Double hydroboration of dienes is the addition of a hydrogen and a boryl group to the two double bonds of a diene molecule and represents a straightforward and effective protocol to prepare synthetically versatile bis(boryl)alkanes, provided that this reaction occurs selectively. However, this reaction can potentially yield several isomeric organoboron products, and it still remains a challenge to control the regioselectivity of this reaction, which allows the selective production of a single organoboron product, in particular, for a broad scope of dienes. By employing a readily available cobalt catalyst, here we show that this double hydroboration yields synthetically useful gem-bis(boryl)alkanes with excellent regioselectivity. In addition, the scope of dienes for this reaction is broad and encompasses a wide range of conjugated and non-conjugated dienes. Furthermore, mechanistic studies indicate that this cobalt-catalyzed double hydroboration occurs through boryl-directed chain-walking hydroboration of alkenylboronates generated from anti-Markovnikov 1,2-hydroboration of 1,n-diene.
ogonoboranes are versatile building blocks for chemical synthesis because of their diverse reactivity in organic reactions. As an important family of organoboron compounds, gem-bis(boryl)alkanes have recently gained increasing attention in organic synthesis due to their unique reactivity. For example, different reactivity of the two boryl groups in gem-bis(boryl)alkanes allows stepwise functionalization of their two C–B bonds. Interestingly, gem-bis(boryl)alkanes can generate two types of carboanions, monoboryl- or gem-bis(boryl)-functionalized carboanions, via deprotonation by LiTMP (lithium tetramethylpiperidide) or alkoxide-induced deborylation. Over past decades, series of catalytic reactions have been developed to access these gem-bis(boryl) compounds, such as double hydroboration of alkenes, diborylation of alkenes, hydroboration of 1-borylalkene, and C–H borylation reactions. Nevertheless, a general and practical approach that combines high catalytic activity, easy accessibility and handling of starting materials, and structural diversity of gem-bis(boryl) products is still lacking.

Metal-catalyzed hydroboration of 1,3-dienes has been developed into selective approaches to prepare allylic or homoallylic organoboron compounds. However, double hydroboration of 1,3-dienes has been rarely studied, mainly because alkynylboron products from the first hydroboration contain an unactivated internal alkene that does not readily undergo the second hydroboration. There was only one early example of rhodium-catalyzed double hydroboration of 1,3-dienes reported by Hayashi, and this reaction selectively afforded 1,3-bis(boryl)alkane products. Catalysts for selective double hydroboration of 1-n-dienes to synthesize gem-bis(boryl)alkanes still remains unknown.

Recently, metal-mediated chain walking has been emerging as a useful tool for remote functionalization of organic molecules. The directions for chain walking can be controlled by catalysts or directing groups in organic substrates. For example, aryl or boryl groups in the substrates can direct the chain walking towards them. Therefore, double hydroboration of 1-n-dienes can be potentially developed into an effective and selective protocol to prepare gem-bis(boryl)alkanes, provided that a trifunctional catalyst can be identified to catalyze these three transformations: selective hydroboration of 1-n-dienes to produce alkynylboronates, the isomerization of alkynylboronates to 1-borylalkenes, and the subsequent hydroboration of 1-borylalkenes to yield gem-bis(boryl)alkanes (Fig. 1).

In recent years, cobalt-catalyzed hydroboration has been extensively studied as catalysts for hydroboration and isomerization of alkenes. In 2015, Chirik and coworkers showed one example of cobalt-catalyzed hydroboration of a boryl-containing terminal alkene to give a gem-bis(boryl)alkane product by taking the advantage of boryl-directed alkene isomerization. During our continuous efforts in developing cobalt-catalyzed hydroboration of unsaturated hydrocarbons, we become interested in identifying a selective cobalt catalyst for double hydroboration of 1-n-dienes to synthesize gem-bis(boryl)alkanes. We envisioned that it would be more challenging to develop a selective double hydroboration of aryl-substituted 1-n-dienes because both aryl and boryl groups in alkynylboronate products of the first hydroboration can control the direction of subsequent alkene isomerization, which would probably decrease the selectivity for the second hydroboration. Indeed, such decreased selectivity has been encountered in a recent study on NiH-catalyzed remote hydroarylation of a phenyl-containing alkynylboronate. Here, we show that double hydroboration of these 1-n-dienes takes place to yield synthetically versatile gem-bis(boryl)alkanes with high regioselectivity in the presence of Co(acac)2 and 1,2-bis(dicyclohexylphosphino)ethane (dcp).

