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Nickel-catalyzed 1,2-dialkenylation of *o*-carboranes with alkenyl bromides

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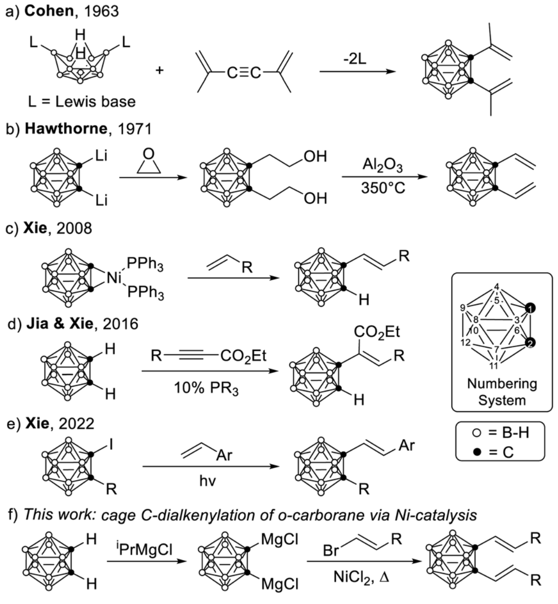
A nickel-catalyzed cross-coupling reaction of *o*-carboranyl with alkenyl bromides has been developed, affording a series of 1,2-dialkenylated *o*-carboranes with a broad substrate scope. This reaction provides an efficient and concise strategy for *C*,*C*′-dialkenylation of *o*-carboranes and supplements the transition-metal catalyzed cage B–H functionalization systems.

Icosahedral carboranes are a class of boron–carbon molecular clusters with characteristic properties, including three-dimensional aromaticity, inherent robustness, high hydrophobicity, and high boron content.[1,2] The carborane derivatives have found wide applications in different fields, ranging from medicine,[3] materials,[4] and coordination/organometallic chemistry[5] to catalysis.[6] In recent years, the development of efficient methodologies for the functionalization of carboranes on either C–H[1,7] or B–H[8] vertices has received increasing research attention and achieved significant progress. A conventional method for cage-*C* functionalization utilized the acidic nature of cage-CH to generate nucleophilic carbon centers with a strong base, which can subsequently react with electrophiles.[1a] Nevertheless, such a synthetic strategy was not practical for alkenylation or arylation of carboranes on the cage C position.

The first synthesis of 1,2-dialkenyl-*o*-$C_2B_{10}H_{10}$ was achieved by Cohen and co-workers through the condensation reaction of decaborane with diisopropenylacetylene giving a very low yield (Scheme 1a).[9] In 1971, Hawthorne and co-workers reported the synthesis of 1,2-diethenylated *o*-carborane *via* an elimination reaction of a carboranyl diol at a very high temperature (350 °C) with only one example (Scheme 1b).[10] In 1986, Zakharkin and co-workers reported that treatment of 1,2-Li_2-*o*-$C_2B_{10}H_{10}$ with perfluoropropylene produced 1,2-di(perfluoropropylenyl)-*o*-carborane in moderate yields.[11] These reactions suffered from low yields and limited substrate scope. In recent years, our group has established diversified methods for the synthesis of 1-alkenyl-*o*-carboranes, including the reaction of nickel carborane with alkenes (Scheme 1c),[12] phosphine-catalyzed coupling of *o*-carborane with electron-deficient alkynes (Scheme 1d)[13] and light-enabled cage *C*-alkenylation with unactivated alkenes *via* a radical process (Scheme 1e).[14] Nevertheless, only mono-alkenylated *o*-carboranes could be prepared by these methods, although with high efficiency and good compatibility with a wide range of substrates. Compared to feasible cage BH dialkenylations *via* transition metal catalysis,[15] there is no reported catalytic method for cage *C*-dialkenylated *o*-carboranes as of now.

In 2015, a nickel-catalyzed 1,2-diarylation of *o*-carboranyl with aryl iodides was developed by our group, offering a practical approach for synthesizing *C*,*C*′-diarylated *o*-carboranes with high efficiency.[16] In this connection, we initiated a study to



Scheme 1 Cage carbon alkenylation of *o*-carboranes.

