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Ring-Expansion Reactivity of Ruthenium BB-Carboryne Metallacycle

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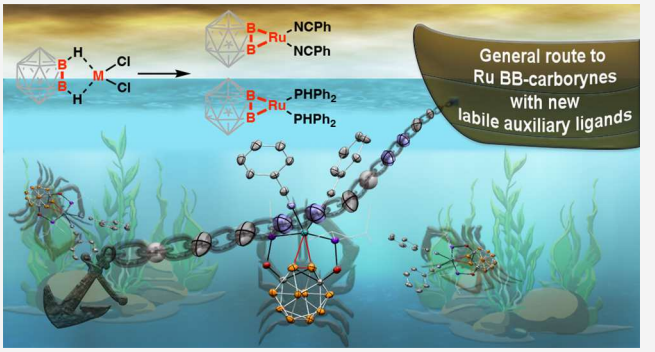
ABSTRACT: A general synthetic approach to the BB-carboryne complexes of ruthenium is reported. Ruthenium dichloride complex supported by two B−H···Ru interactions of a neutral carborane was converted to the carboryne fragment bearing two adjacent B−Ru bonds with either benzonitrile or diphenylphosphine as auxiliary ligands. These ligands proved to be more labile in comparison with the previously reported carbonyl-containing analogue. The lability of new auxiliary ligands enhanced the reactivity of the carboryne fragment and changed the outcome of its reactions with a terminal alkyne and an azide that was inserted into one of the B−Ru bonds of the starting BB>Ru metallacycle. The phenylaldehyde functional group underwent decarbonylation at the metal center producing a bridging borane, carbonyl, and phenyl ligands.



INTRODUCTION

Advances in metal-promoted borylation of organic substrates propelled growth of synthetic, structural, and mechanistic studies of metal−boron complexes.[1−4] Transition metal complexes with metal−boron bonds are active intermediates in these transformations, where coupling of a boryl group with an organic fragment occurs. In the context of ligand design, a boryl group is considered as one of the strongest σ-donors with strong *trans*-influence.[5−9] At the same time, the possibility of the tricoordinate anionic boryl to serve as a π-acceptor has also been noted.[10−12] The variety of potential metal−ligand interactions for boron-based ligand scaffolds stems from the ability to adopt neutral donor borane, neutral acceptor boratrane, and anionic boryl, borate, or borylene coordination modes.[13−16] The switching between these bonding types is often utilized in the activation of chemical bonds of a substrate through metal−ligand cooperativity.[17−24]

One of the common tridentate pincer-type ligand platforms features a combination of two side arm donors and a central anionic center. Several boron-based pincer systems have been introduced in the last two decades.[25−30] Recent discoveries in this area include the activation of dihydrogen across metal-boryl bond with the formation of metal hydride and borane or borohydride.[20,21,31] The recent report of activation of C−H bonds in pyridines highlights the Lewis acidity of boryls where the selectivity of the process is driven by the coordination of nitrogen in a heterocyclic substrate to the boron atom and the iridium center, undergoing oxidative addition.[17] In another example, the addition of O−H and N−H bonds to iridium boryl pincers proceeds with the protonation of the metal center and binding of the anionic fragment to boron.[18]

Boron clusters represent another type of boron-containing molecular platforms.[32−35] Icosahedral *closo*-dicarbadodecaborane cages are among the most widely studied boron clusters. Carboranes $C_2B_{10}H_{12}$ are robust neutral molecules with ten boron and two carbon vertices. These clusters have attracted increasing attention due to their potential use in luminescent materials, batteries, pharmaceuticals, polymers, coordination chemistry, and catalysis.[36−47]

In the realm of ligand design, many examples of boron−metalated icosahedral neutral *closo*-{C_2B_{10}} carboranes have been reported.[48−52] Carboranes possess a unique 3D aromatic character, which imparts unusual electronic and bonding properties.[53,54] Specifically, the exohedral metal−boron bonds in their complexes can be primarily considered as two-center-two-electron σ-bonds, which differentiates them from the metal boryl complexes exhibiting some degree of Lewis acidic π-type metal−boron interactions outlined above. Furthermore, B−H bonds of neutral and anionic boron clusters often strongly coordinate to metal centers.[55,56] The polyhedral geometry of a cluster provides significant steric hindrance around the exohedral metal−boron bond. Furthermore, the 3D structure of boron clusters leads to the possibility of η^2- and even η^3-coordination to the single metal center.

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We have been interested in the exploration of the carboranyl-based pincer complexes within the POBBOP (POBBOP = 1,7-OP(*i*-Pr)$_2$-2,6-dehydro-*m*-carborane) ligand framework where the coordination of a metal center to two phosphinite arms brings it to the proximity of two adjacent boron vertices of the cluster.[57] The potential interplay between metal-boryl M−B bonds, metal-borane bridging B−H···M interactions, and the η^2-bound three-membered carboryne BB>M metallacycle makes this system an attractive platform for interrogation of metal−ligand cooperativity.[58−61]

Our previously reported synthetic route to the first example of BB-carboryne complex of ruthenium utilized $Ru(CO)_3Cl_2$ as a metal precursor, which, upon the reaction with the pincer pro-ligand POBBOP-$(H)_2$ (**1**) in the presence of triethylamine afforded carboryne complex $Ru(CO)_2$(POBBOP) (**2**) that featured two metal−boron bonds to the adjacent vertices of the cluster, two phosphinite arms, and two auxiliary carbonyl ligands.[60] The presence of two electron-accepting carbonyls in the *trans*-positions to two electron-donating boryls likely contributed to the enhanced stability of this six-coordinated 18-electron complex, which was found to tolerate air and moisture in the solid state as well as in solution. The reactivity of the carboryne complex featured the metal−ligand cooperativity where one of the strained electron-rich metal−boron bonds of the BB>Ru fragment interacted with a range of electrophilic substrates, including protonation, halogenation, and insertion of Lewis acidic metal centers (Scheme 1).[60,62,63] In all cases, the strongly bound carbonyl ligands remained coordinated to the metal center.

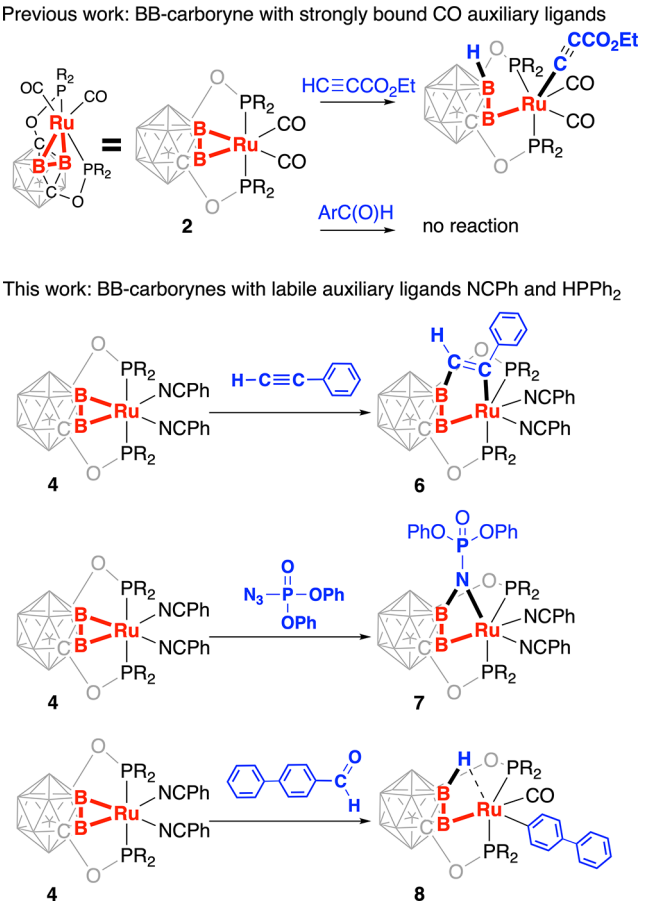
In this work, we present an exploration of ruthenium carboryne complexes that contain more labile auxiliary ligands in place of carbonyls in **2** (Scheme 1). We found a new synthetic method that facilitates double B−H bond activation of the pro-ligand and the formation of the carboryne fragment for a wider range of supporting groups, such as nitriles and phosphines. Owing to the lability of the introduced auxiliary ligands, the resulting carborynes demonstrate new reactivity patterns that are both metal- and ligand-centered.

