ACCOUNTS
of chemical research

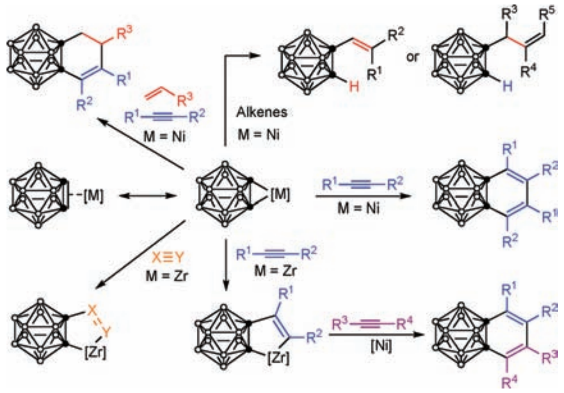
Transition Metal−Carboryne Complexes: Synthesis, Bonding, and Reactivity

ZAOZAO QIU, SHIKUO REN, AND ZUOWEI XIE*
Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong, People's Republic of China

RECEIVED ON DECEMBER 6, 2010

CONSPECTUS

The construction and transformation of metal−carbon (M−C) bonds constitute the central themes of organometallic chemistry. Most of the work in this field has focused on traditional M−C bonds involving tetravalent carbon: relatively little attention has been paid to the chemistry of nontraditional metal−carbon (M−C_{cage}) bonds, such as carborane cages, in which the carbon is hypervalent. We therefore initiated a research program to study the chemistry of these nontraditional M−C_{cage} bonds, with a view toward developing synthetic methodologies for functional carborane derivatives. In this Account, we describe our results in constructing and elucidating the chemistry of transition metal−carboryne complexes.



Our work has shown that the M−C_{cage} bonds in transition metal−carboranyl complexes are generally inert toward electrophiles, and hence significantly different from traditional M−C bonds. This lack of reactivity can be ascribed to steric effects resulting from the carboranyl moiety. To overcome this steric problem and to activate the nontraditional M−C_{cage} bonds, we prepared a series of group 4 and group 10 transition metal−carboryne complexes (where carboryne is 1,2-dehydro-*o*-carborane), because the formation of metallacyclopropane opens up the coordination sphere and creates ring strain, facilitating the reactions of M−C_{cage} bonds with electrophiles. Structural and theoretical studies on metal−carboryne complexes suggest that the bonding interaction between the metal atom and the carboryne unit is best described as a resonance hybrid of the M−C σ and M−C π bonds, similar to that observed in metal−benzyne complexes. The nickel−carboryne complex $(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)_2$ can (i) undergo regioselective [2 + 2 + 2] cycloaddition reactions with 2 equiv of alkyne to afford benzocarboranes, (ii) react with 1 equiv of alkene to generate alkenylcarborane coupling products, and (iii) also undergo a three-component [2 + 2 + 2] cyclotrimerization with 1 equiv of activated alkene and 1 equiv of alkyne to give dihydrobenzocarboranes.

The reaction of carboryne with alkynes is also catalyzed by Ni species. Subsequently, a Pd/Ni co-catalyzed [2 + 2 + 2] cycloaddition reaction of 1,3-dehydro-*o*-carborane with 2 equiv of alkyne was developed, leading to the efficient formation of C,B-substituted benzocarboranes in a single process. In contrast, the zirconium−carboryne species, generated in situ from $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$, reacts with only 1 equiv of alkyne or polar unsaturated organic substrates (such as carbodiimides, nitriles, and azides) to give monoinsertion metallacycles, even in the presence of excess substrates. The resultant five-membered zirconacyclopentenes, incorporating a carboranyl unit, are an important class of intermediates for the synthesis of a variety of functionalized carboranes. Transmetalation of zirconacyclopentenes with other metals, such as Ni and Cu, was also found to be a very useful tool for various chemical transformations.

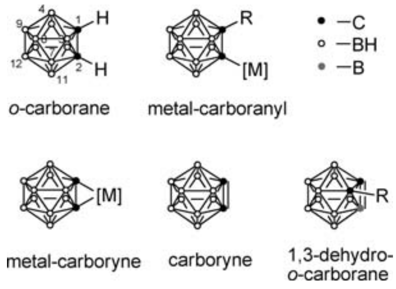
Studies of metal−carboryne complexes remain a relatively young research area, particularly in comparison to the rich literature of metal−benzyne complexes. Other transition metal−carborynes are expected to be prepared and structurally characterized as the field progresses, and the results detailed here will further that effort by providing easy access to a wide range of functionalized carborane derivatives.

Introduction

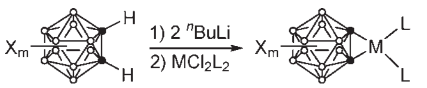
Carboranes are a class of boron hydride clusters in which one or more of the BH vertices are replaced by CH units (Chart 1). They are finding many applications in boron neutron capture therapy (BNCT),[1] in supramolecular design,[2] and as ligands for transition metals;[3] however, their unique structures make

Published on the Web 03/11/2011 www.pubs.acs.org/accounts
10.1021/ar100156f

CHART 1. Carborane Derivatives



SCHEME 1. Synthesis of Group 10 Metal−Carboryne Complexes



1

X = H, 9-I, 9,12-I$_2$, 3-Br, 3-Ph
L$_2$ = (PPh$_3$)$_2$, (PMe$_3$)$_2$, dppe
M = Ni, Pd, Pt

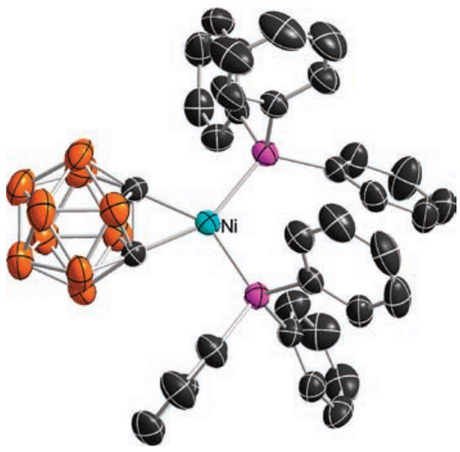
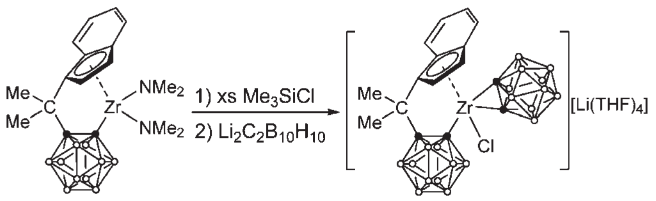


FIGURE 1. Molecular structure of (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$ (**1a**).

SCHEME 2. Synthesis of Zr−Carboryne Complex Anion



2

derivatization difficult. In general, substituted *o*-carboranes can be prepared using the following methods: (1) reaction of alkynes with decaborane,[4] (2) reaction of $Li_2C_2B_{10}H_{10}$ with electrophiles,[5] (3) electrophilic substitution at cage BH vertices,[6] and (4) capitation reaction of *nido*-$C_2B_9H_{11}^{2-}$ with boron halides.[7] For more complex carborane derivatives, such as 1,2-benzo-*o*-carboranes, a multistep procedure is required.[8] We noted however that carboryne (1,2-dehydro-*o*-carborane), a three-dimensional relative of benzyne (Chart 1), can react with alkenes, dienes, and alkynes in [2 + 2], [4 + 2] cycloaddition, and ene-reactions,[9] similar to those of benzyne,[10] to give a mixture of products. Although these reactions have potential for the single step preparation of functionalized carboranes, they are complex and do not proceed in a controlled manner. In view of the widespread use of transition metals in synthetic chemistry however, we wondered whether the use of such metals would result in these reactions taking place in an efficient and controlled manner; hence we initiated a research program to develop transition metal-mediated or -catalyzed synthetic methods for the functionalization of carboranes.

