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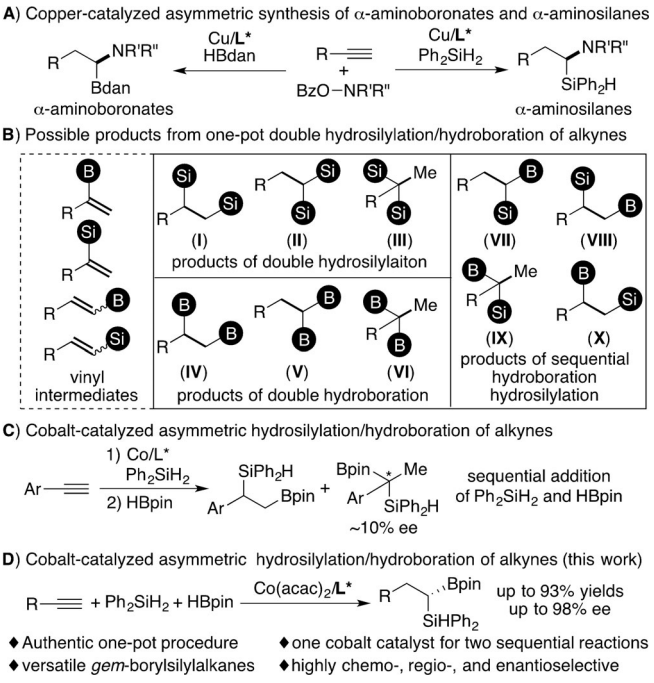
Cobalt-Catalyzed One-Pot Asymmetric Difunctionalization of Alkynes to Access Chiral *gem*-(Borylsilyl)alkanes

*Yang'en You and Shaozhong Ge**

Abstract: *Enantioselective cobalt-catalyzed one-pot hydrosilylation and hydroboration of terminal alkynes has been developed employing a cobalt catalyst generated from Co(acac)$_2$ and (R,R)-Me-Ferrocelane. A variety of terminal alkynes undergo this asymmetric transformation, affording the corresponding gem-(borylsilyl)alkane products with high enantioselectivity (up to 98% ee). This one-pot reaction combines (E)-selective hydrosilylation of alkynes and consecutive enantioselective hydroboration of (E)-vinylsilanes with one chiral cobalt catalyst. This protocol represents the most straightforward approach to access versatile chiral gem-(borylsilyl)alkanes from readily available alkynes with commercially available cobalt salt and chiral ligand.*

The sp^3-geminated organometallic reagents are versatile building blocks in chemical synthesis because they can undergo selective reactions to allow efficient construction of molecular complexity. Compared with conventional geminal bimetallic reagents based on Li, Mg, Al, Zr, Cu, and Zn,[1] geminal compounds containing boron or silicon groups are more facile to handle because of their high stability and functional group compatibility.[2] The majority of these compounds are prochiral *gem*-diborylalkanes and *gem*-disilylalkanes that have two enantiotopic boron or silicon groups,[3] and they can only undergo enantioselective transformations in the presence of chiral catalysts.[4] Considering the distinctive nature of C-B and C-Si functionalities, it can be anticipated that chrial *gem*-(borylsilyl)alkanes, which have both C–B and C–Si bonds on the same carbon, should show more diverse reactivity.[5] These *gem*-(borylsilyl)alkane compounds can be prepared via copper-catalyzed asymmetric boron-addition to aryl-substituted (*E*)-vinylsilanes[5b] or platinum-catalyzed asymmetric hydrosilylation of alkyl-substituted (*E*)-vinylboronates.[5d] Although these two reactions can convert terminal alkynes to *gem*-(borylsilyl)alkanes, the sequential addition of reagents, the preformation of vinyl intermediates, and the use of different catalysts for hydrosilylation and hydroboration steps are required. Therefore, it still remains significant and desirable to develop operationally convenient enantioselective protocols to access *gem*-(borylsilyl)alkanes from readily available feedstock chemicals and chiral catalysts.

