C–H Activation

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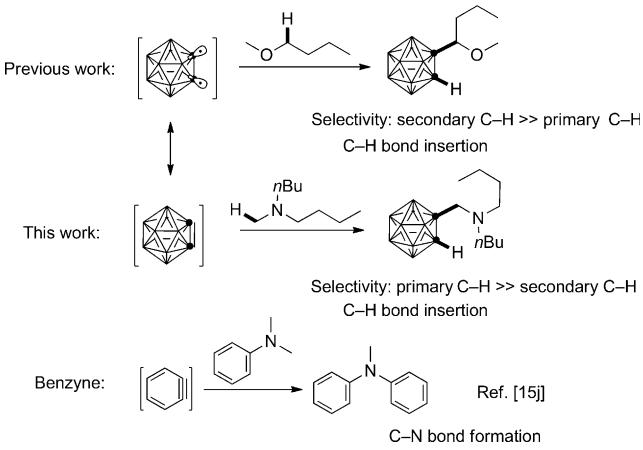
Regioselective Insertion of *o*-Carborynes into the α-C–H Bond of Tertiary Amines: Synthesis of α-Carboranylated Amines**

*Da Zhao, Jiji Zhang, and Zuowei Xie**

Abstract: *o-Carboryne can undergo α-C–H bond insertion with tertiary amines, thus affording α-carboranylated amines in very good regioselectivity and isolated yields. In this process, the nucleophilic addition of tertiary amines to the multiple bond of o-carboryne generates a zwitterionic intermediate. An intramolecular proton transfer, followed by a nucleophilic attack leads to the formation of the final product. Thus, regioselectivity is highly dependent upon the acidity of α-C–H proton of tertiary amines. This approach serves as an efficient methodology for the preparation of a series of 1-aminoalkyl-o-carboranes.*

The α-functionalization of tertiary amines has received considerable attention because of the increasing interest in C–C bond formation[1] and the importance of amines and alkaloids in medicinal chemistry.[2] To achieve this goal, several strategies such as lithiation,[3] amine radical formation,[4] and transition-metal-catalyzed C–H bond activation[5] have been developed. Among them, iminium ions are one of the key intermediates for the construction of amine stereocenters.[5d,6] In contrast, a growing interest has been directed towards the synthesis of *o*-carborane derivatives bearing organic nitrogen groups because of their potential application in medicinal chemistry[7] and catalysis.[8] For instance, carborane/amino acid or carborane/nucleoside combinations serve as excellent candidates for cancer treatment in boron neutron capture therapy (BNCT).[7b–e,9] Moreover, aminoalkyl *o*-carboranes have been extensively employed as ligands for the preparation and characterization of metal complexes.[8,10] Despite the remarkable progress in carborane chemistry, straightforward and general synthesis of such aminoalkyl *o*-carboranes still represents a challenging task.[11] Herein, we describe a highly regioselective α-carboranylation of tertiary amines for the convenient synthesis of 1-aminoalkyl-*o*-carboranes.

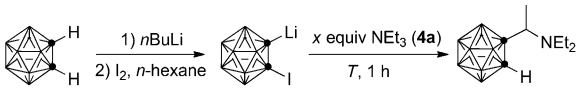
We reported previously that *o*-carboryne (**3a**),[12] a very reactive intermediate, can insert into an ethereal α-C–H bond with the regioselectivity for secondary C–H bonds being much greater than that of primary C–H bonds (Scheme 1).[13a] In view of the α-C–H bond dissociation energy of amines being smaller than that of ethers,[14] we wondered whether α-functionalization of amines could be achieved in a similar manner.



Scheme 1. Reaction of *o*-carboryne (**3a**) with ethers and tertiary amines.

The reaction of 1-iodo-2-lithio-*o*-carborane (**2a**) with triethylamine (**4a**) was chosen as a model to establish the reaction conditions (Table 1). Heating an *n*-hexane suspension of **2a** in the presence of 20 equivalents of **4a** at 60 °C for 1 hour afforded only the α-carboranylated amine **5aa** in 67 % yield upon isolation after workup (Table 1, entry 1). Lowering the amount of **4a** to 10 equivalents gave **5aa** in 72 % (Table 1, entries 2 and 3). Increasing the reaction temperature to 80 °C did not improve the yield (Table 1, entry 4). Heating is necessary for this reaction as only trace amounts of **5aa** were formed at room temperature after 12 hours (Table 1, entry 6).

Table 1: Optimization of reaction conditions.



1a **2a** **5aa**

Entry	**4a** (equiv)	*T* [°C]	**5aa** [%][a]
1	20	60	67
2	10	60	72
3	5	60	55[b]
4	10	80	70
5	10	40	58
6[c]	10	25	trace

[a] Yield of isolated product. [b] **2a** was not completely consumed. [c] 12 h.

