Nickel-catalyzed synthesis of 1,1-diborylalkanes from terminal alkenes

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Organoboron compounds play an irreplaceable role in synthetic chemistry and the related transformations based on the unique reactivity of C–B bond are potentially the most efficient methods for the synthesis of organic molecules. The synthetic importance of multiboron compounds in C–C bond formation and function transformation reactions is growing and the related bortions of activated or nonactivated alkenes have been developed recently. However, introducing directly two boron moieties into the terminal sites of alkenes giving 1,1-diborylalkanes in a catalytic fashion has not been explored yet. Here we describe a synthetic strategy of 1,1-diborylalkanes via a Ni-catalyzed 1,1-diboration of readily available terminal alkenes. This methodology shows high level of chemoselectivity and regioselectivity and can be used to convert a large variety of terminal alkenes, such as vinylarenes, aliphatic alkenes and lower alkenes, to 1,1-diborylalkanes.

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Organoboron compounds are recognized as versatile building blocks and fundamental intermediates in organic synthesis. Particularly because these compounds are usually air and moisture stable and easy to handle compared with Grignard reagents, organolithium reagents, and also enable further transformations based on the unique reactivity of the C–B bond. Transition-metal catalyzed conversion of sp²-hybridized carbon in alkenes to C(sp³)-B bond for the formation of organoboron building blocks is a more recently developed class (Fig. 1a). Several pioneer synthetic methods of monoborylalkanes, 1,2-diborylalkanes and 1,1,1-triborylalkanes from alkenes have been reported recently. Rh-catalyzed synthesis of 1,2-diborylalkanes from terminal vinylarenes was firstly reported by Westcott and co-workers, although the 1,2-diboration product was obtained in very low yield. The enantioselective 1,2-diboration of terminal alkenes catalyzed by platinum catalyst, combined with Suzuki coupling reactions was achieved by Morken’s group. Huang’s group also reported a Co-catalyzed protocol for the formation of 1,1,1-triborylalkanes, but the alkene substrates are restricted to vinylarenes.

As an important class of organoboron compounds, it is undeniable that the 1,1-diborylalkanes show significant applications in organic synthesis. They can either be manipulated in enantioselective catalytic fashion (Fig. 1b) or or provide powerful synthetic module for concise synthesis of complex molecules through multiple C–C bond formation (Fig. 1c), function transformation reactions (Fig. 1d), or both. However, direct synthesis of 1,1-diborylalkanes from terminal alkenes has not been achieved yet. If successful, both synthesis of 1,1-diborylalkanes in synthetic chemistry and applications of alkenes from petrochemical industry will be greatly improved.

**Results**

**Reaction discovery.** As the major research focus of our group, efforts were devoted to discover new C–B bond forming discoveries and alkenes functionalization reactions. We now report the discovery of a synthetic method of 1,1-diborylalkanes, namely, Ni-catalyzed 1,1-diboration of terminal alkenes (Fig. 1e). This reaction provides a convenient strategy for the synthesis of 1,1-diborylalkanes from more stable and less expensive substrates (alkenes and boronic ester). The reaction shows high levels of chemo- and regio-selectivity. As reactions related to organoboron compounds have enjoyed great success in modern organic synthesis, the present reaction is expected to find important applications in synthetic chemistry.

**Investigation of reaction conditions.** Various bases, ligands, solvents and Ni catalysts for the 1,1-diboration reaction of 4-phenyl-1-buten 1 with bis(pinacolato)diboron (B_2pin_2) were screened (Table 1 and Supplementary Tables 1–4). Initially, we tried tricyclohexyl phosphine, a monodentate phosphine ligand that worked well for boration reactions. To our delight, the desired product 2 was obtained in 39% GC yield and only trace amount of 1,2-diboration byproduct 2′ was detected. Some other bases except LiOMe have weakened the 1,1-diboration and only Cs_2CO_3 showed a little effect giving 2 in 22% yield (entry 2–5). We then moved our attention to a sample of 1-analogs and nitrogen heterocyclic carbene (NHC) ligands. To our disappointment, these ligands were found to be ineffective and only trace amount of 2 and 2′ were detected (entries 6–8). We were enlightened by the optimization results that the ligands bearing dicyclohexylphosphine moiety may be good for the 1,1-diboration reaction. Surprisingly, when Cy-XantPhos was used, 2 was increased to 62% yield (entry 9). Higher yield (52%) could also be obtained using THF as solvent (entry 10). Further optimization of the reaction system on the basis of entry 9 and entry 10, we used NEt_3 as an additive, PhMe/THF (v/v 10:1) as solvent and this diboration reaction could proceed smoothly with lower catalyst (5%) and ligand loadings (5%) in 1 h, giving 2 in 78% yield (entry 11). The 1,1-diboration could not be proceeded in the absence of Ni catalyt (entry 12). Some other nickel sources were also tested, but they were not effective (entry 13, 14 and Supplementary Table 4).