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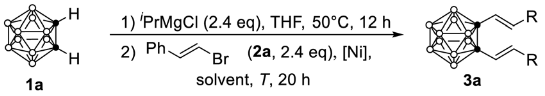
develop a transition metal catalyzed 1,2-dialkenylation of *o*-carboranes. Herein we present a nickel-enabled cross-coupling of *o*-carboranyl with alkenyl bromides for the efficient preparation of a variety of 1,2-dialkenyl-*o*-carboranes.

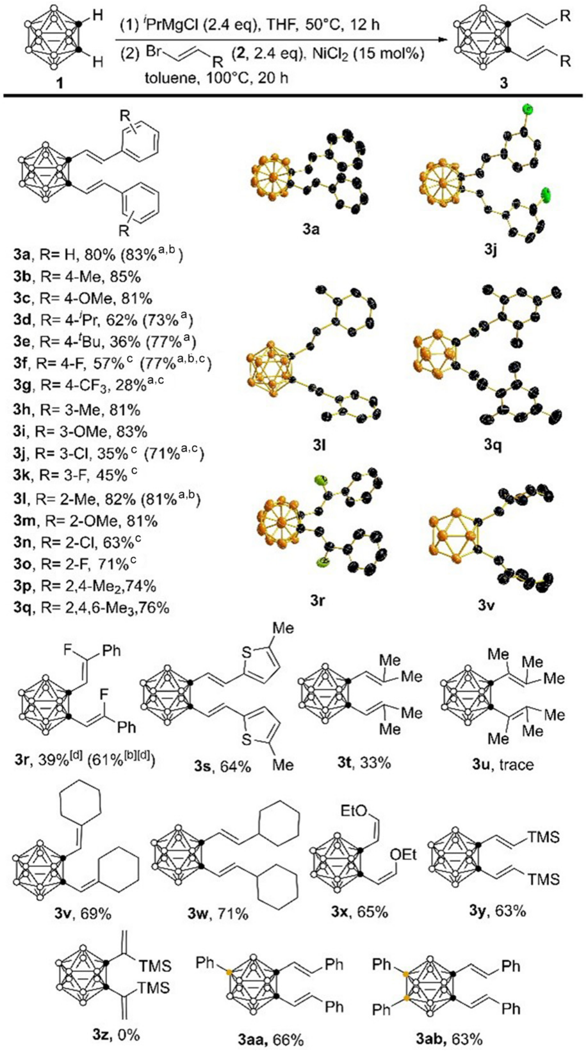
We commenced our study by screening the reaction temperature for the cross-coupling of 1,2-$(MgCl)_2$-*o*-$C_2B_{10}H_{10}$ with β-bromostyrene (**2a**) in toluene with $NiCl_2$ as the catalyst. 1,2-$(MgCl)_2$-*o*-$C_2B_{10}H_{10}$ was prepared *in situ* by treating 1.0 equiv. of *o*-carborane with 2.4 equiv. of ^{i}PrMgCl in THF at 50 °C for 12 h. With 30 mol% of $NiCl_2$ in toluene at 120 °C, the desired product **3a** was obtained in 94% GC yield (entry 1, Table 1). High temperature was required for such a coupling, while the reaction at 80 °C resulted in a decreased yield of **3a** to 81% (entries 2 and 3, Table 1). When the catalyst loading was lowered to 15 mol%, no change was observed in the yield of **3a**. But a further decrease to 10 mol% reduced the yield of **3a** to 88% (entries 4 and 5, Table 1). Other nickel catalysts (entries 6–9, Table 1) and solvents (entries 10–12, Table 1) were less effective. Accordingly, the conditions shown in entry 4 (Table 1) were considered to be the optimum reaction conditions.