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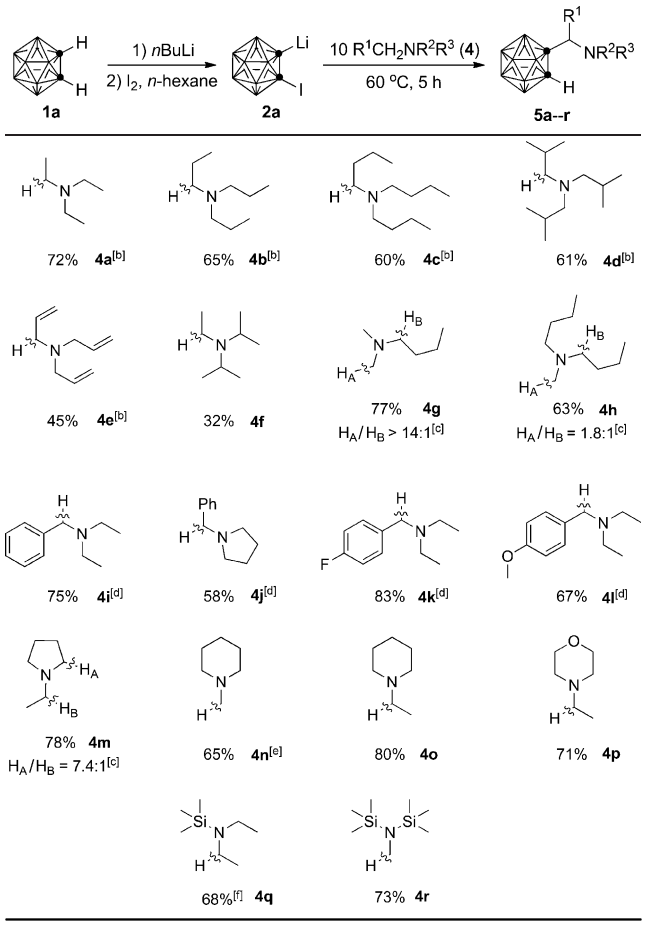
This result suggests that *o*-carboryne favors insertion into the α-C–H bond of amines with the formation of the C–C bond rather than the C–N bond as is observed in the reaction of benzyne (Scheme 1).[15]

Under the optimal reaction conditions (Table 1, entry 2), the substrate scope was examined and the results are compiled in Table 2. Similar to triethylamine (**4a**), the

Table 2: α-Carboranylation of tertiary amines.[a]



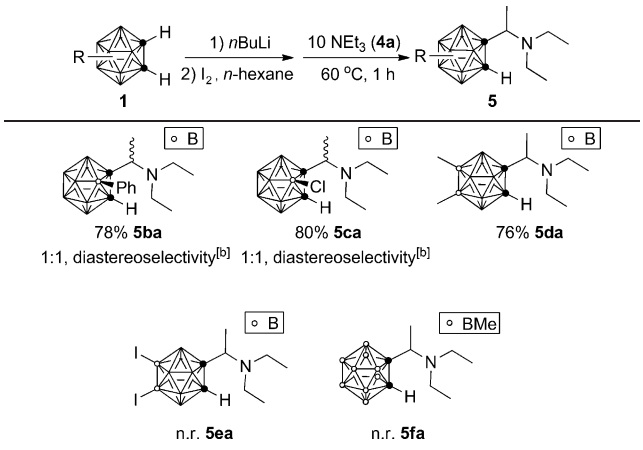
[a] Yield of isolated product. [b] 1 h. [c] Determined by ^{1}H NMR spectroscopy. [d] 2.5 equiv of amine was used. [e] **2a** was not completely consumed. [f] Desilylation occurred during isolation.

symmetrical amines **4b–d** worked well with decreased yields, which might be associated with the increased steric hindrance. Although both GC/MS and NMR spectra indicated a very high conversion, the reaction of triallylamine (**4e**) resulted in only 45% yield, probably because of the loss in purification on silica gel. *N*,*N*-Diisopropylethylamine (**4f**) was a poor substrate because of large steric hindrance imposed by the two isopropyl groups. For unsymmetrical tertiary amines, an intriguing regioselective preference was observed. For instance, *N*,*N*-dimethylbutylamine (**4g**) or *N*-methyldibutylamine (**4h**) underwent α-carboranylation in good yields with greater than 14:1 or 1.8:1 selectivity for methyl C–H bond cleavage over that of a secondary C–H bond, thus reflecting an inherent greater than 4.7:1 or about 2.4:1 selectivity after considering the number of primary and secondary C–H bonds present in either **4g** or **4h**. An exclusive preference for α-carboranylation at the benzylic position over the aliphatic position was observed for the benzylamines **4i–l**. A fluoro substitution (**4k**) at the *para* position of the benzyl group increased the yield, while a methoxy substituent (**4l**) rendered the reaction less efficient. The above results suggest that α-carboranylation occurs preferentially at the more acidic positions or more electron-deficient C–H bonds (methyl versus *n*-butyl; benzyl versus aliphatic).