Alkynes are very versatile feedstocks for chemical synthesis.[6] Asymmetric double hydrofunctionalization of alkynes with the introduction of two different functionalities into the same carbon of the triple bond provides a straightforward approach to prepare chiral sp^3-geminal compounds. Nevertheless, the examples of such enantioselective reactions are very limited.[7] In 2019, the Engle group developed an asymmetric Cu-catalyzed cascade hydroboration/hydroamination of alkynes to synthesize chiral α-amino organoboronates (Scheme 1 A).[7a] In 2020, Hirano and Miura reported a Cu-catalyzed hydrosilylation/hydroamination sequence of alkynes to prepare chiral α-amino organosilanes (Scheme 1 A).[7b] Inspired by these two seminal reports, we envisioned that asymmetric one-pot hydrosilylation/hydroboration of alkynes would provide the most straightforward and convenient protocol to synthesize chiral *gem*-(borylsilyl)alkanes. However, conducting such one-pot hydrosilylation/hydroboration reactions of alkynes without sequential addition of reagents confronts more significant selectivity issues than performing hydrosilylation or hydroboration reactions of well-defined vinylboronate or vinylsilane intermediates,[5b,d] because this one-pot reaction can afford multiple



Scheme 1. Enantioselective reductive *gem*-difunctionalization of alkynes.

[*] Dr. Y.'e. You, Prof. Dr. S. Ge
Department of Chemistry, National University of Singapore
3 Science Drive 3, 117543, Singapore (Singapore)
E-mail: chmgsh@nus.edu.sg
Homepage: http://www.geresearchgroup.com

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202107405.

products, such as disilylalkanes **I**–**III**; diborylalkanes **IV**–**VI**, and borylsilylalkanes **VII**–**X** (Scheme 1 B).

Cobalt catalysts have recently been extensively studied for selective hydrosilylation and hydroboration of terminal alkynes.[8] Nevertheless, chiral cobalt compounds that can catalyze one-pot sequential hydrosilylation and hydroboration of alkynes with high chemo-, regio-, and enantioselectivity are still lacking. In 2016, Lu and Huang independently reported cobalt-catalyzed Markovnikov hydrosilylation/hydroboration of alkynes to form borylsilylalkanes of types **VIII** and **IX**, but sequential addition of Ph_2SiH_2 and HBpin or the isolation of vinylsilane intermediates are required.[9] The asymmetric version of this reaction was also attempted, but low regioselectivity and enantioselectivity (around 10 % *ee*) were obtained (Scheme 1 C).[9a] Herein, we report an enantioselective *anti*-Markovnikov hydrosilation/hydroboration reaction of alkynes to access chiral *gem*-(borylsilyl)alkanes of type **VII** with one cobalt catalyst. This one-pot protocol features high enantioselectivity (up to 98 % *ee*) and operational simplicity with only one addition of all reagents and the cobalt catalyst.

We chose the reaction of phenylacetylene (**1a**) with Ph_2SiH_2 and HBpin to identify a selective chiral cobalt catalyst and reliable conditions that favour the formation of *gem*-(borylsilyl)alkane **2a** (Table 1). After testing various chiral bisphosphine ligands and reaction parameters, we found that alkyne **1a** reacted smoothly with 1 equivalent of Ph_2SiH_2 and 3 equivalents of HBpin in the presence of 3 mol % $Co(acac)_2$ and (*R*,*R*)-Me-Ferrocelane (**L1**) at 0 °C, affording *gem*-(borylsilyl)alkane **2a** in 81 % isolated yield with 92 % *ee* (entry 1 in Table 1). The reactions conducted with chiral ligands **L2**–**L5** produced **2a** in very low yields (5–30 %), and the major product for these reactions was (*E*)-vinylsilane **2a′** (entries 2–5). The reaction performed with $Co(acac)_2$ and Josiphos (**L6**) occurred to full conversion of **1a**, affording **2a** in modest yield (73 %) with modest enantioselectivity (60 % *ee*, entry 6). Various solvents, such as toluene, cyclohexane, and hexane, were tested for this transformation (entries 7–9), and these reactions formed **2a** in significantly lower yields (14–36 %) compared with the reaction conducted in THF. Furthermore, we also attempted this reaction with reduced amounts of HBpin. For example, the reactions run with 1 or 2 equivalents of HBpin produced **2a** with similarly high enantioselectivity (91–92 % *ee*), albeit in slightly lower yields (entries 10 and 11). Temperature had noticeable effect on the enantioselectivity of this reaction, and the reactions carried out at room temperature or 50 °C yielded **2a** with reduced enantioselectivity (84 % and 72 % *ee*, respectively; entries 12 and 13). Other hydrosilanes, such as $PhSiH_3$ and $(EtO)_3SiH$, were also tested for this reaction, but these reactions did not produce the desired *gem*-(borylsilyl)alkane products (entries 14 and 15). The absolute configuration of **2a**