RESULTS AND DISCUSSION

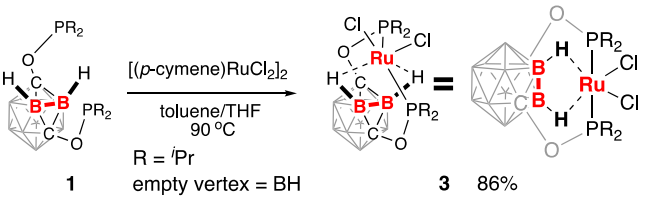
In search for a more general method for the generation of carboryne BB>Ru fragment that does not involve the use of carbonyl ligands, we first turned our attention to the coordination chemistry of the POBBOP-$(H)_2$ pro-ligand **1**.[57] The reaction of POBBOP-$(H)_2$ and $[Ru(p\text{-cymene})Cl_2]_2$ for 48 h at 90 °C in a mixture of toluene and THF in the absence of a base resulted in the complete conversion to a single product, with the signal at 196 ppm in the ^{31}P NMR spectrum. Intriguingly, the ^{11}B and $^{11}B\{^1H\}$ NMR spectra of the product did not contain the signals that could be assigned to the metalated boron atoms for the cluster; in other words, the signals in the spectra only corresponded to boron nuclei coupled to protons. Furthermore, the ^1H NMR spectrum of the product contained the 1:1:1:1 broadened quartet signal at −9.71 ppm, with the relative intensity corresponding to two protons. Normally, the BH groups of the carborane cluster cage give rise to broad signals in the ^1H NMR spectra in the region from 1.5 to 4.5 ppm, whereas the Ru−H hydrides give rise to sharp signals in the region from −15 to −20 ppm. The $^{11}B\{^1H\}-^1H$ NMR correlation experiment clearly demonstrated coupling between boron and hydrogen nuclei with a $^1J_{BH}$ of 111 Hz for the ^1H NMR signal at −9 ppm. These observations led us to assign the product as a complex of the neutral POBBOP-$(H)_2$ ligand that features the coordination of the metal center to two phosphinite arms and no direct metal-boryl bonds. Instead, two bridging B−H···Ru integrations that produced the broadened quartet signal in the ^1H NMR spectrum were established.[64] The product was isolated in 86% yield (Scheme 2). The single-crystal X-ray diffraction experiment confirmed this hypothesis, revealing the molecular structure of $RuCl_2$(POBBOP-$(H)_2$) complex **3** (Figure 1).

The metal center in **3** features a distorted octahedral geometry. The ruthenium atom is coordinated to the carborane cage *via* two B−H···Ru bridging interactions with the interatomic distances Ru1−B1 = 2.250(2) Å and Ru1−B2 = 2.251(2) Å, which are only slightly longer than the direct Ru−B bonds in the carboryne complex **2** (2.174(3) and

Scheme 1. Divergence in the Reactivity of BB-Carboryne Complexes of Ruthenium Driven by the Differences in the Lability of Auxiliary Ligands *trans*- to Boryl Centers



Scheme 2. Synthesis of $RuCl_2$(POBBOP-$(H)_2$) Complex 3 (POBBOP = 1,7-OP(*i*-Pr)$_2$-2,6-dehydro-*m*-carborane)[a]



[a]Unlabeled cluster vertices represent BH units.

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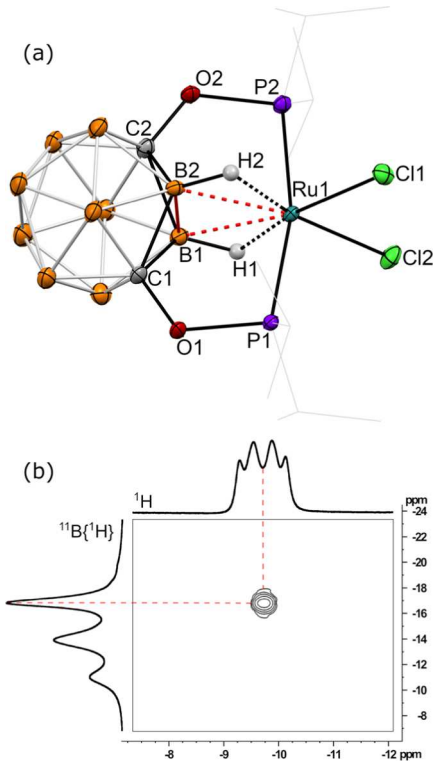
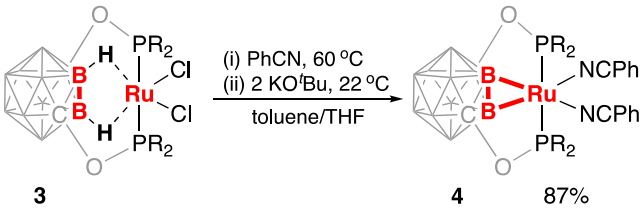


Figure 1. (a) Displacement ellipsoid plot (50% probability) of $RuCl_2(POBBOP\text{-}(H)_2)$ (**3**). Atoms belonging to isopropyl groups of the ligand arms have been omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ru1−B1 = 2.250(2), Ru1−B2 = 2.251(2), B1−B2 = 1.719(3), and P2−Ru1−P1 = 166.7(2). (b) Fragment of the $^{11}B\{^{1}H\}$-^{1}H HSQC NMR spectrum demonstrating a correlation between the ^{11}B NMR signal at −16.8 ppm and the ^{1}H NMR signal in the hydridic region at −9.71 ppm indicating the presence of the bridging B−H···Ru interactions.

2.221(3) Å). The two bridging hydrogen atoms were located and refined freely from the X-ray data (Ru−H = 1.75(2) Å, B−H = 1.16(2) and 1.18(2) Å). Two chloride ligands are located *trans*- to the cluster B(H) atoms. Complex **3** represents a new coordination mode for the unactivated carborane pincer proligand **1** where it acts as a neutral diborane group.

