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Communication

Bimetallic Ru−Pd and Trimetallic Ru−Pd−Cu Assemblies on the Carborane Cluster Surface

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ABSTRACT: The synthesis of well-defined heterometallic complexes remains a frontier challenge in inorganic chemistry. We report an approach that relies on the sequential insertion of electrophilic metal fragments into electron-rich Ru−B bonds of the η^2-BB-carboryne complex (POBBOP)Ru(CO)$_2$ [POBBOP = 1,7-OP(^{i}Pr)$_2$-*m*-2,6-dehydrocarborane]. Utilizing this synthetic strategy, bimetallic (POBBOP)(Ru)(CO)$_2$[Pd(P^{t}Bu$_3$)] and trimetallic (POBBOP)(Ru)(CO)$_2$[Pd(P^{t}Bu$_3$)](CuBr) complexes were selectively prepared. Structural and theoretical analysis of the features of chemical bonding within Ru−B−B−Cu and Ru−B−B−Pd fragments is presented.

Multimetallic transition metal complexes attract significant interest in coordination chemistry, catalysis, spectroscopy, and materials science.[1−3] The synthesis of heterometallic complexes remains challenging because of often nonselective coordination of the metal centers to multiple donor sites. Several approaches to tackling this problem have been discovered, many of which rely on the design of multitopic ligand systems or the generation of electrophile−nucleophile metal pairs.[4−9]

Main group elements have recently emerged as a new type of ligand platform.[10,11] Transition-metal complexes with boron-based scaffolds have attracted considerable attention in part because of their role as reagents or intermediates in hydroboration and borylation reactions.[12] Anionic boryl fragments have been incorporated as donor sites in multidentate ligands, including tridentate pincer-type systems.[13−19] Because of the low electronegativity of boron, boryls are very strong σ donors and display a strong *trans* influence, and in some cases, they can also possess an accessible empty orbital.[20] In addition to the unusual coordination chemistry, cooperative reactivity across the metal−boron bonds has been reported.[21−25]

Being chemically robust and sterically encumbered, polyhedral clusters containing boron represent, among other prominent applications, an attractive ligand platform.[26−37] Neutral carboranes, $C_2B_{10}H_{12}$, contain rather inert B−H bonds that can be activated by late transition metals, providing rare examples of unsupported metal−boron bonds.[38−41] A more general route for the selective formation of carborane-based boryl complexes utilizes donor-containing directing groups, thus giving rise to bidentate and tridentate ligand systems amenable to cyclometalation.[42−45] The polyhedral structure of carboranes affords the possibility of metalation at more than one vertex, either by a single metal center (giving rise to η^2-coordinated carboryne complexes)[46−50] or by two or more metal centers (producing multimetallic complexes).[51,52] Furthermore, a single metal center can migrate on the surface of the cluster from one vertex to another, exhibiting "cage-walking".[53−57]

Recently, we reported the first example of a BB-carboryne complex, (POBBOP)Ru(CO)$_2$ (**1**), where the ruthenium center is coordinated to two adjacent boron atoms of the *m*-carborane-backbone pincer ligand [POBBOP = 1,7-OP(^{i}Pr)$_2$-*m*-2,6-dehydrocarborane].[50] The electron-rich, strained (BB)>Ru metallacycle exhibited cooperative reactivity with organic electrophiles. In addition, Lewis acidic coinage metal cations were able to insert into one of the Ru−B bonds of the parent carboryne, forming unusual Ru−B−B−M metallacycles (M = Cu/Ag/Au; Scheme 1).[58] In this work, we present an expansion of this synthetic strategy to selectively obtain bimetallic (POBBOP)(Ru)(CO)$_2$[Pd(P^{t}Bu$_3$)] (**2**) and trimetallic (POBBOP)(Ru)(CO)$_2$[Pd(P^{t}Bu$_3$)](CuBr) (**3**) complexes supported by the polyhedral carborane cluster (Scheme 1).

