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Synthesis, crystal structure and electrochemical properties of three *isocloso* eleven-vertex ferrocenecarboxylate ruthenaborane clusters

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The reaction of $[RuCl_2(PPh_3)_3]$ with *closo*-$[B_{10}H_{10}]^{2-}$ and $C_5H_5FeC_5H_4COOH$ ($FcCO_2H$) in refluxing CH_2Cl_2 solution affords three ruthenaborane clusters: $[PPh_3(H_2O)(FcCO_2)RuB_{10}H_8Cl]$ (1), $[(PPh_3)_2ClRu(PPh_3)(FcCO_2)RuB_{10}H_9]\cdot 0.5CH_2Cl_2$ ($2\times 0.5CH_2Cl_2$) and $[PPh_3(FcCO_2)_2RuB_{10}H_8]$ (3). All of these compounds are characterized by FT-IR, NMR spectroscopic techniques, elemental analysis and single-crystal X-ray analysis. They are all based on a *closo*-type 1:2:4:2:2 {RuB_{10}} stack with the metal occupying the unique six-connected apical position and can be considered as having *isocloso* structures derived from the complete capping of the open face of an *arachano* geometry to give a completely closed deltahedral cluster. Compounds 1 and 2 both have an *exo*-polyhedral ferrocenecarboxylate that is attached with one {Ru–O} and one {B–O} bond each, resulting in one *exo*-cyclic five-membered Ru–O–C–O–B ring. There is in addition one *exo*-polyhedral ruthenium atom bonded to the center {RuB_{10}} cluster via one {Ru–Ru} linkage and two {$RuH_\mu B$} bridges, which forms a closed *exo*-polyhedral tetrahedron configuration in compound 2. Compound 3 has two *exo*-polyhedral ferrocenecarboxylates to form two five-membered Ru–O–C–O–B rings engendering a symmetrical conformation. All of these new 11-vertex ruthenaboranes can be considered as having *isocloso* structures derived from the complete capping of the open face of an *arachano* geometry to give a completely closed deltahedral cluster. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: ruthenaborane cluster; ferrocenecarboxylate; synthesis; crystal structure; electrochemical property

INTRODUCTION

Since the synthesis of ferrocene in 1951,[1,2] incorporating bulky ferrocene with a unique structure into other molecular architectures has attracted considerable attention. Thus, many ferrocene derivatives have been synthesized and characterized. These compounds have played an important role in many areas of synthesis chemistry, catalytic chemistry, material chemistry, electrochemistry, bioorganometallic chemistry and coordination chemistry.[3–23] Among a great varieties of ferrocene derivatives, ferrocenecarboxylic acid and its sodium salt were early incorporated into coordinated complexes and attracted much interest in coordination chemistry.[24] However, the reported ferrocenecarboxylate complexes structurally characterized by X-ray diffraction analysis have so far been limited to a few examples, such as $[La_2(\mu_2\text{-}FcCO_2)_4(H_2O)_4]\cdot 2FcCO_2H$,[25] $[(Hdmpz)\{HB(dmpz)_3\}VO(\mu\text{-}FcCO_2)]$ (Hdmpz = 3, 5-dimethylpyrazole),[26] $[Cu(FcCO_2)_2(dmim)_2]$ $[Cu(FcCO_2)_2(mim)_2]\cdot H_2O$ (dmim = 1, 2-dimethylimidazole, mim = *N*-dimethylimidazole),[27] $[Cu_2(dpt)_2(\mu\text{-}FcCO_2)](ClO_4)_2$ (dpt = dipropylenetriamine),[28] $[Na_2Mo_6Cl_8(FcCO_2)_6\cdot CH_3OH]$,[29] $[Cu(FcCO_2)_2(py)_2]$ (py = pyridine),[30] $[Cu_2(\mu\text{-}FcCO_2)_2(bpy)_2](ClO_4)_2$

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$\cdot 3/2CH_3OH \cdot H_2O$,[31] [Cu(petdien)($\eta^2$-$FcCO_2$)][$BPh_4$], [Cu(pmdien)($H_2O$)($\eta^2$-$FcCO_2$)]($ClO_4$)] (petdien = *N*,*N*,*N*′,*N*″,*N*″-pentaethyldienthylenetramine, pmdien = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldienthylenetramine),[32] [$HOs_3(CO)_{10}(FcCO_2)$],[33] [$Mo_2(FcCO_2)_2(O_2CCH_3)_2(C_5H_5N)_2$], [$Mo_2(FcCO_2)_4$(*ax*-$CH_3CN)_2$(*ax*-DMSO)$_2$](DMSO)$_2$,[34] [{Cu(dmen)}$_2$($\mu$-OMe){$\mu$-$FcCO_2$}] ($ClO_4$)$_2$ (dmen = *N*,*N*-dimethylethylenediamine) and [{Cu(tmen)}$_2$(μ-OH){μ-$FcCO_2$}](ClO_4)$_2$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[35] Studies revealed that ferrocenecarboxylate anions can act as terminal monodentate(I), bidentate ligand(II) or *O*,*O*′-bridging ligand (III) (Scheme 1).

On the other hand, boron cluster chemistry has made much progress and developed into fruitful area such as boranes, carboranes, heteroboranes of main group, metallaboranes, metallacarboranes and metallaheteroboranes. It has provided many potentially useful applications, including boron neutron capture treatment (BNCT) of tumors, solvent extraction, material science, catalysts and host–guest chemistry.[36–44] Up to the present, there has been little structurally reported on substituted ferrocenyl-borane or ferrocenyl-carborane derivatives, such as arachno-9-dppf-6-SB_9H_{11} (dppf = 1, 1′-bis(diphenylphosphino)ferrocene),[45] [4-{Fc}-2,3,7,8-$(CH_3)_4C_4B_8H_7$],[46] [1-{Fc}-1,2-closo-$C_2B_{10}H_{11}$],[47] [1,1′-{(η^5-C_5H_4)Fe(η^5-C_5H_4)}-{2-Me-1,2-closo-$C_2B_{10}H_{10}$}$_2$], [1-{Fc}-1,2-closo-$C_2B_{10}H_{11}$],[48] and metallacarborane clusters, such as [1-{Fc}-3-(p-cym)-3,1,2-closo-$RuC_2B_9H_{10}$] and [1,1′-{(η^5-C_5H_4)Fe(η^5-C_5H_4)}-{2-Me-3-(p-cym)-3,1,2-closo-$RuC_2B_9H_9$}$_2$] (p-cym = 1-Me-C_6H_4-4-^{i}Pr).[48] To the best of our knowledge, there is no report on metallaborane or metallacarborane clusters containing ferrocenecarboxylate ligand to date. In this study, we first incorporate ferrocenemonocarboxylic acid into borane chemistry and report the synthesis, crystal structures and electrochemical properties of three ruthenaborane clusters containing ferrocenecarboxylate bridging ligand.

RESULT AND DISCUSSION

Synthesis of compounds

Since the first two 11-vertex ruthenaboranes with *exo*-polyhedral metal-to-cluster acetate bridges were prepared by the reaction of [$RuCl_2(PPh_3)_3$] with *closo*-[$B_{10}H_{10}$]$^{2-}$ anion and $MeCO_2H$ in THF solution,[49] a series of such carboxylate- or thiocarboxylate-bridged ruthenaborane compounds, [$(PPh_3)_2(PhCO_2)RuB_{10}H_8Cl] \cdot C_5H_{12}$,[50] [$(PPh_3)$(*p*-$TolCO_2)_2RuB_{10}H_8$],[51] [$(PPh_3)(PhCOS)_2RuB_{10}H_8$][52] and [$(PPh_3)(MeCOS)_2RuB_{10}H_8$],[53] all with one or two Ru–O(or S)–C–O–B five-membered *exo*-cycles, have been isolated from similar reactions with $PhCO_2H$, *p*-$MeC_6H_4CO_2H$, PhCOSH and MeCOSH in CH_2Cl_2 solution. The latter compounds may be obtained according to the idealized equation (1). They only obtained a single compound from the reaction with one carboxylic acid or thiocarboxylic acid. We studied the analogous reaction with $FcCO_2H$ and obtained three compounds. Reaction of [$RuCl_2(PPh_3)_3$], *closo*-[$B_{10}H_{10}$]$^{2-}$ with $FcCO_2H$ in refluxing dichloromethane solution for 5 days, followed by chromatographic separation, yields three new ruthenaborane compounds, [$PPh_3(H_2O)(FcCO_2)RuB_{10}H_8Cl$] (**1**), [$(PPh_3)_2ClRu(PPh_3)(FcCO_2)RuB_{10}H_9$] (**2**) and [$PPh_3(FcCO_2)_2RuB_{10}H_8$] (**3**). Although the reaction mechanism is complex, it may be represented stoicheiometrically by equation (2).

