Late Transition Metal-Carboryne Complexes and Their Reactions with Alkenes and Alkynes

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Abstract

A series of B-substituted nickel-1,2-*o*-carboryne complexes, $(\eta^2\text{-}1,2\text{-}C_2B_{10}R^1_nH_{10-n})Ni(PR^2_3)_2$, were synthesized by salt elimination of phosphine ligated metal halide with dilithiocarboranes. Both the substituents on the carborane cage and the phosphine ligands have significant effects on the stability of these complexes. B-H···Ni interactions were observed in the IR spectra and solid-state structures of $(\eta^2\text{-}3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_9)Ni(PMe_3)_2$ and $(\eta^2\text{-}3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_9)Ni(PPh_3)_2$ due to the steric effect of the phenyl substituent.

The reactivity of $(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)_2$ toward alkenes was studied and a novel nickel-mediated coupling reaction of carboryne with a variety of alkenes was developed, which gives alkenylcarboranes in moderate to very good isolated yields with excellent regio- and stereoselectivity. The intramolecular coordination of the heteroatom in alkenes can suppress β-H elimination reactions, leading to the isolation of the thermodynamically stable inserted intermediates, $[\{[2\text{-}CH_2CH(o\text{-}C_5H_4N)\text{-}1,2\text{-}C_2B_{10}H_{10}]Ni\}_3(\mu_3\text{-}Cl)][Li(DME)_3]$ and $[2\text{-}CH_2CH(CO_2Me)\text{-}1,2\text{-}C_2B_{10}H_{10}]Ni(PPh_3)$. These intermediates react readily with alkynes to give three-component [2+2+2] cycloaddition products. A novel nickel-mediated three-component assembling reaction of carboryne with alkenes and alkynes was then developed to give corresponding dihydro-1,2-benzo-*o*-carboranes. Accordingly, a new method for the synthesis of 1,2-dihydronaphthalenes from readily available starting materials also was developed, which involves nickel-catalyzed carboannulation of arynes, activated alkenes, and alkynes. The

formation of these products can be rationalized by the sequential insertion of alkene and alkyne into the Ni–C bond.

A catalytic version of [2+2+2] cycloaddition reaction of carboryne with alkynes was achieved using 1-iodo-2-lithiocarborane as precursor and $NiCl_2(PPh_3)_2$ as catalyst. The mechanism involved oxidative addition of Ni into the cage C–I bond, elimination of LiI to form Ni-1,2-*o*-carboryne, and sequential alkyne insertion into the $Ni-C_{cage}$ bond and $Ni-C_{vinyl}$ bond, followed by reductive elimination, was proposed after the NMR reaction study and the structural confirmation of the key intermediate, nickelacyclopentene $[\{[2\text{-}C(^{n}Bu)=C(o\text{-}C_5H_4N)\text{-}1,2\text{-}C_2B_{10}H_{10}]Ni\}_2(\mu_2\text{-}Cl)][Li(THF)_4]$, from the reaction of *n*-butyl-2-pyridinylacetylene.

1,3-Dehydro-*o*-carborane was observed for the first time, which can be trapped by unsaturated molecules in the presence of a catalytic amount of transition metal. This leads to a discovery of a palladium/nickel-cocatalyzed [2+2+2] cycloaddition reaction of 1,3-*o*-carboryne with alkynes affording 1,3-benzo-*o*-carboranes. This work offers a new methodology for B-functionalization of carborane and demonstrates the relative reactivity of M–C over M–B bond in metal-1,3-*o*-carboryne complexes toward alkynes.

These methodologies provide exceptionally efficient routes from readily available starting materials to a wide variety of functionalized carboranes, which have potential use in medicinal and materials chemistry.

摘要

本文首先描述了一系列碳硼烷硼原子上有取代基的镍-1,2-碳硼炔配合物(η^2-1,2-$C_2B_{10}R^1{}_nH_{10-n}$)Ni($PR^2{}_3$)$_2$ 的合成与表征。此类化合物可由含膦配体的金属卤化物和碳硼烷二锂盐间的盐消除反应得到。硼笼上的取代基和膦配体对这些化合物的稳定性都有着很大的影响。在(η^2-3-C_6H_5-1,2-$C_2B_{10}H_9$)Ni(PMe_3)$_2$ 和(η^2-3-C_6H_5-1,2-$C_2B_{10}H_9$)Ni(PPh_3)$_2$ 的红外谱图和晶体结构中我们可以观察到B-H···Ni 作用，这种相互作用可归因于苯基的位阻效应。

我们接下来研究了(η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$ 对烯烃的反应活性，从而发现了镍促进的 1,2-碳硼炔与烯烃反应能以很好的区域及立体选择性生成烯基取代的碳硼烷。某些烯烃上杂原子的分子内配位作用可以抑制β-H 消除反应，如甲基丙烯酸甲酯或 2-乙烯基吡啶的反应可以得到稳定的镍杂环戊烷中间体[2-$CH_2CH(CO_2Me)$-1,2-$C_2B_{10}H_{10}$]Ni(PPh_3) 和[{[2-CH_2CH(o-C_5H_4N)-1,2-$C_2B_{10}H_{10}$]Ni}$_3$(μ_3-Cl)][Li(DME)$_3$]。这两个中间体可进一步与炔烃反应生成三组分的[2+2+2]环加成产物。由此我们发现了镍促进的1,2-碳硼炔、烯烃和炔烃的三组分反应得到二氢-1,2-苯并碳硼烷。我们也相应研究了镍催化的芳炔、烯烃和炔烃的三组分环加成反应，得到了一个由简单起始物出发合成 1,2-二氢萘的新方法。这些产物可以理解为由烯烃和炔烃对 Ni–C 键的分步插入反应生成。

我们通过用 1-I-2-Li-1,2-$C_2B_{10}H_{10}$ 作为 1,2-碳硼炔前体和用 $NiCl_2(PPh_3)_2$ 作为催化剂实现了以催化反应的形式来实现碳硼炔与炔烃的[2+2+2]环加成反应。通过核磁反应研究和分离到的关键反应中间体镍杂环戊烯化合物[{[2-C(^{n}Bu)=C(o-C_5H_4N)-1,2-$C_2B_{10}H_{10}$]Ni}$_2$(μ_2-Cl)][Li(THF)$_4$]，我们提出了镍插入

C-I 键后消除 LiI 得到镍-1,2-碳硼炔化合物，之后炔烃分步插入 Ni–C_{cage} 键和 Ni–C_{vinyl} 键，然后还原消除得到最终产物的反应机理。

我们还首次发现了 1,3-脱氢碳硼烷（1,3-碳硼炔）及其在过渡金属存在下与不饱和底物的反应，即 Pd/Ni 共同催化的 1,3-碳硼炔与炔烃的[2+2+2]环加成反应生成 1,3-苯并碳硼烷。通过这个反应还可以证明 1,3-碳硼炔配合物中金属–碳和金属–硼键对炔烃的相对反应活性。

以上对碳硼炔反应的方法学研究为在药物和材料化学方面有潜在应用的碳硼烷化合物的合成提供了非常简便和有效的途径。

Abbreviation

bipy	bipyridine
^{n}Bu (or *n*-Bu)	*n*-butyl
^{n}BuLi	*n*-butyl lithium
^{t}Bu (or *t*-Bu)	*t*-butyl
cat.	catalyst
cod	cyclooctadiene
Cp	cyclopentadienyl
Cy	cyclohexyl
d	doublets
dba	dibenzylideneacetone
dcpe	1,2-bis(dicyclohexylphosphino)ethane
dd	doublet of doublets
DME	dimethoxyethane
dppe	1,2-bis(diphenylphosphino)ethane
dppen	*cis*-1,2-bis(diphenylphosphino)ethene
dppp	1,3-bis(diphenylphosphino)propane
eq. (or equiv)	equivalent
Et	ethyl
Et_2O	diethyl ether
IR	infrared spectroscopy

L	ligand
m	multiplet
M	metal
Me	methyl
Me_2Im	1,3-dimethylimidazol-2-ylidene
MS	mass spectroscopy
NMR	nuclear magnetic resonance spectroscopy
Ph	phenyl
^{n}Pr (or *n*-Pr)	propyl
^{i}Pr (or *i*-Pr)	isopropyl
pyr	pyridine
r.t. (or RT)	room temperature
s	singlet
t	triplet
TBAF	tetrabutylammonium floride
TBDMS	*t*-butyldimethylsilyl
THF	tetrahydrofuran
TMS	trimethylsilyl
Ts	toluenesulfonyl
xs	excess

List of Compounds

IV-5s'	1,2-[MeC=C(^{i}Pr)CH(CO_2Me)CH_2]C_6H_4	70
V-1a	1,2-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_{10}$	81
V-1b	3-Cl-1,2-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$	81
V-1c	3-Ph-1,2-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$	81
V-1d	1,2-[^{n}PrC=C(^{n}Pr)C(^{n}Pr)=C^{n}Pr]-1,2-$C_2B_{10}H_{10}$	81
V-1e	1,2-[^{n}BuC= C(^{n}Bu)C(^{n}Bu)=C^{n}Bu]-1,2-$C_2B_{10}H_{10}$	81
V-1f	1,2-[PhC=C(Ph)C(Ph)=CPh]-1,2-$C_2B_{10}H_{10}$	81
V-1g	1,2-[C(CH_2OMe)=C(CH_2OMe)C(CH_2OMe)=C(CH_2OMe)]--1,2-$C_2B_{10}H_{10}$	81
V-1h	1,2-[MeC=C(^{i}Pr)C(Me)=C^{i}Pr]-1,2-$C_2B_{10}H_{10}$	81
V-1'h	1,2-[MeC=C(^{i}Pr)C(^{i}Pr)=CMe]-1,2-$C_2B_{10}H_{10}$	81
V-1i	1,2-[MeC=C(Ph)C(Me)=CPh]-1,2-$C_2B_{10}H_{10}$	81
V-1j	1,2-[MeC=C(4'-Me-C_6H_4)C(Me)=C(4'-Me-C_6H_4]]--1,2-$C_2B_{10}H_{10}$	81
V-1k	1,2-[MeC=C(4'-CF_3-C_6H_4)C(Me)=C(4'-CF_3-C_6H_4]]--1,2-$C_2B_{10}H_{10}$	81
V-1l	1,2-[EtC=C(Ph)C(Et)=CPh]-1,2-$C_2B_{10}H_{10}$	81
V-1m	1,2-[^{n}BuC=C(Ph)C(^{n}Bu)=CPh]-1,2-$C_2B_{10}H_{10}$	81

VI-1f	3-I-1-($CH_2CH_2OCH_3$)-1,2-$C_2B_{10}H_{10}$	91
VI-1g	3-I-1-[$CH_2CH_2N(CH_3)_2$]-1,2-$C_2B_{10}H_{10}$	91
VI-4a	1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_{10}$	96
VI-4b	2-Me-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$	94
VI-4c	2-^{n}Bu-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$	96
VI-4d	2-TMS-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$	96
VI-4e	2-Ph-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$	96
VI-4f	2-($CH_2CH_2OCH_3$)-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$	96
VI-4g	2-[$CH_2CH_2N(CH_3)_2$]-1,3-[EtC=C(Et)C(Et)= CEt]-1,2-$C_2B_{10}H_9$	96
VI-4h	2-Me-1,3-[^{n}PrC=C(^{n}Pr)C(^{n}Pr)=C^{n}Pr]-1,2-$C_2B_{10}H_9$	96
VI-4i	2-Me-1,3-[^{n}BuC=C(^{n}Bu)C(^{n}Bu)=C^{n}Bu]-1,2-$C_2B_{10}H_9$	96
VI-4j	2-Me-1,3-[PhC=C(Ph)C(Ph)=CPh]-1,2-$C_2B_{10}H_9$	96
VI-4k	2-Me-1,3-[C(4'-Me-C_6H_4)=C(4'-Me-C_6H_4)C(4'-Me-C_6H_4) =C(4'-Me-C_6H_4)]-1,2-$C_2B_{10}H_9$	96
VI-4l	2-Me-1,3-[PhC=C(Me)C(Ph)=CMe]-1,2-$C_2B_{10}H_9$	96
VI-5l	2-Me-1,3-[MeC=C(Ph)C(Ph)=CMe]-1,2-$C_2B_{10}H_9$	
VI-4m	2-Me-1,3-[PhC=C(Et)C(Ph)=CEt]-1,2-$C_2B_{10}H_9$	96
VI-5m	2-Me-1,3-[EtC=C(Ph)C(Ph)=CEt]-1,2-$C_2B_{10}H_9$	

VI-7a	2-Me-1,3-[MeC=C-$(CH_2)_3$-C=CMe]-1,2-$C_2B_{10}H_9$	97
VI-7b	2-Me-1,3-[MeC=C-$(CH_2)_4$-C=CMe]-1,2-$C_2B_{10}H_9$	97
VI-7c	2-Me-1,3-[MeC=C-$(CH_2)_5$-C=CMe]-1,2-$C_2B_{10}H_9$	97

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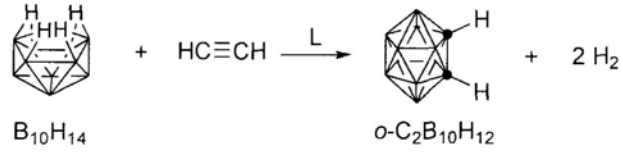
Chapter 1. Introduction

Carboranes (dicarba-*closo*-dodecaboranes), members of the class of carbon-containing boron clusters, have characteristic properties such as spherical geometry, remarkable thermal and chemical stability, and a hydrophobic molecular surface. Medical applications of the carboranes have been mainly in the field of boron neutron capture therapy (BNCT) of cancer, utilizing the high boron content of the carboranes.[1]

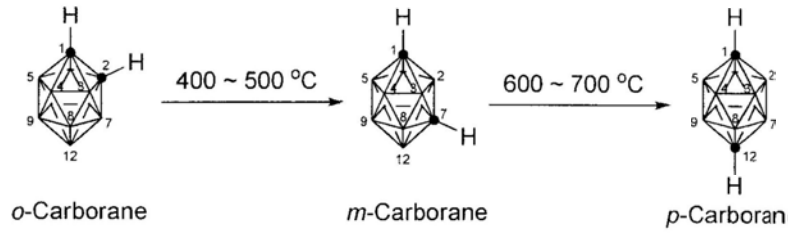
The synthesis and properties of icosohedral carboranes were first reported in 1963[2], which have been the most extensively investigated of all known carboranes during the last 40 years.[3,4] *o*-Carborane was obtained by the reaction of acetylene with complexes prepared from decaborane and Lewis base such as acetonitrile, alkylamines, and alkyl sulfides (Scheme 1.1).[2,5]

Scheme 1.1



Unlike the starting boron hydride, *o*-carborane is stable in the presence of oxidizing agents, alcohols, and strong acids and exhibits phenomenal thermal stability in temperatures up to 400 °C. Under inert atmosphere, it rearranges to *m*-carborane between 400 and 500 °C. This latter compound isomerizes to *p*-carborane between 600 and 700 °C (Scheme 1.2).[3]

Scheme 1.2



One of the most important features of a carborane system is its ability to enter into substitution reactions at both the carbon and boron atoms without degradation of the cage. The stability of the carborane cage is demonstrated under many reaction conditions used to prepare a wide range of C- and B-carborane derivatives.[4a]

1.1 Synthesis of C-Substituted Carboranes

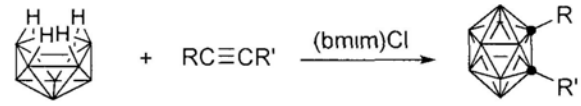
During the past decades investigations in the field of C-substituted carboranes were directed at improving the synthetic methods for the preparation of organic and organometallic carboranyl compounds used in the production of polymeric materials as well as in biological and medical investigations. There are two conventional synthetic methods leading to carbon-substituted carboranes: the reaction of substituted acetylenes with decaborane and electrophilic substitutions of lithiocarboranes.

1.1.1 Reaction of Decaborane with Acetylenes

The reaction of decaborane with acetylenes in the presence of Lewis bases is a general method for carborane synthesis. The typical yields of this method for

terminal alkynes range from 6 to 75%, whereas much lower yields are given or even no reaction takes place for many internal alkynes.[2,5] Recently, Sneddon and co-workers reported an improved method for the synthesis of 1,2-disubstituted *o*-carboranes by direct reaction of $B_{10}H_{14}$ or 6-R-$B_{10}H_{13}$ with terminal or internal alkynes in ionic liquid in high yields (Scheme 1.3).[6]

Scheme 1.3

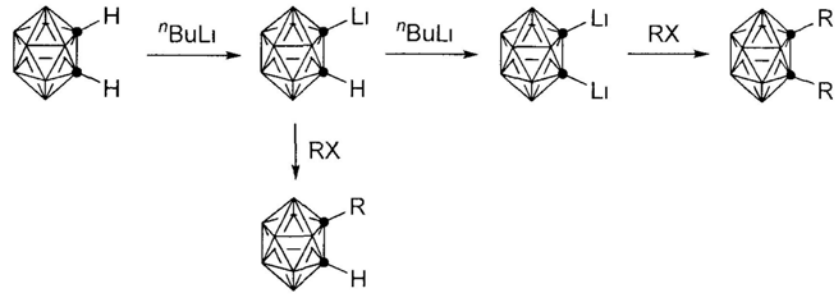


R = R' = Et, Ph, R = Hexyl, R' = H, R = CH_2OH, R' = Me
bmim = 1-butyl-3-methylimidiazolium

1.1.2 Reaction of Lithiocarborane with Electrophiles

The strong electron-withdrawing character of the *o*-carborane unit facilitates the metalation of the carborane CH group. The mildly acidic C–H bonds in *o*-carborane (with the *p*Ka value of ~23) react easily with strong bases such as ^{n}BuLi and PhLi to form C-monolithio-*o*-carborane or C,C'-dilithio-*o*-carborane, which can be converted into the corresponding mono- or di-organosubstituted products (Scheme 1.4).[7]

Scheme 1.4

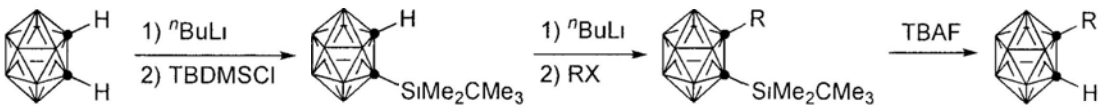


The synthesis of mono-C-substituted *o*-carboranes is not straightforward due to the disproportionation of monolithio-*o*-carborane, which leads to the undesired di-C-substituted products (Scheme 1.5).[7b]

Scheme 1.5

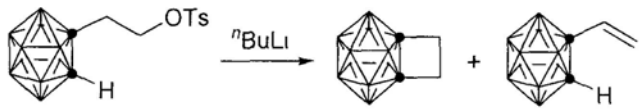
Hawthorne developed an effective method to prepare monosubstituted *o*-carboranes using *tert*-butyldimethylsilyl (TBDMS) as a protecting group, as the reactions between mono- or dilithio-*o*-carborane with TBDMSCl only give monosubstituted product and the TBDMS group can be easily removed by TBAF ($^{n}Bu_4NF$) (Scheme 1.6).[8] The easy functionalization of the cage CH vertices results in the emergence of numerous carborane derivatives, which makes the further application possible.[3a]

Scheme 1.6



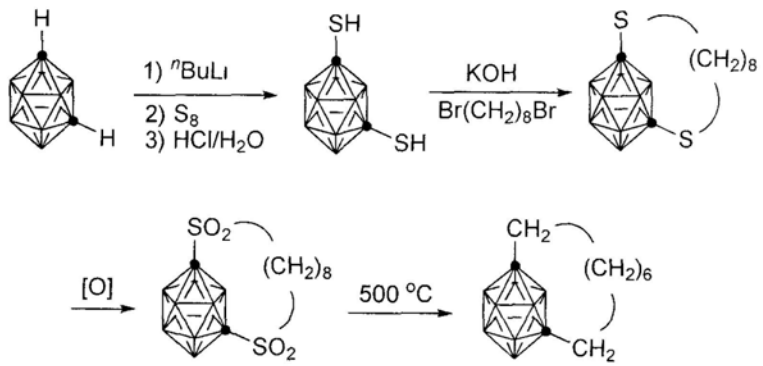
The elimination of *p*-toluenesulfonic acid from the corresponding tosylate gives 1,2-ethano-*o*-carborae in presence of ^{n}BuLi up to 40% yield with the molar ratio of 1,2-ethano-*o*-carborane to 1-vinyl-*o*-carborane as high as 99/1 (Scheme 1.7).[9]

Scheme 1.7



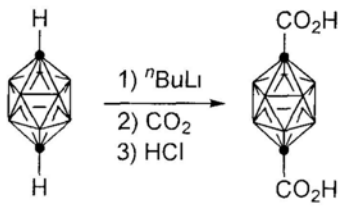
Carboranophanes, *m*-carboranes bridged by a single all-carbon or carbon and sulfur bridge were also synthesized by the action of lithiocarborane on S_8 followed by an alkylation-oxidation-pyrolysis route (Scheme 1.8).[10]

Scheme 1.8



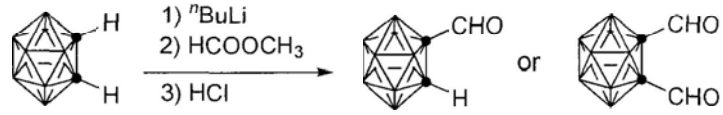
Dilithio-*p*-carborane can be converted to 1,12-bis(hydroxycarbonyl)-*p*-carborane in almost quantitative yield by reaction with carbon dioxide followed by acidification (Scheme 1.9).[11]

Scheme 1.9



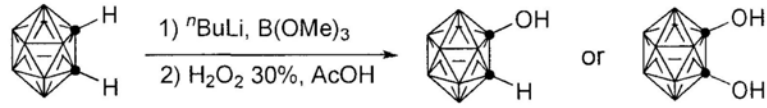
Single-step preparation of C-formyl derivatives directly from *o*-, *m*-, and *p*-carboranes was reported by Dozzo *et al.* in 2005 (Scheme 1.10).[12]

Scheme 1.10



C-hydroxycarboranes and C,C-dihydroxycarboranes can be synthesized by the reaction of lithiocarborane and trimethylborate, followed by oxidation with hydrogen peroxide in the presence of acetic acid through a one-pot procedure (Scheme 1.11).[13]

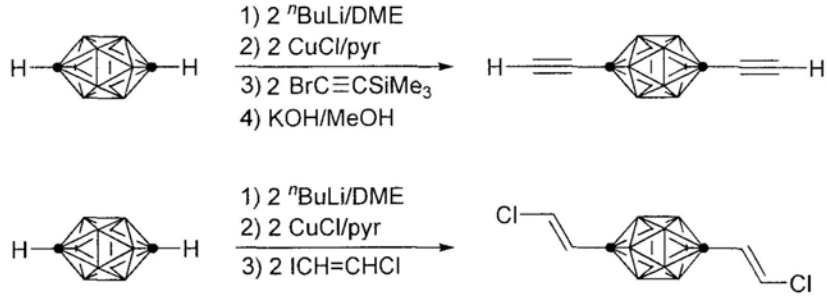
Scheme 1.11



1.1.3 Reaction of Carboranylcopper

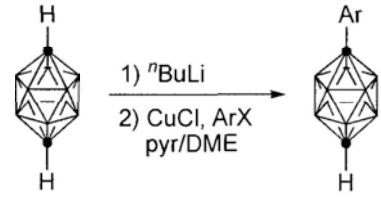
Another method was developed for the synthesis of 1,12-diethynylcarboranes or 1,12-diethenylcarboranes via carboranylcopper compounds. The authors also studied stereochemical aspects of Br_2, HCl, and HI addition to l-ethynylcarboranes (Scheme 1.12).[14]

Scheme 1.12



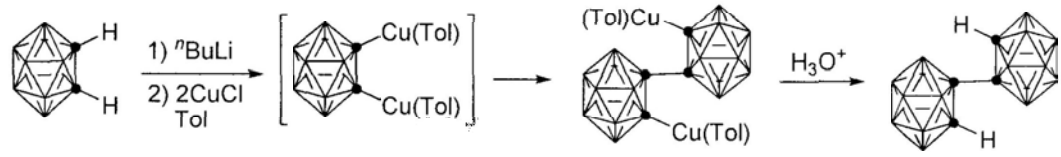
Carboranylcopper compounds can also react with arylhalides to give arylcarborane derivatives (Scheme 1.13).[15]

Scheme 1.13



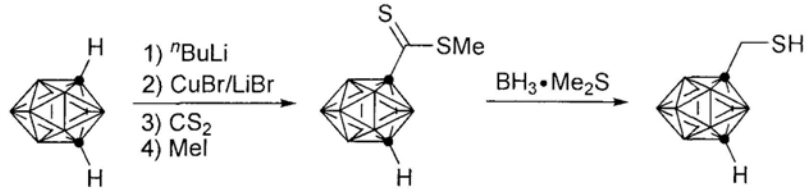
Reaction of dilithio-*o*-carborane with CuCl in toluene afforded a single product, 1,1′:2,2′-$[Cu(toluene)]_2(C_2B_{10}H_{10})_2$, which gave 1,1′-bis(*o*-carborane) after hydrolysis. This serves as the most efficient method for the preparation of 1,1′-bis(*o*-carborane) (Scheme 1.14).[16]

Scheme 1.14



The *m*-carborane was deprotonated with ^{n}BuLi and then treated with CuBr and LiBr followed by CS_2. Addition of MeI gave the dithioester, which was reduced by $BH_3{\cdot}SMe_2$ to afford the thiol (Scheme 1.15).[17]

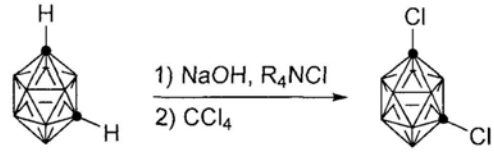
Scheme 1.15



1.1.4 Other Methods

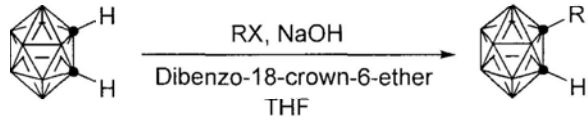
Phase transfer catalysis conditions appear to be more convenient in the preparation of some carborane derivatives. Kabachii *et al.* developed a method for the synthesis of 1,7-dichloro-*m*-carborane by chlorination of *m*-carborane with CCl_4 using phase transfer catalysts (Scheme 1.16).[18]

Scheme 1.16



Zakharkin synthesized 1-alkyl- and 1,2-di-alkyl-*o*-carboranes by alkylating *o*-carborane, and 1-methyl- or 1-phenyl-*o*-carborane with alkyl halides in alkali-THF system using dibenzo-18-crown-6-ether as transferring agent (Scheme 1.17).[19]

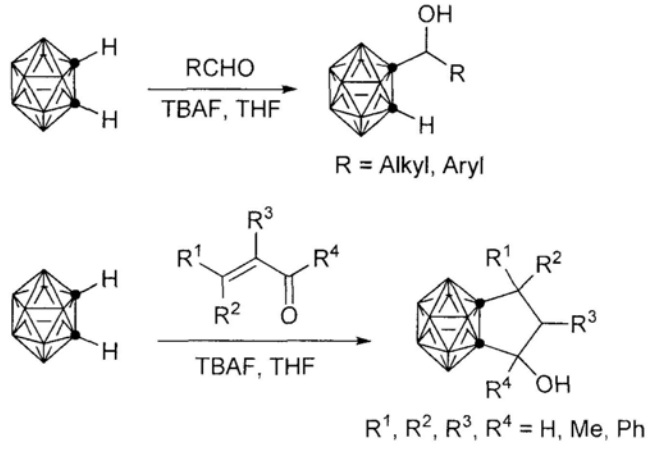
Scheme 1.17



Yamamoto found that the addition of *o*-carborane to aldehydes proceeded very smoothly in the presence of aqueous tetrabutylammonium fluoride (TBAF), giving the corresponding carbinols in high yields. Furthermore, the TBAF-mediated reaction was applied to the [3+2] annulation between *o*-carborane (dianionic C_2 synthons) and α,β-unsaturated aldehydes and ketones (dicationic C_3 synthons) to

give the corresponding five-membered carbocycles in good-to-high yields (Scheme 1.18).[20]

Scheme 1.18



1.2 Synthesis of B-Substituted Carboranes

The chemistry of boron-substituted carboranes is not as developed as that of the carbon analogues due to the difficulty of introducing functional groups at the boron atom of the carborane cage. B-Halogenated carboranes, the first B-substituted species, appear to be inert to substitution reactions. B-Carboranyl compounds can be viewed as analogues of organic compounds because the B-carboranyl group acts as either an alkyl or aryl group in most transformations.[4a]

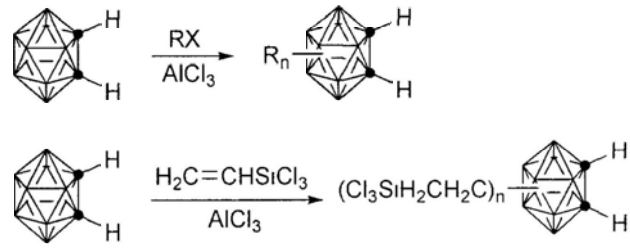
1.2.1 Reaction of Decaborane with Acetylenes

The first compound with a C-B(carborane) bond was obtained by the reaction of acetylene with a mixture of 1- and 2-ethyldecaboranes in acetonitrile, giving a mixture of 8- and 9-ethyl-*o*-carboranes.[2a]

1.2.2 Electrophilic Substitution of Carboranes

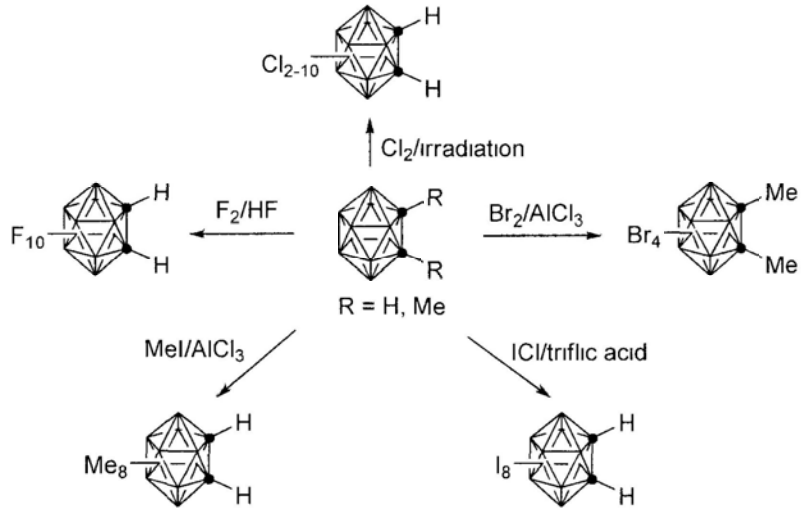
Another route to alkylcarboranes involves the electrophilic alkylation of carboranes with alkyl halide[21] or vinyltrichlorosilane[22] in the presence of $AlCl_3$ (Scheme 1.19).

Scheme 1.19



Direct electrophilic halogenation,[23] alkylation,[21 22 24] and metalation[25] can take place at the boron atom (Scheme 1.20). These reactions are typical for aromatic compounds, and for this reason the carborane molecule has been termed as a "pseudoaromatic" system.[26]

Scheme 1.20

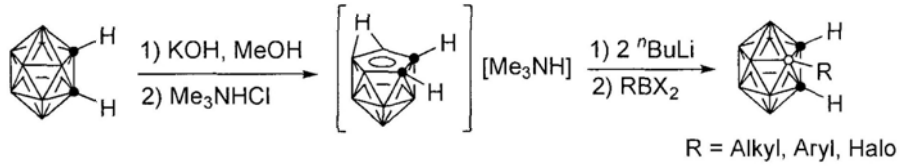


Theoretical calculations on carboranes show that electron density increases in the order 1 (2) < 3 (6) < 4 (5,7,11) < 8 (10) < 9 (12) for *o*-carborane, 1 (7) < 2 (3) < 5 (12) < 4 (6,8,11) < 9 (10) for *m*-carborane, and 1 (12) < 2 (3-11) for *p*-carborane (Scheme 1.2, positions listed in parentheses are chemically equivalent to those in front of the parentheses).[27] Experimental results are in general agreement with theoretical calculations of the charge distribution. Electrophilic substitution usually occurs first at the 9,12 and then at the 8,10 positions of the *o*-carborane cage. The carbon atoms and the adjacent boron atoms do not appear susceptible to electrophilic substitution.

1.2.3 Reaction of Dicarbollide ion ($C_2B_9H_{11}^{2-}$) with Dihalobarane

One of the most important reactions in carborane chemistry was reported by Wiesboeck and Hawthorne in 1964.[28] They showed that *o*-carborane could be degraded using alcoholic alkali removing one boron atom and forming the dicarbollide anion, $C_2B_9H_{11}^{2-}$. Starting from this anion, a number of 3-substituted *o*-caboranes were synthesized by the boron insertion reaction (Scheme 1.21).[29]

Scheme 1.21



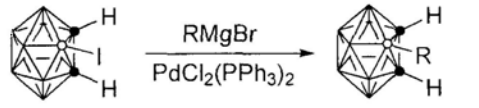
R = Alkyl, Aryl, Halo

1.2.4 Transition Metal-Catalyzed Coupling Reaction

An organic group was introduced at the boron atom of the carborane cage

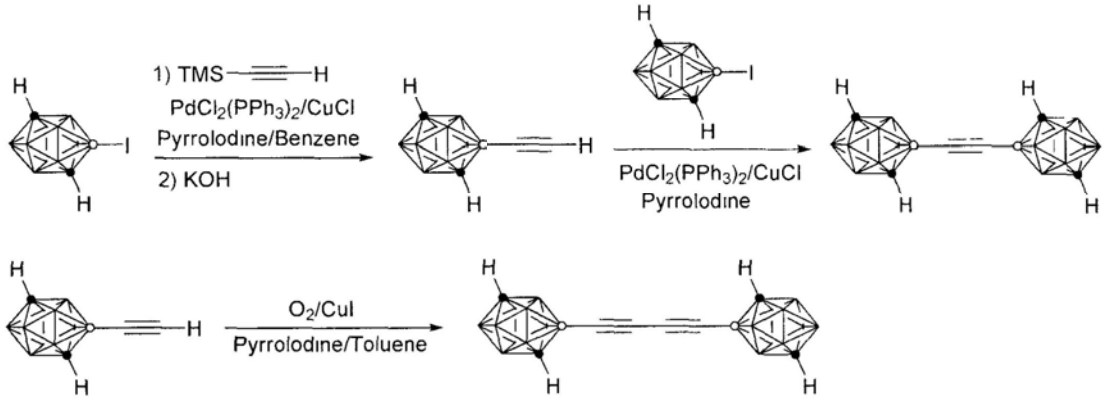
through reaction of iodocarboranes with organomagnesium compounds in the presence of Ni or Pd complexes (Scheme 1.22).[30]

Scheme 1.22



Methodology leading to a new class of rodlike *p*-carborane derivatives is described, involving the palladium-catalyzed coupling of B-iodinated *p*-carboranes with terminal alkynes (Scheme 1.23).[31] The products of these reactions contain an alkyne substituent at a boron vertex of the *p*-carborane cage.

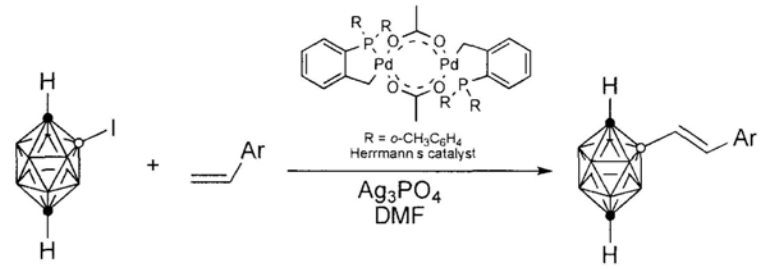
Scheme 1.23



p-Carborane can be vinylated on the 2-*B*-atom in high yields using the Heck reaction (Scheme 1.24).[32] Thus, the reaction between 2-iodo-*p*-carborane and various styrenes resulted in the production of the corresponding

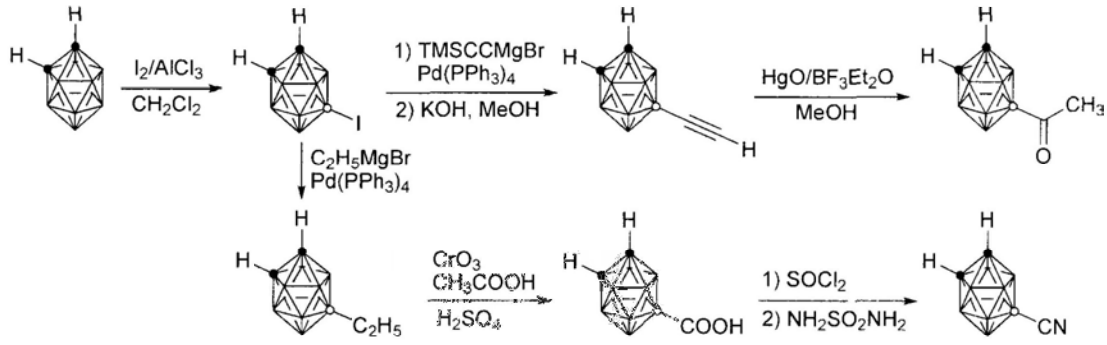
trans-β-(2-B-*p*-carboranyl)-styrene in DMF solution when reacted in the presence of silver phosphate and the palladacycle Herrmann's catalyst.

Scheme 1.24



The syntheses of 9-acetyl-*o*-carborane and 9-cyano-*o*-carborane are outlined in Scheme 1.25.[33] Functionalization of *o*-carborane at the 9-position is readily achieved by iodination followed by reaction with the appropriate Grignard reagent. 9-Ethynyl-*o*-carborane and 9-ethyl-*o*-carborane were obtained by this route from 9-iodo-*o*-carborane. 9-Ethynyl-*o*-carborane is hydrated quantitatively in aqueous methanolic solution under catalysis by HgO and BF_3 with formation of 9-acetyl-*o*carborane. An acid obtained from oxidation of 9-ethyl-*o*-carborane with chromic anhydride, is allowed to react with thionyl chloride to give the corresponding acid chloride, which is converted into nitrile by reaction with sulfonylamide.

Scheme 1.25

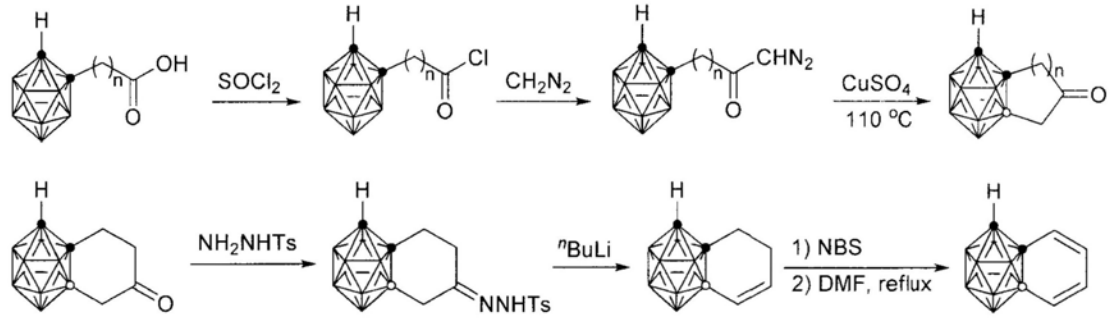


1.2.5 Carbene Reaction

Jones *et al.* reported the reaction of carbomethoxycarbene with the B–H bonds of *o*-carborane can form the products of formal B–H insertion, and the C–H bonds were ignored by the carbene (Scheme 1.26).[34]

An intramolecular version of this reaction can produce a series of carbon-to-boron-bridged *o*-carboranes. The conversion of ketone to bridged benzo-*o*-carborane is presented in Scheme 1.26.[35]

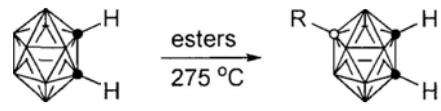
Scheme 1.26



1.2.6 Other Methods

Simple pyrolysis of *o*-carborane in the presence of dialkyl acetylenedicarboxylates and trialkyl methane-tricarboxylates in sealed tubes at 275 °C produces 9-alkyl-*o*-carboranes in reasonable yield (Scheme 1.27).[36]

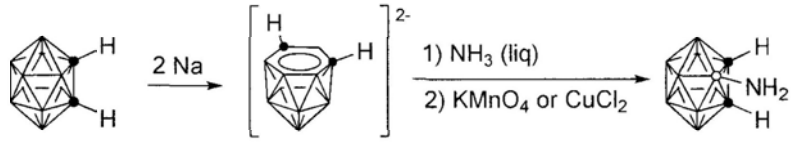
Scheme 1.27



esters = ROOC−C≡C−COOR and $(ROOC)_3CH$
R = Me, Et, ^{i}Pr, ^{n}Bu

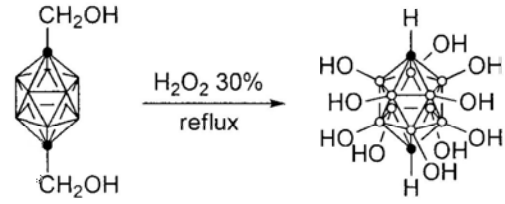
The first B-aminocarborane was obtained by Zakharkin and Kalinin in 1967.[37] They showed that the dicarbadodecaborate anion, formed by the addition of two electrons to the carborane nucleus, reacts with liquid ammonia at low temperature and be oxidized with $KMnO_4$ or $CuCl_2$ to give 3-amino-*o*-carborane (Scheme 1.28). The 3-amino-*o*-carboranes show reactions typical of aliphatic and aromatic primary amines. They are readily arylated and acylated with formic acid or acetic anhydride.

Scheme 1.28



The per-B-hydroxylated carboranes *closo*-1,12-H_2-1,12-$C_2B_{10}(OH)_{10}$, which may be considered to be derivatives of a new type of polyhedral subboric acid, can be prepared by the oxidation of the slightly water-soluble precursor *closo*-1,12-$(CH_2OH)_2$-1,12-$C_2B_{10}H_{10}$ with 30% hydrogen peroxide at the reflux temperature (Scheme 1.29), because *closo*-1,12-$C_2B_{10}H_{12}$ is water-insoluble and hence not available to the hydrogen peroxide reagent. During this reaction sequence, the diol is most likely oxidized to the corresponding dicarboxylic acid, which subsequently decarboxylates during B-hydroxylation.[38]

Scheme 1.29

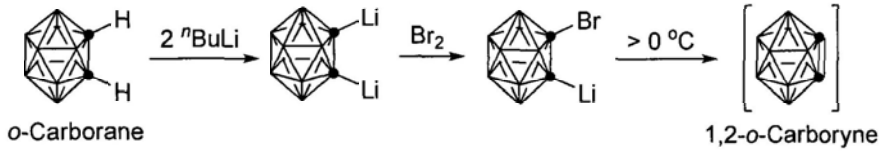


1.3 1,2-*o*-Carboryne

Icosahedral carboranes, *closo*-$C_2B_{10}H_{12}$, are aromatic molecules which resemble benzene in both thermodynamic stability and chemical reactions. For example, carborane and benzene survive heating to several hundred degrees and undergo aromatic substitution reactions with electrophilic reagents.[21-25] Another dramatic aspect of benzene chemistry is the generation of benzyne which found many applications in organic synthesis, mechanistic studies, and synthesis of functional materials since its first report in 1950s.[39] Similar to benzene, *o*-carborane can also form this kind of dehydro-species, 1,2-*o*-carboryne (1,2-dehydro-*o*-carborane).