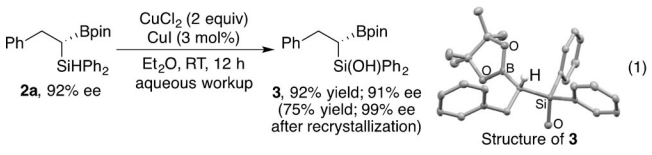


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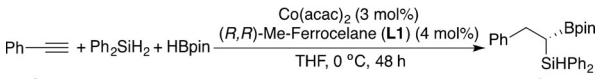
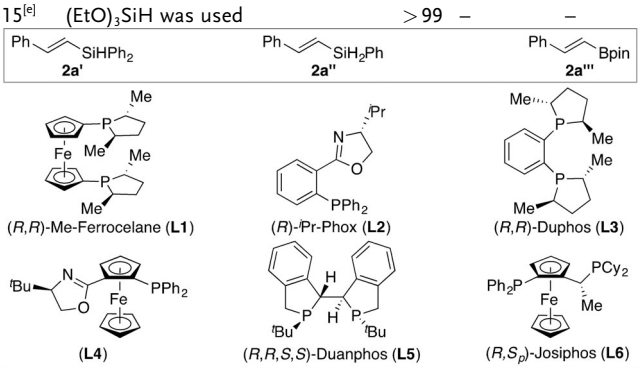
Table 1: Evaluation of conditions for cobalt-catalyzed one-pot hydrosilylation and hydroboraiton of alkyne **1a**.[a]