**Results**

**Evaluation of reaction conditions.** We chose the reaction of (E)-octa-3,7-dien-1-yllbenzene (1a) with HBpin to identify a cobalt catalyst and the conditions that favor the formation of the gem-bis(boryl)alkane product 2a (Fig. 2). The cobalt catalysts we intended to evaluate were generated in situ from Co(acac)2 and bisphosphine ligands and activated by the reaction with HBpin. In general, the targeted double hydroboration reactions were conducted with 2 mol% cobalt catalyst in the presence of 2.5 equivalents of HBpin for 4 h at 100 °C. The selected examples of these reactions are summarized in Fig. 2.

The reaction conducted with Co(acac)2 and dppe proceeded sluggishly to very low conversion (<5%) of 1a and the desired product 2a was not formed (Fig. 2, entry 1). The reaction catalyzed by Co(acac)2 and dpbbz occurred to a low conversion (33%) of 1a and only a trace amount of 2a was detected together with several other isomeric 1-n-dienes that were resulted from the isomerization of 1a (Fig. 2, entry 2). The reactions of 1a with HBpin afforded alkynylboronate 2a as a major product when conducted with Co(acac)2 and dppe or dpbbz (Fig. 2, entries 3 and 4). The reactions run with Co(acac)2, and dpf, dpephos, or xantphos afforded eight isomeric bis(boryl)alkane products (Fig. 2, entries 5–7), and the selectivity for the desired product 2a was only low to modest (28–56%). To our delight, the reaction catalyzed by 2 mol% Co(acac)2/dcp produced 2a in good yield (72%) and high regioselectivity (95% rr, Fig. 2, entry 8). In particular, the reaction conducted with 3 mol% catalyst afforded 2a in high isolated yield (76%) with excellent regioselectivity (97% rr, Fig. 2, entry 9). We also tested various temperatures for this double hydroboration reaction catalyzed by Co(acac)2/dcp. Similar results were obtained for the reactions run at 100 °C and 80 °C (Fig. 2, entries 8 and 10). Further lowering the temperature to 50 °C led to a lower yield of 2a with a diminished regioselectivity (Fig. 2, entry 11). Particularly, the reaction performed at room temperature afforded only the alkynylboronate product 2a, which was formed from hydroboration of the terminal double bond of 1a (Fig. 2, entry 12).

**Substrate scope of conjugated and non-conjugated 1-n-dienes.** With the identified cobalt catalyst and reliable conditions in hand, we studied the scope of 1-n-dienes that undergo this cobalt-catalyzed double hydroboration for the synthesis of gem-bis(boryl)alkanes, and the results are summarized in Fig. 3. In general, a wide range of non-conjugated (Z/E)-1-n-dienes (1a−1h) and conjugated (Z/E)-1,3-dienes (1i−1al) smoothly reacted with HBpin in the presence of 1 mol% Co(acac)2 and 1 mol% dcp, yielding the corresponding gem-bis(boryl)alkanes (2a−2al) in modest to high isolated yields (58–88%) with excellent regioselectivity (up to 99%). Noticeably, carbocyclic products resulted from cyclization of 1,6-diene 1c were not detected.

The scope of 1-n-dienes encompasses both alkyl- and aryl-substituted 1-n-dienes with substituents at various positions (e.g. 1g−1q). Particularly, the double hydroboration of 1-n-dienes (1h and 1i−1q) containing 1,1-disubstituted alkene units afforded β-branched gem-bis(boryl)alkanes (2h and 2l−2q), which are not accessible via double hydroboration of terminal alkynes. In addition, 1,3-dienes containing ortho-substituted aryl groups also smoothly reacted under identified conditions to afforded the corresponding gem-bis(boryl)alkanes (2t and 2u) in high isolated yields. This cobalt-catalyzed double hydroboration can tolerate a range of functional groups, such as ether (2d and 2v), tertiary amine (2y), thioether (2z), fluoride (2ab), carboxylic ester (2ac), and acetal (2ad). Nitrogen- and oxygen-containing 1,3-dienes also reacted to afford the desired products (2aj−2al) in high isolated yields.
Trifunctional catalysts for chain-walking double hydroboration of 1,ₙ-diienes.