Jones and co-workers discovered a way to generate 1,2-*o*-carboryne by treatment of 1,2-dilithio-*o*-carborane with one equiv of bromine (Scheme 1.30).[40] 1-Bromo-2-lithio-*o*-carborane is stable below 0°C, however, upon heating in the presence of unsaturated molecules addition products are formed.[41]

Scheme 1.30

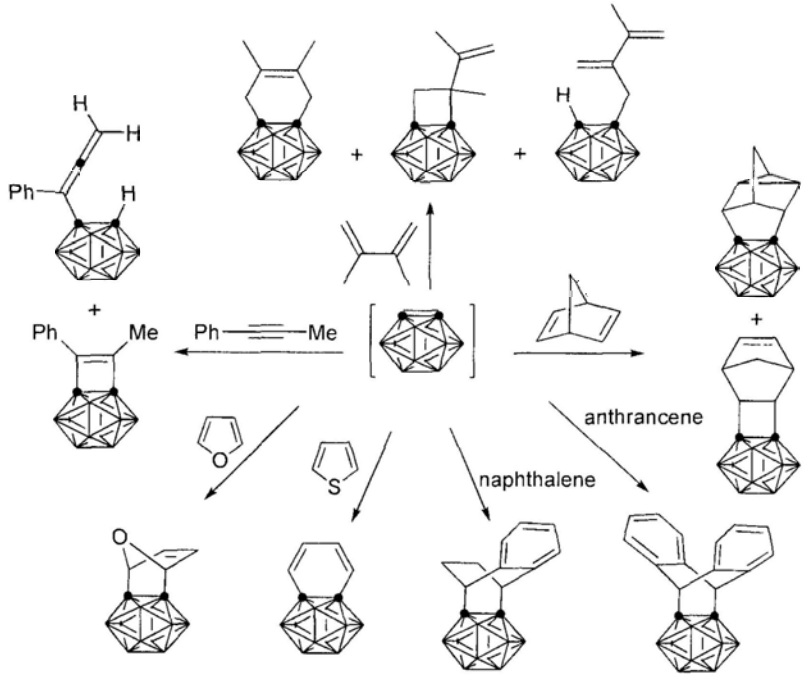


o-Carborane 1,2-*o*-Carboryne

When using diene as a trapping reagent, products of the [2+4] cycloaddition type, the [2+2] cycloaddition type, and ene reaction type are obtained with a very similar ratio to that of the reaction between benzyne and diene.[41] The mechanistic studies on these addition reactions show that both the [2+4] cycloaddition and ene

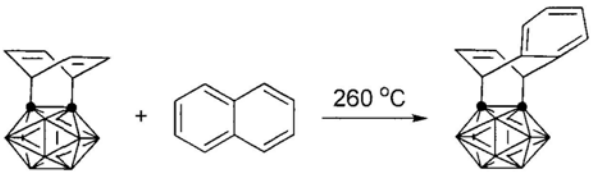
studies on these addition reactions show that both the [2+4] cycloaddition and ene reaction are likely to be concerted, whereas the [2+2] cycloaddition might be stepwise. These are also similar to those of benzyne. Subsequently, the authors studied the reactions of 1,2-*o*-carboryne generated *in situ* with other dienes, alkynes, and alkenes, such as furans, thiophenes, anthracene, naphthalene, benzene, cyclohexene, norbornadiene, hexadiene and so on (Scheme 1.31).[40-42]

Scheme 1.31



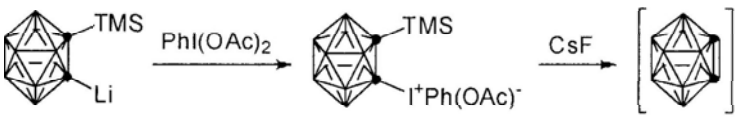
The benzene-1,2-*o*-carboryne adduct has been used as 1,2-*o*-carboryne precursor.[42e] Under heating at 230-260°C, the 1,2-*o*-carboryne moiety transfers from this adduct has been achieved in the presence of acceptors (Scheme 1.32). The naphthalene and anthracene adducts are thermally stable and cannot give similar result.[42e]

Scheme 1.32



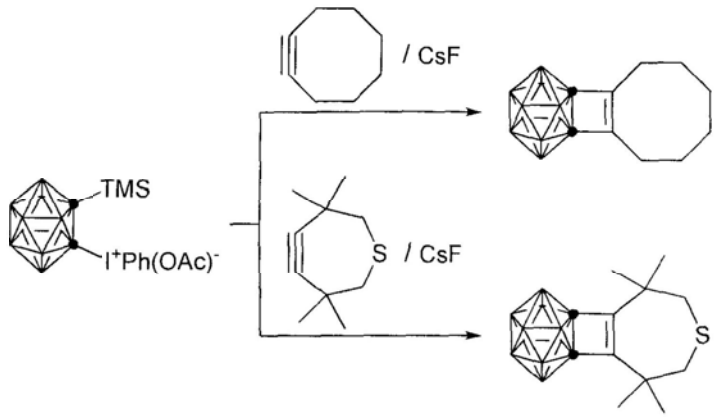
Recently, a more efficient method has been developed for the generation of 1,2-*o*-carboryne under mild reaction conditions. Phenyl[*o*-(trimethylsilyl)carboranyl]iodonium acetate, prepared by the reaction of [*o*-(trimethylsilyl)carboranyl]lithium with $IPh(OAc)_2$, is such a kind of precursor (Scheme 1.33).[43]

Scheme 1.33



The reaction of this salt with anthracene in the presence of desilylating reagents such as CsF or KF/18-crown-6 gives 1,2-*o*-carboryne adduct in much higher yields. Other dienes such as naphthalene, 2,5-dimethylfuran and thiophene also work well as trapping reagents with improved yields compared with Jones' results. In a similar fashion, this precursor also functions well for the [2+2] addition reaction of 1,2-*o*-carboryne and strained cycloalkynes (Scheme 1.34).[43b] It should be mentioned that the cyclization of the *in situ* generated 1,2-*o*-carboryne with some alkynes in the presence of $Ni(PEt_3)_4$, $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ failed.[43b]

Scheme 1.34



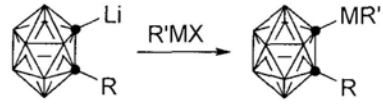
These experimental achievements spurred the theoretical study on this novel species. Although the experimental study only involves 1,2-$C_2B_{10}H_{10}$, the calculations encompass both 1,2-*o*-carboryne and 1,2-dehydro-*o*-silaboranes (*o*-$C_2B_nH_n$ and *o*-$Si_2B_nH_n$, n = 4, 5, 8, and 10).[44] The study shows that the dehydrogeno formation of 1,2-$C_2B_{10}H_{10}$ is energetically comparable to that of benzyne with *ca.* 99 kcal/mol, whereas the dehydrogeno formation of 2,3-$C_2B_5H_5$ is estimated to be even less endothermic than that of 1,2-$C_2B_{10}H_{10}$ by more than 21 kcal/mol. The bond lengths of these dehydrogeno species are also calculated. For 1,2-$C_2B_{10}H_{10}$, the carbon-carbon bond length is 1.356 Å, which is shorter than that of 1.625 Å in 1,2-$C_2B_{10}H_{12}$, indicating the multiple bond character. This bond distance is still significantly longer than that observed in benzyne (1.245 Å). For 2,3-$C_2B_5H_5$, the bond distance of 1.305 Å is more comparable to that in benzyne. The calculation on the frontier molecular orbitals of the [4+2] cycloaddition between dienes and these 1,2-*o*-carboryne intermediate shows that the $E(HOMO_{diene}\text{-}LUMO_{ene})$ is lower than that for ethylene and benzyne. Since Diels-Alder reactions of ethylene, benzyne,

and 1,2-$C_2B_{10}H_{10}$ with butadiene are known, other dehydrogeno carboranes are also expected to have similar reactivity.[44]

1.4 Transition Metal-1,2-*o*-Carboryne Complexes

Transition metals were found capable of forming σ-bonds with the carbon atoms of the carborane cage. Derivatives with M–C(carborane) bonds are known for the following transition metals: Cu, Au, Ti, Zr, Mn, Re, Fe, Co, Rh, Ir, Ni, Pd, and Pt.[4a] The organometallic derivatives of carboranes were mainly obtained from the reaction of lithiocarborane with compounds bearing metal-halogen bond (Scheme 1.35).

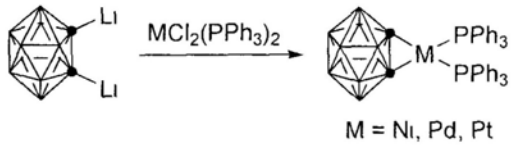
Scheme 1.35



1.4.1 Synthesis of Transition Metal-1,2-*o*-Carboryne Complexes

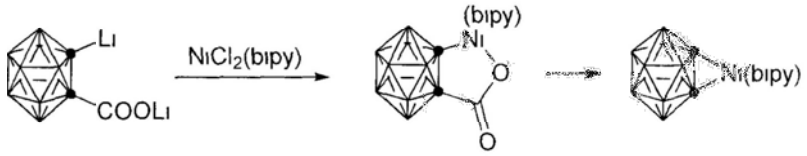
The first example of transition metal-1,2-*o*-carboryne complexes, (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$, was reported in 1973.[45] Treatment of 1,2-dilithio-*o*-caborane with $MiCl_2(PPh_3)_2$ (M = Ni, Pd, Pt) gives unique molecules (Ph_3P)$_2$M(η^2-$C_2B_{10}H_{10}$) (Scheme 1.36).[45,46] The structure of nickel complex was characterized by X-ray analysis. It contains a three-membered ring formed through two Ni–C(cage) bonds and the coordination plane about the nickel atom is essentially planar.[45]

Scheme 1.36



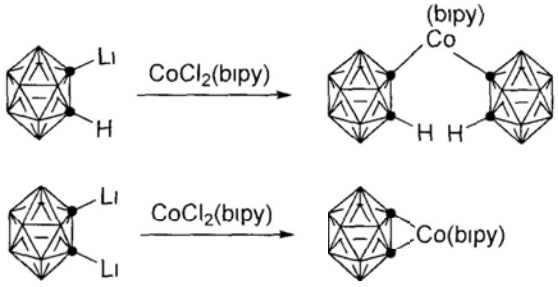
Ol'dekop *et al.* developed a decarboxylation procedure for the preparation of Ni-1,2-*o*-carboryne complexes stabilized by a bipyridyl ligand (Scheme 1.37).[47]

Scheme 1.37



Compounds with a Co–C(carborane) σ-bond were obtained by the interaction of lithiocarboranes with bipyridyl complexes of $CoCl_2$ (Scheme 1.38).[48]

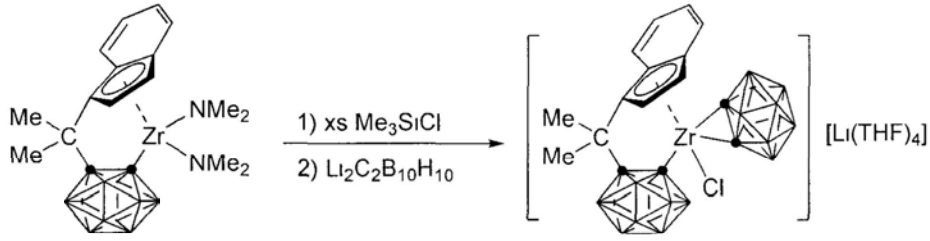
Scheme 1.38



The first example of early transition metal-1,2-*o*-carboryne complex $[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]$ was prepared in 2003 from the reaction of in situ generated $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]ZrCl_2$ with one

equivalent of $Li_2C_2B_{10}H_{10}$ in THF in 60% yield (Scheme 1.39).[49] Many attempts to remove the chloro ligand for the preparation of a neutral complex are not successful. The anionic nature of $[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_{10})(C_2B_{10}H_{10})\}Zr(\eta^3\text{-}C_2B_{10}H_{10})]^-$ does not show any activity toward unsaturated molecules.

Scheme 1.39



Single-crystal X-ray analyses show that the Zr atom is directly bonded to the two adjacent cage carbon atoms which do not have terminal hydrogen atoms. In addition, the metal center also interacts with the cage through an "agostic-like" Zr-H–B bond. Thus, the description Zr-η^3-(*o*-$C_2B_{10}H_{10}$) can be used to exemplify this novel bonding mode. With such a bonding description, the dianionic $[\eta^3\text{-}(o\text{-}C_2B_{10}H_{10})]^{2-}$ ligand formally donates three pairs of electrons to the metal center and is isolobal with Cp^-. Therefore, one can conveniently correlate this zirconium complex anion with complexes having a general formula of d^0 Cp_2MX_2. Alternatively, one can describe the bonding interaction between the metal center and the two carbon atoms of the η^3-(*o*-$C_2B_{10}H_{10}$) ligand in terms of the metal–1,2-*o*-carboryne form. DFT calculations suggest that the bonding interactions between the Zr atom and 1,2-*o*-carboryne are best described as a resonance hybrid of

both the Zr–C σ and Zr–C π bonding forms, similar to that observed in $Cp_2Zr(\eta^2$-benzyne) (Chart 1.1).

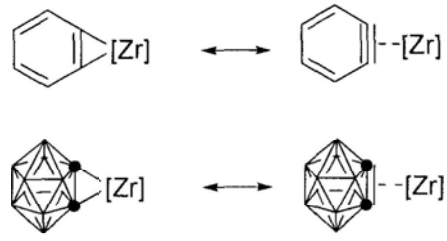
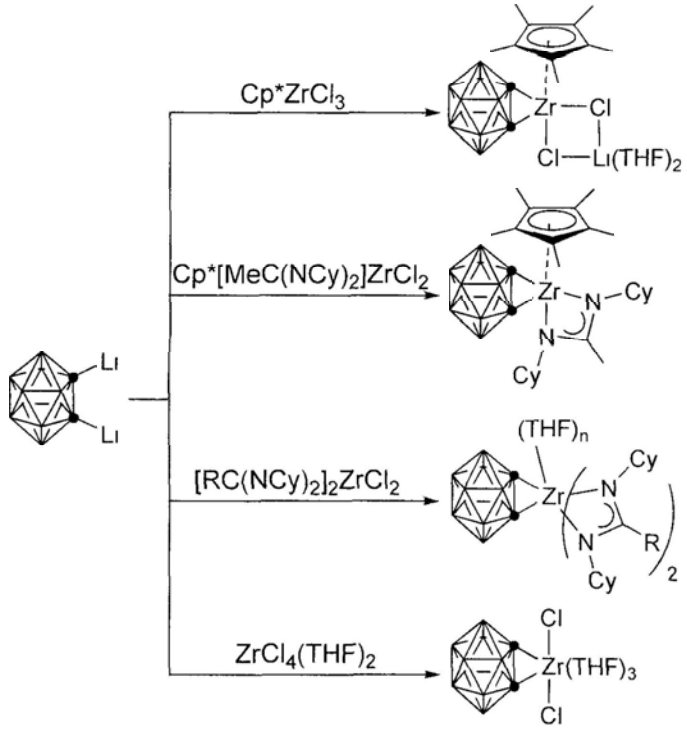


Chart 1.1

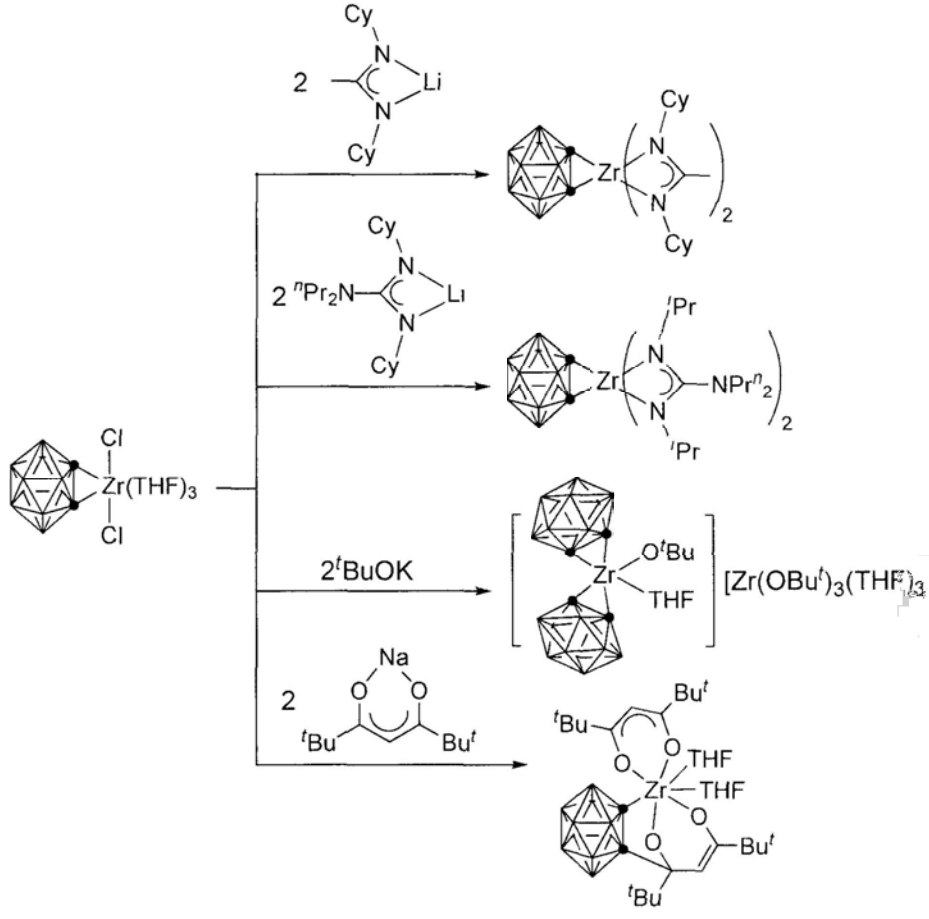
The salt metathesis between organozirconium dichloride and $Li_2C_2B_{10}H_{10}$ gave a class of zirconium-carboryne complexes, including $(\eta^2$-$C_2B_{10}H_{10})ZrCl_2(THF)_3$ (Scheme 1.40). Both the electronic and steric factors of the ligands have significant effects on the formation of the resultant metal complexes.[50]

Scheme 1.40



Treatment of (η^2-$C_2B_{10}H_{10}$)$ZrCl_2(THF)_3$ with 2 equiv of amidinatolithium, guanidinatolithium, or ^{t}BuOK afforded the complex [η^2-CyNC(CH_3)NCy]$_2$Zr(η^2-$C_2B_{10}H_{10}$), [η^2-^{n}Pr$_2$NC(NPr^i)$_2$]$_2$Zr(η^2-$C_2B_{10}H_{10}$), or [(η^2-$C_2B_{10}H_{10}$)$_2$Zr(O^{t}Bu)(THF)][Zr(OBu^t)$_3$(THF)$_3$]. The unexpected product [σ:σ:σ-{^{t}BuC(O)=CHC(^{t}Bu)(O)$C_2B_{10}H_{10}$}]Zr(η^2-^{t}BuCOCHCOBu^t)$(THF)_2$ was isolated from the reaction of (η^2-$C_2B_{10}H_{10}$)$ZrCl_2(THF)_3$ with (^{t}BuCOCHCO^{t}Bu)Na (Scheme 1.41).[50]

Scheme 1.41



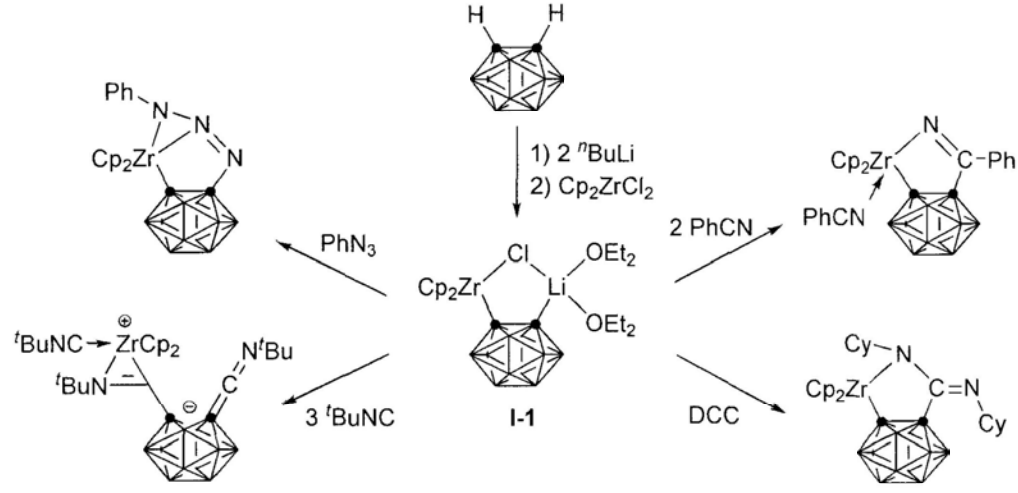
1.4.2 Reactivity of Zr-1,2-*o*-Carboryne Complexes

Attempts to synthesize $Cp_2Zr(\eta^2$-$C_2B_{10}H_{10})$(L), an analogue of

$Cp_2Zr(\eta^2\text{-}C_6H_4)(L)$, *via* treatment of Cp_2ZrCl_2 with one equivalent of $Li_2C_2B_{10}H_{10}$ fail. This reaction gives, instead, the ate-complex $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**I-1**) in 70% isolated yield (Scheme 1.42).[51] Complex **30** can be viewed as a precursor of zirconocene-carboryne $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$.

Treatment of **I-1** with PhCN, CyN=C=NCy, PhN_3, and ^{t}BuNC affords the insertion products $Cp_2Zr[\sigma.\sigma\text{-}N{=}C(Ph)(C_2B_{10}H_{10})](PhCN)$, $Cp_2Zr[\sigma.\sigma\text{-}CyNC(=NCy)(C_2B_{10}H_{10})]$, $Cp_2Zr[\eta^2\text{:}\sigma\text{-}(PhNN{=}N)(C_2B_{10}H_{10})]$, and $Cp_2Zr[\eta^2\text{-}^t BuNC(C_2B_{10}H_{10}){=}CN^tBu](CN^tBu)$, respectively, in moderate to high yields (Scheme 1.42).[51]

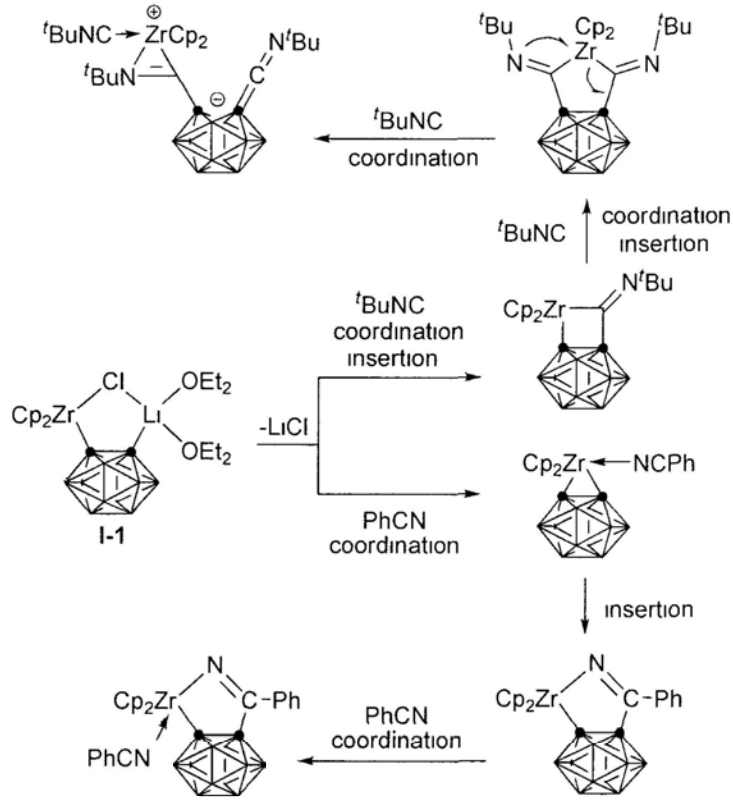
Scheme 1.42



Scheme 1.43 shows the proposed reaction mechanism. Dissociation of LiCl from **I-1** gives the key intermediate $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$. Coordination of PhCN and subsequent insertion generate the five-membered metallacycle. The coordination sphere of the Zr atom is then completed by binding to another equivalent of PhCN

molecule. No further insertion proceeds because of the steric reasons. For ^{t}BuNC, the first insertion of ^{t}BuNC into the Zr–C(cage) bond gives a four-membered metallacycle, followed by the further insertion of the second molecule of ^{t}BuNC to afford a five-membered metallacycle. The coordination of the imine nitrogen and the cleavage of one Zr–C(imine) bond lead to the production of the final product. Back-donation of the carboanion to the cage carbon can lead to the formation of *exo* C(cage)=C double bond and the subsequent cleavage of the cage C–C bond.[51]

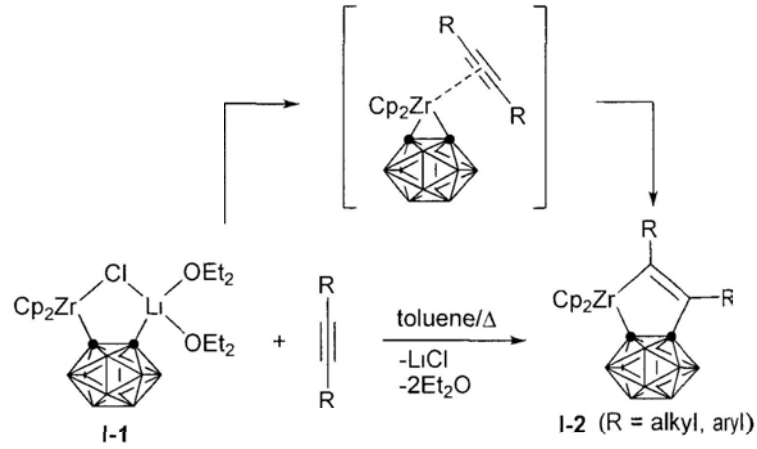
Scheme 1.43



Complex **I-1** can also react with various kinds of alkynes, leading to the formation of metallacyclopentenes. An equimolar reaction of **I-1** with RC≡CR in

refluxing toluene gives 1,2-[$Cp_2ZrC(R)$=$C(R)$]-1,2-$C_2B_{10}H_{10}$ (**I-2**) in very high isolated yield (Scheme 1.44).[52] An alkyne-coordinated complex is suggested to be the intermediate. The polarity of alkynes determines the regioselectivity of the insertion products. Like the reaction with polar unsaturated molecules, no further insertion products are detected even after prolonged heating in the presence of an excess amount of alkynes.[52]

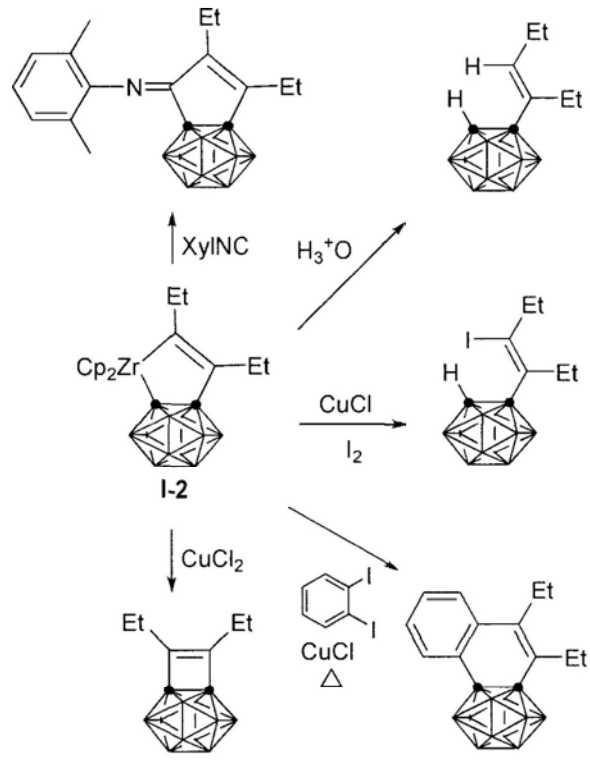
Scheme 1.44



Complex **I-2** are very useful starting materials for the preparation of functionalized carboranes (Scheme 1.45). Hydrolysis under acidic media affords alkenylcarborane 1-[HC(Et)=C(Et)]-1,2-$C_2B_{10}H_{11}$. Interaction of **I-2** with I_2 in the presence of CuCl generates a monosubstituted carborane 1-[CI(Et)=C(Et)]-1,2-$C_2B_{10}H_{11}$ in 71% isolated yield. Disubstituted species 1-I-2[CI(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ is not observed. This result is very different from that of its analogue zirconacyclopentadienes Cp_2Zr[C(R)=C(R)-C(R)=C(R)], in which the diiodo species is the major product in the presence of CuCl. Therefore, it is rational to suggest that, after transmetalation to Cu(I), only the Cu–C(vinyl) bond is

reactive toward I_2 whereas the Cu-C_{cage} bond is inert probably because of steric reasons. Reaction of **I-2** with *o*-diiodobenzene in the presence of CuCl produces naphthalocarborane 1,2-[*o*-$C_6H_4C(Et)=C(Et)$]-1,2-$C_2B_{10}H_{10}$ in 81% isolated yield. Treatment of **I-2** with $CuCl_2$ in toluene at 80 °C gives the C-C coupling product 1,2-[C(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$. 2,6-$(CH_3)_2C_6H_3NC$ can readily insert into the Zr–C_{vinyl} bond to form an insertion product 1,2-[(2',6'-$Me_2C_6H_3N$=)CC(Et)=C(Et)]-1,2-$C_2B_{10}H_{10}$ in refluxing toluene in the absence of CuCl.[53]

Scheme 1.45



1.4.3 Reactivity of Ni-1,2-*o*-Carboryne Complexes

In view of the reactions of nickel-benzyne with alkynes to generate substituted

naphthalenes and the analogy between nickel-benzyne and nickel-1,2-*o*-carboryne complex (Chart 1.2), the reactivity of (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$ was examined.

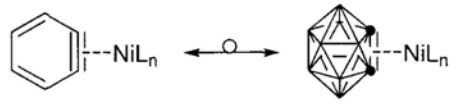
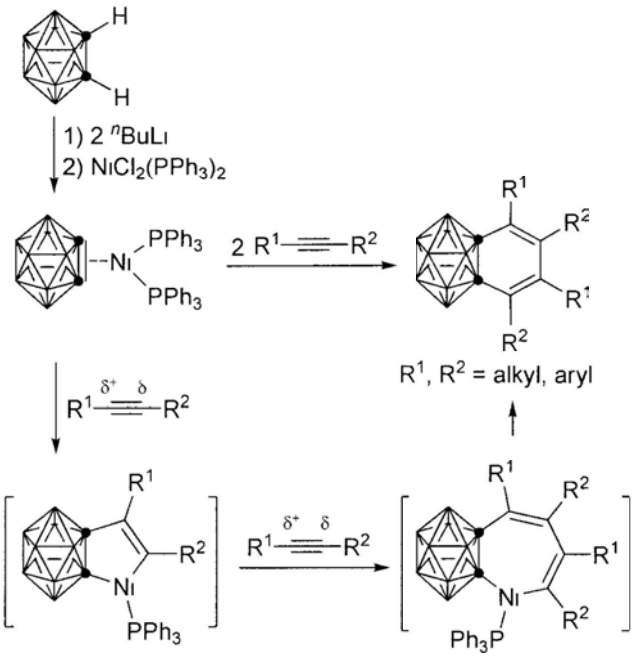


Chart 1.2

Structural data of (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$ show that the C_{cage}–C_{cage} bond distance in (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$ is shorter than the corresponding value observed in Zr-1,2-*o*-carboryne complex,[45] suggestive of the effects of electronic configuration of the metal center on the bonding interactions between the metal atom and carboryne unit. As a result, (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$ does not react with any polar unsaturated molecules, but it reacts well with alkynes.

Treatment of (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$ with internal alkynes gives highly substituted benzocarboranes 1,2-[C(R^1)=C(R^2)C(R^1)=C(R^2)]-1,2-$C_2B_{10}H_{10}$ via a [2+2+2] cycloaddition (Scheme 1.46).[54] The formation of benzocarborane can be rationalized by the sequential insertion of alkynes into the Ni–C bond; followed by reductive elimination. The first insertion into the Ni–C(cage) bond gives a nickelacyclopentene intermediate. 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 highly preferred over the Ni–C(cage) bond, leading to the regioselective products.

Scheme 1.46



1.5 Our Objectives

In view of the rich chemistry displayed by the 1,2-*o*-carboryne and its transition metal complexes, the research objectives of this research are (1) synthesis of new nickel-1,2-*o*-carboryne complexes, (2) exploration of the reaction chemistry of Ni-1,2-*o*-carboryne, and (3) development of new transition metal-1,3-*o*-carboryne chemistry. In the following chapters of this thesis, we would like to describe the details of our efforts on these subjects.

Chapter 2. Nickel-1,2-*o*-Carboryne Complexes

2.1 Introduction

1,2-*o*-Carboryne (1,2-dehydro-*o*-carborane), which was first reported as a reactive intermediate in 1990,[40] is very energetically comparable with its two-dimensional relative benzyne.[44] Reactivity studies also showed that they are quite similar in reactions with unsaturated molecules.[42,43]

Like benzyne, carboryne can be trapped and stabilized by transition metals. The reaction of organozirconium dichloride with 1 equiv of $Li_2C_2B_{10}H_{10}$ or treatment of $(\eta^2\text{-}C_2B_{10}H_{10})ZrCl_2(THF)_3$ with anionic ligands can give a class of zirconium-1,2-*o*-carboryne complexes.[50] Molecular orbital calculations suggested that the bonding interactions between Zr and 1,2-*o*-carboryne are best described as a resonance hybrid of both Zr–C σ and Zr–C π bonding forms which is similar to that observed in Zr-benzyne complex.[49] For late transition metals, salt metathesis is also a good method for the synthesis of metal-1,2-*o*-carboryne complexes by reaction of MCl_2 (M = Ni, Pd, Pt, Co) with $Li_2C_2B_{10}H_{10}$.[45,46,48] A series of Ni-1,2-*o*-carboryne was recently prepared in our group by the reaction of phosphine ligated nickel halide. The C(cage)–C(cage) bonds in these complexes are much shorter than those in Zr-1,2-*o*-carboryne complexes.[50] The reactivity studies on $(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)_2$ show that the coordinated PPh_3 molecules are labile, which can be substituted by other phosphines such as PCy_3, $P(OEt)Ph_2$, and $P(OEt)_3$ to give $(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)(PCy_3)$, $(\eta^2\text{-}C_2B_{10}H_{10})Ni[P(OEt)Ph_2]_2$, and $(\eta^2\text{-}C_2B_{10}H_{10})Ni[P(OEt)_3]_2$, respectively with quantitative conversion.

Our earlier investigation on the B-substituted carborane has revealed that the substituent on carborane plays an important role for the formation of these late transition metal complexes. The reactions of $Li_2C_2B_{10}Me_8H_2$ with $(PPh_3)_2NiCl_2$ or (dppe)$NiCl_2$ gave redox reaction products (σ-$C_2B_{10}Me_8H_3$)Ni$(PPh_3)_2$ or (η^2-$C_2B_{10}Me_8H_2$)Ni(μ-σ:σ:η^2-dppen)Ni(dppe), whereas the complete redox reaction took place for the reactions with $(PPh_3)_2PdCl_2$ and $(PPh_3)_2PtCl_2$. In view of the very rich and exciting chemistry of nickel-benzyne complexes,[55] we are interested in further exploring the nickel-1,2-*o*-carboryne complexes with substituents on the cage boron. In this section we will describe the synthesis and structure of these B-substituted nickel-1,2-*o*-carboryne complexes.

2.2 Synthesis and Structure of B-Substituted Nickel-1,2-*o*-Carboryne Complexes

Treatment of 9-I-1,2-$C_2B_{10}H_{11}$ and 9,12-I_2-1,2-$C_2B_{10}H_{11}$ with 2 equiv of *n*-BuLi in THF at 0 °C, followed by reaction with 1 equiv of $(PPh_3)_2NiCl_2$ in THF at the temperatures -30°C to room temperature gave (η^2-9-I-1,2-$C_2B_{10}H_9$)Ni$(PPh_3)_2$ (**II-1**) as a yellow solid or (η^2-9,12-I_2-1,2-$C_2B_{10}H_8$)Ni$(PPh_3)_2$ (**II-2**) as yellow crystals in 55% or 72% isolated yield, respectively (Scheme 2.1).

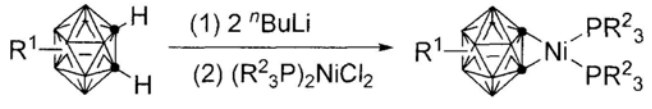
Under the same conditions, the product from the reaction of 3-bromo-1,2-dilithio-*o*-carborane with 1 equiv of $(PPh_3)_2NiCl_2$ was not stable and decomposed to generate 3-Br-1,2-$C_2B_{10}H_{11}$ and Ni(0) species. However, the less bulky and more electron-donating ligand of PMe_3 can stabilize this

Ni-1,2-*o*-carboryne complex and (η^2-3-Br-1,2-$C_2B_{10}H_9$)Ni(PMe_3)$_2$ (**II-3**) can be synthesized as yellow crystals in 31% isolated yield from the interaction of 3-bromo-1,2-dilithio-*o*-carborane with 1 equiv of $(Me_3P)_2NiCl_2$ in THF at the temperatures -30°C to room temperature (Scheme 2.1).

Similarly, complexes (η^2-3-C_6H_5-1,2-$C_2B_{10}H_9$)Ni(PMe_3)$_2$ (**II-4**) and (η^2-3-C_6H_5-1,2-$C_2B_{10}H_9$)Ni(PPh_3)$_2$ (**II-5**) can be isolated as yellow or orange crystals in 42% or 76% isolated yields by the reaction of 3-phenyl-1,2-dilithio-*o*-carborane with 1 equiv of $(Me_3P)_2NiCl_2$ or $(Ph_3P)_2NiCl_2$ in THF, respectively.

In the case of 4,5,7,8,9,10,11,12-octamethyl-*o*-carborane, neither PPh_3 nor PMe_3 can efficiently stabilize the corresponding Ni-1,2-*o*-carboryne species, leading to a mixture of products. A few brown X-ray-quality-crystals of (η^2-4,5,7,8,9,10,11,12-Me_8-$C_2B_{10}H_2$)Ni(PMe_3)$_2$ (**II-6**) was obtained from toluene solution at room temperature during the recrystallization of the product.

Scheme 2.1. Synthesis of B-substituted 1,2-*o*-Carboryne-Ni complexes.



II-1 R^1 = 9-I, R^2 = Ph
II-2 R^1 = 9,12-I_2, R^2 = Ph
II-3 R^1 = 3-Br, R^2 = Me
II-4 R^1 = 3-Ph, R^2 = Me
II-5 R^1 = 3-Ph, R^2 = Ph
II-6 R^1 = 4,5,7,8,9,10,11,12-Me_8, R^2 = Me

Complexes **II-1~4** are sensitive to moisture and air whereas **II-5** is air- and moisture-stable, both in the solid-state and in solution. Interestingly, **II-5** is very thermally stable even in refluxing THF. However heating the THF solution of **II-1~4** can lead to a decomposition, generating neutral carboranes and Ni(0) species. It's

believed that both the interaction between phenyl ring and metal center and the sterically demanding PPh_3 ligand have contributed to the exceptional stability of this complex. Complexes **II-1~5** are slightly soluble in ether and toluene and highly soluble in THF. They were fully characterized by various spectrometric methods and elemental analyses.

The ^{1}H and ^{13}C NMR spectra of **II-1~5**, which only display the signals of PPh_3 or PMe_3 ligand, do not give much information on the solution structures. The cage carbons were not observed for **II-1~5**. The $^{11}B\{^{1}H\}$ NMR spectra display a 3:6:1, 2:6:2, 1:1:2:2:2:2, 2:1:3:4, and 1:1:1:2:5 pattern for **II-1**, **II-2**, **II-3**, **II-4**, and **II-5**, respectively. One singlet at -22 ppm corresponding to *B*I vertex can be observed for **II-1** and **II-2**. The *B*Br signal of **II-3** is overlapped with other BH signals at -10~-14 ppm. In the ^{11}B NMR spectra of **II-4** and **II-5**, the *B*Ph signal can be observed as a singlet at -3 ppm. The ^{31}P NMR spectra show one singlet at ~30 ppm for PPh_3 ligand in **II-1**,**2**,**5** or one singlet at ~-9 ppm for PMe_3 ligand in **II-3**,**4**.

The B-H···M interactions in late-transition-metal complexes usually lead to a significantly reduced J_{BH} value, a very deshielded ^{11}B signal, and a very high-field ^{1}H resonance.[56] It is noted that there is no significant high-field ^{1}H signal and low-field ^{11}B signal observed in the ^{1}H and ^{11}B NMR spectra of **II-1~5**. The IR spectra (KBr) exhibited one very strong and broad stretching band ν_{B-H} at about 2570 cm^{-1} for **II-1~3**, whereas that of **II-4** and **II-5** showed two ν_{B-H} bands at 2550 cm^{-1} and 2530 cm^{-1} (**II-4**)/2510 cm^{-1} (**II-5**). The latter might indicate B-H···Ni interactions in **II-4** and **II-5**.[50,57]

The solid-state structures of **II-2~6** were further confirmed by single-crystal X-ray analyses. As shown in Figures 2.1~2.5, complexes **II-2~6** have similar coordination geometries, which contain a three-membered ring formed through two Ni–C(cage) bonds and the coordination plane about the nickel atom is essentially planar. There are two crystallographically independent molecules in the unit cell of **II-5**. Figure 2.4 shows its representative structure. Selected bond distances and angles around the metal centers are listed in Table 2.1 for comparison.

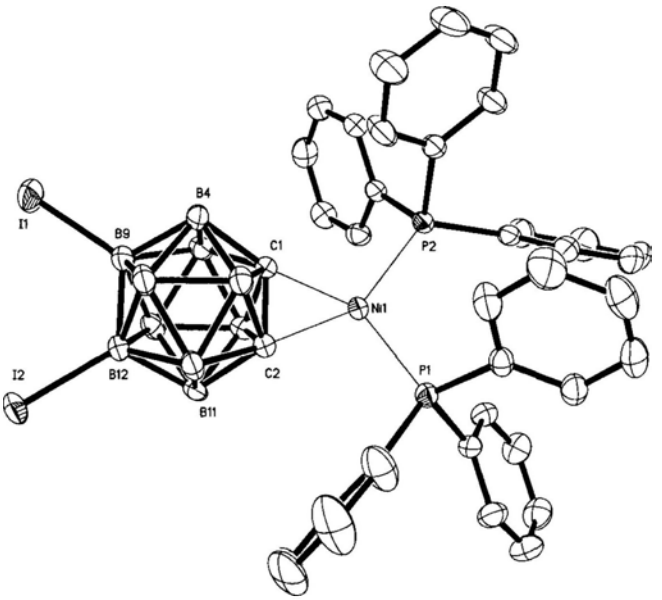


Figure 2.1. Molecular structure of (η^2-9,12-I_2-1,2-$C_2B_{10}H_8$)Ni(PPh_3)$_2$ (**II-2**).

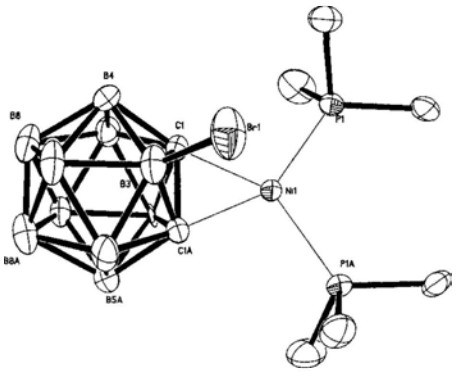


Figure 2.2. Molecular structure of (η^2-3-Br-1,2-$C_2B_{10}H_9$)Ni(PPh_3)$_2$ (**II-3**).

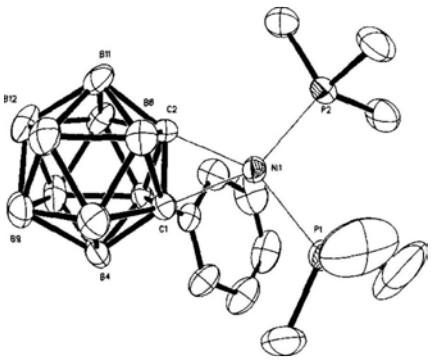


Figure 2.3. Molecular structure of (η^2-3-C_6H_5-1,2-$C_2B_{10}H_9$)Ni(PMe_3)$_2$ (**II-4**).

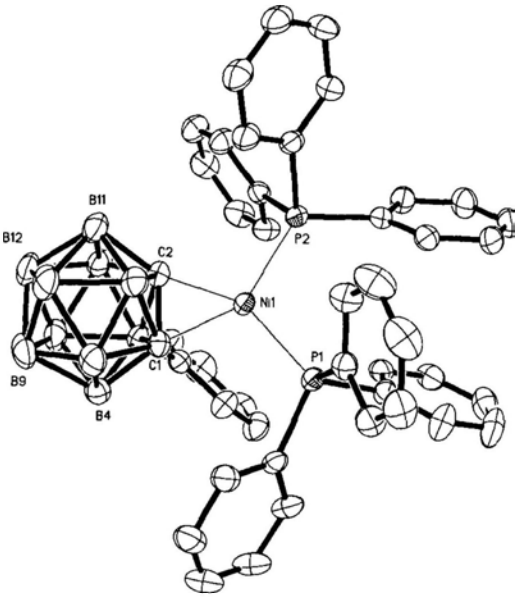


Figure 2.4. Molecular structure of (η^2-3-C_6H_5-1,2-$C_2B_{10}H_9$)Ni(PPh_3)$_2$ (**II-5**), showing one of two independent molecules in the unit cell.

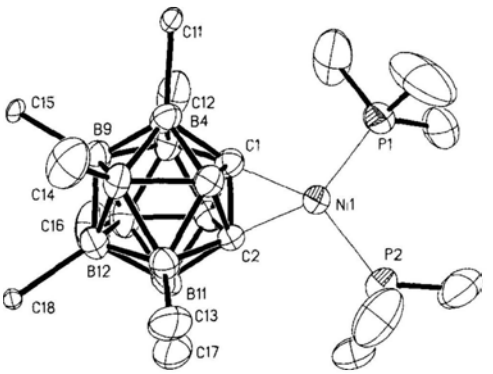


Figure 2.5. Molecular structure of

(η^2-4,5,7,8,9,10,11,12-Me_8-1,2-$C_2B_{10}H_2$)Ni(PMe_3)$_2$ (**II-6**)

Table 2.1 Selected bond distances (Å) and angles (deg) for late transition metal-1,2-*o*-carboryne complexes.

	II-2	**II-3**	**II-4**		**II-5**	**II-6**
C(1)-C(2)	1.550(6)	1.595(14)	1.565(5)	1.576(4)	1.523(3)	1.562(14)
Ni(1)-C(1)	1.926(4)	1.918(6)	1.917(3)	1.927(3)	1.950(2)	1.923(10)
Ni(1)-C(2)	1.917(4)	1.918(6)	1.929(3)	1.924(3)	1.924(2)	1.899(10)
Ni(1)-B(3)	2.647(6)	2.629(15)	2.643(3)	2.672(4)	2.778(2)	2.613(12)
Ni(1)-B(6)	2.626(6)	2.721(20)	2.631(4)	2.583(4)	2.581(3)	2.609(11)
Ni(1)-P(1)	2.190(1)	2.169(2)	2.166(1)	2.164(1)	2.215(1)	2.166(3)
Ni(1)-P(2)	2.214(1)	2.169(2)	2.169(1)	2.163(1)	2.221(1)	2.167(3)
Ni(1)-C(1)-C(2)	65.9(2)	65.4(2)	66.3(2)	65.7(2)	65.9(1)	65.1(5)
Ni(1)-C(2)-C(1)	66.5(2)	65.4(2)	65.6(2)	65.9(2)	67.7(1)	66.7(5)
C(1)-Ni(1)-C(2)	47.6(2)	49.1(4)	48.1(1)	48.3(1)	46.3(1)	48.2(4)

The C(cage)–C(cage) bond distances (1.55~1.57 Å) are close to each other for **II-2,3,4,6** and similar with those observed in the Ni-1,2-*o*-carboryne complexes (1.556(5) Å in (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$, 1.576(6) Å in (η^2-$C_2B_{10}Me_8H_2$)Ni(μ-σ:σ:η^2-dppen)Ni(dppe), 1.551(4) Å in (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)(PCy_3), 1.553(6) Å and 1.561(5) Å in (η^2-$C_2B_{10}H_{10}$)Ni(dppe)), which is much shorter than that of 1.67 Å found in *o*-carborane. The large steric effect results in the shorter C(cage)–C(cage) bond distances of 1.523(3) Å in **II-5**. The shorter bond distances of B(6)-Ni (2.581(3) Å in **II-4**, 2.583(4) Å in **II-5**) over B(3)-Ni (2.778(2) Å in **II-4**, 2.672(4) Å in **II-5**) might indicate some B-H···Ni interactions in the solid-state structures of **II-4** and **II-5** which is consistent with the results derived from IR spectra. These interactions are much weaker than that of 2.313(8) Å in (η^6-$Me_2C_2B_{10}H_{10}$)$MoPt(CO)_4(PPh_3)$.[58] The interactions could be ascribed to the electron requirement nature of the metal centers. It is noteworthy that, since all B-H hydrogen atoms are in calculated positions, a detailed discussion of the B-H distances is not warranted.

2.3 Summary

We have prepared several B-substituted nickel-1,2-*o*-carboryne complexes and fully characterized their structures. Our studies show that the reaction between phosphine ligated metal halide and $Li_2C_2B_{10}H_{10}$ is a good synthetic route for the preparation of these complexes. These late transition metal-1,2-*o*-carboryne

complexes have similar structural features and the C(cage)–C(cage) bonds in these complexes are much shorter than those in Zr-1,2-*o*-carboryne complexes.

Chapter 3. Nickel-Mediated Coupling Reaction of 1,2-*o*-Carboryne with Alkenes

3.1 Introduction

Metal-benzyne complexes have found many applications in organic synthesis, mechanistic studies, and the synthesis of functional materials.[59] In contrast, their analogues, metal-1,2-*o*-carboryne complexes are largely unexplored although the reactivity pattern of 1,2-*o*-carboryne (generated in situ) has been actively investigated.[41-43]

$Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$ (produced in situ from the precursor of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$) has a similar reactivity pattern to that of $Cp_2Zr(\eta^2\text{-}C_6H_4)$ in reactions with polar and nonpolar unsaturated organic substrates.[51,52] It reacts well with isonitrile, nitrile, azide, alkene, and alkyne to give monoinsertion products. One the other hand, $(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)_2$ (**III-1**) undergoes regioselective [2+2+2] cycloaddition with alkynes affording benzocarboranes in a head-to-tail manner, but it does not react with the aforementioned polar unsaturated molecules.[54] These results indicate that the nature of transition metals plays a crucial role in these reactions.