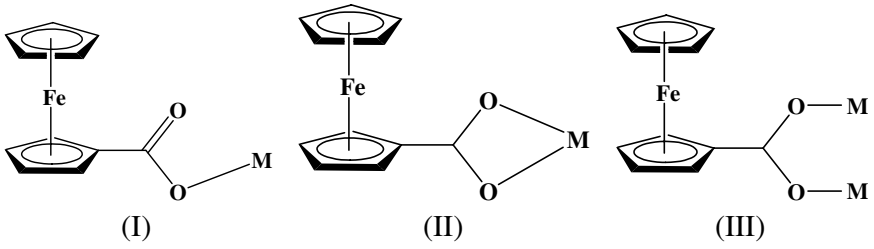
$$[RuCl_2(PPh_3)_3] + closo\text{-}[B_{10}H_{10}]^{2-} + 2RCO_2H/RCOS\,H \longrightarrow [(PPh_3)(RCO_2)_2RuB_{10}H_8]/[(PPh_3)(RCOS)_2RuB_{10}H_8] + 2Cl^- + 2PPh_3 + 2\,H_2 \quad (1)$$

$$4\,[RuCl_2(PPh_3)_3] + 3closo\text{-}[B_{10}H_{10}]^{2-} + 4FcCO_2H + H_2O \longrightarrow [(PPh_3)(H_2O)(FcCO_2)RuB_{10}H_8Cl](\mathbf{1}) + [(PPh_3)_2ClRu(PPh_3)(FcCO_2)RuB_{10}H_9](\mathbf{2}) + [(PPh_3)(FcCO_2)_2RuB_{10}H_8](\mathbf{3}) + 6\,Cl^- + 7\,PPh_3 + 9/2\,H_2 \quad (2)$$

Compound **1** is somewhat air-sensitive, but **2** and **3** are air-stable. They all dissolve in dichloromethane, trichloromethane, acetonitrile and ethanol, and slightly dissolve in pentane and hexane. Compound **2** was isolated as a solvate containing $0.5CH_2Cl_2$.

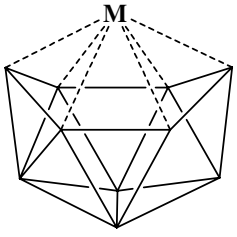
Structures of compounds 1, 2 and 3

The first closed-type ruthenborane cluster [$(PPh_3)_2RuB_{10}H_8(OEt)_2$] was structurally reported by Grook, etc.;[54] there are two views of possible electron structures for this C_{2V} {RuB_{10}} cage. If the ruthenium atom retained a d^6 core, and contributed three orbitals and two electrons to the cluster bonding, so that the closed structure would be deficient by two electrons for a formal *closo* electron count,



Scheme 1.

it would be regarded as 'electron hyper-deficient'.[55,56] This situation is based on the assumption that the metal center is electronically saturated. An alternative view would be that the ruthenium metal vertex supplies contributes four orbitals and four electrons to the cluster, resulting in a 16-electron d^4 ruthenium center with a quasi-octahedral or related disposition of six bonding orbitals. In terms of this latter interpretation the ruthenaundecaboranes reported here would be 11-vertex analogs (IV) of the previously reported 11-vertex *isocloso* metallaboranes $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$[54,57] and $[(PMe_2Ph)_2$-μ-H-$RhB_{10}H_8(OEt)_2]$.[58] Those are formally derived geometrically by the capping of an open *arachno*-type cluster geometry to produce a closed deltahedron. This contrasts with conventional *closo* structures which are formally derived by the capping of an open *nido*-type geometry with a three-orbital contributor. In the *isocloso* structures, the capping atom would contribute four orbitals to the cluster bonding scheme and, conversely, the *arachno*-type borane fragment would have one more orbital available than the nido-type fragment in the metal/borane frontier region (Scheme 2).[58]



(IV)

Scheme 2.

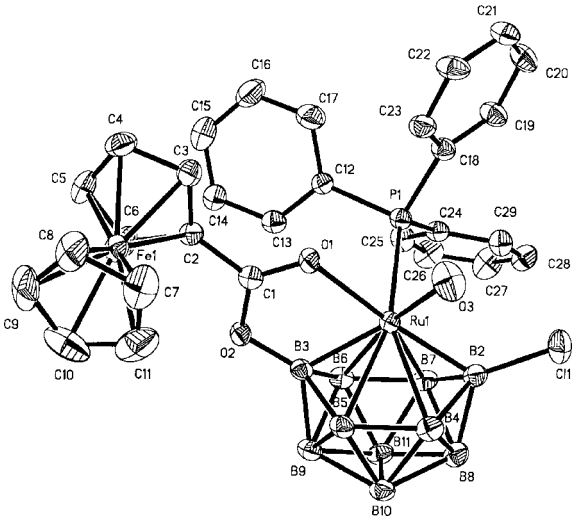


Figure 1. Molecular structure of compound **1**; hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

*$[PPh_3(H_2O)(FcCO_2)RuB_{10}H_8Cl]$ (**1**)*

The molecular structure of compound **1** is shown in Fig. 1. Selected bond lengths and angles of compound **1** are listed in Table 1. The core cluster of **1** is seen to have an 11-vertex *isocloso* $\{RuB_{10}\}$ geometry which engenders the characteristic 11-vertex *isocloso* $\{MB_{10}\}$ metallaborane 1:2:4:2:2 stack. The boron atoms which bond to metal center have a boat-hexaphto conformation. The bond length Ru(1)–B(2) [2.045(8) Å] is slightly longer than that of Ru(1)–B(3) [2.030(7) Å], which shows that *exo*-polyhedral cyclization can strengthen the metal-to-boron bonding.[60,61] The average distance of Ru(1)–B(4), Ru(1)–B(5), Ru(1)–B(6) and Ru(1)–B(7) bonds is 2.331 Å, which is also consistent with that of the reported {Ru–B} bond in $[(PPh_3)_2(PhCO_2)RuB_{10}H_8Cl] \cdot C_5H_{12}$ (average 2.360 Å)[50] and $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$ (average 2.373 Å).[57]

The ruthenium center has three exo-polyhedral ligands: one ferrocenecarboxylate, one triphenylphosphine and one water molecule. In the ferrocenecarboxylate ligand, both cyclopentadienyl rings are planar within experimental error, all deviations from the calculated least-squares plane being less than 0.0135 Å. The distances (1.6442 and 1.650 Å, respectively) from iron atom to planes 1 [C(2)–C(3)–C(4)–C(5)–C(6)] and 2 [C(7)–C(8)–C(9)–C(10)–C(11)] are consistent with the normal range. The conformation of the rings is nearly eclipsed with staggering by 6.3°, as shown in Fig. 1. The dihedral angle between the planes 1 and 2 is 2.1°. The substituted ring does not exhibit significant distortion at C(2) atom, to which the carboxyl is attached. The C(2)–Fe(1) bond length [2.014(6) Å] is slightly shorter than the average distance (2.030 Å) of the other C–Fe bonds. It will be noted that the carbon atom bond to the ferrocenyl moiety is coplanar with the C_5H_4 ring. This would permit a π orbital of suitable symmetry on {C=O} to engage in a π interaction with the cyclopentadienyl system. Moreover, the C(1)–C(2) distance [1.451(9) Å] is slightly shorter than single bond (*ca* 1.500 Å).[51] The distances of C(1)–O(1) and C(1)–O(2) are 1.233(7) and 1.313(7) Å. The ferrocenecarboxylate ligand acts as two donor oxygen atoms and one Ru(1)–O(1)–C(1)–O(2)–B(3) five-member ring is formed between ferrocenecarboxylate and the *closo*-$\{RuB_{10}\}$ group. The bond lengths of Ru(1)–O(1) and B(3)–O(2) are 2.220(4) and 1.441(8) Å, respectively, which is comparable to these in analogous compound $[(PPh_3)_2(PhCO_2)RuB_{10}H_8Cl] \cdot C_5H_{12}$ [2.239(7) and 1.43(1) Å].[50]

It is noted that there is one water molecule which coordinates to the Ru atom in compound **1**. This presumably occurs on work-up in air, which shows that H_2O can partake in the reaction. There is a precedent for similar water molecule in other metallaborane compound, such as $[(H_2O)(PPh_3)PdTeB_{10}H_9(PPh_3)][BF_4]$.[62] The examples which take up water molecule when worked up in air to form a B–OH or B–O group include: $[(\eta^5\text{-}C_5Me_5)_3Ir_3B_{18}H_{15}(OH)]$,[63] [7-($\eta^5$-$C_5Me_5$)-8-Cl-11-($PMe_2Ph$)-*nido*-7,12-$RhOB_{10}H_9$],[64] [$\mu$-9,9′-O-{5-($\eta^5$-$C_5Me_5$)-*nido*-5-$RhOB_9H_{12}$}$_2$],[65] [7-($\eta^5$-$C_5Me_5$)-10-($NEt_3$)-*nido*-7,12-$RhOB_{10}H_{10}$],[66] $[(\eta^5\text{-}C_5Me_5)_2Rh_2S_2B_{15}H_{14}(OH)]$ and $[PPh_4][OB_{18}$

