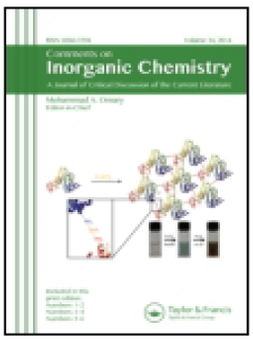

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Coordination Chemistry of Carborane Clusters: Metal-Boron Bonds in Carborane, Carboranyl, and Carboryne Complexes

Bennett J. Eleazer and Dmitry V. Peryshkov

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, USA

Metalated three-dimensional icosahedral boron clusters often exhibit high chemical and thermal stability relative to their simple borane counterparts thus making them a convenient object to study the chemistry of metal-boron bonds. The presence of multiple reactive boron vertices makes carboranes unique ligands with unusual steric and electronic requirements. This article summarizes recent developments in coordination chemistry of neutral $\{C_2B_{10}\}$ carborane clusters with a focus on metal-boron interactions. Several bonding modes are discussed, including neutral borane coordination through bridging B–H…M interactions, boryl complexes with B -M bonds, multimetallic assemblies, and the BB-carboryne complex containing a three-membered (BB)>Ru metallacycle.

Keywords carboranes, ligand design, boryls, carborynes, multimetallic complexes, pincer complexes

1. INTRODUCTION

Boron-based organometallic chemistry has attracted significant attention in the last few decades. Boron-centered ligand systems demonstrate their versatility of

Address correspondence to Dmitry Peryshkov, Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC 29208, USA. E-mail: peryshkov@sc.edu

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bonding modes to metal centers as they can function as borane, boratrane, boryl, borate, or borylene ligands. These complexes represent catalysts and intermediates in various metal-promoted borylation reactions, which have grown into powerful synthetic methodologies.[1–7] There are several recent reviews on electronically precise metal boryl and borylene complexes as well as boratranes.[8–16] This article will focus on recent advances in coordination chemistry of the *closo*-{C_2B_{10}} carborane clusters with specific attention given to exohedral metal-boron bonds that are primarily two-center-two-electron (2c-2e) σ-bond interactions and their transformations. Boron-metalated carborane clusters are different from other metal boryl complexes, which may exhibit some degree of Lewis acidic π-type metal-boron interactions. B-metalated carboranes are also different from metallaborane clusters, which, similarly to cyclopentadienyl complexes, have no distinct 2c-2e metal–boron bonds.

Icosahedral *closo*-dicarbadodecaborane, $C_2B_{10}H_{12}$, referred to in this article simply as carboranes, are remarkably robust neutral boron clusters with two boron vertices replaced by carbon atoms.[17,18] High interest in boron clusters and new synthetic methods of their functionalization is driven by their potential for application in coordination chemistry, polymers, energy storage, medicine, electronic devices, luminescent materials, liquid crystals, ceramics, and catalysis.[18–23] Three isomers of $C_2B_{10}H_{12}$ exist with *ortho*- and *meta*-carborane being readily commercially available (Figure 1). Due to the low total electron count (26 skeletal electrons for 12 vertices), the cluster carbon and boron atoms adopt a six-bonded environment with five bonds to the cluster atoms and one exohedral bond to a hydrogen atom. The steric bulk of the carborane cluster can be demonstrated by comparing the van der Waals volume of *o*-carborane (148 A^3) with that of adamantane (136 A^3) and benzene (79 A^3).

The delocalized electron density of the carborane cage is not uniform and gives rise to extraordinary differences in the electronic effects of the cluster on an exohedral substituent located on the carbon or boron atoms.[24] The presence of two different types of atoms in the cage, as well as the icosahedral geometry of the cluster, result in a large dipole moment of the *o*-carborane

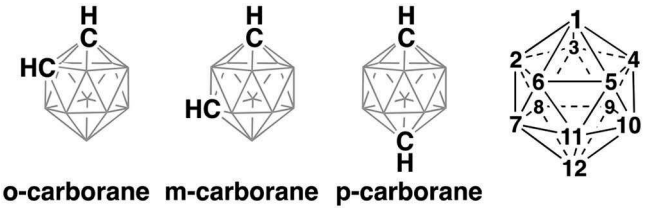


Figure 1: Drawings of three isomers (*ortho-*, *meta-*, and *para-*) of icosahedral carborane $C_2B_{10}H_{12}$ and the numbering scheme of vertices of an icosahedral cluster. Empty vertices represent B–H groups.

isomer (4.5 D) and a significant dipole moment of the *m*-carborane (2.9 D). This unusual anisotropy is also manifested in the anisotropy of the chemical properties of carborane derivatives.[25] Due to the higher electronegativity, the carbon atoms of carboranes are usually regarded as electron withdrawing,[26,27] while the boron atoms of the cluster are strongly electron donating.[28,29] The unusual electronic structure is often highlighted by regarding carboranes as inorganic three-dimensional "aromatic" analogs of arenes.[30] Stability, rigidity, unique and tunable steric bulk, and electronic properties of carboranes make them a highly attractive organomimetic inorganic substituent platform.[31,32]

The utilization of carboranes as ligands is largely constrained to their use as remote auxiliary substituents of phosphines, thiolates, selenides, and N-heterocyclic carbenes.[33–38] Despite the structural and functional diversity of the icosahedral carboranes, studies of their application as metal ligands remain relatively limited. In particular, boron-metalated carboranes remain underexplored.

From the point of view of a coordination chemist, the molecular scaffolds of carboranes are promising for several reasons (Figure 2). First, boryls are likely the strongest σ-donors in the series of anionic ligands based on boron, carbon, nitrogen, and oxygen sites.[39,40] The icosahedral cluster structure can enforce considerable steric hindrance in the vicinity of a metal center. In addition to steric shielding, this unique cluster geometry creates a propensity of the ligand to maintain significant bridging interactions of the type B/C–H···M with the metal that is covalently bound to the adjacent cage atom. Such interactions can potentially stabilize low-coordinate metal center configurations by hemilabile coordination, as well as assist in the cascade-type activation of the B–H bonds vicinal to the metal center, followed by a hydride/group transfer to and from the boron cage.

Second, the 3-D structure of boron clusters can also lead to the possibility of close contact of a single metal center with several atoms of the cage,

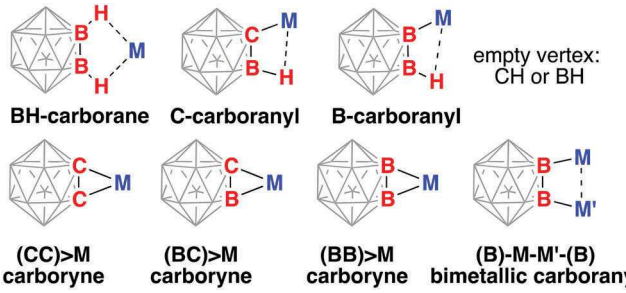


Figure 2: Different modes of metalation of a carborane cage: a neutral carborane coordinated through B–H···M bridging interactions; C–M and B–M carboranyls with possible B–H···M vicinal bridging interactions; η^2-coordinated (CC)>M, (BC)>M, and (BB)>M carborynes; and a bimetallic carboranyl complex featuring a (B)–M–M′–(B) metallacycle.

engendering the formation of η^2-coordinated bisdehydrocarborane (carboryne) metal complexes through a double B–H bond activation. The metal complexes of η^2-carbon-connected (CC)-carborynes are related to those of benzynes and feature similar reactivity with a number of unsaturated substrates such as alkenes, alkynes, and dienes.[41–44] Synthesis of related η^2-coordinated boron-based analogs of benzyne metal complexes, (BB)-carborynes, is interesting for the fundamental understanding of bonding in these unprecedented systems and uncovering the inherent reactivity of strained metal-boron bonds.