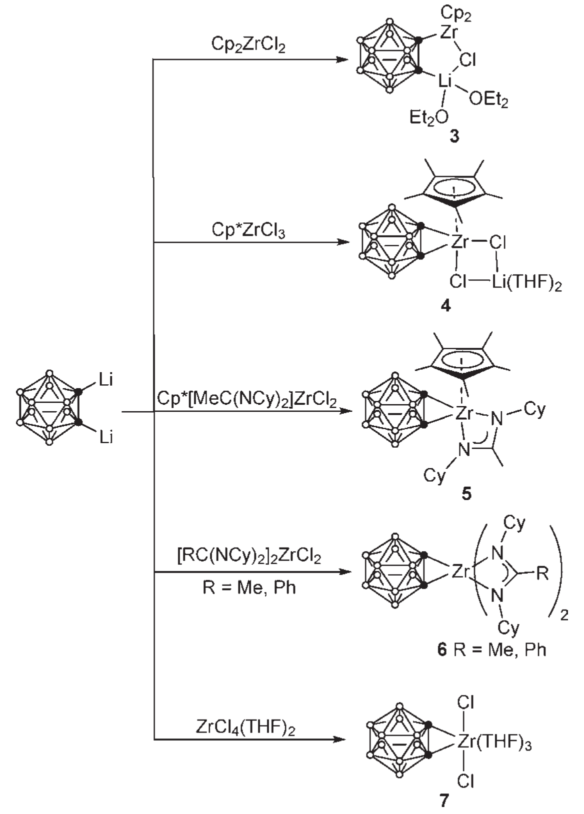
In our previous work, we had determined that, for steric reasons, the M−C_{cage} σ bonds (C_{cage} is the six-coordinate cage carbon, Chart 1) in metal−carboranyl complexes are generally inert toward electrophiles.[11] These results indicated that the reactivity of the M−C_{cage} σ bond is significantly different from that of traditional, tetravalent M−C σ bonds. To overcome this problem, we thought that the construction of a metallacyclopropane (metal−carboryne, Chart 1) would reduce the steric hindrance around the M−C_{cage} bond and also create the ring strain, thus increasing the reactivity of the M−C_{cage} bonds.

With this in mind, we prepared a series of group 4 and group 10 metal−carboryne complexes and found that they can react with various kinds of electrophiles in a controlled fashion and that these reactions are dependent upon both the nature of electrophiles and the electronic configurations of transition metal. This Account summarizes these recent developments in the synthesis, bonding, reactivity, and application of metal−carboryne complexes.

Synthesis

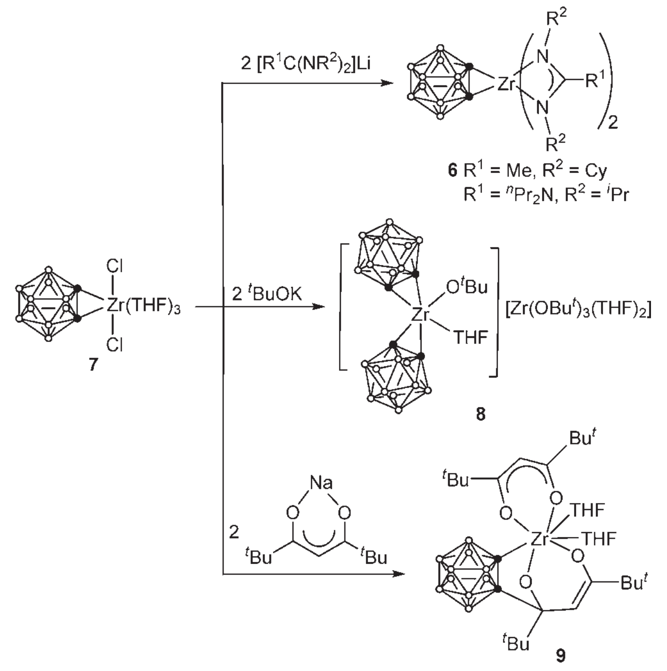
Because dilithiocarborane ($Li_2C_2B_{10}H_{10}$) can be easily prepared from the reaction of *o*-$C_2B_{10}H_{12}$ with 2 equiv of ^{n}BuLi, the salt metathesis between $Li_2C_2B_{10}H_{10}$ and metal halides was an obvious route for the construction of metal−carboryne complexes. In fact, the first example of a metal−carboryne, (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$, was communicated in 1973,[12] much earlier than the parent carboryne intermediate.[9a] This nickel−carboryne was characterized by single-crystal X-ray analyses but without any spectroscopic data, and no chemical properties of this complex have been reported.

SCHEME 3. Synthesis of Zirconium−Carboryne Complexes



Treatment of $Li_2C_2B_{10}H_{10-m}X_m$ with 1 equiv of MCl_2L_2 at 0 °C to room temperature was found to give the corresponding metal−carboryne complex (η^2-$C_2B_{10}H_{10-m}X_m$)ML_2 (M = Ni, Pd, Pt; X = Br, I, Ph; $m = 0, 1, 2$; $L_2 = (PPh_3)_2$, $(PMe_3)_2$, dppe (1,2-bis(diphenylphosphino)ethane)) in 20%−83% isolated yields (Scheme 1).[13] These complexes all have similar solid-state structures, in which the metal atom is bonded to two cage carbon atoms and coordinated to two phosphorus atoms in a square-planar geometry. Figure 1 shows the representative structure of (η^2-$C_2B_{10}H_{10}$)$Ni(PPh_3)_2$ (**1a**). The C_{cage}−C_{cage} bond distances in group 10 transition metal−carboryne complexes are in the range 1.52−1.57 Å and the average Ni−C_{cage} distances fall in the range 1.91−1.94 Å. It is interesting to note that the shortest C_{cage}−C_{cage} distance of 1.523(3) Å, observed in (η^2-3-C_6H_5-1,2-$C_2B_{10}H_9$)$Ni(PPh_3)_2$, is associated with the longest Ni−C_{cage} distance of 1.937(2) Å, which is consistent with that observed in metal−alkyne(alkene) π complexes.[14] It is also noted that the coordinated phosphines in these complexes are labile and can be replaced by other Lewis bases such as dppe, $P(OEt)Ph_2$, $P(OEt)_3$, and PCy_3, which is very important for subsequent reactions.

SCHEME 4. Reaction of Dichlorozirconium−Carboryne with Nucleophiles



Following a similar synthetic route, the first example of an early transition metal−carboryne complex, [{η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$}$ZrCl$($\eta^3$-$C_2B_{10}H_{10}$)][$Li(THF)_4$] (**2**), was prepared in 2003 (Scheme 2).[15] However many attempts to remove the chloro ligand, for the preparation of a neutral complex, using chloride abstracting reagents were not successful. It was then suggested that the replacement of the π, σ constrained-geometry ligand $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ by two cyclopentadienyl (Cp^-) ligands would meet the electronic requirements of the Zr atom, leading to the formation of a neutral complex. Treatment of Cp_2ZrCl_2 with 1 equiv of $Li_2C_2B_{10}H_{10}$ in ether gave the ate-complex Cp_2Zr(μ-Cl)(μ-$C_2B_{10}H_{10}$)$Li(OEt_2)_2$ (**3**) instead of the expected Cp_2Zr(η^2-$C_2B_{10}H_{10}$) (Scheme 3).[16] Complex **3** can be viewed as a precursor of zirconocene−carboryne Cp_2Zr(η^2-$C_2B_{10}H_{10}$). It is believed that the presence of two Cp ligands creates a very crowded environment around the Zr atom, which may destabilize the Zr−carboryne species; hence a monocyclopentadienylzirconium chloride, Cp^*ZrCl_3 ($Cp^* = C_5Me_5$), was chosen as the starting material. Reaction of Cp^*ZrCl_3 with 1 equiv of $Li_2C_2B_{10}H_{10}$ in THF afforded the ate-complex Cp^*(η^2-$C_2B_{10}H_{10}$)Zr(μ-$Cl)_2Li(THF)_2$ (**4**) with a three-membered zirconacyclopropane ring.[17] This result indicates that the monocyclopentadienyl ligand does not meet the electronic and steric requirements of the Zr atom. We then assumed that a proper combination of the π ligands might allow the preparation of neutral complexes. Equimolar reactions of

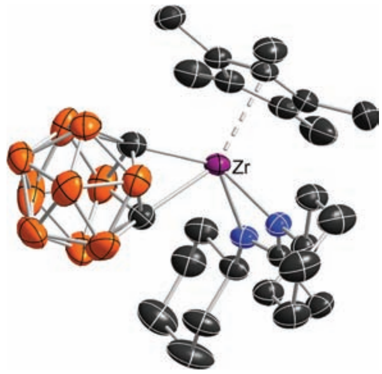
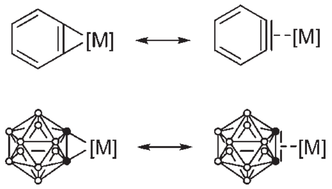


FIGURE 2. Molecular structure of complex **5**.