Table 1. Selected bond lengths (Å) and angles (deg) of compound **1**

Ru(1)–B(2)	2.045(8)	Fe(1)–C(4)	2.054(7)
Ru(1)–B(3)	2.030(7)	Fe(1)–C(5)	2.047(7)
Ru(1)–B(4)	2.318(8)	Fe(1)–C(6)	2.022(6)
Ru(1)–B(5)	2.371(7)	Fe(1)–C(7)	2.031(8)
Ru(1)–B(6)	2.344(7)	Fe(1)–C(8)	2.038(7)
Ru(1)–B(7)	2.292(7)	Fe(1)–C(9)	2.035(8)
Ru(1)–O(1)	2.220(4)	Fe(1)–C(10)	2.001(8)
Ru(1)–O(3)	2.194(5)	Fe(1)–C(11)	2.018(8)
Ru(1)–P(1)	2.4790(18)	C(2)–C(3)	1.422 (8)
B(4)–B(5)	1.710(11)	C(3)–C(4)	1.398 (9)
B(6)–B(7)	1.741(11)	C(4)–C(5)	1.375 (10)
B(2)–Cl(1)	1.788(8)	C(5)–C(6)	1.401 (9)
B(3)–O(2)	1.442(8)	C(2)–C(6)	1.419 (9)
C(1)–O(1)	1.233(7)	C(7)–C(8)	1.348 (11)
C(1)–O(2)	1.313(7)	C(8)–C(9)	1.385 (12)
C(1)–C(2)	1.451(9)	C(9)–C(10)	1.393 (13)
Fe(1)–C(2)	2.014(6)	C(10)–C(11)	1.399 (13)
Fe(1)–C(3)	2.029(7)	C(7)–C(11)	1.365 (13)
O(1)–Ru(1)–P(1)	81.42(11)	B(4)–Ru(1)–B(6)	87.5(3)
O(1)–Ru(1)–O(3)	78.5(2)	B(5)–Ru(1)–B(6)	71.9(3)
O(3)–Ru(1)–P(1)	93.81(18)	B(4)–Ru(1)–B(7)	71.7(3)
B(2)–Ru(1)–P(1)	105.7(2)	B(5)–Ru(1)–B(7)	88.1(3)
B(3)–Ru(1)–P(1)	114.5(2)	B(6)–Ru(1)–B(7)	44.1(3)
B(2)–Ru(1)–O(3)	85.0(3)	Cl(1)–B(2)–Ru(1)	125.8(4)
B(2)–Ru(1)–B(3)	117.6(3)	C(1)–O(1)–Ru(1)	115.7(4)
B(2)–Ru(1)–B(4)	47.5(3)	O(1)–C(1)–O(2)	120.1(6)
B(3)–Ru(1)–B(5)	46.2(3)	C(1)–O(2)–B(3)	112.2(5)
B(4)–Ru(1)–B(5)	42.7(3)	O(2)–B(3)–Ru(1)	118.2(4)
B(2)–Ru(1)–B(7)	46.4(3)	C(3)–C(2)–C(6)	107.6(6)
B(3)–Ru(1)–B(6)	45.5(3)		

H_{21}].[67] The Ru(1)–O(3) distance [2.194(5) Å] is slightly longer than that in Ru complexes $[(bpy)_2(OH_2)RuORu(OH_2)(bpy)_2](ClO_4)_4 \cdot 2H_2O$ (average 2.137 Å),[68] $[(bpy)_2(H_2O)RuORu(OH)(bpy)_2](ClO_4)_4$ [2.148 (11) Å][69] and in $[Ru_3O(O_2CCH_3)_6(OH_2)_3](ClO_4) \cdot 2H_2O$ (average 2.106 Å).[70] The distance from Ru(1) to P(1) is 2.4790(18)Å, which falls into the normal range.

In compound **1**, the hydrogen atom which bound to B(2) atom is substituted by one chlorine atom. This situation is also found in an analogous compound $[(PPh_3)_2(C_6H_5CO_2)RuB_{10}H_8Cl]$.[50] The bond length of B(2)–Cl(1) [1.788(8) Å] is essentially the same as that of reported B–Cl bond length in $[(PPh_3)_2(C_6H_5CO_2)RuB_{10}H_8Cl]$ [1.78 (1) Å].[50]

*$[(PPh_3)_2ClRu(PPh_3)(FcCO_2)RuB_{10}H_9]\cdot 0.5CH_2Cl_2$ (**2**×$0.5CH_2Cl_2$)*

The molecular structure of compound **2** is shown in Fig. 2. Selected bond lengths and angles of compound **2** are listed in Table 2. As shown in Fig. 2, the core cluster unit of compound **2** also has a characteristic 11-vertex $\{RuB_{10}\}$ metallaborane *isocloso* geometry. The Ru(1) ion is η^6-bound to hexacyclic boron ring, which has a boat conformation like cyclohexane, and σ-bound to an oxygen atom from ferrocenecarboxylate ligand, a phosphorus atom of triphenylphosphine and another ruthenium atom. The Ru(1)–B(2) and Ru(1)–B(3) bond lengths are 2.033(7) and 2.043(6) 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 2.310 Å. The ferrocenecarboxylate ligand is two donor atoms to form Ru(1)–O(1)–C(1)–O(2)–B(3) five-membered ring with *closo*-$\{RuB_{10}\}$ group. The distances of Ru(1)–O(1) and B(3)–O(2) are 2.207(4) and 1.423(8) Å, respectively. The bond length of Ru(1)–P(1) is 2.4559(16) Å. All of these are consistent with the corresponding distances found in **1**.

It is very interesting that there is an *exo*-polyhedral ruthenium atom, numbered Ru(2), encompassed in an $\{RuCl(PPh_3)_2\}$ unit bonded to the center $\{RuB_{10}\}$ cluster via one {Ru–Ru} linkage and two $\{RuH_\mu B\}$ bridges (V), which forms a *closo* distorted *exo*-polyhedral Ru(1)–Ru(2)–B(2)–B(4) tetrahedron configuration. The Ru(2) atom is also coordinated with one chlorine atom and two PPh_3 ligands besides B(2), B(4) and Ru(1) atoms. Two ruthenium atoms are attached with an Ru–Ru bond. There is no case previously reported in such ruthenaborane clusters. This type of {Ru–Ru} linkage is different from the compounds $[(PPh_3)_2ClRuClRu(PPh_3)_3B_{10}H_8(OEt)_2]$,[71] $[(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_8\{OCH(CH_3)_2\}_2]$[72] and $[(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_7\{OCH(CH_3)_2\}_3] \cdot 0.4H_2O$,[73] which have one $\{RuCl_2(PPh_3)_2\}$ unit bound to a central 11-vertex *isocloso* $\{RuB_{10}\}$ cluster through one $\{RuCl_\mu Ru\}$ linkage and two $\{RuH_\mu B\}$ bridges and the compound $[\{(PPh_3)_2Cl_2Ru\}_2(PPh_3)RuB_9H_9]$,[74] which has two $\{RuCl_2(PPh_3)_2\}$ units bound to a 10-vertex *isocloso* $\{RuB_9\}$ cluster via an $\{RuCl_\mu Ru\}$ bridge and two $\{RuH_\mu B\}$ bridges. This bonding mode is also different from the metal-to-cluster bonding system in $[\{(PPh_3)_2Ru\}$-μ,μ,μ-$(MeCO_2)_3$-μ,μ-H_2-$\{RuB_{10}H_7\}]$ that

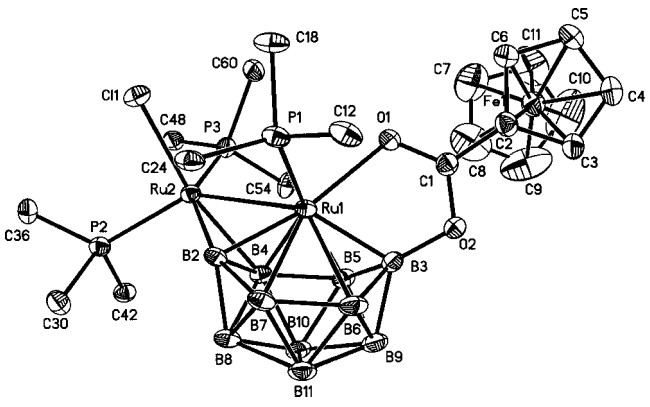


Figure 2. Molecular structure of compound **2**; hydrogen atoms, phenyl group atoms other than the ipso carbon ones and the solvated CH_2Cl_2 molecule have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Table 2. Selected bond lengths (Å) and angles (deg) of compound **2**