**Fig. 1 Hydroboration of dienes.** Trifunctional catalysts for chain-walking double hydroboration of 1,ₙ-diienes.

**Fig. 2 Evaluation of conditions for cobalt-catalyzed double hydroboration of 1,₅-diene 1a.** Reaction conditions: 1a (0.200 mmol), HBpin (0.500 mmol), Co(acac)₂ (4.0 μmol), ligand (4.0 μmol), heptane (0.5 mL), 4 h, yield was determined by GC (gas chromatography) analysis using tridecane as internal standard and yield in parentheses was isolated yield of 2a. *Values in parentheses are regioisomeric ratio and represents the ratio of the desired gem-bis(boryl)alkane product to the sum of all other bis(boryl)alkane isomers as determined by gas chromatography analysis.* 3 mol% cobalt catalyst.

In addition, we also tested this cobalt catalyst for hydroboration reactions of dienes containing two internal or two terminal carbon-carbon double bonds, and the results are shown in Fig. 4. Under standard conditions, bis(alkyl)-substituted 1,₅-diene 1am reacted smoothly with HBpin to afford gem-bis(boryl)alkane product 2ae in 51% isolated yield (Fig. 4a). Product 2ae contains two Bpin groups on the terminal sp³-carbon, indicating the isomerization of both internal double bonds to terminal double bonds. The hydroboration reactions of aryl,alkyl- or aryl,aryl-disubstituted 1,₅-diienes 1an and 1ao produced benzylic boronates 3 and 4, respectively, in high yields (Fig. 4b, c). These benzylic boronate products were formed by cobalt-catalyzed sequential hydroboronation and hydrogenation of 1an and 1ao. The double hydroboration of 1,₅-hexadiene 1ap, a diene containing two terminal double bonds, yielded two bis(boryl)alkane products, 1,1-bis(boryl)hexane 2ap and 1,6-bis(boryl)hexane 2ap′, and the ratios of these two products were temperature dependent. For example, the reaction conducted at 100 °C afforded 1,1-bis(boryl)hexane 2ap as the major product with 2ap:2ap′ of 76:24, and gem-bis(boryl)alkane product 2ap was isolated in 63% yield (Fig. 4d). However, the corresponding reaction run at room temperature gave 1,6-bis(boryl)hexane 2ap′ in 81% isolated yield with high regioselectivity (2ap:2ap′ = 7:93, Fig. 4e).

**Synthetic utilities.** This cobalt-catalyzed chain-walking double hydroboration of 1,ₙ-diienes can be conducted on gram-scales with a decreased catalyst loading. For example, the reaction of (Z/E)-buta-1,3-dien-1-yllbenzene 1s (Z:E = 45:55) with HBpin on a 8.0-mmol scale proceeded to full conversion of 1s in the presence of 0.5 mol% Co(acac)₂/dcpe and afforded the desired product 2s (2.53 g) in 82% isolated yield (Fig. 5a). We subsequently show the utility of gem-Bis(boryl)alkane 2s as a versatile building block in organic synthesis by conducting a series of organic transformations with 2s (Fig. 5b–f). For example, 2s could undergo a Boron-Wittig reaction with an aldehyde to afford ketone 5 after oxidative workup with NaBO₂·4H₂O (ref.10) (Fig. 5b). 2s could also be used as an alkylation reagent for the alkylation of quinoline N-oxide to prepare 2-allylquinoline 6.
(ref.67) (Fig. 5c). In addition, the carbanion generated by the deprotonation of 2s with LiTMP, NaHMDS, or NaO\textsubscript{T}Bu reacted with iodomethane or 5-bromopent-1-ene to afford boryl-functionalized alkenes 7, 8, and 9, respectively11 (Fig. 5d–f). Furthermore, gem-bis(boryl)alkane 2s readily underwent Pd-catalyzed Suzuki-Miyaura coupling with 4-iodoanisole to give alkylboronate 10 in 81% isolated yield (Fig. 5g).

