Coupling Reactions

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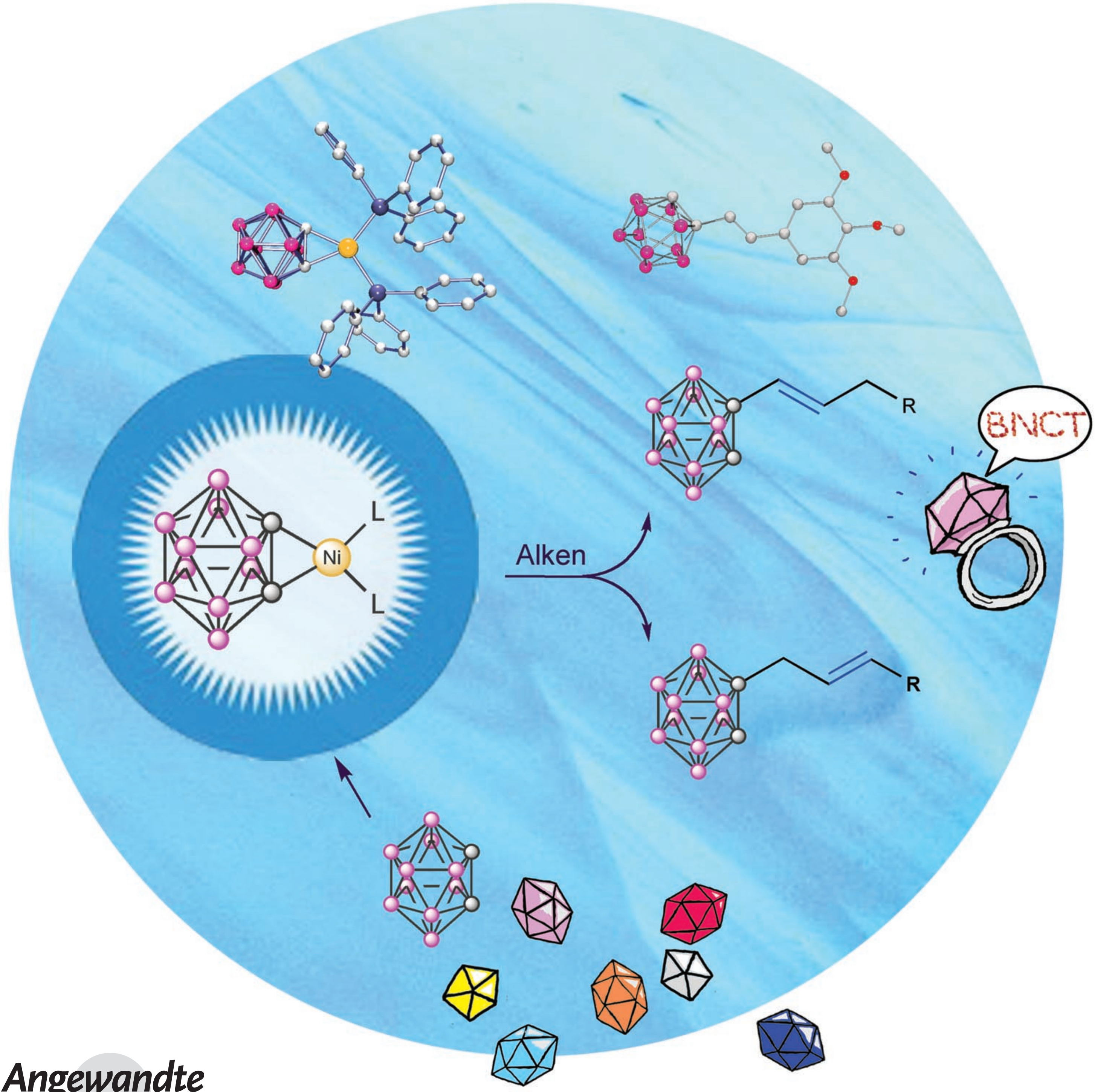
Nickel-Mediated Coupling Reactions of Carboryne with Alkenes: A Synthetic Route to Alkenylcarboranes**