Third, the polyhedral structure of carboranes allows for metalation of more than one vertex of a cage, leading to the synthesis of multimetallic complexes supported by the curved boron cluster surface. These systems may feature metal-metal interactions along with multiple metal-boron contacts that can lead to metal-metal and metal-ligand cooperative reactivity.

This article will review recent developments in coordination chemistry of neutral icosahedral $\{C_2B_{10}\}$ carborane clusters with emphasis on the formation and reactivity of metal-boron bonds, highlighting the three structural motifs described earlier (Figure 2).

2. CARBORANES AS ANIONIC BORYL LIGANDS

Unsubstituted carborane clusters are relatively inert, weakly coordinating neutral ligands, so the direct formation of unsupported metal-boron bonds on the surface of *closo*-$\{C_2B_{10}\}$ cages by B–H bond activation has been reported only for several Hg, Tl, Ir and, recently, Os complexes.[45–50] Herein, we would like to highlight two recently reported systems containing unsupported B–M bonds.

Interestingly, oxidative addition of B–I bonds of iodocarboranes to low-valent Pd(0) centers has not yet led to isolation of palladium boryl complexes. The Grushin group and, later, the Teixidor group concluded that such oxidative addition is rapid but reversible, and the equilibrium is shifted predominantly towards starting materials.[51,52] One interesting approach to construction of unsupported B–M bonds on the surface of carboranes is the transmetallation reaction of known B-mercurocarboranes with late transition metals such as palladium or platinum. This approach was utilized by Spokoyny and co-workers to structurally characterize $[PtCl(PPh_3)_2(9\text{-B-}m\text{-}C_2B_{10}H_{11})]$ (**1**), featuring a Pt–B bond with bond length 2.102(2) Å (Figure 3a).[53] The synthesis of the palladium-containing analog, with the use of a similar method, failed to produce a Pd-boryl complex, instead resulting in the isolation of a bimetallic complex containing the Pd–Hg bond.

Another new synthetic approach for the formation of unsupported metal-boron bonds was recently demonstrated by the Adams and Peryshkov groups. In that work, the reaction of triosmium carbonyl cluster, $Os_3(CO)_{10}(NCMe)_2$,

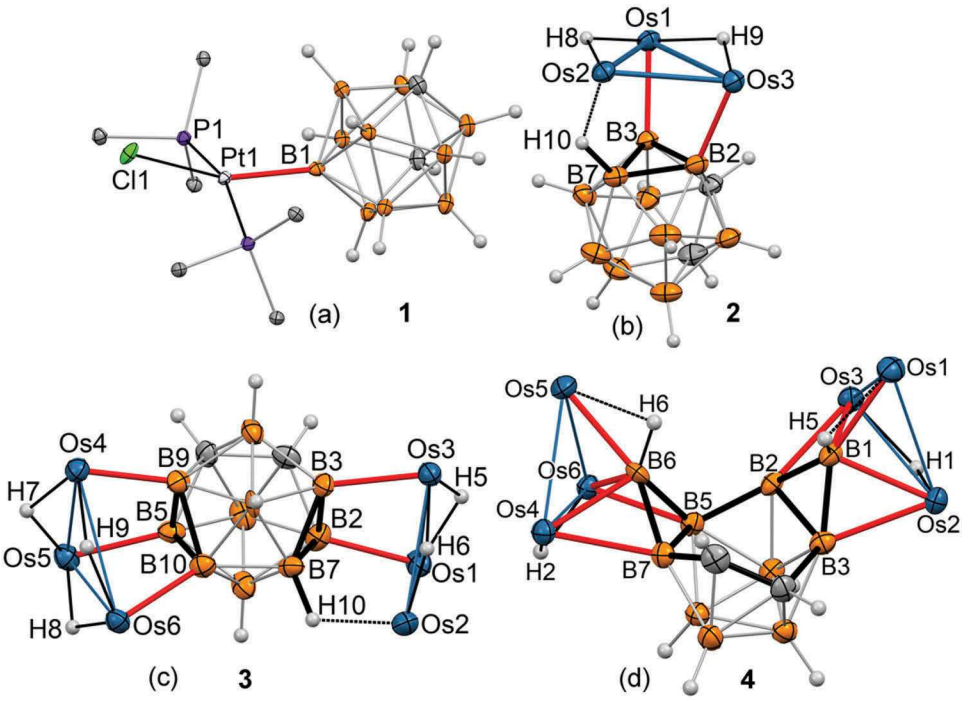


Figure 3: Displacement ellipsoid plots (40% probability) of complexes featuring unsupported metal-boron bonds: (a) $[PtCl(PPh_3)_2(9\text{-B-}m\text{-}C_2B_{10}H_{11})]$ (**1**)[53]; (b) $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}o\text{-}C_2B_{10}H_{10})$ (**2**)[50]; (c) $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3,\mu_3\text{-}o\text{-}C_2B_{10}H_7)Os_3(CO)_9(\mu\text{-}H)_3$ (**3**)[50]; (d) $Os_3(CO)_9(\mu\text{-}H)(\mu_3,\mu_3\text{-}C_2B_{10}H_8)Os_3(CO)_9(\mu\text{-}H)$ (**4**).[50] Phenyl groups of PPh_3 ligands and carbonyl groups of $Os_3(CO)_9$ fragments were omitted for clarity. © John Wiley and Sons/Wiley-VCH. Adapted with permission of John Wiley and Sons/Wiley-VCH. Permission to reuse must be obtained from the rightsholder.

and $o\text{-}C_2B_{10}H_{12}$ led to the isolation of a series of compounds containing Os–B bonds.[50] The use of 1:1 stoichiometry led to double B–H bond activation and coordination of the triosmium cluster to the carborane cage surface through two Os–B bonds and one Os···H–B bridging interaction (**2**, Figure 3b). Interestingly, this complex reacts with another equivalent of $Os_3(CO)_{10}(NCMe)_2$ to afford a hexaosmium complex (**3**) that contains a carborane cage sandwiched between two triosmium carbonyl clusters that are coordinated through a total of five 2c-2e Os–B bonds and one bridging Os···H–B 3c-2e bond (Figure 3c). Heating of **3** in nonane at reflux resulted in the rupturing of the *closo*-carborane cluster, so a pair of B–H groups became triply-bridging ligands for each of three osmium atoms on each hemisphere, in addition to two pairs of Os–B bonds (**4**, Figure 3d). A more detailed follow-up study revealed migration of triosmium clusters on the surface of the boron cage, as evidenced by thermal rearrangement leading to isolation of several positional isomers.[54]

A more general strategy for the activation of B–H bonds is the utilization of directing groups attached to a $\{C_2B_{10}\}$ carborane cage. The corresponding cyclometalated products have been reported for a number of transition metals, primarily for Ni, Pd, Pt, Rh, Ir, and Ru.[45,55–60] Metalation of boron atoms of carboranes has been recently thoroughly reviewed by Jin and co-workers.[61] The interest in metal-boron bonds of boron clusters also stems from the attractiveness of the direct metal-promoted B–H bond activation as a functionalization tool.[62–68] The use of organic donor groups attached to a boron cage has been demonstrated to direct metal-catalyzed derivatization to neighboring boron vertices.[69–71] In several cases, metalated carboranyl complexes have been isolated, suggesting their role as intermediates in these catalytic cycles.-[72–74] In addition, a number of tridentate pincer-type complexes with carborane backbones have been synthetized through directed B–H bond activation with thioethers,[75] selenoethers,[75] pyridines,[76] and oxazoline[77] groups as donor arms. Recently, the Peryshkov group introduced the POBOP pincer ligand framework[78] (POBOP = 1,7-OP(i-Pr)$_2$-m-carboranyl) containing phosphinite donor groups, which enjoy a great popularity in traditional carbon-metalated pincers.[79–82]