CHART 2. Bonding Interactions between Metal and Carboryne



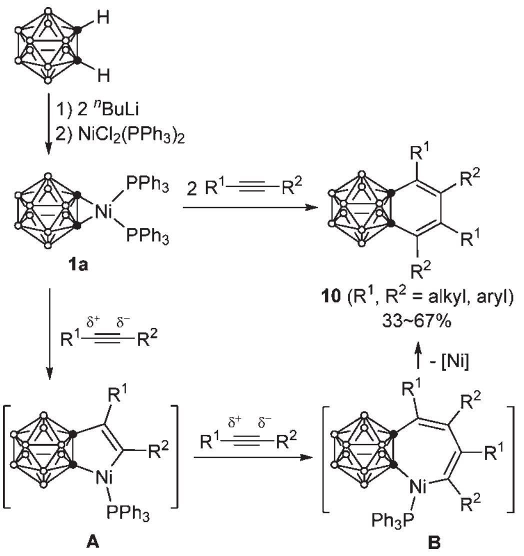
Cp*[η^2-CyNC(Me)NCy]ZrCl$_2$ (Cy = cyclohexyl), [η^2-RC(NCy)$_2$]$_2$ ZrCl$_2$, and ZrCl$_4$(THF)$_2$ with Li$_2$C$_2$B$_{10}$H$_{10}$ generated the neutral species Cp*[η^2-CyNC(Me)NCy]Zr(η^2-C$_2$B$_{10}$H$_{10}$) (**5**), [η^2-RC(NCy)$_2$]$_2$Zr(η^2-C$_2$B$_{10}$H$_{10}$) (**6**, R = Me, Ph), and (η^2-C$_2$B$_{10}$H$_{10}$) ZrCl$_2$(THF)$_3$ (**7**), respectively (Scheme 3).[17] Complex **7** should be a good starting material for further reactions because it contains two chloro groups, and in fact treatment of **7** with 2 equiv of [η^2-R^{1}C(NR^2)$_2$]Li produced [η^2-R^{1}C(NR^2)$_2$]$_2$Zr (η^2-C$_2$B$_{10}$H$_{10}$) (**6**) (R^1 = Me, R^2 = Cy; R^1 = ^{n}Pr$_2$N, R^2 = ^{i}Pr) in high yields. Reaction of **7** with 2 equiv of ^{t}BuOK led to the isolation of an ionic complex, [(η^2-C$_2$B$_{10}$H$_{10}$)$_2$Zr(O^{t}Bu)(THF)] [Zr(OBu^t)$_3$(THF)$_2$] (**8**). In contrast, reaction of **7** with 2 equiv of [^{t}BuCOCHCO^{t}Bu]Na gave an unexpected product, [σ:σ:σ-{^{t}BuC(O)=CHC(^{t}Bu)(O)C$_2$B$_{10}$H$_{10}$}]Zr(η^2-^{t}BuCOCHCOBu^t)(THF)$_2$ (**9**) (Scheme 4), though no pure products were isolated from the reactions of **7** with 1 equiv of Li$_2$C$_2$B$_{10}$H$_{10}$ or either 1 or 2 equiv of CpNa.[17] These results show that a proper selection of the ligands is important for the preparation of neutral Zr−carboryne complexes.

Most of the Zr−carboryne complexes were structurally characterized, and the structure of **5**, shown in Figure 2, is a typical representative. The C$_{\text{cage}}$−C$_{\text{cage}}$ distances range from 1.61−1.71 Å, and the average Zr−C$_{\text{cage}}$ distances fall in the range 2.26−2.35 Å.

Bonding

It is found that the C$_{\text{cage}}$−C$_{\text{cage}}$ bond distances (1.52−1.57 Å) in Ni−carboryne complexes are generally 0.1 Å shorter than those observed in the Zr−carboryne complexes (1.61−1.71 Å) with the shortest C$_{\text{cage}}$−C$_{\text{cage}}$ bonds being associated with the longest M−C$_{\text{cage}}$ ones. Such a phenomenon is also observed in metal−alkyne π complexes.[14] To understand the bonding interactions between the metal atom and the carboryne ligand, DFT calculations were performed on a Zr−carboryne model complex. The results suggest that the bonding interactions are best described as a resonance hybrid of both the M−C σ and M−C π bonds (Chart 2),[15] similar to those described for metal−benzyne complexes.[18] It is believed that the Zr(II) has a higher tendency than Ni(0) to donate its d electrons to the π* orbital of the carboryne ligand,[13,19] resulting in the much longer C$_{\text{cage}}$−C$_{\text{cage}}$ bond distances observed in Zr−carboryne complexes. In other words, the interactions between the Ni atom and carboryne have more π character than those observed in Zr−carboryne complexes, which facilitates the reactivity studies on these metal complexes.

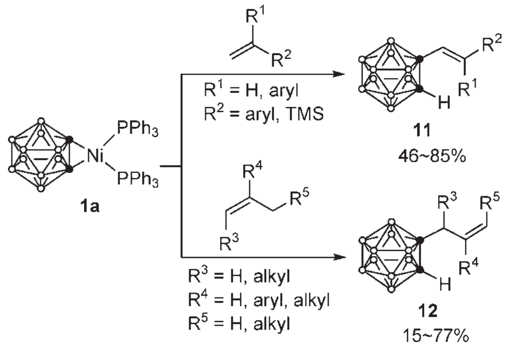
SCHEME 5. Reaction of Nickel−Carboryne with Alkynes



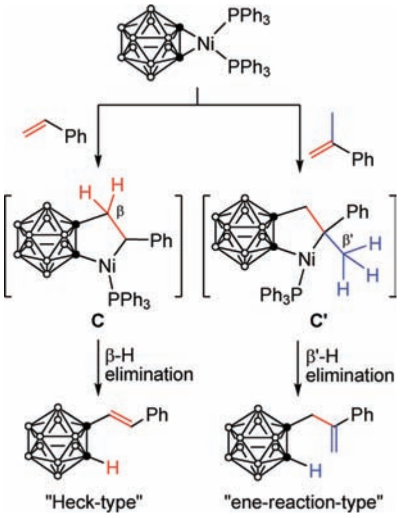
Reactivity

[2 + 2 + 2] Cycloaddition of Ni−Carboryne with Alkynes. In view of the analogous behavior of nickel−benzyne and nickel−carboryne complexes, we envisaged that the latter might react with unsaturated substrates in a similar manner to the reactions of nickel−benzynes with alkynes to generate substituted naphthalenes.[20] In fact, treatment of (η^2-C$_2$B$_{10}$H$_{10}$) Ni(PPh$_3$)$_2$ (**1a**) with internal alkynes R^{1}C≡CR^2 gave highly substituted 1,2-benzo-*o*-carboranes 1,2-[C(R^1)=C(R^2)C(R^1)=C(R^2)] −1,2-C$_2$B$_{10}$H$_{10}$ (**10**) via a [2 + 2 + 2] cycloaddition (Scheme 5).[21] Steric factors play an important role in the

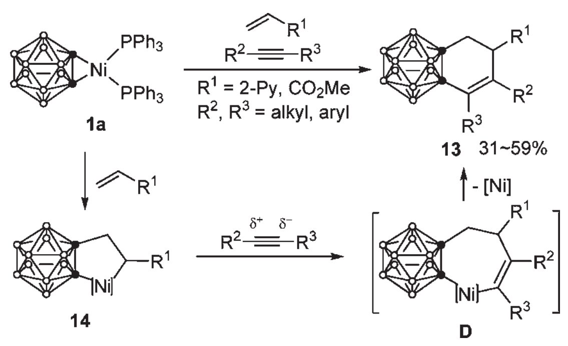
SCHEME 6. Reaction of Nickel–Carboryne with Alkenes



SCHEME 7. Proposed Mechanism for the Formation of Alkenylcarboranes



SCHEME 8. Nickel-Mediated Three-Component [2 + 2 + 2] Cycloaddition Reaction of Carboryne, Alkenes, and Alkynes



reactions, with the sterically less hindered linear dialkylalkynes producing better yields than phenyl- and *tert*-butyl-substituted ones.

Important mechanistic information is obtained through the exclusive formation of the head-to-tail product in the reaction with unsymmetrical aryl alkynes, suggesting that the insertion regioselectivity is determined by the polarity of the alkyne.[20a,22] The formation of **10** can be rationalized by the sequential insertion of alkynes into the Ni–C bond, followed by reductive elimination (Scheme 5). The first insertion into the Ni–C_{cage} bond in **1a** gives a nickelacyclopentene intermediate **A**. The exclusive formation of the head-to-tail products suggests that the insertion of the second equivalent of alkyne into the Ni–C_{vinyl} bond is strongly preferred over the Ni–C_{cage} bond due to steric effects, leading to the regioselective products.

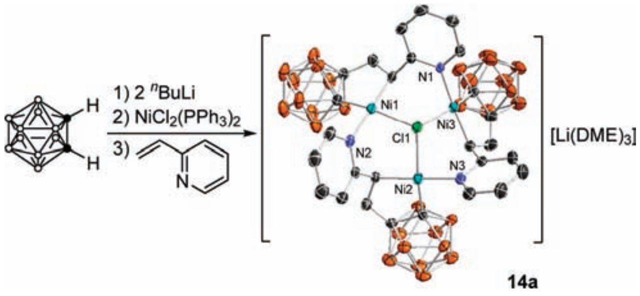
Compared with the reactions of Ni–benzyne with alkynes, those of Ni–carboryne have a limited substrate scope but higher regioselectivity. Terminal alkynes do not react with Ni–carboryne since they can protonate the Ni–carboryne complex, also those containing an ester group undergo self-trimerization in the presence of Ni(0).[21] On the other hand, large steric effects imposed by carborane cage make such reactions highly regioselective.

