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Dearomative C2-borylation of indoles†

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The dearomative borylation of indoles is challenging and typically requires transition metal catalysts, strong bases, or harsh conditions. We report the metal- and base-free C2-borylation of indoles using bis(1-methyl-ortho-carboranyl)borane as an electrophilic borylating reagent to generate borylated indolenium species under mild conditions.

The dearomative functionalization of indoles is an effective strategy to convert aromatic compounds into functionalized products.1 However, dearomative borylation reactions are scarce. Most established indole dearomatization strategies involve the use of transition metal catalysts using a diborane (B₂pin₂) or organoboron species (RBpin) as the boron source, typically specific to substrates with directing groups that orient catalyst binding (Fig. 1a).2,3 In metal-free approaches,4 Fontaine demonstrated the dearomative C3-borylation of indoles using pinacolborane (HBpin) as the boron source in the presence of a B/N frustrated Lewis pair (FLP) catalyst (Fig. 1b).^{5,6} Resconi and coworkers demonstrated the reaction of the electrophilic borane B(C₆F₅)₃ with 1-methyl-1*H*-indole to selectively furnish the C2-borylated indolenium (Fig. 1c).⁷ The reaction took 10 days to complete and 1-methyl-1H-indole was the only substrate. We surmised that such a reaction could be a fruitful means to access borylated indolenium species and that more electrophilic boranes could be effective reagents to achieve the desired products. It has recently been shown that ortho-carboranes as substituents on boron amplify the Lewis acidity of boranes.8 For example, tris(ortho-carboranyl)borane (BoCb₃)9 and bis(1-methyl-ortho-carboranyl)borane (HB^{Me}oCb₂)¹⁰ are more Lewis acidic than $B(C_6F_5)_3^{11}$ and $HB(C_6F_5)_2^{12}$ making them promising reagents for dearomative borylation.

Department of Chemistry and Biochemistry, Baylor University, One Bear Place #97348, Waco, Texas 76798, USA. E-mail: caleb_d_martin@baylor.edu † Electronic supplementary information (ESI) available: Experimental procedures, multinuclear NMR spectra, and X-ray crystallographic data (PDF). CCDC 2419318 and 2419319. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d5dt00579e

Replicating the Resconi reaction for a baseline, the C-H borylation of 1-methyl-1H-indole with B(C₆F₅)₃ was monitored by 1H NMR spectroscopy that revealed conversion into the borylated indolenium A after 5 days (120 h) with an isolated yield of 85% (87% conversion, Table 1, entry 1), half the time from their report with comparable yield (88%). Switching the solvent from CH2Cl2 to benzene had little effect, resulting only in a slight decrease in conversion (85% conversion, entry 2). The sluggish reaction may be due to either the Lewis acid strength or the steric bulk of B(C₆F₅)₃. Switching to the less bulky secondary borane $HB(C_6F_5)_2$ (buried volume = 47%) presents the possibility of hydroboration or dehydrogenative borylation reactivity. 13 When HB(C₆F₅)₂ was treated with 1-methyl-1H-indole in CH₂Cl₂ or benzene, it did not lead to any reaction at all even after heating to 80 °C (entries 3 and 4). This implies that reducing the electrophilicity has a deleterious effect on the reaction. Replacing B(C₆F₅)₃ with the stronger Lewis acid BoCb₃ resulted in no conversion in either CH₂Cl₂ or benzene, even after heating to 80 °C (entries 5 and 6). This is presumably due to the larger steric profile of the borane (buried volume of $BoCb_3 = 72\%$ and $B(C_6F_6)_3 = 59\%$. ¹⁴ Switching to

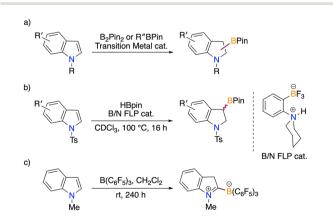


Fig. 1 Dearomative borylations by (a) transition metal catalysis, (b) B/N frustrated Lewis pair (FLP) catalysis, and (c) under catalyst-free conditions.