In the POBOP-H pincer proligand, two phosphinite donor arms enforce a close contact of the coordinated metal center to two B–H bonds of the boron cage, which predisposes at least one of these bonds to be activated (B1–H1 and B2–H2, Figure 4a). Indeed, the reaction of the POBOP-H ligand and Wilkinson's catalyst led to the clean formation of (POBOP)Rh(H)(Cl)(PPh_3) (**5**) through the oxidative addition of the B–H bond of the cluster to the Rh(I) center. Dehydrohalogenation of **5** in the presence of NEt_3, followed by oxidative addition of iodobenzene, afforded the (POBOP)Rh(Ph)(I) complex (**6**). This compound features a five-coordinate Rh(III) center and a strained metal-boron bond, as indicated by an acute exohedral bond angle of 85.2(1)° (Figure 4b and 4c). The bond strain in **6** can be highlighted by the comparison to the unstrained B2–B1–H1 angle in the POBOP-H ligand precursor (116.1 (9)°) or the B2–B1–Rh1 angle of 109.8(2)° in (POBOP)Rh(H)(Cl)(PPh_3) (**5**) (Figure 4c, dashed red line). The bond strain in (POBOP)Rh(Ph)(I) can be caused by the possible attractive interaction between the metal center and the vicinal B–H bond, as evidenced by the relatively close Rh1···B2 contact of 2.582(2) Å and an apparent short Rh1···H2A(B2) contact of 2.20(1) Å. It has to be noted, however, that the ^{1}H and ^{11}B NMR spectra of **6** at room temperature did not exhibit any discernible features that could be attributed to such a 3c-2e interaction. The complex (POBOP)Rh(Ph)(I) was the first example of a B-metalated $\{C_2B_{10}\}$ cluster containing a metal aryl fragment, even though these intermediates have been implied in several catalytic cycles for a long time. Heating of **6** in the presence of acetonitrile led to the cascade process starting with reductive elimination of the phenyl group to the boron cage. This resulted in the formation of a transient Rh(I) species that, in turn, oxidatively

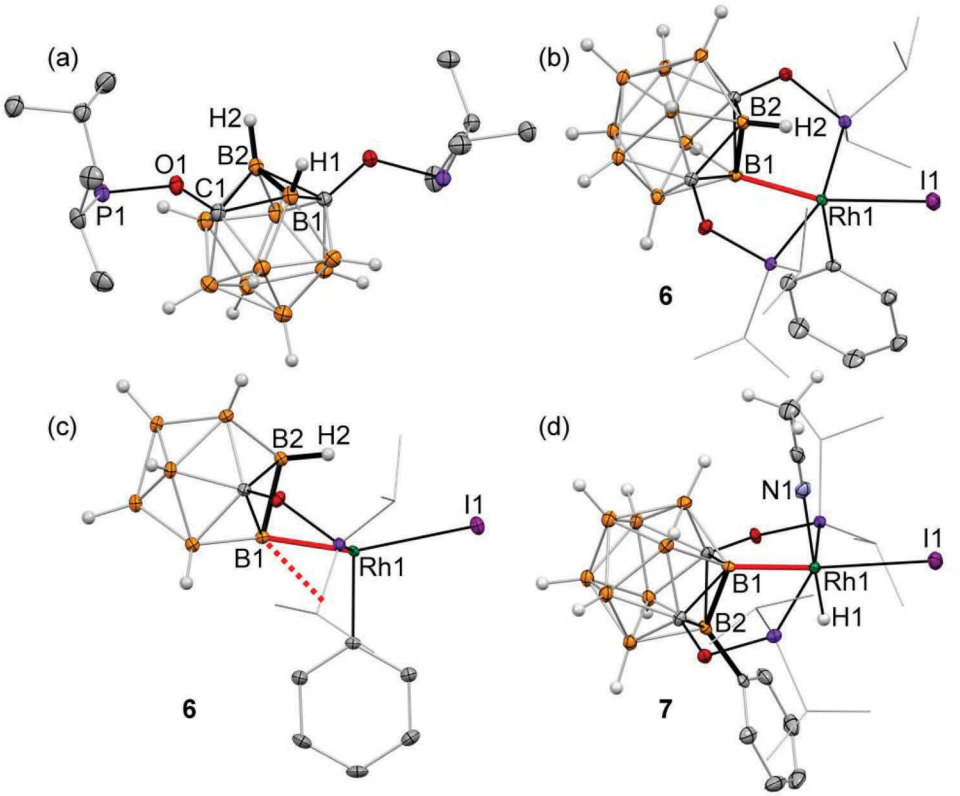
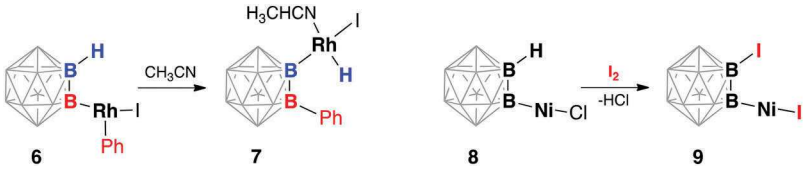


Figure 4: Displacement ellipsoid plots (50% probability) of (a) 1,7-OP(*i*-Pr)$_2$-*m*-$C_2B_{10}H_{10}$ (POBOP-H) proligand; (b) (POBOP)Rh(Ph)(I) complex (**6**), a general view; (c) (POBOP)Rh(Ph)(I) complex, a view perpendicular to the B2–B1–Rh1–C2 plane, where the idealized angle for an unstrained exohedral bond for the carborane cluster is shown by the dashed red line; (d) (POB(BPh)OP)Rh(H)(I)(CH_3CN) complex (**7**) that formed upon heating of (POBOP)Rh(Ph)(I), resulting in the transfer of the phenyl ring to the carborane cage and the migration of the metal center to the adjacent boron vertex. Isopropyl groups of the ligand and most hydrogen atoms have been omitted for clarity. Adapted with permission from reference [78]. © 2016 American Chemical Society. Permission to reuse must be obtained from the rightsholder.

added the vicinal B–H bond, which led to the re-formation of a Rh(III) B-carboranyl complex (**7**, Figure 4d). The overall transformation is the transfer of the aryl group to one boron atom of the cage and the metal center migration to the adjacent boron atom (Scheme 1, left).[78] This metal- and ligand-centered reactivity of boron-containing complexes recently attracted increased attention due to implications of metal-ligand cooperativity.[83,84]

In a related work on (POBOP)Ni(Cl) (**8**), we have demonstrated that the B–H bond vicinal to the Ni–B bond can be activated and functionalized.[85] The reaction of (POBOP)Ni(Cl) and I_2 led to the iodination of the adjacent B–H bond (**9**, Scheme 1, right). It is not currently clear whether the formation of this new B–I bond occurs through a high-valent nickel center



Scheme 1: (left): Migration of the phenyl group and activation of the adjacent B–H bond in (POBOP)Rh(Ph)(I) (**6**) and formation of (POB(BPh)OP)Rh(H)(I)(CH_3CN) (**7**). (right) Iodination of the B–H bond adjacent to the B–Ni bond in (POBOP)Ni(Cl) (**8**) and formation of (POB(BI)OP)Ni(I) (**9**). The phosphinite arms of the pincer POBOP ligand have been omitted for clarity.

intermediate with its subsequent migration from one boron atom to another, as it was in the case for the conversion of **6** to **7** in the rhodium system (see earlier), or through the polarization and activation of an axially coordinated I_2 ligand generating an iodonium cation, leading to halogenation of the vicinal boron vertex.