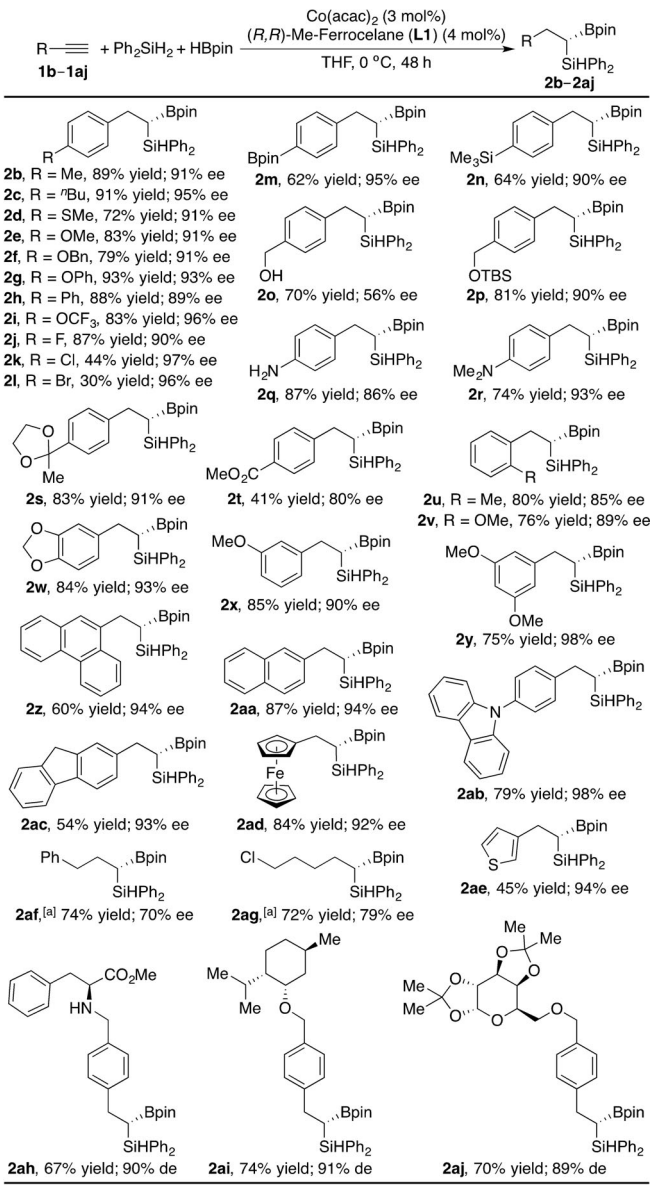
Entry	Variation from the standard conditions	Conversion of **1a** [%]	Yield of **2a** [%]	*ee* of **2a** [%]
1	none	> 99	87 (81[b])	92
2[c]	**L2** instead of **L1**	> 99	< 5	–
3[c]	**L3** instead of **L1**	> 99	26	92
4[c]	**L4** instead of **L1**	> 99	30	54
5[c]	**L5** instead of **L1**	> 99	16	27
6	**L6** instead of **L1**	> 99	73	60
7[c]	toluene as solvent	> 99	18	90
8[c]	hexane as solvent	95	36	82
9[c]	cyclohexane as solvent	95	14	86
10	1 equivalent of HBpin	> 99	52	91
11	2 equivalents of HBpin	> 99	70	92
12	RT instead of 0 °C	> 99	89	84
13	50 °C instead of 0 °C	> 99	93	72
14[d]	$PhSiH_3$ was used	> 99	< 5	–
15[e]	$(EtO)_3SiH$ was used	> 99	–	–



[a] Conditions: phenylacetylene (0.200 mmol), Ph_2SiH_2 (0.260 mmol), HBpin (0.600 mmol), $Co(acac)_2$ (6.0 μmol), ligand (8.0 μmol), THF (1 mL) at 0 °C for 48 h, conversion of **1a** and yield of **2a** were determined by GC analysis with tridecane as internal standard, and *ee* was determined by chiral HPLC analysis. [b] Isolated yield. [c] These reactions predominantly afforded a mixture of vinylsilane and vinylboronate products that were resulted from hydrosilylation and hydroboration reactions of alkyne **1a**. [d] Vinylsilane **2a″** was isolated in 88 % yield. [e] Vinylboronate **2a‴** was isolated in 70 % yield.

from the reaction catalyzed by $Co(acac)_2$/**L1** (entry 1) was assigned as (*S*) by single-crystal X-ray analysis on silanol **3** obtained by Cu-catalyzed chlorination of hydrosilane **2a** followed by the hydrolysis of the resulting Si–Cl bond [Eq. (1)].[10]