Table 1 Screening of electrophilic boranes for the C2-borylation of 1-methyl-1H-indole

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Entry	BR_3	Solvent	Time (h)	Conversion ^b (%)
1	B(C ₆ F ₅) ₃	CH ₂ Cl ₂	120	A , 87 (85)
2	$B(C_6F_5)_3$	C_6H_6	120	A, 85 (82)
3^c	$HB(C_6F_5)_2$	CH_2Cl_2	24	NR
4^d	$HB(C_6F_5)_2$	C_6H_6	24	NR
5 ^c	$BoCb_3$	CH_2Cl_2	24	NR
6^d	$BoCb_3$	C_6H_6	24	NR
7	$\mathrm{HB}^{\mathrm{Me}}o\mathrm{Cb}_2$	CH_2Cl_2	24	1 , 37 (30)
8	$HB^{Me}oCb_2$	C_6H_6	1	1 , >97 (97)
9	$HB^{Me}oCb_2$	$CHCl_3$	7	1 , >97 (97)
10	$\mathrm{HB}^{\mathrm{Me}}o\mathrm{Cb}_2$	C_7H_8	3	1 , >97 (97)
11	$\mathrm{HB}^{\mathrm{Me}}o\mathrm{Cb}_2$	THF	24	1, NR

^a Standard reaction conditions: 1-methyl-1H-indole (0.1 mmol), BR₃ (0.1 mmol), solvent (1 mL), and 23 °C. BoCb₃ = tris(ortho-carboranyl) borane, HBMeoCb₂ = bis(1-methyl-ortho-carboranyl)borane, and NR = no reaction. ^b Conversions are calculated from ¹H NMR spectroscopy using mesitylene as an internal standard and isolated yields are given in the parenthesis. c Reaction heated to 40 °C. d Reaction heated to

HB^{Me}oCb₂, a secondary borane with a smaller steric profile than BoCb₃ (buried volume = 64%) and higher electrophilicity than B(C₆F₅)₃, gave encouraging results. Carrying out the reaction with HBMeoCb2 in CH2Cl2 at 23 °C resulted in 37% conversion after 24 h, but in benzene, quantitative conversion was achieved within an hour, enabling the isolation of 1 in 97% yield (entries 7 and 8, respectively). The structure of 1 was confirmed by a single-crystal X-ray diffraction study (Fig. 2).

The ¹H NMR spectrum features a singlet integrating to two protons for the α methylene group at 4.78 ppm. The tricoordinate resonance for HBMeoCb2 in the 11B NMR spectrum at 70.9 ppm disappears, leaving only peaks in the tetracoordinate/cluster region, notably a diagnostic doublet for the borate at -17.8 ppm (${}^{1}J_{B-H} = 90$ Hz). The ${}^{13}C$ NMR spectrum revealed a singlet at 79.4 ppm assigned to C3 that is consistent with the methylene group of the iminium species. Reactions in chloroform and toluene led to comparable yields but in both cases the reaction took a longer time to complete (entries 9 and 10), while THF completely suppressed the reactivity (entry 11). Using the optimized conditions for 1, the reactivity of other indole substrates with HBMeoCb2 was investigated (Scheme 1). First, we examined substitution on nitrogen. Indoles bearing n-butyl and benzyl groups on the nitrogen worked efficiently to generate borylated products 2 and 3 in 80% and 86% yields, respectively (Scheme 1a). A more electron-withdrawing tosyl (Ts) substituent or a bulky triisopropylsilyl (TIPS) group failed to enable any reaction. Interestingly, the parent indole did not undergo C2-boryla-

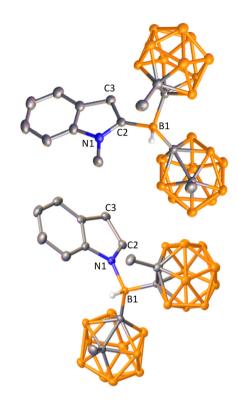


Fig. 2 Solid-state structures of 1 (top) and 4 (bottom). Hydrogen atoms (except for H attached to the central boron atom) and solvates are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) of 1: N(1)-C(2) 1.315(3), C(2)-C(3) 1.512(3), C(2)-B(1) 1.631(3), and N(1)-C(2)-B(1) 124.52(17); 4: B(1)-N(1) 1.597(17), C(2)-C(3) 1.483(18), N(1)-C(2) 1.293(17), and C(2)-N (1)-B(1) 126.56(11).