3. CARBORANES AS NEUTRAL BORANE LIGANDS: VICINAL B–H···M INTERACTIONS

Neutral unsubstituted *closo*-{C_2B_{10}} carboranes are relatively weak ligands and generally do not form isolable complexes to transition metals through the coordination by only B–H···M interactions. The related classes of *exo-nido*-metallacarboranes, as well as complexes of anionic *closo*-{CB_{11}}$^-$ clusters, are represented by a large number of compounds that feature multiple borane-to-metal coordination motifs, as demonstrated by the work of the Hawthorne, Teixidor, Weller, and Stone groups and others.[86–96] An interesting fluxional system involving a series of cationic rhodium complexes partnered with the *closo*-$CB_{11}H_{12}^-$ anion $Rh(PR_3)(H)_2(CB_{11}H_{12})$ (R = isopropyl, cyclohexyl, cyclopentyl) (**10**) has been reported by Weller and co-workers.[97] Cationic fragments $[Rh(PR_3)(H)_2]^+$ in these compounds are coordinated to the boron cluster anion through three Rh···H − B bridging interactions. The coordination of the metal center is fluxional over the surface of the carborane anion in solution. Sequential addition of ethylene and dihydrogen to **10** resulted in functionalization of boron atoms of the cluster with the ethyl group, indicating the formation of intermediates containing Rh–B bonds. Intriguingly, complexes **10** were found to be stable only under dihydrogen atmosphere. Under argon, the spontaneous loss of H_2 and the formation of complexes with an empirical formula $Rh_2(PR_3)_2(CB_{11}H_{12})_2$ (**11**) occurred. Crystal structure determination revealed that these compounds are dimers with two carborane monoanions and a $[Rh^{III}(H)(PR_3)Rh^{I}(PR_3)]^{2+}$ core. One carborane cluster is coordinated with the bimetallic cation through three Rh···H–B bridging interactions, while the other interacts through two Rh···H–B interactions and one direct Rh–B bond. Complexes **11** revert to **10** after addition of H_2.

A direct comparison between behavior of *closo*-{C_2B_{10}} and *closo*-{CB_{11}} clusters towards B–H bond activation has been recently carried out by Lavallo and co-workers. An Ir(I) complex containing the neutral *o*-carboranyl phosphine ligand $C_2B_{10}H_{11}(P(C_3H_7)_2)$ is not isolable and undergoes intramolecular oxidative addition of a B–H bond to afford Ir(III) cyclometalated products. In contrast, an isoelectronic Ir(I) complex supported by an anionic phosphine $CB_{11}H_{11}(P(C_3H_7)_2)$ (**12**) is stable towards B–H bond activation.[60] Notably, a related zwitterionic Ir(I) complex of the $CB_{11}H_{11}(P(C_3H_7)_2)$ (**13**) ligand features two bridging B–H···Ir interactions.[98]

The three-dimensional icosahedral geometry of carboranes opens a possibility of multiple metal-boron interactions within a B-carboranyl complex. A metalated vertex of the cluster is surrounded by five B–H/C–H bonds and, therefore, additional vicinal bridging B–H···M interactions become feasible. Furthermore, this coordination arrangement can affect reactivity, as indicated by the example of the (POBOP)Rh(Ph)(I) complex, where the metal center can move from one boron atom of the cage to another, leaving a functional group or a hydrogen atom behind.

One of the first crystallographically characterized carborane complexes containing a metalated cage and the vicinal coordinated borane fragment was synthesized by the Hawthorne group, and its crystal structure was reported by Bau and co-workers in 1972.[99,100] The structure of a cobalt(III) complex containing two chelating anionic 1,1′-biscarborane ligands (**14**) was disclosed. This compound also exhibited a B–H···Co bridging interaction between one of the carborane cages and the metal center with a short Co–B distance of 2.29(1) Å. One biscarborane unit, therefore, acts as an X_2L ligand while the other is an X_2 ligand.

A more recent related example comes from the Sivaev and Welch groups, which reported a similar biscarborane complex of ruthenium (**15**).[101] The biscarborane ligand was used as a dianionic chelating ligand featuring an additional bridging 3c-2e B–H···Ru interaction (Figure 5a). One of the carbon-metal bonds in **15** is strained with a B11–C4–Ru1 angle of 78.9(1)° due to the presence of the vicinal B–H···Ru interaction ((H)B···Ru distance 2.429(3)Å). This borane coordination was shown to alternate between two equivalent boron sites of a carborane cage in solution, as evidenced by ^{11}B NMR spectroscopy. After treatment with CO, the metal center became saturated by one CO ligand, breaking the bridging borane interaction. Reaction with phosphines, however, yielded a more drastic change. Addition of dppe or PPh_3 replaces the auxiliary *p*-cymene ligand and enforced activation of the coordinated B–H bond of biscarborane, forming a new B–Ru bond (**16**, Figure 5b). In the product, one boron cage still features its original C–Ru bond with a newly formed agostic B–H···Ru interaction. Overall, this is a transformation of biscarborane from a C, C-coordinated X_2L type ligand in **15** to a C,B-coordinated X_2L type in **16**. Notably, the Ru−C to Ru−B bond conversion in the presence of dihydrogen

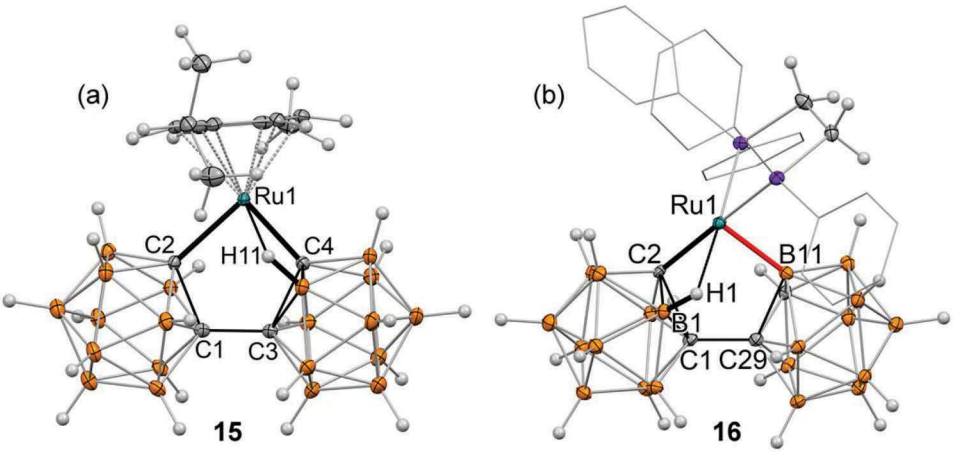


Figure 5: Displacement ellipsoid plots (50% probability) of (a) [Ru(1,1′-$C_2B_{10}H_{10}$–$C_2B_{10}H_{10}$)(*p*-cymene)] (**15**) and (b) [Ru(1,3′-$C_2B_{10}H_{10}$–$C_2B_{10}H_{10}$)(dppe)] (**16**). Phenyl groups of the dppe ligand have been omitted for clarity.[101] Adapted from reference [101] with permission from © The Royal Society of Chemistry. Adapted with permission of The Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

has been reported by the Xie group for cyclopentadienylcarboranyl complexes, which likely proceeds through intermediates similar to [Ru(1,1′-$C_2B_{10}H_{10}$–$C_2B_{10}H_{10}$)(*p*-cymene)].[102]

Metalation of the POBOP pincer ligand framework with ruthenium led to the synthesis of complexes featuring an exohedral Ru–B bond, as well as a vicinal B–H···Ru bridging interaction (Figure 6a).[103] The bridging B–H···Ru interactions in the carboranyl ruthenium complexes are surprisingly strong and lead to extreme distortion of the adjacent covalent B–Ru metal-boryl bond. For example, one of the features in the structure of the (POBOP)Ru(H)(PPh_3) complex (**17**) containing metal-boryl, metal-borane, and metal-hydride functionalities is the extreme strain of the B–Ru bond, as demonstrated by the acute B2–B1–Ru1 angle of 69.4(2)° (Figure 6b). This extreme bond strain is the result of the strong vicinal 3c–2e borane coordination that exhibits a (H2)B2···Ru1 distance of 2.276(3) Å, which is remarkably close to the 2c-2e B1–Ru1 bond length (2.208(3) Å) in the same complex.