For cyclic amines, the reaction was dependent upon the ring size probably because of steric reasons (Table 2).[16] For example, the five-membered cyclic amine **4m** was found to undergo α-carboranylation with about a 3.7:1 selectivity for cyclic positions over the aliphatic chain positions, whereas the cyclic positions of six-membered cyclic amines **4n** and **4o** were completely inactive. Similarly, the reaction of *N*-ethylmorpholine (**4p**) furnished only the ethyl carboranylated amine, no ethereal C–H cleavage was observed. *N*,*N*-Diethyltrimethylsilylamine (**4q**) and *N*,*N*-bistrimethylsilylmethylamine (**4r**) also worked well to give **5q** (68%) and **5r** (73%), respectively.

Effects of cage B substituents on α-carboranylation were also examined (Table 3). Two diastereoisomers were formed in a 1:1 ratio for 3-substitued carboranes (**5ba** and **5ca**).[13,17] A significant electronic effect was observed (**5da–fa**). For example, the 9,12-dimethyl carboranylated amine **5da**[18] was obtained in 76% yield, whereas no reaction was observed for either 9,12-diiodo-*o*-carborane (**1e**)[19] or 4,5,7,8,9,10,11,12-octamethyl-*o*-carborane (**1f**).[20]

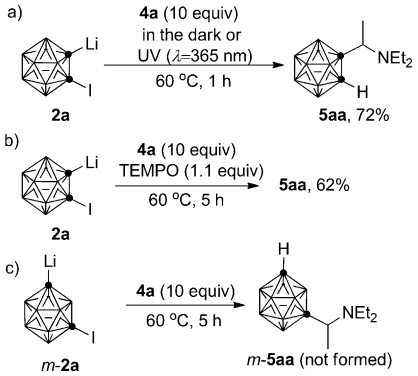
Table 3: Effects of cage B-substituents on α-carboranylation.[a]



[a] Yield of isolated product. [b] Determined by ^{1}H NMR spectroscopy. n.r. = no reaction.

All the compounds **5** were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR techniques and HRMS. The molecular structures of **5b**, **5d**, and **5f** were further confirmed by single-crystal X-ray analyses (see the Supporting Information).

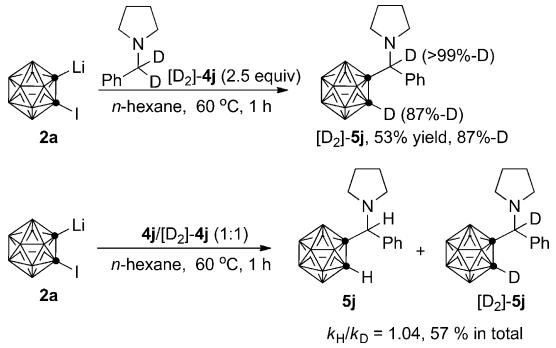
To gain some insight into the reaction pathway, several control experiments were conducted (Scheme 2). The reaction proceeded well either under UV irradiation ($\lambda = 365$ nm) or in the dark (Scheme 2a). The desired α-carboranylated



Scheme 2. Control experiments.

amine **5aa** was still isolated in 62% yield in the presence of 1.1 equivalent of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), thus indicating that a radical pathway was not necessarily involved in this process (Scheme 2b). In addition, no desired product was detected from the reaction of 1-iodo-7-lithio-*m*-carborane (*m*-**2a**) with **4a** (Scheme 2c). These experimental results, together with the regioselectivity observed in the results from Table 2, are significantly different from those reported in our previous work on the reaction of *o*-carboryne with ethers,[13a] which probably suggests the absence of the biradical-form of *o*-carboryne in current reactions.

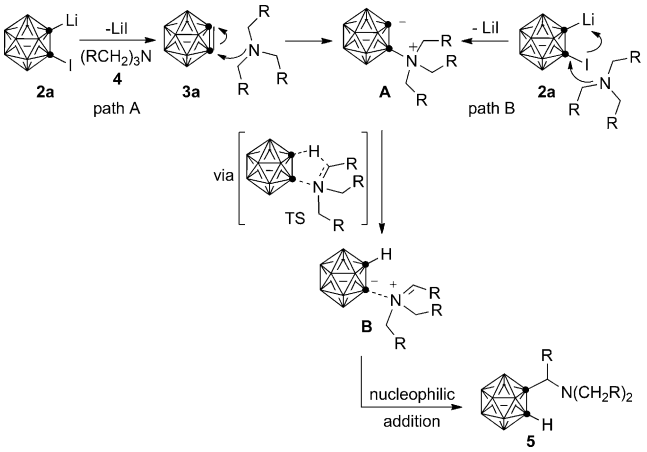
To determine the proton source, the deuterium-labeled substrate [D_2]-**4j** (> 99% D) was subjected to the reaction (Scheme 3). The product [D_2]-**5j** with 87% deuterium