Coupling Reactions of Ni–Carboryne with Alkenes. Complex **1a** reacted with alkenes to afford the C–C coupling alkenylcarborane products **11** or **12**, in moderate to very good yields with excellent regio- and stereoselectivity (Scheme 6).[23] For substituted styrenes, the "Heck-type" of products **11** were single regioisomers. In contrast, the "ene-reaction-type" of products **12** were isolated for aliphatic alkenes and α-methylstyrene. No double insertion products were observed and bulky alkenes such as *cis*- and *trans*-stilbene did not undergo this reaction.

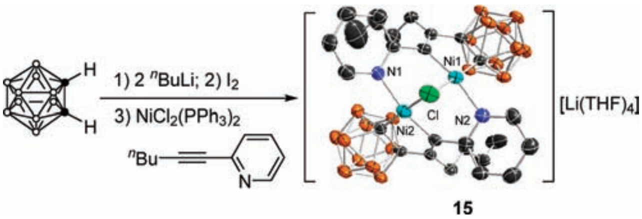
It was noteworthy that treatment of **1** with cyclohexene gave 1-(2-cyclohexen-1-yl)-*o*-carborane in 67% yield, which is much higher than the 10–20% yield from the direct reaction of carboryne (generated *in situ*) with cyclohexene.[9a] Furthermore, **1** did not react with anthracene, furan, or thiophene, whereas these 4π systems reacted readily with carboryne to give [4 + 2] cycloaddition products.[9] These results suggest that carboryne and Ni–carboryne have different chemical properties.

Scheme 7 shows the plausible mechanism for the formation of coupling products. Coordination and insertion of the alkene give a five-membered nickelacycle **C** or **C′**. The regioselectivity observed in the reaction can be ascribed to the large steric effect of the carborane moiety. β-H or β'-H elimination prior to the insertion of the second equivalent of alkene and reductive elimination produces alkenylcarboranes, 1-[HC=CH(Ph)]–1,2-$C_2B_{10}H_{11}$ ("Heck-type" product) or 1-[CH_2C(Ph)=CH_2]–1,2-$C_2B_{10}H_{11}$ ("ene-reaction-type" product). It is also observed that the ring strain makes β-H elimination more

SCHEME 9. Synthesis of Nickelacyclopentane Intermediate



SCHEME 10. Synthesis of Nickelacyclopentene Intermediate

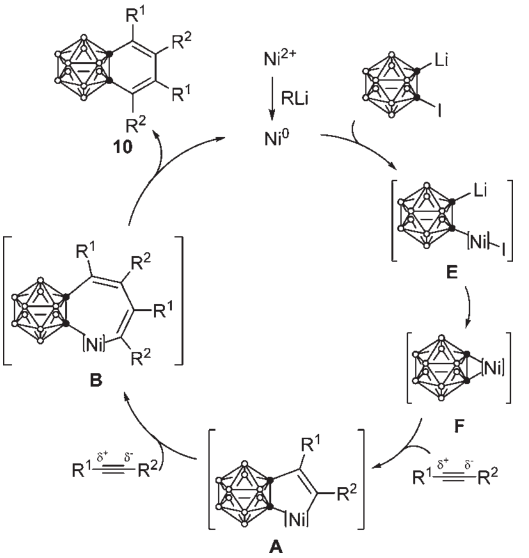


difficult than β'-H elimination.[24] This mechanism is supported by a labeling experiment; treatment of **1** with styrene-d_3 in THF at 90 °C gave 1-[DC=CD(Ph)]–2-D–1,2-$C_2B_{10}H_{10}$ with >95% deuterium incorporation.

[2 + 2 + 2] Cycloaddition of Ni–Carboryne with Activated Alkenes and Alkynes. In the reaction of **1a** with activated alkenes such as methyl acrylate and 2-vinylpyridine, only the alkylcarboranes 1-[$CH_2CH_2(CO_2Me)$]–1,2-$C_2B_{10}H_{11}$ and 1-[CH_2CH_2(*o*-C_5H_4N)]–1,2-$C_2B_{10}H_{11}$ were obtained after hydrolysis. This result implies that the donor atom of the olefin may stabilize the five-membered nickelacyclopentane intermediates, preventing β-H elimination reactions. These intermediates can readily undergo three-component [2 + 2 + 2] cycloaddition reactions with alkynes to give dihydrobenzocarboranes **13** (Scheme 8). This reaction can be carried out in one-pot because activated alkenes are much more reactive than alkynes toward Ni–carboryne. These techniques result in a synthetic process that is capable of excellent control over the chemo- and regioselectivity of the dihydrobenzocarborane products.[25]

The key intermediate, nickelacyclopentane **14a**, was isolated from the reaction of **1** with 2-vinylpyridine and structurally confirmed by X-ray analysis (Scheme 9). Treatment of **14a** with 3-hexyne afforded the expected dihydrobenzocarborane in >90% yields. Accordingly, the formation of product **13** can be rationalized by the sequential insertion of alkene and alkyne, as illustrated in Scheme 8, with the electronic effect playing a dominant role in controlling the regioselectivity.[20a,22] Alkynes insert selectively into the Ni–C_{alkyl} bond of the nickelacyclopentane leaving the Ni–C_{cage} bond intact. This work furnishes a new method of assembling substituted dihydrobenzocarboranes from very simple molecules in a single operation.

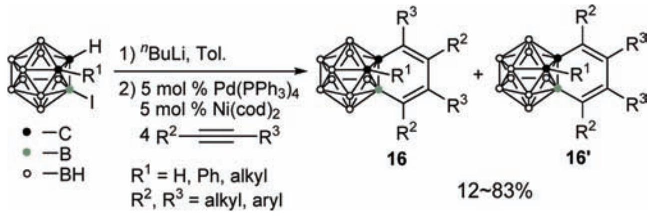
SCHEME 11. Proposed Mechanism for Nickel-Catalyzed [2 + 2 + 2] Cycloaddition



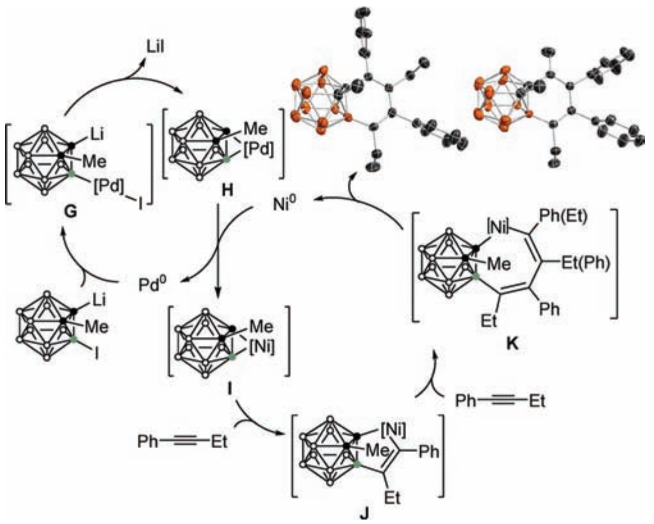
Ni-Catalyzed [2 + 2 + 2] Cycloaddition of Carboryne with Alkynes. In the above Ni-mediated reactions of carboryne with unsaturated substrates, a stoichiometric amount of the Ni reagent is required and a Ni(0) species is the end metal complex. Benzyne undergoes Ni-catalyzed reactions with alkenes or alkynes,[26] so consideration was given to producing a catalytic cycle by making use of the Ni(0) species produced via appropriate design of the starting material. We anticipated that the carboryne precursor, 1-iodo-2-lithiocarborane,[9f] might undergo oxidative addition on Ni(0) to give, after elimination of LiI, the Ni–carboryne complex required for a catalytic cycle.[27] Screening experiments suggested that $NiCl_2(PPh_3)_2$ was the best catalyst, although all nickel complexes showed some catalytic activity in [2 + 2 + 2] reactions. Reaction of 1-I-2-Li-1,2-$C_2B_{10}H_{10}$ with 2 equiv of alkynes in the presence of 20 mol % of $NiCl_2(PPh_3)_2$ in hot toluene gave [2 + 2 + 2] cycloaddition products, 1,2-benzo-*o*-carboranes, which were isolated in yields very comparable to those of stoichiometric reactions. The yield drops significantly, however, if the catalyst loading is reduced from 20 mol % to 10 mol %. It is also noted that internal diynes can undergo these [2 + 2 + 2] cycloaddition reactions, giving the desired products with a good fused-ring size tolerance.