The ruthenium carboranyl hydride complex **17** was found to exhibit an unprecedented rapid intramolecular exchange between the metal-bound hydride and the vicinal B–H bond of the cluster (Figure 6c). This process occurs by shuttling of the metal center between two adjacent boron atoms of the cage at temperatures above –50 °C with an activation energy for the exchange transformation of 12.2 kcal/mol. This unique system can be considered as an isolable intermediate in metal-promoted B–H activation reactions and it directly demonstrates the possibility of regioisomerization of metalated boron

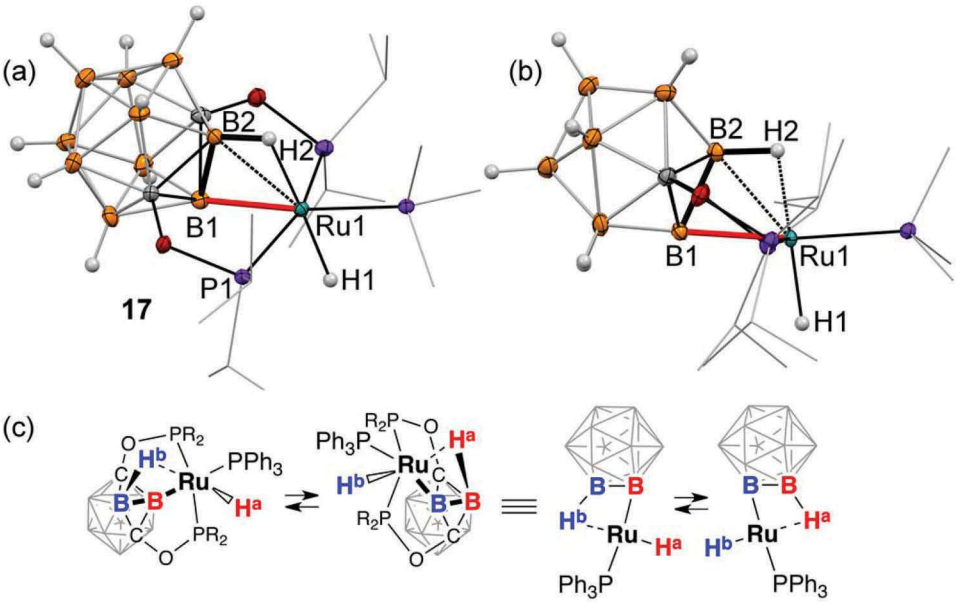


Figure 6: Displacement ellipsoid plots (50% probability) of the (POBOP)Ru(H)(PPh_3) complex (**17**): (a) a general view; (b) a view perpendicular to the B1–B2–Ru1 plane.[103] Isopropyl groups of POBOP and phenyl groups of PPh_3 have been omitted for clarity. Note the closeness of values of the B1–Ru1 bond length (2.208(3) Å) and the B2···Ru1 distance (2.276(3) Å), as well as an extremely acute B2–B1–Ru1 angle (69.4(2)°). (c) Scheme of the rapid exchange process of the metal hydride and the coordinated borane group in **17**. Note "walking" of the metal center on the carborane cage. Adapted by permission of The Royal Society of Chemistry. © The Royal Society of Chemistry. Adapted with permission of The Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.[103]

clusters. Recently, the Spokoyny group reported Pd-catalyzed regioizomerization of 9-bromo-*m*-carborane that also likely proceeds through a palladium analog of **17** as an intermediate.[104] In this case, the "cage-walking" process proceeded through all B–H vertices of the *m*-carborane cluster.

Reactivity of the unusual ruthenium boryl hydride complex (POBOP)Ru(H)(PPh_3) featuring a latent open coordination site with the bridging B–H···Ru interaction that acts as a hemilabile neutral ligand and a distorted electron-rich metal-boron bond was probed in reactions with H_2, D_2, and in catalytic dehydrogenation of cyclooctane. The transfer dehydrogenation of cyclooctane promoted by **17** was found to be facile and efficient under both nitrogen (TON = 400) and air (TON = 288), with some of the highest TON values for a ruthenium-based catalyst reported to date.[105,106] This high efficiency of the catalyst can be attributed to the stabilization of the unsaturated metal center by borane coordination and high thermal stability of the carborane cluster and its exohedral bonding.

4. CARBORANES AS η^2-COORDINATED (BB)-CARBORYNES

Transition metal benzyne complexes have been extensively studied because of their rich chemistry and synthetic utility.[107–114] Metal-coordinated benzynes are involved in a range of insertion reactions with nitriles, ketones, alkenes, and alkynes. In 1979, the Schrock group reported the first structure of a complex containing a benzyne ligand η^2-coordinated to a metal center.[109] Interestingly, in 1973, Beall and co-workers isolated and crystallographically characterized a nickel complex containing an η^2-coordinated 1,2-dehydro-*o*-carborane cluster (**18**, Figure 7a).[115] This 1,2-dehydro-*o*-carborane $C_2B_{10}H_{10}$ ligand can be considered a three-dimensional analog to benzyne, and this type of species was later named "carboryne" in the literature, as the two share many reactivity manifolds.[30,41,116–118] A number of complexes containing this C,C-bound carboryne ligand have been isolated for Group 4 and Group 10 transition metals (Figure 7).[42,119,120] The synthesis and utilization of this class of compounds in insertion and cycloaddition reactions with unsaturated substrates were pioneered by the Xie group, resulting in regioselective synthesis of numerous carborane cage derivatives.[121–126]

Apart from the carboryne ligand bound to a metal center through two carbon atoms (CC-carboryne), one can envisage its isomer that is bound through two boron atoms in the η^2 fashion (BB-carboryne). The POBOP pincer framework has been shown to enforce a close contact of a metal center and two cage vertices, as was demonstrated by the acute B2–B1–Ru1 angle in (POBOP)Ru(H)(PPh_3) (**17**) (69.4(1)°, described earlier) and the presence of a strong vicinal B–H···Ru interaction. The fluxionality of the B–H/B–Ru–H fragment in that complex led to a hypothesis that the second B–H bond of the ligand can be irreversibly activated by the metal center if an appropriate auxiliary ligand

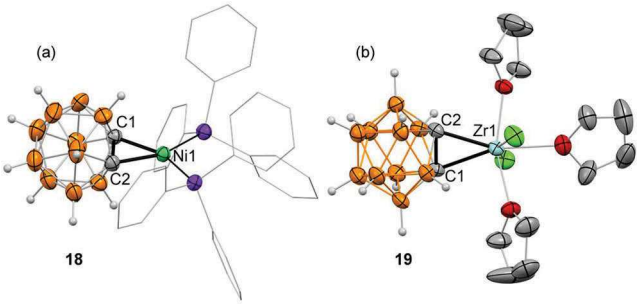


Figure 7: Displacement ellipsoid plots (40% probability) of the selected CC-carboryne complexes: (a) Ni(η^2-1,2-*o*-$C_2B_{10}H_{10}$)(PPh_3)$_2$ (**18**)[115,120]; (b) Zr(η^2-1,2-*o*-$C_2B_{10}H_{10}$)Cl_2(THF)$_3$ (**19**).[153] Phenyl groups of PPh_3 and most of the hydrogen atoms have been omitted for clarity. Note the strain of exohedral carbon-metal bonds as indicated by acute C2–C1–Ni1 and C2–C1–Zr1 angles (65.3(2)° and 69.5(2)°, respectively). Adapted with permission from references [115,120,153]. ©1973, 2009, 2010 American Chemical Society. Permission to reuse must be obtained from the rightsholder.

set it present. Strong π-acceptors, such as carbonyl ligands, were the primary choice, as they would stabilize coordination of the resulting presumably highly electron-donating BB-carboryne ligand to a metal center. Indeed, the reaction of the ligand precursor POBOP-H and $[Ru(CO)_3Cl_2]_2$ after addition of a base led to the clean formation of a single product.[127] A single-crystal X-ray diffraction experiment confirmed the target η^2 coordination of the carborane cluster through two adjacent boron atoms to the ruthenium center (Figure 8a). The metal center was found in the distorted octahedral coordination environment with two Ru–B bonds, two phosphinite pincer ligand arms, and two carbonyl ligands. This (POBBOP)$Ru(CO)_2$ complex (**20**, POBBOP = 1,7-OP(*i*-Pr)$_2$–2,6-dehydro-*m*-carborane) was the first example of a metal complex of the η^2-coordinated 2,6-dehydro-*m*-carborane (BB-carboryne). Similarities between the BB-carboryne and benzyne complexes in structure, bonding, and reactivity patterns will be discussed later in this article.