Table 1 Optimization of the reaction conditions[a]



Entry	[Ni] (mol%)	Solvent	*T* [°C]	Yield[b] (%)
1	$NiCl_2$ (30)	Toluene	120	94
2	$NiCl_2$ (30)	Toluene	100	93
3	$NiCl_2$ (30)	Toluene	80	81
4	$NiCl_2$ (15)	Toluene	100	93
5	$NiCl_2$ (10)	Toluene	100	88
6	$NiBr_2$ (15)	Toluene	100	80
7	$Ni(PMe_3)Cl_2$ (15)	Toluene	100	24
8	$Ni(PPh_3)Cl_2$ (15)	Toluene	100	29
9	Ni(dppe)Cl_2 (15)	Toluene	100	61
10	$NiCl_2$ (15)	THF	100	76
11	$NiCl_2$ (15)	Hexane	100	Trace
12	$NiCl_2$ (15)	Et_2O	100	Trace

THF = tetrahydrofuran. Et_2O = diethyl ether. [a] Reactions were conducted on a 0.2 mmol scale of **1a** in 2 mL of solvent in a closed flask for 20 h. [b] GC yield.



Scheme 2 Synthesis of 1,2-dialkenyl-*o*-carboranes (isolated yields are presented). [a] General conditions: **1** (0.20 mmol), **2** (0.48 mmol), $NiCl_2$ (15%), toluene (2.0 mL), 100 °C, 20 h. Isolated yield. [b] $NiCl_2$ (30%), 130 °C, 72 h. [c] 2.0 mmol scale instead of 0.2 mmol. [d] Tol/THF = 50 : 1.

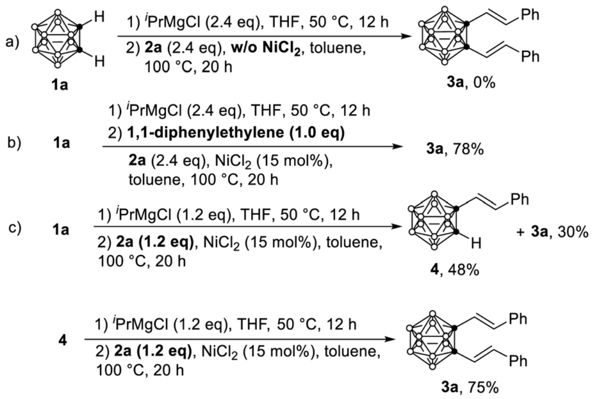
Subsequently, the substrate scope of this coupling was examined, and the results are shown in Scheme 2. β-Bromostyrenes with various functional groups, including alkyl, methoxyl, thienyl, trifluoromethyl and halides, were well tolerated to afford the corresponding 1,2-dialkenyl-*o*-carboranes in 28%–85% yields (**3a**–**3s**). In general, electron-donating substituents led to higher yields than the corresponding electron-withdrawing ones, regardless of their positions on the phenyl rings. However, for **3d** with an ^{i}Pr group and **3e** with a ^{t}Bu group, the lower yields of dialkenylated products might be related to the difficult installation of the second alkenyl group probably due to the steric effect, since monoalkenylated carboranes were observed in the reaction mixture. Harsher conditions, including higher temperature, a larger dose of the catalyst, a longer reaction time, and/or a small amount of THF, could effectively increase the yields of **3d**–**3g**, **3j**–**3k**, **3n**–**3o** and **3r**, which bear either a sterically-bulky or electron-withdrawing group. Also, alkyl, alkoxyl and trimethylsilyl bromoalkenes were compatible, giving **3t** and **3v**–**3y** in 33%–71% yields, comparable to those of β-bromostyrenes. Moreover, substitution on the α-carbon of bromoalkenes would inhibit such a coupling reaction, comparing **3t** with **3u** (33% *vs.* trace) and **3y** with **3z** (63% *vs.* 0%). The reason might be ascribed to the increased steric hindrance around the reaction center, which might impede oxidative addition or the subsequent reductive elimination step. Notably, the isolation of **3x** as a single isomer confirmed the retention of the *E* or *Z* configuration of the alkenyl group in this coupling as the double bond remains intact during the reaction. On the other hand, the coupling of B(9)-phenyl- and B(9,12)-diphenyl-*o*-carborane worked well to produce the desired products **3aa** and **3ab** in 63%–66% yields. In addition, the isolated yields remained almost unchanged if the reactions were scaled up by 10 times (**3a**, **3f** and **3l** in Scheme 2).