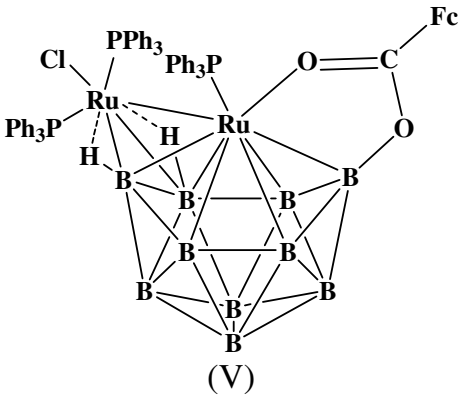
Ru(1)–B(2)	2.033(7)	Fe(1)–C(7)	2.031(10)
Ru(1)–B(3)	2.043(6)	Fe(1)–C(8)	2.000(12)
Ru(1)–B(4)	2.240(6)	Fe(1)–C(9)	2.001(11)
Ru(1)–B(5)	2.360(7)	Fe(1)–C(10)	2.013(11)
Ru(1)–B(6)	2.358(7)	Fe(1)–C(11)	2.011(10)
Ru(1)–B(7)	2.282(6)	Ru(2)–B(2)	2.227(6)
Ru(1)–O(1)	2.207(4)	Ru(2)–B(4)	2.269(6)
Ru(1)–P(1)	2.4559(16)	Ru(2)–P(2)	2.3853(16)
B(4)–B(5)	1.713(9)	Ru(2)–P(3)	2.3259(16)
B(6)–B(7)	1.751(11)	C(1)–O(2)	1.306(7)
Ru(1)–Ru(2)	3.0076(7)	C(2)–C(3)	1.430(9)
B(3)–O(2)	1.423(8)	C(3)–C(4)	1.417(10)
C(1)–O(1)	1.246(7)	C(4)–C(5)	1.380(10)
C(1)–O(2)	1.306(7)	C(5)–C(6)	1.414(10)
C(1)–C(2)	1.447(8)	C(2)–C(6)	1.414(9)
Fe(1)–C(2)	2.008(6)	C(7)–C(8)	1.357(15)
Fe(1)–C(3)	2.020(7)	C(8)–C(9)	1.325(17)
Fe(1)–C(4)	2.028(8)	C(9)–C(10)	1.44(2)
Fe(1)–C(5)	2.042(8)	C(10)–C(11)	1.361(18)
Fe(1)–C(6)	2.029(7)	C(7)–C(11)	1.398(15)
O(1)–Ru(1)–P(1)	86.31(11)	O(2)–B(3)–Ru(1)	118.4(4)
O(1)–Ru(1)–Ru(2)	116.08(11)	B(2)–Ru(1)–Ru(2)	47.76(18)
Ru(2)–Ru(1)–P(1)	103.61(4)	B(4)–Ru(1)–Ru(2)	48.58(16)
B(2)–Ru(1)–P(1)	95.79 (19)	P(2)–Ru(2)–P(3)	100.46(6)
B(3)–Ru(1)–P(1)	125.5(2)	P(2)–Ru(2)–Cl(1)	98.02(6)
B(4)–Ru(1)–P(1)	141.84(17)	P(3)–Ru(2)–Cl(1)	88.55(6)
B(2)–Ru(1)–B(3)	118.7(3)	P(2)–Ru(2)–B(2)	100.86(17)
B(2)–Ru(1)–B(7)	47.1(3)	B(4)–Ru(2)–Cl(1)	152.14(17)
B(7)–Ru(1)–B(6)	44.3(3)	B(4)–Ru(2)–P(3)	105.84(17)
B(3)–Ru(1)–B(6)	45.9(3)	Ru(1)–Ru(2)–Cl(1)	105.24(4)
B(5)–Ru(1)–B(3)	46.1(2)	Ru(1)–Ru(2)–P(3)	109.43(4)
B(5)–Ru(1)–B(4)	43.6(2)	B(2)–Ru(2)–B(4)	44.7(2)
B(2)–Ru(1)–B(4)	46.8(2)	B(2)–Ru(2)–Ru(1)	42.53(17)
B(4)–Ru(1)–B(7)	72.0(2)	B(4)–Ru(2)–Ru(1)	47.75(16)
B(6)–Ru(1)–B(5)	71.5(3)	Ru(2)–B(2)–B(4)	69.0(3)
B(4)–Ru(1)–B(6)	87.6(2)	Ru(2)–B(2)–Ru(1)	89.7(2)
B(5)–Ru(1)–B(7)	88.6(3)	Ru(2)–B(4)–B(2)	66.3(3)
B(3)–Ru(1)–O(1)	71.7(2)	Ru(2)–B(4)–Ru(1)	83.7(2)
C(1)–O(1)–Ru(1)	115.8(4)	B(2)–B(4)–Ru(1)	60.2(3)
O(1)–C(1)–O(2)	120.2(5)	B(4)–B(2)–Ru(1)	73.0(3)
C(1)–O(2)–B(3)	112.7(5)		

is based on a central 11-vertex *isocloso* $\{RuB_{10}\}$ cluster via two $\{RuH_{\mu}Ru\}$ and two $\{Ru(CH_3CO_2)_{\mu}Ru\}$ bridges respectively (Scheme 3).[49]

The Ru–Ru bond length [3.0076(7) Å] in compound **2** is comparable to that of the reported Ru–Ru bond in metallaborane compound $[\{(\eta_6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)_2\}RuB_{10}H_8(OEt)_2]$ (average 3.103 Å)[75] and longer than that in compounds $[\{(\eta_6\text{-}C_6Me_6)_2Ru_2H_2(CO)_2\}RuB_{10}H_8(OEt)_2]$ (average 2.802 Å)[76] and $[\{(\eta_6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$ (average 2.809 Å).[77,78] The distances of Ru(2)–B(2) and Ru(2)–B(4) are 2.227(6) and 2.269(6) Å respectively, which are slightly shorter than those in analogous compound $[(PPh_3)_2ClRuClRu(PPh_3)_3B_{10}H_8(OEt)_2]$ [2.325(1) and 2.460(12)Å respectively].[71]

*[PPh$_3$(FcCO$_2$)$_2$RuB$_{10}$H$_8$] (**3**)*

The molecular structure of compound **3** is shown in Fig. 3. The selected bond lengths and bond angles for compound **3** are listed in Table 3. The core cluster unit of compound **3** is



(V)

Scheme 3.

also the same as **1** and **2** that both have an 11-vertex *iso*closo $\{RuB_{10}\}$ geometry with the characteristic 11-vertex *isocloso* $\{MB_{10}\}$ metallaborane 1 : 2 : 4 : 2 : 2 stack. The Ru center also has three donor atoms of *exo*-polyhedral ligands, one P atom of PPh_3 ligand and two O atoms from two ferrocenecarboxylate ligands. The average distances of Ru(1)–B(2), Ru(1)–B(3) and Ru(1)–B(4), Ru(1)–B(5), Ru(1)–B(6), Ru(1)–B(7) are 2.017 and 2.329 Å respectively, which are consistent with the corresponding values in compounds **1** and **2**.