*Zaozao Qiu and Zuowei Xie**



Metal–benzyne complexes have found many applications in organic synthesis, mechanistic studies, and the synthesis of functional materials.[1] In contrast, the isolobally analogous metal–carboryne complexes[2] are largely unexplored, although the reactivity pattern of carboryne (generated in situ) has been actively investigated.[3–5] We have recently demonstrated the complementary reactivities of $[Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})]$ (produced in situ, $Cp = C_5H_5$)[6] and $[(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)_2]$ (**1**).[7] The former reacts readily with polar unsaturated organic substrates, such as those containing isonitrile, nitrile, and azide groups to give monoinsertion products; however, it does not show any activity toward internal alkynes.[6] The latter (**1**) undergoes regioselective [2+2+2] cycloaddition with alkynes to afford benzocarboranes, but it does not react with the polar unsaturated molecules listed above.[7] These results indicate that the nature of the transition metals plays a crucial role in these reactions. We have extended our research to include alkenes, and report herein their reaction with nickelcarboryne to afford alkenylcarboranes.

In a typical procedure, the alkene (2 equiv) was added to a solution of nickel–carboryne **1**, prepared in situ by the reaction of $Li_2C_2B_{10}H_{10}$ with $[NiCl_2(PPh_3)_2]$ in THF, and the reaction mixture was heated at 90 °C in a closed vessel overnight. Standard workup procedures afforded the coupled products in excellent regio- and steroselectivity for most alkenes (Table 1). The temperature is crucial for this reaction; no reaction occurred at less than 60 °C. In contrast, higher reaction temperatures (> 90 °C) led to the decomposition of **1**, as indicated by ^{11}B NMR spectroscopy. Toluene and diethyl ether were not suitable for this reaction because of the poor solubility of **1** in these solvents. Reactions that employed other phosphine compounds such as PEt_3, $P(OEt)_3$, and 1,2-bis(diphenylphosphino)ethane (dppe) gave very similar results to those obtained using PPh_3. The use of the isolated pure complex **1** as the starting material gave the same results as the complex used in situ.

As shown in Table 1, a variety of alkenes are compatible with this nickel-mediated cross-coupling reaction. Substituted styrene derivatives reacted efficiently to give "Heck-type" products **3** as single regioisomers with excellent stereoselectivity and in very good yields. The nature of the substituents on the phenyl ring has no apparent effect on the reactions (entries 1–5). The yields were lower for 1,1-diphenylethene and vinyltrimethylsilane because of steric effects (entries 7 and 8). The "ene-reaction-type" products were isolated in good yields for aliphatic alkenes and α-methylstyrene (**2f**, entries 6, 9–11). For example, **4k** was isolated in 67 % yield, which is much higher than the 10–20 % yield from the direct reaction of carboryne with cyclohexene.[3] Vinyl ethers **2n** and **2o** also reacted with nickel carboryne **1**, but the coupled products were formed in low yields, probably because of the coordination of the oxygen atom that occupies the vacant site of the nickel atom (entries 14 and 15). Such interactions may alter the regioselectivity of the olefin insertion and stabilize the inserted product, which leads to the formation of **5n** after hydrolysis. In the case of norbornene (**2l**), the corresponding inserted product was thermodynamically very stable,[8] and afforded only hydrolysis product **5l** in 60 % isolated yield (entry 12). No double-insertion product was observed. For indene (**2m**), both hydrolysis product **5m** and "ene-reaction-type" product **3m** were isolated in 27 % and 31 % yield, respectively (entry 13). No reaction was observed with *cis*- and *trans*-stilbene, 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 mass spectrometry.[9a] The molecular structure of **3e** was further confirmed by single-crystal X-ray analyses (Figure 1).[9b]

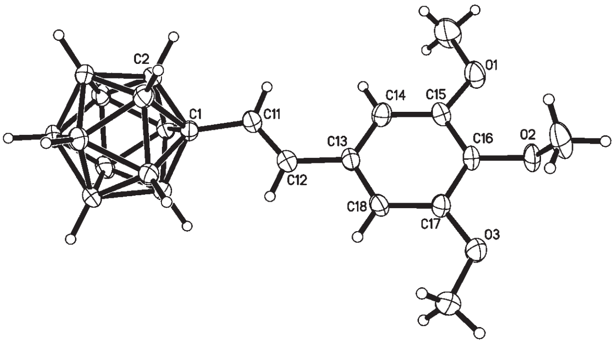


Figure 1. Molecular structure of **3e**. Selected bond lengths (Å) and angles (°): C1–C2 1.626(3), C1–C11 1.495(3), C11–C12 1.302(3), C12–C13 1.475(3), C1-C11-C12 122.2(2), C11-C12-C13 129.1(2).