The crystal structure of (POBBOP)$Ru(CO)_2$ revealed a remarkable strain in the (BB)>Ru metalacycle as indicated by the acute B–B–Ru angles of 65.5 (1)° and 68.4(1)°. These values correspond to the smallest exohedral B–B–X angles for icosahedral boron clusters. The Ru–B bond lengths are 2.174(3) Å and 2.221(3) Å. Interestingly, the B–B distance in the (BB)>Ru metalacycle is 1.720(4) Å, which is shorter than that in the POBOP-H proligand (1.788(3) Å). Such bond length decrease indicates the stronger bonding interaction between two metalated boron atoms of the carboryne complex.

Electron-donating ability of the BB-carboryne ligand could be assessed by the analysis of carbonyl ligand stretching frequencies. In (POBBOP)$Ru(CO)_2$, the values of ν(CO) are 2010 cm^{-1} and 1958 cm^{-1} ($\nu(CO)_{average}$ = 1984 cm^{-1}). It

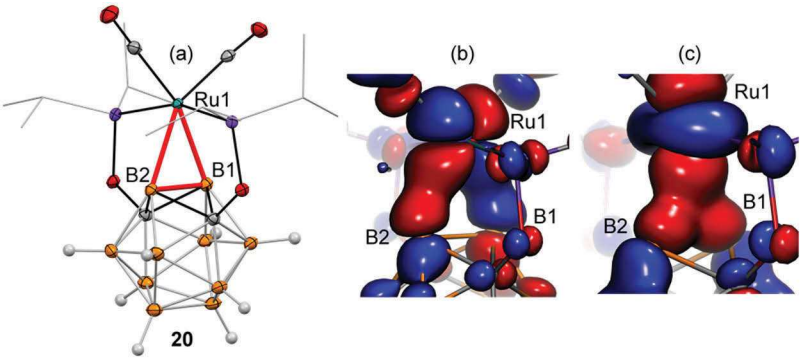
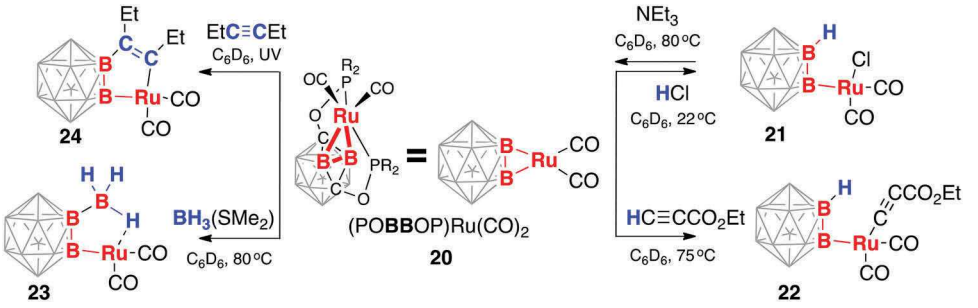


Figure 8: (a) Displacement ellipsoid plot (50% probability) of the BB-carboryne complex (POBBOP)$Ru(CO)_2$ (**20**); (b) highest-occupied molecular orbital (HOMO) in the vicinity of the (BB)>Ru metallacycle in **20**; and (c) lower-energy occupied molecular orbital (HOMO-15) in the vicinity of the (BB)>Ru metallacycle in **20**.[127] Isopropyl group of the POBOP ligand has been omitted for clarity. Note the strain of exohedral boron-metal bonds as indicated by the acute B2–B1–Ru1 angles (68.4(1)°). Adapted with permission from reference [127]. © 2016 American Chemical Society. Permission to reuse must be obtained from the rightsholder.

is instructive to compare these values to those for mononuclear Ru(II) and Ru (0) *cis*-dicarbonyl complexes. Six-coordinate Ru(II) complexes $Ru(CO)_2L_2X_2$ (X = an anionic ligand, L = a neutral donor ligand, in most cases being a phosphine) exhibit $\nu(CO)_{average}$ in the range from 1981 to 2060 cm^{-1}, which is higher than that for **20**. Five-coordinate Ru(0) complexes $Ru(CO)_2L_3$ exhibit $\nu(CO)_{average}$ in the range from 1863 to 1976 cm^{-1}, which is lower than that for **20**. Notably, six-coordinate Ru(0) η^2-alkene and η^2-alkyne complexes $Ru(CO)_2L_2(\eta^2\text{-L'})$ exhibit $\nu(CO)_{average}$ values in the range 1927 cm^{-1} to 2003 cm^{-1}, which is close to that for the (BB)-carboryne complex **20**.[127]

The electronic structure of the (BB)-carboryne complex was studied using DFT calculations. The highest occupied molecular orbital (HOMO) and a lower-lying occupied molecular orbital (HOMO–15) closely resemble a bonding situation in a metal olefin complex, corresponding to the Dewar-Chatt-Duncanson description (Figure 8b and 8c). Thus, the HOMO fragment corresponds to the back donation from a *d*-orbital of the metal center to the π*-orbital of the B–B bond. At the same time, the HOMO–15 represents a donation from the π-orbital of the BB-carboryne to a *d*-orbital of the metal center. This representation provides some analogy of η^2 bonding of the BB-carboryne ligand to that of alkenes in metal complexes. The molecular bonding graph in the QTAIM analysis for the (BB)>Ru fragment is triangular with one B–B and two Ru–B bond paths. In the ELF representation, Ru–B bonding is represented by two disynaptic V(Ru,B) valence basins, which are shifted outwards from Ru–B connectivity lines. The ELF analysis also localized a three-center V(Ru,B,B) basin, which can be interpreted as bonding between the metal center and the B–B bond in the (BB)>Ru metallacycle. Interestingly, the QTAIM analysis indicated a stronger B–B bond with the bond critical point in the carboryne complex, in comparison to a weaker B–B interaction with no direct bond path in the starting POBOP-H ligand or in the mono-B-metalated complex (POBOP) $Ru(Cl)(CO)_2$ (**21**).

The reactivity pattern for **20** is consistent with its bonding description as a combination of two extreme cases of ruthenacycloborapropene and an olefin-type complex. We hypothesized that the highly strained, electron-rich ruthenium-boron bonds in BB-carboryne can themselves act as nucleophilic reaction centers, thus exhibiting metal-ligand cooperativity (Scheme 2). One of the metal-boron bonds in **20** can be reversibly protonated with HCl, forming the (POBOP)$Ru(Cl)(CO)_2$ complex (**21**), featuring a chloride ligand on the metal center and a newly formed B–H bond. A similar reactivity was observed in the case of a terminal alkyne, with the formal oxidative addition of the substrate across one of the metal-boron bonds in BB-carboryne leading to the formation of a B-carboranyl acetylide (POBOP)$Ru(C \equiv C\text{–}CO_2Et)(CO)_2$ (**22**). A nucleophilic character of Ru–B bonds in the carboryne **20** was further demonstrated by the reaction with Lewis acid $BH_3{\cdot}SMe_2$. In this case, the borane moiety attached to one of the boron vertices of carboryne through the formation of a



Scheme 2: Reactivity of the BB-carboryne complex (POBBOP)Ru(CO)$_2$.[127] Adapted with permission from reference [127]. © 2016 American Chemical Society. Permission to reuse must be obtained from the rightsholder.

B–B bond and a bridging (B)–BH$_3$···Ru interaction. The complex (POB(BH$_3$)OP)Ru(CO)$_2$ (**23**) is a rare example of a carborane cluster with an exohedral B–B bond to a simple borane formed by the coupling of nucleophilic boryl and electrophilic borane fragments.