After isolation and structural characterization of the monoalkyne insertion species, nickelacyclopentene **15**

SCHEME 12. Pd/Ni-Cocatalyzed [2 + 2 + 2] Cycloaddition of 1,3-Dehydro-*o*-carborane with Alkynes



SCHEME 13. Proposed Mechanism of Pd/Ni-Cocatalyzed [2 + 2 + 2] Cycloaddition



(Scheme 10),[27] the mechanism of the catalytic cycle shown in Scheme 11 was proposed. The catalysis is likely to be initiated by Ni(0) species generated from the reduction of Ni(II) by the lithiocarborane salt.[28] Oxidative addition of C_{cage}—I bond on Ni(0), followed by the elimination of LiI affords Ni—carboryne intermediate **F**; then sequential insertion of alkynes into the Ni—C bond produces the seven-membered nickelacycle **B**. Reductive elimination yields the cycloaddition product **10** and regenerates the Ni(0) species to complete the catalytic cycle.

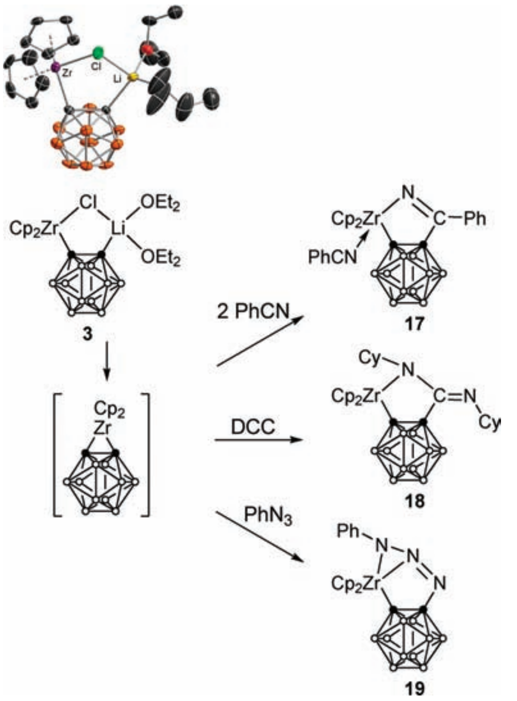
Pd/Ni Cocatalyzed [2 + 2 + 2] Cycloaddition of 1,3-Dehydro-*o*-carborane with Alkynes. Having achieved the aforementioned catalytic process, one question that arose was whether this strategy could be extended to the unknown species 1,3-dehydro-*o*-carborane (Chart 1). Experimental results show that unlike 1-Li-2-I-1,2-$C_2B_{10}H_{10}$,[9f] 1-Li-3-I-1,2-$C_2B_{10}H_{10}$ is very thermally stable, and no decomposition is observed after heating in toluene for several days. Taking into account the fact that the cage B—I bond can undergo oxidative addition in the presence of Pd(0),[6] we anticipated that oxidative addition of the cage B—I in 1-Li-3-I-1,2-$C_2B_{10}H_{10}$ on Pd(0), followed by subsequent elimination of LiI, would afford the target complex Pd-1,3-dehydro-*o*-carborane. Indeed the almost quantitative yield of 1-methyl-*o*-carborane obtained by heating 1-Li-2-Me-3-I-1,2-$C_2B_{10}H_9$ in the presence of 5 mol % of $Pd(PPh_3)_4$, using toluene as a solvent, can be ascribed to the decomposition of the resultant metal complex Pd-2-methyl-1,3-dehydro-*o*-carborane at high temperatures. No 1-methyl-*o*-carborane was detected at reaction temperatures below 70 °C, suggesting that a high temperature is essential for the oxidative addition of B—I on Pd(0) to proceed. Unlike (η^2-1,2-*o*-$C_2B_{10}H_{10}$)$Pd(PPh_3)_2$, (η^2-1,3-*o*-$C_2B_{10}H_9$Me)$Pd(PPh_3)_2$ cannot be isolated by an analogous process because it is not stable at the high reaction temperature; however, this reactive intermediate can be trapped by alkynes, leading to the formation of the [2 + 2 + 2] cycloaddition products 1,3-benzo-*o*-carboranes, **16**/**16**′ (Scheme 12).[29] It is noted that the addition of a Ni(0) species to the Pd catalyst can significantly accelerate the above reactions and a combination of 5 mol % of $Pd(PPh_3)_4$ with 5 mol % of $Ni(cod)_2$ exhibits the highest catalytic activity.

Both aliphatic and aromatic alkynes, as well as diynes, can undergo such [2 + 2 + 2] cycloaddition reactions, and steric factors are found to play a crucial role. No cycloaddition reaction proceeded, for example, with sterically demanding alkynes bearing trimethylsilyl or *o*-tolyl groups. Alkynes bearing carbonyl groups also did not undergo this reaction because they reacted with the carboryne precursor 1-Li-2-Me-3-I-1,2-$C_2B_{10}H_9$.

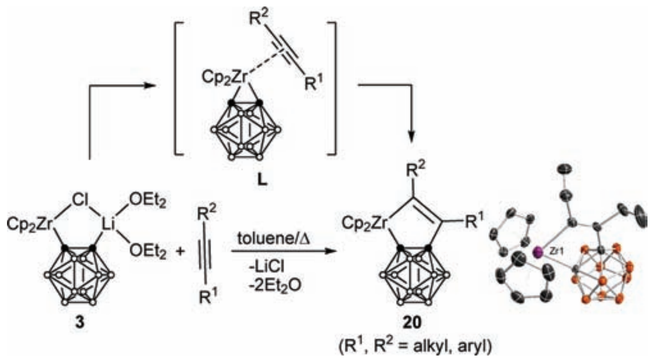
A cooperative mechanism involving two catalytic cycles, in which each metal plays its own role, is proposed in Scheme 13. Since Ni(0) can hardly insert into the B—I bond, the Pd-1,3-dehydro-*o*-carborane **H** is formed via oxidative addition of B—I on Pd(0) followed by subsequent LiI elimination. Because a two-component system is much more effective in catalyzing the reaction of 1,3-dehydro-*o*-carborane with alkynes than using Pd on its own, a transmetalation process between Pd and Ni may occur, affording the more reactive nickel-1,3-dehydro-*o*-carborane **I**.[30] In the reaction with PhC≡CEt, the electronically controlled regioselective insertion of an unsymmetrical alkyne[20a,22] into the Ni—B bond gives the nickelacyclopentene intermediate **J**. Subsequent insertion of the second equiv of PhC≡CEt into the Ni—C_{vinyl} bond, in both head-to-tail and head-to-head manners, followed by reductive elimination yields the final products. It is postulated that the insertion of alkynes into the M—C_{cage} bond in **J** is prohibited due to steric reasons.

The alkyne insertion in the above reactions can be viewed as a nucleophilic attack of the M—C/B σ-bond (the

SCHEME 14. Reaction of Zr−Carboryne with Polar Unsaturated Substrates

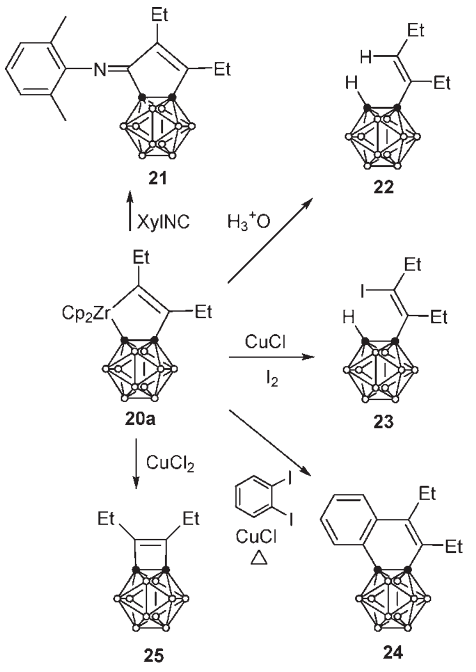


SCHEME 15. Reaction of Zr−Carboryne with Alkynes



bonding electron pair) on one of the two alkyne carbons. The absence of 2-Me-1,3-[EtC=C(C_6H_5)—C(Et)=C(C_6H_5-)]−1,2-$C_2B_{10}H_{10}$ in the products indicates the exclusive insertion of the first equivalent of alkyne into the Ni−B bond with electronically controlled regioselectivity, which is consistent with the M−B bond being much more nucleophilic than the M−C bond.[31] The relatively higher reactivity of the Ni species could be explained by the Pd−B bond being stronger than the Ni−B bond or perhaps by the Ni−B bonding pair being more nucleophilic than the Pd−B.[31] This work offers a new method for the cage B-functionalization of carboranes and demonstrates that metal−1,3-*o*-carborynes can be viewed as a new kind of boron nucleophile.