Compound **3** is stable in THF or in toluene, but changes in the ^{31}P NMR spectra were observed in the presence of stronger ligands, such as phosphines or nitriles, and upon addition of base such as triethylamine or potassium *tert*-butoxide. The changes in the ^{11}B spectra under these conditions are indicative of B−H bond activation and the formation of metal−boron bonds. The B−H bond activation in **3** is arrested when no π-accepting auxiliary ligands are present, as it has been demonstrated for metal−boron bond formation with related diazaborole scaffolds.[65] Therefore, **3** can serve as a precursor for a wider range of B-coordinated carboranyl and carboryne complexes of ruthenium. Indeed, its reaction with benzonitrile in the presence of KO^{t}Bu led to the formation of product **4** that exhibited the spectral feature of the carboryne fragment, namely, two equivalent metalated boron vertices. Compound **4** was then prepared in a one-pot reaction by the sequential addition of PhCN and KO^{t}Bu to **3** (Scheme 3). First, benzonitrile was added in excess to **3** and the mixture was heated at 60 °C for 4 h resulting in the formation of multiple products according to the ^{31}P NMR spectroscopy. The subsequent addition of potassium *tert*-butoxide and

Scheme 3. Synthesis of $Ru(NCPh)_2(POBBOP)$ Complex 4[a]



3 **4** 87%

[a]Unlabeled cluster vertices represent BH units.

stirring of the reaction mixture at room temperature for 72 h resulted in the complete conversion to a single product **4**, which featured a signal at 207 ppm in the ^{31}P NMR spectrum. Two metalated boron atoms of the carborane cage gave rise to a singlet at −3.4 ppm in the ^{11}B NMR spectrum. No signals were observed from −20 to 0 ppm in the ^{1}H spectrum, corroborating the absence of bridging B−H···Ru groups and terminal Ru−H hydrides.

The product was isolated in an 87% yield. Single crystals of $Ru(NCPh)_2(POBBOP)$ complex (**4**) were obtained by the slow evaporation of a saturated hexane solution at room temperature. The crystal structure confirmed the formation of the BB>Ru carboryne fragment with two metal−boron bonds of 2.110(7) and 2.185(7) Å (Figure 2). These bond lengths are

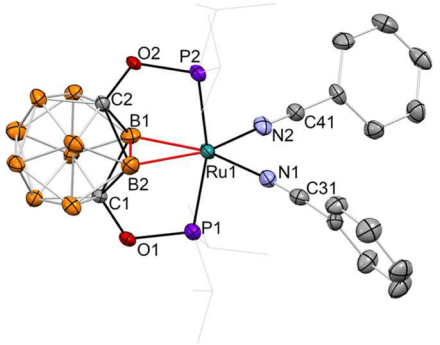


Figure 2. Displacement ellipsoid plot (50% probability) of $Ru(NCPh)_2(POBBOP)$ (**4**). Atoms belonging to isopropyl groups of the ligand arms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1−B1 = 2.110(7), Ru1−B2 = 2.185(7), B1−B2 = 1.730(10), Ru1−N1 = 2.068(5), Ru1−N2 = 2.073(5), P2−Ru1−P1 = 163.7(1), and N1−Ru1−N2 = 89.4(2).

slightly shorter than those in our previously reported carboryne complex $Ru(CO)_2(POBBOP)$ (**2**) (2.174(3) and 2.221(3) Å).[60] The exohedral B2−B1−Ru1 angle of 68.5(3)° and B1−B2−Ru1 angle of 64.0(3)° are the most acute among the reported exohedral B−B−M angles for icosahedral boron clusters. These, along with the B1−Ru1−B2 angle of 47.5(3)° demonstrate significant bond strain in the BB>Ru three-membered metallacycle. Two benzonitrile ligands that are *trans*- to the carboryne fragment exhibit an unstrained N1−Ru1−N2 angle of 89.4(2)°.

With the new carboryne complex $Ru(NCPh)_2(POBBOP)$ in hand, we first probed the lability of its benzonitrile ligands. The addition of CO at room temperature led to a quick conversion to carbonyl congener $Ru(CO)_2(POBBOP)$. The addition of 2 equiv. of PPh_3 or PEt_3 led to the binding of only one phosphine per metal center according to the ^{31}P NMR spectroscopy. Apparently, the POBBOP ligand exerts substantial steric hindrance around the metal center so that the

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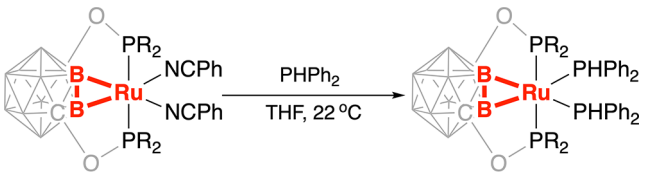
two remaining coordination sites that are *trans*- to the boron cluster can be occupied by only smaller ligands. Even for triethylphosphine, with its relatively small cone angle, only one PEt_3 can displace one benzonitrile in **4**, forming Ru(NCPh)-(PEt_3)(POBBOP). In contrast, the addition of a less crowded phosphine, $PHPh_2$, led to complete displacement of benzonitrile with the phosphine ligands and the formation of $Ru(PHPh_2)_2$(POBBOP) in 60% yield (**5**) (Scheme 4). The

Scheme 4. Synthesis of $Ru(PHPh_2)_2$(POBBOP) Complex 5[a]



[a]Unlabeled cluster vertices represent BH units.

formation of this carboryne complex was corroborated by the appearance of two signals in the ^{31}P NMR spectrum: a triplet signal at 195 ppm corresponding to two phosphinite donor arms of POBBOP and a broader singlet signal at 15.1 ppm corresponding to two coordinated diphenylphosphine ligands. Notably, the diphenylphosphine complex **5** is stable upon prolonged heating at 100 °C in toluene solution, and no P−H bond activation by the metal center or metal−boron bonds was observed.

The single crystals of complex **5** were obtained by slow evaporation of its solution in diethyl ether at room temperature. The exohedral Ru−B bond distances for **5** (Figure 3)

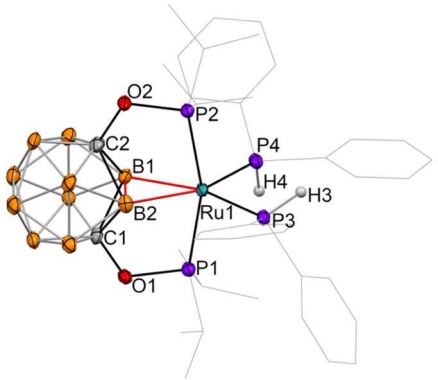
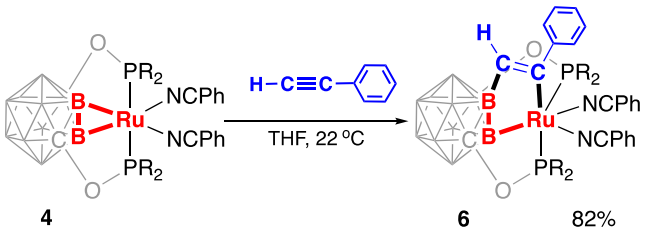


Figure 3. Displacement ellipsoid plot (50% probability) of Ru-$(PHPh_2)_2$(POBBOP) (**5**). Atoms belonging to isopropyl groups of the ligand arms and phenyl rings on phosphines have been omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ru1−B1 = 2.192(6), Ru1−B2 = 2.176(6), B1−B2 = 1.715(7), Ru1−P3 = 2.342(1), Ru1−P4 = 2.323(1), P2−Ru1−P1 = 161.8(1), and P3−Ru1−P4 = 99.3(1).

(Ru1−B1 = 2.192(6) Å and Ru1−B2 = 2.176(6) Å) are slightly longer than those in $Ru(NCPh)_2$(POBBOP) (**4**). The P3−Ru1−P4 angle is relatively large at 99.3(1)°, which indicates the substantial degree of steric hindrance exerted by the phenyl groups of diphenylphosphine ligands. Other structural metrics of **5** are similar to those of **4** and **2**.