In view of the reactions of nickel-benzynes with alkene to generate mono-insertion products (Scheme 3.1)[60] and the analogy between nickel-benzyne and nickel-1,2-*o*-carboryne complexes (Chart 3.1), we are interested in exploring the

reactivity of nickel-1,2-*o*-carboryne with alkenes In this section we will describe the reaction of nickel-1,2-*o*-carboryne with alkenes affording alkenylcarboranes

Scheme 3.1

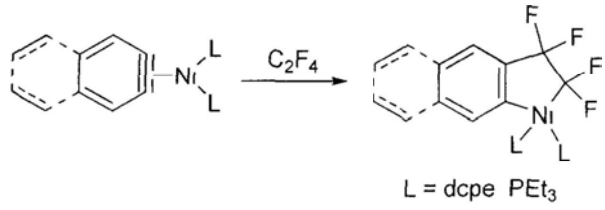


Chart 3.1 Isolobal analog

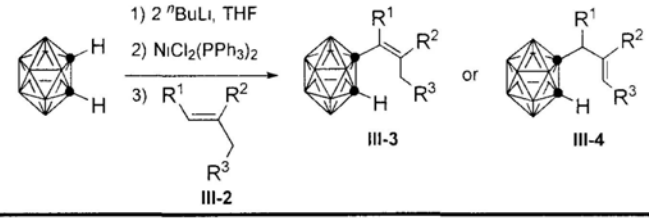
Ni-benzyne Ni-1 2-*o*-carboryne

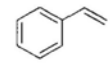
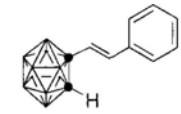
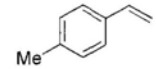
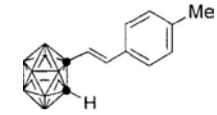
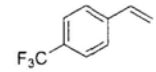
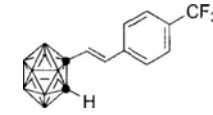
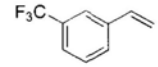
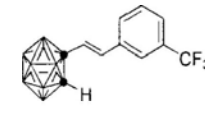
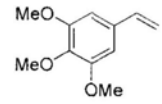
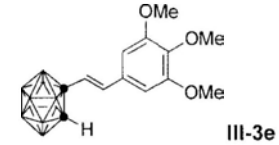
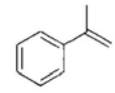
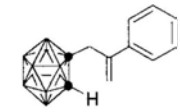
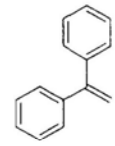
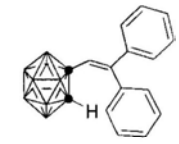
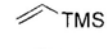
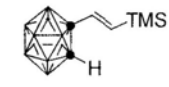
3.2 Results and Discussion

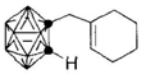
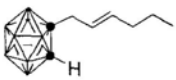
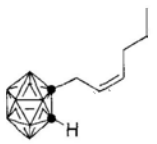
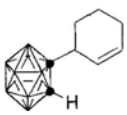
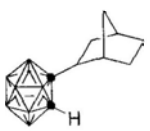
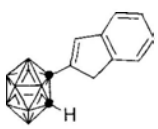
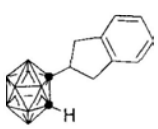
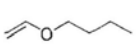
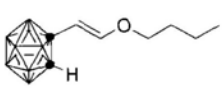
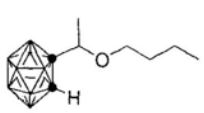
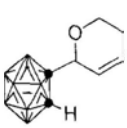
A typical procedure is as follows To a THF solution (10 mL) of $Li_2C_2B_{10}H_{10}$ (1 0 mmol), prepared in situ from the reaction of ^{n}BuLi (2 0 mmol) with *o*-carborane (1 0 mmol), was added $(PPh_3)_2NiCl_2$ (1 0 mmol) at 0 °C The reaction mixture was further stirred for 0 5 h at room temperature giving the Ni-1,2-*o*-carboryne intermediate (η^2-$C_2B_{10}H_{10}$)Ni$(PPh_3)_2$ (**III-1**) [45 54] Alkene (2 equiv) was added at room temperature, and the reaction mixture was heated at 90 °C in a closed vessel overnight The reaction mixture was then cooled to room temperature and quenched with $NaHCO_3$ solution Normal workup afforded the coupling products in excellent regio- and steroselectivity for most alkene as shown in Table 3 1

The temperature is crucial for this reaction No reaction proceeded at $T < 60$ °C

Table 3.1. Nickel-mediated coupling reaction of 1,2-*o*-carboryne with alkene.



Entry	Alkene	Product	Yield (%)[a]
1	 **III-2a**	 **III-3a**	82
2	 **III-2b**	 **III-3b**	85
3	 **III-2c**	 **III-3c**	80
4	 **III-2d**	 **III-3d**	73
5	 **III-2e**	 **III-3e**	76
6	 **III-2f**	 **III-4f**	59
7	 **III-2g**	 **III-3g**	46
8	 **III-2h**	 **III-3h**	46

Entry	Alkene	Product	Yield (%)[a]
9	 **III-2i**	 **III-4i**	77
		 **III-4j**	
10	 **III-2j**	 **III-5j**	74 (1:1)[b]
11	 **III-2k**	 **III-4k**	67
12	 **III-2l**	 **III-5l**	60[c]
13	 **III-2m**	 **III-3m**	31
		 **III-5m**	27[c]
14	 **III-2n**	 **III-3n**	18
		 **III-5n**	12[c]
15	 **III-2o**	 **III-4o**	15

[a] Isolated yields [b] **III-4j/5j** were inseparable and their ratio was estimated by ^{1}H NMR
[c] Isolated after hydrolysis

On the other hand, higher reaction temperatures (>90 °C) led to the decomposition of **III-1** as indicated by ^{11}B NMR. Toluene and diethyl ether were not suitable for this reaction because of the poor solubility of **III-1**. Other phosphines such as PEt_3, $P(OEt)_3$, and dppe gave very similar results to that of PPh_3. It is noted that the same results were obtained if the isolated pure complex **III-1** was used for the reactions.

As shown in Table 3.1, a variety of alkenes is compatible with this nickel-mediated cross-coupling reaction. Substituted styrenes reacted efficiently to give "Heck type" of products **III-3** as single regioisomers with excellent stereoselectivity in very good isolated yields. The nature of the substituents on phenyl ring has no obvious effect on the reaction results (entries 1–5). The yields were lower for 1,1-diphenylethene and vinyltrimethylsilane due to steric effects (entries 7 and 8). The "ene-reaction type" of products was isolated in good yields for aliphatic alkenes and α-methylstyrene (**III-2f**) (entries 6, 9–11). For example, **III-4k** was isolated in 67% yield, which is much higher than the 10–20% yield from the direct reaction of 1,2-*o*-carboryne with cyclohexene.[42] Vinylethers **III-2n** and **III-2o** also reacted with Ni-1,2-*o*-carboryne **III-1** but to a less extent probably due to the coordination of oxygen atom occupying the vacant site of the Ni atom (entries 14 and 15). Such interactions may alter the regioselectivity of the olefin insertion and stabilize the inserted product, leading to the formation of **III-5n** after hydrolysis. In the case of norbornene (**III-2l**), the corresponding inserted product was thermodynamically very stable,[61] affording only hydrolysis product **III-5l** in 60%

isolated yield (entry 12). No double insertion product was observed. For indene (**III-2m**), both hydrolysis product **III-5m** and "ene- reaction type" of species **III-3m** were isolated in 27% and 31% yield, respectively (entry 13). No reaction was proceeded with *cis*- and *trans*-stillbene, 6,6-dimethylfulvene, 1,1-dimethylallene, 1-phenylallene, 2-propenenitrile, diphenylvinylphosphine, ethylvinylsulfide, anthracene, furan, and thiophene.

All new products were fully characterized by various spectroscopic techniques and high resolution MS. In the ^{1}H NMR spectra of **III-3a**~**e**, **h**, and **n**, ^{3}J (~15 Hz) for olefinic protons indicates a *trans*-conformation. In the reaction of 1-hexene, *trans*- and *cis*-isomers were observed with the molar ratio of 1:1 in the ^{1}H NMR spectrum of the crude product. The ^{11}B NMR spectra generally exhibited a 1:1:2:2:2:2 splitting pattern for all these mono-substituted carboranes.

The molecular structures of **III-3c**, **III-3e**, and **III-3g** were further confirmed by single-crystal X-ray analyses (Figure 3.1~3.3).

It has been documented that the reaction of 1,2-*o*-carboryne (generated in situ) with anthracene, furan, or thiophene gave [2+4] cycloaddition products.[41-43] The Ni-1,2-*o*-carboryne complex **III-1**, however, did not react with any of them. This result suggests that 1,2-*o*-carboryne and Ni-1,2-*o*-carboryne should undergo different reaction pathways in the reactions with alkene.

Scheme 3.2 shows the plausible mechanism for the formation of coupling products. Dilithiocarborane reacts with $(PPh_3)_2NiCl_2$ to generate the

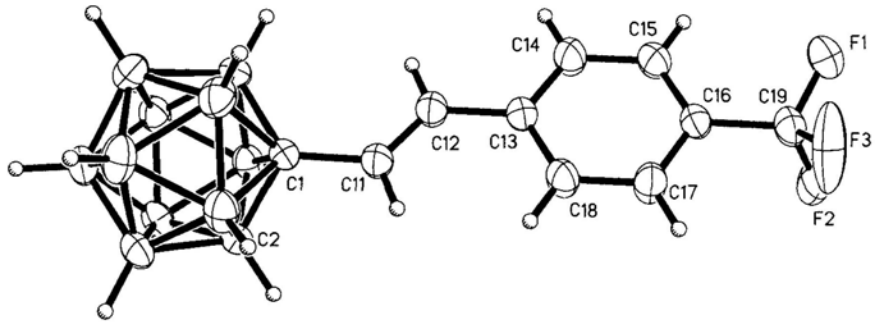


Figure 3.1. Molecular structure of **III-3c**.

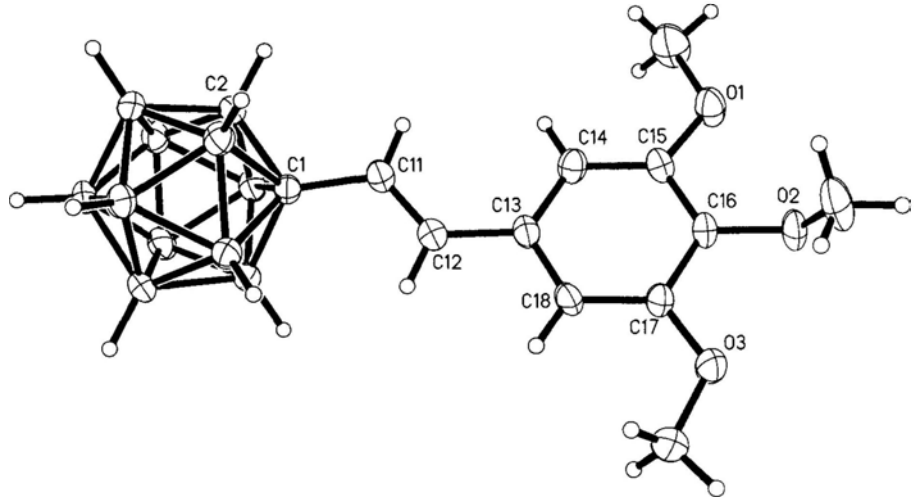


Figure 3.2. Molecular structure of **III-3e**.

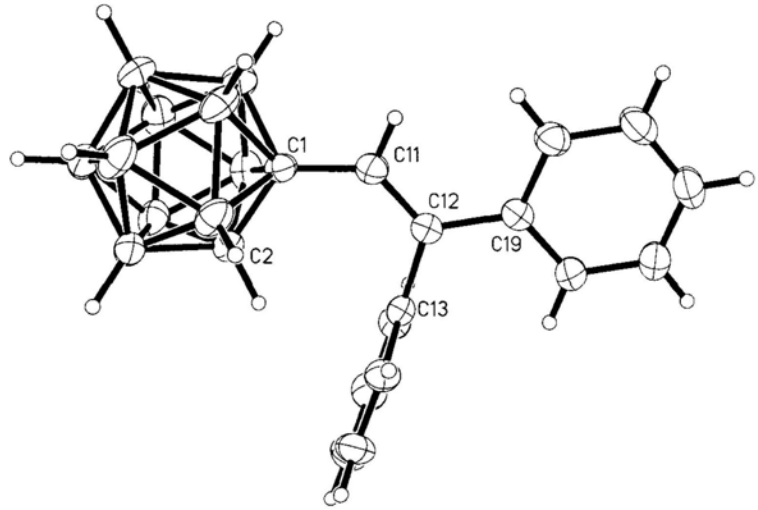
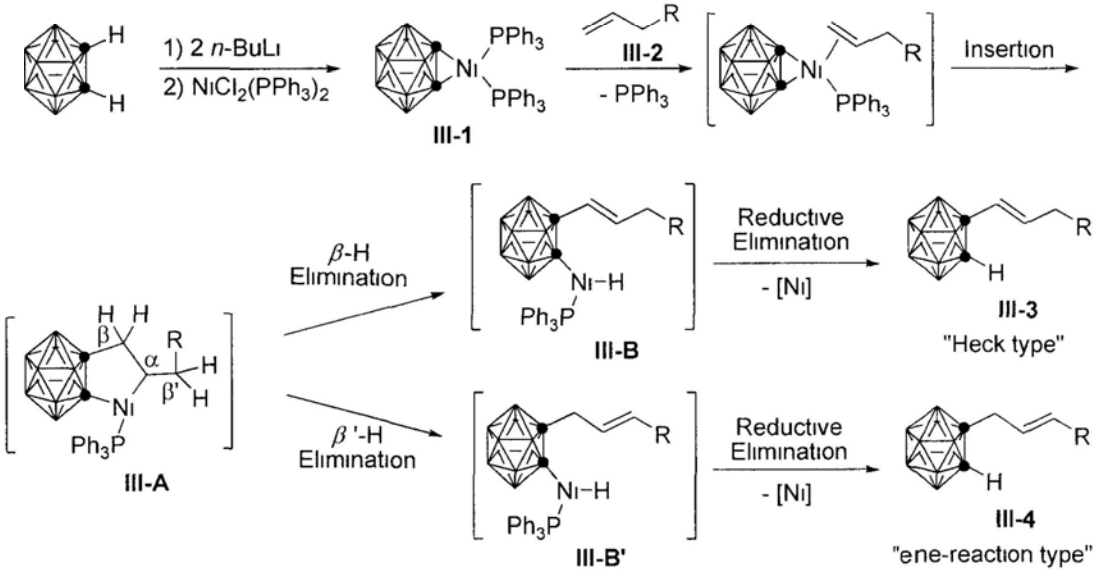


Figure 3.3. Molecular structure of **III-3g**.

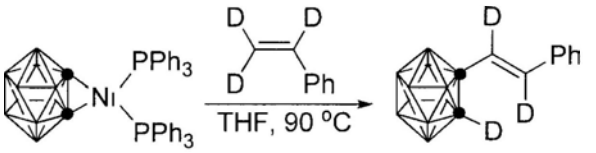
Ni-1,2-*o*-carboryne complex **III-1**.[45] Coordination and insertion of alkene give a nickelacycle **III-A**.[62] The regioselectivity observed in the reaction can be rationalized by the large steric effect of carborane moiety. β-H/β'-H elimination prior to the insertion of the second molecule of alkene produces the intermediate **III-B/B'**.[63] Reductive elimination affords the alkenylcarboranes **III-3** ("Heck type" of products) or **III-4** ("ene-reaction type" of products). In general, β-H elimination of five-membered metallacycles is more difficult than β'-H elimination (vide infra).[63] Such hydrogen elimination reactions may be suppressed due to steric reasons[61a] or intramolecular coordination of the heteroatom, which leads to the formation of alkylcarboranes after hydrolysis (Table 3.1, entries 12–14).

Scheme 3.2. Proposed mechanism for the formation of coupling products



The aforementioned mechanism is supported by the following experiment. Treatment of **III-1** with styrene-d_3 in THF at 90 °C gave [D_3]-**III-3a** in 80% isolated yield with >95% deuterium incorporation (Scheme 3.3).

Scheme 3.3. Reaction of **III-1** with styrene-d_3.



III-1 [D_3]-**III-3a**

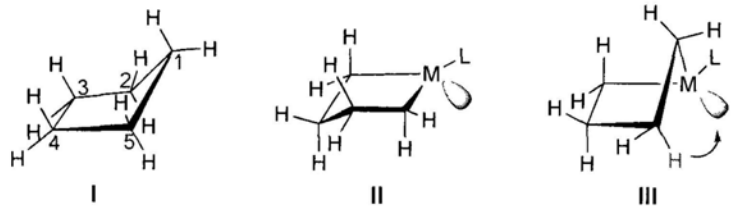
It has been suggested that many metallacycles, such as six-, five-, four-, and three-membered metallacycles, cannot undergo β-H elimination readily, because the M-C_α-C_β-H dihedral angles in these compounds are constrained to values far from 0°. In addition, the β-hydrogen atoms are constrained to positions far away from the metal center. These theories are conformed to our result that β-H elimination of five-membered metallacycles is more difficult than β'-H elimination. However, there is increasing evidence that β-H elimination reactions of five-membered-ring intermediates to afford hydridometal alkene complexes are possible (Scheme 3.4).[63]

Scheme 3.4

It is well-known that cyclopentane actually assumes a slightly puckered "envelope" conformation that reduces the eclipsing and lowers the torsional strain. This puckered shape is not fixed but undulates by the thermal up-and-down motion

of the five methylene groups (Scheme 3.5, **I**). In the metallacycle, there are three types of unique positions in the five-membered ring. In consideration of the steric effect of the ligand, the metal atom can only be located at two positions (Scheme 3.5, **II** and **III**). The two conformational isomers are both 14 electron species. Because of their coordinatively unsaturated feature, each isomer is expected to have a low-lying unoccupied orbital, which should have the maximum amplitude along the direction of the missing leg in the four-legged piano-stool structure. The low-lying unoccupied orbital is ready to accept the β-hydrogen to form the metal-hydride bond in the eliminated product. It can be seen that in **II** all the β-hydrogens orient themselves away from the maximum amplitude of the low-lying unoccupied orbital. However, there is a β-hydrogen in close proximity to the maximum amplitude of the low-lying unoccupied orbital in **III**. The close proximity of the transferring β-hydrogen to the accepting unoccupied orbital is essential to facilitate the β-hydrogen elimination process.[63d]

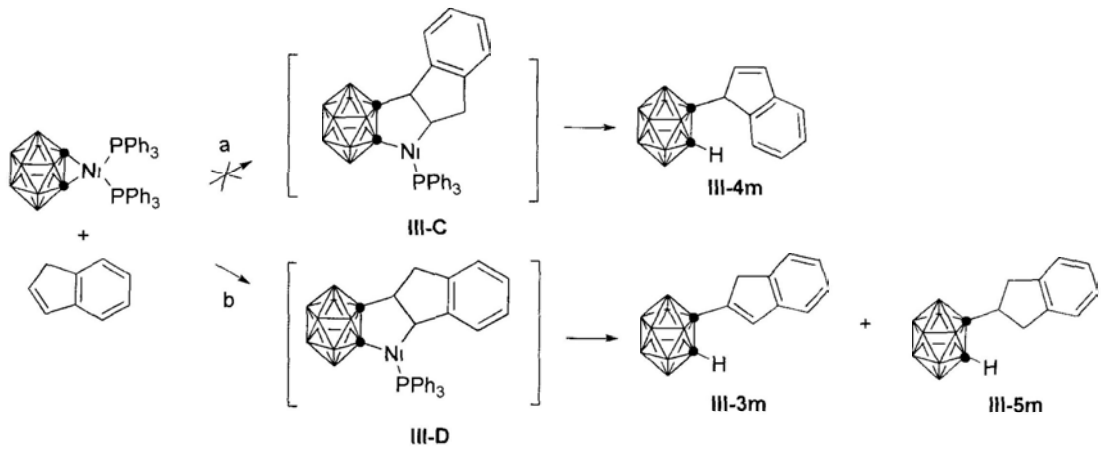
Scheme 3.5



In the reaction of indene (**III-2m**), due to the steric reason, indene prefers to insert as showed in pathway b to give intermediate **III-D** than afford **III-4m** through intermediate **III-C** in pathway a (Scheme 3.6). After quenching, the hydrolysis

product **III-5m** without β-H elimination is observed along with the normal product **III-3m** in 0.9:1 molar ratio. It can be considered that there are two β-H conformations in **III-D** (*exo* and *endo* to Ni). The β-H_{endo} elimination affords **III-3m**. Due to the fused ring structure, the coplanar conformation is difficult to be achieved by β-H_{exo} and Ni atom, and the hydrolysis species **III-5m** is obtained as the final product.

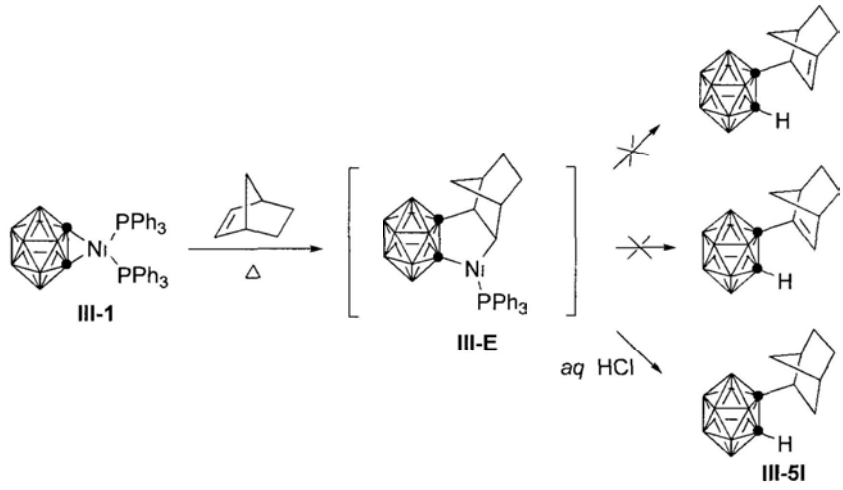
Scheme 3.6



In the reaction of norbornene (**III-2l**), the metallacycle **III-E** is especially stable owing to the absence of β-H atom with appropriate geometric requirements for elimination, the alkyl-substituted product was obtained after quenching (Scheme 3.7).[61]

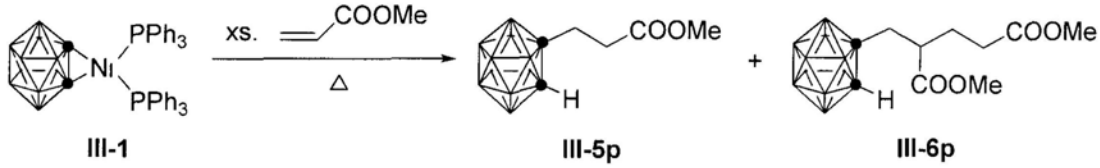
The reactions of nickel-1,2-*o*-carboryne **III-1** with alkenes having donor atom such as methyl acrylate and 2-vinylpyridine were also investigated (Schemes 3.8 and 3.10). The coordination of these donor atoms in olefin may stabilize the intermediate, preventing the β-H elimination.

Scheme 3.7



In case of methyl acrylate, the absence of alkenylcarborane can be rationalized by the coordination of the carbonyl to the Ni atom, stabilizing the nickelacycle intermediate. Product **III-6p**, generated from the second molecule of methyl acrylate insertion into the Ni–C_{alkyl} bond, was obtained by extending the reaction time to 5 days.

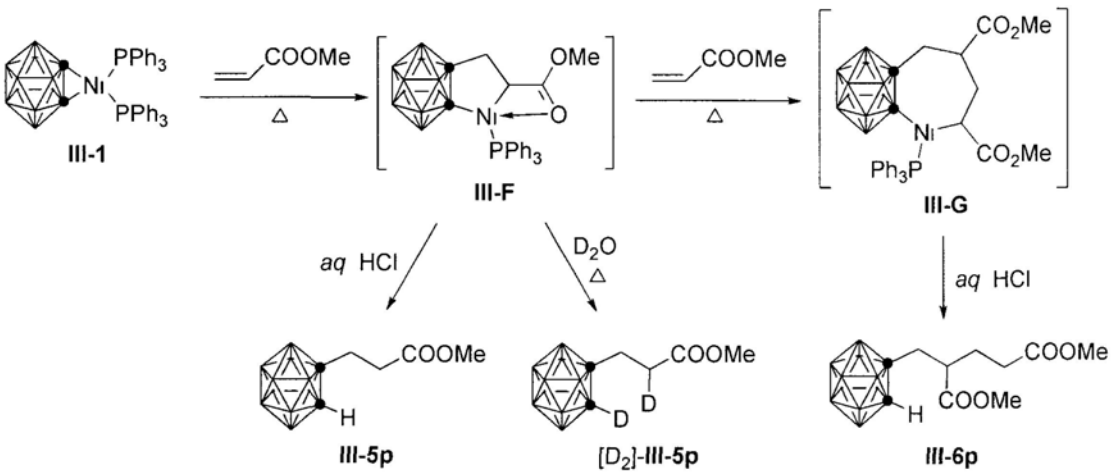
Scheme 3.8. Reaction of **III-1** with methyl acrylate.



1 day	62%	-
5 days	57%	14%

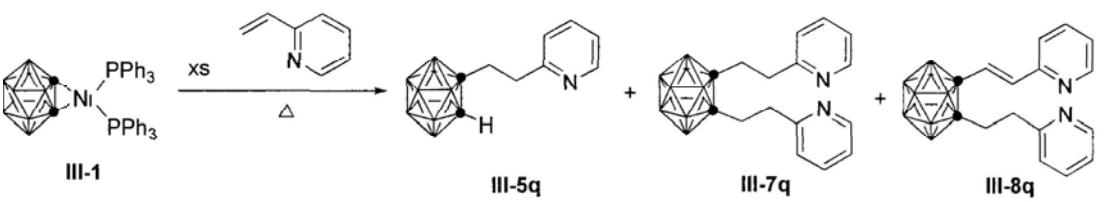
To investigate the reaction mechanism, the following labeling experiment was performed. Quenching the reaction mixture with D_2O can afford the desired product [D_2]**III-5p** with greater than 95% deuterium incorporation (Scheme 3.9).

Scheme 3.9. Proposed mechanism for the formation of alkylcaborane product.



The reaction of 2-vinylpyridine is different from that of methyl acrylate. Although similar mono-alkylcarborane was obtained after heating at 90°C overnight and quenching, extension of reaction time can lead to the isolation of two new products, **III-7q** and **III-8q**, which should be generated by the insertion of the second molecule of 2-vinylpyridine into the Ni–C(cage) bond (Scheme 3.10). It's a very rare example for a M–C(cage) bond to be involved in the reactions because the unique electronic and steric properties of carboranyl moiety can make the M–C(cage) bond in metal-carboranyl complexes inert toward unsaturated molecules.[64]

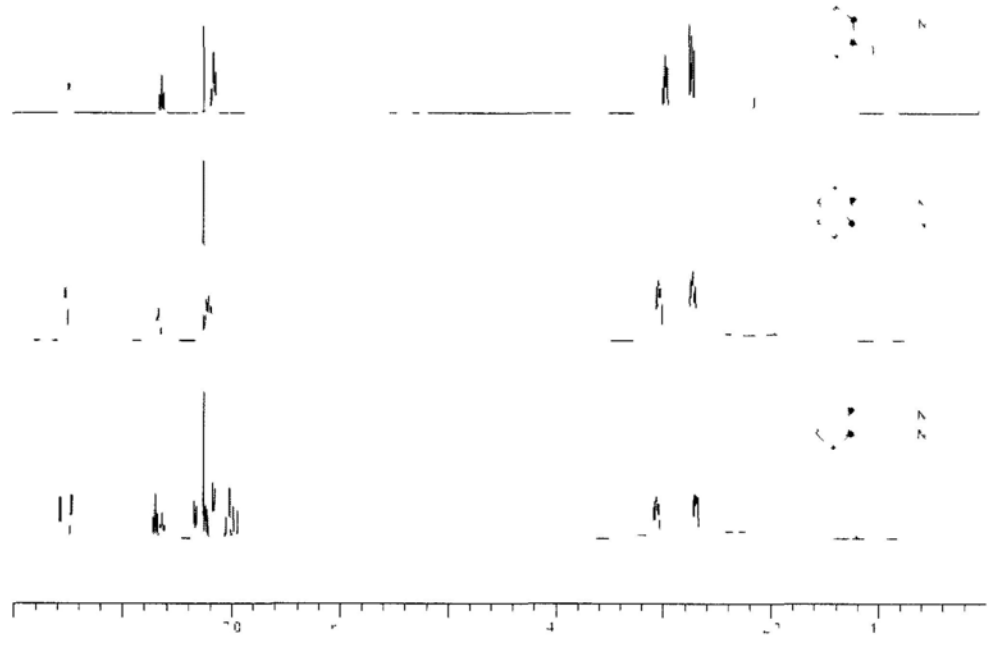
Scheme 3.10. Reaction of **III-1** with 2-vinylpyridine.



	III-5q	III-7q	III-8q
overnight	59%	trace	trace
3 days	22%	16%	10%

The ^{1}H NMR spectra of **III-5q** and **III-8q** are compared with that of **III-7q** (Figure 3.4). In the ^{1}H NMR spectrum of **III-5q**, one singlet at 3.80 ppm corresponding to the cage C*H* can be clearly observed. The ^{1}H NMR spectrum of **III-8q** clearly showed two doublets at 6.97 ppm and 7.03 ppm with ^3J = 15.3 ppm corresponding to *trans*-olefinic protons. And two sets of pyridinyl signals indicate the unsymmetrical structure of **III-8q**.

Figure 3.4. ^{1}H NMR spectra of **III-5q**, **III-7q**, and **III-8q**



The molecular structures of **III-7q**, **III-8q**, and **III-5p** were further confirmed by single-crystal X-ray analyses as shown in Figures 3.5~3.7.

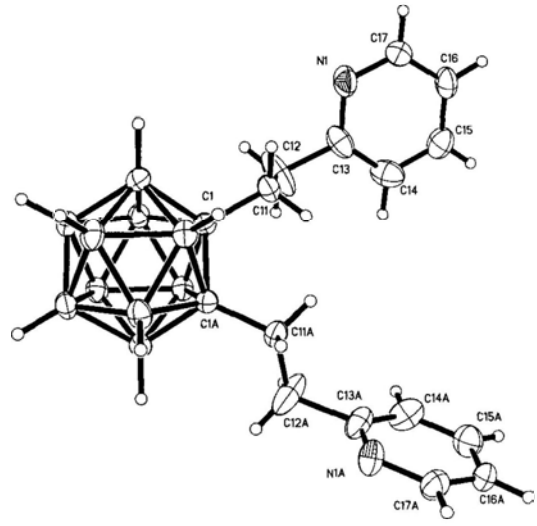


Figure 3.5. Molecular structure of **III-7q**.

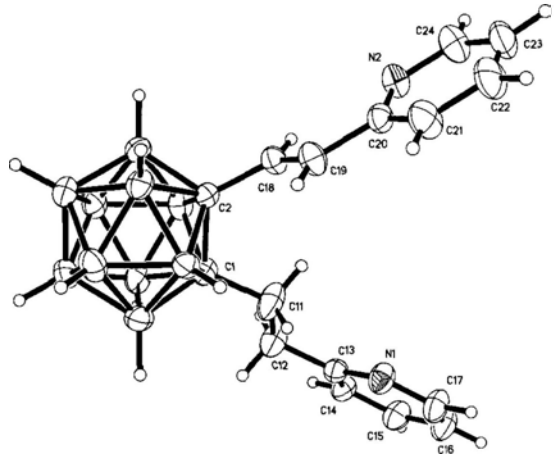


Figure 3.6. Molecular structure of **III-8q**.

Table 3.2. Selected bond distances(Å) and angles (°) for **III-7q** and **III-8q**.

III-7q		**III-8q**			
C1-C11	1.522(3)	C1-C11	1.513(3)	C2-C18	1.497(2)
C11-C12	1.482(4)	C11-C12	1.406(3)	C18-C19	1.347(3)
C12-C13	1.510(3)	C12-C13	1.492(3)	C19-C20	1.474(3)
C1-C11-C12	116.2(2)	C1-C11-C12	118.4(2)	C2-C18-C19	123.3(2)
C11-C12-C13	112.2(2)	C11-C12-C13	117.8(2)	C18-C19-C20	122.6(2)

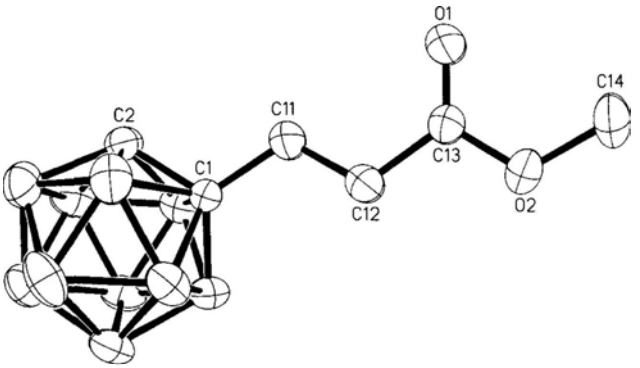
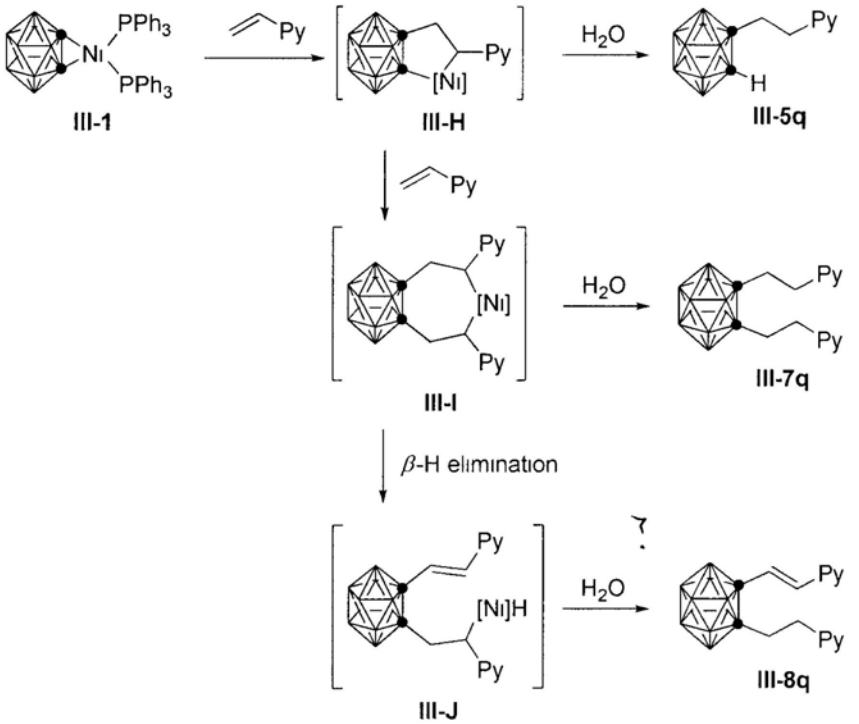


Figure 3.7. Molecular structure of **III-5p**.

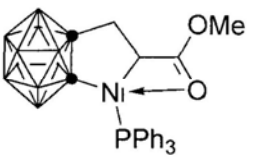
Scheme 3.11 shows the plausible mechanism for the formation of **III-7q** and **III-8q**. A second equiv of 2-vinylpyridine can insert into the Ni–C(cage) bond in nickelacyclopropane **III-H** to afford nickelacycloheptane **III-I**, which can undergo β-H elimination to give Ni-H species **III-J**. Quenching of these coexisting intermediates of **III-H**, **III-I**, and **III-J** in the reaction mixture leads to the formation of **III-5q**, **III-7q**, and **III-8q**, respectively.

Scheme 3.11. Proposed mechanism for the formation of **III-7q** and **III-8q**.

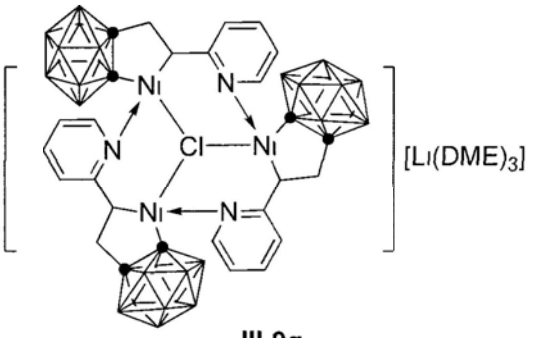


The mono-alkene insertion species nickelacyclopentanes **III-9p,q** (Chart 3.2) were isolated and fully characterized from the reaction of **III-1** with methyl acrylate and 2-vinylpyridine, respectively. Complex **III-9q** was further confirmed by single-crystal X-ray analyses. It is an ionic complex, in which the anion consists of three square-planar Ni moieties sharing one μ_3-Cl atom (Figure 3.8). The proposed molecular structure of **III-9p** is shown in Chart 3.2, which is supported by ^{1}H, ^{13}C and ^{11}B NMR as well as elemental analyses.

Chart 3.2



III-9p



III-9q

3.3 Summary

We have developed a nickel-mediated coupling reaction of 1,2-*o*-carboryne with a variety of alkenes, which gives alkenylcarboranes in moderate to very good isolated yields with excellent regio- and stereoselectivity. This serves a new methodology for the synthesis of alkenylcarboranes. This work also demonstrates that Ni-1,2-*o*-carboryne exhibits different reactivity patterns toward alkynes and alkenes.

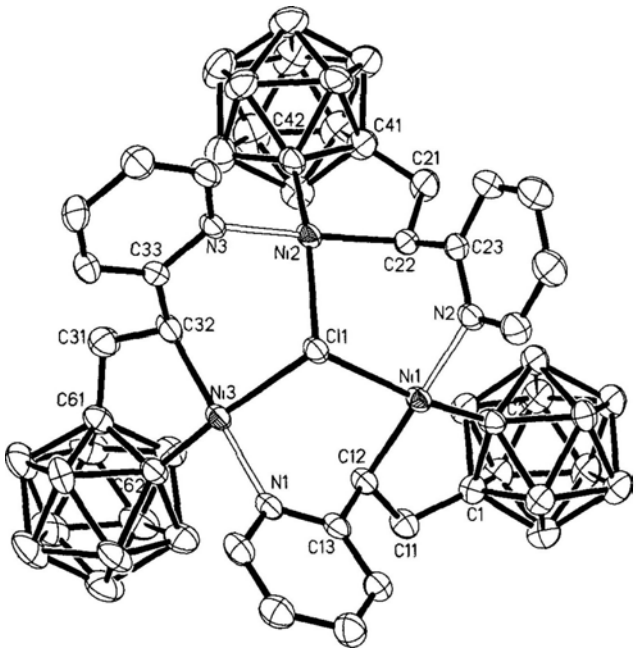


Figure 3.8. Molecular structure of the anion in **III-9q**. Selected bond lengths (Å) and angles (deg): Ni1-C2 1.884(5), Ni1-C12 1.966 (5), Ni1-Cl1 2.292(1), Ni1-N2 1.937(4), Ni2-C42 1.884(6), Ni2-C22 1.970(5), Ni2-Cl1 2.307(1), Ni2-N3 1.946(4), Ni3-C62 1.880(5), Ni3-C32 1.974(6), Ni3-Cl1 2.285(1), Ni3-N1 1.948(4), C2-Ni1-C12 88.3(2), C42-Ni2-C22 87.7(2), C62-Ni3-C32 87.6(2).

The β-H elimination reactions may be suppressed due to steric reasons or intramolecular coordination of the heteroatom leading to the formation of alkylcarboranes after hydrolysis. The thermodynamically stable inserted intermediate offered us an opportunity to investigate its reactivity and to synthesize novel carborane derivatives.

Chapter 4. Nickel-Mediated/Catalyzed Three-Component Cycloaddition Reaction of 1,2-*o*-Carboryne/Arynes, Alkenes, and Alkynes

4.1 Introduction

Transition metal-mediated cycloadditions of alkynes and/or alkenes serve as a powerful strategy to construct a wide range of compounds since complexation of the metal center to an olefin or alkyne significantly modifies the reactivity of this moiety.[65]

1,2-*o*-Carboryne can react with alkenes in ene- and [2+2] reaction manner.[40-43] In contrast, nickel-1,2-*o*-carboryne reacts with alkenes to afford the 'Herk type" and "ene-reaction type" cross-coupling products. In the reaction of nickel-1,2-*o*-carboryne with alkenes, when methyl acrylate or 2-vinylpyridine was used as the starting material, only alkylcarboranes were obtained after hydrolysis. The nickelacyclopentane intermediates were isolated in which the donor atom of the olefin can stabilize the intermediates, preventing the β-H elimination. We then studied the reactivity of these intermediates and found that they can react readily with alkynes to give three-component [2+2+2] cycloaddition products.

Multicomponent cross-coupling reactions are a powerful strategy to assemble complex molecules from very simple precursors in a single operation.[66] Arynes, a class of very reactive analogues of alkynes, have recently been reported to undergo metal-catalyzed conversion.[67-76] For examples, the cyclotrimerization of arynes[67] and

the cocyclization of arynes with alkynes,[68] allylic halides,[69] or activated alkenes[70] can all be catalyzed by palladium. Palladium can also catalyze three-component cross-coupling reactions of arynes, allylic halides[71] (allylic epoxides,[72] aromatic halides[73]) and alkynylstannanes[71a] (boronic acids[71b]) to form substituted benzenes, and three-component cyclization of arynes, aryl halides, and alkynes[74] or alkenes[75] to produce phenanthrene derivatives. In contrast, nickel-catalyzed transformations of arynes is much less explored.[76]

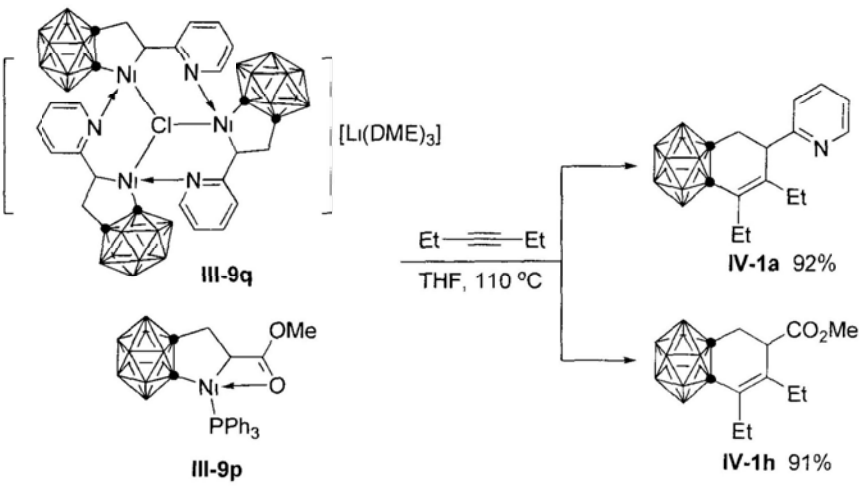
In view of the analogy between 1,2-*o*-carboryne and its two dimensional relative benzyne, we are also interested in exploring the three-component reaction of benzyne with alkenes and alkynes. In this section we will describe the nickel-mediated three-component cycloaddition reaction of 1,2-*o*-carboryne with alkenes and alkynes to afford dihydrobenzo-1,2-*o*-carboranes and nickel-catalyzed three-component cycloaddition reaction of arynes with alkenes and alkynes to afford dihydronaphthalenes.

4.2 Results and Discussion

The mono-alkene insertion species **III-9p** or **III-9q** do not show any activity toward olefins such as styrene and 1-hexene (except for excess of activated alkenes such as methyl acrylate and 2-vinylpyridine). But they can react readily with alkynes to give three-component [2+2+2] cycloaddition products. In an initial attempt, the THF solution of **III-9q** or **III-9p** was added with 10 equiv of 3-hexyne and heated at

110 °C for 3 days to afford dihydrobenzo-1,2-*o*-carborane **IV-1a** and **IV-1h** in 92% and 91% isolate yields, respectively (Scheme 4.1). These results show that alkynes are more reactive than alkenes toward these nickelacyclopentane complexes.

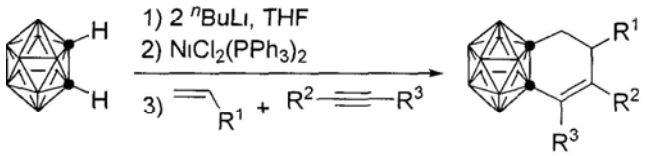
Scheme 4.1. Reactions of nickelacyclopentanes with 3-hexyne.



We then examined the reaction in the three-component manner. In a typical procedure, alkene (1.2 equiv) and alkyne (4 equiv) were added to a THF solution of nickel-1,2-*o*-carboryne, prepared in situ by the reaction of $Li_2C_2B_{10}H_{10}$ with $NiCl_2(PPh_3)_2$,[45] and the reaction mixture was heated at 110 °C in a closed vessel. Standard workup procedures afforded the cyclization products in very good chemo- and regioselectivity (Table 4.1). An excess amount of alkynes were necessary as hexasubstituted benzenes were isolated from all reactions, which were generated via Ni-mediated cyclotrimerization of alkynes.[65] It is noted that alkynes do not react with nickelacyclopentanes till the reaction temperature reaches ~80 °C and the optimal

temperature is 110 °C as suggested by GC-MS analyses. On the other hand, activated alkenes can react well with Ni-1,2-*o*-carboryne in THF at room temperature to give the nickelacycls. Therefore, a separate addition of alkene and alkyne is not necessary for this system.

Table 4.1. Nickel-mediated three-component cycloaddition.



IV-1

Entry	R^1	R^2	R^3	Products	Yield[a]
1	2-Py	Et	Et	**IV-1a**	57
2	2-Py	^{n}Bu	^{n}Bu	**IV-1b**	32
3	2-Py	Me	^{i}Pr	**IV-1c**	34
		^{i}Pr	Me	**IV-1c'**	(1.6 :1)
4	2-Py	Me	Ph	**IV-1d**	40
5	2-Py	Me	*p*-Tolyl	**IV-1e**	35
6	2-Py	Et	Ph	**IV-1f**	39
7	2-Py	^{n}Bu	Ph	**IV-1g**	31
8	2-Py	Ally	Ph	**IV-1h**	36
9	2-Py	Ph	Ph	NR	-
10	2-Py	TMS	TMS	NR	-
11	CO_2Me	Et	Et	**IV-1i**	59
12	CO_2Me	^{n}Pr	^{n}Pr	**IV-1j**	50
13	CO_2Me	^{n}Bu	^{n}Bu	**IV-1k**	48
14	CO_2Me	Ph	Ph	NR	-
15	CO_2Me	TMS	TMS	NR	-

[a] Isolated Yields

As shown in Table 4.1, a variety of alkynes are compatible with this nickel-mediated three-component cyclization. Steric factors played an important role

in the reactions. Sterically less demanding 3-hexyne offered the highest yield (entries 1 and 11). No reaction proceeded for diphenylacetylene (entries 9 and 14) and bis(trimethylsilyl)acetylene (entries 10 and 15). 4-Methyl-2-pentyne offered two regio-isomers in a molar ratio of 1.6:1 (entry 3). Other unsymmetrical alkynes gave only one isomer of **IV-1** due to the electronic effects as phenyl can be viewed as electron-withdrawing group (entries 4–8).[60,77] In the case of CH_2=$CHCH_2C{\equiv}CC_6H_5$, no C=C insertion product was observed (entry 8). It is noteworthy that terminal alkynes quenched the reaction intermediates to afford **III-9q,r**, and nitriles, isonitriles, or carbodiimides did not yield any insertion products.