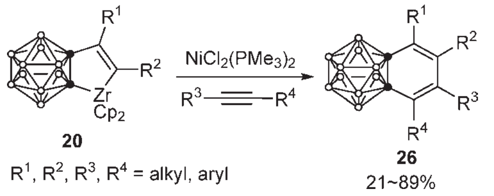
SCHEME 16. Reactivity of Zirconacyclopentene



Reaction of Zirconocene−Carboryne with Polar Unsaturated Molecules. As described above, the nature of the metal has a large effect on the bonding interactions between the metal atom and carboryne unit,[13,17] and this in turn influences their chemical properties. The Ni−carboryne complexes react well with alkynes and alkenes but are inert toward polar unsaturated molecules such as nitriles and carbodiimides. On the other hand, the Zr−carboryne reacts with a variety of polar unsaturated organic molecules. For example, treatment of the zirconocene−carboryne precursor, $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**3**), with PhCN, Cy—N=C=N—Cy (DCC), and PhN_3 gave the corresponding monoinsertion products, zirconacycles $Cp_2Zr[\sigma{:}\sigma\text{-}N{=}C(Ph)(C_2B_{10}H_{10})](PhCN)$ (**17**), $Cp_2Zr[\sigma{:}\sigma\text{-}CyNC({=}NCy)(C_2B_{10}H_{10})]$ (**18**), and $Cp_2Zr[\eta^2{:}\sigma\text{-}(PhNN{=}N)(C_2B_{10}H_{10})]$ (**19**), respectively, in moderate to high yields (Scheme 14).[16] It should also be noted that, even in the presence of excess substrate, **3** reacted with only 1 equiv of the unsaturated molecule. These reactions may proceed via the intermediate $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$, followed by the insertion of polar unsaturated molecules.

Reaction of Zirconocene−Carboryne with Alkynes. Complex **3** can also react with various alkynes to form five-membered zirconacyclopentenes, 1,2-[$Cp_2ZrC(R){=}C(R)$]−1,2-$C_2B_{10}H_{10}$ (**20**) (Scheme 15).[32] Steric factors are important in these reactions, which occur with symmetrical and unsymmetrical alkynes bearing alkyl or aryl substituents.

SCHEME 17. Reaction of Zirconacyclopentene with Alkynes in the Presence of $NiCl_2(PMe_3)_2$

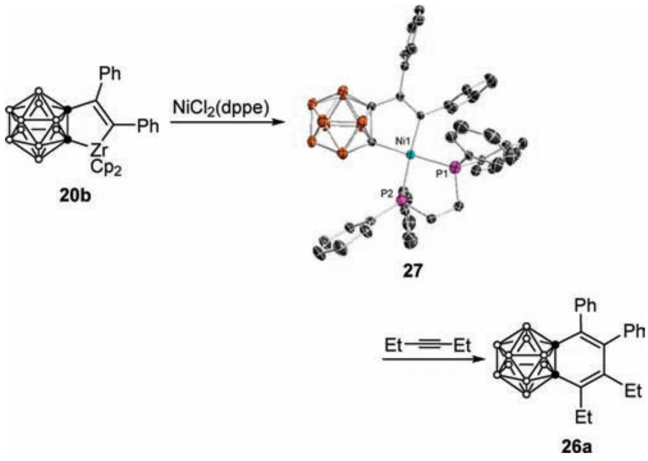


The regioselectivity of the insertion product is generally determined by the polarity of the alkyne, and in case of unsymmetrical alkyl alkynes, both regioisomers are obtained. In contrast to Ni−carborynes, only monoinsertion products were isolated even after prolonged heating in the presence of an excess amount of alkynes. A reaction pathway for the formation of complexes **20**, involving Zr−carboryne $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$, is proposed (Scheme 15).

These complexes are very useful starting materials for the preparation of functionalized carboranes. For example, upon refluxing in toluene, 2,6-$(CH_3)_2C_6H_3NC$ readily inserted into the Zr−C_{vinyl} bond of 1,2-[$Cp_2ZrC(Et)$=C(Et)]−1,2-$C_2B_{10}H_{10}$.[33] to form an insertion product 1,2-[(2′,6′-$Me_2C_6H_3N$=)CC(Et)=C(Et)]−1,2-$C_2B_{10}H_{10}$ (**21**) as outlined in Scheme 16. Hydrolysis of **20a** under acidic conditions afforded the alkenylcarborane 1-[HC(Et)=C(Et)]−1,2-$C_2B_{10}H_{11}$ (**22**). Reaction of **20a** with I_2 in the presence of CuCl generated a monoiodosubstituted carborane 1-[CI(Et)=C(Et)]−1,2-$C_2B_{10}H_{11}$ (**23**). Reaction of **20a** with *o*-diiodobenzene in the presence of CuCl produced naphthalocarborane 1,2-[*o*-C_6H_4C(Et)=C(Et)]−1,2-$C_2B_{10}H_{10}$ (**24**). Treatment of **20a** with $CuCl_2$ in toluene at 80 °C gave the C−C coupling product 1,2-[C(Et)=C(Et)]−1,2-$C_2B_{10}H_{10}$ (**25**). These results indicate that zirconacyclopentenes incorporating a carboranyl unit (**20**) resemble their analogues zirconacyclopentadienes Cp_2Zr[C(R)=C(R)—C(R)=C(R)] in some reactions.[34] On the other hand, complexes **20** have unique properties of their own due to the presence of the highly sterically demanding carboranyl unit.

Zr/Ni Co-mediated [2 + 2 + 2] Cycloaddition of Carboryne with Two Different Types of Alkynes. Previous work showed that nickel can mediate, or catalyze, [2 + 2 + 2] cycloaddition of carboryne with 2 equiv of alkynes to afford 1,2-benzo-*o*-caboranes with four identical substituents on the butadiene fragment[21,27] and that no selectivity was observed if two different kinds of alkynes were used in the reaction system. We noted that zirconacyclopentenes **20** were inert toward alkynes whereas the corresponding nickelacyclopentenes were very reactive toward alkynes, so the question arose as to whether transmetalation of zirconacyclopentenes to nickel[35] could result in the formal three-component [2 + 2 + 2] cycloaddition of carboryne with two types of alkynes.

SCHEME 18. Synthesis and Reaction of Transmetalation Intermediate



Reaction in hot toluene of **20** with alkynes in the presence of a stoichiometric amount of $NiCl_2(PMe_3)_2$ afforded the expected 1,2-benzo-*o*-caborane **26** (Scheme 17).[36] Both alkyl and aryl alkynes work well except for those containing ester and amino groups. Unsymmetrical alkynes produce two regioisomers in ratios apparently dependent on steric and electronic factors.

The transmetalation of zirconacycle to nickel is unambiguously supported by the isolation and structural characterization of the nickelacyclopentene 1,2-[(dppe)NiC(Ph)=C(Ph)]−1,2-$C_2B_{10}H_{10}$ (**27**) from the reaction of **20b** with 1 equiv of $NiCl_2$(dppe) (Scheme 18). The presence of the dppe ligand and two phenyl groups makes complex **27** thermodynamically stable. Treatment of **27** with EtC≡CEt yielded the substituted 1,2-benzo-*o*-carborane 1,2-[C(Ph)=C(Ph)-C(Et)=C(Et)]−1,2-$C_2B_{10}H_{10}$ (**26a**), and hence this serves as a very efficient one-pot [2 + 2 + 2] protocol for the preparation of various 1,2-benzo-*o*-carborane derivatives with different substituents.

Conclusions and Perspectives

Salt metathesis between $Li_2C_2B_{10}H_{10}$ and metal halides has been found to be a very useful and efficient synthetic method for metal−carboryne complexes. On the basis of DFT calculations and structural studies, the bonding interactions between the metal and carboryne unit are best described as a resonance hybrid of both the M−C σ and M−C π bonding forms, with the interactions between Ni atom and carboryne having more π character than those observed in Zr−carboryne complexes. Both Ni− and Zr−carboryne complexes show a diverse array of reactions with unsaturated molecules. Ni–carboryne can undergo reaction with 2 equiv of alkynes to afford benzo-*o*-carboranes, with 1 equiv of alkenes to generate alkenylcarborane coupling products, and with 1 equiv of activated alkene and 1 equiv of alkyne, through a three-component $[2+2+2]$ cycloaddition, to give dihydrobenzo-*o*-carboranes. Ni–carboryne however does not show any activity toward polar unsaturated molecules. In contrast, Zr–carboryne can react with both alkynes and polar unsaturated molecules to afford monoinsertion product zirconacycles. Such zirconacyclopentenes are very useful intermediates for the synthesis of various kinds of functionalized carboranes, while transmetalation to nickel and copper creates further synthetic opportunities. These techniques offer a new method for the functionalization of carboranes that cannot be achieved by other means.

Our work shows that the metal–carbon bonds in metal–carboryne complexes are reactive toward electrophiles, whereas those in metal–carboranyl complexes are inert, and this leads to very high chemoselectivity. The results also suggest that the metal–boron bond is more reactive toward alkynes than the metal–carbon bond in metal–1,3-dehydro-*o*-carborane complexes.