The *exo*-polyhedral ruthenium-bound ligand phosphorus atom is almost in the reflection plane which bisects the two B(5)–B(6) and B(4)–B(7) vectors. The two ferrocenecarboxylate groups 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 bound to B(2) and B(3), respectively. This results in two nearly symmetric *exo*-polyhedral five-membered Ru–O–C–O–B rings, which is different from the analogous compounds **1** and **2** that both have one identical ring only. The bond lengths of Ru(1)–P(1) and the average

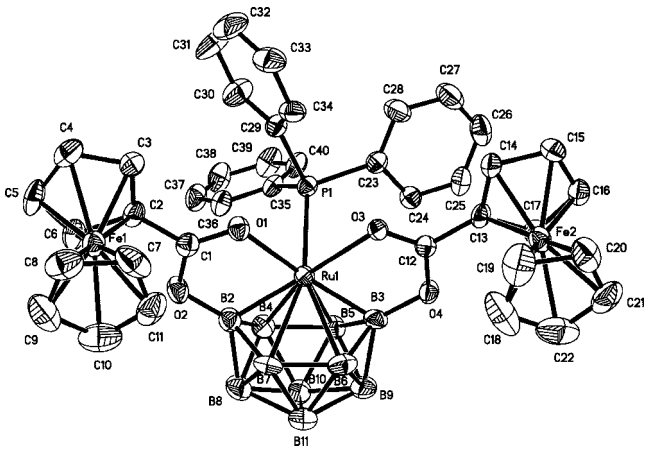


Figure 3. Molecular structure of compound **3;** hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Table 3. Selected bond lengths (Å) and angles (deg) of compound **3**

Ru(1)–B(2)	2.029(8)	Fe(1)–C(3)	2.040(6)
Ru(1)–B(3)	2.005(8)	Fe(1)–C(4)	2.049(7)
Ru(1)–B(4)	2.298(7)	Fe(1)–C(5)	2.048(7)
Ru(1)–B(5)	2.290(7)	Fe(1)–C(6)	2.046(6)
Ru(1)–B(6)	2.349(8)	Fe(1)–C(7)	2.024(7)
Ru(1)–B(7)	2.378(7)	Fe(1)–C(8)	2.045(7)
Ru(1)–O(1)	2.237(4)	Fe(1)–C(9)	2.014(8)
Ru(1)–O(3)	2.254(4)	Fe(1)–C(10)	1.998(9)
Ru(1)–P(1)	2.4826(17)	Fe(1)–C(11)	2.014(8)
B(4)–B(5)	1.748(11)	Fe(2)–C(13)	2.016(6)
B(6)–B(7)	1.707(12)	Fe(1)–C(14)	2.013(7)
B(2)–O(2)	1.446(8)	Fe(2)–C(15)	2.065(7)
B(3)–O(4)	1.427(8)	Fe(1)–C(16)	2.049(6)
C(1)–O(1)	1.239(7)	Fe(1)–C(17)	2.042(6)
C(1)–O(2)	1.331(7)	Fe(2)–C(18)	2.026(9)
C(1)–C(2)	1.462(8)	Fe(1)–C(19)	2.026(7)
C(12)–O(3)	1.240(6)	Fe(2)–C(20)	2.052(7)
C(12)–O(4)	1.322(7)	Fe(2)–C(21)	2.041(8)
C(12)–C(13)	1.448(8)	Fe(2)–C(22)	2.030(10)
Fe(1)–C(2)	2.031(6)		
O(3)–Ru(1)–P(1)	80.05(10)	B(5)–Ru(1)–B(7)	88.2(3)
O(1)–Ru(1)–O(3)	89.72(14)	B(5)–Ru(1)–B(6)	72.1(3)
O(1)–Ru(1)–P(1)	84.29(11)	B(6)–Ru(1)–B(7)	42.3(3)
B(2)–Ru(1)–P(1)	115.0(2)	B(3)–Ru(1)–O(3)	72.1(2)
B(3)–Ru(1)–P(1)	108.9(2)	B(2)–Ru(1)–O(1)	72.9(2)
B(2)–Ru(1)–B(3)	117.4(3)	C(1)–O(1)–Ru(1)	113.3(4)
B(2)–Ru(1)–B(4)	45.9(3)	O(1)–C(1)–O(2)	121.3(6)
B(2)–Ru(1)–B(7)	46.0(3)	C(1)–O(2)–B(2)	112.0(5)
B(3)–Ru(1)–B(5)	46.6(3)	O(2)–B(2)–Ru(1)	116.4(5)
B(3)–Ru(1)–B(6)	46.9(3)	O(4)–B(3)–Ru(1)	118.3(5)
B(4)–Ru(1)–B(5)	44.8(3)	C(12)–O(3)–Ru(1)	112.7(3)
B(4)–Ru(1)–B(6)	88.1(3)	O(3)–C(12)–O(4)	121.1(5)
B(4)–Ru(1)–B(7)	72.2(3)	C(12)–O(4)–B(3)	112.2(5)

Ru–O, O–B of the compound **3** are similar to those observed in reported 11-vertex *closo*-ruthenaundecaborane compounds in the literature.[49–53,79]

IR spectra

The compounds **1–3** are also characterized by FT-IR spectrum analysis. The IR spectroscopies of these three compounds are similar to each other. The skeleton vibration of borane and halogeno-borane is very complex.[80] Most of the B–H stretching vibrations range from 2650 to 2450 cm^{-1} and the strong absorption peaks at 2516, 2518 and 2517 cm^{-1}, respectively, of compounds **1–3** are within this range.[81,82] The absorption peak at 3049 cm^{-1} can be assigned to the v_{C-H} stretching vibration of benzene rings. There are three or four peaks from 1632 to 1430 cm^{-1}, which can be assigned to $v_{C=C}$ stretching vibration. The absorption peaks at 2953 and 2925 cm^{-1} can be assigned to the v_{C-H} stretching vibration of cyclopentadienyl rings. Two strong absorption bands around 1570 and 1383 cm^{-1} which are assigned to v(C=O) and v(C–O) of ferrocene carboxylates, respectively, correspond to reported data (1575 and 1380 cm^{-1}).[83] At 1100 cm^{-1}, presenting the peak of ν_{P-C}, and at 545–490 cm^{-1} of ν_{P-C} absorption, these peaks indicate that PPh_3 exist in compounds.[84] Both $B_{10}Cl_{10}^{2-}$ and $B_{12}Cl_{12}^{2-}$ have absorptions of ν_{B-Cl} in the range 1150–1100 cm^{-1}.[85] There is a moderate absorption at 1095 cm^{-1} of compound **1**, so we infer there is a Cl atom bonded to B atom in compound **1**. In addition, a strong absorption at 3441 cm^{-1} of compound **1** is attributable to v(H–O) of water.

Electrochemical study

The electrochemical data for compounds **1, 2** and **3** are summarized in Table 5. The cyclic voltammograms (CVs) of compounds **1, 2** and **3** in CH_2Cl_2 containing 0.10 M *n*-Bu_4NClO_4 are shown in Figs 4–6, respectively. It can be seen from Fig. 4 that compound **1** exhibited three quasi-reversible waves at 0.83 V [$\Delta E_p(1) = 0.20$ V, $i_{pa}/i_{pc} \approx 1$], −1.09 V [$\Delta E_p(2) = 0.15$ V, $i_{pa}/i_{pc} \approx 1$] and −1.49 V [$\Delta E_p(3) = 0.14$ V, $i_{pa}/i_{pc} \approx 1$] in the scan range of −1.8 to 1.3 V, showing that, at the electrode surface, the neutral bimetallic compound underwent three successive one-electron oxidations to yield the mono-, di- and trication, respectively. Similarly, the compound **3** also exhibited three quasi-reversible waves at 0.88 V [$\Delta E_p(1) = 0.18$ V, $i_{pa}/i_{pc} \approx 1$], −1.13 V [$\Delta E_p(2) = 0.14$ V, $i_{pa}/i_{pc} \approx 1$] and −1.52 V [$\Delta E_p(3) = 0.15$ V, $i_{pa}/i_{pc} \approx 1$] in the same scan range as shown in Fig. 5. In addition, both compounds **1** and **3** have an irreversible oxidation wave at −1.60 and −1.64 V, respectively. Differently, compound **2** only exhibited two quasi-reversible waves at 0.86 V [$\Delta E_p(1) = 0.16$ V, $i_{pa}/i_{pc} \approx 1$] and −1.16 V [$\Delta E_p(2) = 0.10$ V, $i_{pa}/i_{pc} \approx 1$] and one irreversible wave at −1.40 V, which can be seen from Fig. 6. The cyclic voltammogram of reactant [$RuCl_2(PPh_3)_3$] showed only one couple of quasi-reversible redox peak at −1.30 V. (The formal potential of ferrocene–ferrocenium redox couple was located at 0.49 V under the experimental conditions of Yuan *et al*.[86])

In compound **1**, the quasi-reversible waves at −1.49 and −1.09 V in the cyclic voltammogram are tentatively ascribed to the ruthenium center ($Ru^{II/III}$ and $Ru^{III/IV}$, respectively). The wave at 0.83 V is attributed to the oxidation of the ferrocenyl ligand ($Fe^{II/III}$). Compound **3** also shows three quasi-reversible waves. Compound **2** shows one quasi-reversible wave at −1.16 V of the ruthenium center ($Ru^{III/IV}$) and one quasi-reversible wave at 0.88 V of the ferrocenyl ligand ($Fe^{II/III}$), while the irreversible wave at −1.40 V is also assigned to the redox of the ruthenium center ($Ru^{II/III}$). The CV data show that the redox potentials of these compound s are influenced by ligand substitution at the Ru and Fe centers.