Compounds **IV-1** were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR as well as high-resolution mass spectrometry. The regioisomers of **IV-1c** were assigned using NOESY analyses (Chart 4.1).

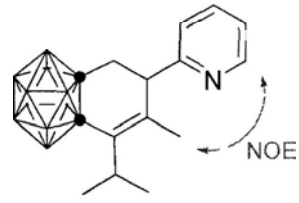


Chart 4.1

In the ^{1}H NMR spectra ($CDCl_3$) of **IV-1a~1h**, which generated from the reaction of Ni-1,2-*o*-carboryne, 2-vinylpyridine, and alkynes, two doublet of doublets at ~2.8 ppm with ^2J = 14.8 Hz, ^3J = 7.2 Hz and ~3.0 ppm with ^2J = 14.8 Hz, ^3J = 10.8 Hz assignable to the carborane cage connected CH_2 unit and one doublet of doublet at ~3.9 ppm with ^3J = 7.2 and 10.8 Hz corresponding to the C*H* proton, were observed. In case of methyl acrylate insertion products **IV-1i~1k**, the C*H* signal was

shifted upfield to ~3.3 ppm as a multiplet. The two CH_2 signals moved to ~2.5 ppm with ^2J = 14.7 Hz, ^3J = 7.3 Hz and ~3.2 pp with ^2J = 14.7 Hz, ^3J = 6.0 Hz. Their ^{13}C NMR spectra were consistent with the ^{1}H NMR results. The ^{13}C NMR spectra showed the signals of C*H* and CH_2 unit at 47~41 and 37~32 ppm, respectively. The ^{11}B NMR spectra exhibited a 1:1:8 splitting pattern for **IV-1a~1h** and a 1:1:1:1:6 splitting pattern for **IV-1i~1k**.

The solid-state structures of **IV-1d** and **IV-1i** were further confirmed by single-crystal X-ray analyses. In the molecular structure of **IV-1d** (Figure 4.1), the bond distances and angles indicate that C(11) and C(12) are sp^3-carbons whereas C(18) and C(20) are sp^2-carbons. There are two crystallographically independent molecules in the unit cell of **IV-1i**. Figure 4.2 shows the representative structure. The bond distances and angles are very close to those observed in **IV-1d**.

Scheme 4.2 shows the plausible mechanism for the formation of [2+2+2] cycloaddition products. The trinuclear Ni complex in **III-9r** may be dissociated into mononuclear Ni complex during the reaction. Accordingly, the formation of products **IV-1** can be rationalized by the sequential insertion of alkene and alkyne into the Ni–C bond. The insertion of alkene affords the nickelacyclopentane **III-9**. Subsequent insertion of alkyne into the nickel–C(alkyl) bond gives the seven-membered intermediate **IV-A**.[54,64] Reductive elimination yields the final products **IV-1**.

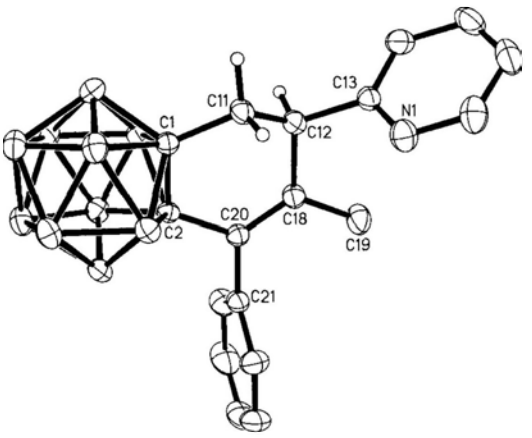


Figure 4.1. Molecular structure of **IV-1d**. Selected bond lengths (Å) and angles (deg): C1-C2 1.640(2), C1-C11 1.519 (2), C11-C12 1.536(2), C12-C18 1.531(2), C18-C20 1.340(2), C2-C20 1.503(2), C2-C1-C11 115.8(1), C1-C11-C12 114.4(1), C11-C12-C18 112.8(1), C12-C18-C20 122.6(1), C18-C20-C2 122.2(1), C20-C2-C1 115.9(1).

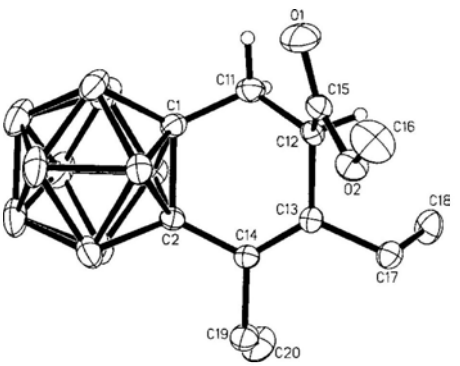
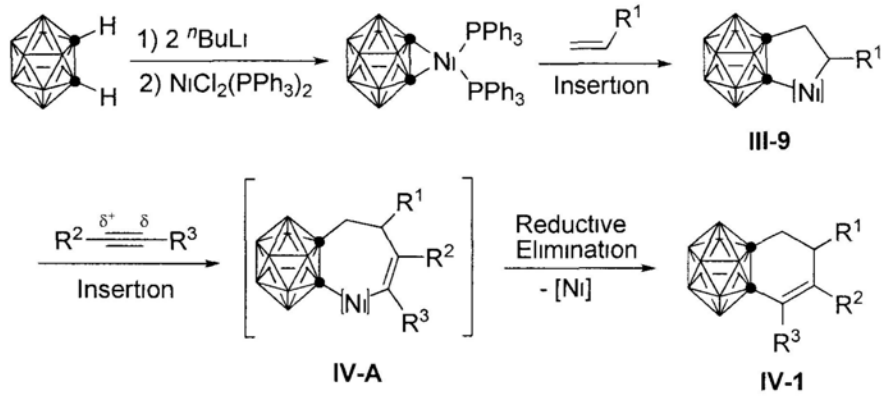


Figure 4.2. Molecular structure of **IV-1i**. Selected bond lengths (Å) and angles (deg): C1-C2 1.650(3), C1-C11 1.507 (4), C11-C12 1.516(4), C12-C13 1.532(4), C13-C14 1.335(4), C2-C14 1.493(4), C2-C1-C11 115.6(2), C1-C11-C12 113.5(2), C11-C12-C13 114.7(2), C12-C13-C24 122.5(2), C13-C14-C2 121.6(2), C14-C2-C1 116.5(2).

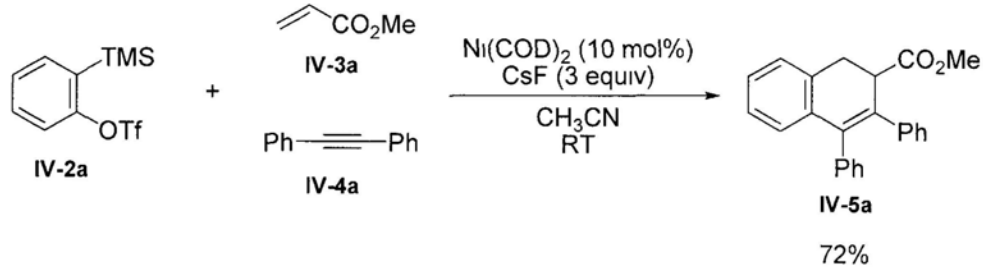
Scheme 4.2. Proposed mechanism for three-component cycloaddition.



We then extended our research to include arynes and found that nickel can efficiently catalyze three-component [2+2+2] cyclization of arynes, alkenes, and alkynes to afford a series of substituted dihydronaphthalenes that cannot be prepared from readily available starting materials.[78]

In an initial attempt, a CH_3CN solution of benzyne precursor **IV-2a** (1 equiv, 2-(trimethylsilyl)phenyltriflate), methyl acrylate **IV-3a** (2 equiv), and diphenyl acetylene **IV-4a** (1.2 equiv) in the presence of $Ni(cod)_2$ (10 mol %) and CsF (3 equiv) was stirred at room temperature for 5 h to give the cyclization product **IV-5a** in 72% isolated yield (Scheme 4.3 and Table 4.2, entry 6).

Scheme 4.3. Three-component reaction of benzyne, methyl acrylate, and diphenylacetylene.

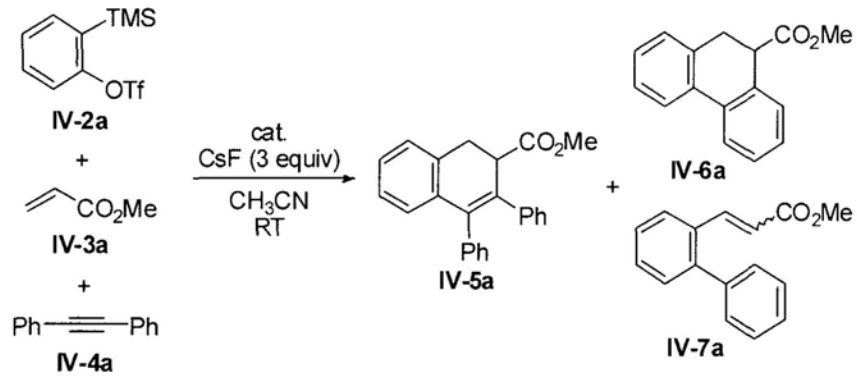


Subsequent work focused on optimization of this reaction (Table 4.2). Changing the ligand from cod to PPh_3 or adding PPh_3 to $Ni(cod)_2$ led to a big drop in the isolation of **IV-5a** from 72% to 50% yield (entries 6 and 9). Addition of bidentate ligand dppe further decreased the isolated yield of **IV-5a** to 21% (entry 10). No detectable **IV-5a** was observed when $NiCl_2(PBu^n_3)_2$/Zn or $NiCl_2$(dppp)/Zn was used as catalyst (Table 4-2, entries 3 and 5). In contrast, palladium complexes such as $Pd(dba)_2$, $PdCl_2(PPh_3)_2$/Zn, and $Pd(PPh_3)_4$ did not mediate three-component benzyne-alkene-alkyne cyclization, rather they catalyzed two-component benzyne-alkene-benzyne cycloaddition and cross-coupling[70] to afford 9,10-dihydrophenanthrene **IV-6a** and methyl 3-(1,1'-biphenyl-2-yl)-2-propenate **IV-7a** (entries 11–13).

These results showed that (1) both metal and ligand had significant effects on the reactions; (2) activated alkene is more reactive than alkyne, otherwise two-component benzyne-alkyne-alkyne cycloaddition products should be observed; and (3) $Ni(cod)_2$ exhibited the highest catalytic activity in three-component [2+2+2] cyclization. The same results were observed when the catalyst loading was decreased from 10 mol % to 5 mol % (Table 4.2, entry 8) or the reaction temperature was increased from room temperature (20 °C) to 50 °C (Table 4.2, entry 7).

The scope and limitation of this Ni-catalyzed cyclization process were then examined using various alkenes and aryne precursors. The results were summarized in Table 4.3. Acrylates **IV-3a**,**b**,**c** gave very high isolated yields (72~76%) of the

Table 4.2. Optimization of three-component cycloaddition reaction[a]



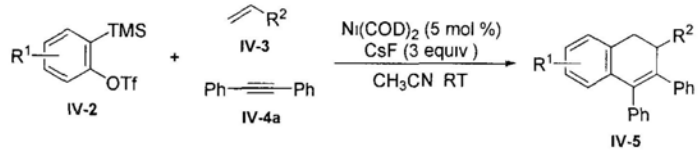
Entry	Catalyst	Loading [mol %]	Yield of **IV-5a** (%)[b] (**IV-5a** : **IV-6a** : **IV-7a**)[c]
1	$Ni(PPh_3)_4$	10	50 (55 : <2 : 43)
2	$NiCl_2(PPh_3)_2$/Zn (1:3)	10	52 (67 : 8 : 25)
3	$NiCl_2(PBu^n_3)_2$/Zn (1:3)	10	0 (<2 : 51 : 47)
4	$NiCl_2$(dppe)/Zn (1:3)	10	11 (17 : 32 : 51)
5	$NiCl_2$(dppp)/Zn (1:3)	10	0 (<1 : 27 : 72)
6	$Ni(cod)_2$	10	72 (90 : <5 : <5)
7	$Ni(cod)_2$	10	73[d] (90 : <5 : <5)
8	$Ni(cod)_2$	5	72 (90 : <5 : <5)
9	$Ni(cod)_2/PPh_3$ (1:2)	10	51 (55 : <2 : 43)
10	$Ni(cod)_2$/dppe (1:1)	10	21 (23 : 16 : 61)
11	$Pd(dba)_2$	10	0 (<2 : 37 : 61)
12	$PdCl_2(PPh_3)_2$/Zn (1:3)	10	0 (<2 : 52 : 46)
13	$Pd(PPh_3)_4$	10	0 (<1 : 88 : 11)

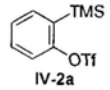
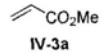
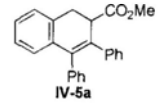
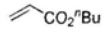
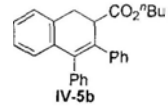
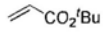
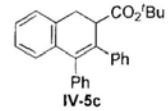
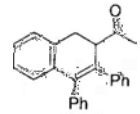
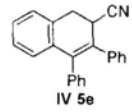
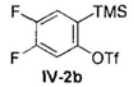
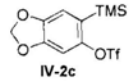
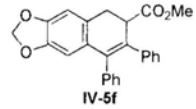
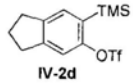
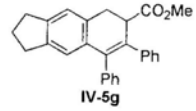
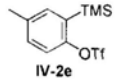
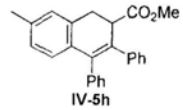
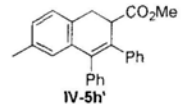
[a] Condition: **IV-2a** (0.3 mmol), **IV-3a** (0.6 mmol), **IV-4a** (0.36 mmol), and CsF (0.9 mmol) in CH_3CN (1 mL) at r.t. for 5 h. [b] Isolated yields of **IV-5a**. [c] Ratio determined by ^1H NMR spectroscopy on the crude product mixture. [d] The reaction was carried out at 50 °C.

corresponding cocyclization products **IV-5a**,**b**,**c** (entries 1–3). Methyl vinyl ketone **IV-4d** and acrylonitrile **IV-5e** offered very low yields of the desired aryne-alkene-alkyne cocyclization product of **IV-5d** (3%) and **IV-5e** (15%) (entries 4 and 5). In these reactions, the major products were aryne-alkene-aryne cyclization species. If unactivated alkenes were used, no desired products **IV-5** were detected. Functionalized aryne precursors with electron-donating groups (**IV-2c**,**d**,**e**) were less effective, producing dihydronaphthalene derivatives **IV-5f**,**g**,**h/h'** in moderate yields (entries 7–9). The electron-poor benzyne precursor **IV-2b** afforded an inseparable complex mixture (entry 6).

A variety of alkynes were compatible with this nickel-catalyzed cocyclization reaction and gave the desired products **IV-5** in very good yields (Table 4.4). An excellent regioselectivity was observed for all unsymmetrical alkynes because of the polarity of these molecules (entries 1–8). It is noteworthy that no C=C or C≡N insertion product was observed when **IV-4f** or **IV-4g** was used as the starting material (entries 5 and 6). In case of methyl 2-butynoate **IV-4i**, the low yield was due to the trimerization of **IV-4i** catalyzed by Ni(0) (entry 8).[65,79] It's known that an alkyne with electron-withdrawing substituents is more reactive than one with electron-donating groups in Ni(0)- or Pd(0)-catalyzed [2+2+2] cocyclization,[68d,80] which is consistent with the result of entries 9–11. Dialkylacetylene **IV-4j~l** (2 equiv) afforded **IV-5q~s/s'** in 22–44% yields. When 3 equiv of alkyne was used, the

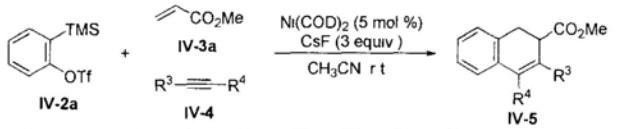
Table 4.3. Nickel-catalyzed three-component cycloaddition of arynes with activated alkenes and diphenylacetylene[a]

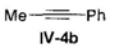
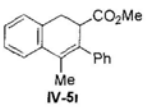
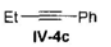
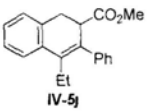
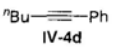
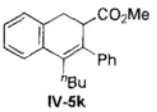
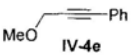
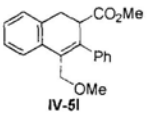
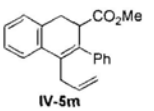
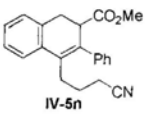
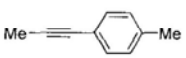
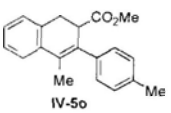
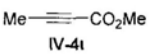
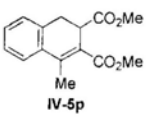
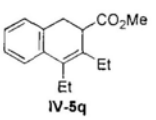
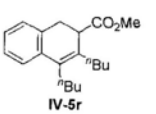
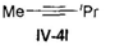
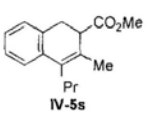
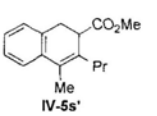


Entry	IV-2	IV-3	IV-5	Yield (%)[b]
1	 IV-2a	 IV-3a	 IV-5a	76
2	IV-2a	 IV-3b	 IV-5b	72
3	IV-2a	 IV-3c	 IV-5c	74
4	IV-2a	 IV-3d	 IV-5d	3
5	IV-2a	 IV-3e	 IV 5e	15
6	 IV-2b	IV-3a	-	-
7	 IV-2c	IV-3a	 IV-5f	29[c]
8	 IV-2d	IV-3a	 IV-5g	46[c]
9	 IV-2e	IV-3a	 IV-5h  IV-5h'	57[c] (IV-5h: IV-5h' = 1.3:1)[d]

[a]Condition **IV-2** (0 3 mmom), **IV-3** (0 6 mmol), **IV-4a** (0 6 mmol), CsF (0 9 mmol) in CH_3CN (1 mL) at r t for 5 h [b]Isolated yields [c]The reaction was carried out at r t overnight [d]The ratio was estimated by ^{1}H NMR

Table 4.4. Nickel-catalyzed three-component cycloaddition of benzyne with methyl acrylate and alkynes[a]



Entry	IV-4	IV-5	Yield (%)[b]
1	 IV-4b	 IV-5i	71
2	 IV-4c	 IV-5j	78
3	 IV-4d	 IV-5k	71
4	 IV-4e	 IV-5l	75
5	 IV-4f	 IV-5m	68
6	 IV-4g	 IV-5n	32
7	 IV-4h	 IV-5o	66
8	 IV-4i	 IV-5p	19
9	 IV-4j	 IV-5q	31(63)[c]
10	 IV-4k	 IV-5r	22(47)[c]
11	 IV-4l	 IV-5s  IV-5s'	44(51)[c] (**IV-5s**: **IV-5s'** = 2:1)[d]

[a] Condition **IV-2a** (0 3 mmol), **IV-3a** (0 6 mmol), **IV-4** (0 6 mmol), and CsF (0 9 mmol) in CH_3CN (1 mL) at r t for 5 h [b] Isolated yields [c] 3 mmol of Alkyne was used [d] The ratio was estimated by ^1H NMR

yields can be raised to 47-63%. And two regioisomers **IV-5s** and **IV-5s'** were obtained in 2:1 molar ratio in the reaction of 4-methyl-2-pentyne **IV-4l**.

Compounds **IV-5** were fully characterized by ^{1}H and ^{13}C NMR as well as high-resolution mass spectrometry. In the ^{1}H NMR spectrum of **IV-5**, three doublet of doublets or one triplet and two doublet of doublets can be observed at 3~4 ppm corresponding to the C*H* and CH_2 protons. Their ^{13}C NMR spectra were also consistent with the results observed with **IV-1**, which showed the signals of C*H* and CH_2 unit at ~46 and ~32 ppm, respectively. The relative regiochemical assignments of **IV-5h** and **IV-5h'** were determined using HH COSY analyses and the diagnostic correlation is shown in Chart 4.2.

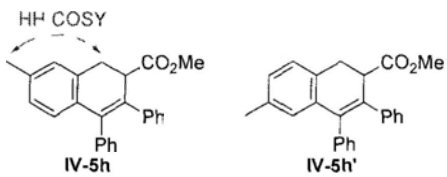


Chart 4.2.

The relative regiochemical assignments of 1,2-dihydronaphthalene **IV-5** were determined using NOESY analyses and the diagnostic correlations are shown in Chart 4.3.

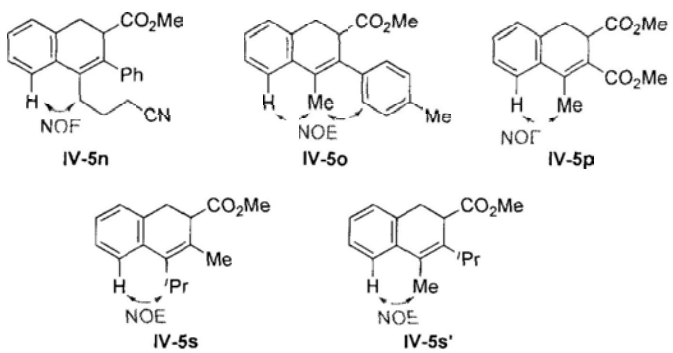


Chart 4.3.

The molecular structures of **IV-5e** and **IV-5l** were further confirmed by single-crystal X-ray analyses (Figure 4.3 and 4.4).

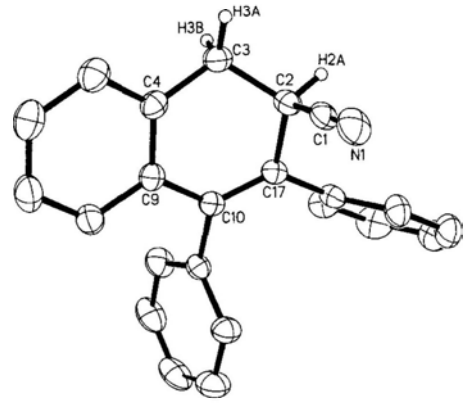


Figure 4.3. Molecular structure of **IV-5e.** Selected bond lengths (Å) and angles (deg): C4-C9 1.401(3), C4-C3 1.500 (3), C3-C2 1.524(3), C2-C17 1.537(2), C17-C10 1.342(2), C10-C9 1.476(3), C9-C4-C3 118.2(2), C4-C3-C2 112.1(2), C3-C2-C17 111.5(2), C2-C17-C10 119.3(2), C17-C10-C9 121.3(2), C10-C9-C4 119.7(2).

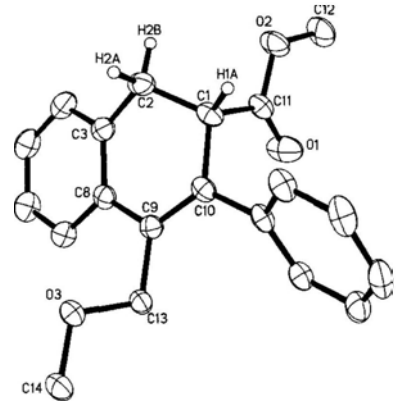
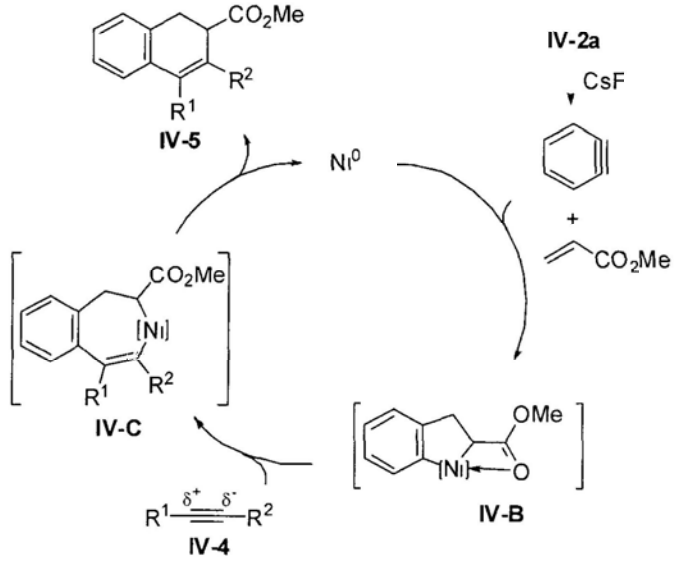


Figure 4.4. Molecular structure of **IV-5l.** Selected bond lengths (Å) and angles (deg): C8-C3 1.404(3), C3-C2 1.500 (3), C2-C1 1.530(3), C1-C10 1.517(3), C10-C9 1.347(2), C9-C8 1.490(2), C8-C3-C2 118.5(2), C3-C2-C1 112.7(2), C2-C1-C10 112.5(2), C1-C10-C9 120.8(2), C10-C9-C8 120.8(2), C9-C8-C3 119.5(2).

A plausible mechanism for the nickel-catalyzed three-component cocyclization is shown in Scheme 4.4. The catalysis is likely initiated by oxidative coupling of benzyne and alkene on Ni(0) to form a nickelacycle **IV-B,** which is probably stabilized by an intramolecular coordination of the heteroatom. Subsequent insertion of alkyne into the nickel–C(aryl) bond gives the seven-membered intermediate **IV-C**.[60,77] The regioselectivity observed in the reactions can be rationalized by the polarity of alkynes.[77] Reductive elimination of **IV-B** yields the final product **IV-5** and regenerates the catalyst.

Scheme 4.4. Proposed mechanism of nickel-catalyzed [2+2+2] cyclization reaction.



4.3 Summary

We have developed a novel nickel-mediated three-component assembling reaction of 1,2-*o*-carboryne with alkenes and alkynes and a novel nickel-catalyzed three-component [2+2+2] carboannulation of arynes, activated alkenes, and alkynes.

This work offers an exceptionally efficient route to the synthesis of dihydrobenzocarborane and 1,2-dihydronaphthalenes derivatives from readily available starting materials.

Chapter 5. Nickel-Catalyzed [2+2+2] Cycloaddition of 1,2-*o*-Carboryne with Alkynes

5.1 Introduction

Reactivity studies showed that 1,2-*o*-carboryne can react with alkenes, dienes, and alkynes in [2+2], [2+4] cycloaddition and ene-reaction patterns,[40-43] similar to that of benzyne. The carboryne reactions are usually complicated and not in a controlled manner. On the other hand, nickel-1,2-*o*-carboryne complex (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$[45] can undergo regioselective [2+2+2] cycloaddition reactions with 2 equiv of alkynes to afford benzocarboranes.[54] This reaction requires a stoichiometric amount of Ni reagent. Transition metal-catalyzed cocyclization of π-component molecules has received much attention because of its highly atom-economical nature.[65] In view of the analogy between metal-benzyne[55] and metal-1,2-*o*-carboryne complexes and the metal-catalyzed reactions of benzyne with alkenes and alkynes,[67-76] we wondered if a catalytic version of nickel-mediated reactions of 1,2-*o*-carboryne could be developed.

In the stoichiometric reactions, high temperature was necessary for the insertion of alkynes into the Ni–C_{cage} bond in Ni-1,2-*o*-carboryne and the Ni(0) species was the end metal complex.[54] On the other hand, 1-bromo-2-lithiocarborane was reported as a precursor of 1,2-*o*-carboryne.[40-42] It is rational to assume that 1-bromo-2-lithiocarborane may undergo oxidative addition with Ni(0) to give, after elimination of LiBr, the desired Ni-1,2-*o*-carboryne complex to construct a catalytic

cycle. In this section we will report the nickel-catalyzed [2+2+2] cycloaddition of 1,2-*o*-carboryne with 2 equiv of alkynes to afford benzocarboranes.

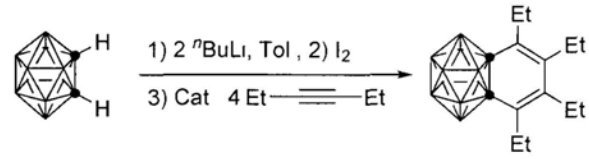
5.2 Results and Discussion

1-Iodo-2-lithiocarborane was chosen as the precursor to realize the catalytic cycle because it is more efficient than 1-bromo-2-lithiocarborane (*vide infra*) and iodine is easy to handle with. 1-Iodo-2-lithiocarborane, conveniently prepared in situ from the reaction of dilithiocarborane with 1 equiv of iodine in toluene at room temperature, was thermally stable at room temperature. Heating a benzene solution of 1-iodo-2-lithiocarborane overnight afforded a [4+2] cycloaddition product 1,2-(2,5-cyclohexadiene-1,4-diyl)-*o*-carborane in 25% isolated yield, which is much higher than the 8% yield from 1-bromo-2-lithiocarborane precursor.[42e] This result suggests that 1-iodo-2-lithiocarborane is a more efficient precursor than the bromo one.

We then examined the catalytic activity of various metal complexes in the reaction of 1-iodo-2-lithiocarborane with an excess amount of 3-hexyne in toluene at 110 ^{o}C for 2 h. The results were summarized in Table 5.1. The Ni(0) complexes were all catalytically active with $Ni(cod)_2$ being the most active one, giving the desired [2+2+2] cycloaddition product **V-1a** in 33~49% isolated yields (entries 1–3). Addition of PPh_3 led to a big drop in the yield of **V-1a** from 49% to 33%, probably suggesting that free PPh_3 and alkyne compete the coordination site of the Ni atom.

The Ni(II) salts were also active. Their activities depended largely on the ligands (entries 4–12). $NiCl_2(PPh_3)_2$ was found to be the best catalyst, producing **V-1a** in 65% isolated yield, suggesting that the in situ generated Ni(0) species is more active than $Ni(cod)_2$ (*vide infra*) (entry 6). Lower catalyst loading (10 mol %) resulted in a significant decrease of the yield from 65% to 31% (entry 7). Extension of reaction time from 2 h to 4 h did not affect the yield of **V-1a** (entry 8).

Table 5.1. Optimization of reaction conditions[a]



V-1a

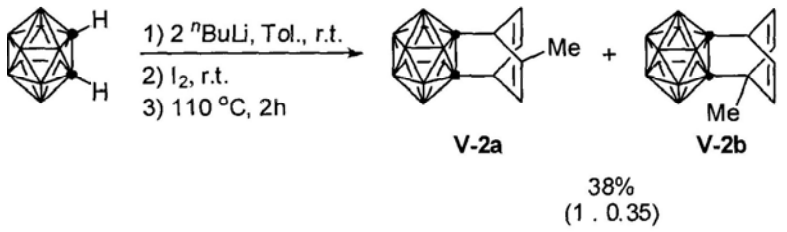
Entry	Catalyst[b]	Loading mol %	Time h	T °C	Yield %[c]
1	$Ni(cod)_2$	20	2	110	49
2	$Ni(cod)_2/4PPh_3$	20	2	110	33
3	$Ni(PPh_3)_4$	20	2	110	37
4	$NiCl_2(PMe_3)_2$	20	2	110	17
5	$NiCl_2(P^nBu_3)$	20	2	110	57
6	$NiCl_2(PPh_3)_2$	20	2	110	65
7	$NiCl_2(PPh_3)_2$	10	2	110	31
8	$NiCl_2(PPh_3)_2$	20	4	110	63
9	$NiCl_2(PPh_3)_2$	20	4	90	60
10	$NiCl_2$(dppe)	20	2	110	29
11	$NiCl_2$(dppp)	20	2	110	22
12	$NiI_2(Me_2Im)_2$	20	2	110	16
13	$Pd(PPh_3)_4$	20	2	110	1
14	$PdCl_2(PPh_3)_2$	20	2	110	1
15	$FeCl_2/2PPh_3$	20	2	110	-
16	$CoCl_2(PPh_3)_2$	20	2	110	-

[a] Condition 1) carborane (0 5 mmol), *n*-BuLi (1 0 mmol), in toluene at room temperature for 1 h, 2) I_2 (0 5 mmol), at room temperature for 0 5 h, 3) catalyst, 3-hexyne (2 mmol) [b] cod = cyclooctadiene, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, Me_2Im = 1,3-dimethylimidazol-2-ylidene, [c] Isolated yields

Temperature was crucial to the reaction. Compound **V-1a** was not observed if the reaction temperatures were < 60 °C. The reaction proceeded well at 90 °C, but needed a longer time to completion (entry 9). It was noted that in addition to **V-1a** other products were *o*-carborane with small amounts of 1,2-*o*-carboryne–alkyne ene-reaction product **V-3** (Scheme 5.2) and 1,2-*o*-carboryne–toluene [2+4] cycloaddition reaction products **V-2** (Scheme 5.2) in the above reactions. In sharp contrast, palladium complexes such as $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ showed almost no activity (entries 13 and 14). $FeCl_2/2PPh_3$ and $CoCl_2(PPh_3)_2$ were inactive (entries 15 and 16).

To further investigate the reaction, we examined the following control experiments. The toluene solution of the in situ prepared 1-iodo-2-lithiocarborane was heated at 110 °C for 2 h. [4+2] cycloaddition products **V-2a** and **V-2b** were obtained as inseparable mixture in 38% isolated yield (Scheme 5.1).

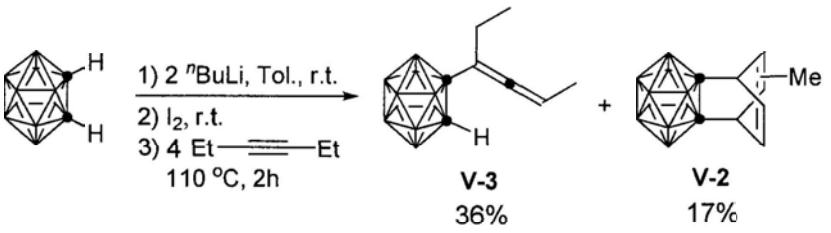
Scheme 5.1. Reaction of 1,2-*o*-carboryne precursor with toluene.



When 4 equiv of 3-hexyne was used, the ene-reaction product **V-3** was obtained as the major product in 36% yield after heating. [4+2] cycloaddition product was

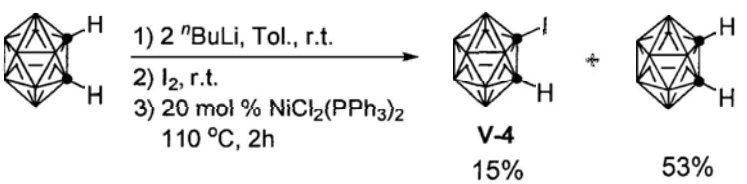
isolated in 17% yield, and carborane was recovered in 27% yield (Scheme 5.2). This result implies that alkynes are more efficient reagents than arenes in the reaction with 1,2-*o*-carboryne.

Scheme 5.2. Reaction of 1,2-*o*-carboryne precursor with 3-hexyne in toluene.



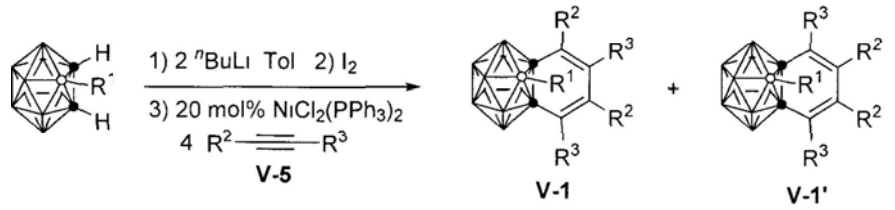
When 1-iodo-2-lithiocarborane toluene solution was heated in the presence of 20 mol % $NiCl_2(PPh_3)_2$, only 15 mol% of 1-iodocarborane was recovered along with the isolation of carborane (53%) (Scheme 5.3). The transition-metal species can largely change the reaction pathway and prohibit the [4+2] cycloaddition reaction of 1,2-*o*-carboryne with toluene.

Scheme 5.3. Heating of 1,2-*o*-carboryne precursor in toluene in the presence of $NiCl_2(PPh_3)_2$.



We then expanded the substrates scope of the catalytic cycloaddition reaction to include various carboranes and alkynes using the above optimal reaction condition (Table 5.1, entry 6). The results were compiled in Table 5.2. The isolated yields of **V-1** were very comparable with those of stoichiometric reactions of Ni-1,2-*o*-carboryne with alkynes (entries 1, 4–6, and 9).[54] Steric factors played an important role in the reactions. Sterically less demanding 3-hexyne offered the highest yield (entry 1). Carboranes with 3-chloro and 3-phenyl resulted in a big decrease in the isolated yields of **V-1b,c** from 65% to 31~38% (entries 2 and 3). 4-Methyl-2-pentyne **V-5f** offered two inseparable regio-isomers **V-1h/ V-1'h** in a molar ratio of 7:3 (entry 8). However, an excellent regioselectivity was observed for unsymmetrical arylalkynes due to the electronic effects as phenyl can be viewed as electron-withdrawing group (entries 9–14).[60,77] For alkynes bearing ether groups **V-5e** and **V-5m**, the products were formed in low yields, probably due to the coordination of oxygen atom occupying the vacant site of the Ni atom (entries 7 and 15). Such interactions may also alter the regioselectivity of the alkyne insertion and stabilize the inserted product, which leads to the formation of **V-1'o** and a small amount of mono-alkyne insertion products after hydrolysis (*vide infra*) (entry 15). Alkynes bearing amido group or carbonyl group such as **V-5n** and **V-5o** were incompatible with this reaction because they can react with the carboryne precursor 1-iodo-2-lithiocarborane (entries 16 and 17). For methyl 2-butynoate **V-5o**, the homocyclotrimerization product was observed.[79]

Table 5.2. Nickel-catalyzed cycloaddition of 1,2-*o*-carborynes with alkynes.

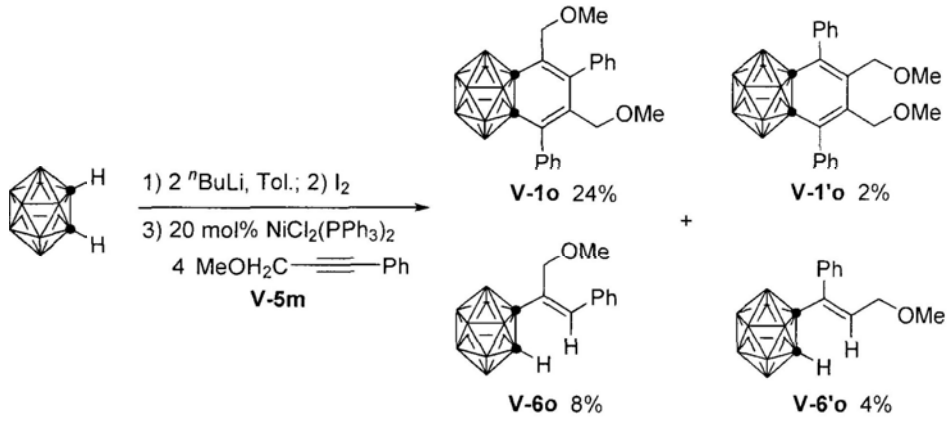


Entry	R^1	R^2 / R^3	V-5	Product	Yield (%)[a b]
1	H	Et / Et	**V-5a**	**V-1a**	65 (67)
2	3-Cl	Et / Et	**V-5a**	**V-1b**	31
3	3-Ph	Et / Et	**V-5a**	**V-1c**	38
4	H	^{n}Pr / ^{n}Pr	**V-5b**	**V-1d**	59 (65)
5	H	^{n}Bu / ^{n}Bu	**V-5c**	**V-1e**	54 (65)
6	H	Ph / Ph	**V-5d**	**V-1f**	28 (33)
7	H	CH_2OMe / CH_2OMe	**V-5e**	**V-1g**	13
8	H	Me / ^{i}Pr	**V-5f**	**V-1h** + **V-1'h**	44 (**V-1g/V-1'g** = 70/30)[c]
9	H	Me / Ph	**V-5g**	**V-1i**	50 (54)
10	H	Me / *p*-Tolly	**V-5h**	**V-1j**	39
11	H	Me / *p*-CF_3-C_6H_4	**V-5i**	**V-1k**	49
12	H	Et / Ph	**V-5j**	**V-1l**	49
13	H	^{n}Bu / Ph	**V-5k**	**V-1m**	43
14	H	C≡CPh / Ph	**V-5l**	**V-1n**	51
15	H	CH_2OMe / Ph	**V-5m**	**V-1o / V-1'o**	24 / 2
16	H	CH_2NMe_2 / Ph	**V-5n**	-	-
17	H	CO_2Me / Me	**V-5o**	-	-

[a]Isolated yields [b]Yields in parentheses are corresponding to those of stoichiometric reactions of Ni-1,2-*o*-carboryne with 2 equiv of alkynes, reported in ref 54 [c]Molar ratio was determined by ^{1}H NMR spectroscopy on the crude product mixture

In the reaction of **V-5m**, four new products of **V-1o**, **V-1'o**, **V-6o**, and **V-6'o** were isolated after hydrolysis in 24%, 2%, 8%, and 4% yields, respectively. The electronic-controlled regioselective alkyne insertion products **V-1o** and **V-6o** are the major products. The formation of reversed alkyne insertion species **V-1'o** and **V-6'o** may be due to the interaction between O and Ni atom in the reaction intermediates.

Scheme 5.4. The nickel-catalyzed cycloaddition of 1,2-*o*-carborynes with **V-5m**.



The regiochemical assignment of **V-1'o** was determined by the facts that there is no correlation between the cage *C* (74.2 ppm) and OCH_2 (3.84 ppm) can be observed in the HMBC analysis. On the other hand, the HMBC NMR spectrum of **V-1o** apparently illustrates the correlation between the proton on OCH_2 group (3.86 ppm) and the cage *C* (74.6 ppm) (Chart 5.1).

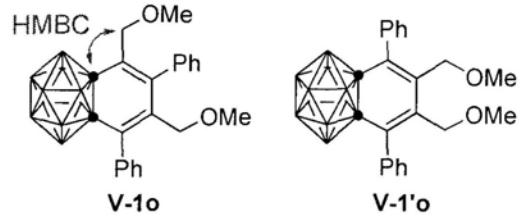


Chart 5.1

The relative regiochemical assignments of V-**6o** and **V-6'o** were determined using HH COSY analyses and the diagnostic correlation is shown in Chart 5.2 .

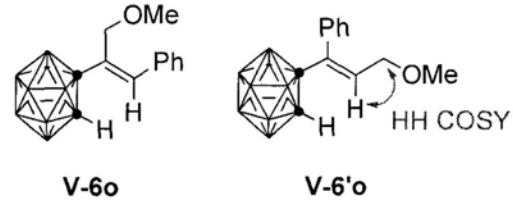
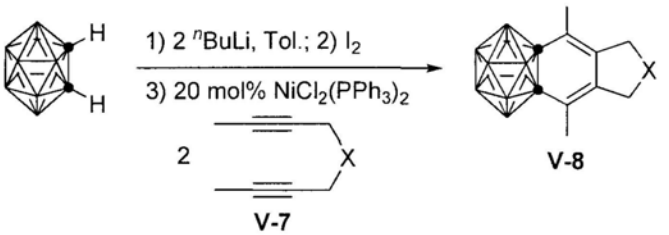


Chart 5.2

Internal diynes **V-7a-c** were also compatible with these nickel-catalyzed cycloaddition reactions and gave the desired products **V-8** in 15~39% isolated yields with a good fused-ring size tolerance (Scheme 5.4). The yield was rather low for seven-membered fused-ring species **V-8c**. No reaction proceeded for the oxo-bridged diyne **V-7d**. It's noteworthy that this condition is not suitable for the reaction involving alkenes and produces the coupling product in very low yield.

Scheme 5.5. Nickel-catalyzed cycloaddition of 1,2-*o*-carboryne with diynes.



V-7a X = CH_2 **V-8a** 38%
V-7b X = $(CH_2)_2$ **V-8b** 39%
V-7c X = $(CH_2)_3$ **V-8c** 15%
V-7d X = O **V-8d** -

Compounds **V-1**, **V-6**, and **V-8** were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectra as well as high-resolution mass spectrometry. For products **V-1** without substituent on the B atom, the $^{11}B\{^{1}H\}$ NMR spectra generally exhibited a 2:6:2 or a 2:4:4 splitting pattern. And the $^{11}B\{^{1}H\}$ NMR spectra exhibited a 4:2:2:1:1 splitting pattern for **V-1b** and a 1:2:3:3:1 splitting pattern for **V-1c**. A singlet assignable to *B*-Ph in **V-1c** can be observed in the ^{1}H coupled ^{11}B NMR spectrum, whereas the signal of *B*-Cl is overlapped with other *B*-H signals and cannot be identified.

The molecular structures of **V-1h**, **V-1n**, **V-1o**, **V-6o** and **V-8b** were further

confirmed by single-crystal X-ray analyses (Figure 5.1~5.5). The localized double bonds suggest there is no π-delocalization in the six-membered ring of the benzocarborane products (Table 5.3).

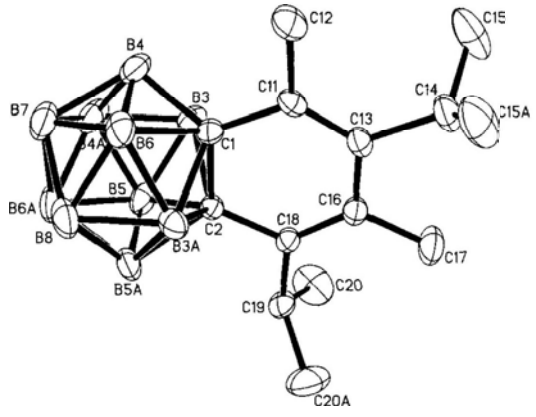


Figure 5.1. Molecular structure of **V-1h**.

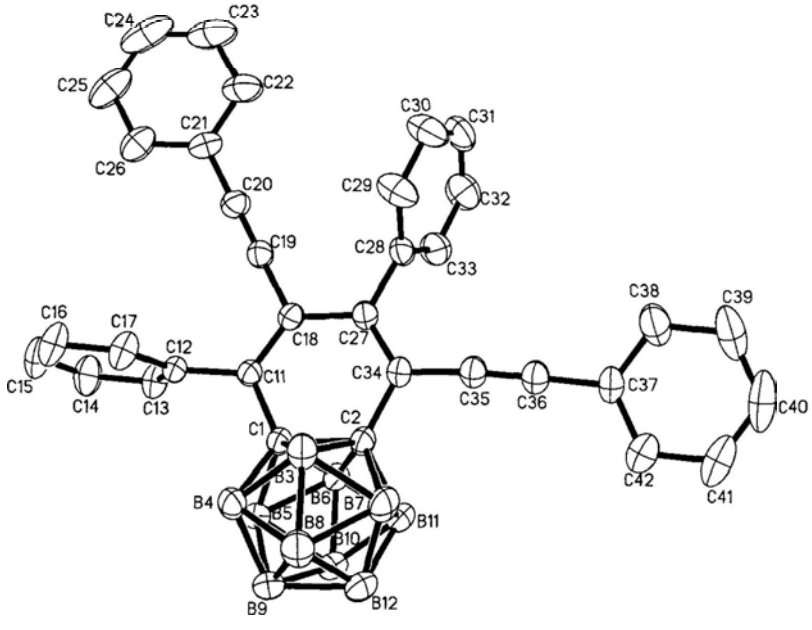


Figure 5.2. Molecular structure of **V-1n**.