One of the characteristic reactions of benzyne complexes and (CC)-carboryne complexes is [2 + 2] cycloaddition reactions with internal alkynes. The reaction of **20** and 3-hexyne under UV irradiation led to the selective formation of the crystallographically characterized cycloaddition complex containing the bridging B–CEt=CEt–Ru fragment (**24**). The second B–Ru bond of the complex, as well as two carbonyl ligands, remained intact. This reaction highlights a direct analogy of the BB-carboryne complex to benzynes and CC-carborynes.

In summary, utilization of a unique geometry of the *m*-carborane POBOP pincer framework led to the synthesis of the first metal complex of a *closo*- boron cluster containing an exohedral (BB)>M metallacycle. Reactivity of this ruthenium BB-carboryne complex is reminiscent of the aryne-aryl transformations of metal benzynes or amine–amide and carbene-alkyl conversion reported for pincer systems.

5. RATIONAL SYNTHESIS OF CARBORANE-SUPPORTED HETEROMETALLIC COMPLEXES: EXPANSION OF (BB)>RU METALLACYCLE WITH METAL-BASED ELECTROPHILES

The synthesis of well-defined heterobimetallic complexes remains a frontier challenge in inorganic chemistry due to unusual electronic effects of metalloligands, potential for cooperative metal-metal reactivity in the activation of strong bonds, and the relevance to heterogeneous catalysts.[128–132] Carborane and other polyhedral boron clusters show promise as useful tools

in the construction of multiple metal–boron interactions and as building blocks for multimetallic architectures because of their unique three-dimensional cluster structure. However, *closo*-carborane cages, as mentioned previously, are weakly coordinating neutral ligands and thus do not feature many examples of multiple metals interacting with the carborane cage. The related class of anionic metallacarbollides has been shown by the Stone group to facilitate formation of B–M, B–H···M, and M–M interactions. For example, it has been demonstrated that anionic molybdenum, iron, and rhenium carbollide complexes could bind transition metal cations (Ru(II), Cu(I), Ag(I), Fe(II)) with either two or three bridging B–H···M interactions.[90,91,133] In some cases, the incoming metal can also form a M–M bond with the metal center of carbollide featuring a compound containing B–M, B–H···M and M–M bonds.

Closo-{C_2B_{10}} carborane dichalcogenolates have been used as a backbone for multimetallic architectures. The Jin group explored reactivity of 16-electron "pseudo-aromatic" iridium complexes Cp*Ir($Se_2C_2B_{10}H_{10}$) and Cp*Ir ($S_2C_2B_{10}H_{10}$) with rhodium, molybdenum, and tungsten sources to form multinuclear heterometallic complexes with Ir–M bonds.[134,135] Interestingly, in some cases for Ir–Rh products, B–H bond activation by the iridium center has been observed along with rhodium center insertion into the C–S/Se bonds of carborane ligands, resulting in the formation of two analogous tetranuclear complexes that contained Ir and Rh centers coordinated to the carborane cage through adjacent Ir–B and Rh–C bonds.[136]

A bimetallic rhodium complex with the Rh–Rh bond that is supported by the pair of adjacent exohedral Rh–C and Rh–B bonds on the carborane cage surface was synthesized and structurally characterized by the Jin group through metalation of the *o*-carboranylthioamidate ligand with a cationic Rh (III) source (**25**, Figure 9a).[137] An analogous Ir(III) complex was also prepared.

Another bimetallic complex with exohedral metal-boron bonds was synthesized by the Jin group using *m*-carborane dicarboxylic acid as a directing ligand for double B–H bond activation by two iridium centers (**26**, Figure 9b).[59] In this complex, two IrCp* fragments are bridged by a chloride ligand and bound to two adjacent boron atoms of the *m*-carborane cage. The Ir···Ir distance of 4.006(1) Å implies no bonding between metal centers. Two Ir–B bond lengths in the complex are 2.04(2) Å and 2.08(2) Å, indicating two independent exohedral iridium boryl fragments. Interestingly, the B–B bond length in **26** between two metalated boron atoms in this compound is rather long at 1.89(3) Å, which can be compared to the corresponding B–B bond length of 1.720(4) Å in the (BB)>Ru carboryne metallacycle in **20**, highlighting the difference between the dimetalated diboryl and carboryne bonding descriptions.

Reactivity of strained, electron-rich metal-boron bonds of the ruthenium BB-carboryne complex towards organic electrophiles led us to the hypothesis that the bonding pair of Ru–B bonds in the (BB)>Ru metallacycle can interact

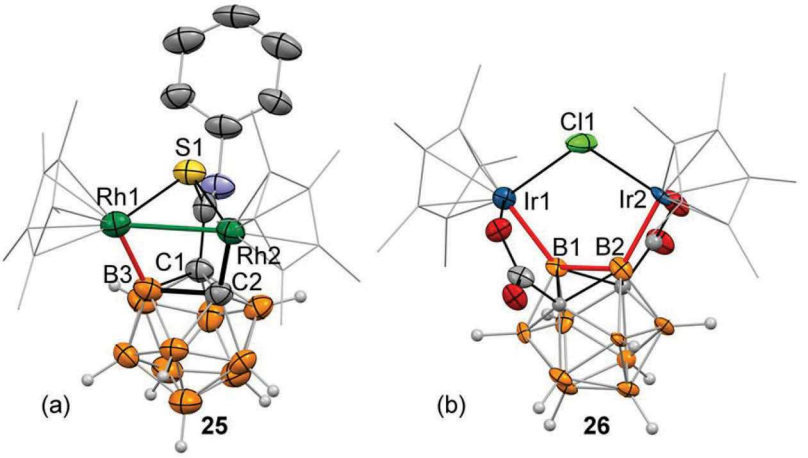


Figure 9: Displacement ellipsoid plots (50% probability) of (a) a bimetallic C,B-carboranyl complex $(RhCp^*)_2(2,3\text{-}o\text{-}C_2B_{10}H_9)(CSNHPh)$ (**25**)[137] and (b) a bimetallic B,B-carboranyl complex $(IrCp^*)_2(\mu\text{-}Cl)(2,6\text{-}C_2B_{10}H_8)(COO)_2$ (**26**).[59] Most of the hydrogen atoms have been omitted for clarity. Note the relatively long B1–B2 bond (1.89(3) Å) and the lack of metal-metal bonding in **26**. Adapted from reference [137] with permission from The Royal Society of Chemistry; adapted with permission from reference [59]. © The Royal Society of Chemistry. Adapted with permission of The Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder. © 2014 The American Chemical Society. Adapted with permission of the American Chemical Society.

with inorganic Lewis acids such as Group 11 cations. Reactions of (POBBOP)$Ru(CO)_2$ with CuCl, $AgNO_3$, and $Au(SMe_2)Cl$ resulted in the selective formation of heterobimetallic complexes (**27–30**, Figure 10a).[138] In case of all three products, a coinage metal cation inserted into one of the Ru–B boron bonds of the parent carboryne with the second Ru–B bond remaining intact, forming unusual Ru–B–B–M metallacycles. Two carbonyl ligands remained bound to the ruthenium center. These compounds are the first examples of coinage metal B-carboranyls.

The copper (**27**) and gold (**28**) complexes crystalized as chloride-bridged dimers where the M(I) coinage metal cations have a four-coordinate planar geometry that is uncharacteristic for Cu(I) and Au(I). Copper-boron bond length in $[(POBBOP)(Ru)(CO)_2(Cu)(Cl)]_2$ (**27**) is 2.029(2) Å, which is slightly longer than Cu–B bonds in copper boryl complexes (1.980(2)–2.002(3) Å) (Figure 10b).[139–143] Interestingly, the Ru···B(Cu) distance in **27** (2.475(2) Å) is in the range for boron cluster complexes with bridging 3c-2e B–H···Ru interactions.