**Scope of the methodology.** The substrate scope for the 1,1-diboration of aliphatic alkenes was shown in Table 2. A variety of nonactivated terminal aliphatic alkenes could be readily converted to the desired products with modest to high yields (25–78%). Substrates with different chain lengths (2–7)
Table 1 Screening of conditions for the preparation of 1,1-diborylalkanes from alkenes

| Entry | Ni cat. | Ligand | Base | Solvent | Yield (%) |
|-------|---------|--------|------|---------|-----------|
| 1     | Ni(COD)₂ | PCy₃   | LiOMe | PhMe    | 39        |
| 2     | Ni(COD)₂ | PCy₃   | LiOBU₄| PhMe    | <5        |
| 3     | Ni(COD)₂ | PCy₃   | Cs₂CO₃| PhMe    | 22        |
| 4     | Ni(COD)₂ | PCy₃   | NaIOBU₄| PhMe   | Trace     |
| 5     | Ni(COD)₂ | PCy₃   | KOBU₄ | PhMe    | <5        |
| 6     | Ni(COD)₂ | PCpent₃| LiOMe | PhMe    | Trace     |
| 7     | Ni(COD)₂ | PCyPh₂ | LiOMe | PhMe    | Trace     |
| 8     | Ni(COD)₂ | IMesHCl| LiOMe | PhMe    | Trace     |
| 9     | Ni(COD)₂ | Cy-XantPhos | LiOMe | PhMe | 62 |
| 10    | Ni(COD)₂ | Cy-XantPhos | LiOMe | THF | 52 |
| 11c   | Ni(COD)₂ | Cy-XantPhos | LiOMe/NEt₃ | PhMe/THF | 78 |
| 12    | -       | Cy-XantPhos | LiOMe/NEt₃ | PhMe/THF | 0 |
| 13    | Ni(PP₃H)₄ | PCy₃ | LiOMe | PhMe | 0 |
| 14    | NiCl₂(PCy₂)₂ | PCy₃ | LiOMe | PhMe | 12 |

Standard reaction conditions: 5% Ni(COD)₂, 5% Cy-XantPhos, 2.0 equiv. B₂pin₂, 1.0 equiv. LiOMe, 0.5 equiv. NEt₃, 0.55 mL PhMe/THF(v:v/10:1) with Ar protection at 130 °C for 1 h

*For entry 1-10 and 13-14, 10% Ni(COD)₂; and 20% Ligand; at 130 °C for 12 h

*GC yield average of two runs using n-tetracosane as internal standard

1,1-Diboration of sugar derivatives, LCs and lower alkenes.

This 1,1-diboration reaction of terminal alkenes was utilized for the modification of sugar derivatives, liquid crystals (LCs) and even ethylene shown in Fig. 2. C-alkyl or O-alkyl glycosides are important bioactive candidates. It would therefore be interesting to use our reaction to modify glycosides to form 1,1-diboron-containing bioactive synthons. C-alkyl D-glucose derivative was synthesized from tetrabenzyl-protected D-glucose via fluorination and subsequent allylation. 1,1-Diboration of was utilized and it could be successfully 1,1-diborated.

Next, we turned our attention to validate the generality of our 1,1-diboration protocol for vinylarenes (Table 3). To our disappointment, the optimized reaction conditions for terminal aliphatic alkenes have little effect on vinylarenes. However, fine-tuning of ligands on the basis of the reaction parameters, we found that tricyclohexylphosphine could afford the desired product in satisfactory yields. Notably, similar results were obtained regardless of the electron-donating (e.g., 27, 29, 30) or electron-withdrawing (32, 33) groups on the substrates. Steric hindrance (e.g., 30) shows subtle influence on the yield of the desired products.

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The desired product 43 was isolated in 82% yield. Performing diboration of another kind of lower alkenes ethylene 44 afforded the 1,1-diboration product 45 and 1,2-diboration undesired product 46 in 45% combined yield, and the ratio of 45/46 was 1:2 (Supplementary Fig. 56). Diboration results of 42 and 44 indicate that steric hindrance in alkenes plays a positive role in this site-selective matter. The above transformations demonstrated a vast application prospect of our developed reaction.

Discussion
A set of experiments were executed as additional evidence in support of our proposed catalytic cycle (Supplementary Discussions). The cross-over experiment of 1 with B2pin2 and B2pai2 to yield 2, 47 and 24 indicates that the two boron motifs in the products were supplied by two molecular bisboronic ester (Fig. 3a). The result of cross-over experiment of 1 with B2pin2 and B2pin2-d12 is also in accordance with the above observations (Supplementary Discussions and Supplementary Fig. 61 for more details). Deuterium labeling studies were conducted by using 4-(2,2-dideuterovinyl)-1,1′-biphenyl (29a-d2) as the substrate (93% deuterium content) and one of benzyl hydrogen atoms in the product was 92% deuterated (Fig. 3b). This deuterium experiment illustrated that one of the benzyl hydrogen atoms is originated from hydrogen atoms bonded in terminal site of alkenes. Through nickel-catalyzed alkenes boration and subsequent hydroboration process, we realize the 1,1-selective diboration of alkenes. Diboration of alkenes was all proceeded in a 1,2-selective manner before this study.