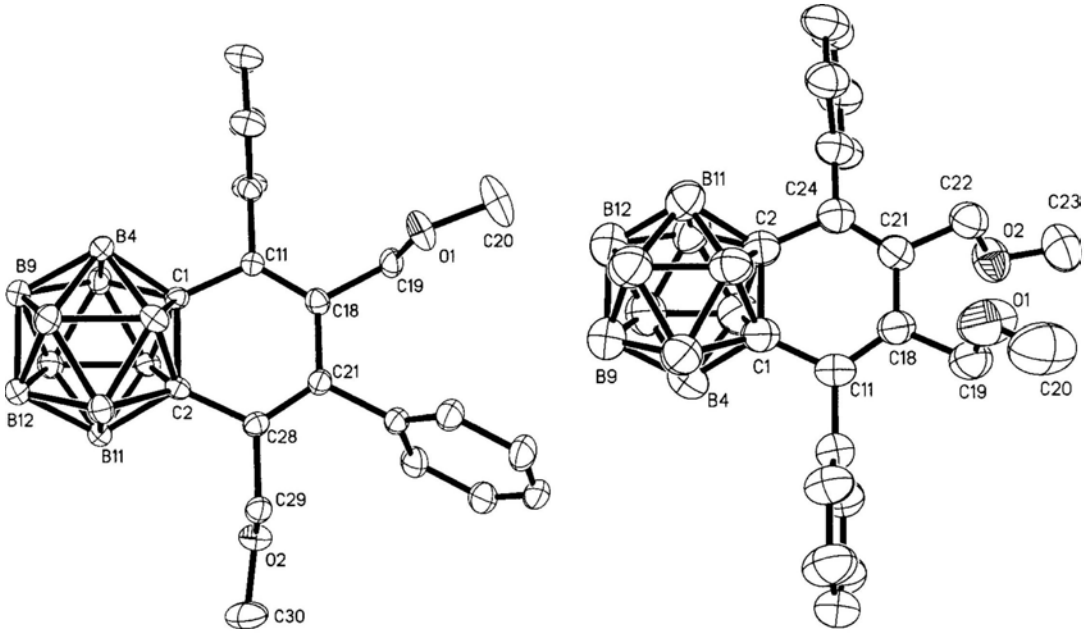


Figure 5.3. Molecular structures of **V-1o** and **V-1'o**.

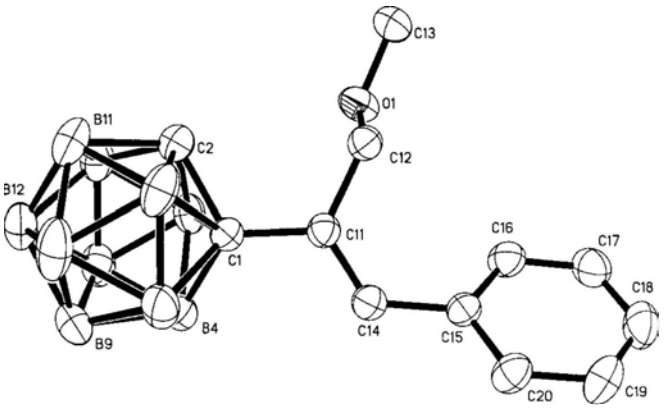


Figure 5.4. Molecular structure of **V-6o**.

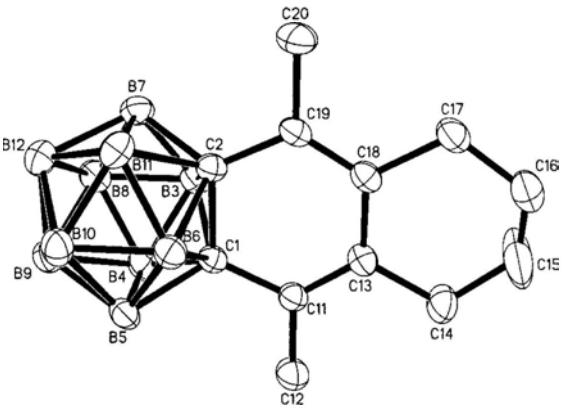


Figure 5.5. Molecular structure of **V-8b**.

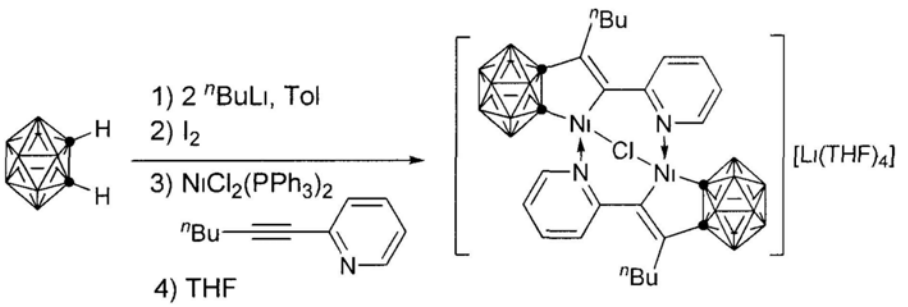
Table 5.3. Selected Bond Distances(Å) for **V-1h**, **V-1n**, **V-1o**, **V-1'o** and **V-8b**.

V-1h		**V-1n**		**V-1o**		**V-1'o**		**V-8b**	
C1-C2	1.629(5)	C1-C2	1.641(3)	C1-C2	1.639(6)	C1-C2	1.637(6)	C1-C2	1.643(4)
C1-C11	1.494(5)	C1-C11	1.486(3)	C1-C11	1.497(6)	C1-C11	1.502(6)	C1-C11	1.487(5)
C11-C13	1.347(5)	C11-C18	1.354(3)	C11-C18	1.350(6)	C11-C18	1.342(6)	C11-C13	1.346(5)
C13-C16	1.477(5)	C18-C27	1.473(3)	C18-C21	1.467(6)	C18-C21	1.460(6)	C13-C18	1.470(5)
C16-C18	1.346(5)	C27-C34	1.350(3)	C21-C28	1.347(6)	C21-C24	1.331(6)	C18-C19	1.343(5)
C18-C2	1.488(5)	C34-C2	1.496(3)	C28-C2	1.498(6)	C24-C2	1.508(6)	C19-C2	1.486(5)

To gain some insight into the reaction mechanism, an NMR reaction of 1-I-2-Li-1,2-$C_2B_{10}H_{10}$ with 1 equiv of $Ni(cod)_2/2PPh_3$ in toluene was conducted and monitored by ^{11}B and ^{31}P NMR spectra. The results suggested the formation of (η^2-$C_2B_{10}H_{10}$)$Ni(PPh_3)_2$ even at room temperature, which indicates that an oxidative addition of I–C_{cage} bond to Ni(0) proceeded. On the other hand, treatment of in situ generated 1-I-2-Li-1,2-$C_2B_{10}H_{10}$ with 1 equiv of $NiCl_2(PPh_3)_2$ in the presence of 2 equiv of *n*-butyl-2-pyridinylacetylene in refluxing toluene gave, after recrystallization from THF, a mono alkyne insertion product **V-9** [{[2-C(^{n}Bu)=C(*o*-C_5H_4N)-1,2-$C_2B_{10}H_{10}$]Ni}$_2$(μ_2-Cl)][Li(THF)$_4$] as red crystals in 25% yield (Scheme 5.6). It was fully characterized by various NMR spectra and elemental analyses.

Single-crystal X-ray analyses revealed that **V-9** is an ionic complex consisting of dimeric complex anions and tetrahedral cations. In the anion, two square-planar Ni moieties share one μ-Cl atom (Figure 5.6). Coordination of the pyridinyl to the Ni atom can stabilize complex **V-9** and prevent the further insertion of the second equiv of *n*-butylpyridinylacetylene.

Scheme 5.6. Reaction of Ni-1,2-*o*-carboryne with *n*-butyl-2-pyridinylacetylene.



V-9

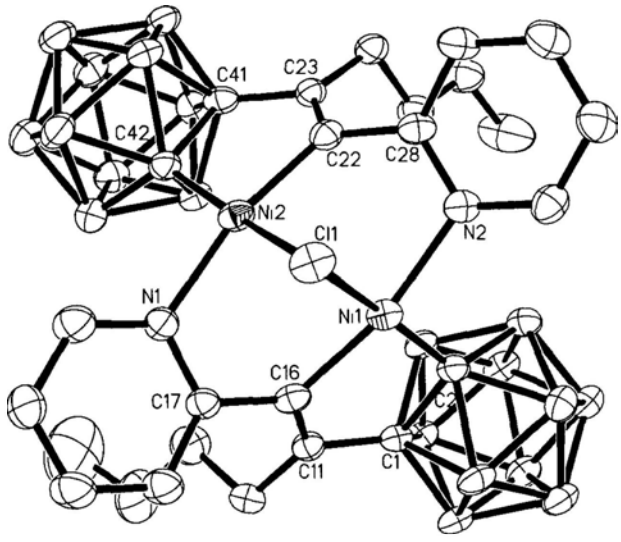
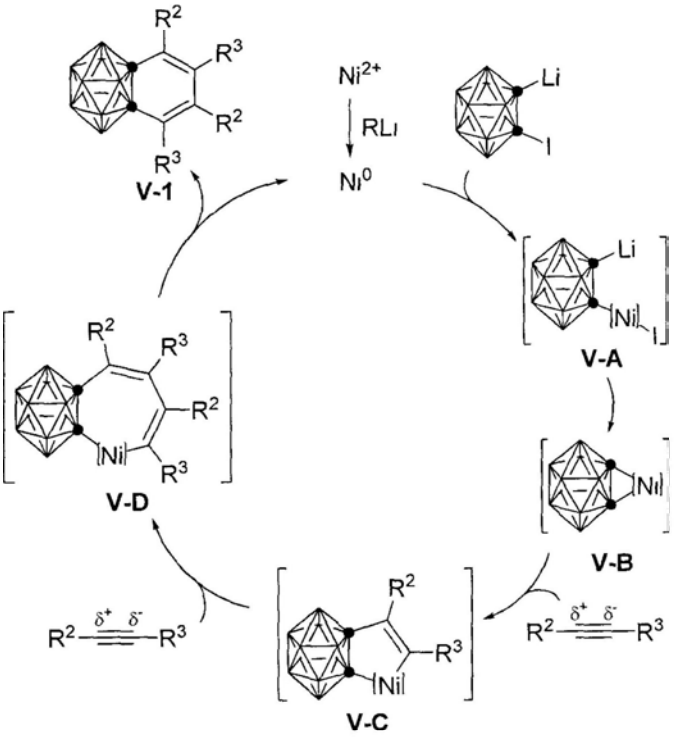


Figure 5.6. Molecular structure of the anion in **V-9**. Selected bond lengths (Å) and angles (deg): Ni1-C2 1.890(7), Ni1-C16 1.929 (8), Ni1-Cl1 2.267(2), Ni1-N2 1.965(6), C1-C2 1.655(9), C1-C11 1.487(9), C11-C16 1.378(9), Ni2-C42 1.910(7), Ni2-C22 1.925(8), Ni2-Cl1 2.267(2), Ni2-N1 1.946(6), C41-C42 1.640 (10), C41-C23 1.507 (13), C23-C22 1.346 (10), C2-Ni1-C16 86.8(3), C16-Ni1-Cl1 95.7(2), Cl1-Ni1-N2 83.8(2), N2-Ni1-C2 96.8(3), C42-Ni2-C22 85.6(3), C22-Ni2-Cl1 97.1(2), Cl1-Ni2-N1 82.7(2), N1-Ni2-C42 97.6(3), Ni1-Cl1-Ni2 70.8(1).

Given the above experimental evidence, a plausible mechanism for the nickel-catalyzed cycloaddition is shown in Scheme 5.7. The catalysis is likely initiated by Ni(0) species generated via the reduction of Ni(II) with lithiocarborane salt.[81] Oxidative addition between I–C(cage) bond and Ni(0), followed by a subsequent elimination of lithium iodide produces a Ni-1,2-*o*-carboryne intermediate **V-B**. An alternative pathway proceeded by the elimination of lithium iodide to form 1,2-*o*-carboryne and subsequent coordination to the metal center cannot be ruled out. Insertion of the first equiv of alkyne into the Ni–C(cage) bond of Ni-1,2-*o*-carboryne

gives a nickelacyclopentene intermediate **V-C**. The second equiv of alkyne inserts into the Ni–C(vinyl) bond to afford the seven-membered intermediate **V-D**.[54,64] Reductive elimination yields the cycloaddition product **V-1** and releases Ni(0) species to complete the catalytic cycle. The regioselectivity observed in the reactions can be rationalized by the polarity of alkynes.[60,77]

Scheme 5.7. Proposed mechanism of nickel-catalyzed [2+2+2] cyclization reaction.



5.3 Summary

We have developed the first metal-catalyzed reaction of 1,2-*o*-carboryne with unsaturated molecules using 1-iodo-2-lithiocarborane as precursor and $NiCl_2(PPh_3)_2$ as catalyst. The mechanism was proposed after the structural confirmation of the key intermediate, nickelacyclopentene.

Chapter 6. Palladium/Nickel-Cocatalyzed [2+2+2] Cycloaddition of 1,3-*o*-Carboryne with Alkynes

6.1 Introduction

1,2-*o*-Carboryne is a three-dimentional relative of benzyne (Chart 6.1).[44] It can react with alkenes, dienes, and alkynes in [2+2], [2+4] cycloaddition and ene-reaction patterns[40-43] similar to those of benzyne[39]. This reactive species can be stabilized by transition metals, leading to the formation of metal-1,2-*o*-carboryne complexes.[45-50] Molecular orbital calculations on the Zr-carboryne complex suggest that the bonding interactions between Zr and carboryne are best described as a resonance hybrid of both Zr–C σ and Zr–C π bonding forms,[49] which is similar to that observed in Zr-benzyne complex (Chart 6.1).[82] This type of metal-1,2-*o*-carboryne complexes can react with unsaturated molecules in a control manner to produce alkenylcarboranes, benzocarboranes[54], dihydrobenzocarboranes, and other functionalized carboranes[51-53]. In view of these unique features of 1,2-*o*-carboryne and the important application of boron-centered nucleophiles,[83~85] we became interested in the unknown species 1,3-dehydro-*o*-carborane (1,3-*o*-carboryne) (Chart 6.1). In this section, we report our work on palladium/nickel-cocatalyzed reaction of 1,3-*o*-carboryne with 2 equiv of alkynes to afford [2+2+2] cycloaddition products, 1,3-benzo-*o*-carborane.

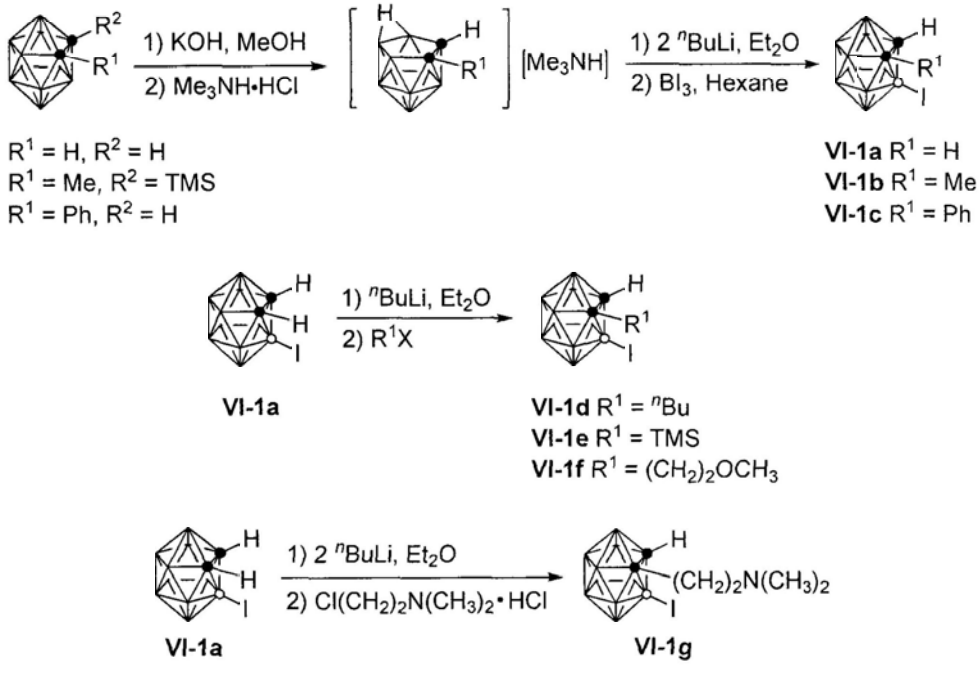
Chart 6.1 Structures of benzyne and carborynes.

6.2 Results and Discussion

6.2.1 Synthesis of 1,3-*o*-Carboryne Precursor

As 1,2-*o*-carboryne can be generated in situ by heating 1-X-2-Li-1,2-$C_2B_{10}H_{10}$ (X = Br[40-42], I) via the elimination of LiX, we attempted to produce 1,3-*o*-carboryne in a similar manner using 1-Li-3-X-1,2-$C_2B_{10}H_{10}$ as precursors. Unfortunately, both 1-Li-3-X-1,2-$C_2B_{10}H_{10}$ and 1-Li-2-CH_3-3-X-1,2-$C_2B_{10}H_9$ are all very thermally stable even after prolonged heating in THF or toluene. Considering that the cage B–I bond can undergo oxidative addition in the presence of Pd(0),[86] we speculate that an oxidative addition of the cage B–I in 1-Li-3-I-1,2-$C_2B_{10}H_{10}$ on the Pd(0), followed by subsequent elimination of LiI would afford the target complex Pd-1,3-*o*-carboryne, which could be trapped by alkynes.

A series 1,3-*o*-carboryne precursors **VI-1a~c** were synthesized by the boron insertion reaction of the dicarbollide anion $C_2B_9H_{11}^{2-}$ with BI_3.[29] Compounds **VI-1d~g** can be synthesized with lithiated **VI-1a** and alkyl chloride (Scheme 6.1).

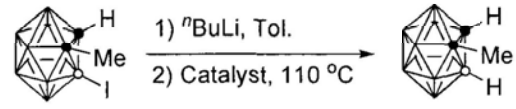


Scheme 6.1

6.2.2 Reaction of 1,3-*o*-Carboryne Precursor

The reactions of these precursors were next studied. In an initial attempt, a toluene solution of the 1-Li-2-Me-3-I-1,2-$C_2B_{10}H_9$, prepared in situ by treatment of 2-Me-3-I-1,2-$C_2B_{10}H_{10}$ (**VI-1b**) with 1 equiv of ^{n}BuLi, was heated in the presence of $Pd(PPh_3)_4$ (10 mol %) to give 1-methyl-*o*-carborane (**VI-3b**) in almost quantitative yield in 14 h. The formation of **VI-3b** may probably result from the decomposition of Pd-2-methyl-1,3-*o*-carboryne at high temperatures (Table 6.1, entry 1). If the catalyst loading was reduced to 5 mol%, the reaction was slow down (Table 6.1, entry 2). $Ni(cod)_2$ was almost inactive in the activation of cage B–I bond (Table 6.1, entry 4). However a combination of 5 mol% of $Ni(cod)_2$ and 5 mol% $Pd(PPh_3)_4$ can improve the formation of **VI-3b** (Table 6.1, entry 3) (*vide infra*).[87] Grinard reagent (MeMgBr) is less effective than ^{n}BuLi in the reaction with cage CH. On the other hand, MeMgBr can react with 3-iodo-*o*-carborane in the presence of Pd(0) to give 3-methyl-*o*-carborane.[30] 3-Bromo-*o*-carborane and 3-chloro-*o*-carborane are not suitable for this reaction because Pd(0) cannot add to the boron-bromine or boron-chlorine bond efficiently.[31e] It is noted that no reaction proceeded at $T < 70$ °C, and only compound **VI-3b** can be observed at higher temperatures by ^{11}B NMR spectroscopy in the reaction of 3-iodo-1-lithio-2-methyl-*o*-carborane with a catalytic amount of $Pd(PPh_3)_4$. Attempts to isolate (η^2-1,3-*o*-$C_2B_{10}H_{10}$)Pd(L), an analogue of (η^2-1,2-*o*-$C_2B_{10}H_{10}$)Ni(L),[45] in the presence of PPh_3 or dppe (dppe = 1,2-bis(diphenylphosphino)ethane) failed.

Table 6.1. Reaction of 1,3-*o*-carboryne precursor **VI-1b**.[a]



VI-1b **VI-3b**

Entry	Catalyst	Loading (mol %)	Reaction time	Yield (%)[b] **VI-1b**	**VI-3b**
1	$Pd(PPh_3)_4$	10	14 h	<1	>99
2	$Pd(PPh_3)_4$	5	30 h	10	90
3	$Pd(PPh_3)_4/Ni(cod)_2$	5 / 5	30 h	<1	>99
4	$Ni(cod)_2$	5	30 h	>99	<1

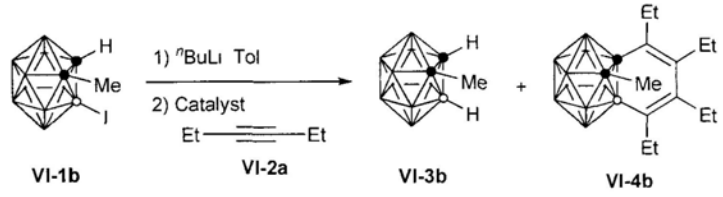
[a] Conditions: 1) ^{n}BuLi (1 equiv), toluene, r.t., 0.5 h; 2) Catalyst, 110 °C. [b] Yields determined by GC-MS on the crude product mixture.

6.2.3 Metal-Catalyzed [2+2+2] Cycloaddition of 1,3-*o*-Carboryne with Alkynes

Subsequent work focused on trapping the 1,3-*o*-carboryne intermediate with alkynes. The optimization of this reaction is listed in Table 6.2. Pd(II) species can effectivly catalyze the [2+2+2] cycloaddition reaction of 2-methyl-1,3-*o*-carboryne with 3-hexyne to afford **VI-4b** (entries 2–8). Adding PPh_3 to $PdCl_2(cod)$ or $[Pd(Ally)Cl]_2$ led to a big increase in the isolation of **VI-4b** probably due to the reduction of Pd(II) to Pd(0) by PPh_3 (entries 5 and 8).[81a] Pd(0) species is more effective but with a big ligand effect. $Pd(PPh_3)_4$ can catalyze the [2+2+2] cycloaddition reaction affording **VI-4b** in 90% yield. In comparison, $Pd(dba)_2$ (dba = dibenzylideneacetone) gives **VI-4b** in 43% yield only (Table 2, entries 9 and 10). $Ni(cod)_2$ exhibited very low catalytic activity (Table 2, entry 11), but the addition of nickel species to palladium catalyst can significantly accelerate the reaction (entries 12–18).[87] Combination of $Pd(PPh_3)_4$ with $Ni(cod)_2$ exhibited the highest catalytic activity in this [2+2+2] cyclization. The similar results were observed when the catalyst loading was decreased from 10 mol % to 2 mol % or 2 equiv of PPh_3 was

add in the reaction (entries 14–17). $Ni(cod)_2$ can also accelerate the catalytic reaction of $PdCl_2(PPh_3)_2$ giving **4b** in 84% yield in 3 h (entry 18).

Table 6.2. Optimization of Pd/Ni-Catalyzed Cycloaddition Reaction[a]



VI-1b VI-2a VI-3b VI-4b

Entry	Catalyst	Loading (mol %)	Reaction time	Yield[b] VI-1b	VI-3b	VI-4b
1	none	0	7 d[c]	100	-	-
2	$Pd(OAc)_2$	10	3 d[c]	56	19	25
3	$PdCl_2(PPh_3)_2$	10	3 d[c]	9	12	79
4	$PdCl_2(cod)$	10	3 d[c]	87	12	<1
5	$PdCl_2(cod)$ /$2PPh_3$	10	30 h	<1	8	91
6	$Pd(CH_2TMS)_2(cod)$	10	3 d[c]	90	9	<1
7	$[Pd(Ally)Cl]_2$	5	3 d[c]	6	25	69
8	$[Pd(Ally)Cl]_2/4PPh_3$	5	1 h	<1	7	92
9	$Pd(dba)_2$	10	7 d[c]	21	36	43
10	$Pd(PPh_3)_4$	10	7 h	2	8	90
11	$Ni(cod)_2$	10	7 d[c]	72	13	15
12	$Pd(PPh_3)_4/Ni(PPh_3)_4$	10 / 10	3 h	3	6	91
13	$Pd(dba)_2/Ni(cod)_2$	10 / 10	3 d[c]	25	43	32
14	$Pd(PPh_3)_4/Ni(cod)_2$	10 / 10	0.5 h	<1	6	93
15	$Pd(PPh_3)_4/Ni(cod)_2$	5 / 5	2 h	<1	3	96
16	$Pd(PPh_3)_4/Ni(cod)_2/2PPh_3$	5 / 5	2 h	<1	4	95
17	$Pd(PPh_3)_4/Ni(cod)_2$	2 / 2	4 h	<1	6	93
18	$PdCl_2(PPh_3)_2/Ni(cod)_2$	10 / 10	3 h	9	7	84

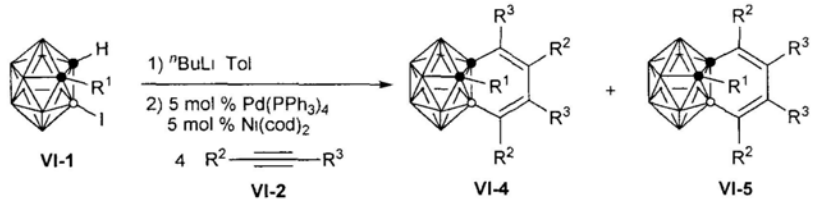
[a] Conditions 1) ^{n}BuLi (1 equiv), toluene, r t , 0 5 h, 2) Catalyst, 3-hexyne (4 equiv), 110 °C [b] Yields determined by GC-MS on the crude product mixture [c] The reaction was quenched with H_2O

Listed in Table 6.3 are representative results obtained from the palladium/nickel-cocatalyzed cycloaddition reactions with various alkynes. 1,3-*o*-Carboryne without protecting group at 2-C position gives very low isolated yield (12%) of **VI-4a** (entry 1). The steric factor on the 2-C of 1,3-*o*-carboryne has no significant effect on the reactions (entries 2–4). Functionalized 1,3-*o*-carboryne with electron-withdrawing group such as phenyl leading to the isolation of corresponding cyclization product **VI-4e** in moderate yield (entry 5). And substituents bearing heteroatom also afford moderate yields (entries 6 and 7). Both aliphatic and aromatic alkynes underwent [2+2+2] cycloaddition reactions. Steric factors played an important role in the reactions. No reaction proceeded for sterically more demanding alkynes bearing trimethylsilyl or *o*-tolyl group (entries 10 and 15). Alkynes bearing carbonyl group such as **VI-2e** and **VI-2f** were incompatible with this reaction because they can react with the carboryne precursor 1-Li-2-Me-3-I-1,2-$C_2B_{10}H_9$ (entries 11 and 12). Unsymmetrical alkynes gave two isomers of **VI-4l,m** and **VI-5l,m** (entries 16 and 17). It is noted that alkenes only give trace amount insertion products, and nitriles, isonitriles, or carbodiimides are ineffective under this condition.

The palladium/nickel-cocatalyzed cycloaddition reaction was successfully extended to various diynes (Scheme 6.2). Thus, 2-methyl-1,3-*o*-carboryne underwent cycloaddition with diynes (**VI-6a~d**) to provide the 1,3-benzo-*o*-carborane products, **VI-7a~c** in 6~34% yields, with a good fused-ring size tolerance.

Compounds **VI-4**, **VI-5** and **VI-7** were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectra as well as high-resolution mass spectrometry. For compounds **VI-4a~g**, four triplets at 0.5 to 1.2 ppm and a multiplet at ~2.5 ppm corresponding to the ethyl groups can observed in the ^{1}H NMR spectra. The CH_3 (cage) signals appear at 1.2

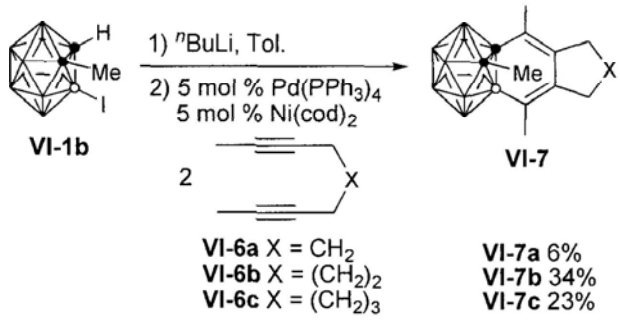
Table 6.3. Pd/Ni-Catalyzed Cycloaddition of 1,3-*o*-Carboryne with Alkynes[a]



Entry	R^1/ **VI-1**	R^2/R^3/ **VI-2**	Product	Yield (%)[b]
1	H/ **VI-1a**	Et/Et/ **VI-2a**	**VI-4a**	12
2	Me/ **VI-1b**	Et/Et/ **VI-2a**	**VI-4b**	79
3	^{n}Bu/ **VI-1c**	Et/Et/ **VI-2a**	**VI-4c**	67
4[c]	TMS/ **VI-1d**	Et/Et/ **VI-2a**	**VI-4d**	69
5	Ph/ **VI-1e**	Et/Et/ **VI-2a**	**VI-4e**	43
6	$(CH_2)_2OMe$/ **VI-1f**	Et/Et/ **VI-2a**	**VI-4f**	58
7	$(CH_2)_2NMe_2$/ **VI-1g**	Et/Et/ **VI-2a**	**VI-4g**	51
8	Me/ **VI-1b**	^{n}Pr/^{n}Pr/ **VI-2b**	**VI-4h**	55
9	Me/ **VI-1b**	^{n}Bu/^{n}Bu/ **VI-2c**	**VI-4i**	43
10	Me/ **VI-1b**	^{n}Bu/TMS/ **VI-2d**	**NR**[d]	-
11	Me/ **VI-1b**	COOMe/COOMe/ **VI-2e**	**NR**[e]	-
12	Me/ **VI-1b**	Me/COOMe/ **VI-2f**	**NR**[e]	-
13	Me/ **VI-1b**	Ph/Ph/ **VI-2g**	**VI-4j**	55
14	Me/ **VI-1b**	*p*-Tolly/*p*-Tolly/ **VI-2h**	**VI-4k**	51
15	Me/ **VI-1b**	*o*-Tolly/*o*-Tolly/ **VI-2i**	**NR**[d]	-
16	Me/ **VI-1b**	Me/Ph/**2j**	**VI-4l** **VI-5l**	49 (**VI-4l**/**VI-5l** = 62/38)[f]
17	Me/ **VI-1b**	Et/Ph/ **VI-2k**	**VI-4m** **VI-5m**	47(**VI-4m**/**VI-5m** = 80/20)[f]

[a] Conditions 1) ^{n}BuLi (1 equiv), toluene, r t , 0 5 h, 2) $Pd(PPh_3)_4$ (5 mol %), $Ni(cod)_2$ (5 mol %), alkyne (4 equiv), 110 °C, overnight [b] Isolated yields [c] 5 mol % $Pd(PPh_3)_4$ used as catalyst [d] **VI-3** was obtained as the product [e] **VI-1** was recovered [f] Ratio was determined by ^{1}H NMR spectroscopy on the crude product mixture

Scheme 6.2. Pd/Ni-Cocatalyzed Cycloaddition of 1,3-*o*-Carboryne with Diynes



ppm in the ^{1}H NMR spectra of **VI-4b**,**h**,**i** and **VI-7a**~**c**. In case of phenyl substituted products **VI-4j**,**k** the CH_3(cage) signals were shifted lowfield to 2.1 ppm. In the ^{1}H NMR spectra of **VI-4l**,**m** and **VI-5l**,**m**, which have both alkyl and aryl substitutents, the CH_3(cage) signals were observed at 1.7 ppm. Their ^{13}C NMR spectra were consistent with the ^{1}H NMR results. The olefin carbons which connected to the boron atom were not observed for **VI-4**, **VI-5** and **VI-7**.[88] The ^{11}B{^{1}H} NMR spectra generally exhibited a 3:5:2 splitting pattern for **VI-4b**,**h**~**m**, **VI-5m** and **VI-7a**~**c**, bearing methyl groups on the cage carbon. And the ^{11}B{^{1}H} NMR spectra displayed a 1:2:1:3:1:1:1, 3:4:1:1:1, 1:4:3:1:1, 2:1:1:3:3, 1:1:5:1:1:1, and 3:5:1:1 pattern for **VI-4a**, **4c**, **4d**, **4e**, **4f** and **4g**, respectively. The signal of *B*-C is overlapped with other *B*-H signals and cannot be identified.

The molecular structures of **VI-4a**, **VI-4b**, **VI-4d**, **VI-4j**, **VI-4m**, **VI-5m** and **VI-7b** were further confirmed by single-crystal X-ray analyses (Figure 6.1~6.6). The localized double bonds suggest there is no substantial π-delocalization in the six-membered ring.

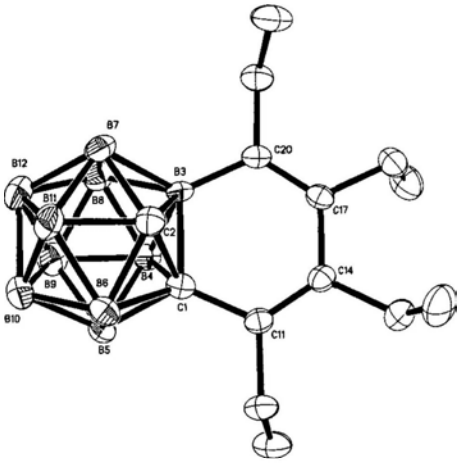


Figure 6.1. Molecular structure of **VI-4a**.

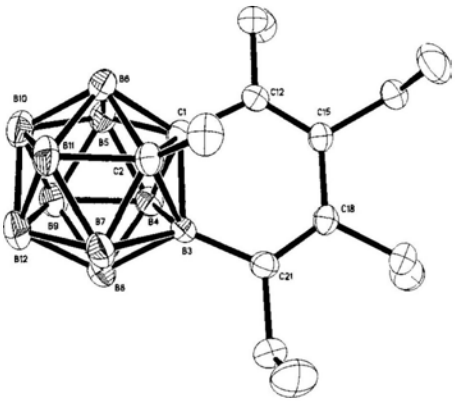


Figure 6.2. Molecular structure of **VI-4b**.

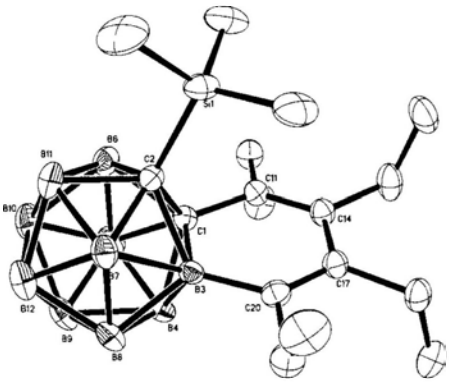


Figure 6.3. Molecular structure of **VI-4d**.

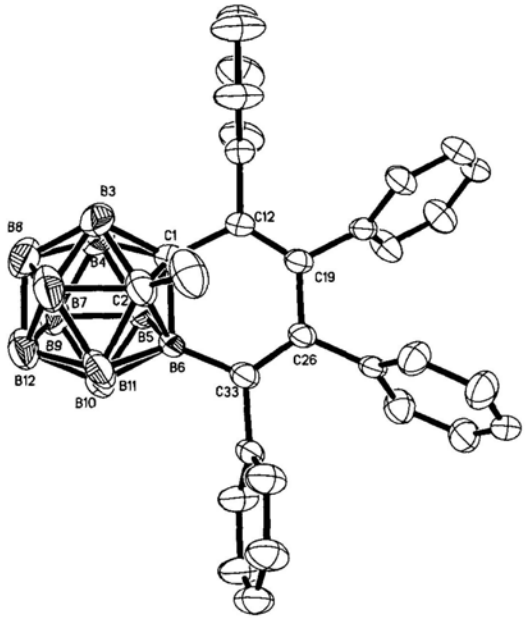


Figure 6.4. Molecular structure of **VI-4j**.

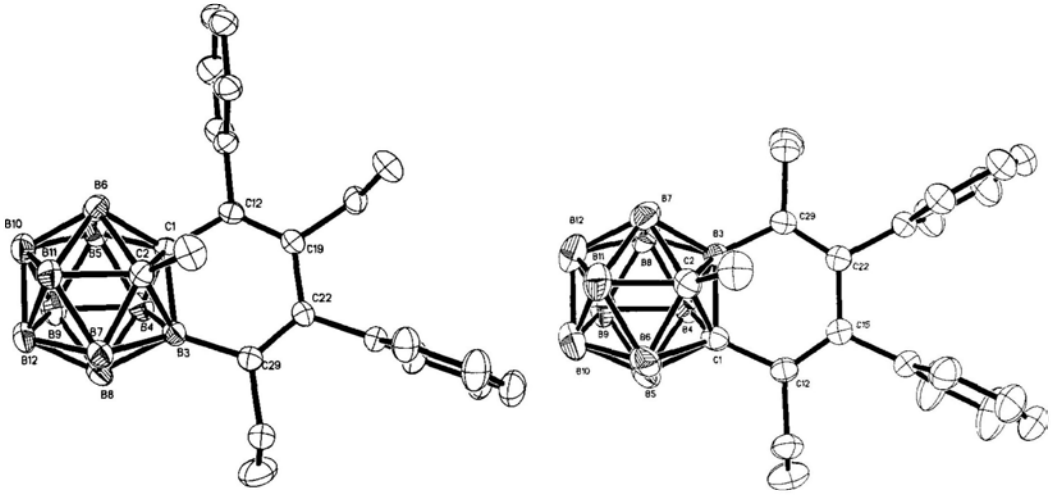


Figure 6.5. Molecular structures of **VI-4m** and **VI-5m**.

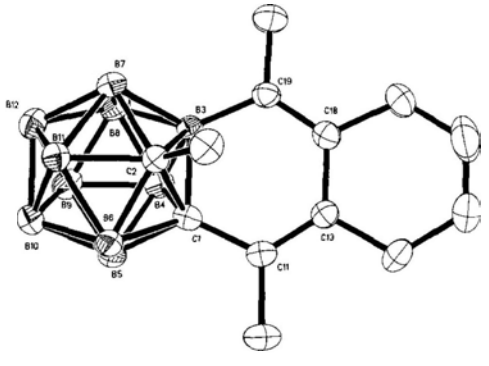


Figure 6.6. Molecular structure of **VI-7b**.

Table 6.4. Selected bond lengths (Å)

VI-4a	C(1)-B(3)	C(1)-C(11)	C(11)-C(14)	C(14)-C(17)	C(17)-C(20)	C(20)-B(3)
	1.706(5)	1.507(4)	1.340(4)	1.482(4)	1.351(4)	1.524(5)
VI-4b	C(1)-B(3)	C(1)-C(12)	C(12)-C(15)	C(15)-C(18)	C(18)-C(21)	C(21)-B(3)
	1.708(4)	1.502(4)	1.353(4)	1.479(4)	1.351(4)	1.527(5)
VI-4d	C(1)-B(3)	C(1)-C(11)	C(11)-C(14)	C(14)-C(17)	C(17)-C(20)	C(20)-B(3)
	1.707(2)	1.518(2)	1.366(3)	1.498(2)	1.366(3)	1.546(3)
VI-4j	C(1)-B(6)	C(1)-C(12)	C(12)-C(19)	C(19)-C(26)	C(26)-C(33)	C(33)-B(6)
	1.706(4)	1.520(4)	1.347(3)	1.487(3)	1.357(3)	1.527(4)
VI-4m	C(1)-B(3)	C(1)-C(12)	C(12)-C(19)	C(19)-C(22)	C(22)-C(29)	C(29)-B(3)
	1.707(5)	1.481(5)	1.350(4)	1.481(5)	1.344(5)	1.537(6)
VI-5m	C(1)-B(3)	C(1)-C(12)	C(12)-C(15)	C(15)-C(22)	C(22)-C(29)	C(29)-B(3)
	1.701(4)	1.514(4)	1.352(4)	1.492(4)	1.351(4)	1.531(4)
VI-7b	C(1)-B(3)	C(1)-C(11)	C(11)-C(13)	C(13)-C(18)	C(18)-C(19)	C(19)-B(3)
	1.689(5)	1.508(5)	1.359(5)	1.483(5)	1.356(5)	1.533(5)

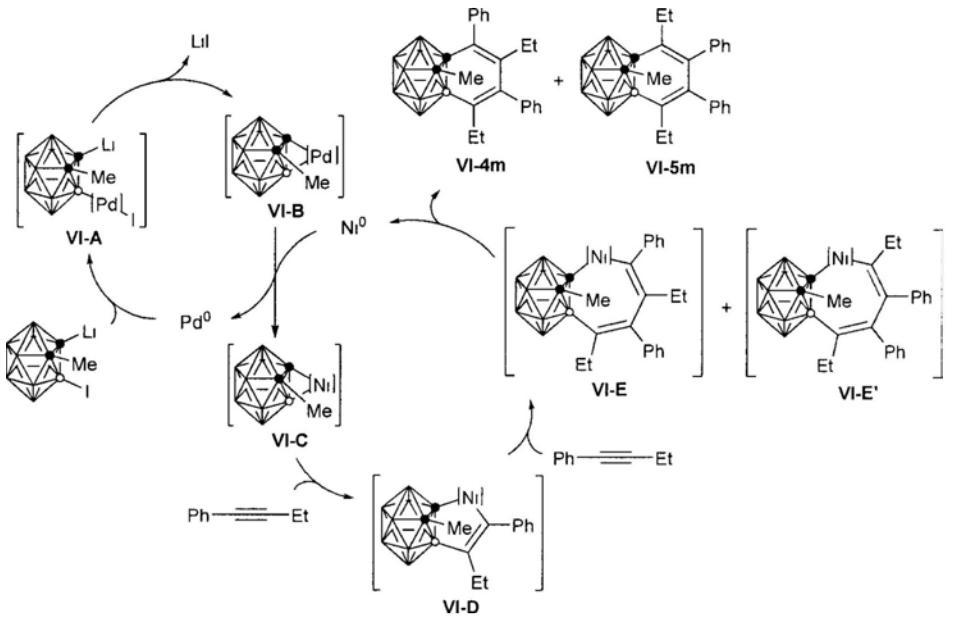
6.2.4 Proposed Mechanism

It is believed that the reaction is through a metal-1,3-*o*-carboryne intermediate because the catalytic amount of Pd species can convert **VI-1b** to **VI-3b** quantitatively. A mixture of **VI-1b** and 3-hexyne was refluxed in toluene in the presence of 5 mol % $Pd(PPh_3)_4$ and 5 mol % $Ni(cod)_2$ did not give any alkyne insertion products, rather afforded the isomers of **VI-1b** with iodo being located at different cage boron positions as suggested by GC-MS analyses.

A plausible mechanism for palladium/nickel-cocatalyzed [2+2+2] cocyclization is shown in Scheme 6.3. As Ni(0) cannot insert into the B–I bond efficiently (Table 6.1, entry 4), the Pd-1,3-*o*-carboryne **VI-B** is formed by the oxidative addition of B–I on Pd(0), followed by LiI elimination. It is noteworthy that the reactions were very slow (>5 days) and inefficient with more bulky alkynes **VI-2b~k** when only $Pd(PPh_3)_4$ or $[Pd(Ally)Cl]_2/PPh_3$ was employed as catalyst. In view of that the two-component catalyst is more effective than Pd species alone in the reaction of 1,3-*o*-carboryne with alkynes, it is rational to propose a transmetallation process between Pd and Ni, affording a more reactive nickel-1,3-*o*-carboryne **VI-C**. The relatively higher activity of Ni species is probably due to that the Pd–B bond is stronger than the Ni–B bond or the Ni–B bonding pair is more nucleophilic than that of Pd–B. In the reaction with PhC≡CEt, the electronically controlled regio-selective insertion of unsymmetrical alkyne into the Ni–B bond gives the nickelacyclopentene intermediate **VI-D**.[60,77] The absence of 2-Me-1,3-{1',4'-[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 Ni–B bond. As the insertion of alkynes into the Ni–C(cage) bond in metal-carboranyl complexes is prohibited due to steric reasons,[64] the second equivalent of alkyne inserts into the Ni–C(vinyl) bond in both head-to-tail

and head-to-head manners. Subsequent reductive elimination yields the final products **VI-4m** and **VI-5m**.

Scheme 6.3. Proposed Mechanism of Pd/Ni-Cocatalyzed [2+2+2] Cyclization Reaction



The M–B bond is much more reactive than the M–C bond in the alkyne insertion as the bonding pair of M–B is very high in energy. This is consistent with the result from the reaction of metal-borataalkene with alkynes[88] and the conclusion based on metal-catalyzed borylation reactions[89]. Due to the low electronegativity of boron, an M–B bond is much more nucleophilic than an M–C bond. The alkyne insertion into an M–B bond step can be considered as a nucleophilic attack of the M–B σ-bond (the bonding electron pair) on one of the two alkyne carbons. The nucleophilic attack in nature also explains the regioselectivity observed in the unsymmetrical alkynes, i.e., in the insertion product **VI-D**, boron is bonded to the carbon having the electron-donating ethyl substituent.

6.3 Summary

In summary, we have shown for the first time a 1,3-*o*-carboryne, which can be regarded as a new boron nucleophile and can be trapped by unsaturated molecules in the presence of transition metal. This serves a palladium/nickel-cocatalyzed [2+2+2] cycloaddition reaction of 1,3-*o*-carboryne with alkynes to afford 1,3-benzo-*o*-carboranes. This work offers a new methodology for B-functionalization of carborane and demonstrates the relative reactivity of M–C over M–B bond in 1,3-*o*-carboryne complexes toward alkynes.

Chapter 7. Conclusion

This thesis describes (1) the synthesis and structural characterization of B-substituted nickel-1,2-*o*-carboryne complexes, (2) the reaction chemistry of Ni-1,2-*o*-carboryne with alkenes or/and alkynes, and (3) the formation of 1,3-*o*-carboryne and ite reaction with alkynes catalyzed by transition metal.

Complexes (η^2-1,2-$C_2B_{10}R^1{}_nH_{10-n}$)Ni($PR^2{}_3$)$_2$ (R^1 = I, n = 1, R_2 = Ph (**II-1**); R^1 = I, n = 2, R_2 = Ph (**II-2**); R^1 = Br, n = 1, R_2 = Me (**II-3**); R^1 = Ph, n = 1, R_2 = Me (**II-4**); R^1 = Ph, n = 1, R_2 = Ph (**II-5**)) were synthesized by salt elimination of phosphine ligated metal halide with dilithiocarboranes. The substituents on the carborane cage have significant effects on these complexes and **II-5** exhibits exceptional stability toward heat and moisture. B-H···Ni interactions were observed in the IR spectra and solid-state structures of **II-4** and **II-5** due to the steric effect of the phenyl substituent.