Next, we probed the reactivity of the new carboryne complexes described above in order to ascertain the effect of the auxiliary ligands, especially their increased lability. The reaction of $Ru(NCPh)_2$(POBBOP) (**4**) with phenylacetylene at room temperature resulted in the clean formation of a single product with the signal at 198.4 ppm in the ^{31}P NMR spectrum (Scheme 5). The single crystals of the product were

Scheme 5. Synthesis of Complex 6[a]



[a]Unlabeled cluster vertices represent BH units.

grown by the slow evaporation of a hexane solution. The crystal structure determination revealed the addition product $Ru(NCPh)_2$(HCCPh)(POBBOP) (**6**) that formed upon [2 + 2] cycloaddition/1,2-insertion of the alkyne to one of the boron−ruthenium bonds of carboryne (Figure 4). Another

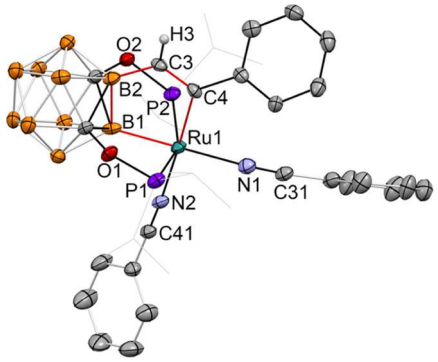


Figure 4. Displacement ellipsoid plot (50% probability) of **6**. Atoms belonging to isopropyl groups of the ligand arms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1−B1 = 2.045(5), Ru1−C4 = 2.108(4), B1−B2 = 1.813(7), Ru1−N1 = 2.106(4), Ru1−N2 = 2.071(4), C3−C4 = 1.349(6), B2−C3 = 1.525(7), P2−Ru1−P1 = 153.0(1), N1−Ru1−N2 = 87.9(2), B2−B1−Ru1 = 105.0(3).

metal−boron bond remained intact with a Ru1−B1 distance of 2.045(5) Å. The alkyne fragment added across the former B−Ru bond forming the five-membered metallacycle with a Ru1−C4 distance of 2.108(4) Å and a C3−C4 distance of 1.349(6) Å corresponding to a double bond character. Although there is the possibility of two isomers of the cycloaddition products, where the terminal carbon atom of the alkyne binds to either the boron atom of the cluster or the metal center, only a single isomer is being formed, according to the NMR spectroscopy. Both benzonitrile ligands remained bound to the metal center, with noticeably different ruthenium−nitrogen bond distances (Ru1−N1 = 2.106(4) Å and Ru1−N2 = 2.071(4) Å), likely due to the strong *trans*-influence of the electron-rich boryl ligand.

Notably, the reaction of phenylacetylene and Ru-$(CO)_2$(POBBOP) (**2**) proceeded differently from that of $Ru(NCPh)_2$(POBBOP) (**4**) described above. For the carbonyl analogue **2**, it instead required elevated temperatures and resulted in the deprotonation of the alkyne by the B−Ru bond

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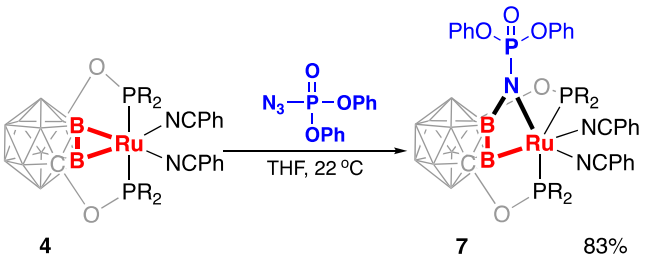
Organometallics XXXX, XXX, XXX−XXX

and the formation of the B−H bond at the cluster and the terminal acetylide ligand at the metal center.[60] The cycloaddition reactivity of **4** presented herein is analogous to the chemistry of metal benzyne and CC-carboryne complexes.[66,67] Similarly, the 1,2-insertion of alkynes into metal-boryl bonds has been established with the isolation of a number of 2-boryl-1-alkenyl metal complexes in the studies of hydroboration and related reactions.[68−72]

The reaction of diphenylphosphoryl azide with **4** in THF resulted in the clean formation of a new product **7** at room temperature (Scheme 6). According to ^{31}P NMR spectroscopy,

Scheme 6. Synthesis of Complex 7[a]



[a]Unlabeled cluster vertices represent BH units.

the product formation occurred essentially immediately upon mixing, which was confirmed by the appearance of a new singlet signal at 193.7 ppm and another singlet at 3.6 ppm in the 2:1 ratio. Single-crystal X-ray diffraction revealed the structure of $Ru(NCPh)_2(NP(O)(OPh)_2)(POBBOP)$ (**7**). The starting azide apparently lost N_2 and the remaining nitrene was inserted into one boron−ruthenium bond of carboryne **4** forming the four-membered B−N−Ru−B metallacycle (Figure 5). The remaining Ru1−B1 bond in **7** is 2.086(2) Å, which is

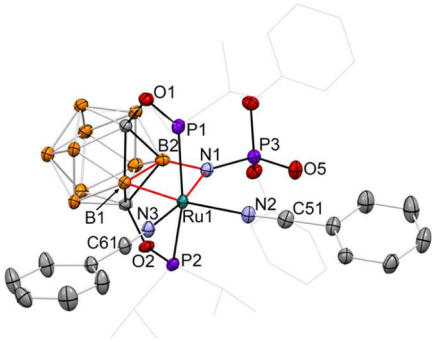
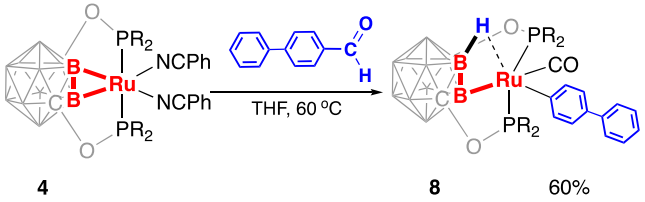


Figure 5. Displacement ellipsoid plot (50% probability) of **7**. Atoms belonging to isopropyl groups of the ligand arms and the phenyl rings on the phosphoryl group have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1−B1 = 2.086(2), Ru1−N1 = 2.188(2), B1−B2 = 1.826(4), Ru1−N2 = 2.120(2), Ru1−N3 = 1.980(2), B2−N1 = 1.429(3), N1−P3 = 1.588(2), P3−O5 = 1.467(2), B2−N1−Ru1 = 94.4(1), B2−N1−P3 = 127.9(2), P2−Ru1−P1 = 158.8(1), N2−Ru1−N3 = 96.9(1), and B2−B1−Ru1 = 87.1(1).

typical for B-carboranyls. Interestingly, the borylamide bond B2−N1 is relatively short at 1.429(3) Å (B−N single bond lengths are typically 1.58 Å and double bond lengths are 1.40 Å).[73,74] This bond length value is among the shortest reported for the exohedral B−N bond for boron clusters and, together with the trigonal planar geometry around the amide nitrogen atom (the sum of bond angles at N1 is 359.9°) implies significant π-bonding interaction between the cage boron atom and the amide nitrogen.[75−78] Additionally, the Ru1−N1 bond in **7** for the formally anionic amide group is rather long at 2.188(2) Å, which is even longer than two ruthenium−nitrogen distances for its neutral benzonitrile ligands (1.980(2) and 2.120(2) Å). The N1−P3 distance is relatively short at 1.588(2) Å.