a)
$$\begin{array}{c} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{array} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2 \\ \hline C_6H_6, 23 \, ^{\circ}C \end{pmatrix} \\ \hline \begin{pmatrix} HB^{Me}oCb_2$$

Scheme 1 Substrate scope of HBMeoCb2 mediated C2-borylation of indoles with nitrogen substitution (a), parent indole (b), substitution on the aryl group (c), and methyl at the C3 position (d). Reaction conditions: indole (0.1 mmol), $HB^{Me}oCb_2$ (0.1 mmol), and C_6H_6 (1 mL). TIPS = triisopropylsilyl and Ts = tosyl.

tion; instead, dearomative N-borylation occurred to afford 4 in 90% yield (Scheme 1b). The structure was confirmed by a single crystal X-ray diffraction study (Fig. 2).15

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Substitution on the 6-membered ring of N-methylindole was tolerated for bromo-substituted N-methylindoles at the C5and C6-positions to furnish the borylated products 5 and 6 in 88% and 82% yields, respectively (Scheme 1c). Inductive donating groups (4-Me and 7-Me) and a strong π donor (5-OMe) were tolerated to afford borylated indoleniums 7-9 in excellent yields (90-97%). A decrease in yield (75%) was observed for a π -electron withdrawing -Bpin substituent at the C5-position (10).

Installing a methyl group at the C3-position resulted in only trace amounts of borylated product (11) with the lack of reactivity attributed to steric bulk. The method proved to be scalable to multigram quantities, as exemplified in the synthesis of 2.25 g of 1 with no change in yield (97%). We examined the addition of several bases (nBuLi, pyridine, 2,6-lutidine, and NEt₃) to attempt to convert the indolenium species into either the C3-borylation product or a functionalized indole. At 23 °C in THF, reactions with pyridine, NEt3, and 2,6-lutidine did not result in any conversion, but heating at 80 °C for a day resulted in conversion into N-methylindole, the starting material. Reaction with nBuLi at 23 °C in THF yielded an intractable mixture.

In the structures of 1 and 4 (Fig. 2), the C(2)–C(3) bonds are similar in length [1: 1.512(3) Å and 4: 1.483(18) Å], considerably longer than that in indole [1.355(11) Å] and consistent with dearomatization. The N(1)-C(2) bond lengths [1: 1.315(3) Å and 4: 1.293(17) Å] are shortened compared to that in indole [N(1)-C(2) 1.332(11) Å], in agreement with the iminium structure.7,15,16

The borylation mechanism was investigated by conducting the reaction with DBMeoCb2 (Scheme 2). The outcome of the reaction was the borylated product with deuterium exclusively on boron based on ²H NMR spectroscopy (1-d) that eliminates the possibility of a hydroboration sequence. The reaction took an hour, the same time as HBMeoCb2, ruling out any kinetic isotope effect and consistent with the deuterium staying on boron throughout the reaction. A rational mechanism leading to 1-d involves olefin attack to afford the C2- or C3-functionalized carbocation intermediates (I and II, respectively). In the C2 pathway, an amine facilitates hydride migration from I to generate 1-d. In the C3 pathway, the migration of the borate in intermediate II leads to I, which subsequently results in 1-d. In

Scheme 2 Deuterium labelled study and proposed mechanism.

an attempt to observe intermediates, the reaction was monitored by ¹H and ¹H{¹¹B} NMR spectroscopy at 23 °C and −50 °C. Unfortunately, no intermediates were observed, only starting materials (N-methylindole and HBMeoCb2) and 1 were detected.

In summary, the high Lewis acidity of bis(1-methyl-orthocarboranyl)borane is leveraged for the uncatalyzed dearomative C2-borylation of indoles. Borane screening revealed that both steric effects and Lewis acidity are essential, with HB^{Me}oCb₂ performing better than fluoroaryl boranes. Despite the hydride on boron, no hydroboration reactivity was observed for any substrates. Substrate screening indicated that substitution on the 6-membered ring is well tolerated but bulky groups on nitrogen or a methyl group at the C3 position inhibit the reaction. The parent indole undergoes N-borylation rather than C2-borylation. In all reactions, mild conditions are used and atom economy is preserved. This work demonstrates the potential of HB^{Me}oCb₂ as a borylation reagent that will continue to be investigated.

Data availability

The data underlying this study are available in the published article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

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