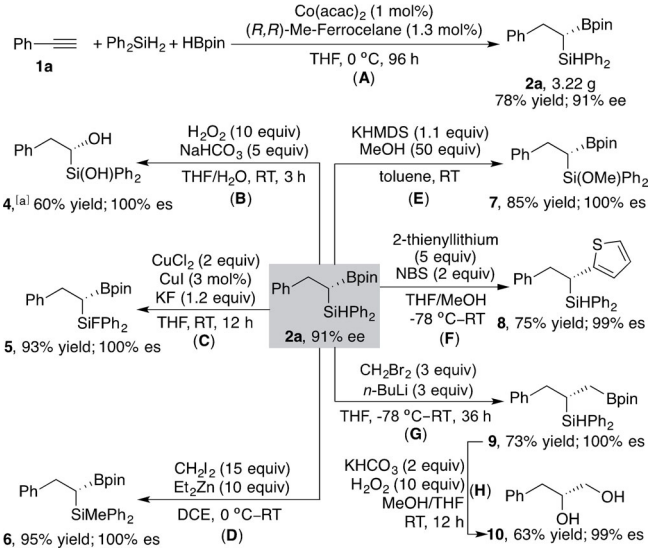
With the identified chiral cobalt catalyst and conditions, we explored the scope of terminal alkynes that undergo this cobalt-catalyzed enantioselective difunctionalization reaction, and the results are summarized in Scheme 2. In general, a variety of aryl-substituted alkynes (**1b**–**1ac**) reacted smoothly with Ph_2SiH_2 and HBpin in the presence of 3 mol % $Co(acac)_2$ and 4 mol % (*R*,*R*)-Me-Ferrocelane to produce the corresponding enantioenriched *gem*-(borylsilyl)alkanes (**2b**–**2ac**) in high yields with high enantioselectivity. In addition, ferrocenylacetylene (**1ad**) and (3-thienyl)acetylene (**1ae**) reacted to give *gem*-(borylsilyl)alkanes **2ad** and **2ae** with 92 % *ee* and 94 % *ee*, respectively. Furthermore, the



Scheme 2. Scope of terminal alkynes. Conditions: alkyne (0.200 mmol), Ph_2SiH_2 (0.260 mmol), HBpin (0.600 mmol), $Co(acac)_2$ (6.0 μmol), (*R*,*R*)-Me-Ferrocelane (8.0 μmol), THF (1 mL), 0 °C, 48 h, yields of isolated products, *ee* and *de* values were determined by chiral HPLC analysis. [a] This reaction was conducted in 1,4-dioxane. Bn = benzyl, TBS = *tert*-butyldimethylsilyl.

alkyl-substituted alkynes **1af** and **1ag** also underwent this cobalt-catalyzed process to afford chiral *gem*-(borylsilyl)alkanes **2af** and **2ag** as major products in high yields, albeit with slightly lower enantioselectivity. This cobalt-catalyzed reaction tolerates various functional groups, such as sulfide (**2d**), trifluoromethoxy (**2i**), fluoro (**2j**), chloro (**2k** and **2af**), bromo (**2l**), boronic ester (**2m**), silyl (**2n**), unprotected hydroxyl (**2o**) and amine (**2q**), siloxyl (**2p**), acetal (**2s**), and carboxylic ester (**2t** and **2ah**) moieties. Noticeably, the alkynes containing unprotected hydroxyl (**1o**) and amine (**1q**) groups reacted with lower enantioselectivity compared with their corresponding protected congeners (**1p** and **1r**), presumably because free hydroxy and amine groups coordinate more strongly to the cobalt catalyst. Alkynes containing L-phenylalanine, L-menthol and D-protection-galactopyranose units also underwent this asymmetric transformation, providing *gem*-(borylsilyl)alkanes **2ah**–**2aj** with high enantioselectivity (89–91% de).

To show the synthetic utility of this enantioselective protocol for the preparation of chiral *gem*-(borylsilyl)alkanes, we carried out the hydrosilylation/hydroboration reaction of alkyne **1a** on a gram scale with a reduced catalyst loading (1 mol%), and this reaction occurred smoothly at 0 °C to afford chiral *gem*-(borylsilyl)alkane **2a** (3.22 g, 78% yield and 91% *ee*), although a longer reaction time was needed (Scheme 3A). The C–B bond in compound **2a** could be



Scheme 3. Gram-scale one-pot hydrosilylation/hydroboration reaction of **1a** and derivatization of chiral *gem*-(borylsilyl)alkane **2a**. [a] The absolute configuration of **4** was assigned as (*R*) by single-crystal X-ray diffraction analysis;[10] NBS = N-bromosuccinimide, KHMDS = potassium hexamethyldisilazide.

