–P(3)	95.03(11)		

tetrahedron. The Ru(2) atom is coordinated by one Cl and two PPh_3 ligands besides one prow B(2), one bilge B(4) and Ru(1) of the cluster core. The Ru(2)–P(2), Ru(2)–P(3) bond lengths and P(2)–Ru(2)–P(3) bond angle are 2.348(3), 2.318(3) Å and 99.68(10)°, respectively, comparable to those of $[(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_7\{OCH(CH_3)_2\}_3] \cdot 0.4H_2O$ (2.299(3), 2.326(3) Å and 99.31(9)°, respectively) [23]. Two kinds of bridges of the two ruthenium atoms in double nucleus ruthenaborane clusters are reported: (a) via $\{RuCl_{\mu}Ru\}$ bridges in $[(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_7\{OCH(CH_3)_2\}_3] \cdot 0.4H_2O$ [23], $[(PPh_3)_2ClRuClRu(PPh_3)_3B_{10}H_8(OEt)_2]$ [15a] and $[(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_8\{OCH(CH_3)_2\}_2]$ [24] and (b) via two $\{RuH_{\mu}Ru\}$ and two $\{Ru(CH_3CO_{2\mu}Ru\}$ bridges in $[\{(PPh_3)_2Ru\}\text{-}\mu,\mu,\mu\text{-}(MeCO_2)_3\text{-}\mu,\mu\text{-}H_2\text{-}\{RuB_{10}H_7\}]$ [8a]. In cluster **2**, two ruthenium atoms are directly attached with a Ru–Ru bond, which is different from those reported above with $\{RuX_{\mu}Ru\}$ ($X = Cl$, H or (CH_3CO_2)) bridges. In addition, the boron atoms which bond to Ru(2) are different from those of previously reported clusters with both bilge boron atoms bound to the *exo*-polyhedral ruthenium atom [15, 23, 24]. The Ru–Ru bond length (3.0076(7) Å) in **2** is consistent with the Ru–Ru distance in 11-vertex ruthenaborane cluster $[\{(\eta_6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)_2\}RuB_{10}H_8(OEt)_2]$ (average 3.103 Å) [22] and longer than this in $[\{(\eta_6\text{-}C_6Me_6)_2Ru_2H_2(CO)_2\}RuB_{10}H_8(OEt)_2]$ (average 2.802 Å) [25] and $[\{(\eta_6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$ (average 2.809 Å) [26]. The Ru(2)–B(2) and Ru(2)–B(4) distances are 2.227(6) and 2.269(6) Å, respectively, which fall in the normal range.

3.2. *FT-IR, ^{1}H, and ^{13}C NMR spectra study*

Clusters **1** and **2** are also characterized by FT-IR, ^{1}H and ^{13}C NMR spectral analysis. Some important assignments are shown in the experimental section. The IR spectra of the two clusters are similar to each other. The band at 3050 cm^{-1} is due to the ν(Ar–H) vibrations of the phenyl (C_6H_5) or substituted phenyl (C_6H_4) units in clusters **1** and **2**. There are 3–4 peaks from 1634 to 1434 cm^{-1}, which can be assigned to ν(C=C) stretching vibrations. The skeleton vibration of the borane cluster is very complex [27]. Most B–H stretching vibrations range from 2650 to 2450 cm^{-1} and the strong absorption peak around 2515 cm^{-1} of clusters **1** and **2** [28, 29] indicate a boron skeleton. The main feature in the IR spectrum is the absence of a band in the region between 2671 and 3100 cm^{-1}, where the ν(O–H) of carboxylic acid vibration in the free carboxylic acid appears, indicating metal–ligand bond formation through this site. Two strong absorption bands around 1582 and 1384 cm^{-1}, assigned to ν(C=O) and ν(C–O) of iodobenzoates, respectively, are in accord with reported data (1575 and 1380 cm^{-1}) [30]. The ν(C–I) appeared at 1055 and 1056 cm^{-1} as expected [31]. At 1100 cm^{-1}, ν_{P-C}, and at 545–490cm^{-1} of δ_{P-C} indicate that PPh_3 exists in clusters [32].

The ^{1}H NMR spectra show the expected integration and peak multiplicities. In the spectra of free *para*-iodoobenzoic acid, single resonances are observed at 7.69, 7.83 and 11.0 ppm, respectively. The resonances at 11.0 ppm of the proton on hydroxy is absent in the spectra of the clusters indicating replacement of the carboxylic acid proton by ruthenaborane in cluster formation. The chemical shifts of the protons of triphenylphosphine exhibit signals at 7.08–7.35 ppm and the chemical shifts of the protons of iodobenzoate are at 7.53–7.83 ppm as multiplets in clusters **1** and **2** consistent with literature values [8e, 31, 33]. The singlets of B–H fall in the 0.87–1.62 ppm range. The ^{13}C NMR data for the two clusters are also similar to each other. In the ^{13}C NMR spectra of **1**, four resonances were assigned as follows: at 103.89 and 102.35 ppm for the carbon atoms attach to iodine, at 126.00–134.15 ppm for the phenyl carbon atoms, 138.89 and 138.04 ppm for the aryl carbon atoms meta- to carboxy, and at 175.16 and 167.74 ppm for the carbonyl carbon atoms [34, 35].

4. Conclusion

Two *iso-closo exo*-cyclic 11-vertex ruthenaborane clusters $[(PPh_3)(p\text{-}IPhCO_2)_2RuB_{10}H_8]$ (**1**) and $[(PPh_3)_2ClRu(PPh_3)(p\text{-}IPhCO_2)RuB_{10}H_9] \cdot CH_2Cl_2$ (**2**) are reported herein. Both clusters are based on an 11-vertex *closo*-type $\{RuB_{10}\}$ cluster-geometry with the metal atom occupying the six-connected apical position. The former has two *exo*-cyclized *para*-iodobenzoates that act as terminal bidentate ligands attached by $\{COO\}_\mu$ bridges to the cluster center engendering a symmetrical conformation. For **2**, there is one *exo*-cyclized *para*-iodobenzoate ligand as in cluster **1** forming a five-membered ring on one side. There also exists another ruthenium atom bounding to the cluster center via one Ru–Ru linkage and two Ru–B bonds, forming a *closo* distorted *exo*-polyhedral Ru(1)–Ru(2)–B(2)–B(4) tetrahedron on the other side. Two ruthenium atoms are attached with a Ru–Ru bond, different than previously reported clusters with $\{RuX_\mu Ru\}$ (X=Cl, H or (CH_3CO_2)) bridges.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 269164 and 273098. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: C44-1223-336-033; E-mail: deposite@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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