Results from the CV experiment suggest the assignment of the waves that are present in negative potential to the

Table 4. Crystal data and structure refinement details for compounds **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{29}H_{34}B_{10}ClFeO_3PRu$	$C_{65.50}H_{64}B_{10}O_2Cl_2P_3FeRu_2$	$C_{40}H_{41}B_{10}Fe_2O_4PRu$
Formula weight	762.00	1413.070	937.57
Wavelength (Å)	0.710 73	0.710 73	0.710 73
Crystal size (mm^3)	0.45 × 0.28 × 0.16	0.45 × 0.36 × 0.29	0.39 × 0.31 × 0.27
Temperature (K)	298(2)	298(2)	298(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2(1)/n	P2(1)/c	P2(1)/c
a (Å)	12.487(5)	22.196(3)	17.166(6)
b (Å)	23.780(11)	15.3753(19)	14.823(5)
c (Å)	12.759(6)	19.412(2)	19.409(7)
α (deg)	90	90	90
β (deg)	114.226(6)	99.314(2)	100.094(6)
γ (deg)	90	90	90
Vol ($Å^3$)	3455(3)	6537.4(14)	4862(3)
Z	4	4	4
Dc (mg m^{-3})	1.465	1.436	1.281
Absorption coefficient (mm^{-1})	1.011	0.874	0.963
Limiting indices	$-14 \le h \le 8$, $-28 \le k \le 24$, $-15 \le l \le 14$	$-24 \le h \le 26$, $-18 \le k \le 18$, $-23 \le l \le 12$	$-19 \le h \le 20$, $-17 \le k \le 15$, $-22 \le l \le 23$
Completeness to theta	99.9%	99.9%	98.5%
Maximum and minimum transmission	0.8549 and 0.6589	0.7857 and 0.6945	0.7809 and 0.7050
Goodness-of-fit on F^2	1.022	1.057	1.008
Data/restraints/parameters	6098/3/421	11533/41/790	8433/0/523
F (000)	1536	2864	1896
Theta range (deg)	1.95–25.03	0.93–25.03	1.83–25.00
Reflection collected	17 870	26 859	24 366
Independent reflections	6098	11 533	8433
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0553$, $wR_2 = 0.1312$	$R_1 = 0.0575$, $wR_2 = 0.1580$	$R_1 = 0.0650$, $wR_2 = 0.1434$
R indices (all data)	$R_1 = 0.1009$, $wR_2 = 0.1642$	$R_1 = 0.0741$, $wR_2 = 0.1699$	$R_1 = 0.1172$, $wR_2 = 0.1693$
Largest difference peak and hole (e $Å^{-3}$)	1.206, −0.789	2.032, −0.495	0.979, −0.664

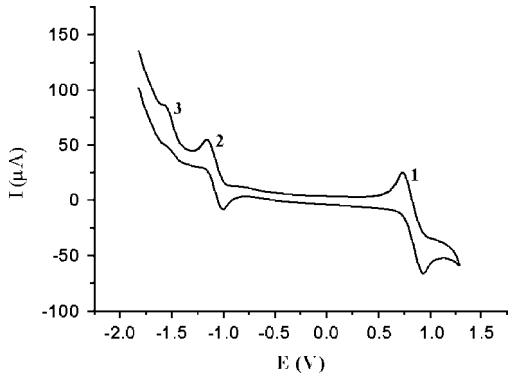


Figure 4. CV of compound **1** in CH_2Cl_2, scan from −1.8 to 1.3 V (scan rate 100 mV/s).

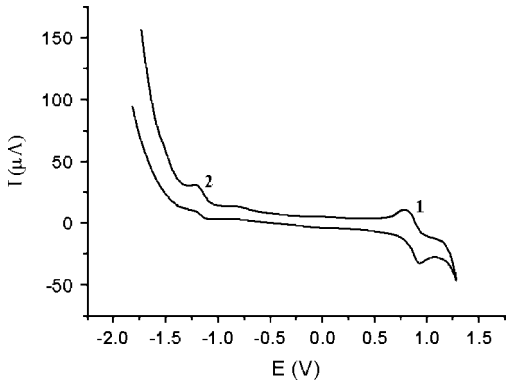


Figure 5. CV of compound **2** in CH_2Cl_2, scan from −1.8 to 1.3 V (scan rate 100 mV/s).

oxidation of the Ru center and the waves around 0.85 V to the oxidation of the Fc center. This results disagree with those of some heterobimetallic ferrocenyl complexes.[87–91] The more negative shift of the formal potential of the ruthenium center may be attributed to a better electron-donating ability of PPh_3 units. The positive shift of the formal potential of the

Table 5. CV data (V) for compounds **1**, **2** and **3**[a]

Cluster	$E_{1/2}$[b] (1)	$E_{pa}(1)$	$E_{pc}(1)$	$E_{1/2}(2)$	$E_{pa}(2)$	$E_{pc}(2)$	$E_{1/2}(3)$	$E_{pa}(3)$	$E_{pc}(3)$	$E_{pa}(4)$
1	0.83	0.93	0.73	−1.09	−1.01	−1.16	−1.49	−1.42	−1.56	−1.6
2	0.86	0.93	0.79	−1.16	−1.12	−1.22	—	−1.40	—	—
3	0.88	0.97	0.79	−1.13	−1.06	−1.20	−1.52	−1.44	−1.59	−1.64

[a] Electrolyte 0.1 M n-Bu_4NClO_4 in CH_2Cl_2; scan rate 100 mV/s.
[b] $E_{1/2}(n) = (1/2)[E_{pa}(n) + E_{pc}(n)]$.

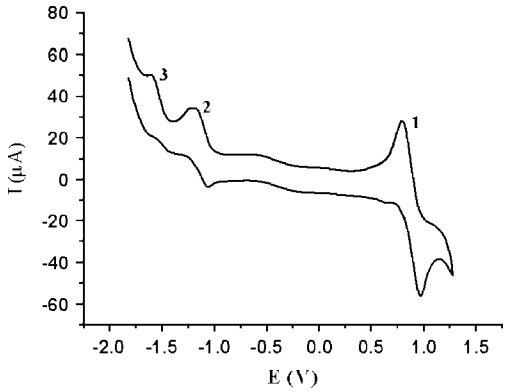


Figure 6. CV of compound **3** in CH_2Cl_2, scan from −1.8 to 1.3 V (scan rate 100 mV/s).

ferrocene center may be attributed to the electrophilic effect of the carbonyl group.

CONCLUSION

Three *isocloso* 11-vertex ferrocene carboxylate ruthenaborane clusters $[(PPh_3)(H_2O)FcCO_2RuB_{10}H_8Cl]$ (**1**), $[(PPh_3)_2ClRu(PPh_3)FcCO_2RuB_{10}H_9] \cdot 0.5CH_2Cl_2$ (**2** × $0.5CH_2Cl_2$) and $[PPh_3(FcCO_2)_2RuB_{10}H_8]$ (**3**) were prepared and characterized by FT-IR spectra, NMR spectroscopic techniques, elemental analysis and single crystal X-ray diffraction. In compounds **1**–**3**, the ferrocenyl unit which acts as terminal bidentate ligand was attached by $\{COO\}_\mu$ bridge to the cluster center. An interesting uptake of one water molecule to generate the Ru–water group is noted in compound **1**. This instance is rare in ruthenaborane compounds. Interestingly, two ruthenium atoms are attached with {Ru–Ru} bond in compound **2**, which is different from the previously reported analogous compounds via $\{RuH_\mu Ru\}$ or $\{RuCl_\mu Ru\}$ bridge.

EXPERIMENTAL

General procedures

The starting compounds $[RuCl_2(PPh_3)_3]$[92] and $(Et_3NH)_2[B_{10}H_{10}]$[93] were prepared by previously published methods. 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 AR grade and used without further purification. The reaction was carried out under an atmosphere of dry nitrogen 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 × 1 mm, made in the laboratory as required. FT-IR spectra were recorded in the range 400–4000 cm^{-1} with a Nicolet-460 FT-IR spectrophotometer, and samples were prepared as KBr pellets. NMR spectra were measured on a Varian Mercury 400 (400 MHz) nuclear magnetism resonance system.

Cyclic voltammetric measurements were performed on a Potentiostatl/Gawanostat (EG&G) 273A with 270 electrochemical analysis software. A conventional electrochemical cell was used with a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, and Ag–AgCl (saturated KCl) as the reference electrode. All measurements were carried out under nitrogen in anhydrous deoxygenated dichloromethane. The cyclic voltammograms were recorded with a scan rate 100 mV/s in CH_2Cl_2 containing 0.10 M n-Bu_4NClO_4 as the supporting electrolyte. All peak potentials were measured against Ag–AgCl. The ferrocene–ferrocenium redox couple was located at 0.53 V under our experimental conditions.