Scheme 3. Deuterium experiments.

incorporation was obtained in 53% yield. This finding reveals that D (H) incorporated into the cage H mainly comes from the amine substrate. Meanwhile, the intermolecular primary kinetic isotope effect (KIE) experiments were also carried out under standard reaction conditions (Scheme 3). The results showed a k_H/k_D value of 1.04, which reveals that the C–H bond cleavage was not the rate-determining step.[21]

To gain further insight into the reaction pathway and to understand the origin of the selectivity for the α-carboranylation of tertiary amines, DFT calculations were carried out.[21] On the basis of both experimental and theoretical results, a plausible mechanism is proposed in Scheme 4.



Scheme 4. Proposed pathways for α-carboranylation of amines.

Elimination of LiI from **2a** gives the reactive intermediate *o*-carboryne (**3a**). Nucleophilic attack of tertiary amine **4** generates the zwitterionic intermediate **A** (path A).[15j] Alternatively, an S_N2 type nucleophilic substitution at the cage C–I bond and elimination of LiI can also lead to the formation of **A** (path B). **A** then undergoes an intramolecular hydrogen transfer to afford the iminium salt **B**. Intramolecular addition yields the final product **5**.

Many attempts to isolate the proposed *N*-carboranyl ammonium salt intermediate **A** failed. The computational results suggest that path A is energetically more favorable than path B (see the Supporting Information). The calculations also reveal that the rate-determining step for path A is the formation of *o*-carboryne, and the hydrogen shift is a fast process. The nature of the hydrogen transfer is likely to be a proton transfer, as indicated by DFT calculations. In this regard, α-carboranylation at a benzylic position is dominant over that of aliphatic position (Table 2; **4i–l**) since a benzylic proton is much more acidic than an aliphatic one. The calculated results also show that the hydrogen shift from a methyl group is more favorable than that from an ethyl group by 1.4 kcal mol^{-1}. Such a preference for primary C–H bonds over secondary C–H ones is caused by the developing negative charge at α-carbon atom as the primary carbon anion is more stable than the secondary carbon anion.

In summary, *o*-carborynes can undergo an α-C–H insertion reaction with tertiary amines on the order of primary ≫ secondary C–H, thus producing α-carboranylated amines in very good regioselectivity and yields. In this process, more acidic C–H bonds are favored. Mechanistic studies as well as DFT calculations suggest that the bonding form of the *o*-carboryne intermediate is involved in this reaction. This work represents another unique reactivity pattern of *o*-carboryne, and serves as an efficient method for the generation of a series of 1-aminoalkyl-*o*-carboranes which might find applications in medicine and catalysis.

Experimental Section

Typical procedure: Iodine (253.8 mg, 1.0 mmol) was added to a suspension of 1,2-dilithio-*o*-$C_2B_{10}H_{10}$ (1.0 mmol) in *n*-hexane

(10 mL), prepared in situ from the reaction of *n*BuLi (1.25 mL, 1.6 M in *n*-hexane, 2.0 mmol) with *o*-carborane (**1a**; 144.2 mg, 1.0 mmol) at 0 °C, at room temperature. After stirring for 15 min at room temperature, iodine completely disappeared and a white suspension was obtained. Next, 10 equiv of the amine **4a** was added to this suspension by a syringe at room temperature. The resulting mixture was stirred at room temperature for 15 min and heated at 60 °C for 1 h, and then quenched by wet *n*-hexane. After removal of solvents in vacuo, the residue was examined by ^{1}H NMR spectroscopy and then subjected to flash column chromatography on silica gel (230–400 mesh) using *n*-hexane as eluent to give **5aa** (175.2 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.08$ (br, 1H) (cage C*H*), 3.43 (q, $J = 6.8$ Hz, 1H) (NC*H*), 2.52 (br, 2H), 2.31 (br, 2H) (NCH*H*), 1.23 (d, $J = 6.8$ Hz, 3H), 0.98 ppm (br, 6H) (CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 81.0$ (cage *C*), 60.0, 59.3 (cage *C*), 46.8, 41.3, 14.8, 19.8, 12.9 ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): $\delta = -3.6$ (1B), −5.2 (1B), −9.6 (2B), −11.1 (1B), −12.0 (1B), −12.6 (1B), −13.3 (1B), −14.3 ppm (2B). HRMS (EI) calcd for $C_8H_{25}{}^{11}B_8{}^{10}B_2N^+$: 243.3103. Found 243.3101.

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