Reaction of the (POBBOP)Ru(CO)$_2$ carboryne complex **1** with Pd(P^{t}Bu$_3$)$_2$ led to the formation of a single product and the release of 1 equiv of P^{t}Bu$_3$ according to the ^{31}P NMR spectrum of the reaction mixture. The ^{11}B NMR spectrum of the product contains two signals corresponding to the two metalated boron atoms at −2.8 and 2.1 ppm. The crystal structure determination revealed the identity of bimetallic complex **2** (Figure 1). In the molecular structure of **2**, the Pd(P^{t}Bu$_3$) fragment is inserted into one of the B−Ru bonds of **1**. The palladium center is coordinated to one boron atom, one remaining phosphine, and the ruthenium center. The Pd−B2 bond length is 2.049(3) Å, which is typical for exohedral

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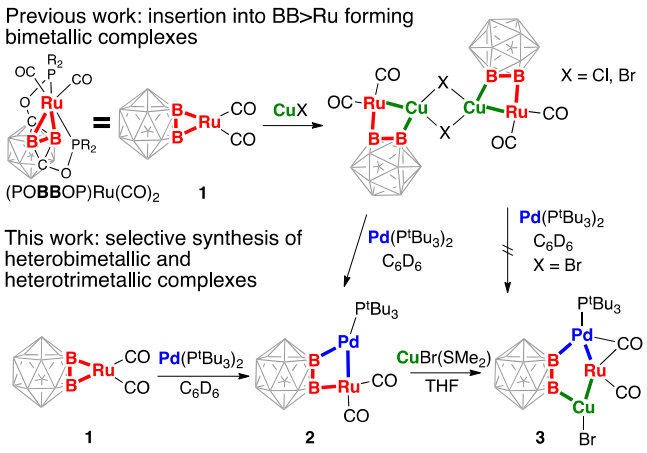
Scheme 1. (Top) Insertion of Coinage Metals into BB>Ru Metallacycle of BB-Carboryne Complex 1, Affording Bimetallic Complexes, and (Bottom) Sequential Insertion of Pd and Cu, Leading to the Selective Formation of Bimetallic (2) and Trimetallic (3) Complexes



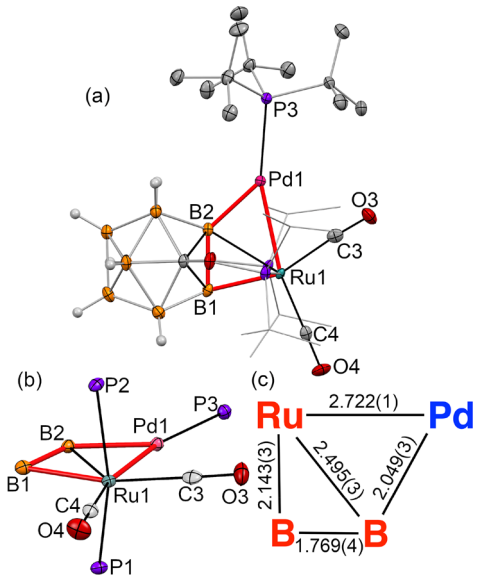


Figure 1. Displacement ellipsoid plots (50% probability) of **2**: (a) View perpendicular to the B1−B2−Pd1−Ru1 plane. (b) Coordination environment of the metal centers. Atoms belonging to the isopropyl groups of the ligand arms and hydrogen atoms of the alkylphosphine ligand are omitted for clarity. Only one of the two crystallographically independent, chemically identical molecules is shown. (c) Selected bond distances (Å).