In the reactivity study of (η^2-$C_2B_{10}H_{10}$)Ni(PPh_3)$_2$, we found alkenes can regioselectively react with nickelacarboryne in an insertion manner followed by a β-H elimination to afford alkenylcarboranes. Both aliphatic and aromatic, terminal and internal, cyclic and acyclic alkenes underwent the insertion reactions, and among them substituted styrenes gave the best results. The mechanism was supported by the D-substitued experiments. The β-H elimination cannot occur with some substrates such as methyl acrylate and 2-vinyl pyridine leading to the isolation of the thermodynamically stable inserted intermediates, nickelacyclopentanes.

In view of that nickelacyclopentane intermediates can react readily with alkynes to give dihydrobenzocarborane derivatives, a novel nickel-mediated three-component assembling reaction of 1,2-*o*-carboryne with alkenes and alkynes was developed. The formation of products can be rationalized by the sequential insertion of alkene and alkyne into the Ni–C(cage) and Ni–C(alkyl) bond, followed by reductive elimination.

By the analogy between benzyne and 1,2-*o*-carboryne, nickel-catalyzed three-component cycloaddition reactions of arynes, activated alkenes, and alkynes have been achieved, leading to a series of substituted dihydronaphthalenes in moderate to very good isolated yields with excellent chemo- and regioselectivity.

1-Iodo-2-lithiocarborane, conveniently prepared in situ from the reaction of dilithiocarborane with 1 equiv of iodine, was used as the 1,2-*o*-carboryne precursor to develop a catalytic version of the reactions of 1,2-*o*-carboryne with alkynes. The isolated yields of the benzocarborane products were very comparable with those of stoichiometric reactions of Ni-1,2-*o*-carboryne with alkynes. The key intermediate, nickelacyclopentene $[\{[2\text{-}C(^{n}Bu)=C(o\text{-}C_5H_4N)\text{-}1,2\text{-}C_2B_{10}H_{10}]Ni\}_2(\mu_2\text{-}Cl)][Li(THF)_4]$ was isolated and structurally confirmed.

1,3-*o*-Carboryne, which can be regarded as a new boron nucleophile, can be formed by salt elimination of 3-iodo-1-lithio-*o*-carborane catalyzed by palladium(0). Due to high reaction temperatures, 1,3-*o*-carboryne cannot be stabilized by transition-metal, but can be trapped by alkynes to form [2+2+2] cycloaddition products. These studies introduce a direct and efficient route to the synthesis of 1,3-benzo-*o*-carborane derivatives and demonstrate the relative reactivity of M–C over M–B bond in 1,3-*o*-carboryne complexes toward alkynes.

Chapter 8. Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents (except CH_2Cl_2) were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. CH_2Cl_2 was refluxed over CaH_2 for several days and distilled immediately prior to use. All chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. $(Ph_3P)_2NiCl_2$,[90] $(Me_2Im)_2NiI_2$,[91] aryne precursors **IV-2b~e**,[67b,68a] 3-bromo-*o*-carborane,[29e] 3-iodo-*o*-carborane,[92] 9-iodo-*o*-carborane,[23a] 9,12-diiodo-*o*-carborane,[28b] 1-phenyl-*o*-carborane[93] were prepared according to literature methods. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^1H NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 300 MHz or a Bruker DPX 400 spectrometer at 400 MHz. $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 75 MHz or a Bruker DPX 400 spectrometer at 100 MHz. $^{11}B\{^1H\}$ NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 96 MHz or a Bruker DPX 400 spectrometer at 128 MHz. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts, and to external 85% H_3PO_4 (0.00 ppm) for phosphorous chemical shifts. Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, CAS, China.

Preparation of (η^2-9-I-1,2-$C_2B_{10}H_9$)Ni(PPh_3)$_2$ (II-1). A 1.6 M solution of *n*-BuLi in *n*-hexane (0.625 mL, 1.0 mmol) was slowly added to a stirring solution of 9-I-1,2-$C_2B_{10}H_{11}$ (135 mg, 0.5 mmol) in THF (10 mL) at 0°C, and the mixture was stirred at room temperature for 1 h. The resulting 1,2-Li_2-9-I-1,2-$C_2B_{10}H_9$ suspension was then cooled to 0°C, to which was added $(Ph_3P)_2NiCl_2$ (327 mg, 0.5 mmol). The reaction mixture was then stirred for 0.5 h at room temperature, giving a brown solution. After removal of the solvent, the deep brown residue was extracted with toluene (10 mL × 3). The brown filtrate was concentrated to 5 mL. Complex **II-1**·0.5toluene was obtained as a yellow solid after it stood at room temperature for 2 days (247 mg, 55%). ^{1}H NMR (benzene-d_6): δ 7.28 (m, 12H, C_6H_5), 6.86 (m, 18H, C_6H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 133.7 (d, $^2J_{C\text{-}P}$ = 11.5 Hz), 131.9 (d, $^1J_{C\text{-}P}$ = 44.5 Hz), 130.6, 128.7 (d, $^3J_{C\text{-}P}$ = 6.1 Hz), the cage carbons are not observed. $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -1.1 (3B), -13.9 (6B), -22.9 (1B). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 33.9. IR (KBr, cm^{-1}): ν_{BH} 2578 (vs). Anal. Calcd for $C_{83}H_{86}B_{20}Ni_2P_4I_2$ (**II-1**+0.5toluene): C, 55.54; H, 4.83. Found: C, 55.68; H, 5.06.

Preparation of (η^2-9,12-I_2-1,2-$C_2B_{10}H_8$)Ni(PPh_3)$_2$ (II-2). A 1.6 M solution of *n*-BuLi in *n*-hexane (0.625 mL, 1.0 mmol) was slowly added to a stirring solution of 9,12-I_2-1,2-$C_2B_{10}H_{10}$ (198 mg, 0.5 mmol) in THF (10 mL) at 0°C, and the mixture was stirred at room temperature for 1 h. The resulting 1,2-Li_2-9,12-I_2-1,2-$C_2B_{10}H_8$ suspension was then cooled to 0°C, to which was added $(Ph_3P)_2NiCl_2$ (327 mg, 0.5 mmol). The reaction mixture was then stirred for 0.5 h at room temperature, giving a brown solution. After removal of the solvent, the deep brown residue was extracted with CH_2Cl_2 (20 mL). The brown filtrate was concentrated to 3 mL. Complex **II-2** was obtained as yellow crystals after this solution stood at -30°C overnight (352 mg, 72%). ^{1}H NMR (CD_2Cl_2): δ 7.40 (m, 6H, C_6H_5), 7.25 (m, 24H, C_6H_5). $^{13}C\{^1H\}$

NMR (CD_2Cl_2): δ 133.1 (dd, $^2J_{C\text{-}P}$ = 6.0 Hz), 130.3, 128.2 (dd, $^3J_{C\text{-}P}$ = 4.9 Hz), the cage carbons are not observed. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ -0.5 (2B), -14.0 (6B), -21.6 (2B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 32.4. IR (KBr, cm^{-1}): ν_{BH} 2592 (vs). Anal. Calcd for $C_{38}H_{38}B_{10}NiP_2I_2$ (**II-2**): C, 46.70; H, 3.92. Found: C, 47.19; H, 3.97.

Preparation of (η^2-3-Br-1,2-$C_2B_{10}H_9$)Ni(PMe_3)$_2$ (II-3). A 1.6 M solution of *n*-BuLi in *n*-hexane (0.625 mL, 1.0 mmol) was slowly added to a stirring solution of 3-Br-1,2-$C_2B_{10}H_{11}$ (112 mg, 0.5 mmol) in THF (10 mL) at 0°C, and the mixture was stirred at room temperature for 1 h. The resulting 1,2-Li_2-3-Br-1,2-$C_2B_{10}H_9$ suspension was then cooled to 0°C, to which was added $(Me_3P)_2NiCl_2$ (141 mg, 0.5 mmol). The reaction mixture was then stirred for 0.5 h at room temperature, giving a brown solution. After removal of the solvent, the deep brown residue was extracted with toluene (10 mL × 3). The brown filtrate was concentrated to 5 mL. Complex **II-3** was obtained as yellow crystals after it stood at room temperature for 2 days (67 mg, 31%). ^1H NMR (benzene-d_6): δ 0.73 (m, 18H, CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 16.6 (m), the cage carbons are not observed. $^{11}B\{^1H\}$ NMR (benzene-d_6): δ -1.5 (1B), -8.4 (1B), -10.8 (2B), -11.6 (2B), -12.6 (2B), -14.1 (2B). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ -9.4. IR (KBr, cm^{-1}): ν_{BH} 2551 (vs). Anal. Calcd for $C_8H_{27}B_{10}BrNiP_2$ (**II-3**): C, 22.25; H, 6.30. Found: C, 22.61; H, 6.18.

Preparation of (η^2-3-C_6H_5-1,2-$C_2B_{10}H_9$)Ni(PMe_3)$_2$ (II-4). A 1.6 M solution of *n*-BuLi in *n*-hexane (0.625 mL, 1.0 mmol) was slowly added to a stirring solution of 3-C_6H_5-1,2-$C_2B_{10}H_{11}$ (110 mg, 0.5 mmol) in THF (10 mL) at 0°C, and the mixture was stirred at room temperature for 1 h. The resulting 1,2-Li_2-3-C_6H_5-1,2-$C_2B_{10}H_9$ suspension was then cooled to 0°C, to which was added $(Me_3P)_2NiCl_2$ (141 mg, 0.5 mmol). The reaction mixture was then stirred for 0.5 h at room temperature, giving a brown solution. After removal of the solvent, the deep brown residue was extracted

with toluene (10 mL × 3). The brown filtrate was concentrated to 6~7 mL. Complex **II-4** was obtained as yellow crystals after it stood at room temperature for 3 days (90 mg, 42%). ^{1}H NMR (CD_2Cl_2): δ 7.82 (m, 2H, C_6H_5), 7.30 (m, 3H, C_6H_5), 1.16 (m, 18H, CH_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 133.6, 127.6, 126.9 (C_6H_5), 16.3 (m) (CH_3), the cage carbons are not observed. $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2): δ -2.8 (1B), -3.8 (1B), -8.2 (1B), -12.2 (2B), -15.2 (5B). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ -9.1. IR (KBr, cm^{-1}): ν_{BH} 2550, 2531 (vs). Anal. Calcd for $C_{14}H_{32}B_{10}NiP_2$ (**II-4**): C, 39.18; H, 7.52. Found: C, 38.96; H, 7.71.

Preparation of (η^2-3-C_6H_5-1,2-$C_2B_{10}H_9$)Ni(PPh_3)$_2$ (II-5). A 1.6 M solution of *n*-BuLi in *n*-hexane (0.625 mL, 1.0 mmol) was slowly added to a stirring solution of 3-C_6H_5-1,2-$C_2B_{10}H_{11}$ (110 mg, 0.5 mmol) in THF (10 mL) at 0°C, and the mixture was stirred at room temperature for 1 h. The resulting 1,2-Li_2-3-C_6H_5-1,2-$C_2B_{10}H_9$ suspension was then cooled to 0°C, to which was added $(Ph_3P)_2NiCl_2$ (327 mg, 0.5 mmol). The reaction mixture was then stirred for 0.5 h at room temperature, giving a brown solution. After removal of the solvent, the deep brown residue was extracted with toluene (10 mL × 3). The brown filtrate was concentrated to 10 mL. Complex **II-5** was obtained as orange crystals after it stood at room temperature for 3 days (305 mg, 76%). ^{1}H NMR (CD_2Cl_2): δ 7.70 (d, J = 7.2 Hz, 2H, BC_6H_5), 7.45 (t, J = 7.2 Hz, 1H, BC_6H_5), 7.33 (m, 6H, PC_6H_5), 7.18 (m, 14H, BC_6H_5 & PC_6H_5), 7.06 (m, 12H, PC_6H_5). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 135.3 (s, BC_6H_5), 134.0 (m, PC_6H_5), 131.9 (d, $^{1}J_{C\text{-}P}$ = 44.2 Hz, PC_6H_5), 130.5 (s, PC_6H_5), 128.6 (m, PC_6H_5), 128.1 (BC_6H_5), the cage carbons are not observed. $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2): δ -1.7 (2B), -7.7 (1B), -11.9 (3B), -13.4 (4B). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 29.6. IR (KBr, cm^{-1}): ν_{BH} 2557, 2512 (vs). Anal. Calcd for $C_{44}H_{44}B_{10}NiP_2$ (**II-5**): C, 65.93; H, 5.53. Found: C, 66.12; H, 5.54.

General Procedure for Nickel-Mediated Cycloaddition Reaction of 1,2-*o*-Carboryne with Alkynes. To a THF solution (5 mL) of $Li_2C_2B_{10}H_{10}$ (1.0 mmol), prepared in situ from the reaction of *n*-BuLi (2.0 mmol) with *o*-carborane (1.0 mmol), was added $(PPh_3)_2NiCl_2$ (1.0 mmol). The reaction mixture was stirred at room temperature for 0.5 h to give the Ni-1,2-*o*-carboryne complex (η^2-$C_2B_{10}H_{10}$)Ni$(PPh_3)_2$.[53] Alkene (2.0 mmol) was then added and the reaction vessel was closed and heated at 90 °C overnight. After removal of the precipitate, the resulting solution was concentrated to dryness in vacuo. The residue was subject to column chromatography on silica gel (40-230 mesh) to give the coupling product.

***trans*-1-(HC=CHPh)-1,2-$C_2B_{10}H_{11}$ (III-3a)**. Yield: 82%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 5H) (Ph), 6.85 (d, J = 16.0 Hz, 1H), 6.28 (d, J = 16.0 Hz, 1H) (olefinic), 3.72 (s, 1H) (cage C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.7, 129.5, 128.9, 126.9, 122.5 (olefinic and Ph), 60.9 (cage *C*), another cage carbon was not observed. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -1.9 (1B), -4.5 (1B), -8.6 (2B), -10.2 (4B), -12.0 (2B). ^{1}H NMR (300 MHz, benzene-d_6): δ 6.99 (m, 3H), 6.88 (m, 2H) (Ph), 6.48 (d, J = 15.9 Hz, 1H), 5.76 (d, J = 15.9 Hz, 1H) (olefinic), 2.47 (s, 1H) (cage C*H*). ^{11}B{^{1}H} NMR (96 MHz, benzene-d_6): δ -2.2 (1B), -5.0 (1B), -9.4 (2B), -11.3 (2B), -12.2 (2B), -13.2 (2B). HRMS: *m/z* calcd for $C_{10}H_{18}{}^{11}B_8{}^{10}B_2{}^+$: 246.2406. Found: 246.2407.

***trans*-1-[DC=CD(Ph)]-2-D-1,2-$C_2B_{10}H_{11}$ ([D_3]-III-3a)**. Yield: 80%. Colorless oil. ^{1}H NMR (400 MHz, benzene-d_6): δ 6.99 (m, 3H), 6.87 (m, 2H) (Ph). ^{2}H NMR (61 MHz, benzene): δ 6.47 (1^2H), 5.76 (1^2H) (olefinic), 2.42 (1^2H) (cage C^2*H*). HRMS: *m/z* calcd for $C_{10}H_{15}{}^2H_3{}^{11}B_8{}^{10}B_2{}^+$: 249.2595. Found: 249.2588.

***trans*-1-{HC=CH[(2'-CH_3)C_6H_4]}-1,2-$C_2B_{10}H_{11}$ (III-3b)**. Yield: 85%. White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz,

2H) (Ph), 6.81 (d, J = 15.9 Hz, 1H), 6.23 (d, J = 15.9 Hz, 1H) (olefinic), 3.71 (s, 1H) (cage C*H*), 2.35 (s, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 139.7, 137.6, 131.4, 129.6, 126.9, 121.4 (olefinic and Ph), 74.4, 61.0 (cage *C*), 21.3 (*C*H_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.7 (1B), -5.8 (1B), -9.9 (2B), -11.7 (2B), -12.3 (2B), -13.6 (2B). HRMS: *m/z* calcd for $C_{11}H_{20}{}^{11}B_8{}^{10}B_2{}^+$: 260.2563. Found: 260.2561.

***trans*-1-{HC=CH[(4'-CF$_3$)C$_6$H$_4$]}-1,2-C$_2$B$_{10}$H$_{11}$ (III-3c)**. Yield 80%. White solid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H) (Ph), 6.88 (d, J = 15.9 Hz, 1H), 6.36 (d, J = 15.9 Hz, 1H) (olefinic), 3.74 (s, 1H) (cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.5, 136.2, 127.2, 125.9, 125.2 (*C*F_3, olefinic and Ph), 73.3, 60.7 (cage *C*). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.5 (1B), -5.3 (1B), -9.7 (2B), -11.7 (2B), -12.3 (2B), -13.4 (2B). HRMS: *m/z* calcd for $C_{11}H_{17}{}^{11}B_8{}^{10}B_2F_3{}^+$: 314.2280. Found: 314.2275.

***trans*-1-{HC=CH[(3'-CF$_3$)C$_6$H$_4$]}-1,2-C$_2$B$_{10}$H$_{11}$ (III-3d)**. Yield 73%. White solid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.52 (m, 4H) (Ph), 6.90 (d, J = 15.9 Hz, 1H), 6.35 (d, J = 15.9 Hz, 1H) (olefinic), 3.74 (s, 1H) (cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.2, 134.9, 130.1, 129.5, 126.0, 124.5, 123.6, 123.5 (*C*F_3, olefinic and Ph), 73.4, 60.7 (cage *C*). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.0 (1B), -4.8 (1B), -9.2 (2B), -11.2 (2B), -11.9 (2B), -12.9 (2B). HRMS: *m/z* calcd for $C_{11}H_{17}{}^{11}B_8{}^{10}B_2F_3{}^+$: 314.2280. Found: 314.2276.

***trans*-1-{HC=CH[3',4',5'-(OMe)$_3$C$_6$H$_2$]}-1,2-C$_2$B$_{10}$H$_{11}$ (III-3e)**. Yield 76%. White solid. ^1H NMR (300 MHz, $CDCl_3$): δ 6.78 (d, J = 15.6 Hz, 1H) (olefinic), 6.54 (s, 2H) (Ph), 6.17 (d, J = 15.6 Hz, 1H) (olefinic), 3.88 (s, 6H), 3.85 (s, 3H) (OCH_3), 3.72 (s, 1H) (cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.5, 139.4, 137.7, 129.6, 121.7, 104.2 (olefinic and Ph), 74.1(cage *C*), 61.0, 56.2 (O*C*H_3), another cage carbon was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.5 (1B), -5.6 (1B),

-9.8 (2B), -11.6 (2B), -12.3 (2B), -13.5 (2B). HRMS: *m/z* calcd for $C_{13}H_{24}{}^{11}B_8{}^{10}B_2{}^+$: 336.2723. Found: 336.2718.

1-[$H_2CC(Ph)=CH_2$]-1,2-$C_2B_{10}H_{11}$ (III-4f). Yield: 59%. Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.36 (m, 5H) (Ph), 5.48 (s, 1H), 5.20 (s, 1H) (olefinic), 3.49 (s, 2H) (CH_2), 3.37 (s, 1H) (cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.8, 139.1, 128.9, 128.6, 126.2, 119.7 (olefinic and Ph), 73.8, 58.8 (cage *C*), 42.5 (CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.5 (1B), -5.9 (1B), -9.9 (2B), -11.1 (2B), -12.7 (2B), -13.4 (2B). HRMS: *m/z* calcd for $C_{11}H_{20}{}^{11}B_8{}^{10}B_2{}^+$: 260.2563. Found: 260.2563.

1-[HC=$C(Ph)_2$]-1,2-$C_2B_{10}H_{11}$ (III-3g). Yield: 46%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (m, 3H), 7.28 (m, 3H), 7.17 (m, 4H) (Ph), 6.27 (s, 1H) (olefinic), 3.00 (s, 1H) (cage C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.2, 140.0, 136.0, 129.1, 129.0, 128.9, 128.8, 128.5, 126.9, 122.0 (olefinic and Ph), 73.2, 57.5 (cage *C*). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.5 (1B), -4.2 (1B), -9.8 (4B), -10.4 (2B), -13.1 (2B). HRMS: *m/z* calcd for $C_{16}H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 322.2719. Found: 322.2716.

***trans*-1-[HC=CH($SiMe_3$)]-1,2-$C_2B_{10}H_{11}$ (III-3h)**. Yield: 46%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.24 (d, J = 18.4 Hz, 1H), 6.01 (d, J = 18.4 Hz, 1H) (olefinic), 3.65 (s, 1H) (cage C*H*), 0.08 (s, 9H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 139.4, 137.2 (olefinic), 59.8 (cage *C*), -1.8 (CH_3), another cage carbon was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -2.3 (1B), -5.0 (1B), -9.2 (2B), -11.5 (4B), -13.0 (2B). HRMS: *m/z* calcd for $C_7H_{22}{}^{11}B_8{}^{10}B_2Si^+$: 242.2488. Found: 242.2483.

1-[$H_2C\overline{C=CH(CH_2)_3CH_2}$]-1,2-$C_2B_{10}H_{11}$ (III-4i). Yield: 77%. Colorless oil. ^1H NMR (400 MHz, benzene-d_6): δ 5.07 (s, 1H) (olefinic), 2.62 (s, 1H) (cage C*H*), 2.20 (s, 2H) (CB-CH_2), 1.72 (m, 2H), 1.62 (m, 2H), 1.30 (m, 4H) (CH_2). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 132.8 (olefinic), 74.9, 60.6 (cage *C*), 45.9 (acyclic CH_2), 29.3, 25.3,

22.7, 21.7 (cyclic CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ -3.2 (1B), -6.5 (1B), -9.8 (2B), -11.6 (2B), -13.7 (4B). HRMS: *m/z* calcd for $C_9H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 238.2719. Found: 238.2718.

***cis-/trans*-1-[$H_2CCH=CH(^nPr)$]-1,2-$C_2B_{10}H_{11}$ (III-4j).** Yield: 74%. Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 5.64 (m, 1H), 5.53 (m, 1H), 5.31 (m, 2H) (olefinic), 3.60 (s, 1H), 3.56 (s, 1H) (cage C*H*), 2.98 (d, J = 7.8 Hz, 2H), 2.88 (d, J = 7.5 Hz, 2H), 2.00 (m, 4H), 1.40 (m, 4H) (CH_2), 0.90 (t, J = 7.5 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.5, 135.7, 122.9, 122.1 (olefinic), 74.5, 59.4 (cage C), 40.7, 34.8, 34.3, 29.3, 22.5, 22.2 (CH_2), 13.7, 13.6 (CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -1.3 (1B), -4.7 (1B), -8.2 (2B), -10.2 (2B), -12.4 (4B). HRMS: *m/z* calcd for $[C_7H_{22}{}^{11}B_8{}^{10}B_2 - 2H]^+$: 224.2563. Found: 224.2552.

1-[HCC=CH$(CH_2)_2$CH$_2$]-1,2-$C_2B_{10}H_{11}$ (III-4k). Yield: 67%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.86 (m, 1H), 5.57 (d, J = 10.4 Hz, 1H) (olefinic), 3.70 (s, 1H) (cage C*H*), 2.97 (m, 1H) (C*H*), 1.98 (m, 3H), 1.79 (m, 1H), 1.54 (m, 2H) (CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 131.3, 125.8 (olefinic), 80.0, 59.7 (cage C), 40.8, 29.6, 24.4, 21.1 (CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -1.8 (1B), -3.8 (1B), -8.3 (2B), -10.7 (2B), -12.8 (4B). These data are identical with those reported in the literature.[42a]

1-bicyclo[2.2.1]hept-2-yl-1,2-carborane (III-5l). Yield: 60%. Colorless oil. ^1H NMR (400 MHz, benzene-d_6): δ 2.43 (s, 1H) (cage C*H*), 1.85 (m, 2H), 1.46 (m, 1H) (C*H*), 1.16 (m, 2H), 1.04 (m, 2H) 0.70 (m, 4H) (CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ 81.3, 62.5 (cage *C*), 49.0, 43.8, 39.6 (*C*H), 36.6, 35,7, 30.2, 28.4 (CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6): δ -3.1 (1B), -5.2 (1B), -9.5 (2B), -12.2 (2B), -13.6 (4B). ^1H NMR (300 MHz, $CDCl_3$): δ 3.57 (s, 1H) (cage C*H*), 2.31 (m,

2H), 2.12 (m, 1H) (C*H*), 1.61 (m, 2H), 1.53 (m, 1H), 1.35 (m, 1H), 1.13 (m, 4H) (CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.4 (2B), -5.6 (1B), -9.8 (2B), -12.3 (2B), -12.6 (2B), -13.9 (2B). HRMS: *m/z* calcd for $C_9H_{22}{}^{11}B_8{}^{10}B_2{}^+$: 238.2719. Found: 238.2710.

1-(1H-inden-2-yl)-1,2-carborane (III-3m). Yield: 31%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 4H), 6.98 (s, 1H) (aromatic), 3.85 (s, 1H) (cage C*H*), 3.50 (s, 2H) (CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.5, 142.3, 139.9., 133.9, 127.2, 126.6, 123.8, 122.0 (aromatic and olefinic), 73.6, 61.4 (cage *C*), 42.0 (*C*H_2). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.3 (1B), -4.8 (1B), -9.2 (2B), -11.0 (2B), -11.4 (2B), -12.9 (2B). These data are identical with those reported in the literature.[94]

1-(2,3-dihydro-1H-inden-2-yl)-1,2-carborane (III-5m). Yield: 27%. Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.17 (s, 4H) (aromatic), 3.68 (s, 1H) (cage C*H*), 3.03 (m, 5H) (C*H* and CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.4, 127.28, 124.3 (aromatic), 61.2 (cage *C*), 47.3 (*C*H), 39.9 (*C*H_2). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.1 (1B), -4.4 (1B), -8.6 (2B), -10.9 (2B), -12.1 (2B), -12.5 (2B). HRMS: *m/z* calcd for $C_{11}H_{20}{}^{11}B_8{}^{10}B_2{}^+$: 260.2563. Found: 260.2561.

***trans*-1-[HC=CH(O^{n}Bu)]-1,2-$C_2B_{10}H_{11}$ (III-3n).** Yield: 18%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.81 (d, J = 12.4 Hz, 1H), 5.07 (d, J = 12.4 Hz, 1H) (olefinic), 3.66 (t, J = 6.4 Hz, 2H) (OCH_2), 3.54 (s, 1H) (cage C*H*), 1.61 (m, 2H), 1.38 (m, 2H) (CH_2), 0.93 (t, J = 7.6 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.2, 100.2 (olefinic), 70.4 (cage *C*), 62.4 (O*C*H$_2$), 31.0, 19.0 (*C*H_2), 13.7 (*C*H_3), another cage carbon was not observed.. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -1.3 (1B), -5.5 (1B), -9.5 (2B), -10.3 (2B), -11.4 (2B), -12.5 (2B). HRMS: *m/z* calcd for $C_8H_{22}O{}^{11}B_8{}^{10}B_2{}^+$: 242.2688. Found: 242.2682.

1-[HC(Me)(O^{n}Bu)]-1,2-$C_2B_{10}H_{11}$ (III-5n): Yield: 12%. Colorless oil. ^1H NMR

(400 MHz, $CDCl_3$): δ 4.08 (s, 1H) (cage C*H*), 3.86 (q, J = 6.8 Hz, 1H) (OC*H*), 3.56 (m, 1H) (OC*H*H), 3.31 (m, 1H) (OCH*H*), 1.52 (m, 2H), 1.33 (m, 5H) (CH_2 and CH_3), 0.91 (t, J = 6.8 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 78.2, 58.3 (cage *C*), 75.5 (O*C*H), 70.3 (O*C*H_2), 31.7, 19.7, 19.3 (CH_2), 13.8 (CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.9 (1B), -4.7 (1B), -9.3 (3B), -12.1 (3B), -13.4 (1B), -14.3 (1B). HRMS: *m/z* calcd for $C_8H_{24}O^{11}B_8{}^{10}B_2{}^+$: 244.2825. Found: 244.2823.

1-[HCC=CH(CH$_2$)$_2$O]-1,2-C$_2$B$_{10}$H$_{11}$ (III-4o): Yield 15%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.04 (m, 1H) (olefinic), 5.72 (d, J = 6.9 Hz, 1H) (olefinic), 4.54 (s, 1H) (O*C*H), 4.09 (s, 1H) (cage C*H*), 3.98 (ddd, J = 1.2, 4.2, 8.4 Hz, 1H) (OC*H*H), 3.65 (dt, J = 2.7, 8.4 Hz, 1H) (OCH*H*), 2.28 (m, 1H) (C*H*H), 1.93 (ddd, J = 1.2, 2.7, 13.2 Hz, 1H) (CH*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 127.5, 126.0 (olefinic), 73.3 (O*C*H), 64.3 (cage *C*), 58.3 (O*C*H_2), 25.3 (CH_2), another cage carbon was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -3.4 (1B), -4.4 (1B), -9.4 (2B), -12.1 (3B), -13.8 (3B). HRMS: *m/z* calcd for $C_7H_{18}O^{11}B_8{}^{10}B_2{}^+$: 226.2355. Found: 226.2357.

1-[CH$_2$CH$_2$(CO$_2$Me)]-1,2-C$_2$B$_{10}$H$_{11}$ (III-5p). Yield: 62%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 4H) (OCH_3 and cage C*H*), 2.55 (m, 4H) (CH_2). ^1H NMR (400 MHz, benzene-d_6): δ 3.21 (s, 3H) (OCH_3), 2.58 (s, 1H) (cage C*H*), 1.88 (s, 4H) (CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.8 (*C*=O), 73.9, 61.5 (cage *C*), 52.2 (O*C*H_3), 33.2, 32.7 (CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.3 (1B), -5.7 (1B), -9.6 (2B), -11.8 (2B), -12.3 (2B), -13.0 (2B). HRMS: *m/z* Calcd for $C_6H_{18}O_2{}^{11}B_8{}^{10}B_2{}^+$: 230.2304. Found: 230.2302.

1-[CH$_2$CH(D)(CO$_2$Me)]-2-D-1,2-C$_2$B$_{10}$H$_{11}$ ([D$_2$]-III-5p). Methyl acrylate (172 mg, 2.0 mmol) was added to the THF suspension of Ni-1,2-*o*-carboryne (1.0 mmol) prepared in situ from dilithiocarborane and $NiCl_2(PPh_3)_2$,[53] and the mixture was

heated at 90 °C overnight. D_2O (2 mL) was added and the reaction mixture was heated at 60 °C for 3 h. After removal of the solvent under vacuum, the oily residue was purified by column chromatography on silica gel (230-400 mesh) using hexane/ether (v/v = 15/1) as eluent to afford **[D_2]-III-5p** as a white solid (125 mg, 54%). ^{1}H NMR (300 MHz, benzene-d_6): δ 3.19 (s, 3H) (OC*H*$_3$), 1.88 (s, 3H) (C*H*D and C*H*$_2$). ^{2}H NMR (61 MHz, benzene-d_6): δ 2.63 (1^2H) (cage C^2*H*), 1.87 (1^2H) (CH^2*H*). HRMS: *m/z* Calcd for $C_6H_{16}{}^2H_2O_2{}^{11}B_8{}^{10}B_2{}^+$: 232.2430. Found: 232.2430.

1-[$CH_2CH(CO_2Me)CH_2CH_2CO_2Me$]-1,2-$C_2B_{10}H_{11}$ (III-6p). Yield: 14%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.29 (s, 3H), 3.18 (s, 3H) (OC*H*$_3$), 2.98 (s, 1H) (cage C*H*), 2.40 (m, 2H), 1.90 (m, 2H), 1.63 (m, 1H), 1.39(m, 2H) (C*H* & C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 174.4, 172.6 (*C*=O), 73.7, 61.2 (cage *C*), 52.4, 51.9 (O*C*H$_3$), 44.4 (*C*H), 39.2, 31.0, 28.2 (*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -2.8 (1B), -6.1 (1B), -10.3 (3B), -13.6 (5B). HRMS: *m/z* Calcd for $C_{10}H_{24}O_4{}^{11}B_8{}^{10}B_2$ [M-H]$^+$: 315.2594. Found: 315.2594.

1-[CH_2CH_2(*o*-C_5H_4N)]-1,2-$C_2B_{10}H_{11}$ (III-5q). Yield: 59%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 4.4 Hz, 1H), 7.65 (dt, J = 2.0, 7.6 Hz, 1H), 7.18 (m, 2H) (Py), 3.80 (s, 1H) (cage C*H*), 2.98 (t, J = 8.0 Hz, 2H), 2.74 (t, J = 8.0 Hz, 2H) (C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.2, 149.1, 137.0, 123.2, 122.0 (Py), 74.8, 61.5 (cage *C*), 36.9, 36.8 (*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -2.6 (1B), -6.0 (1B), -9.6 (2B), -11.7 (2B), -12.4 (2B), -13.3 (2B). HRMS: *m/z* Calcd for $C_9H_{17}N^{11}B_8{}^{10}B_2{}^+$: 247.2364. Found: 247.2373.

1,2-[CH_2CH_2(*o*-C_5H_4N)]$_2$-1,2-$C_2B_{10}H_{10}$ (III-7q). Yield: 16%. Colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, J = 4.4 Hz, 2H), 7.67 (m, 3H), 7.21 (m, 4H) (Py), 3.07 (m, 4H), 2.77 (m, 4H) (C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.6, 149.3, 136.9, 123.2, 121.9 (Py), 79.5 (cage *C*), 37.5, 34.1 (*C*H$_2$). ^{11}B{^{1}H}

NMR (128 MHz, $CDCl_3$): δ -4.8 (2B), -10.5 (8B). HRMS: *m/z* Calcd for $C_{16}H_{26}N_2{}^{11}B_8{}^{10}B_2{}^+$: 354.3099. Found: 354.3098.

***trans*-1-[CH=CH(*o*-C_5H_4N)]-2-[CH_2CH_2(*o*-C_5H_4N)]-1,2-$C_2B_{10}H_{10}$ (III-8q).** Yield: 10%. Colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 4.8 Hz, 1H), 8.47 (d, J = 5.6 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 6.40 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.24 (dd, J = 4.8, 7.6 Hz, 1H), 7.16 (m, 2H) (Py), 3.06 (m, 2H), 2.70 (m, 2H) (CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.6, 152.4, 149.9, 149.2, 140.0, 136.9, 136.7, 124.8, 123.9, 123.7, 123.1, 121.7 (Py & olefinic *C*), 80.0, 79.0 (cage *C*), 37.6, 34.5 (CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -4.3 (2B), -10.4 (8B). HRMS: *m/z* Calcd for $C_{16}H_{24}N_2{}^{11}B_8{}^{10}B_2{}^+$: 352.2943. Found: 352.2931.

Preparation of Nickelacyclopentane (III-9p, III-9q). To a THF solution (5 mL) of $Li_2C_2B_{10}H_{10}$ (1.5 mmol), prepared in situ from the reaction of ^{n}BuLi (3.0 mmol) with *o*-carborane (1.5 mmol), was added $NiCl_2(PPh_3)_2$ (1.5 mmol). The reaction mixture was stirred at room temperature for 0.5 h to give the Ni-1,2-*o*-carboryne complex.[53] After the addition of alkene (1.8 mmol), the reaction vessel was closed and heated at 90 °C overnight. Removal of the solvent gave a red residue which was extracted with ether (10 mL) twice. The combined ether solution was concentrated to dryness and washed with hexane (50 mL) three times. Removal of the solvent afforded **III-9** as a red solid. Recrystallization of **III-9p** from THF/hexane gave red microcrystals. Recrystallization of **III-9q** from DME (1,2-dimethoxyethane) afforded X-ray-quality crystals.

[{[2-CH_2CH(*o*-C_5H_4N)-1,2-$C_2B_{10}H_{10}$]Ni}$_3$(μ_3-Cl)][Li(DME)$_3$] (III-9q): Yield: 32%. Red crystals. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.21 (m, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.42 (m, 1H), 6.70 (m, 1H) (Py), 6.08 (dd, J = 6.1, 10.3 Hz, 1H) (Ni-C*H*), 3.65 (s, 4H), 3.47 (s, 6H) (DME), 2.65 (dd, J = 10.3, 14.6 Hz, 1H) (C*H*H), 2.40 (dd,

J = 6.1, 14.6 Hz, 1H) (CH*H*). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 172.1, 149.0, 135.6, 121.3, 115.6 (Py), 91.3, 76.5 (cage *C*), 70.5, 59.0 (DME), 43.8 (*C*H_2), 43.2 (Ni-*C*H). $^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2): δ -5.9 (2B), -8.7 (4B), -10.8 (4B). IR (KBr, cm^{-1}): ν 2976 (s), 2876 (s), 2575 (vs), 1598 (s), 1471 (s), 1045 (s), 1017 (s), 889 (m), 734 (m). Anal. Calcd for $C_{39}H_{81}B_{30}ClLiN_3Ni_3O_6$ (**III-9q**): C, 38.06; H, 6.63; N, 3.41. Found: C, 37.80; H, 6.47; N, 3.13.

[2-$CH_2CH(CO_2Me)$-1,2-$C_2B_{10}H_{10}$]Ni(PPh_3) (III-9r): Yield: 39%. Red solid. ^1H NMR (400 MHz, benzene-d_6): δ 7.60 (m, 6H), 6.99 (m, 9H) (PPh_3), 4.12 (dd, J = 7.6, 16.0 Hz, 1H) (C*H*H), 2.89 (s, 3H) (OCH_3), 2.67 (dd, J = 9.2, 16.0 Hz, 1H) (CH*H*), 1.74 (dd, J = 7.6, 9.2 Hz, 1H) (Ni-C*H*). ^1H NMR (400 MHz, pyridine-d_5): δ 7.42 (m, 6H), 7.32 (m, 9H) (PPh_3), 3.61 (m, 1H) (C*H*H), 3.01 (m, 1H) (CH*H*), 2.78 (s, 3H) (OCH_3), 2.00 (m, 1H) (Ni-C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, pyridine-d_5): δ 181.5 (C=O), 137.6, 134.3, 129.4, 129.2, 129.0, 128.7 (PPh_3), 88.2, 80.4 (cage *C*), 49.8 (OCH_3), 42.4 (Ni-*C*H), 35.1 (*C*H_2). $^{11}B\{^1H\}$ NMR (96 MHz, pyridine-d_5): δ -3.1 (1B), -4.7 (1B), -8.1 (3B), -9.6 (4B), -13.6 (1B). IR (KBr, cm-1): ν 3055 (w), 2955 (w), 2880 (w), 2573 (vs), 1714 (m), 1619 (s), 1443 (s), 1274 (s), 1047 (s), 898 (m), 735 (m), 695 (m). Anal. Calcd for $C_{28}H_{39}B_{10}NiO_2P$ (**III-9r**+THF): C, 53.99; H, 6.32. Found: C, 53.75; H, 5.95.

Reaction of Complex III-9q with 3-Hexyne. Complex **III-9q** (20 mg, 0.018 mmol) was dissolved in THF (0.5 mL) and 3-hexyne (17 mg, 0.21 mmol) was then added. The reaction vessel was closed and heated at 110 °C for 3 days. After removal of the solvent, the residue was subject to column chromatography on silica gel (230-400 mesh) using hexane/ether (v/v = 12:1) as eluent to give **IV-1a** as a white solid (16 mg, 92%).

Reaction of Complex III-9r with 3-Hexyne. To a THF solution (0.5 mL) of

III-9r (22 mg, 0.035 mmol) was added 3-hexyne (12 mg, 0.146 mmol). The reaction vessel was closed and heated at 110 °C for 3 days. Following the same workup procedure as described for **III-9q** gave **IV-1h** as a white solid (10 mg, 91%).

General Procedure for Nickel-Mediated Three-Component Reaction of 1,2-*o*-Carboryne with Alkenes and Alkynes. To a THF suspension (5 mL) of $Li_2C_2B_{10}H_{10}$ (1.0 mmol), prepared in situ from the reaction of ^{n}BuLi (2.0 mmol) with *o*-carborane (1.0 mmol), was added $NiCl_2(PPh_3)_2$ (1.0 mmol). The reaction mixture was stirred at room temperature for 0.5 h to give the Ni-1,2-*o*-carboryne complex.[53] Alkene (1.2 mmol) and alkyne (4.0 mmol) were added. The reaction vessel was closed, stirred at room temperature for 3 h and then heated at 110 °C for 3 days. After removal of the precipitate, the resulting solution was concentrated to dryness in vacuo. The residue was subject to column chromatography on silica gel to give the product **IV-1**.

1,2-[EtC=C(Et)CH(*o*-C_5H_4N)CH_2]-1,2-$C_2B_{10}H_{10}$ (IV-1a). Yield: 57%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (m, 1H), 7.70 (t, J = 7.4 Hz, 1H), 7.23 (m, 1H), 7.15 (d, J = 7.7 Hz, 1H) (Py), 3.93 (m, 1H) (C*H*), 2.89 (dd, J = 10.5, 14.6 Hz, 1H) (C*H*HCH), 2.75 (dd, J = 7.2, 14.6 Hz, 1H) (CH*H*CH), 2.43 (m, 1H), 2.34 (m, 1H), 2.25 (m, 1H), 1.53 (m, 1H) (CH_2CH_3), 1.15 (t, J = 7.4 Hz, 3H), 0.79 (t, J = 7.4 Hz, 3H) (CH_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.1, 149.8, 137.0, 136.7, 130.8, 123.7, 122.1 (olefinic and Py), 73.4, 69.5 (cage *C*), 44.2 (*C*HCH_2), 37.0, (CH*C*H_2), 25.4, 24.1 (*C*H_2CH_3), 14.7, 12.6 (*C*H_3). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -4.1 (1B), -5.5 (1B), -9.8 (2B), -10.7 (3B), -11.5 (3B). HRMS: *m/z* calcd for $C_{15}H_{27}N^{11}B_8{}^{10}B_2{}^+$: 329.3147. Found: 329.3149.

1,2-[^{n}BuC=C(^{n}Bu)CH(*o*-C_5H_4N)CH_2]-1,2-$C_2B_{10}H_{10}$ (IV-1b). Yield: 32%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 4.8 Hz,1H), 7.64 (t, J = 7.6

Hz, 1H), 7.18 (dd, J = 4.8, 7.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H) (Py), 3.84 (dd, J = 7.2, 10.8 Hz,1H) (C*H*), 2.84 (dd, J = 10.8, 14.4 Hz, 1H) (C*H*HCH), 2.69 (dd, J = 7.2, 14.4 Hz, 1H) (CH*H*CH), 2.38 (m, 1H), 2.21 (m, 3H), 1.63 (m, 1H), 1.48 (m, 1H), 1.36 (m, 3H), 1.24 (m, 1H), 1.10 (m, 2H) (CH_2), 0.94 (t, J = 7.2 Hz, 3H), 0.71 (t, J = 7.2 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.2, 149.7, 136.7, 135.8, 130.0, 123.8, 122.1 (olefinic and Py), 73.6, 69.6 (cage *C*), 44.8 (*C*HCH_2), 37.2, (CH*C*H_2), 32.4, 32.2, 30.7, 30.1, 22.9, 22.4 (*C*H_2CH_3), 13.7, 13.6 (CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -4.0 (1B), -5.4 (1B), -9.3 (2B), -10.7 (3B), -11.7 (3B). HRMS: *m/z* calcd for $C_{19}H_{35}N^{11}B_8{}^{10}B_2{}^+$: 385.3773. Found: 385.3765.

1,2-[^{i}PrC=C(Me)CH(*o*-C_5H_4N)CH_2]-1,2-$C_2B_{10}H_{10}$ (IV-1c) + 1,2-[MeC=C(^{i}Pr)CH(*o*-C_5H_4N)CH_2]-1,2-$C_2B_{10}H_{10}$ (IV-1c'). Yield: 34%. Colorless oil. IV-1c:IV-1c' = 1.6:1. **IV-1c**: ^1H NMR (400 MHz, $CDCl_3$): δ 8.59 (m, 1H), 7.64 (m, 1H), 7.19 (m, 1H), 7.09 (d, J = 8.0 Hz, 1H) (aromatic *H*), 3.74 (m, 1H) (C*H*CH_2), 3.04 (m, 1H) (C*H*$(CH_3)_2$), 2.96 (dd, J = 10.4, 14.8 Hz, 1H), 2.73 (dd, J = 8.0, 14.8 Hz, 1H) (CHCH_2), 1.55 (s, 3H) (C=C-CH_3), 1.25 (d, J = 7.2 Hz, 6H) (CH(CH_3)$_2$). **IV-1c'**: ^1H NMR (400 MHz, $CDCl_3$): δ 8.56 (m, 1H), 7.64 (m, 1H), 7.17 (m, 2H) (aromatic *H*), 3.81 (m, 1H) (C*H*CH_2), 3.25~2.70 (m, 3H) (C*H*$(CH_3)_2$ & CHCH_2), 2.12 (s, 3H) (C=C-CH_3), 0.97 (d, J = 7.2 Hz, 3H), 0.80 (d, J = 7.2 Hz, 3H) (CH(CH_3)$_2$). Compound **IV-1c** and **IV-1c'** was isolated as a mixture and cannot be separated. Their molar ratio was determined by ^1H NMR spectrum on a crude product mixture.

1,2-[PhC=C(Me)CH(*o*-C_5H_4N)CH_2]-1,2-$C_2B_{10}H_{10}$ (IV-1d). Yield: 40%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (m, 1H), 7.68 (t, J = 7.6, 1H), 7.36 (m, 3H), 7.16 (m, 4H) (Py, Ph), 3.95 (dd, J = 7.2, 10.8 Hz, 1H) (C*H*CH_2), 3.11 (dd, J = 10.8, 14.8 Hz, 1H) (C*H*H), 2.84 (dd, J = 7.2, 14.8 Hz, 1H) (CH*H*), 1.15 (s, 3H)

(=CCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.1, 149.8, 137.8, 136.9, 134.5, 131.5, 130.1, 129.5, 128.4, 128.3, 127.9, 124.1, 122.4 (olefinic, Ph, and Py), 72.6, 70.0 (cage *C*), 46.3 (*C*HCH$_2$), 36.9 (CH*C*H$_2$), 20.4 (=C*C*H$_3$). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -3.9 (1B), -5.4 (1B), -10.5 (8B). HRMS: *m/z* calcd for $C_{18}H_{25}N^{11}B_8{}^{10}B_2{}^+$: 363.2990. Found: 363.2995.

1,2-[(4'-Me-C$_6$H$_4$)C=C(Me)CH(*o*-C$_5$H$_4$N)CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-1e). Yield: 35%. White solid. ^1H NMR (300 MHz, $CDCl_3$): δ 8.60 (m, 1H), 7.66 (t, J = 10.4 Hz, 1H), 7.17 (m, 4H), 7.03 (m, 2H) (Py, Ph), 3.93 (dd, J = 9.6, 14.8 Hz, 1H) (C*H*), 3.09 (dd, J = 14.8, 19.2 Hz, 1H) (C*H*H), 2.83 (dd, J = 9.6, 19.2 Hz, 1H) (CH*H*), 2.36 (s, 3H) (Ph-CH_3), 1.15 (s, 3H) (=CCH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.3, 149.9, 137.6, 136.8, 134.8, 134.5, 131.4, 129.9, 129.4, 129.1, 129.0, 124.0, 122.3 (olefinic, Ph, and Py), 72.8, 70.0 (cage *C*), 46.4 (*C*HCH$_2$), 36.9 (CH*C*H$_2$), 21.3 (Ph-CH_3), 20.4 (=C*C*H$_3$). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.7 (1B), -5.1 (1B), -10.8 (8B). HRMS: *m/z* calcd for $C_{19}H_{27}N^{11}B_8{}^{10}B_2{}^+$: 377.3141. Found: 377.3143.