The gold-containing complex $[(POBBOP)(Ru)(CO)_2(Au)(Cl)]_2$ (**28**) is isostructural to the copper analog (Figure 10c). The gold-boron bond is the shortest reported to date with a Au–B bond length of 2.027(2) Å. It is comparable to that in a few recently reported 2c-2e gold–boron bonds in gold boryl complexes

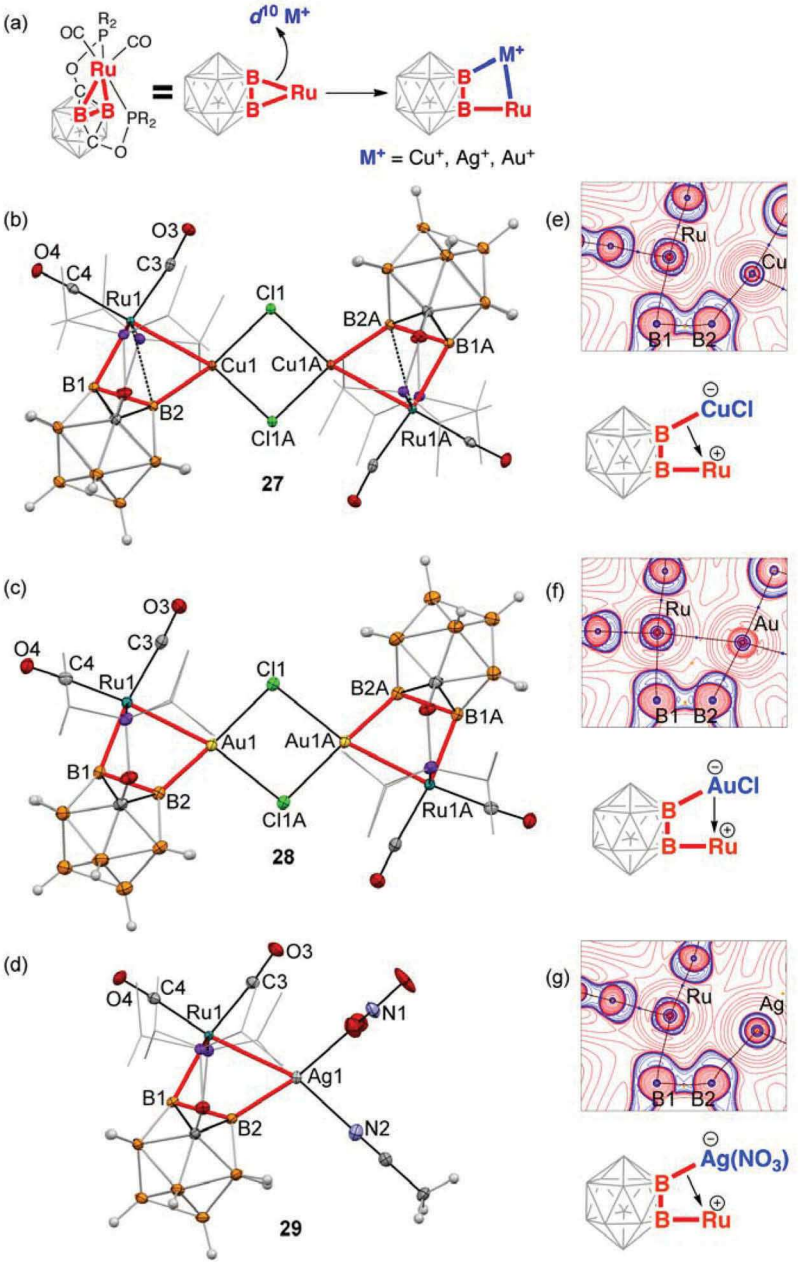


Figure 10: (a) Synthesis of heterobimetallic complexes by insertion of coinage metal cations into ruthenium-boron bonds of the (BB)>Ru metallacycle; (b)-(d) displacement ellipsoid plots (50% probability) of $[(POBBOP)(Ru)(CO)_2(Cu)(Cl)]_2$ (**27**), $[(POBBOP)Ru(CO)_2(Au)(Cl)]_2$ (**28**), $(POBBOP)(Ru)(CO)_2(Ag)(CH_3CN)(NO_3)$ (**29**); (e)-(f) contour maps of electron density Laplacians and QTAIM molecular graphs and bonding descriptions in the (B1–B2–Ru1–M) fragment for these complexes.[138] © The Royal Society of Chemistry. Adapted with permission of The Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

(2.069(3)–2.144(4) Å).[140,142,144] The Au–Ru distance in **28** is 2.682(1) Å, which is similar to that in bimetallic complexes. In contrast to its copper congener **27**, the distance between the ruthenium center and the vicinal boron atom Ru···B (Au) in **28** is 2.723(3) Å and does not correspond to a significant bonding interaction.

The silver-containing complex (POBBOP)(Ru)$(CO)_2$(Ag)$(CH_3CN)(NO_3)$ (**29**) has a short Ag–B bond (2.182(3) Å), which is comparable to those in two other reported silver boryl complexes (2.118(2) Å and 2.122(4) Å) (Figure 10d).[140] The Ru···B(Ag) distance is relatively short at 2.444(3) Å, indicating a bridging bonding interaction similar to that in the copper-containing complex **27**.

Values of stretching frequencies of carbonyl ligands coordinated to the ruthenium center in these bimetallic complexes provide information about changes of electronic structure upon coordination of coinage metal cations to the (BB)>Ru metalacycle. For the starting carboryne complex **20**, the $\nu(CO)_{average}$ is 1984 cm^{-1}, which increases to 1995 cm^{-1}, 2002 cm^{-1}, and 2017 cm^{-1} upon coordination of Lewis acidic copper, gold, and silver cations, respectively.

Theoretical calculations revealed a difference in the bonding situation for Cu and Ag vs. Au-containing complexes. Insertion of copper or silver in one of the bonds of the parent BB-carboryne resulted in the formation of a new 3c-2e B–M···Ru interaction that is isolobal to bridging B–H···Ru interactions described earlier (Figure 10e and 10g). Bonding in the gold-containing complex **28** is best described as distinct B–Au and Au–Ru bonds (Figure 10f). This representation is consistent with the Au–B bond length in **28** being the shortest reported to date.

Insertion of coinage metal cations into the single Ru–B bond of the carboryne metallacycle is related to coordination of electrophilic metals to alkylidene, silylene, and borylene/boryl complexes.[145–148] Interestingly, coordination of Au^+ to Pt–C bonds in aryl complexes has been recently reported.[149] Formation of these heterobimetallic complexes represents a novel synthetic strategy for exohedral metal–boryl bonds in icosahedral $\{C_2B_{10}\}$ clusters and Group 11 metals as the direct B–H bond activation by these cations remains unknown.

6. SUMMARY AND OUTLOOK

Icosahedral *closo*-$\{C_2B_{10}\}$ carborane clusters as ligands for transition metals exhibit rich coordination chemistry with several binding motifs: neutral borane ligands, anionic boryls, and formally dianionic carborynes. The three-dimensional polyhedral structure of carboranes allows a combination of some of these bonding modes in one complex; for example, a B–H···M bridging interaction vicinal to the B–M boryl group. Furthermore, assembly of multimetallic complexes on the surface of carborane clusters offers a wide flexibility in the number of metal centers and their mutual arrangement and bonding. The stability of B-metalated carboranyls in comparison to other boryl complexes

will undoubtedly be one of the key factors in expansion of a number of isolated examples of this class of coordination compounds. The development of synthetic protocols for the formation of metal-boron bonds is still an underexplored area, and some new experimental routes are expected to emerge. The use of carborane clusters as ligands for multiple metal centers may lead to a design of well-defined molecular analogs of borophene-type structures on metallic surfaces.[150–152]

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ORCID

Dmitry V. Peryshkov http://orcid.org/0000-0002-5653-9502

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