**Discussion**

We subsequently conducted a series of experiments to gain insights into the mechanism of this cobalt-catalyzed double hydroboration reactions of 1,n-dienes, and the results of these experiments are summarized in Fig. 6. Similar to mono-hydroboration of 1,5-diene 1a at room temperature (Fig. 2, entry 12), monohydroboration of 1,3-diene 1s with 1.1 equiv. of HBpin occurred to completion in 30 min at room temperature and afforded alkynylboronate 11s selectively (Fig. 6a). Subsequent heating the reaction mixture at 100 °C for 2 h resulted in the isomerization of 11s to a mixture of alkynylboronates 11s, 11s′, and 11s″ with a ratio of 51:17:32 (Fig. 6a). We then tested a mixture of these alkynylboronates for hydroboration with HBpin in the presence of 1 mol % of Co(acac)\textsubscript{2}/dcpe, and all these isomeric alkynylboronates were converted to gem-bis(boryl)alkane 2s in high yield (Fig. 6b). The conversion of 11s, 11s′, and 11s″ to a single product 2s indicates that boryl group has a stronger directing ability for this cobalt-catalyzed chain-walking hydroboration than phenyl group, which may stem from the interaction of the d-electrons of the cobalt catalyst with the empty p-orbital on boron68.

A control experiment of this double hydroboration was conducted with a substrate containing an oxygen-tethered 1,6-diene.
Fig. 4 Hydroboration of dienes containing two internal double bonds or two terminal double bonds. a Double hydroboration of diene 1am. b Sequential hydroboration/hydrogenation of diene 1an. c Sequential hydroboration/hydrogenation of diene 1ao. d Double hydroboration of diene 1ap at 100 °C. e Hydroboration of diene 1ap at room temperature.

Fig. 5 Gram-scale synthesis of gem-bis(boryl)alkane 2s and its further transformations. a Gram-scale synthesis of 2s. b Synthesis of 5. c Synthesis of 6. d Synthesis of 7. e Synthesis of 8. f Synthesis of 9. g Synthesis of 10.
This reaction afforded 1,7-bis(boryl)alkane 13 and chain-walking double hydroboration was not observed. This suggests that the chain walking takes place through reversible β-hydrogen elimination and reinsertion steps. A deuterium-labeling experiment of the double hydroboration of 1,3-diene (E)-1s was then conducted with DBpin, and deuterium incorporation at all positions of the aliphatic chain of 2s-D was observed (Fig. 6d). When the deuterium-labeling experiment was performed with (E)-1s-D and HBpin, deuterium scrambling at all positions of the aliphatic chain of 2s-D was observed as well (Fig. 6d). In addition, when a crossover experiment of this double hydroboration was run with (E)-1s-D and (E/Z)-1x, similar deuterium incorporation and deuterium scrambling map was also observed for gem-bis(boryl)alkane products 2s-D and 2x-D (Fig. 6e). The results of this crossover experiment indicate that dissociation and re-association of Co-H/D from the Co-H/D-olefin complex occurs during the chain walking process.

We then tested this cobalt catalyst, Co(acac)2/dcpe, for chain-walking hydroboration of phenyl- and boryl-containing alkenes with double bonds at various positions, and the results are summarized in Fig. 7. (E)-But-1-en-1-ylbenzene (14) reacted smoothly with 1.5 equivalents HBpin in the presence of 3 mol% Co(acac)2 (1 mol%) dcpe (1 mol%) Heptane, 100 °C, 2 h Ph

Bpin

2s-D, 77%
Co(acac)$_2$/dcpe at 100 °C to give alkylboraante 15 as a major product together with a trace amount (4%) of alkylboraante 16, a byproduct from chain-walking hydroboration (Fig. 7a). Similarly, the reaction between (E)-but-2-en-1-ylbenzene (17) and HBpin under standard conditions afforded alkylboraante products 15 and 16, albeit with a low regioselectivity (15:16 = 61:39), and both products were resulted from chain-walking hydroboration (Fig. 7b). But-3-en-1-ylbenzene (18) also underwent this cobalt-catalyzed chain-walking hydroboration, but the major product (16) of this reaction was from the hydroboration of terminal double bond of 18 (Fig. 7c). For comparison, we also conducted the reaction between a boryl-containing terminal alkene 19 and HBpin under standard conditions (Fig. 7d), and the major product, gem-bis(boryl)alkane 20, was formed by the cobalt-catalyzed chain-walking hydroboration. The results of chain-walking hydroboration reactions conducted with but-3-en-1-ylbenzene (18) and but-3-en-1-ylboronic pinacol ester (19) indicate that the Bpin group has a stronger directing ability for chain-walking hydroboration than the phenyl group.