palladium B-carboranyl complexes. The Pd−Ru distance of 2.722(1) Å is comparable to the Pd−Ru interatomic distances in multimetallic complexes and clusters. The Ru−B1 bond length is 2.143(3) Å, which is typical for exohedral ruthenium B-carboranyl complexes. Interestingly, the Ru···B2 distance is 2.495(3) Å, which is longer than a two-center two-electron (2c-2e) Ru−B bond but close to the range of 3c-2e bridging Ru···H−B interactions found in boron cluster complexes [2.355(3)−2.462(3) Å].[59−63] Furthermore, the Ru−B bond is strained, as evidenced by the dramatically acute B2−B1−Ru angle of 78.6(1)°, while the analogous exohedral B2−B1−H angle in the ligand precursor POBOP-H is 116.1(1)°.[19] This distortion of the metal−boron bond is likely caused by the attractive Ru···Pd and Ru···B2 interactions. The B1−B2 bond length in bimetallic **2** is 1.769(4) Å, which is longer than that in the metallacycle of the parent η^2-carboryne **1** [1.720(4) Å]. The two metal atoms and two boryl centers lie in one plane.

The formation of **2** can be considered to be an electrophilic attack by a 14e neutral $Pd^0(P^tBu_3)$ moiety on the electron-rich and strained Ru−B bond in the carboryne **1**. This PdL fragment has been reported to insert into metal−metal bonds.[64] Importantly, the product **2** still contains one strained electron-rich Ru−B bond. We hypothesized that a stronger Lewis acid, such as a coinage metal d^{10} cation, could interact with the remaining ruthenium boryl moiety. The reaction of **2** with $CuBr(SMe_2)$ in tetrahydrofuran (THF) at room temperature afforded a single product according to the ^{31}P NMR data. The ^{11}B NMR spectrum of the product indicated that signals at −7.5 and −0.7 ppm belong to two metalated boron atoms. The crystal structure determination revealed formation of the new trimetallic complex **3**. As proposed, the copper(I) cation fragment inserted into the Ru−B bond in **2**, forming a copper boryl (Figure 2).

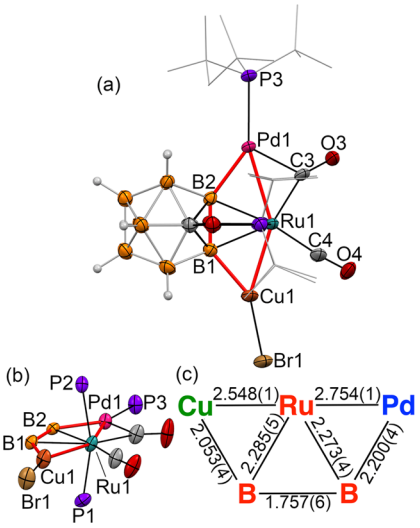


Figure 2. Displacement ellipsoid plots (50% probability) of **3**: (a) View perpendicular to the B1−B2−Pd1−Cu1−Ru1 plane. (b) Coordination environment of the metal centers. Atoms belonging to the isopropyl groups of the ligand arms and the alkylphosphine ligand are omitted for clarity. Only one out of the two crystallographically independent, chemically identical molecules is shown. (c) Selected bond distances (Å).

The ruthenium center in **3** is no longer directly bound to the boron cluster atoms with 2c-2e bonds, as evidenced by the elongated Ru−B1 and Ru−B2 distances of 2.285(5) and 2.273(4) Å, respectively. The palladium atom is still coordinated to one boron atom with an elongated Pd−B2 bond [2.200(4) Å in **3** vs 2.049(3) Å in **2**]. One carbonyl ligand bridges the ruthenium and palladium centers. The Ru−Pd distance is 2.754(1) Å, which is effectively unchanged from that in **2**. The Cu−B1 bond length is 2.053(4) Å, which is close to the 2c-2e bonds in copper boryl complexes [1.980(2)−2.002(3) Å].[65−71] The Ru−Cu distance of 2.548(1) Å is comparable to that in other heterobimetallic complexes. The three metal atoms and two boryl centers lie in one plane. The bromide ligand completes the distorted trigonal-planar environment around the copper center.