Synthesis of compounds

$[RuCl_2(PPh_3)_3]$ (384 mg, 0.4 mmol), $(Et_3NH)_2[B_{10}H_{10}]$ (129 mg, 0.4 mmol) and $FcCO_2H$ (184 mg, 0.8 mmol) were stirred together in refluxing CH_2Cl_2 (80 ml) solution under nitrogen atmosphere for 120 h. The resulting brown-red solution was reduced (rotary evaporator, 30 °C, water pump) to ca 8 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 gave compounds **1** (orange-red, $R_f = 0.30$, 18.2 mg, 3.3%), **2** (brown-red, $R_f = 0.78$, 33 mg, 6.0%) and **3** (orange-red, Rf = 0.83, 133 mg, 23.7%). The single crystals of the compounds were recrystallized from dichloromethane–n-pentane solution. Compound **1**: anal. calcd for $C_{29}H_{34}B_{10}O_3ClPFeRu$: C, 45.71; H, 4.50; found: C, 46.13; H, 4.37. Selected FT-IR (KBr, cm^{-1}): 3441 (vs), 3054 (m), 2974 (m), 2516 (vs), 1631 (m), 1573 (vs), 1466 (m), 1435 (m), 1383 (m), 1331 (w), 1174 (m), 1114 (m), 748 (m), 696 (s), 522 (s); ^1H NMR ($CDCl_3$): δ 0.88 (2H, BH), δ 1.25 (4H, BH), δ 1.55 (2H,

BH), δ 1.65 (2H, H_2O), δ 4.26 (5H, C_5H_5), δ 4.35 (2H, C_5H_4), δ 4.44 (2H, C_5H_4), δ 7.32-7.36 (15H, Ph); ^{13}C NMR ($CDCl_3$): 70.43 (s, 5C, C_5H_5), 73.11 (s, 1C, C_5H_4 C_{ipso}), 74.0 (C_5H_4C, CH), 171.3 (1C, C═O), 128.62–133.47 (18C, Ph). Compound **2** × 0.5CH_2Cl_2: anal. calcd for $C_{65.50}H_{64}B_{10}O_2Cl_2P_3FeRu_2$: C, 55.67; H, 4.56; found: C, 56.0; H, 4.40; Selected FT-IR (KBr, cm^{-1}): 3049 (s), 2518 (s), 1632 (m), 1564 (vs), 1481 (m), 1434 (s), 1383 (m), 1327 (w), 1115 (m), 1093 (m), 844 (m), 742 (s), 695 (s), 520 (s), 490 (m); ^1H NMR ($CDCl_3$): δ 0.89 (2H, BH), δ 0.94 (1H, BH), δ 0.98 (1H, BH), δ 1.25 (3H, BH), δ 1.59 (2H, BH), δ 4.23 (5H, C_5H_5), δ 4.30 (2H, C_5H_4), δ 4.50 (2H, C_5H_4), δ 5.30 (1H, CH_2Cl_2), δ 6.77–7.79 (45H, Ph); ^{13}C NMR ($CDCl_3$): 70.04 (s, 5C, C_5H_5), 70.57 (s, 1C, C_5H_4 C_{ipso}), 70.27 (C_5H_4C, CH), 70.34 (C_5H_4C, CH), 174.7 (1C, C═O), 127.78–134.49 (36C, Ph). Compound **3**: anal. calcd for $C_{40}H_{41}B_{10}PO_4Fe_2Ru$: C, 51.24; H, 4.41; found: C, 51.02; H, 4.37. Selected FT-IR (KBr, cm^{-1}): 2953 (m), 2924 (m), 2517 (s), 1631 (m), 1569 (s), 1535 (s), 1461 (s), 1434 (s), 1382 (s), 1326 (m), 1170 (s), 1117 (m), 1054 (m), 997 (m), 826 (m), 740 (s), 693 (s) 521 (s), 494 (m); ^1H NMR ($CDCl_3$): δ 0.88 (2H, BH), δ 1.28 (4H, BH), δ 1.56 (2H, BH), δ 4.03 (5H, C_5H_5), δ 4.11 (5H, C_5H_5), δ 4.23 (4H, C_5H_4), δ 4.52 (4H, C_5H_4), δ 7.12–7.46 (15H, Ph); ^{13}C NMR($CDCl_3$): 67.84 (10C, C_5H_5), 73.18 (2C, C_5H_4 C_{ipso}), 73.01 (4C, C_5H_4C, CH), 72.06 (4C, C_5H_4C, CH), 175.1 (2C, C═O), 128.44–134.46 (18C, Ph).

Crystallography

Crystallographic data for the complexes **1–3** were collected on a Bruker Smart 1000 CCD diffractometer using Mo–Kα radiation ($\lambda = 0.71073$ Å) with $\omega/2\theta$ scan mode at 298(2) K. All 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 package.[93] Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Center as Supplementary Publication Numbers CCDC-265294 (**1**), CCDC-265295 (**2**) and CCDC-269161 (**3**). Details of the crystal parameters, data collection and refinement are summarized in Table 5. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336033; email: deposit@ccdc.cam.ac.uk).

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REFERENCES

1. Kealy TJ, Pauson PL. *Nature* 1951; **168**: 1039.
2. Miller SA, Tebboth JA, Tremaine JF. *J. Chem. Soc.* 1952; 632.
3. Togni A. *Angew. Chem. Int. Edn Engl.* 1996; **35**: 1475.
4. Murray JH, Harding MM. *J. Med. Chem.* 1994; **37**: 1936.
5. Garcia MM, Perez GE, Ochoa FL, Cruz-Almanza R. *Tetrahedron* 1997; **53**: 12 369.
6. Bucci E, De Napoli L, Du Fabio G, Messere A, Montesarchio D, Romanelli A, Piccialli G, Varra M. *Tetrahedron* 1999; **55**: 14 435.
7. Togni A, Hayashi T. *Ferrocenes, Homogenous Catalysis, Organic Synthesis, Materials Science*. VCH: Weinheim, 1995.
8. Sawamura M, Ito Y. *Chem. Rev.* 1992; **92**: 857.
9. Hudson SA, Maitlis PM. *Chem. Rev.* 1993; **93**: 861.
10. Miller JS, Epstein AJ, Reiff WM. *Acc. Chem. Res.* 1988; **21**: 114.
11. Miller JS, Epstein AJ. *Angew. Chem. Int. Edn Engl.* 1994; **33**: 385.
12. Long NG. *Angew. Chem. Int. Edn Engl.* 1995; **34**: 21.
13. Kaifer AE. *Acc. Chem. Res.* 1999; **32**: 62.
14. Saweczko P, Kraatz HB. *Coord. Chem. Rev.* 1999; **190**(192): 185.
15. Horie M, Suzaki Y, Osakada K. *J. Am. Chem. Soc.* 2004; **126**: 3684.
16. Sun WY, Kusukawa T, Fujita M. *J. Am. Chem. Soc.,* 2002; **124**: 11 570.
17. Matsue T, Evans DH, Osa T, Kobayashi N. *J. Am. Chem. Soc.* 1985; **107**: 3411.
18. Steudel R, Hassenberg K, Pickardt J. *Organometallics* 2002; **21**: 2604.
19. Liu J, Tian S, Tiefenauer L, Nielsen PE, Knoll W. *Anal. Chem.* 2005; **77**: 2756.
20. Kraatz HB, Leek DM, Houmam A, Enright GD, Lusztyk J, Wayner DDM. *J. Organomet. Chem.* 1999; **589**: 38.
21. Dave RVS, Nils MN. *Chem. Rev.* 2004; **104**: 5931.
22. Kopf-Maier P, Kopf H. *Chem. Rev.* 1987; **87**: 1137.
23. Nguyen P, Gomez-Elipe P, Manners I. *Chem. Rev.* 1999; **99**: 1515.
24. Slocum DW, Ernst CR. *Adv. Organomet. Chem.* 1972; **10**: 106.
25. Li G, Hou HW, Li LK, Wang YF, Meng XR, Zhu Y, Fan YT. *Acta Chim. Sin.* 2004; **62**: 1060.
26. Collison D, Mabbs FE, Turner SS, Powell AK, Mclnnes EJL, Yellowlees LJ. *J. Chem. Soc., Dalton Trans.* 1997; 1201.
27. Abuhijleh AL, Woods C. *J. Chem. Soc., Dalton Trans.* 1992; 1249.
28. Concepcion L, Ramon C, Francesc I, Elies M, Enric E. *Inorg. Chem.* 2000; **39**: 4560.
29. Nicholas P, Duward FS. *Inorg. Chem.* 1997; **36**: 5609.
30. Abuhijleh AL, Pollitte J, Woods C. *Inorg. Chim. Acta.* 1994; **215**: 131.
31. Costa R, Lopez C, Molins E, Epsinosa E. *Inorg. Chem.* 1998; **37**: 5686.
32. Costa R, Lopez C, Molins E, Epsinosa E, Perez J. *J. Chem. Soc., Dalton Trans.* 2001; 2833.
33. Lee SM, Cheung KK, Wong WT. *J. Organomet. Chem.* 1996; **506**: 77.
34. Cotton FA, Falvello LR, Reid AH, Tocher JH. *J. Organomet. Chem.* 1987; **319**: 87.
35. Lopez C, Costa R, Illas F, Graaf C, Turnbull MM, Landee CP, Espinosa E, Mata I, Molins E. *J. Chem. Soc., Dalton Trans.* 2005; 2322.
36. Hawthorne MF. *Angew. Chem. Int. Edn Engl.* 1993; **32**: 950.
37. Plesek J. *Chem. Rev.* 1992; **92**: 269.
38. Grimes RN. *J. Chem. Educ.* 2004; **81**: 658.
39. Hawthorne MF, Yang XG, Zheng ZP. *Pure Appl. Chem.* 1994; **66**: 245.
40. Hawthorne MF, Zheng ZP. *Acc. Chem. Res.* 1997; **30**: 267.
41. Hardie MJ, Raston CL. *Angew. Chem. Int. Engl.* 2000; **39**: 3835.
42. Hardie MJ, Raston CL. *Chem. Commun.* 2001; 905.
43. Malic N, Nichols PJ, Raston CL. *Chem. Commun.* 2002; 16.
44. Shea SL, Bould J, Londesborough MGS, Perera SD, Franken A, Ormsby DL, Jelinek T, Stibr B, Holub JC, Thornton-Pett M, Kennedy JD. *Pure Appl. Chem.* 2003; **75**: 1239.
45. Donaghy KJ, Carroll PJ, Sneddon LG. *Inorg. Chem.* 1997; **36**: 547.
46. Grimes RN, Maxwell WM, Maynard RB, Sinn E. *Inorg. Chem.* 1980; **19**: 2981.
47. Zakharkin LI, Kalinin VN, Snyakin AP. *Zh. Obshch. Khim.* 1970; **40**: 2246.