Compounds **3** were fully characterized using ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy and high-resolution mass spectrometry (HRMS). Their ^{11}B{^{1}H} NMR spectra exhibited either a 2 : 8 or a 2 : 2 : 6 pattern, consistent with that of 1,2-disubstituted *o*-carboranes. The signals of cage-carbon atoms were found at about 80 ppm in the ^{13}C{^{1}H} NMR spectra. The molecular structures of **3a**, **3j**, **3l**, **3q**, **3r**, and **3v** were further confirmed by single-crystal X-ray analyses.

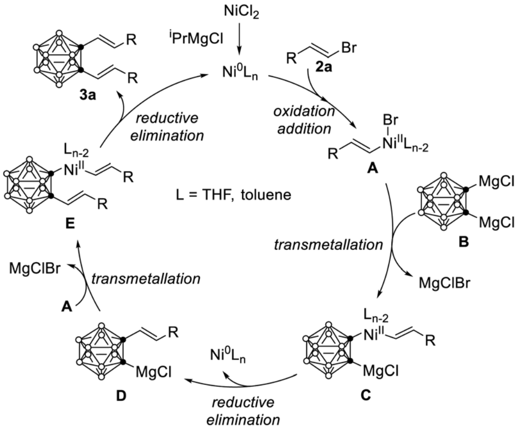
To gain some insights into the mechanism, the following control experiments were conducted. No reaction occurred in the absence of $NiCl_2$, indicating the indispensability of nickel catalysts (Scheme 3a). The yield of **3a** remained unaffected in the presence of 1.0 equiv. of 1,1-diphenylethylene as the radical trapping agent, obviating the involvement of a radical pathway (Scheme 3b).[17] The coupling reaction of 1-MgCl-*o*-$C_2B_{10}H_{11}$ and **2a** gave mono-substituted product **4** in a yield of 48%. Treatment of **4** with 1.2 equiv. of ^{i}PrMgCl and subsequent coupling with **2a** generated **3a** in 75% isolated yield, revealing that such a Kumada-type coupling proceeded in a stepwise manner (Scheme 3c).[18]

Based on the aforementioned experimental results and literature reports,[16,18] a plausible mechanism is proposed in Scheme 4. The catalytic cycle starts from *in situ* generation of Ni0 species *via* the reduction of $NiCl_2$ by Grignard reagents. Oxidative addition of alkenyl bromides on Ni0 leads to the formation of an [alkenyl-$Ni^{II}Br(solvent)_2$] complex (**A**). Transmetallation between **A** and 1,2-$(MgCl)_2$-*o*-carborane (**B**) affords intermediate **C**, followed by reductive elimination to give 1-alkenyl-2-MgCl-*o*-carborane (**D**) and regenerate catalytic Ni0 species. From **D**, a repeat of this catalytic cycle produces **3a** as the final product.

In summary, a nickel-catalyzed cross-coupling reaction of *o*-carboranyl with alkenyl bromides has been developed. Electronic effects are distinct where electron-rich substrates surpass electron-deficient ones. The reaction scales can be properly enlarged with high yields. This reaction demonstrates a broad substrate scope with good compatibility towards various functional groups, enabling the synthesis of a series of *C*,*C*′-dialkenylated *o*-carboranes. This method offers a straightforward and efficient approach for one-step incorporation of two alkenyl functionalities into *o*-carborane frameworks, providing valuable synthons for the construction of complex structures with potential applications in materials science.



Scheme 3 Control experiments.



Scheme 4 Proposed mechanism.

Conflicts of interest

There are no conflicts to declare.

Data availability

Supplementary information (SI): experimental details and characterization data. See DOI: https://doi.org/10.1039/d5dt02451j.

CCDC 2491517–2491522 (**3a**, **3j**, **3l**, **3q**, **3r** and **3v**) contain the supplementary crystallographic data for this paper.[19a–f]

Acknowledgements

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