In addition, we also tested a cobalt catalyst generated from Co(acac)$_2$ and dppe (1,2-bis(diphenylphosphino)ethane), a bisphosphine ligand having a similar steric but different electronic property, for hydroboration of terminal alkenes 18 and 19 with HBpin (Fig. 7e and f). These two reactions proceeded very sluggishly and approximately 30% of 18 and 19 were converted at 100 °C in 24 h. Interestingly, major products (16 and 20) of these two reactions were resulted from direct anti-Markovnikov hydroboration of 18 and 19, and much less byproducts (15 and 21) were formed by chain-walking hydroboration relative to the corresponding reactions catalyzed by the cobalt catalyst generated from Co(acac)$_2$ and dcpe (Fig. 7c, d). The results of these four reactions (Fig. 7c–f) suggest that the electron-rich property of dcpe ligand facilitates the chain-walking process, thus promoting chain-walking hydroboration.

Based on the results of mechanistic studies, we proposed a catalytic pathway for this cobalt-catalyzed chain-walking double hydroboration of 1,4-diene 1b, as depicted in Fig. 8. The activation of Co(acac)$_2$ with HBpin in the presence of dcpe (L) forms a cobalt hydride species (L)Co-H (ref. 69). Migratory insertion of the terminal alkene of 1b into (L)Co-H generates an alkylcobalt intermediate A, which then undergoes σ-bond metathesis with HBpin to produce alkylcobaltinate 2b′ and regenerates (L)Co-H. The double bond in 2b′ then inserts into (L)Co-H to form an alkylcobalt species B, which undergoes isomerization to form the alkylcobalt intermediate C through reversible β-hydrogen elimination and reinsertion. In the last step, σ-bond metathesis between alkylcobalt species...
gem-bis(boryl)alkanes via a selective cobalt-catalyzed double hydroboration of 1,1-diienes. A wide range of conjugated and non-conjugated 1,1-diienes reacted with pincer-catalyzed bis(pinacolato)boryl complexes to produce gem-bis(boryl)alkanes in high isolated yields with excellent regioselectivity in the presence of a catalyst generated in situ from Co(acac)2 and dcppe ligand. Mechanistic studies suggest that this cobalt-catalyzed double hydroboration occurs through an initial anti-Markovnikov mono-hydroboration of 1,1-diienes followed by a sequential boryl-directed chain-walking hydroboration of the resulting alkynylboronates. This cobalt-catalyzed double hydroboration provides a straightforward approach to access structurally diverse and synthetically versatile gem-bis(boryl)alkanes from readily available 1,1-diienes.

Methods

General procedure for double hydroboration of 1,1-diienes. In an Argon-filled glovebox, a 4-mL screw-capped vial was charged with Co(acac)2 (0.8 mg, 3.0 µmol), dcppe (1.3 mg, 3.0 µmol), 1,1-diene (0.30 mmol), heptane (0.5 mL) and a magnetic stirring bar. The solution was stirred for 5 min and pincolborane (96.0 mg, 0.75 mmol) was added to the vial. The vial was sealed with a cap containing a PTFE septum and a stirring bar. The solution was stirred for 5 min and pincolborane (96.0 mg, 0.75 mmol) was added to the vial. The vial was sealed with a cap containing a PTFE septum and a magnetic stirring bar. The solution was stirred for 5 min and pincolborane (96.0 mg, 0.75 mmol) was added to the vial. The vial was sealed with a cap containing a PTFE septum and a magnetic stirring bar.

Data availability

The authors declare that all data supporting the findings of this study are available within the article and Supplementary Information files, and also are available from the corresponding author upon reasonable request.

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