The related $Ru(CO)_2(POBBOP)$ (**2**) complex did not exhibit any reactivity toward aldehydes or ketones. The increased lability of benzonitrile ligands in $Ru(NCPh)_2(POBBOP)$ prompted us to explore their reactivity with organic carbonyl compounds. The reaction of $Ru(NCPh)_2(POBBOP)$ (**4**) and biphenyl-4-carboxaldehyde in THF did not proceed at room temperature but led to the formation of a single product according to ^{31}P NMR spectroscopy (a singlet at 206.7 ppm) upon heating at 60 °C (Scheme 7). The single crystals of the product Ru(CO)-

Scheme 7. Synthesis of Complex 8[a]



[a]Unlabeled cluster vertices represent BH units.

$(C_6H_4C_6H_5)(POBBOP\text{-}H)$ (**8**) were obtained by the slow evaporation of a hexane solution at room temperature. The crystal structure determination revealed the *B*-carboranyl complex with the biphenyl and carbonyl groups coordinated to the metal center (Figure 6). Two benzonitrile ligands of

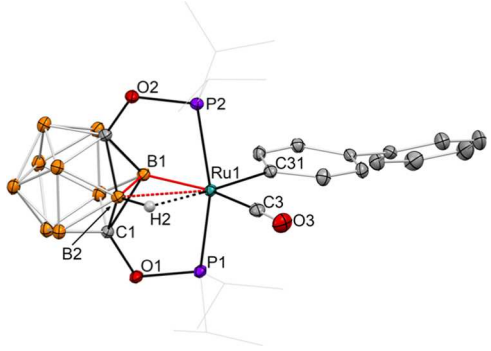


Figure 6. Displacement ellipsoid plot (50% probability) of compound **8**. Atoms belonging to isopropyl groups of the ligand arms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1−B1 = 2.153(2), Ru1−B2 = 2.413(2), Ru1−C3 = 1.915(2), Ru1−C31 = 2.081(2), B1−B2 = 1.750(2), P2−Ru1−P1 = 160.3(1), C31−Ru1−C3 = 93.7(1), B2−B1−Ru1 = 75.6(1).

compound **4** were removed in the formation of compound **8**. Another important feature of this product is the presence of the bridging B−H···Ru interaction in the place of one of the former B−Ru bonds of the starting carboryne. This coordinated neutral borane fragment is strongly bound to the metal center, which manifests in the relatively short Ru1−B2(H2) distance of 2.413(2) Å, which can be compared with the metal-boryl bond length Ru1−B1 of 2.153(2) Å. The aryl

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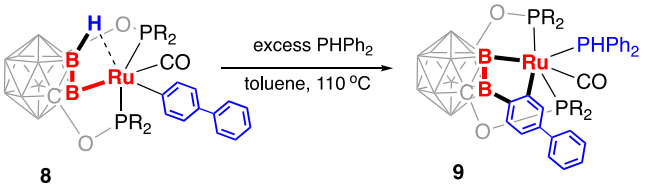
Organometallics XXXX, XXX, XXX−XXX

group in **8** is *trans-* to the bridging B−H···Ru hydride. Similarly to the formation of **8**, an analogous reaction of **4** and benzaldehyde produced decarbonylation product Ru(CO)-(C_6H_5)(POBBOP-H) **8b** that features bridging borane B−H··· Ru, carbonyl, and phenyl groups at the metal center.

Aldehydes are known to undergo decarbonylation at transition metal centers, mostly *via* initial oxidative addition of their C−H bonds.[79−82] The decarbonylation of acetaldehyde formed *in situ* by the rhodium boryl pincer complex has been proposed as one of the steps in its reaction with ethanol. The reaction of the rhodium boryl pincer complex with ethanol has been proposed to proceed to form acetaldehyde *in situ*, which then underwent oxidative addition to form hydridoacyl species and subsequent decarbonylation and reductive elimination of methane to form metal carbonyl.[27] In the case of **8**, the bridging B−H···Ru group probably originated from the cooperative B−Ru involvement, as the oxidative addition to the Ru(II) center in **4** is less likely. Subsequent decarbonylation of the acyl group produced **8**. Only one isomer of **8** is observed in the NMR spectra of the reaction mixture indicating that decarbonylation step produces the aryl group *trans-* to the bridging hydride. In this configuration of the rigid pincer complex geometry, reductive elimination of the corresponding arene would require either dissociation of one of the pincer phosphinite arms or loss of CO. Apparently, these rearrangements do not occur, as complex **8** is stable upon heating at 110 °C in toluene with and without the presence of added benzonitrile, indicating no formation of biphenyl or reversibility of the decarbonylation step. In the presence of the excess aldehyde at 110 °C, Ru(NCPh)$_2$(POBBOP) produced the same single organometallic product **8** along with the ester product of the Claisen−Tishchenko reaction.[83] The ester formation is not catalytic, with respect to **4**.

The reaction of Ru(PHPh$_2$)$_2$(POBBOP) (**5**) with biphenyl-4-carboxaldehyde also proceeded gradually at 60 °C in THF solution and produced the same product **8** indicating a similar lability of the auxiliary phosphine ligands. While compound **8** was found to be thermally stable in the presence of benzonitrile, it slowly converted to a mixture of new products with one predominant component at 100 °C for 7 days in the presence of PHPh$_2$, either added exogenously or released *in situ* during the conversion of **5** to **8**. In the ^{31}P NMR spectrum of the reaction mixtures, the singlet signal of **8** at 206.7 ppm mostly converted to a new doublet at 211.7 ppm along with a broader singlet at 26.4 ppm (Scheme 8). Purification of the product proved difficult; nevertheless, single crystals (**9**) were obtained by slow evaporation of a saturated hexane solution at room temperature. The single-crystal X-ray crystallography analysis revealed the attachment of the biphenyl group to both the boron atom of the cluster and the metal center (Figure 7). Notably, the *ipso*-position of the biphenyl ligand, which was

Scheme 8. Formation of Complex 9[a]



8 9

[a]Unlabeled cluster vertices represent BH units.

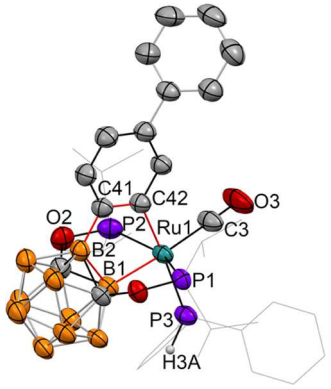


Figure 7. Displacement ellipsoid plot (50% probability) of **9**. Atoms belonging to isopropyl groups of the ligand arms and phenyl rings of the phosphine have been omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ru1−B1 = 2.116(3), Ru1−C42 = 2.134(3), Ru1−P3 = 2.379(1), B2−C41 = 1.546(4), C41−C42 = 1.405(4), B1−B2 = 1.823(4), P2−Ru1−P1 = 148.4(1), and B2−B1−Ru1 = 105.8(2).

attached to the metal center in **8**, is bound to the boron atom in **9**. The ruthenium center in **9** apparently activated the *adjacent*-C−H bond along with the loss of the bridging hydride from **8**. The carbonyl group remained attached *trans-* to the metal−boron bond. Additionally, one diphenylphosphine ligand becomes coordinated in **9**. The metal−boron bond length Ru1−B1 is 2.116(3) Å in **9**; the Ru1−C42 bond distance is 2.134(3) Å.