The reaction of carboryne (generated in situ) with anthracene, furan, or thiophene has been shown to yield [2+4] cycloaddition products.[5] The nickel carboryne **1**, however, did not react with any of these molecules. This result suggests that carboryne and nickel carboryne should undergo different reaction pathways in reactions with alkenes.

Scheme 1 shows a plausible mechanism for the formation of the coupled products. Dilithiocarborane reacts with $[NiCl_2(PPh_3)_2]$ to generate the nickel carboryne **1**.[2a] Coordination and insertion of the alkene gives a nickelacycle **A**.[10] The regioselectivity observed in the reaction can be rationalized by the large steric effect of the carborane moiety. β-H/β′-H elimination prior to the insertion of the second molecule of alkene produces the intermediate **B**/**B′**.[11] Reductive elimination affords the alkenylcarboranes **3** ("Heck-type" products) or **4** ("ene-reaction-type" products). In general, β-H elimination of five-membered metallacycles is more difficult

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[*] Z. Qiu, Prof. Dr. Z. Xie
Department of Chemistry and
Center of Novel Functional Molecules
The Chinese University of Hong Kong
Shatin, N.T., Hong Kong (China)
Fax: (+852) 2603-5057
E-mail: zxie@cuhk.edu.hk

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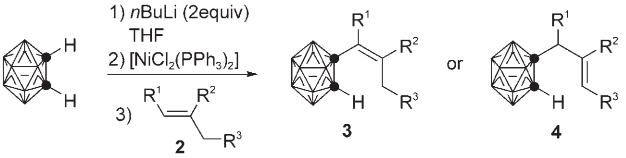
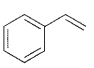
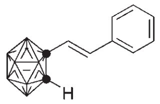
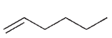
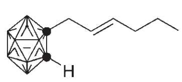
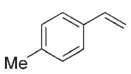
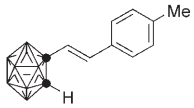
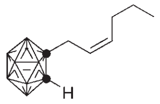
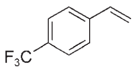
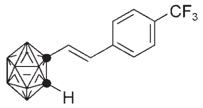
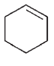
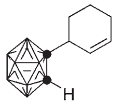
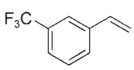
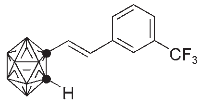
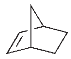
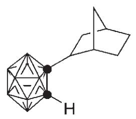
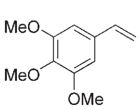
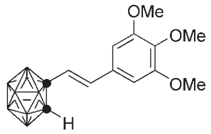
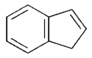
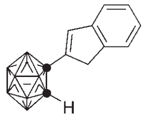
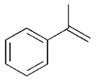
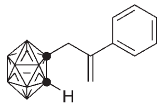
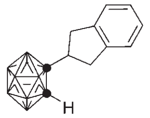
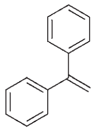
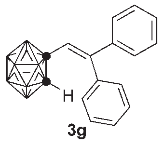
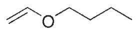
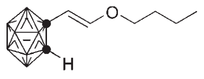
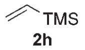
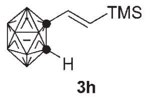
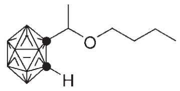
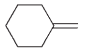
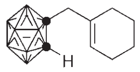
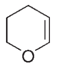
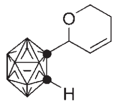
Table 1: Nickel-mediated coupling reaction of carboryne with alkenes.