Compared with the very rich literature concerning the chemistry of metal–benzyne complexes, studies of metal–carboryne complexes are just beginning, and it is expected that other transition metal–carborynes will be prepared and structurally characterized. The reaction scope requires further exploration, especially with regard to multicomponent reactions. The possibility of generating a "carbordiyne", containing two "C=B" units in one carborane cage also remains to be addressed. Whether these methods for the preparation of metal–carboryne complexes can be extended to supercarboranes is also an open question.

We are grateful to all co-workers involved in the studies described in this paper for their valuable contributions. Financial support from The Research Grants Council of The Hong Kong Special Administration Region (Project No. 404108) and The Chinese University of Hong Kong is also gratefully acknowledged.

BIOGRAPHICAL INFORMATION

Zaozao Qiu received her B.Sc. in 2002 and M.Sc. in 2005, both from Lanzhou University, for work on organic synthesis. After serving for one year as a Research Assistant in the Shanghai Institute of Organic Chemistry (SIOC), the Chinese Academy of Sciences, she moved to The Chinese University of Hong Kong (CUHK), and earned her Ph.D. degree in 2010 under the supervision of Prof. Zuowei Xie. Currently, she is working as a postdoctoral fellow in the laboratory of Prof. Xie. Her research interests include the synthesis and reactivity of late transition metal–carboryne complexes.

Shikuo Ren obtained his B.Sc. and M.Sc. from Lanzhou University in 1998 and 2001, respectively, majoring in organic chemistry under the supervision of Prof. Yongqiang Tu. After working as a Research Assistant for one year in SIOC and serving as a Group Leader & Safety Manager in Sundia MediTech Co. Ltd. in Shanghai for years, he continued his study at CUHK and obtained his Ph.D. degree in 2010 under the supervision of Prof. Zuowei Xie. He is currently a postdoctoral fellow in the laboratory of Prof. Xie. His research interests include the synthesis and reactivity of early transition metal–carboryne complexes.

Zuowei Xie was born in Zhejiang, China, in 1964. He obtained his B.Sc. at Hangzhou University in 1983, a M.Sc. at SIOC in 1986, and his Ph.D. in 1990, working in a special joint program between SIOC and the Technische Universität Berlin. After serving as a Research Associate in SIOC and a postdoctoral fellow at the University of Southern California, he joined the chemistry faculty of CUHK in 1995, where he is now a Chair Professor. He has received several prestigious awards including State Natural Science Awards in 1997 and 2008, the Chinese Chemical Society Yao-Zeng Huang Award in Organometallic Chemistry in 2010, and the Croucher Award from the Croucher Foundation (Hong Kong) in 2003.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: zxie@cuhk.edu.hk.

REFERENCES

1 (a) Hawthorne, M. F. The Role of Chemistry in the Development of Boron Neutron Capture Therapy of Cancer. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950–984. (b) Soloway, A. H.; Tjarks, W.; Barnum, J. G. The Chemistry of Neutron Capture Therapy. *Chem. Rev.* **1998**, *98*, 1515–1562. (c) Valliant, J. F.; Guenther, K. J.; King, A. S.; Morel, P.; Schaffer, P.; Sogbein, O. O.; Stephenson, K. A. The Medicinal Chemistry of Carboranes. *Coord. Chem. Rev.* **2002**, *232*, 173–230. (d) Armstrong, A. F.; Valliant, J. F. The Bioinorganic and Medicinal Chemistry of Carboranes: From New Drug Discovery to Molecular Imaging and Therapy. *Dalton Trans.* **2007**, 4240–4251.

2 Selected examples: (a) Yang, X.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. Rigid-Rod Molecules: Carborods. Synthesis of Tetrameric p-Carboranes and the Crystal Structure of Bis(tri-n-butylsily1)tetra-p-carborane. *J. Am. Chem. Soc.* **1992**, *114*, 9719–9721. (b) Colquhoun, H. M.; Herbertson, P. L.; Wade, K.; Baxter, I.; Williams, D. J. A Carborane-Based Analogue of Poly(p-phenylene). *Macromolecules* **1998**, *31*, 1694–1696. (c) Jude, H.; Disteldorf, H.; Fischer, S.; Wedge, T.; Hawkridge, A. M.; Arif, A. M.; Hawthorne, M. F.; Muddiman, D. C.; Stang, P. J. Coordination-Driven Self-Assemblies with a Carborane Backbone. *J. Am. Chem. Soc.* **2005**, *127*, 12131–12139.

3 (a) Hosmane, N. S.; Maguire, J. A. Metallacarborane of d- and f-Block Metals. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007; Vol. 3, Chapter 5. (b) Xie, Z. Advances In the Chemistry of Metallacarboranes of f-Block Elements. *Coord. Chem. Rev.* **2002**, *231*, 23–46. (c) Xie, Z. Cyclopentadienyl-Carboranyl Hybrid Compounds: A New Class of Versatile Ligands for Organometallic Chemistry. *Acc. Chem. Res.* **2003**, *36*, 1–9. (d) Deng, L.; Xie, Z. Advances in the Chemistry of Carboranes and Metallacarboranes with More Than 12 Vertices. *Coord. Chem. Rev.* **2007**, *251*, 2452–2476. (e) Zhang, J.; Xie, Z. Recent Progress in the Chemistry of Supercarboranes. *Chem.—Asian. J.* **2010**, *5*, 1742–1757.

4 Selected examples: (a) Heying, T. L.; Ager, J. W., Jr.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. A New Series of Organoboranes. I. Carboranes from the Reaction of Decaborane with Acetylenic Compounds. *Inorg. Chem.* **1963**, *2*, 1089–1092. (b) Kusari, U.; Li, Y.; Bradley, M. G.; Sneddon, L. G. Polyborane Reactions in Ionic Liquids: New Efficient Routes to Functionalized Decaborane and o-Carborane Clusters. *J. Am. Chem. Soc.* **2004**, *126*, 8662–8663.

5 Selected examples: (a) Heying, T. L.; Ager, J. W.; Clark, S. L.; Alexander, R. P.; Papetti, S.; Reid, J. A.; Trotz, S. I. A New Series of Organoboranes. III. Some Reactions of 1,2-Dicarbaclovododecaborane(12) and its Derivatives. *Inorg. Chem.* **1963**, *2*, 1097–1105. (b) Gomez, F. A.; Johnson, S. E.; Hawthorne, M. F. Versatile Protecting Group for 1,2-Dicarba-closo-dodecaborane(12) and the Structure of a Silylcarborane Derivative. *J. Am. Chem. Soc.* **1991**, *113*, 5915–5917.

6 Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. Facile Electrophilic Iodination of Icosahedral Carboranes. Synthesis of Carborane Derivatives with Boron−Carbon Bonds via the Palladium-Catalyzed Reaction of Diiodocarboranes with Grignard Reagents. *Inorg. Chem.* **1995**, *34*, 2095–2100.

7 Selected examples: (a) Li, J.; Logan, C. F.; Jones, M., Jr. Simple Syntheses and Alkylation Reactions of 3-Iodo-o-carborane and 9,12-Diiodo-o-carborane. *Inorg. Chem.* **1991**, *30*, 4866–4868. (b) Clara Vinas, C.; Barberà, G.; Oliva, J. M.; Teixidor, F.; Welch, A. J.; Rosair, G. M. Are Halocarboranes Suitable for Substitution Reactions? The Case for 3-I-1,2-closo-$C_2B_{10}H_{11}$: Molecular Orbital Calculations, Aryldehalogenation Reactions, ^{11}B NMR Interpretation of closo-Carboranes, and Molecular Structures of 1-Ph-3-Br-1,2-closo-$C_2B_{10}H_{10}$ and 3-Ph-1,2-closo-$C_2B_{10}H_{11}$. *Inorg. Chem.* **2001**, *40*, 6555–6562.

8 (a) Hota, N. K.; Matteson, D. S. Benzocarborane. High Stability but Little Aromatic Character. *J. Am. Chem. Soc.* **1971**, *93*, 2893–2897. (b) Wu, S.; Jones, M., Jr. A Carbon-to-Boron-Bridged Benzo-o-carborane. *Inorg. Chem.* **1988**, *27*, 2005–2008.