This type of biphenyl ring migration and activation was not observed in the reaction of the analogous benzonitrile-ligated carboryne complex **4** with biphenyl-4-carboxaldehyde even at elevated temperatures for prolonged periods of time, which resulted in only the formation of the decarbonylation product **8**. In the case of complex **5**, it is possible that apparent reductive elimination of the biphenyl and boryl from the metal center leads to the formation of the boron−carbon bond and the unsaturated low-valent ruthenium intermediate. Subsequently, either C−H bond activation of the proximal aryl ring or B−H bond activation of the bridging hydride occurs. The presence of diphenylphosphine in the reaction mixture may assist these steps, possibly acting as a base for the removal of the metal hydride as well as trapping the activation product. The observation of a signal corresponding to the cationic P(H)$_2$Ph$_2^+$ at 26.4 ppm during the formation of **9** from **8** in the presence of PHPh$_2$ corroborates this conjecture.[84]

Decarbonylation of aldehyde at the metal centers of BB-carborynes **4** and **5** can be contrasted with the behavior of CC-carboryne complexes of Zr and Sc or a ruthenium benzyne complex in the presence of aldehydes.[85−87] In those cases, insertion of the carbonyl group into metal−carbon bonds and the formation of cyclic alkoxy fragments have been observed instead. The difference in reactivity observed herein might be attributed to the reported instability of bora-acyl complexes toward decarbonylation where a direct metal-boryl bond is a more favorable configuration.[88,89]

CONCLUSIONS

The ruthenium dichloride complex (**3**) of a neutral pincer proligand POBBOP-(H)$_2$ was synthesized. This complex features two neutral borane groups B and H coordinated to the metal center. While the complex **3** is stable in weakly coordinating

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Organometallics XXXX, XXX, XXX−XXX

solvents, addition of stronger donors causes B−H bond activation and the formation of B−Ru bonds. From this starting material, the BB-carboryne complexes Ru(NCPh)$_2$(POBBOP) (**4**) containing auxiliary benzonitrile and Ru(PHPh$_2$)$_2$(POBBOP) (**5**) containing a diphenylphosphine ligand were prepared. The reactivity of these complexes was compared with that of the previously reported carbonyl-containing variant Ru(CO)$_2$(POBBOP) (**2**). We found that the lability of auxiliary ligand plays a significant role in the reactivity of metal−boron bonds of the BB>Ru metallacycle. The reaction of Ru(NCPh)$_2$(POBBOP) (**4**) with the terminal alkyne PhCCH led to the formation of the cycloaddition product **6** with the B−C═C−Ru−B cycle. In contrast, the reaction of Ru(CO)$_2$(POBBOP) with phenylacetylene led to deprotonation of the alkyne by the B−Ru bond and formation of B−H and Ru−C≡CPh groups. The reaction of Ru(NCPh)$_2$(POBBOP) (**4**) and diphenylphosphoryl azide led to the insertion of the nitrene into B−Ru bond, while Ru(CO)$_2$(POBBOP) did not react with the azide. The newly formed B−N bond in the insertion product **7** is short and closer to the bond length of B═N double bonds, implying some degree of π-bonding between the cluster and the exohedral nitrogen atom. The reaction of Ru(NCPh)$_2$(POBBOP) (**4**) and biphenylaldehyde C$_6$H$_5$−C$_6$H$_4$−C(O)H resulted in the formation of bridging borane B−H···Ru and decarbonylation of the aldehyde in complex **8**. The carbonyl analogue Ru(CO)$_2$(POBBOP) did not react with aldehydes, even under more forcing conditions. The reaction of Ru(PHPh$_2$)$_2$(POBBOP) (**5**) and C$_6$H$_5$−C$_6$H$_4$−C(O)H formed the decarbonylation product **8**, which, upon further heating, led to aryl group transfer to the boron atom of the cluster and the C−H bond activation of the aryl ring and the formation of C−Ru bond (**9**). These experimental results demonstrate differences in reactivity manifolds of the BB>Ru metallacycle introduced by the change in auxiliary ligands.

EXPERIMENTAL SECTION

All synthetic manipulations, unless stated otherwise, were carried out either in a nitrogen-filled VAC drybox or on a dual manifold Schlenk-style vacuum line. The solvents were sparged with nitrogen, passed through activated alumina, and stored over activated 4 Å m Linde-type molecular sieves. Benzene-d_6 was degassed and stored over activated 4 Å Linde-type molecular sieves. NMR spectra were recorded using Varian spectrometers at 400 (^{1}H), 500 (^{1}H), 100 (^{13}C), 126 (^{13}C), 162 (^{31}P), 203 (^{31}P) and 128 (^{11}B) MHz, reported in δ (parts per million) and referenced to the residual ^{1}H/^{13}C signals of the deuterated solvent or an external 85% phosphoric acid (^{31}P(δ): 0.0 ppm) and BF$_3$(Et$_2$O) (^{11}B(δ): 0.0 ppm) standards. *J* values are given in hertz.

(POBBOP)-H$_2$ (1,7-OP(*i*-Pr)$_2$-*m*-carborane) was prepared according to the previously reported literature procedure.[52] [Ru(*p*-cymene)Cl$_2$]$_2$, *m*-carborane (Katchem), P(CH(CH$_3$)$_2$)$_2$Cl, benzonitrile, diphenylphosphine, phenylacetylene, biphenyl-4-carboxaldehyde, diphenylphosphoryl azide, benzaldehyde, and potassium *tert*-butoxide were used as received.

Synthesis of RuCl$_2$(POBBOP-(H)$_2$) (3). 1,7-OP(*i*-Pr)$_2$-*m*-carborane (114 mg; 0.279 mmol) was dissolved in a mixture of THF and toluene (5 mL) and transferred to a Schlenk flask. [Ru(*p*-cymene)Cl$_2$]$_2$ (86 mg; 0.140 mmol; 0.5 equiv) was added to the reaction mixture and heated at 90 °C for 48 h. The resulting reddish-orange color solution was filtered inside the glovebox, and the volatiles were removed under vacuum from the filtrate. The resulting reddish-orange color solid was triturated with hexane (2 mL) and dried under vacuum. Subsequently, the solid was washed with diethyl ether (1 mL × 3) and then with hexane (1 mL × 3) and further dried under vacuum. Yield: 140 mg, 86%. ^{1}H (C$_6$D$_6$): δ 4.00−1.60 (br m, 8H, B*H*), 2.19 (m, 4H, P(C*H*(CH$_3$)$_2$)$_2$), 1.29 (m, 12H, P(CH(C*H*$_3$)$_2$)$_2$,), 1.08 (m, 12H, P(CH(C*H*$_3$)$_2$)$_2$,), −9.71 (q, 2H, B-*H*···Ru, $^1J_{B-H}$ = 111 Hz). ^{13}C{^{1}H} (C$_6$D$_6$): δ 111.1 (C$_2$B$_{10}$H$_8$), 29.0 (P(*C*H(CH$_3$)$_2$)$_2$), 16.6 (P(CH(*C*H$_3$)$_2$)$_2$), 15.9 (P(CH(*C*H$_3$)$_2$)$_2$). ^{11}B{^{1}H} (C$_6$D$_6$): δ −11.05 (*B*-H), −13.96 (*B*-H), −16.84 (*B*−H···Ru). ^{31}P{^{1}H} (C$_6$D$_6$): δ 196.88 (Ru-*P*). Found: C, 28.67; H, 6.49. Calcd. for C$_{14}$H$_{38}$B$_{10}$O$_2$P$_2$Cl$_2$Ru: C, 28.97; H, 6.60.