Table 2 Substrate scope for 1,1-diboration of aliphatic alkenes

| Alkyl        | 5% Ni(COD)2, 5% Cy-XantPhos | LiOMe (1.0 equiv.), NEt3 (0.5 equiv.) | PhMe/THF (10:1), Ar, 130°C, 1h |
|--------------|------------------------------|---------------------------------------|----------------------------------|
| Bpin         | Bpin                         | 0.2 mmol                              | 2.0 equiv.                       |

| Ph                    | Bpin | 11 64% |
|-----------------------|------|--------|
| MeO                  | Bpin | 12 64% |
| 3 n = 1, 60%          |      |        |
| 2 n = 2, 59%          |      |        |
| 4 n = 3, 62%          |      |        |

| Bpin                  | Bpin | 13 70% (66%)† |
|-----------------------|------|---------------|
| 5 n = 4, 57%          |      |               |
| 6 n = 6, 63% (55%)‡   |      |               |
| 7 n = 8, 59%          |      |               |

| 8 R = Me, 72%         |      |               |
| 9 R = Bu, 65%         |      |               |
| 10 R = OMe, 71%       |      |               |

| 14 48%§               |      |               |

Discussion
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In summary, we have successfully developed a chemo- and regio-selective Ni-catalyzed 1,1-diboration reaction of terminal alkenes. Tremendous variety of terminal alkenes (vinylarenes, aliphatic alkenes and low alkenes) could react smoothly in this methodology. This reaction provides an effective and convenient way for the synthesis of 1,1-diborylalkanes. The obtained products provides an excellent platform for achieving complex structures and via C–C bond formation, function

Table 3 Substrate scope for 1,1-diboration of vinylarenes

| Substrate | Yield (%) |
|-----------|-----------|
| Diboration of tetrabenzyl-D-glucose | 51(45) |
| Diboration of diacetone-D-glucose | 57(52) |
| Diboration of liquid crystals material | 66% |
| Diboration of lower alkenes | 41(40) |

The reactions were conducted in 0.2 mmol scale. Isolated yield

Fig. 2 1,1-Diboration of sugar derivatives, LCs and lower alkenes. a (1) DAST (diethylaminotrifluorosulfur, 1.1 equiv.), THF, –30 °C. (2) Allyltrimethylsilane (2.0 equiv.), 20% BF₃·Et₂O, DCM. (3) 10% Ni(COD)₂, 10% Cy-Xantphos. b (1) NaH, DMF, 5-bromopent-1-ene, 0 °C. (2) Standard conditions, 4 h. c Standard conditions. d Standard conditions, 12 h.
transformations and even enantioselective catalytic cross-coupling reactions. Novel reactions of 1,1-diborylalkanes are being explored in our laboratory.

**Methods**

**General procedure for 1,1-diboration of aliphatic alkenes.** In a glove box, a mixture of 5% Ni(COD)$_2$ (2.8 mg, 0.01 mmol), 5% Cy-XantPhos (6.0 mg, 0.01 mmol), LiOMe (7.6 mg, 0.2 mmol, 1.0 equiv.) and B$_2$pin$_2$ (101.6 mg, 0.4 mmol, 2.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The vessel was filled with argon for three cycles. 0.55 mL PhMe/THF (v/v, 10:1), 10% PCy$_3$ (1.0 equiv.), NEt$_3$ (1.0 equiv.) and alkenes (0.2 mmol, 1.0 equiv.) were added respectively under a positive flow of argon. The reaction mixture was stirred at room temperature (r.t.) for 4 h and then transferred to a pre-heated 130 °C oil bath. After 1 h, the reaction mixture was cooled to r.t. and then diluted with DCM, filtered through silica gel with copious washings by EtOAc, concentrated, and purified by silica gel chromatography to afford the desired product.

**Data availability.** The authors declare that the data supporting the findings of this study are available within the article and its Supplementary Information files. For the experimental procedures, see Supplementary Methods. For NMR, GC-MS and HRMS analysis of the compounds in this article, see Supplementary Figs 1–62. For X-ray data of compound 41 (CCDC No. 1525017), see Supplementary Table 5 and Supplementary Fig. 63. The crystal data can be obtained free of charge from the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk).

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**Fig. 3** Mechanism study experiments. a Cross-over experiments of 1 with B$_2$pin$_2$ and B$_2$pai$_2$ to afford 1,1-diboron compounds 2, 47 and 24 respectively. GC peak area ratio of 2, 47, 24 is 1/2.2/1.1 (Correction factor is not taken into account). b Deuterium labeling experiment was conducted using 29a–d$_2$ as starting material.

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