9 (a) Gingrich, H. L.; Ghosh, T.; Huang, Q.; Jones, M., Jr. 1,2-Dehydro-o-carborane. *J. Am. Chem. Soc.* **1990**, *112*, 4082–4083. (b) Ghosh, T.; Gingrich, H. L.; Kam, C. K.; Mobraaten, E. C. M.; Jones, M., Jr. Reactions of 1,2-Dehydro-o-carborane with Dienes. *J. Am. Chem. Soc.* **1991**, *113*, 1313–1318. (c) Cunningham, R. J.; Bian, N.; Jones, M., Jr. Reaction of 1,2-Dehydro-o-carborane with Acetylenes. Ene Reactions and Cycloaddition To Give an Analogue of Benzocyclobutadiene. *Inorg. Chem.* **1994**, *33*, 4811–4812. (d) Jeon, J.; Kitamura, T.; Yoo, B.-W.; Kang, S. O.; Ko, J. Synthesis and Reactivity of an Efficient 1,2-Dehydrocarborane Precursor, Phenyl[o-(trimethylsilyl)carboranyl]iodonium Acetate. *Chem. Commun.* **2001**, 2110–2111. (e) Lee, T.; Jeon, J.; Song, K. H.; Jung, I.; Baik, C.; Park, K.-M.; Lee, S. S.; Kang, S. O.; Ko, J. Generation and Trapping Reaction of an Efficient 1,2-Dehydrocarborane Precursor, Phenyl[o-(trimethylsilyl)carboranyl]iodonium Acetate. *Dalton Trans.* **2004**, 933–937. (f) Wang, S. R.; Qiu, Z.; Xie, Z. Insertion of Carboryne into Aromatic Rings: Formation of Cyclooctatetraenocarboranes. *J. Am. Chem. Soc.* **2010**, *132*, 9988–9989.

10 (a) Franzen, V.; Joschek, H. I. Conversion of Acetylenes with Dehydrobenzene. *Justus Liebigs Ann. Chem.* **1967**, *703*, 90–95. (b) Jones, M., Jr.; Levin, R. H. Stereochemistry of the 2 + 2 and 2 + 4 Cycloadditions of Benzyne. *J. Am. Chem. Soc.* **1969**, *91*, 6411–6415.

11 (a) Xie, Z. Group 4 Metallocenes Incorporating Constrained-Geometry Carboranyl Ligands. *Coord. Chem. Rev.* **2006**, *250*, 259–272. (b) Shen, H.; Xie, Z. Constrained-Geometry Ruthenium Carboranyl Complexes and Their Unique Chemical Properties. *Chem. Commun.* **2009**, 2431–2445. (c) Qiu, Z.; Xie, Z. Unique Chemical Properties of Metal−Carbon Bonds in Metal-Carboranyl and Metal-Carboryne Complexes. *Sci. China, Ser. B: Chem.* **2009**, *52*, 1544–1558.

12 Sayler, A. A.; Beall, H.; Sieckhaus, J. F. Unusual Chelated o-Carborane Transition Metal Complex. *J. Am. Chem. Soc.* **1973**, *95*, 5790–5792.

13 Qiu, Z.; Deng, L.; Chan, H.-S.; Xie, Z. Synthesis and Structural Characterization of Group 10 Metal-Carboryne Complexes. *Organometallics* **2010**, *29*, 4541–4547.

14 Elschenbroich, C.; Salzer, A. *Organometallics. A Concise Introduction*, VCH: New York, 1992; Chapter 15, p 256.

15 Wang, H.; Li, H.-W.; Huang, X.; Lin, Z.; Xie, Z. Synthesis, Structure, and Bonding of a Zirconocene-1,2-dehydro-o-carborane Complex. *Angew. Chem., Int. Ed.* **2003**, *42*, 4347–4349.

16 Deng, L.; Chan, H.-S.; Xie, Z. Synthesis, Structure, and Reactivity of a Zirconocene−Carboryne Precursor. *J. Am. Chem. Soc.* **2005**, *127*, 13774–13775.

17 Ren, S.; Deng, L.; Chan, H.-S.; Xie, Z. Synthesis and Structural Characterization of Zirconium−Carboryne Complexes. *Organometallics* **2009**, *28*, 5749–5756.

18 Buchwald, S. L.; Watson, B. T. Trimethylphosphine Adduct of the Zirconocene−Benzyne Complex: Synthesis, Reactions, and X-ray Crystal Structure. *J. Am. Chem. Soc.* **1986**, *108*, 7411–7413.

19 Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: Hoboken, NJ, 2005; Chapter 2, p 47.

20 (a) Bennett, M. A.; Wenger, E. Insertion Reactions of Benzyne−Nickel(0) Complexes with Acetylenes. *Organometallics* **1995**, *14*, 1267–1277. (b) Retbøll, M.; Edwards, A. J.; Rae, A. D.; Willis, A. C.; Bennett, M. A.; Wenger, E. Preparation of Benzyne Complexes of Group 10 Metals by Intramolecular Suzuki Coupling of ortho-Metalated Phenylboronic Esters: Molecular Structure of the First Benzyne−Palladium(0) Complex. *J. Am. Chem. Soc.* **2002**, *124*, 8348–8360.

21 Deng, L.; Chan, H.-S.; Xie, Z. Nickel-Mediated Regioselective [2 + 2 + 2] Cycloaddition of Carboryne with Alkynes. *J. Am. Chem. Soc.* **2006**, *128*, 7728–7729.

22 Bennett, M. A.; Macgregor, S. A.; Wenger, E. Insertion of Unsymmetric Alkynes into the Metal−Carbon Bonds of Nickelacycles: What Determines the Regioselectivity? *Helv. Chim. Acta* **2001**, *84*, 3084–3104.

23 Qiu, Z.; Xie, Z. Nickel-Mediated Coupling Reactions of Carboryne with Alkenes: A Synthetic Route to Alkenylcarboranes. *Angew. Chem., Int. Ed.* **2008**, *47*, 6572–6575.

24 Huang, X.; Zhu, J.; Lin, Z. β-Hydrogen Elimination of Five-Membered-Ring Metallacycles. Is It Possible? *Organometallics* **2004**, *23*, 4154–4159.

25 Qiu, Z.; Xie, Z. Nickel-Mediated Three-Component Cycloaddition Reaction of Carboryne, Alkenes, and Alkynes. *J. Am. Chem. Soc.* **2009**, *131*, 2084–2085.

26 (a) Hsieh, J.-C.; Cheng, C.-H. Nickel-Catalyzed Cocyclotrimerization of Arynes with Diynes; a Novel Method for Synthesis of Naphthalene. *Chem. Commun.* **2005**, 2459–2461. (b) Qiu, Z.; Xie, Z. Nickel-Catalyzed Three-Component [2 + 2 + 2] Cycloaddition Reaction of Arynes, Alkenes, and Alkynes. *Angew. Chem., Int. Ed.* **2009**, *48*, 5729–5732.

27 Qiu, Z.; Wang, S. R.; Xie, Z. Nickel-Catalyzed Regioselective [2 + 2 + 2] Cycloaddition of Carboryne with Alkynes. *Angew. Chem., Int. Ed.* **2010**, *49*, 4649–4652.

28 Terao, J.; Tomita, M.; Singh, S. P.; Kambe, N. Nickel-Catalyzed Regioselective Carbomagnesation of Methylenecyclopropanes through a Site-Selective Carbon−Carbon Bond Cleavage. *Angew. Chem., Int. Ed.* **2010**, *49*, 144–147.

29 Qiu, Z.; Xie, Z. Palladium/Nickel-Cocatalyzed Cycloaddition of 1,3-Dehydro-o-carborane with Alkynes. Facile Synthesis of C,B-Substituted Carboranes. *J. Am. Chem. Soc.* **2010**, *132*, 16085–16093.

30 Cho, C. S.; Lee, J. W.; Lee, D. Y.; Shim, S. C.; Kim, T. J. Synthesis of Isoindolines via Carbonylative Cyclisation of 2-(2-Bromophenyl)-2-oxazolines by a Bimetallic Palladium-Nickel Catalyst System. *Chem. Commun.* **1996**, 2115–2116.

31 Dang, L.; Lin, Z.; Marder, T. B. Boryl Ligands and Their Roles in Metal-Catalysed Borylation Reactions. *Chem. Commun.* **2009**, 3987–3995.

32 Ren, S.; Chan, H.-S.; Xie, Z. Reaction of Zirconocene−Carboryne Precursor with Alkynes: An Efficient Route to Zirconacyclopentenes Incorporating a Carboranyl Unit. *Organometallics* **2009**, *28*, 4106–4114.

33 Ren, S.; Chan, H.-S.; Xie, Z. Synthesis, Structure, and Reactivity of Zirconacyclopentene Incorporating a Carboranyl Unit. *J. Am. Chem. Soc.* **2009**, *131*, 3862–3863.

34 Marek., I. *Titanium and Zirconium in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2002.

35 (a) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. Cycloaddition Reaction of Zirconacyclopentadienes to Alkynes: Highly Selective Formation of Benzene Derivatives from Three Different Alkynes. *J. Am. Chem. Soc.* **1998**, *120*, 1672–1680. (b) Takahashi, T.; Tsai, F.-Y.; Li, Y.; Nakajima, K.; Kotora, M. Carbon−Carbon Bond Formation Reaction of Zirconacyclopentadienes with Alkynes in the Presence of Ni(II)-complexes. *J. Am. Chem. Soc.* **1999**, *121*, 11093–11100.

36 Ren, S. Synthesis, Structure, and Reactivity of Group 4 Metal-Carboryne Complex. Ph.D. Thesis, The Chinese University of Hong Kong, 2010.