Synthesis of Ru(NCPh)$_2$(POBBOP) (4). The synthesis of Ru(NCPh)$_2$(POBBOP) complex was carried out in a similar manner to the synthesis of complex **3** above in a one-pot reaction with the addition of benzonitrile and a base without the isolation of the intermediate complex **3**. The ligand precursor 1,7-OP(^{i}Pr)$_2$-*m*-carborane (150 mg; 0.367 mmol) and [Ru(*p*-cymene)Cl$_2$]$_2$ (112 mg; 0.184 mmol; 0.5 equiv) was transferred to a Schlenk flask using a mixture of THF and toluene (5 mL). The reaction mixture was heated at 90 °C for 48 h. Benzonitrile (189 mg; 1.835 mmol; 5 equiv) was added to the subsequent solution and further heated the reaction mixture at 60 °C for 6 h. Finally, potassium *tert*-butoxide (86 mg; 0.771 mmol; 2.1 equiv) was added using THF (2 mL) to the reddish-orange color solution resulting in a color change to a dark reddish-brown color. The reaction mixture was stirred at room temperature for 72 h. The final reaction mixture was filtered inside the glovebox and volatiles were removed under vacuum from the filtrate resulting in a reddish-brown color solid. The solid was triturated with hexane (2 mL) and dried under vacuum. Next, the solid was washed with hexane (1 mL × 3) and further dried under vacuum to obtain a fine reddish-brown solid. The product was extracted from the solid using benzene (1 mL × 3). Volatiles were removed under vacuum to obtain a dark-red color solid which was triturated with hexane (2 mL) and further dried under vacuum. Yield: 227 mg, 87%. ^{1}H NMR (C$_6$D$_6$): δ 7.14−6.66 (m, 10H, C$_6$*H*$_5$-CN), 4.00−1.50 (br m, 8H, B*H*), 2.28 (m, 4H, P(C*H*(CH$_3$)$_2$)$_2$), 1.40 (m, 24H, P(CH(C*H*$_3$)$_2$)$_2$). ^{13}C{^{1}H} (C$_6$D$_6$): δ 132.0−126.1 (C$_6$H$_5$CN), 119.0 (C$_6$H$_5$CN), 116.7 (C$_6$H$_5$*C*N), 113.9 (C$_2$B$_{10}$H$_8$), 113.0 (C$_2$B$_{10}$H$_8$), 29.7 (P(*C*H(CH$_3$)$_2$)$_2$), 18.1 (P(CH(*C*H$_3$)$_2$)$_2$), 17.4 (P(CH(*C*H$_3$)$_2$)$_2$). ^{11}B{^{1}H} (C$_6$D$_6$): δ −3.43 (*B*-Ru), −13.67 (*B*-H), and −18.70 (*B*-H). ^{31}P{^{1}H} (C$_6$D$_6$): δ 207.43 (Ru-*P*). Found: C, 46.88; H, 6.84. Calcd. for C$_{28}$H$_{46}$B$_{10}$N$_2$O$_2$P$_2$Ru: C, 47.11; H, 6.50.

Synthesis of Ru(PHPh$_2$)$_2$(POBBOP) (5). Ru(NCPh)$_2$(POBBOP) complex (**4**) (35 mg; 0.049 mmol) was dissolved in THF (2 mL) and diphenylphosphine (10% w/w in hexane, 183 mg; 0.098 mmol; 2 equiv) was added to the solution. The reaction mixture was stirred for 5 min at room temperature. The color of the solution changed to a darker reddish-brown color. The reaction mixture was dried under vacuum to remove the volatiles to obtain a brownish-orange solid. The solid was triturated with hexane (2 mL) and dried under vacuum. The brown-orange solid was washed with hexane (1 mL × 3) and dried under vacuum. Subsequently, the product was extracted from the solid using diethyl ether (1 mL × 3). Volatiles were removed under vacuum to obtain a brown-orange solid which was triturated with hexane (2 mL) and dried under vacuum. Finally, further purification of the solid was done by washing with acetonitrile (1 mL × 3) and drying under vacuum. The final product was triturated with hexane (2 mL) and dried under vacuum to obtain a pale orange solid. Yield: 26 mg, 60%. ^{1}H NMR (C$_6$D$_6$): δ 7.98 (m, 8H, PH(C$_6$*H*$_5$)$_2$), 7.22 (br m, 2H, P*H*(C$_6$H$_5$)$_2$), 7.12 (m, 8H, PH(C$_6$*H*$_5$)$_2$), 7.03 (m, 4H, PH(C$_6$*H*$_5$)$_2$), 4.00−1.50 (br m, 8H, B*H*), 1.50 (m, 4H, P(C*H*(CH$_3$)$_2$)$_2$), 0.93 (m, 12H, P(CH(C*H*$_3$)$_2$)$_2$), 0.68 (m, 12H, P(CH(C*H*$_3$)$_2$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 137.1−129.7 (PH(*C*$_6$H$_5$)$_2$), 115.1 (C$_2$B$_{10}$H$_8$), 33.6 (P(*C*H(CH$_3$)$_2$)$_2$), 19.5 (P(CH(*C*H$_3$)$_2$)$_2$), 17.2 (P(CH(*C*H$_3$)$_2$)$_2$). ^{11}B{^{1}H} (C$_6$D$_6$): δ −1.18 (*B*-Ru), −12.18 (*B*-H), and −17.18 (*B*-H). ^{31}P{^{1}H} (C$_6$D$_6$): δ 195.03 (t, 2P, Ru-*P-donor arm*), 15.11 (br, 2P, Ru-*PHPh*$_2$). Found: C, 51.53; H, 6.91. Calcd. for C$_{38}$H$_{58}$B$_{10}$O$_2$P$_4$Ru: C, 51.87; H, 6.64.

Synthesis of Ru(NCPh)$_2$(HCCPh)(POBBOP) (6). Phenylacetylene (6.4 mg; 0.063 mmol; 1.5 equiv) was added to a solution of Ru(NCPh)$_2$(POBBOP) complex (**4**) (30 mg; 0.042 mmol) in THF (1 mL; with few drops of C$_6$D$_6$) in a J. Young valve. The reaction was carried out at room temperature, and the immediate formation of the complex **6** was confirmed by ^{31}P{^{1}H} NMR spectroscopy. The

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Organometallics XXXX, XXX, XXX−XXX

reaction mixture was filtered inside the glovebox, and the volatiles were removed from the filtrate under vacuum to obtain a brown-orange solid. The solid was triturated with hexane (2 mL) and dried under vacuum. Afterward, the solid was washed with hexane (1 mL × 3) and dried thoroughly under vacuum to obtain a dark-orange solid. Yield: 28.4 mg, 82%. ^{1}H (C_6D_6): δ 7.80−6.79 (m, 15H, −C_6H_5), 4.39 (s, 1H, Ph−C═C−H), 4.00−1.50 (br m, 8H, BH), 3.10 (m, 2H, P(CH(CH_3)$_2$)$_2$), 2.93 (m, 2H, P(CH(CH_3)$_2$)$_2$), 1.32 (m, 12H, P(CH(CH_3)$_2$)$_2$), 1.21 (m, 6H, P(CH(CH_3)$_2$)$_2$), 1.14 (m, 6H, P(CH(CH_3)$_2$)$_2$). ^{13}C{^{1}H} (C_6D_6): δ 132.3 (Ph−C═C−H), 131.8 (Ph-C═C−H), 129.2−125.3 (−C_6H_5), 113.3 (C_6H_5CN), 105.2 ($C_2B_{10}H_8$), 32.9 (P(CH(CH$_3$)$_2$)$_2$), 32.2 (P(CH(CH$_3$)$_2$)$_2$), 30.2 (P(CH(CH$_3$)$_2$)$_2$), 18.9 (P(CH(CH$_3$)$_2$)$_2$), 17.6 (P(CH(CH$_3$)$_2$)$_2$), 17.0 (P(CH(CH$_3$)$_2$)$_2$). ^{11}B{^{1}H} (C_6D_6): δ 11.77 (B-C), −1.19 (B-Ru), −14.91 (B-H), −18.36 (B-H), −23.28 (B-H). ^{31}P{^{1}H} (C_6D_6): δ 198.36 (Ru-P). Found: C, 53.68; H, 6.75. Calcd. for $C_{36}H_{52}B_{10}N_2O_2P_2Ru$: C, 52.99; H, 6.42. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