48. Carsten LB, Georgina MR, Andrew SW. *J. Organomet. Chem.* 1998; **556**: 55.
49. Fontaine XLR, Greenwood NN, Kennedy JD, Thornton-Pett M, Zheng PJ. *J. Chem. Soc., Chem. Commun.* 1987; 1717.
50. Yao HJ, Fu J, Jin RS, Wei JD, Chen J, Zheng PJ. *Chin. J. Struc. Chem.* 1995; **14**: 364.
51. Nie Y, Hu CH, Wu QJ, Lu SF, Jin RS, Zheng PJ. *Acta. Crystallogr.* 2000; **C56**: 536.
52. Yao HJ, Hu CH, Dou JM, Wei JD, Jin RS, Li W, Zheng PJ. *Polyhedron* 1998; **17**: 1877.
53. Nie Y, Hu CH, Sun J, Jin RS, Zheng PJ. *Acta. Crystallogr.* 1999; **C55**: 1224.
54. Crook JE, Elrington M, Greenwood NN, Kennedy JD, Woollins JD. *Polyhedron* 1984; **3**: 901.
55. Baker RT. *Inorg. Chem.* 1986; **25**: 109.
56. Johnston RL, Mingos DMP. *Inorg. Chem.* 1986; **25**: 3321.
57. Crook JE, Elrington M, Greenwood NN, Kennedy JD, Thornton-Pett M, Woollins JD. *J. Chem. Soc., Dalton Trans.* 1985; 2407.
58. Fowkes H, Greenwood NN, Kennedy JD, Thornton-Pett M. *J. Chem. Soc., Dalton Trans.* 1986; 517.
59. Kennedy JD, Stibr B, Jelinek T, Fontaine XLR, Thornton-Pett M. *Collect. Czech. Chem. Commun.* 1993; **58**: 2090.
60. Dou JM, Hu CH, Li W, Yao HJ, Jin RS, Zheng PJ. *Polyhedron* 1997; **16**: 2323.
61. Dou JM, Hu CH, Sun J, Wei JD, Zheng PJ. *Polyhedron* 1997; **16**: 3873.
62. Sheehan JP, Spalding TR, Ferguson G, Gallagher JF, Kaitner B, Kennedy JD. *J. Chem. Soc., Dalton Trans.* 1993; 35.
63. Shea SL, Jelinek T, Stibr B, Thornton-Pett M, Kennedy JD. *Inorg. Chem. Commun.* 2000; **3**: 169.
64. Fontaine XLR, Fowkes H, Greenwood NN, Kennedy JD, Thornton-Pett M. *J. Chem. Soc., Chem. Commun.* 1985; 1722.
65. Ditzel EJ, Fontaine XLR, Fowkes H, Greenwood NN, Kennedy JD, Mackinnon P, Zhu SS, Thornton-Pett M. *J. Chem. Soc., Chem. Commun.* 1990; 1692.
66. Kaur P, Kennedy JD, Thornton-Pett M, Jelinek T, Stibr B. *J. Chem. Soc., Dalton Trans.* 1996; 1775.
67. Jelinek T, Kennedy JD, Stibr B, Thornton-Pett M. *J. Chem. Soc., Chem. Commun.* 1995; 1665.
68. Gilbert JA, Eggleston DS, Murphy WR, Geselowitz DA, Gersten SW, Hodgson DJ, Meyer TJ. *J. Am. Chem. Soc.* 1985; **107**: 3855.
69. Schoonover JR, Ni JF, Roecker L, White PS, Meyer TJ. *Inorg. Chem.* 1996; **35**: 5885.
70. Powell G, Richens DT, Bino A. *Inorg. Chim. Acta.* 1995; **232**: 167.
71. Elrington M, Kennedy JD, Greenwood NN, Thornton-Pett M. *J. Chem. Soc., Chem. Commun.* 1984; 1398.
72. Yao HJ, Li W, Hu CH, Dou JM, Jin RS, Huang ZE, Zheng PJ. *Chin. J. Struct. Chem.* 1998; **17**: 13.
73. Li X, Yao HJ, Hu CH, Dou JM, Sun J, Jin RS, Zheng PJ. *Chin. J. Struct. Chem.* 1999; **18**: 378.
74. Kim YH, Barton L, Rath NP, Kennedy JD. *Inorg. Chem. Commun.* 2005; **8**: 147.
75. Bown M, Waters JM. *J. Am. Chem. Soc.* 1990; **112**: 2442.
76. Bown M, Waters JM, Fontaine XLR, Kennedy JD. *J. Organomet. Chem.* 1990; **390**: 379.
77. Bown M, Fontaine XLR, Greenwood NN, Mackinnon P, Kennedy JD, Thornton-Pett M. *J. Chem. Soc., Dalton Trans.* 1987; 2781.
78. Bown M, Fontaine XLR, Greenwood NN, Mackinnon P, Kennedy JD, Thornton-Pett M. *J. Chem. Soc., Chem. Commun.* 1987; 442.
79. Bown M, Fontaine XLR, Greenwood NN, Kennedy JD, Thornton-Pett M. *J. Chem. Soc., Dalton Trans.* 1990; 3039.
80. Leites LA. *Chem. Rev.* 1992; **92**: 279.
81. Kazuo N. *Infrared and Raman spectra of Inorganic and Coordination Compounds* (Translated by Huang DR and Wang RQ). Beijing: Chemical Industry Press: 1986; 175.
82. Crook JE, Greenwood NN, Kennedy JD, McDonald WS. *J. Chem. Soc., Dalton Trans.* 1984; 2487.
83. Abuhijjleh AL, Pollitte J, Woods C. *Inorg. Chim. Acta* 1994; **215**: 131.
84. Deacon GB, Green JHS. *Spectrochim. Acta* 1968; **A24**: 845.
85. Yuan P, Liu SH, Xiong W, Yin J, Yu G, Sung HY, Williams ID, Jia G. *Organometallics* 2005; **24**: 1452.
86. Li ZH, Beatty AM, Fehlner TP. *Inorg. Chem.* 2003; **42**: 5707.
87. Li ZH, Fehlner TP. *Inorg. Chem.* 2003; **42**: 5715.
88. Zhu Y, Clot O, Wolf MO, Yap GPA. *J. Am. Chem. Soc.* 1998; **120**: 1812.
89. Biani FF, Graiff C, Opromolla G, Predieri G, Tiripicchio A, Zanello P. *J. Organomet. Chem.* 2001; **637**(639): 586.
90. Hallman PS, Stephenson TA, Wilkinson G. *Inorg. Synth.* 1970; **9**: 16.
91. Zhang GM, Zhu H. *Acta. Chim. Sin.* 1978; **36**(4): 315.
92. Sheldrick GM. SHELXTL 5.10 for Windows NT: Structure Determination Software Programs. Bruker Analytical X-ray Systems Inc.: Madison, USA, 1997.