1,2-[PhC=C(Et)CH(*o*-C$_5$H$_4$N)CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-1f). Yield: 39%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (m, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.37 (m, 3H), 7.16 (m, 4H) (Py, Ph), 4.03 (dd, J = 7.1, 10.8 Hz, 1H) (C*H*CH$_2$), 3.10 (dd, J = 10.8, 14.7 Hz, 1H) (C*H*HCH), 2.84 (dd, J = 7.1, 14.7 Hz, 1H) (CH*H*CH), 1.73 (m, 1H), 1.42 (m, 1H) (=CCH_2), 0.62 (t, J = 7.5 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.2, 149.8, 140.2, 137.4, 136.7, 131.3, 130.0, 129.7, 128.2, 128.1, 127.9, 123.9, 122.3 (olefinic, Ph, and Py), 72.4, 69.7 (cage *C*), 44.0 (*C*HCH$_2$), 37.0 (CH*C*H$_2$), 25.9 (=C*C*H$_2$), 12.8 (*C*H$_3$). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -4.3 (1B), -5.6 (1B), -10.9 (8B). HRMS: *m/z* calcd for $C_{19}H_{27}N^{11}B_8{}^{10}B_2{}^+$: 377.3141. Found: 377.3131.

1,2-[PhC=C(^{n}Bu)CH(*o*-C$_5$H$_4$N)CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-1g). Yield: 31%.

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (m, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.35 (m, 3H), 7.18 (m, 4H) (Py, Ph), 4.00 (dd, J = 7.1, 10.8 Hz, 1H) (C*H*CH_2), 3.08 (dd, J = 10.8, 14.6 Hz, 1H) (C*H*HCH), 2.83 (dd, J = 7.1, 14.6 Hz, 1H) (CH*H*CH), 1.66 (m, 1H), 1.39 (m, 1H) (=CCH_2), 1.08 (m, 1H), 0.96 (m, 1H), 0.83 (m, 1H), 0.79 (m, 1H) (CH_2), 0.50 (t, J = 7.3 Hz, 3H) (CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 160.4, 149.8, 139.0, 137.5, 136.6, 131.6, 130.1, 129.9, 128.2, 128.0, 127.9, 124.0, 122.3 (olefinic, Ph, and Py), 72.5, 69.8 (cage *C*), 44.9 (*C*HCH_2), 37.1 (CH*C*H_2), 32.4, 30.2, 22.2 (*C*H_2), 13.4 (*C*H_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -4.5 (1B), -5.9 (1B), -11.0 (8B). HRMS: *m/z* calcd for $C_{21}H_{31}N^{11}B_8{}^{10}B_2{}^{+}$: 405.3454. Found: 405.3442.

1,2-[PhC=C(CH$_2$CH=CH$_2$)CH(*o*-C$_5$H$_4$N)CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-1h). Yield: 36%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (m, 1H), 7.63 (m, 1H), 7.35 (m, 3H), 7.18 (m, 4H) (Py, Ph), 5.33 (m, 1H) (C*H*=CH_2), 4.87 (d, J = 10.2 Hz, 1H), 4.59 (d, J = 17.1 Hz, 1H) (CH=CH_2), 4.01 (dd, J = 7.1, 10.6 Hz, 1H) (cyclic C*H*CH_2), 3.16 (dd, J = 10.6, 14.7 Hz, 1H) (cyclic C*H*H), 2.83 (dd, J = 7.1, 14.7 Hz, 1H) (cyclic CH*H*), 2.48 (dd, J = 4.8, 15.3 Hz, 1H), 2.15 (dd, J = 7.3, 15.3 Hz, 1H) (acyclic CH_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.9, 149.9, 137.1, 136.5, 136.3, 134.5, 133.1, 129.8, 129.7, 128.1, 124.5, 122.3, 116.5 (olefinic, Ph, and Py), 72.3, 69.9 (cage *C*), 44.1 (*C*HCH_2), 36.8, 36.7 (*C*H_2). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -3.4 (1B), -4.9 (1B), -10.2 (8B). HRMS: *m/z* calcd for $C_{20}H_{27}N^{11}B_8{}^{10}B_2{}^{+}$: 389.3141. Found: 389.3135.

1,2-[EtC=C(Et)CH(CO$_2$Me)CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (IV-1i). Yield: 59%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3H) (OCH_3), 3.28 (m, 1H) (C*H*CH_2), 3.13 (dd, J = 5.2, 14.8 Hz, 1H) (C*H*HCH), 2.54 (dd, J = 7.2, 14.8 Hz, 1H) (CH*H*CH), 2.46 (m, 2H), 2.29 (m, 1H), 2.05 (m, 1H), 1.11 (t, J = 7.6 Hz, 3H), 0.99 (t, J = 7.6 Hz,

3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.4 (C=O), 133.3, 131.6 (olefinic), 73.2, 69.0 (cage *C*), 52.6 (OCH_3), 41.6 ($CHCH_2$), 32.6 ($CHCH_2$), 25.8, 25,2 (CH_2CH_3), 14.2, 12.7 (CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -4.2 (1B), -5.7 (1B), -7.3 (1B), -9.2 (1B), -11.5 (6B). HRMS: *m/z* calcd for $C_{12}H_{26}O_2{}^{11}B_8{}^{10}B_2{}^+$: 310.2930. Found: 310.2922.

1,2-[^{n}PrC=C(^{n}Pr)CH(CO_2Me)CH_2]-1,2-$C_2B_{10}H_{10}$ (IV-1j). Yield: 50%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3H) (OCH_3), 3.28 (m, 1H) ($CHCH_2$), 3.06 (dd, J = 6.0, 14.7 Hz, 1H) ($CHHCH$), 2.55 (dd, J = 7.3, 14.7 Hz, 1H) ($CHHCH$), 2.27 (m, 3H), 1.98 (m, 1H), 1.50 (m, 3H), 1.25 (m, 1H) (CH_2), 0.95 (t, J = 7.3 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.4 (C=O), 132.1, 130.8 (olefinic), 73.3, 69.0 (cage *C*), 52.6 (OCH_3), 42.2 ($CHCH_2$), 34.7, 34.4, 32.6, 23.0, 21.6 (CH_2), 14.1 (CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -3.8 (1B), -5.3 (1B), -7.3 (1B), -8.3 (1B), -11.0 (6B). HRMS: *m/z* calcd for $C_{14}H_{30}O_2{}^{11}B_8{}^{10}B_2{}^+$: 338.3249. Found: 338.3237.

1,2-[^{n}BuC=C(^{n}Bu)CH(CO_2Me)CH_2]-1,2-$C_2B_{10}H_{10}$ (IV-1k). Yield: 48%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3H) (OCH_3), 3.29 (m, 1H) ($CHCH_2$), 3.07 (dd, J = 6.1, 14.7 Hz, 1H) ($CHHCH$), 2.55 (dd, J = 7.3, 14.7 Hz, 1H) ($CHHCH$), 2.31 (m, 3H), 1.97 (m, 1H), 1.45 (m, 3H), 1.32 (m, 4H), 1.20 (m, 1H) (CH_2), 0.94 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.5 (C=O), 132.2, 130.6 (olefinic), 73.3, 69.0 (cage *C*), 52.6 (OCH_3), 42.2 ($CHCH_2$), 32.6, 32.5, 32.1, 31.7, 30.4, 22.9, 22.8 (CH_2), 13.9, 13.7 (CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -3.8 (1B), -5.4 (1B), -7.1 (1B), -8.5 (1B), -11.0 (6B). HRMS: *m/z* calcd for $C_{16}H_{34}O_2{}^{11}B_8{}^{10}B_2{}^+$: 366.3562. Found: 366.3550.

General Procedure for Nickel-Catalyzed Three-Component Cyclization of Arynes with Alkenes and Alkynes. To a flask containing $Ni(cod)_2$ (0.015 mmol)

and CsF (0.9 mmol) were added CH_3CN (1 mL), alkyne (0.6 mmol), alkene (0.6 mmol) and aryne precursor (0.3 mmol). The reaction mixture was stirred at room temperature for 5 h. After extraction with ether, the resulting solution was dried over Na_2SO_4 and concentrated to dryness in vacuo. The residue was subject to column chromatography on silica gel (40 - 230 mesh) using hexane/ethyl acetate as eluent to give the product.

1,2-[PhC=C(Ph)CH(CO_2Me)CH_2]C_6H_4 (IV-5a). Yield: 76%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (m, 5H), 7.08 (m, 8H), 6.79 (d, *J* = 7.6 Hz, 1H) (aromatic *H*), 3.76 (t, *J* = 6.4 Hz, 1H) (C*H*), 3.56 (s, 3H) (OCH_3), 3.38 (dd, *J* = 6.4, 15.6 Hz, 1H) (C*H*H), 3.30 (dd, *J* = 6.4, 15.6 Hz, 1H) (CH*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 174.1 (*C*=O), 141.3, 139.1, 137.8, 136.1, 134.3, 133.3, 131.0, 129.8, 128.9, 127.9, 127.6, 127.3, 126.7, 126.3 (olefinic and aromatic *C*), 52.0 (O*C*H$_3$), 46.7 (*C*HCH$_2$), 32.3 (CH*C*H$_2$). HRMS: *m/z* calcd for $C_{24}H_{20}O_2^+$: 340.1458. Found: 340.1455.

1,2-[PhC=C(Ph)CH(CO_2^{n}Bu)CH_2]C_6H_4 (IV-5b). Yield: 72%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (m, 5H), 7.08 (m, 8H), 6.78 (d, *J* = 6.9 Hz, 1H) (aromatic *H*), 3.97 (t, *J* = 6.3 Hz, 1H) (OCH_2), 3.72 (t, *J* = 6.0 Hz, 1H) (C*H*), 3.38 (dd, *J* = 6.0, 15.3 Hz, 1H) (C*H*H), 3.31 (dd, *J* = 6.0, 15.3 Hz, 1H) (CH*H*), 1.41 (m, 2H), 1.18 (m, 2H) (CH_2), 0.81 (t, *J* = 7.5 Hz, 3H) (CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 173.7 (*C*=O), 141.4, 139.2, 137.6, 136.2, 134.4, 133.3, 131.0, 128.8, 127.9, 127.5, 127.3, 127.2, 126.6, 126.3 (olefinic and aromatic *C*), 64.6 (O*C*H$_2$), 46.9 (*C*HCH$_2$), 32.5 (CH*C*H$_2$), 30.5, 18.9 (*C*H$_2$), 13.6 (*C*H$_3$). HRMS: *m/z* calcd for $C_{27}H_{26}O_2^+$: 382.1927. Found: 382.1932.

1,2-[PhC=C(Ph)CH(CO_2^{t}Bu)CH_2]C_6H_4 (IV-5c). Yield: 74%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (m, 5H), 7.08 (m, 8H), 6.75 (d, *J* = 7.2 Hz, 1H)

(aromatic *H*), 3.64 (t, *J* = 6.4 Hz, 1H) (C*H*), 3.33 (dd, *J* = 6.4, 15.2 Hz, 1H) (C*H*H), 3.28 (dd, *J* = 6.4, 15.2 Hz, 1H) (CH*H*), 1.21 (s, 9H) ($C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 172.9 (*C*=O), 141.4, 139.3, 137.2, 136.5, 135.1, 133.6, 131.0, 128.8, 127.9, 127.5, 127.2, 127.1, 126.6, 126.5, 126.4, 126.2 (olefinic and aromatic *C*), 80.7 ($OC(CH_3)_3$), 48.1 ($CHCH_2$), 32.8 ($CHCH_2$), 27.6 (CH_3). HRMS: *m/z* calcd for $C_{27}H_{26}O_2^+$: 382.1927. Found: 382.1921.

1,2-{PhC=C(Ph)[CHC(=O)Me]CH_2}C_6H_4 (IV-5d). Yield: 3%. Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.24 (m, 4H), 7.13 (m, 7H), 7.05 (m, 2H), 6.83 (d, *J* = 7.5 Hz, 1H) (aromatic *H*), 3.67 (dd, *J* = 4.8, 6.9 Hz, 1H) (C*H*), 3.41 (dd, *J* = 6.9, 15.6 Hz, 1H) (C*H*H), 3.20 (dd, *J* = 4.8, 15.6 Hz, 1H) (CH*H*), 2.10 (s, 1H), (CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 209.9 (*C*=O), 141.4, 139.0, 138.1, 136.2, 134.8, 133.0, 130.9, 128.8, 128.0, 127.8, 127.5, 127.3, 126.8, 126.7, 126.5 (olefinic and aromatic *C*), 54.8 ($CHCH_2$), 32.4 ($CHCH_2$), 28.7 6 (CH_3). HRMS: *m/z* calcd for $C_{24}H_{20}O_2^+$: 324.1509. Found: 324.1498.

1,2-[PhC=C(Ph)CH(CN)CH_2]C_6H_4 (IV-5e). Yield: 15%. Colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (m, 5H), 7.16 (m, 6H), 7.12 (m, 2H), 6.84 (d, *J* = 8.0 Hz, 1H) (aromatic *H*), 3.84 (dd, *J* = 4.4, 5.6 Hz, 1H) (C*H*), 3.40 (dd, *J* = 5.6, 15.2 Hz, 1H) (C*H*H), 3.20 (dd, *J* = 4.4, 15.2 Hz, 1H) (CH*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 139.8, 139.2, 138.1, 135.3, 131.3, 130.7, 129.5, 128.2, 128.1, 127.7, 127.5, 127.3, 127.2 (olefinic and aromatic *C*), 120.4 (*C*N), 32.4, 32.2 ($CHCH_2$ & $CHCH_2$). HRMS: *m/z* calcd for $C_{23}H_{17}N^+$: 307.1356. Found: 307.1361.

1,2-(OCH_2O)-4,5-[PhC=C(Ph)CH(CO_2Me)CH_2]C_6H_2 (IV-5f). Yield: 29%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (m, 3H), 7.07 (m, 7H), 6.74 (s, 1H), 6.31 (s, 1H) (aromatic *H*), 5.88 (s, 2H) (OCH_2O), 3.67 (t, *J* = 6.0 Hz, 1H) (C*H*), 3.60 (s, 3H) (OCH_3), 3.28 (dd, *J* = 6.0, 15.6 Hz, 1H) (C*H*H), 3.23 (dd, *J* = 6.0, 15.6

Hz, 1H) (CH*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 174.2 (*C*=O), 146.3, 146.1, 141.4, 139.3, 137.5, 132.3, 130.9, 130.4, 128.8, 127.9, 127.5, 127.4, 126.7, 126.1, 108.1, 107.7 (olefinic and aromatic *C*), 100.9 (OCH_2O), 52.1 (OCH_3), 46.7 ($CHCH_2$), 32.4 ($CHCH_2$). HRMS: *m/z* calcd for $C_{25}H_{20}O_4^+$: 384.1356. Found: 384.1350.

4,5-$(CH_2)_3$-1,2-[PhC=C(Ph)CH(CO_2Me)CH_2]C_6H_4 (IV-5g). Yield: 46%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (m, 3H), 7.07 (m, 8H), 6.64 (s, 1H) (aromatic *H*), 3.73 (t, *J* = 6.0 Hz, 1H) (C*H*), 3.57 (s, 3H) (OCH_3), 3.35 (dd, *J* = 6.0, 15.6 Hz, 1H) (C*H*H), 3.26 (dd, *J* = 6.0, 15.6 Hz, 1H) (CH*H*), 2.88 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H) ($CH_2CH_2CH_2$), 2.01 (m, 2H) ($CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.3 (*C*=O), 143.5, 142.5, 141.5, 139.5, 138.2, 134.3, 133.2, 131.3, 131.0, 128.9, 127.8, 127.5, 126.5, 126.1, 123.4, 122.7 (olefinic and aromatic *C*), 52.0 (OCH_3), 47.0 ($CHCH_2$), 32.7, 32.6 ($CHCH_2$ & $CH_2CH_2CH_2$), 25.4 ($CH_2CH_2CH_2$). HRMS: *m/z* calcd for $C_{27}H_{24}O_2^+$: 380.1771. Found: 380.1778.

4-Me-1,2-[PhC=C(Ph)CH(CO_2Me)CH_2]C_6H_4 (IV-5h) + 5-Me-1,2-[PhC=C(Ph)CH(CO_2Me)CH_2]C_6H_4 (IV-5'h): Yield: 57%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (m, 6H), 7.04 (m, 16H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.60 (s, 1H) (aromatic *H*), 3.73 (m, 2H) (C*H*), 3.57 (s, 3H), 3.56 (s, 3H) (OCH_3), 3.34 (m, 2H) (C*H*H), 3.26 (m, 2H) (CH*H*), 2.32 (s, 3H), 2.18 (s, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.2 (*C*=O), 141.4, 139.3, 139.2, 137.9, 137.7, 137.2, 136.1, 135.9, 134.3, 133.2, 131.0, 130.2, 129.6, 128.9, 128.8, 128.2, 128.0, 127.8, 127.5, 127.4, 127.3, 127.2, 126.6, 126.2, 126.1 (olefinic and aromatic *C*), 52.0 (OCH_3), 46.9, 46.7 ($CHCH_2$), 32.3, 31.9 ($CHCH_2$), 21.3, 21.2 (CH_3). HRMS: *m/z* calcd for $C_{25}H_{22}O_2^+$: 354.1614. Found: 354.1606.

1,2-[MeC=C(Ph)CH(CO_2Me)CH_2]C_6H_4 (IV-5i). Yield: 71%. Colorless oil. ^1H

NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 3H), 7.27 (m, 4H), 7.17 (m, 2H) (aromatic *H*), 3.57 (m, 1H) (C*H*), 3.43 (s, 3H) (OCH_3), 3.29 (dd, J = 4.7, 15.5 Hz, 1H) (C*H*H), 3.19 (dd, J = 7.0, 15.5 Hz, 1H) (CH*H*), 2.00 (s, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.5 (*C*=O), 142.0, 135.8, 133.6, 133.3, 130.3, 129.1, 128.1, 127.4, 127.1, 126.8, 123.9 (olefinic and aromatic *C*), 51.7 (O*C*H_3), 46.1 (*C*HCH$_2$), 32.0 (CH*C*H$_2$), 16.2 (*C*H$_3$). HRMS: *m/z* calcd for $C_{19}H_{18}O_2^+$: 278.1301. Found: 278.1299.

1,2-[EtC=C(Ph)CH(CO$_2$Me)CH$_2$]C$_6$H$_4$ (IV-5j). Yield: 78%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (m, 3H), 7.23 (m, 4H), 7.17 (m, 2H) (aromatic *H*), 3.52 (t, J = 6.4 Hz, 1H) (C*H*), 3.43 (s, 3H) (OCH_3), 3.25 (dd, J = 6.4, 15.4 Hz, 1H) (CHC*H*H), 3.12 (dd, J = 6.4, 15.4 Hz, 1H) (CHCH*H*), 2.46 (q, J = 7.5 Hz, 2H) (CH_2CH$_3$), 0.99 (t, J = 7.5 Hz, 3H) (CH$_2$CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 173.8 (*C*=O), 141.9, 136.4, 134.1, 133.9, 133.3, 128.6, 128.1, 127.7, 126.9, 126.8, 123.9 (olefinic and aromatic *C*), 51.7 (O*C*H$_3$), 46.4 (*C*HCH$_2$), 32.2 (CH*C*H$_2$), 22.0 (*C*H$_2$CH$_3$), 14.1 (CH$_2$*C*H$_3$). HRMS: *m/z* calcd for $C_{20}H_{20}O_2^+$: 292.1458. Found: 292.1461.

1,2-[^{n}BuC=C(Ph)CH(CO$_2$Me)CH$_2$]C$_6$H$_4$ (IV-5k). Yield: 71%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (m, 3H), 7.22 (m, 4H), 7.18 (m, 2H) (aromatic *H*), 3.54 (m, 1H) (C*H*), 3.44 (s, 3H) (OCH_3), 3.27 (dd, J = 5.7, 15.4 Hz, 1H) (CHC*H*H), 3.14 (dd, J = 6.8, 15.4 Hz, 1H) (CHCH*H*), 2.45 (t, J = 7.8 Hz, 2H) (CH_2 CH$_2$), 1.36 (m, 2H), 1.21 (m, 2H) (*C*H$_2$), 0.76 (t, J = 7.2 Hz, 3H) (CH$_2$CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.7 (*C*=O), 142.0, 135.0, 134.2, 134.1, 133.7, 128.8, 128.1, 127.7, 126.9, 126.7, 124.0 (olefinic and aromatic *C*), 51.7 (O*C*H$_3$), 46.4 (*C*HCH$_2$), 32.2 (CH*C*H$_2$), 31.2, 28.5, 22.5 (*C*H$_2$), 13.8 (CH$_2$*C*H$_3$). HRMS: *m/z* calcd for $C_{22}H_{24}O_2^+$: 320.1771. Found: 320.1777.

1,2-[C(CH$_2$OMe)=C(Ph)CH(CO$_2$Me)CH$_2$]C$_6$H$_4$ (IV-5l). Yield: 75%.

Colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.6 Hz, 1H), 7.24 (m, 5H), 7.17 (m, 1H), 7.10 (m, 2H) (aromatic *H*), 4.17 (d, J = 10.8 Hz, 1H) (C*H*HOCH$_3$), 4.10 (d, J = 10.8 Hz, 1H) (CH*H*OCH$_3$), 3.55 (dd, J = 4.4, 6.8 Hz, 1H) (C*H*), 3.37 (s, 3H) (CO_2CH_3), 3.24 (dd, J = 4.4, 15.5 Hz, 1H) (CHC*H*H), 3.19 (s, 3H) (CH_2OCH_3), 3.13 (dd, J = 6.8, 15.5 Hz, 1H) (CHCH*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 173.0 (*C*=O), 140.7, 138.2, 133.6, 133.3, 131.3, 128.9, 128.0, 127.5, 127.4, 127.3, 127.0, 124.7 (olefinic and aromatic *C*), 69.3 (OCH_2), 57.7 (CH_2OCH_3), 51.9 (CO_2CH_3), 46.2 (*C*HCH$_2$), 31.8 (CH*C*H$_2$). HRMS: *m/z* calcd for $C_{20}H_{20}O_3^+$: 308.1407. Found: 308.1415.

1,2-[C(CH$_2$CH=CH$_2$)=C(Ph)CH(CO$_2$Me)CH$_2$]C$_6$H$_4$ (IV-5m). Yield: 68%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 6H), 7.19 (m, 3H) (aromatic *H*), 5.90 (m, 1H) (C*H*=CH$_2$), 5.05 (m, 2H) (CH=C*H*$_2$), 3.59 (dd, J = 5.4, 6.6 Hz, 1H) (C*H*), 3.48 (s, 3H) (OCH_3), 3.30 (dd, J = 5.2, 15.5 Hz, 1H) (CHC*H*H), 3.21 (m, 3H) (CHCH*H* & C*H*$_2$CH=CH$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 173.6 (*C*=O), 141.7, 136.8, 135.2, 134.3, 133.6, 132.1, 128.4, 128.1, 127.5, 127.1, 127.0, 126.7, 124.7, 116.0 (olefinic and aromatic *C*), 51.8 (OCH_3), 46.4 (*C*HCH$_2$), 33.5, 31.8 (CH*C*H$_2$ & *C*H$_2$CH=CH$_2$). HRMS: *m/z* calcd for $C_{21}H_{20}O_2^+$: 304.1458. Found: 304.1457.

1,2-{C[(CH$_2$)$_3$CN]=C(Ph)CH(CO$_2$Me)CH$_2$}C$_6$H$_4$ (IV-5n). Yield: 32%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (m, 9H) (aromatic *H*), 3.52 (dd, J = 5.3, 6.8 Hz, 1H) (C*H*), 3.43 (s, 3H) (OCH_3), 3.26 (dd, J = 5.3, 15.5 Hz, 1H) (CHC*H*H), 3.14 (dd, J = 6.8, 15.5 Hz, 1H) (CHCH*H*), 2.60 (m, 2H), 2.13 (m, 2H), 1.72 (m, 2H) (CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 173.2 (*C*=O), 141.3, 135.8, 134.0, 133.3, 132.7, 128.7, 128.4, 128.0, 127.4, 127.2, 127.0, 123.6 (olefinic and aromatic *C*), 119.4 (*C*N), 51.8 (OCH_3), 46.4 (*C*HCH$_2$), 32.0 (CH*C*H$_2$), 27.6, 24.6, 16.7 (CH_2).

HRMS: *m/z* calcd for $C_{22}H_{21}NO_2^+$: 331.1567. Found: 331.1564.

1,2-[MeC=C(4'-Me-C_6H_4)CH(CO_2Me)CH_2]C_6H_4 (IV-5o). Yield: 66%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (m, 1H), 7.18 (m, 1H), 7.17 (m, 6H) (aromatic *H*), 3.56 (dd, *J* = 4.4, 6.8 Hz, 1H) (C*H*), 3.44 (s, 3H) (OCH_3), 3.29 (dd, *J* = 4.4, 15.2 Hz, 1H) (C*H*H), 3.18 (dd, *J* = 6.8, 15.2 Hz, 1H) (CH*H*), 2.36 (s, 3H) (C_6H_4-CH_3), 2.02 (s, 3H) (C=C-CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 173.6 (*C*=O), 139.0, 136.4, 135.9, 133.4, 133.3, 130.1, 129.0, 128.7, 127.4, 126.9, 126.8, 123.8 (olefinic and aromatic *C*), 51.7 (O*C*H$_3$), 46.0 (*C*HCH$_2$), 32.0 (CH*C*H$_2$), 21.2 (C_6H_4-*C*H$_3$), 16.3 (C=C-*C*H$_3$). HRMS: *m/z* calcd for $C_{20}H_{20}O_2^+$: 292.1458. Found: 292.1457.

1,2-[MeC=C(CO_2Me)CH(CO_2Me)CH_2]C_6H_4 (IV-5p). Yield: 19%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (m, 1H), 7.26 (m, 2H), 7.18 (m, 1H) (aromatic *H*), 3.91 (dd, *J* = 4.0, 7.2 Hz, 1H) (C*H*), 3.81 (s, 3H), 3.56 (s, 3H) (OCH_3), 3.24 (dd, *J* = 4.0, 15.6 Hz, 1H) (C*H*H), 3.05 (dd, *J* = 7.2, 15.6 Hz, 1H) (CH*H*), 2.51 (s, 3H) (s, 3H) (C=C-CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 173.3, 168.4 (*C*=O), 143.7, 135.0, 134.5, 129.1, 127.6, 127.0, 126.6, 125.4 (olefinic and aromatic *C*), 52.1, 51.7 (O*C*H$_3$), 40.5 (*C*HCH$_2$), 30.9 (CH*C*H$_2$), 16.8 (*C*H$_3$). HRMS: *m/z* calcd for $C_{15}H_{16}O_4^+$: 260.1043. Found: 260.1040.

1,2-[EtC=C(Et)CH(CO_2Me)CH_2]C_6H_4 (IV-5q). 3 mmol of 3-hexyne was used in the reaction. Yield: 63%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15 (m, 4H) (aromatic *H*), 3.56 (s, 3H) (O*C*H$_3$), 3.21 (m, 2H) (C*H* & C*H*H), 2.96 (dd, *J* = 6.9, 15.3 Hz, 1H) (CH*H*), 2.56 (m, 3H), 2.16 (m, 1H) (CH_2CH$_3$), 1.11 (t, *J* = 7.5 Hz, 3H), 1.10 (t, *J* = 7.5 Hz, 3H) (CH$_2$CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 174.0 (*C*=O), 134.7, 134.1, 133.8, 133.7, 127.5, 126.6, 126.1, 123.0 (olefinic and aromatic *C*), 51.8 (O*C*H$_3$), 42.7 (*C*HCH$_2$), 32.0 (CH*C*H$_2$), 26.1, 20.9 (*C*H$_2$CH$_3$), 14.1, 13.6 (CH$_2$*C*H$_3$).

HRMS: *m/z* calcd for $C_{16}H_{20}O_2^+$: 244.1458. Found: 244.1455.

1,2-[^{n}BuC=C(^{n}Bu)CH(CO_2Me)CH_2]C_6H_4 (IV-5r). 3 mmol of 5-decyne was used in the reaction. Yield: 47%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (m, 4H) (aromatic *H)*, 3.56 (s, 3H) (OCH_3), 3.12 (m, 2H) (C*H* & C*H*H), 2.93 (dd, *J* = 6.9, 15.3 Hz, 1H) (CH*H*), 2.54 (m, 3H), 2.09 (m, 1H), 1.43 (m, 8H) (CH_2CH_3), 0.93 (m, 6H) (CH_2CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 174.0 (*C*=O), 135.0, 133.8, 133.1, 132.7, 127.5, 126.5, 126.1, 123.1 (olefinic and aromatic *C*), 51.8 (OCH_3), 43.1 ($CHCH_2$), 32.9 ($CHCH_2$), 31.8, 31.6, 31.3, 27.8, 23.1, 23.0 (CH_2), 14.1 (CH_2CH_3). HRMS: *m/z* calcd for $C_{20}H_{28}O_2^+$: 300.2084. Found: 300.2079.

1,2-[^{i}PrC=C(Me)CH(CO_2Me)CH_2]C_6H_4 (IV-5s) + 1,2-[MeC=C(^{i}Pr)CH(CO_2Me)CH_2]C_6H_4 (IV-5s'). Yield: 51%. Colorless oil, **IV-5s**:**IV-5s'** = 2:1. **IV-5s**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41~7.07 (m, 4H) (aromatic *H*), 3.50 (s, 3H) (OCH_3), 3.23~2.89 (m, 4H) ($CHCH_2$, $CHCH_2$, & $CH(CH_3)_2$), 2.13 (s, 3H) (C=C-CH_3), 1.10 (d, *J* = 7.2 Hz, 3H), 0.99 (d, *J* = 7.2 Hz, 3H) ($CH(CH_3)_2$). **IV-5s'**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41~7.07 (m, 4H) (aromatic *H*), 3.59 (s, 3H) (OCH_3), 3.23~2.89 (m, 4H) ($CHCH_2$, $CHCH_2$, & $CH(CH_3)_2$), 2.02 (s, 3H) (C=C-CH_3), 1.35 (d, *J* = 7.2 Hz, 3H), 1.30 (d, *J* = 7.2 Hz, 3H) ($CH(CH_3)_2$). Compounds **IV-5s** and **IV-5s'** were isolated as a mixture and cannot be separated. Their molar ratio was determined by ^{1}H NMR spectrum on a crude product mixture.

Control Experiment: Reaction of 1,2-*o*-carboryne precursor with toluene. To a toluene solution (10 mL) of $Li_2C_2B_{10}H_{10}$, prepared in situ from the reaction of ^{n}BuLi (1.6 M, 1.25 mL, 2.0 mmol) with *o*-carborane (144 mg, 1.0 mmol), was added I_2 (254 mg, 1.0 mmol). The reaction mixture was stirred at room temperature for 0.5 h and then heated at 110 °C for 2h. After addition of water and extraction with ether,

the resulting solution was concentrated to dryness in vacuo. The residue was subject to column chromatography on silica gel (230-400 mesh) using hexane as eluent to give **V-2** as a white solid (89 mg, 38%).

1,2-(2-methyl-2,5-cyclohexadiene-1,4-diyl)-*o*-carborane (V-2a): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.67 (m, 2H), 6.22 (dd, J = 1.6, 4.4 Hz, 1H) (olefinic *H*), 4.03 (td, J = 1.6, 6.4 Hz, 1H), 3.78 (d, J = 5.6 Hz, 1H) (C*H*), 1.87 (s, 3H) (CH_3). **1,2-(1-methyl-2,5-cyclohexadiene-1,4-diyl)-*o*-carborane (V-2b)**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.67 (m, 2H), 6.36 (d, J = 7.6 Hz, 2H) (olefinic *H*), 4.07 (m, 1H) (C*H*), 1.64 (s, 3H) (CH_3).

Control Experiment: Reaction of 1,2-*o*-carboryne precursor with 3-hexyne in toluene. To a toluene solution (10 mL) of $Li_2C_2B_{10}H_{10}$, prepared in situ from the reaction of ^{n}BuLi (1.6 M, 1.25 mL, 2.0 mmol) with *o*-carborane (144 mg, 1.0 mmol), was added I_2 (254 mg, 1.0 mmol). The reaction mixture was stirred at room temperature for 0.5 h. 3-Hexyne (328 mg, 4.0 mmol) was then added and the reaction vessel was closed and then heated at 110 °C for 2h. After addition of water and extraction with ether, the resulting solution was concentrated to dryness in vacuo. The residue was subject to column chromatography on silica gel (230-400 mesh) using hexane as eluent to give [4+2] cycloaddition product **V-2** as a white solid (40 mg, 17%), the ene-reaction product **V-3** as a colorless oil (81 mg, 36%), and carborane as a white solid (39 mg, 27%). **1-[C(Et)=C=CH(Me)]-1,2-$C_2B_{10}H_{11}$ (V-3)**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.53 (m, 1H) (C*H*), 3.75 (s, 1H) (cage *H*), 2.08 (m, 2H) (CH_2), 1.72 (d, J = 7.2 Hz, 3H) ($CHCH_3$), 0.96 (t, J = 7.2 Hz, 3H) (CH_2CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 202.6 (C=*C*=CH), 104.8, 94.0 (olefinic *C*), 74.6, 60.7 (cage *C*), 24.7 (*C*H), 14.0, 12.2 (CH_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -3.6 (1B), -6.1 (1B), -10.4 (2B), -11.6 (2B), -13.3 (2B), -14.2 (2B). HRMS: m/z Calcd for

$[M-2H]^+$ ($C_8H_{20}B_{10}^+$): 222.2406. Found: 222.2403.

Control Experiment: Heating of 1,2-*o*-Carboryne precursor in toluene in the presence of $NiCl_2(PPh_3)_2$. To a toluene solution (10 mL) of $Li_2C_2B_{10}H_{10}$, prepared in situ from the reaction of ^{n}BuLi (1.6 M, 1.25 mL, 2.0 mmol) with *o*-carborane (144 mg, 1.0 mmol), was added I_2 (254 mg, 1.0 mmol). The reaction mixture was stirred at room temperature for 0.5 h. $NiCl_2(PPh_3)_2$ (654 mg, 1.0 mmol) was then added and the reaction vessel was closed and then heated at 110 °C for 2h. After addition of water and extraction with ether, the resulting solution was concentrated to dryness in vacuo. The residue was subject to column chromatography on silica gel (230-400 mesh) using hexane as eluent to give 1-iodocarborane **V-4** as a white solid (41 mg, 15%), and carborane as a white solid (76 mg, 53%).

General Procedure for Nickel-Catalyzed Regioselective [2+2+2] Cycloaddition of 1,2-*o*-Carboryne with Alkynes or Diynes. To a toluene solution (5 mL) of $Li_2C_2B_{10}H_{10}$ (0.5 mmol), prepared in situ from the reaction of ^{n}BuLi (1.0 mmol) with *o*-carborane (0.5 mmol), was added I_2 (0.5 mmol), and the reaction mixture was stirred at room temperature for 0.5 h. $NiCl_2(PPh_3)_2$ (0.1 mmol), and alkyne (2.0 mmol) or diyne (1.0 mmol) were then added, and the reaction vessel was closed and heated at 110 °C overnight. After addition of 5 mL of water and extraction with ether (10 mL × 3), the resulting ether solutions were concentrated to dryness in vacuo. The residue was subject to flash column chromatography on silica gel (230-400 mesh) using hexane as eluent to give the cycloaddition product.

1,2-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_{10}$ (V-1a). Yield: 65%. Colorless crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (q, J = 7.5 Hz, 4H), 2.01 (q, J = 7.5 Hz, 4H) (CH_2), 1.02 (t, J = 7.5 Hz, 6H), 0.78 (t, J = 7.5 Hz, 6H) (CH_3). $^{13}C\{^1H\}$ NMR

(75 MHz, $CDCl_3$): δ 135.1, 134.0 (olefinic *C*), 76.3 (cage *C*), 26.3, 21.9 (CH_2CH_3), 15.0, 14.8 (CH_2CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.4 (2B), -10.2 (6B), -13.1 (2B). These data are identical with those reported in the literature.[53]

3-Cl-1,2-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$ (V-1b). Yield: 31%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 2.51 (q, *J* = 7.4 Hz, 4H), 2.37 (q, *J* = 7.4 Hz, 4H) (CH_2), 1.15 (t, *J* = 7.4 Hz, 6H), 1.05 (t, *J* = 7.4 Hz, 6H) (CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 136.9, 132.6 (olefinic *C*), 26.4, 22.2 (CH_2), 15.1, 14.6 (CH_3), cage *C* atoms were not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -8.9 (4B), -10.7 (2B), -12.5 (2B), -14.0 (1B), -17.9 (1B). HRMS: m/z Calcd for $C_{14}H_{29}B_{10}Cl^+$: 340.2955. Found: 340.2954.

3-Ph-1,2-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$ (V-1c). Yield: 38%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 2H), 7.23 (m, 1H), 7.18 (m, 2H) (Ph), 2.63 (m, 4H), 2.06 (m, 4H) (CH_2), 1.19 (t, *J* = 7.2 Hz, 6H), 0.56 (t, *J* = 7.2 Hz, 6H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.5, 134.1, 133.7, 128.9, 127.3 (Ph & olefinic *C*), 26.5, 21.8 (CH_2), 15.0, 14.0 (CH_3), cage *C* atoms were not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -5.9 (1B), -7.7 (2B), -11.1 (3B), -12.0 (3B), -15.4 (1B). HRMS: m/z Calcd for $C_{20}H_{34}B_{10}^+$: 382.3658. Found: 382.3658.

1,2-[^{n}PrC=C(^{n}Pr)C(^{n}Pr)=C^{n}Pr]-1,2-$C_2B_{10}H_{10}$ (V-1d). Yield: 59%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 2.45 (m, 4H), 2.17 (m, 4H), 1.53 (m, 4H), 1.32 (m, 4H) (CH_2), 0.97 (m, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 134.1, 132.8 (olefinic *C*), 76.4 (cage *C*), 35.8, 31.4, 23.9, 23.8 (CH_2), 14.3 (CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -8.3 (2B), -11.2 (6B), -14.0 (2B). These data are identical with those reported in the literature.[53]

1,2-[^{n}BuC=C(^{n}Bu)C(^{n}Bu)=C^{n}Bu]-1,2-$C_2B_{10}H_{10}$ (V-1e). Yield: 54%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 2.49 (m, 4H), 2.20 (m, 4H), 1.45 (m, 4H), 1.39

(m, 8H), 1.24 (m, 4H) (CH_2), 0.95 (m, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 134.0, 132.8 (olefinic *C*), 76.5 (cage *C*), 33.4, 32.6, 29.0, 23.1, 23.0 (CH_2), 13.8, 13.7 (CH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -8.2 (2B), -11.2 (6B), -14.0 (2B). These data are identical with those reported in the literature.[53]

1,2-[PhC=C(Ph)C(Ph)=CPh]-1,2-$C_2B_{10}H_{10}$ (V-1f). Yield: 28%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.12 (m, 10H), 6.74 (m, 6H), 6.62 (m, 4H) (Ph). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 137.8, 137.7, 137.1, 137.0, 130.9, 129.9, 127.6, 127.2, 126.8, 126.1 (Ph & olefinic *C*), 74.8 (cage *C*). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -5.1 (2B), -8.8 (4B), -11.3 (4B). These data are identical with those reported in the literature.[53]

1,2-[C(CH_2OMe)=C(CH_2OMe)C(CH_2OMe)=C(CH_2OMe)]-1,2-$C_2B_{10}H_{10}$ (V-1g). Yield: 13%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 4.29 (s, 4H), 4.27 (s, 4H) (OCH_2), 3.38 (s, 6H), 3.33 (s, 6H) (OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 136.2, 133.2 (olefinic *C*), 74.7 (cage *C*), 70.1, 67.4 (OCH_2), 58.3, 58.2 (OCH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -6.7 (2B), -10.6 (6B), -13.1 (2B). HRMS: m/z Calcd for $C_{14}H_{30}B_{10}O_4^+$: 370.3149. Found: 370.3145.

1,2-[MeC=C(^{i}Pr)C(Me)=C^{i}Pr]-1,2-$C_2B_{10}H_{10}$ (V-1h) + 1,2-[MeC=C(^{i}Pr)C(^{i}Pr)=CMe]-1,2-$C_2B_{10}H_{10}$ (V-1'h).: Yield: 44%. White solid. V-**1h**:**V-1'h** = 70:30. **V-1h:** ^1H NMR (400 MHz, $CDCl_3$): δ 3.23 (m, 1H), 3.10 (m, 1H) (C*H*), 2.26 (s, 3H), 2.02 (s, 3H) (CH_3), 1.29 (d, J = 7.2 Hz, 6H), 1.19 (d, J = 7.2 Hz, 6H) ($CHCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.2, 129.7, 129.0 (olefinic *C*), 34.6 (C_{cage}-C-CH_3), 29.7, 28.5 (*C*H), 20.9, 20.7 ($CHCH_3$), 18.5 (C_{cage}-C=C-CH_3), cage *C* atoms were not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -7.6 (2B), -10.5 (6B), -13.8 (2B). HRMS: *m/z* calcd for $C_{14}H_{30}B_{10}^+$: 306.3345. Found: 306.3346. **V-1'h**: ^1H NMR (400 MHz, $CDCl_3$): δ 3.21 (m, 2H) (C*H*), 1.97 (s, 6H) (CH_3), 1.26

(d, J = 7.2 Hz, 12H) (CHCH_3). Compound **V-1h** was isolated as a pure product whereas **V-1'h** was always contaminated with **V-1h**. Their molar ratio was determined by ^{1}H NMR spectrum of a crude mixture.

1,2-[MeC=C(Ph)C(Me)=CPh]-1,2-$C_2B_{10}H_{10}$ (V-1i). Yield: 50%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 6H), 7.16 (m, 2H), 7.02 (m, 2H) (Ph), 1.97 (s, 3H), 1.22 (s, 3H) (CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 139.1, 137.8, 135.4, 133.4, 132.9, 130.2, 129.8, 128.7, 128.3, 128.1, 127.5 (Ph & olefinic *C*), 75.6 (cage *C*), 21.1, 20.6 (*C*H_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -6.5 (2B), -10.1 (5B), -12.4 (3B). These data are identical with those reported in the literature.[53]

1,2-[MeC=C(4'-Me-C_6H_4)C(Me)=C(4'-Me-C_6H_4)]-1,2-$C_2B_{10}H_{10}$ (V-1j). Yield: 39%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (m, 4H), 7.03 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H) (aromatic *H*), 2.38 (s, 3H), 2.37 (s, 3H), 1.97 (s, 3H), 1.24 (s, 3H) (CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 137.8, 137.1, 136.2, 135.4, 134.9, 133.2, 132.7, 130.0, 129.4, 128.7, 128.2 (Ph & olefinic *C*), 75.8, 75.7 (cage *C*), 21.3, 21.2, 21.1, 20.7 (*C*H_3). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -7.5 (2B), -10.3 (5B), -13.0 (3B). HRMS: m/z Calcd for $C_{22}H_{30}B_{10}^+$: 402.3345. Found: 402.3357.

1,2-[MeC=C(4'-CF_3-C_6H_4)C(Me)=C(4'-CF_3-C_6H_4)]-1,2-$C_2B_{10}H_{10}$ (V-1k). Yield: 49%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (m, 4H), 7.30 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H) (aromatic *H*), 1.97 (s, 3H), 1.20 (s, 3H) (CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 142.5, 140.9, 134.3, 134.1, 132.5, 130.6, 129.5, 128.9, 126.0, 125.3 (Ph & olefinic *C*), 75.2, 74.7 (cage *C*), 21.3, 20.7 (*C*H_3). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -7.4 (2B), -11.5 (5B), -13.4 (3B). HRMS: m/z Calcd for $C_{22}H_{24}B_{10}F_6^+$: 510.2780. Found: 510.2775.

1,2-[EtC=C(Ph)C(Et)=CPh]-1,2-$C_2B_{10}H_{10}$ (V-1l). Yield: 49%. White solid. ^{1}H

NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 6H), 7.16 (m, 4H) (Ph), 2.35 (q, J = 7.2 Hz, 2H), 1.65 (q, J = 7.2 Hz, 2H) (CH_2), 0.93 (t, J = 7.2 Hz, 3H), 0.48 (t, J = 7.2 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 139.5, 137.7, 137.2, 135.8, 135.6, 133.8, 130.5, 129.4, 128.1, 127.7, 127.6 (Ph & olefinic *C*), 75.3, 75.2 (cage *C*), 27.4, 25.0 (*C*H_2), 14.4, 13.9 (*C*H_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -7.2 (2B), -10.5 (6B), -13.1 (2B). HRMS: m/z Calcd for $C_{22}H_{30}B_{10}^+$: 402.3345. Found: 402.3345.

1,2-[^{n}BuC=C(Ph)C(^{n}Bu)=CPh]-1,2-$C_2B_{10}H_{10}$ (V-1m). Yield: 43%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 6H), 7.17 (m, 2H), 7.12 (m, 2H) (Ph), 2.27 (m, 2H), 1.58 (m, 2H), 1.32 (m, 2H), 1.06 (m, 2H), 0.88 (m, 2H) (CH_2), 0.64 (t, J = 7.6 Hz, 3H) (CH_3), 0.57 (m, 2H) (CH_2), 0.33 (t, J = 7.6 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 138.4, 137.7, 137.3, 135.7, 134.7, 133.7, 130.5, 129.5, 128.1, 128.0, 127.7, 127.5 (Ph & olefinic *C*), 75.5, 75.3 (cage *C*), 34.1, 31.8, 31.4, 31.3, 22.7, 22.3 (*C*H_2), 13.3, 13.0 (*C*H_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -7.1 (2B), -10.4 (4B), -12.9 (4B). HRMS: m/z Calcd for $C_{26}H_{38}B_{10}^+$: 458.3971. Found: 458.3967.

1,2-[C(C≡CPh)=C(Ph)C(C≡CPh)=CPh]-1,2-$C_2B_{10}H_{10}$ (V-1n). Yield: 51%. Yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 8H), 7.35 (m, 4H), 7.18 (m, 4H), 7.16 (m, 2H), 6.48 (d, J = 8.0 Hz, 2H) (Ph). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 142.6, 140.2, 137.8, 137.6, 131.6, 131.2, 129.9, 129.5, 129.2, 128.7, 128.3, 128.0, 127.9, 127.6, 122.0, 121.9, 119.9 (Ph & olefinic *C*), 101.0, 100.0, 87.2, 86.3 (alkyne *C*), 73.9, 72.2 (cage *C*). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -7.1 (3B), -10.4 (4B), -13.0 (3B). HRMS: m/z Calcd for $C_{34}H_{30}B_{10}^+$: 546.3345. Found: 546.3336.