Synthesis of Ru(NCPh)$_2$(NP(O)(OPh)$_2$)(POBBOP) (7). Diphenylphosphoryl azide (12.7 mg; 0.046 mmol; 1.1 equiv) was added to a solution of Ru(NCPh)$_2$(POBBOP) complex (**4**) (30 mg; 0.042 mmol) in THF (1 mL; with few drops of C_6D_6) in a J. Young valve. The reaction was carried out at room temperature, and the immediate formation of complex **7** was confirmed by ^{31}P{^{1}H} NMR spectroscopy. The color of the reaction mixture changed from red-brown color to a darker brown color. The reaction mixture was filtered inside the glovebox and the volatiles were removed from the filtrate under vacuum to obtain a brown color solid. The solid was triturated with hexane (2 mL) and dried under vacuum. Subsequently, the solid was washed with diethyl ether (1 mL × 3) and then with hexane (2 mL × 3). The final product was dried under vacuum to obtain complex **7** as a brown solid. Yield: 33.8 mg, 83%. ^{1}H (C_6D_6): δ 7.94−6.71 (m, 20H, −C_6H_5), 4.00−1.50 (br m, 8H, BH), 3.65 (m, 2H, P(CH(CH$_3$)$_2$)$_2$), 2.97 (m, 2H, P(CH(CH$_3$)$_2$)$_2$), 1.55 (m, 6H, P(CH(CH_3)$_2$)$_2$), 1.40 (m, 6H, P(CH(CH_3)$_2$)$_2$), 1.34 (m, 6H, P(CH(CH_3)$_2$)$_2$), 1.24 (m, 6H, P(CH(CH_3)$_2$)$_2$). ^{13}C{^{1}H} (C_6D_6): δ 133.2−121.2 (−C_6H_5), 113.8 (C_6H_5CN), 102.1 ($C_2B_{10}H_8$), 32.2 (P(CH(CH$_3$)$_2$)$_2$), 19.0 (P(CH(CH$_3$)$_2$)$_2$), 18.3 (P(CH(CH$_3$)$_2$)$_2$), 17.8 (P(CH(CH$_3$)$_2$)$_2$), 17.5 (P(CH(CH$_3$)$_2$)$_2$). ^{11}B{^{1}H} (C_6D_6): δ 1.66 (B-N), −0.89 (B-Ru), −16.46 (B-H), −21.84 (B-H), −25.47 (B-H). ^{31}P{^{1}H} (C_6D_6): δ 193.68 (Ru-P), 3.55 (N-P). Found: C, 50.32; H, 5.43. Calcd. for $C_{40}H_{56}B_{10}N_3O_5P_3Ru$: C, 49.99; H, 5.87.

Synthesis of Ru(CO)($C_6H_4C_6H_5$)(POBBOP-H) (8). Biphenyl-4-carboxaldehyde (14 mg; 0.077 mmol; 1.1 equiv) was added to a solution of Ru(NCPh)$_2$(POBBOP) complex (**4**) (50 mg, 0.07 mmol) in THF (1 mL; with few drops of C_6D_6) in a J. Young valve. The reaction mixture was heated at 60 °C for 6 h. The color of the solution changed to a darker red color. The reaction mixture was filtered inside the glovebox and the volatiles were removed from the filtrate under vacuum to obtain a brown-orange solid. The solid was triturated with hexane (2 mL) and dried under vacuum. Finally, the solid was washed with hexane (1 mL × 3) and dried under vacuum to obtain the product. Yield: 29 mg, 60%. The residual Claisen−Tishchenko ester side-product could not be completely removed from the sample. ^{11}B{^{1}H} (C_6D_6): δ 1.36 (B-Ru), −13.11 (B-H), −17.24 (B-H), and −18.25 (B-H). ^{31}P{^{1}H} (C_6D_6): δ 206.69 (Ru-P).

Synthesis of Ru(CO)(C_6H_5)(POBBOP-H) (8b). The synthesis of complex **8b** was carried out analogously to that for complex **8** with the use of benzaldehyde. ^{1}H (C_6D_6): δ 8.08 (m, 2H, −C_6H_5), 7.02 (m, 1H, −C_6H_5), 6.90 (m, 2H, −C_6H_5), 4.00−1.60 (br m, 8H, BH), 2.72 (m, 2H, P(CH(CH$_3$)$_2$)$_2$), 1.94 (m, 2H, P(CH(CH$_3$)$_2$)$_2$), 0.96 (m, 12H, P(CH(CH_3)$_2$)$_2$), 0.82 (m, 6H, P(CH(CH_3)$_2$)$_2$), 0.32 (m, 6H, P(CH(CH_3)$_2$)$_2$), −6.44 (q, 1H, B-H···Ru, $^{1}J_{B-H}$ = 131 Hz). ^{13}C{^{1}H} (C_6D_6): δ 157.4 (Ru-C_6H_5), 145.9 (Ru-CO), 130.0−121.7 (−C_6H_5), 110.9 ($C_2B_{10}H_8$), 32.5 (P(CH(CH$_3$)$_2$)$_2$), 27.8 (P(CH(CH$_3$)$_2$)$_2$), 18.4 (P(CH(CH$_3$)$_2$)$_2$), 17.2 (P(CH(CH$_3$)$_2$)$_2$), 16.4 (P(CH(CH$_3$)$_2$)$_2$), 15.6 (P(CH(CH$_3$)$_2$)$_2$). ^{11}B{^{1}H} (C_6D_6): δ 1.66 (B-Ru), −12.59 (B-H), −17.06 (B-H), −17.74 (B-H). ^{31}P{^{1}H} (C_6D_6): δ 206.42 (Ru-P).

Synthesis of Ru(CO)(PHPh$_2$)($C_6H_3C_6H_5$)(POBBOP-H) (9). Biphenyl-4-carboxaldehyde (8 mg; 0.045 mmol, 1.0 equiv) was added to a solution of Ru(PHPh$_2$)$_2$(POBBOP) complex (**5**) (40 mg; 0.045 mmol) in THF (1 mL; with a few drops of C_6D_6) in a J. Young valve. The reaction mixture was heated at 70 °C for 16 h. The initial formation of complex **8** was observed in ^{31}P{^{1}H} NMR spectroscopy. Then, toluene and another 1 equiv of biphenyl-4-carboxaldehyde (8 mg; 0.045 mmol, 1.0 equiv) were added to the reaction mixture and heated at 100 °C for a prolonged period of time (7 days) which resulted in the formation of complex **9** along with other unidentified products. Volatiles were removed from the reaction mixture inside the glovebox under vacuum to obtain a dark-red solid. The solid was triturated with hexane (2 mL) and dried under vacuum. Subsequently, the solid was washed with hexane (1 mL × 3) and dried under vacuum to obtain a dark-orange solid (20 mg). Other unidentified products were present in the product. Single crystals of **9** were grown from a benzene/hexanes mixture.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.4c00225.

Characterization data (NMR spectra and crystallographic details) (PDF)

Accession Codes

CCDC 2357012−2357018 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, 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

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