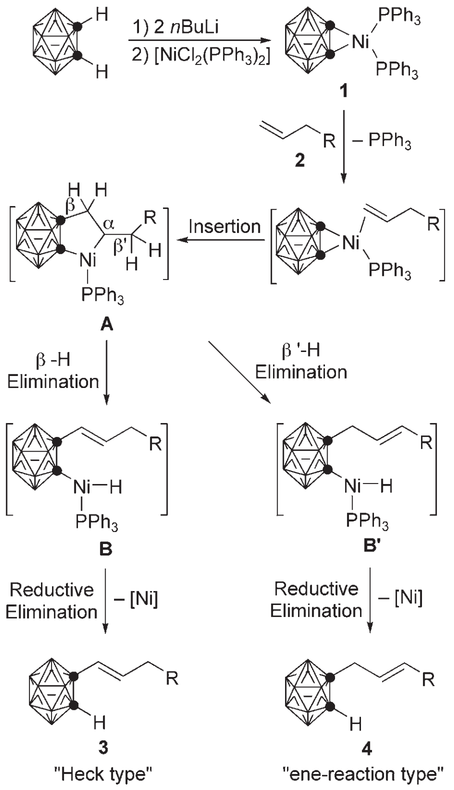
Entry	Alkene	Product	Yield [%][a]	Entry	Alkene	Product	Yield [%][a]
1	 **2a**	 **3a**	82	10	 **2j**	 *trans*-**4j**	74 (1:1)[b]
2	 **2b**	 **3b**	85			 *cis*-**4j**	
3	 **2c**	 **3c**	80	11	 **2k**	 **4k**	67
4	 **2d**	 **3d**	73	12	 **2l**	 **5l**	60[c]
5	 **2e**	 **3e**	76	13	 **2m**	 **3m**	31
6	 **2f**	 **4f**	59			 **5m**	27[c]
7	 **2g**	 **3g**	46	14	 **2n**	 **3n**	18
8	 **2h**	 **3h**	46			 **5n**	12[c]
9	 **2i**	 **4i**	77	15	 **2o**	 **4o**	15

[a] Isolated yields. [b] *cis/trans*-**4j** were inseparable and their ratio was estimated from ^{1}H NMR spectra. [c] Isolated after hydrolysis.

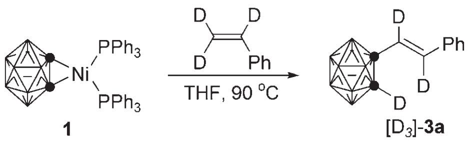
than β′-H elimination.[11] Such hydrogen elimination reactions may be suppressed for steric reasons[8] or because of intramolecular coordination of the heteroatom, which leads to the formation of alkylcarboranes after hydrolysis (Table 1, entries 12–14).

The aforementioned mechanism is supported by the following experiment. Treatment of **1** with [D$_3$]styrene in THF at 90 °C gave [D$_3$]-**3a** in 80 % yield with greater than 95 % deuterium incorporation (Scheme 2).

In summary, we have developed a nickel-mediated coupling reaction of carboryne with a variety of alkenes, which affords alkenylcarboranes in moderate to very good yields and excellent regio- and stereoselectivity. This provides a new methodology for the synthesis of alkenylcarboranes.



Scheme 1. Proposed mechanism for the formation of coupled products.



Scheme 2. Reaction of **1** with [D$_3$]styrene.

This work also demonstrates that nickel carboryne **1** exhibits different reactivity patterns toward alkynes and alkenes.

Experimental Section

General procedure: [NiCl$_2$(PPh$_3$)$_2$] (1.0 mmol) was added to a solution of Li$_2$C$_2$B$_{10}$H$_{10}$ (1.0 mmol) in THF (5 mL), prepared in situ from the reaction of *n*BuLi (2.0 mmol) with *o*-carborane (1.0 mmol). The reaction mixture was stirred at room temperature for 0.5 h to give the nickel carboryne complex **1**.[2a] The 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 subjected to column chromatography on silica gel to give the coupled product.

Keywords: alkenes · C—C coupling · carboranes · metalation · nickel

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[9] a) Complete characterization data are provided in the Supporting Information; b) crystal data for **3e**: C$_{13}$H$_{24}$B$_{10}$O$_3$, $M_r = 336.4$, monoclinic, space group $P2_1$, $a = 7.275(7)$, $b = 10.326(10)$, $c = 13.105(13)$ Å, $\beta = 103.60(2)°$, $V = 956.85(16)$ Å^3, $T = 296$ K, $Z = 2$, $\rho_{calcd} = 1.168$ g cm^{-3}, $2\theta_{max} = 50°$, $\mu(\mathrm{Mo}_{K\alpha}) = 0.71073$ Å. A total of 7002 reflections were collected and led to 3224 unique reflections, 3224 of which with $I > 2\sigma(I)$ were considered as observed, $R_1 = 0.0432$, wR_2 (F^2) = 0.1081. This structure was solved by direct methods and refined by full-matrix least-squares on F^2 by using the SHELXTL/PC package of crystallographic software.[12] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were geometrically fixed using the riding model. CCDC 685436 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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