1,2-[C(CH_2OMe)=C(Ph)C(CH_2OMe)=CPh]-1,2-$C_2B_{10}H_{10}$ (V-1o). Yield: 24%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 6H), 7.22 (m, 4H) (Ph), 3.86 (s, 2H), 3.22 (s, 2H) (OCH_2), 3.09 (s, 3H), 2.58 (s, 3H) (OCH_3). $^{13}C\{^1H\}$ NMR

(100 MHz, $CDCl_3$): 140.9, 139.8, 136.1, 135.9, 133.1, 130.4, 130.1, 129.2, 128.5, 127.7, 127.6, 127.4 (Ph & olefinic *C*), 74.7, 74.6 (cage *C*), 70.9, 69.4 (OCH_2), 58.0, 57.7 (OCH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -6.6 (2B), -10.4 (4B), -12.7 (4B). HRMS: m/z Calcd for $C_{22}H_{30}B_{10}O_2^+$: 434.3254. Found: 434.3251.

1,2-[PhC=C(CH$_2$OMe)C(CH$_2$OMe)=CPh]-1,2-C$_2$B$_{10}$H$_{10}$ (V-1'o). Yield: 2%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 6H), 7.25 (m, 4H) (Ph), 3.84 (s, 4H) (OCH_2), 3.09 (s, 6H) (OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 140.7, 136.1, 130.2, 130.1, 128.6, 127.7 (Ph & olefinic *C*), 74.2 (cage *C*), 69.3 (OCH_2), 58.2 (OCH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -6.3 (2B), -10.4 (4B), -12.7 (4B). HRMS: m/z Calcd for $C_{22}H_{30}B_{10}O_2^+$: 434.3254. Found: 434.3249.

1-[C(CH$_2$OMe)=CH(Ph)]-1,2-C$_2$B$_{10}$H$_{11}$ (V-6o). Yield: 8%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 3H), 7.22 (m, 3H) (Ph & olefinic), 4.10 (s, 1H) (cage C*H*), 3.96 (s, 2H) (OCH_2), 3.27 (s, 3H) (OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 140.0, 134.9, 130.4, 128.7, 128.6, 128.5 (Ph & olefinic *C*), 69.4 (cage *C*), 59.4 (OCH_2), 57.9 (OCH_3), the other cage *C* was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -3.3 (2B), -10.0 (2B), -11.6 (4B), -13.7 (2B). HRMS: m/z Calcd for $C_{12}H_{22}B_{10}O^+$: 290.2674. Found: 290.2670.

1-[C(Ph)=CH(CH$_2$OMe)]-1,2-C$_2$B$_{10}$H$_{11}$ (V-6'o). Yield: 4%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 3H), 7.13 (m, 2H) (Ph), 7.01 (br s, 1H) (olefinic), 4.08 (d, J = 0.8 Hz, 2H) (OCH_2), 3.72 (s, 1H) (cage C*H*), 3.43 (s, 3H) (OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 135.2, 133.0, 129.9, 128.8, 128.1, 127.6 (Ph & olefinic *C*), 76.1, 73.9 (cage *C*), 58.9 (OCH_2), 58.1 (OCH_3). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -3.3 (2B), -10.0 (2B), -11.6 (4B), -13.7 (2B). HRMS: m/z Calcd for $C_{12}H_{22}B_{10}O^+$: 290.2674. Found: 290.2672.

1,2-[MeC=C-(CH$_2$)$_3$-C=CMe]-1,2-C$_2$B$_{10}$H$_{10}$ (V-8a). Yield: 38%. White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (t, J = 7.2 Hz, 4H) (C=CCH_2), 2.12 (s, 6H) (CH_3), 1.81 (m, 2H) ($CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 136.1, 125.1 (olefinic *C*), 79.1 (cage *C*), 31.6, 23.9 (*C*H_2) 18.9 (*C*H_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.5 (2B), -11.0 (5B), -12.3 (3B). HRMS: m/z Calcd for $C_{11}H_{22}B_{10}^+$: 262.2719. Found: 262.2710.

1,2-[MeC=C-(CH$_2$)$_4$-C=CMe]}-1,2-$C_2B_{10}H_{10}$ (V-8b). Yield: 39%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (m, 4H) (C=CCH_2), 2.12 (s, 6H) (CH_3), 1.58 (m, 4H) ($CH_2CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 128.9, 128.0 (olefinic *C*), 76.7 (cage *C*), 27.7, 21.9 (*C*H_2) 18.9 (*C*H_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.0 (2B), -10.6 (4B), -12.9 (4B). HRMS: m/z Calcd for $C_{12}H_{24}B_{10}^+$: 276.2876. Found: 262.2868.

1,2-[MeC=C-(CH$_2$)$_5$-C=CMe]}-1,2-$C_2B_{10}H_{10}$ (V-8c). Yield: 15%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (m, 4H) (C=CCH_2), 2.20 (s, 6H) (CH_3), 1.54 (m, 6H) (CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 134.1, 126.9 (olefinic *C*), 29.4, 28.6, 27.5 (*C*H_2), 19.4 (*C*H_3), cage *C* was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -8.0 (2B), -11.1 (6B), -13.9 (2B). HRMS: m/z Calcd for $C_{13}H_{26}B_{10}^+$: 290.3032. Found: 290.3032.

Preparation of [{[2-C(^{n}Bu)=C(*o*-C_5H_4N)-1,2-$C_2B_{10}H_{10}$]Ni}$_2$(μ_2-Cl)][Li(THF)$_4$] (V-9). To a toluene solution (5 mL) of $Li_2C_2B_{10}H_{10}$ (0.5 mmol), prepared in situ from the reaction of ^{n}BuLi (1.6 M, 0.63 mL, 1.0 mmol) with *o*-carborane (72 mg, 0.5 mmol), was added I_2 (127 mg, 0.5 mmol), and the reaction mixture was stirred at room temperature for 0.5 h. $NiCl_2(PPh_3)_2$ (327 mg, 0.5 mmol), and *n*-butyl-2-pyridinylacetylene (159 mg, 2.0 mmol) were then added and the reaction vessel was closed and heated at 90 °C

overnight. Removal of the solvent gave a red residue which was washed with hexane (50 mL × 3). Recrystallization from THF at room temperature afforded **V-9**·THF as red crystals (70 mg, 25%). ^{1}H NMR (300 MHz, [D$_5$]pyridine): δ 8.16 (d, J = 4.2 Hz, 2H), 7.08 (m, 2H), 6.76 (d, J = 8.1 Hz, 2H), 6.57 (m, 2H) (Py), 3.64 (m, 10H) (CH_2O THF), 2.11 (t, J = 8.1 Hz, 4H) (CH_2), 1.59 (m, 10H) (CH_2 THF), 1.54 (m, 4H), 1.07 (m, 4H) (CH_2), 0.64 (t, J = 7.5 Hz, 6H) (CH_3). ^{13}C{^{1}H} NMR (100 MHz, [D$_5$]pyridine): 167.3, 158.8, 148.1, 146.8, 133.9, 121.5, 117.5 (Py & olefinic *C*), 90.8, 75.1 (cage *C*), 67.1 (*C*H$_2$O THF), 31.4, 31.0 (*C*H$_2$), 25.1 (*C*H$_2$ THF), 22.3 (*C*H$_2$), 13.2 (*C*H$_3$). ^{11}B{^{1}H} NMR (96 MHz, [D$_5$]pyridine): δ -3.6 (6B), -6.6 (4B), -9.5 (8B), -12.9 (2B). Anal. Calcd for $C_{46}H_{86}B_{20}ClLiN_2Ni_2O_5$ (**V-7**+THF): C, 49.19; H, 7.72; N, 2.49. Found: C, 49.07; H, 7.57; N, 2.27.

Preparation of 3-I-1,2-$C_2B_{10}H_{11}$ (VI-1a). *o*-Carborane (1.44 g, 10 mmol) and KOH (2.24 g, 40 mmol) were dissolved in 100 mL of MeOH and the resulting solution was refluxed for 4 h. After removal of the solvent, the residue was dissolved in 20 mL of water. Addition of a saturated Me_3NH • HCl aq. solution gave [Me_3NH][$C_2B_9H_{12}$] as a white solid (1.60 g, 83%). To a ether suspension (10 mL) of [Me_3NH][$C_2B_9H_{12}$] (1.60 g, 8.3 mmol) was added ^{n}BuLi (1.6 M, 1.66 mol, 1.04 mL) at 0 °C. The reaction mixture was stirred at r. t. for 2 h and then refluxed for 4 h. After removal of solvent in vacuo, hexane (20 mL) was added to the resulting solid. A solution of BI_3 (4.88 g, 12.5 mmol) in hexane (10 mL) was slowly added to the above suspension at 0 °C. The reaction mixture was stirred at r.t. for another 6 h and then hydrolyzed with 2 mL of water. The organic layer was separated, dried over $MgSO_4$, and concentrated. The residue was subject to column chromatography on silica gel (230-400 mesh) using hexane as eluent to give **VI-1a** (1.46 g, 65%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 2H) (cage *H*). These data are

identical with those reported in the literature.[92]

Preparation of 3-I-1-Me-1,2-$C_2B_{10}H_{10}$ (VI-1b). To an Et_2O solution (20 mL) of *o*-carborane (1.44 g, 10 mmol) was added dropwise ^{n}BuLi (1.6 M, 6.25 mL, 10 mmol) at 0°C, and the mixture was stirred at r. t. for 1 h. To the resulting reaction mixture was added TMSCl (1.27 mL, 10 mmol) at 0 °C, and the solution was stirred at room temperature for another 4 h. ^{n}BuLi (1.6 M, 6.25 mL, 10 mmol) was added at 0 °C, and the reaction mixture was stirred at room temperature for 1 h before 2 equiv of MeI (1.25 mL, 20 mmol) was added at 0 °C. After stirring at room temperature overnight, the reaction was quenched with 20 mL of water and extracted with Et_2O (10 mL × 3). After removal of the solvents in vacuo, 1-methyl-2-trimethylsilyl-*o*-carborane was obtained as a white solid, which was used in the next step reaction without further purification (2.28 g, 99%). 1-Methyl-2-trimethylsilyl-*o*-carborane (2.28 g, 9.9 mmol) and KOH (2.24 g, 40 mmol) were dissolved in 100 mL of MeOH and the resulting solution was refluxed for 4 h. After removal of the solvent, the residue was dissolved in 20 mL of water. Addition of a saturated Me_3NH •HCl aq. solution gave [Me_3NH][3-Me-7,8-$C_2B_9H_{11}$] as a white solid (1.82 g, 88%). To a ether suspension (10 mL) of [Me_3NH][3-Me-7,8-$C_2B_9H_{11}$] (1.82 g, 8.7 mmol) was added ^{n}BuLi (1.6 M, 1.74 mol, 1.09 mL) at 0 °C. The reaction mixture was stirred at r. t. for 2 h and then refluxed for 4 h. After removal of solvent in vacuo, hexane (20 mL) was added to the resulting solid. A solution of BI_3 (5.12 g, 13.1 mmol) in hexane (10 mL) was slowly added to the above suspension at 0 °C. The reaction mixture was stirred at r.t. for another 6 h and then hydrolyzed with 2 mL of water. The organic layer was separated, dried over $MgSO_4$, and concentrated. The residue was subject to column chromatography on silica gel (230-400 mesh) using hexane as eluent to give **VI-1b** (1.51 g, 61%) as a

white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.61 (s, 1H) (cage *H*), 2.24 (s, 3H) (C*H*$_3$). These data are identical with those reported in the literature.[30d]

Preparation of 3-I-1-Ph-1,2-$C_2B_{10}H_{10}$ (VI-1c). VI-1c (640 mg, 37%) was prepared as a white solid from 1-phenyl-*o*-carborane (1.10 g, 5 mmol) using the same method for **VI-1a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (m, 3H), 7.34 (m, 2H) (Ph), 4.24 (s, 1H) (cage *H*). These data are identical with those reported in the literature.[30d]

Preparation of 1-^{n}Bu-3-I-1,2-$C_2B_{10}H_{10}$ (VI-1d). To an ether solution (5 mL) of 3-iodo-*o*-carborane (400 mg, 1.5 mmol) was added ^{n}BuLi (1.6 M, 1.5 mmol, 0.93 mL) and the mixture was stirred at 0 °C for 1 h. After adding ^{n}BuBr (1.5 mmol, 0.16 mL), the reaction mixture was stirred for at 0 °C 5 h and then hydrolyzed with water. The organic layer was separated, dried over $MgSO_4$, and concentrated. The residue was subject to column chromatography on silica gel (230-400 mesh) using hexane as eluent to give **VI-1d** (254g, 53%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.61 (s, 1H) (cage *H*), 2.47 (m, 1H), 2.30 (m, 1H), 1.50 (m, 2H), 1.35 (m, 2H) (C*H*$_2$), 0.94 (t, *J* = 7.2 Hz, 3H) (C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 75.0, 64.7 (cage *C*), 38.9, 30.9, 22.0 (*C*H$_2$), 13.6 (*C*H$_3$). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -2.6 (1B), -5.2 (1B), -7.5 (1B), -10.0 (1B), -11.3 (4B), -13.3 (1B), -25.3 (1B). HRMS: *m/z* calcd for $C_6H_{19}B_{10}I^+$: 326.1529. Found: 326.1532.

Preparation of 3-I-1-TMS-1,2-$C_2B_{10}H_{10}$ (VI-1e). VI-1e was prepared as a white solid from TMSCl using the same method for **VI-1d**. Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (s, 1H) (cage *H*), 0.41 (s, 9H) (C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 67.4, 64.1 (cage *C*), -0.9 (*C*H$_3$). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -0.2 (1B), -1.7 (1B), -4.7 (1B), -9.0 (2B), -9.7 (1B), -11.0 (1B), -12.1 (1B), -13.0 (1B), -28.1 (1B). HRMS: *m/z* calcd for $C_5H_{20}B_{10}ISi$ $[M-H]^+$: 342.1298. Found: 342.1302.

Preparation of 3-I-1-($CH_2CH_2OCH_3$)-1,2-$C_2B_{10}H_{10}$ (VI-1f). **VI-1f** was prepared as a colorless oil from 2-chloroethyl methyl ether using the same method for **VI-1d**. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 1H) (cage *H*), 3.56 (m, 2H) (OC*H*$_2$), 3.32 (s, 3H) (OC*H*$_3$), 2.79 (m, 1H), 2.63 (m, 1H) (OCH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 72.8, 64.4 (cage *C*), 70.0 (O*C*H$_2$), 58.7 (O*C*H$_3$), 38.3 (OCH$_2$*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -2.2 (1B), -4.7 (1B), -7.7 (1B), -9.7 (1B), -11.3 (4B), -12.7 (1B), -24.5 (1B). HRMS: *m/z* calcd for $C_5H_{17}B_{10}IO^+$: 328.1322. Found: 328.1323.

Preparation of 3-I-1-[$CH_2CH_2N(CH_3)_2$]-1,2-$C_2B_{10}H_{10}$ (VI-1g). **VI-1g** was prepared as a light yellow oil from 2 equiv ^{n}BuLi and 2-chloro-*N,N*-dimethylethylamine hydrochloride using the same method for **VI-1d**. Yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00 (s, 1H) (cage *H*), 2.59 (m, 3H), 2.41 (m, 1H) (C*H*$_2$), 2.23 (s, 6H) (NC*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 73.7, 64.4 (cage *C*), 57.8 (NCH$_2$), 45.4 (N*C*H$_3$), 35.8 (*C*H$_2$CH$_2$N). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -1.9 (1B), -4.3 (1B), -7.4 (1B), -9.5 (1B), -11.0 (4B), -12.5 (1B), -24.2 (1B). HRMS: *m/z* calcd for $C_6H_{20}B_{10}IN^+$: 341.1638. Found: 341.1639.

General Procedure for Palladium/Nickel-Cocatalyzed Cycloaddition Reaction of 1,3-*o*-Carboryne with Alkynes. To a toluene solution (5 mL) of 3-iodo-1-methyl-*o*-carborane (0.5 mmol) was added 1 equiv of ^{n}BuLi (0.5 mmol), and the reaction mixture was stirred at room temperature for 0.5 h. Pd(PPh_3)$_4$ (5 mol%), Ni(cod)$_2$ (5 mol%), and alkyne (2.0 mmol) [or diyne (1.0 mmol)] were then added, and the reaction vessel was closed and heated at 110 °C overnight. After addition of water and extraction with ether, the resulting solution was concentrated to dryness in vacuo. The residue was subject to column chromatography on silica gel (230-400 mesh) using hexane as eluent to give the desired cycloaddition product.

1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_{10}$ (VI-4a). Yield: 12%. Colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61 (m, 4H), 2.39 (m, 5H) (cage C*H* & CH_2), 1.19 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H), (CH_3). ^{1}H NMR (400 MHz, benzene-d_6): δ 2.54 (q, *J* = 7.6 Hz, 2H), 2.23 (m, 2H), 2,15 (m, 1H), 2.02 (m, 3H) (CH_2), 1.83 (s, 1H) (cage C*H*), 1.15 (t, *J* = 7.6 Hz, 3H), 0.87 (t, *J* = 7.6 Hz, 3H), 0.82 (t, *J* = 7.6 Hz, 3H), 0.74 (t, *J* = 7.6 Hz, 3H), (CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.3, 142.0, 130.6 (olefinic *C*), 60.4 (cage *C*), 28.3, 27.0, 23.3, 21.9 (*C*H$_2$), 15.5, 15.1, 15.0, 14.8 (*C*H$_3$), the olefinic *C* connected to B atom and another cage *C* were not observed. ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -4.8 (1B), -7.8 (2B), -10.0 (1B), -11.7 (3B), -13.2 (1B), -14.0 (1B), -16.8 (1B). HRMS: *m/z* calcd for $C_{14}H_{30}B_{10}^+$: 306.3345. Found: 306.3349.

2-Me-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$ (VI-4b). Yield: 54%. Colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (m, 3H), 2.44 (m, 5H) (CH_2), 1.29 (s, 3H) (CH_3), 1.15 (t, *J* = 7.6 Hz, 3H), 1.12 (t, *J* = 7.6 Hz, 3H), 1.05 (t, *J* = 7.6 Hz, 3H), 1.04 (t, *J* = 7.6 Hz, 3H) (CH$_2$CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.6, 143.5, 128.8 (olefinic *C*), 81.3, 67.9 (cage *C*), 28.2, 26.9, 23.5, 21.9 (*C*H$_2$), 20.2 (*C*H$_3$), 15.6, 15.3, 15.2, 14.7 (CH$_2$*C*H$_3$), the olefinic *C* connected to B atom was not observed. ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -8.0 (3B), -9.9 (1B), -11.2 (3B), -12.8 (1B), -14.4 (2B). HRMS: *m/z* calcd for $C_{15}H_{32}B_{10}^+$: 320.3502. Found: 320.3504.

2-^{n}Bu-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$ (VI-4c). Yield: 67%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (m, 10H), 1.33 (m, 2H), 1.25 (m, 2H) (CH_2), 1.15 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H) (CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.8, 143.3, 128.7 (olefinic *C*), 82.9, 72.7 (cage *C*), 31.4, 31.2, 28.1, 27.0,

23.5, 22.4, 21.8 (CH_2), 15.4, 15.3, 15.2, 14.8, 13.6 (CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -7.8 (3B), -11.2 (5B), -14.4 (1B), -16.2 (1B). HRMS: *m/z* calcd for $C_{18}H_{38}B_{10}^+$: 362.3971. Found: 392.3967.

2-TMS-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$ (VI-4d). Yield: 69%. Colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 2.46 (m, 8H) (CH_2), 1.26 (t, *J* = 7.6 Hz, 3H), 1.18 (t, *J* = 7.6 Hz, 3H), 1.08 (t, *J* = 7.6 Hz, 3H), 1.06 (t, *J* = 7.6 Hz, 3H) (CH_2CH_3), 0.03 (s, 9H) ($Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.4, 142.2, 131.5 (olefinic *C*), 83.8, 68.5 (cage *C*), 29.0, 27.8, 23.5, 21.8 (CH_2), 15.2, 15.0, 14.7, 14.6 (CH_2CH_3), 0.56 ($Si(CH_3)_3$), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.6 (1B), -7.2 (2B), -7.8 (2B), -11.1 (3B), -12.3 (1B), -14.3 (1B). HRMS: *m/z* calcd for $C_{17}H_{38}B_{10}Si^+$: 378.3740. Found: 378.3748.

2-Ph-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$ (VI-4e). Yield: 43%. Colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (m, 3H), 7.14 (m, 2H) (Ph), 2.63 (m, 4H), 2.13 (m, 3H), 1.98 (m, 1H) (CH_2), 1.27 (t, *J* = 7.6 Hz, 3H), 1.15 (t, *J* = 7.6 Hz, 3H), 0.64 (t, *J* = 7.6 Hz, 3H), 0.49 (t, *J* = 7.6 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.3, 143.4, 130.3, 129.9, 129.4, 128.8, 127.4 (olefinic *C* & Ph), 84.9, 75.5 (cage *C*), 28.5, 27.5, 23.1, 21.6 (CH_2), 15.0, 14.7, 14.6, 14.0 (CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -6.0 (2B), -7.6 (1B), -10.0 (1B), -11.4 (3B), -13.7 (3B). HRMS: *m/z* calcd for $C_{20}H_{34}B_{10}^+$: 382.3658. Found: 382.3657.

2-($CH_2CH_2OCH_3$)-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$ (VI-4f). Yield: 58%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.25 (t, *J* = 7.2 Hz, 2H) (OCH_2), 3.23 (s, 3H) (OCH_3), 2.52 (m, 3H), 2.38 (m, 5H), 1.64 (m, 2H) (CH_2), 1.16 (t, *J* = 7.6

Hz, 3H), 1.12 (t, J = 7.6 Hz, 3H), 1.05 (t, J = 7.6 Hz, 3H), 1.03 (t, J = 7.6 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.0, 143.6, 128.7 (olefinic *C*), 82.8, 69.5 (cage *C*), 70.7 (OCH_2), 58.5 (OCH_3), 31.1, 28.2, 27.0, 23.5, 21.9 (CH_2), 15.4, 15.2, 15.1, 14.7 (CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -7.1 (1B), -7.8 (1B), -11.1 (5B), -12.7 (1B), -14.2 (1B), -16.1 (1B). HRMS: *m/z* calcd for $C_{17}H_{36}B_{10}O^+$: 364.3764. Found: 364.3760.

2-[$CH_2CH_2N(CH_3)_2$]-1,3-[EtC=C(Et)C(Et)=CEt]-1,2-$C_2B_{10}H_9$ (VI-4g). Yield: 51%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 2.44 (m, 10H) (CH_2), 2.10 (s, 6H) ($N(CH_3)_2$), 1.54 (m, 2H) (CH_2), 1.16 (t, J = 7.6 Hz, 3H), 1.14 (t, J = 7.6 Hz, 3H), 1.08 (t, J = 7.6 Hz, 3H), 1.04 (t, J = 7.6 Hz, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.0, 143.6, 128.7 (olefinic *C*), 83.1, 70.5 (cage *C*), 58.4 (NCH_2), 45.3 ($N(CH_3)_2$), 29.1, 28.2, 27.0, 23.5, 21.9 (CH_2), 15.5, 15.4, 15.3, 14.9 (CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -7.6 (3B), -10.9 (5B), -14.1 (1B), -16.2 (1B). HRMS: *m/z* calcd for $C_{18}H_{39}B_{10}N$: 377.4080. Found: 377.4076.

2-Me-1,3-[^{n}PrC=C(^{n}Pr)C(^{n}Pr)=C^{n}Pr]-1,2-$C_2B_{10}H_9$ (VI-4h). Yield: 55%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 2.48 (m, 3H), 2.27 (m, 5H) ($=CCH_2$), 1.51 (m, 4H), 1.36 (m, 4H) (CH_2CH_2), 1.26 (s, 3H) (CH_3), 0.98 (m, 12H) (CH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.4, 142.4, 127.8 (olefinic *C*), 81.3, 68.0 (cage *C*), 37.9, 36.5, 33.2, 31.6 ($=CCH_2$), 24.6, 24.2, 23.6 (CH_2CH_2), 20.2 (CH_3), 14.8, 14.7, 14.6, 14.4 (CH_2CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -8.3 (3B), -11.4 (5B), -14.6 (2B). HRMS: *m/z* calcd for $C_{19}H_{40}B_{10}^+$: 376.4128. Found: 376.4114.

2-Me-1,3-[^{n}BuC=C(^{n}Bu)C(^{n}Bu)=C^{n}Bu]-1,2-$C_2B_{10}H_9$ (VI-4i). Yield: 33%. The reaction of 5-nonyne catalyzed by 10 mol % $Pd(PPh_3)_4$ or 10 mol % $[Pd(Ally)Cl]_2$/

20 mol % PPh_3 was completed in about 7 days and 5 days to give **VII-4i** in 26 and 23% yields, respectively. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 2.48 (m, 5H). 2.31 (m, 7H), 1.40 (m, 12H) (CH_2), 1.27 (s, 3H) (CH_3), 0.95 (m, 12H) (CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 144.4, 142.3, 127.6 (olefinic *C*), 81.4, 68.0 (cage *C*), 35.4, 34.0, 33.4, 33.2, 32.9, 32.4 30.7, 29.1, 23.4, 23.3, 23.2, 23.1(CH_2), 20.2 (CH_3), 14.0, 13.9, 13.8, 13.7 (CH_2CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -8.4 (4B), -11.5 (4B), -14.6 (2B). HRMS: *m/z* calcd for $C_{23}H_{48}B_{10}^+$: 432.4754. Found: 432.4758.

2-Me-1,3-[PhC=C(Ph)C(Ph)=CPh]-1,2-$C_2B_{10}H_9$ (VI-4j). Yield: 55%. Yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.09 (m, 9H), 6.89 (d, J = 8.0 Hz, 1H), 6.77 (m, 10H) (aromatic C*H*), 2.12 (s, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.5, 145.4, 142.2, 139.7, 139.5, 139.0, 131.9, 131.5, 130.4, 130.1, 129.7, 128.7, 127.5, 127.3, 127.2, 127.1, 126.8, 126.6, 126.5, 126.0, 125.9, 125.7 (aromatic & olefinic *C*), 78.7, 67.8 (cage *C*), 21.0 (CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -8.2 (3B), -10.5 (4B), -13.6 (3B). HRMS: *m/z* calcd for $C_{31}H_{32}B_{10}^+$: 512.3502. Found: 512.3520.

2-Me-1,3-[C(4'-Me-C_6H_4)=C(4'-Me-C_6H_4)C(4'-Me-C_6H_4)=C(4'-Me-C_6H_4)]-1,2-$C_2B_{10}H_9$ (VI-4k). Yield: 51%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 6.90 (m, 6H), 6.83 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.50 (m, 8H) (aromatic C*H*), 2.23 (s, 3H), 2.21 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.7, 145.5, 139.6, 137.0, 136.8, 136.5, 136.4, 135.1, 135.0, 134.8, 131.6, 131.3, 130.2, 129.9, 129.5, 128.6, 128.2, 127.9, 127.7, 127.5, 127.2 (aromatic & olefinic *C*), 79.1, 67.9 (cage *C*), 21.0, 20.9 (CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -7.8 (4B), -10.1 (4B), -13.3 (2B). HRMS: *m/z* calcd for $C_{35}H_{40}B_{10}^+$: 568.4128. Found: 568.4150.

2-Me-1,3-[PhC=C(Me)C(Ph)=CMe]-1,2-$C_2B_{10}H_9$ (VI-4l) +

2-Me-1,3-[MeC=C(Ph)C(Ph)=CMe]-1,2-$C_2B_{10}H_9$ (VI-5l). Yield: 49%. White solid. **VI-4l**: **VI-5l** = 62:38. **VII-4l**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 6H), 7.12 (m, 2H), 6.93 (m, 2H) (aromatic C*H*), 1.93 (s, 3H), 1.70 (s, 3H), 1.34 (s, 3H) (CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 144.8, 140.8, 139.8, 130.8, 129.6, 128.7, 128.5, 128.2, 128.1, 127.7, 126.9 (aromatic & olefinic *C*), 79.8, 67.9 (cage *C*), 22.9, 21.7, 20.5 (*C*H$_3$), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.3 (3B), -10.4 (5B), -13.2 (2B). HRMS: *m/z* calcd for $C_{21}H_{28}B_{10}^+$: 388.3189. Found: 388.3189. Compound **VI-4l** was isolated as a pure product whereas **VI-5l** was always contaminated with **VI-4l**. Their molar ratio was determined by ^{1}H NMR spectrum of a crude mixture.

2-Me-1,3-[PhC=C(Et)C(Ph)=CEt]-1,2-$C_2B_{10}H_9$ (VI-4m) +

2-Me-1,3-[EtC=C(Ph)C(Ph)=CEt]-1,2-$C_2B_{10}H_9$ (VI-5m). Yield: 47%. White solid. **VI-4m**: **VI-5m** = 80:20. **VII-4m**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 6H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.16 (m, 1H), 7.06 (m, 1H), 6.97 (m, 1H) (aromatic C*H*), 2.27 (m, 2H), 1.78 (m, 2H) (CH_2), 1.73 (s, 3H) (CH_3), 1.01 (t, *J* = 7.6 Hz, 3H), 0.55 (t, *J* = 7.6 Hz, 3H) (CH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.9, 144.7, 139.6, 139.2, 131.1, 129.9, 129.4, 128.0, 127.9, 127.8, 127.7, 127.6, 127.0 (aromatic & olefinic *C*), 79.7, 67.5 (cage *C*), 28.4, 26.8 (*C*H$_2$), 20.6 (*C*H$_3$), 14.3 (CH_2CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.7 (3B), -10.9 (4B), -13.6 (3B). HRMS: *m/z* calcd for $C_{23}H_{32}B_{10}^+$: 416.3502. Found: 416.3489. **VI-5m**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (m, 6H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 6.4 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.61 (m, 1H) (aromatic C*H*), 2.23 (m, 4H) (CH_2), 1.71 (s, 3H) (CH_3), 0.98 (t, *J* = 7.6 Hz, 3H), 0.81 (t, *J* = 7.6 Hz, 3H) (CH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.1, 144.8, 140.0, 130.6, 129.7,

129.6, 129.5, 129.1, 127.4, 127.3, 127.2, 126.4, 126.0 (aromatic & olefinic *C*), 80.7, 68.0 (cage *C*), 29.0, 28.2 (*C*H_2), 20.5 (*C*H_3), 14.5, 14.4 (CH_2CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.4 (3B), -10.6 (4B), -13.6 (3B). HRMS: *m/z* calcd for $C_{23}H_{32}B_{10}^+$: 416.3502. Found: 416.3506.

2-Me-1,3-[MeC=C-(CH$_2$)$_3$-C=CMe]-1,2-C$_2$B$_{10}$H$_9$ (VI-7a). Yield: 6%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 2.57 (m, 4H) (=CC*H*$_2$), 2.09 (s, 3H), 2.02 (s, 3H) (=CC*H*$_3$), 1.83 (m, 2H) (CH_2CH_2), 1.24 (s, 3H) (C*H*$_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 147.2, 145.3, 118.7 (olefinic *C*), 81.7, 67.7 (cage *C*), 33.1, 31.3 (=C*C*H$_2$), 23.8 (CH_2CH_2), 20.3, 20.1, 19.5 (*C*H_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -6.2 (1B), -7.3 (2B), -9.6 (1B), -11.0 (3B), -12.6 (1B), -13.8 (2B). HRMS: *m/z* calcd for $[C_{12}H_{24}B_{10}]^+$: 276.2876. Found: 276.2867.

2-Me-1,3-[MeC=C-(CH$_2$)$_4$-C=CMe]-1,2-C$_2$B$_{10}$H$_9$ (VI-7b). Yield: 34%. Colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 2.45 (m, 4H) (=CC*H*$_2$), 2.11 (s, 3H), 2.04 (s, 3H) (=CC*H*$_3$), 1.65 (m, 4H) (CH_2CH_2), 1.23 (s, 3H) (C*H*$_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 140.8, 139.0, 121.3 (olefinic *C*), 81.1, 67.4 (cage *C*), 29.3, 27.2 (=C*C*H$_2$), 22.1, 21.9 (CH_2CH_2), 21.0, 20.1, 19.3 (*C*H_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.5 (3B), -9.3 (1B), -10.9 (3B), -12.2 (1B), -14.0 (2B). HRMS: *m/z* calcd for $C_{13}H_{26}B_{10}^+$: 290.3032. Found: 290.3029.

2-Me-1,3-[MeC=C-(CH$_2$)$_5$-C=CMe]-1,2-C$_2$B$_{10}$H$_9$ (VI-7c). Yield: 23%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 2.61 (m, 4H) (=CC*H*$_2$), 2.16 (s, 3H), 2.11 (s, 3H) (=CC*H*$_3$), 1.67 (m, 1H), 1.58 (m, 4H), 1.48 (m, 1H) (CH_2CH_2), 1.30 (s, 3H)

(CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 146.0, 144.0, 124.4 (olefinic *C*), 81.1, 68.3 (cage *C*), 31.0, 29.0 (=CCH_2), 28.3, 28.0 (CH_2CH_2), 21.6, 20.2, 19.9 (CH_3), the olefinic *C* connected to B atom was not observed. $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -7.9 (3B), -9.9 (1B), -11.2 (3B), -12.6 (1B), -14.4 (2B). HRMS: *m/z* calcd for $C_{14}H_{28}B_{10}^+$: 304.3189. Found: 304.3179.

X-ray Structure Determination. Single-crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. All data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[95] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[96] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Appendix II. CIF files are given in Appendix III in electronic format.

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Appendix

Appendix I. Publications Based on the Research Findings

1. Zaozao Qiu and Zuowei Xie. "Nickel-Mediated Coupling Reaction of Carboryne with Alkenes: New Synthetic Route to Alkenylcarboranes" *Angew. Chem. Int. Ed.* **2008**, *47*, 6572–6575.
2. Zaozao Qiu and Zuowei Xie. "Nickel-Mediated Three-Component Cycloaddition Reaction of Carboryne, Alkenes, and Alkynes" *J. Am. Chem. Soc.* **2009**, *131*, 2084–2085.
3. Zaozao Qiu and Zuowei Xie. "Nickel-Catalyzed Three-Component [2+2+2] Cycloaddition Reaction of Arynes, Alkenes, and Alkynes" *Angew. Chem. Int. Ed.* **2009**, *48*, 5729–5732.
4. Zaozao Qiu and Zuowei Xie. "Unique chemical properties of metal-carbon bonds in metal-carboranyl and metal-carboryne complexes" *Sci. China Ser. B-Chem.* **2009**, *52*, 1544–1558.
5. Zaozao Qiu, Sunewang R. Wang, and Zuowei Xie. "Nickel-Catalyzed Regioselective [2+2+2] Cycloaddition of Carboryne with Alkynes" *Angew. Chem. Int. Ed.* **2010**, *49*, in press.
6. Zaozao Qiu, Yi Sun, and Zuowei Xie. "Reaction of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NCCH_3)_2$ with Internal Alkynes. Synthesis and Structural Characterization of Ruthenium Cyclobutadiene and Ruthenacyclopentatriene Complexes" *Sci. China Ser. B-Chem.* **2010**, *54*, in press.
7. Zaozao Qiu and Zuowei Xie. "Palladium/Nickel-Cocatalyzed [2+2+2] Cycloaddition of 1,3-Dehydro-*o*-carborane with Alkynes", manuscript in preparation.

8. Zaozao Qiu, Liang Deng, Hoi-Shan Chan, and Zuowei Xie. "Synthesis, Structural Characterization and Reactivity of Nickel-1,2-*o*-Carboryne Complexes", manuscript in preparation.

Appendix II. Crystal Data and Summary of Data Collection and Refinement

	II-2	II-3	II-4	II-5
formular	$C_{38}H_{38}B_{10}I_2NiP_2$	$C_8H_{27}B_{10}BrNiP_2$	$C_{14}H_{32}B_{10}NiP_2$	$C_{44}H_{44}B_{10}NiP_2$
crystal size (mm)	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.20
fw	977.23	431.96	429.15	801.54
crystal system	triclinic	orthorhombic	monoclinic	monoclinic
space group	*P*(-1)	*A*ma2	$P2_1$	$P2_1/n$
a, Å	12.597(2)	15.253(2)	8.937(1)	12.958(1)
b, Å	12.615(2)	11.484(2)	15.886(1)	21.107(1)
c, Å	14.992(2)	11.858(2)	17.545(2)	15.398(1)
α, deg	71.936(3)	90	90	90
β, deg	78.406(3)	90	104.205(2)	92.682(1)
γ, deg	71.484(2)	90	90	90
V, Å^3	2133.9(5)	2077.0(5)	2414.9(4)	4188.9(4)
Z	2	4	4	4
D_{calcd}, Mg/m^3	1.521	1.381	1.180	1.271
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073
2θ range, deg	2.9 to 50.0	5.3 to 50.5	3.5 to 50.5	3.3 to 50.5
μ, mm^{-1}	2.004	2.998	0.934	0.572
F(000)	960	872	896	1664
no. of obsd reflns	7460	1936	8695	7596
no. of params refnd	478	109	487	514
goodness of fit	1.095	1.144	1.018	1.051
R1	0.041	0.055	0.033	0.031
wR2	0.098	0.149	0.084	0.081

	II-6	**III-3c**	**III-3e**	**III-3g**
formular	$C_{16}H_{44}B_{10}NiP_2$	$C_{11}H_{17}B_{10}F_3$	$C_{13}H_{24}B_{10}O_3$	$C_{16}H_{22}B_{10}$
crystal size	0.40 x 0.30 x	0.50 x 0.40 x	0.40 x 0.30 x	0.50 x 0.40 x
(mm)	0.30	0.30	0.20	0.30
fw	465.26	314.35	336.42	322.44
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1$	$P2_1/c$
a, Å	10.290(1)	12.322(2)	7.275(1)	12.518(1)
b, Å	25.985(3)	18.702(2)	10.326(1)	7.549(1)
c, Å	11.492(1)	7.547(1)	13.105(1)	20.712(2)
α, deg	90	90	90	90
β, deg	110.827(2)	105.034(3)	103.601(2)	97.800(2)
γ, deg	90	90	90	90
V, Å^3	2872.2(5)	1679.5(4)	956.9(2)	1938.9(3)
Z	4	4	2	4
D_{calcd}, Mg/m^3	1.076	1.243	1.168	1.105
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073
2θ range, deg	3.1 to 50.0	3.4 to 56.0	5.1 to 50.0	3.3 to 56.0
μ, mm^{-1}	0.789	0.085	0.069	0.054
F(000)	992	640	352	672
no. of obsd reflns	5059	4031	3224	4655
no. of params refnd	262	217	235	235
goodness of fit	1.838	1.032	1.036	1.005
R1	0.153	0.072	0.043	0.063
wR2	0.426	0.198	0.108	0.157

	III-5q	**III-7r**	**III-8r**	**III-9r**
formular	$C_6H_{18}B_{10}O_2$	$C_{16}H_{26}B_{10}N_2$	$C_{16}H_{24}B_{10}N_2$	$C_{39}H_{81}B_{30}Cl$ $LiN_3Ni_3O_6$
crystal size (mm)	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30
fw	230.30	354.49	352.47	1230.89
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	*P*nma	*C*2/c	$P2_1/n$
a, Å	21.807(4)	10.636(2)	19.594(1)	15.252(3)
b, Å	10.773(2)	19.055(4)	10.876(1)	23.471(4)
c, Å	24.597(5)	10.113(2)	19.714(1)	18.257(4)
α, deg	90	90	90	90
β, deg	108.21 (1)	90	100.018(1)	91.51(1)
γ, deg	90	90	90	90
V, Å^3	5489(2)	2050(1)	4137(1)	6533(2)
Z	16	4	8	4
D_{calcd}, Mg/m^3	1.115	1.149	1.132	1.251
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073
2θ range, deg	2.1 to 50.0	4.3 to 56.1	4.2 to 55.6	2.8 to 56.0
μ, mm^{-1}	0.062	0.060	0.059	0.939
F(000)	1920	744	1472	2552
no. of obsd reflns	9652	2549	4841	15772
no. of params refnd	649	133	253	748
goodness of fit	1.079	1.023	1.036	1.010
R1	0.076	0.069	0.062	0.062
wR2	0.217	0.181	0.174	0.146

	IV-1d	**IV-1i**	**IV-5e**	**IV-5l**
formular	$C_{18}H_{25}B_{10}N$	$C_{12}H_{26}B_{10}O_2$	$C_{23}H_{17}N$	$C_{20}H_{20}O_3$
crystal size	0.50 x 0.40 x	0.40 x 0.30 x	0.40 x 0.30 x	0.50 x 0.40 x
(mm)	0.30	0.20	0.20	0.30
fw	363.49	310.43	307.38	308.36
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1$	$P2_1/c$	$P2_1/n$
a, Å	12.961(2)	10.412(1)	11.313(2)	12.573(3)
b, Å	7.054(1)	14.952(2)	15.952(3)	9.332(2)
c, Å	23.025(3)	12.096(1)	9.467(2)	13.657(3)
α, deg	90	90	90	90
β, deg	98.98(1)	102.44(1)	98.285(4)	90.587(4)
γ, deg	90	90	90	90
V, Å^3	2079.1(5)	1839.0(4)	1722.6(5)	1602.4(6)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.161	1.121	1.185	1.278
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073
2θ range, deg	3.2 to 56.0	3.4 to 56.0	3.6 to 56.1	4.4 to 56.0
μ, mm^{-1}	0.059	0.062	0.068	0.085
F(000)	760	656	648	656
no. of obsd reflns	5023	8294	4147	3861
no. of params refnd	262	433	217	208
goodness of fit	1.023	1.005	0.972	1.027
R1	0.057	0.059	0.051	0.054
wR2	0.158	0.122	0.129	0.137

	V-1h	**V-1n**	**V-1o**	**V-1'o**
formular	$C_{14}H_{30}B_{10}$	$C_{34}H_{30}B_{10}$	$C_{22}H_{30}B_{10}O_2$	$C_{22}H_{30}B_{10}O_2$
crystal size	0.40 x 0.30 x	0.40 x 0.30 x	0.40 x 0.30 x	0.30 x 0.20 x
(mm)	0.20	0.20	0.20	0.20
fw	306.48	546.68	434.56	434.56
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/m$	$P(-1)$	$P(-1)$	$P(-1)$
a, Å	9.932(1)	11.171(2)	6.546(6)	8.871(1)
b, Å	10.652(1)	11.415(2)	12.647(11)	9.580(1)
c, Å	10.052(1)	13.505(3)	15.303(14)	15.712(1)
α, deg	90	94.33(1)	93.46(2)	80.99(1)
β, deg	115.14(1)	106.82(1)	90.41(2)	88.55(1)
γ, deg	90	99.08 (1)	100.42(2)	71.30(1)
V, Å^3	962.6(1)	1614.3(5)	1243.5(19)	1248.7(2)
Z	2	2	2	4
D_{calcd}, Mg/m^3	1.057	1.125	1.161	1.156
radiation (λ), Å	0.71073	0.71073	0.71073	1.54178
2θ range, deg	4.5 to 50.0	3.2 to 50.0	2.7 to 50.5	5.7 to 135.4
μ, mm^{-1}	0.051	0.059	0.065	0.484
$F(000)$	328	568	456	456
no. of obsd reflns	1787	5668	4079	4282
no. of params refnd	127	397	307	308
goodness of fit	1.020	1.045	1.119	0.942
R1	0.069	0.059	0.113	0.076
wR2	0.192	0.151	0.307	0.176

	V-6o	**V-8b**	**V-9**	**VI-4a**
formular	$C_{12}H_{22}B_{10}O$	$C_{12}H_{24}B_{10}$	$C_{46}H_{86}B_{20}Cl$ $LiN_2Ni_2O_5$	$C_{14}H_{30}B_{10}$
crystal size (mm)	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30
fw	290.40	276.41	1123.18	306.48
crystal system	triclinic	orthorhombic	triclinic	monoclinic
space group	*P*(-1)	*Pbca*	*P*(-1)	$P2_1/c$
a, Å	7.807(8)	18.004(3)	11.388(3)	9.63(1)
b, Å	9.509(1)	18.596(3)	14.951(3)	17.65(1)
c, Å	12.428(1)	19.838(3)	19.334(4)	12.05(1)
α, deg	73.32(1)	90	86.53(1)	90
β, deg	84.61(1)	90	83.80(1)	111.74(1)
γ, deg	77.33(1)	90	74.03(1)	90
V, $Å^3$	861.8(1)	6639(2)	3145(1)	1901(2)
Z	2	16	2	4
D_{calcd}, Mg/m^3	1.119	1.106	1.186	1.071
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073
2θ range, deg	3.4 to 50.5	3.8 to 50.0	2.1 to 50.0	4.3 to 50.0
μ, mm^{-1}	0.058	0.053	0.683	0.052
F(000)	304	2336	1184	656
no. of obsd reflns	3107	5845	11023	3355
no. of params refnd	208	397	694	217
goodness of fit	1.014	1.044	1.025	1.044
R1	0.056	0.072	0.080	0.075
wR2	0.143	0.184	0.205	0.161

	VI-4b	**VI-4d**	**VI-4j**	**VI-4m**
formular	$C_{15}H_{32}B_{10}$	$C_{17}H_{38}B_{10}Si$	$C_{31}H_{32}B_{10}$	$C_{23}H_{32}B_{10}$
crystal size	0.40 x 0.30 x	0.50 x 0.40 x	0.50 x 0.40 x	0.40 x 0.30 x
(mm)	0.20	0.30	0.30	0.20
fw	320.51	378.66	512.67	416.59
crystal system	orthorhombic	orthorhombic	trigonal	monoclinic
space group	$Pna2_1$	$P2_12_12_1$	$R(-3)$	$P2_1$
a, Å	17.16(2)	9.771(3)	38.990(1)	12.641(1)
b, Å	9.76(1)	14.550(5)	38.990(1)	8.951(1)
c, Å	12.10(1)	16.814(6)	12.161(1)	22.288(2)
α, deg	90	90	90	90
β, deg	90	90	90	98.53(1)
γ, deg	90	90	120	90
V, Å^3	2026(3)	2390(1)	16011(1)	2493.8(4)
Z	4	4	18	4
D_{calcd}, Mg/m^3	1.051	1.052	0.957	1.110
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073
2θ range, deg	4.7 to 50.0	3.7 to 50.5	3.5 to 50.0	1.8 to 50.0
μ, mm^{-1}	0.051	0.100	0.050	0.056
$F(000)$	688	816	4824	880
no. of obsd reflns	2873	4328	6196	8299
no. of params refnd	226	253	371	595
goodness of fit	1.082	1.049	1.056	1.001
R1	0.048	0.039	0.069	0.052
wR2	0.106	0.108	0.205	0.103

	VI-5m	**VI-7b**
formular	$C_{23}H_{32}B_{10}$	$C_{13}H_{22}B_{10}$
crystal size	0.50 x 0.40 x	0.50 x 0.40 x
(mm)	0.30	0.30
fw	416.59	286.41
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	8.939(1)	9.31(1)
b, Å	17.671(2)	7.73(1)
c, Å	16.068(2)	24.42(2)
α, deg	90	90
β, deg	91.45(1)	91.05(1)
γ, deg	90	90
V, Å^3	2537.3(5)	1757(2)
Z	4	4
D_{calcd}, Mg/m^3	1.091	1.083
radiation (λ), Å	0.71073	0.71073
2θ range, deg	3.4 to 50.5	3.3 to 50.0
μ, mm^{-1}	0.055	0.052
F(000)	880	600
no. of obsd reflns	4575	3092
no. of params refnd	298	208
goodness of fit	1.094	1.035
R1	0.082	0.090
wR2	0.248	0.251

Appendix III. X-ray crystallographic data in CIF (electronic form)