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The stretching frequencies of the carbonyl ligands at the ruthenium center provided insight into changes in the electronic structure upon conversion of **1** to **2** and **2** to **3**. The values of the carbonyl stretching frequencies, ν(CO), are 2010 and 1958 cm^{-1} for the starting monometallic complex **1**. The insertion of $Pd^0(P^tBu_3)$ into one Ru−B bond in **1** resulted in a decrease of ν(CO) to 1974 and 1935 cm^{-1} for **2**. The addition of the CuBr moiety to the remaining Ru−B bond further shifted ν(CO) to 1977 and 1830 cm^{-1} for **3**. The larger change in the carbonyl group's IR bands in **3** is caused by switching of the coordination mode of one of the terminal Ru(CO) groups to the bridging Ru(CO)Pd carbonyl.

The solution of the colorless parent carboryne complex **1** in THF contains a band in the UV region (240 nm) of the absorption spectrum. Incorporation of the palladium center leads to the appearance of absorption bands at 322 and 394 nm for **2**. The trimetallic complex **3** features two bands at 296 and 372 nm.

Both **2** and **3** are soluble in common organic solvents (benzene and THF) and sparingly soluble in hexanes. Carbonyl ligands in **1**−**3** do not undergo insertion into metal−boron bonds, in line with previous observations on the relative stabilities of boraacyl and boryl complexes.[72] Complex **2** is thermally stable in a benzene solution at 80 °C, while **3** decomposes forming **2** and other unidentified products upon heating.

Carboryne **1** binds only 1 equiv of $Pd^0(P^tBu_3)$, thus allowing for the stepwise assembly of **3**. We found that the order of metal attachment (first palladium and then copper) is important. If it is reversed, the reaction of **1** and excess CuBr produces a bimetallic ruthenium−copper complex,[58] which reacts at 80 °C with $Pd(P^tBu_3)_2$, extruding the copper center and forming **2** (Scheme 1). Therefore, the observed formation of complexes **2** and **3** in excellent yields is an example of the remarkably selective synthetic route to heterobimetallic and heterotrimetallic complexes.

Given the unusual bimetallic and trimetallic compositions of **2** and **3**, we investigated their features of chemical bonding by employing analysis of the electron density in the framework of the quantum theory of atoms in molecules (QTAIM; AIMAll and Multiwfn codes) as well as analysis of the electron localization function (ELF; TopMode code) for the electron density computed at the PBE0/def-TZVP level with zeroth-order regular approximation correction with the *ORCA* suite.[73−75]

ELF representations are shown in Figure 3. Analysis of **2** shows the presence of a disynaptic valence basin V(Ru,B1), which is similar to that in the starting complex **1**,[50] and a trisynaptic valence basin V(Pd,Ru,B2). The population of this trisynaptic basin is 2.25 electrons, with the contributions of 0.88*e* from Pd, 0.3*e* from Ru, and 1.07*e* from B2. Thus, the bonding environment for the ruthenium center appears as one 2c-2e Ru−B1 bond and one 3c-2e Ru···Pd−B2 bond.

Topological analysis in the QTAIM description revealed that the palladium atom has bond paths to both Ru and B2, whereas there is no direct Ru−B2 bond path. A more nuanced description was obtained using delocalization indices (DIs), which are defined as the number of electron pairs shared between two atoms, thus being an analogue of the bond order. The Ru−B1 bonding with a DI value of 0.73 is similar to that in the starting complex **1**; however, the Ru···Pd−B2 situation is more peculiar. The Ru···Pd interaction is a bond with a nonnegligible DI value of 0.47 and a well-defined bond path.

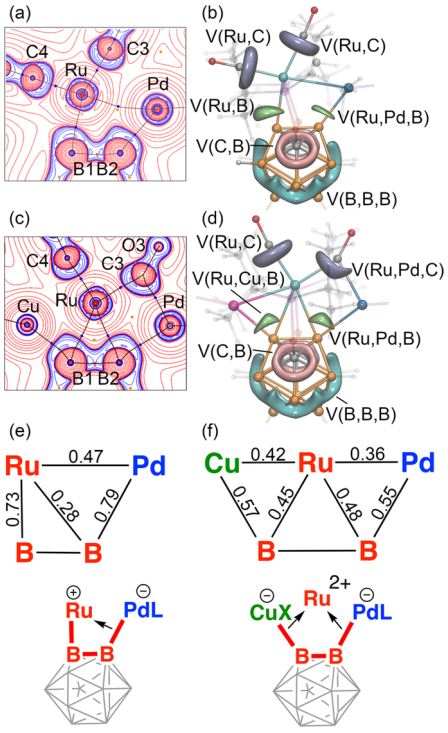

Figure 3. (a and c) Contour maps of the electron density, Laplacian, and molecular graphs (based on the QTAIM bond paths) in the B1−B2−Ru1−Pd plane for **2** and the B1−B2−Ru1−Pd−Cu plane for **3**. Red curves indicate electron density depletion, blue curves indicate electron density concentration, and blue dots are bond critical points. (b and d) ELF isosurfaces for selected valence basins for **2** and **3**. The V(B,B,B) and V(B,C) basins are shown at η = 0.8; the V(Ru,C), V(Ru,B1), V(Ru,Pd,B2), and V(Ru,Cu,B2) basins are shown at η = 0.72. Other basins are omitted for clarity. (e and f) Selected DIs and bonding descriptions for **2** and **3**.

The palladium center is also bonded to B2 with a DI value of 0.79. Although the Ru−B2 bond path is not present, there is a residual Ru···B2 bonding interaction with a DI value of 0.28. This description is in agreement with the ELF representation of 3c-2e Ru···Pd−B2 bonding dominated by the Pd−B2 interaction. A similar description is often used for isolobal bridging M···H−B interactions in boranes. For example, we reported bonding analysis of a ruthenium B-carboranyl complex, with the 3c-2e Ru···H−B bond exhibiting a DI value of 0.23 for the analogous Ru···B2 interaction.[55]

For complex **3**, both QTAIM and ELF analysis showed predominantly 3c-2e bonding character for M−Ru−B fragments. ELF analysis demonstrated the presence of trisynaptic basins V(Ru,Cu,B1) and V(Ru,Pd,B2). Additionally, there is a trisynaptic V(Ru,Pd,C) basin for the carbonyl ligand bridging two metals. The topological analysis shows that there are metal−ligand Ru−B1, Ru−B2, Pd−B2, and Cu−B1 bond paths. The DI values for the Ru−B1 and Ru−B2 bonds are 0.45 and 0.48, respectively, which are only slightly smaller than the DI values for the Cu−B1 (0.57) and Pd−B2 (0.55) bonds and close to the DI values for the Ru−Pd (0.36) and Ru−Cu (0.42) bonds. These results suggest that there is an extensive delocalization of metal−boron and metal−metal bonding in **3**, with two sets of 3c-2e Ru−Cu−B1 and Ru−Pd−B2 bonds (Figure 3).

In summary, we report the selective stepwise synthesis of heterobimetallic and heterotrimetallic complexes through the

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insertion of electrophilic metal fragments into strained electron-rich Ru−B bonds of BB-carboryne **1**. According to the theoretical study, the bonding environment of metal centers is best described as a pair of 2c-2e Ru−B and 3c-2e Ru···Pd−B bonds in **2** and a pair of highly delocalized 3c-2e Ru···Pd−B and Ru···Cu−B interactions in **3** (Figure 3). We aim to expand this synthetic strategy for the synthesis of other multimetallic complexes supported by metal−boron bonds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02799.

Experimental details, characterization data (NMR and absorption spectra and crystallographic data), and computational details (PDF)

Accession Codes

CCDC 2108336 and 2108337 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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