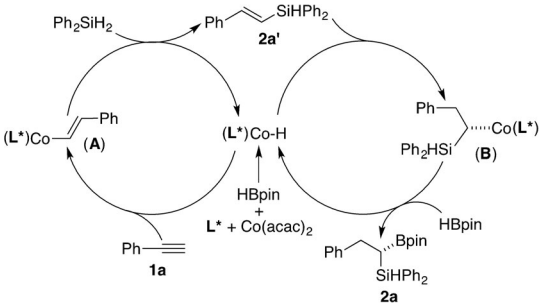
oxidized by H_2O_2, with the concomitant oxidation of Si–H bond to silanol, to form alcohol **4** in 60% isolated yield (Scheme 3B). The Si–H bond in *gem*-(borylsilyl)alkane **2a** could undergo several transformations without converting its C–B bond. For example, it could undergo Cu-catalyzed fluorination in the presence of CuI, $CuCl_2$, and KF to afford fluorosilane **5** in 93% yield with 100% es (Scheme 3C).[11] Carbene generated from CH_2I_2 and Et_2Zn could insert into the Si–H bond of **2a** to produce tertiary silane **6** in 95% yield with 100% es (Scheme 3D).[12] The hydrosilane **2a** could be converted to silylether **7** in high yield in the presence of LiHMDS and methanol (Scheme 3E).[12] Furthermore, the C–B bond in **2a** can also be converted selectively while keeping the Si–H bond intact. *gem*-(Borylsilyl)alkane **2a** underwent enantiospecific C–C coupling with 2-thienyllithium in the presence of NBS to afford chiral alkylsilane **8** in 75% yield with 99% es (Scheme 3F).[13] In addition, homologation of **2a** with $LiCH_2Br$ formed chiral 1-boryl-2-silylalkane **9** in 73% isolated yield with 100% es (Sche-

me 3G), and compound **9** could be further converted to chiral 1,2-diol **10** with 99% es (Scheme 3H).

To provide some insights into the high chemoselectivity of this cobalt-catalyzed double hydrofunctionalization of alkynes, some control experiments were conducted, and the results are summarized in Scheme 4. The hydrosilylation of alkyne **1a** occurred to complete conversion of **1a** and afforded (*E*)-vinylsilane **2a′** with excellent regio- and stereoselectivity under standard conditions (Scheme 4A). However, the hydroboration of **1a** proceeded with only modest chemoselectivity and produced (*E*)-vinylboronate **2a″** and *gem*-diborylalkane **11** with the ratio of 3:1 (Scheme 4B). We then tested the reactions of (*E*)-vinylsilane **2a′** and (*E*)-vinylboronate **2a″** with Ph_2SiH_2 and HBpin under standard conditions. The reaction of **2a′** with Ph_2SiH_2 was very sluggish and the hydrogenation of **2a′** occurred to form alkylsilane **12** in 19% GC yield; however, the hydroboration of **2a′** occurred smoothly in the presence of 1 or 3 equivalents of HBpin to form *gem*-(borylsilyl)alkane **2a** in good isolate yields with 91% *ee* (Scheme 4C). On the contrary, the hydrosilylation and hydroboration reactions of (*E*)-vinylboronate **2a″** occurred with <2% conversion under standard conditions (Scheme 4D). The results of these control experiments suggest that *gem*-(borylsilyl)alkane **2a** is formed through the hydrosilylation of **1a** followed by the asymmetric hydroboration of (*E*)-vinylsilane **2a′**.

We subsequently monitored this one-pot reaction of alkyne **1a** with Ph_2SiH_2 and HBpin (Scheme 4E, see the Supporting Information for the detailed monitoring of the reaction process). This experiment was set up in an argon-filled glovebox at room temperature and the reaction vial was then transferred to an ethanol bath at 0 °C. The GC analysis on the mixture indicated that alkyne **1a** was fully consumed before the reaction was cooled to 0 °C and (*E*)-vinylsilane **2a′** was selectively formed, together with a trace amount (<2%) of (*E*)-vinylboronate **2a″**. Further monitoring of the reaction showed that (*E*)-vinylsilane **2a′** was then smoothly converted to *gem*-(borylsilyl)alkane **2a** with high enantioselectivity.

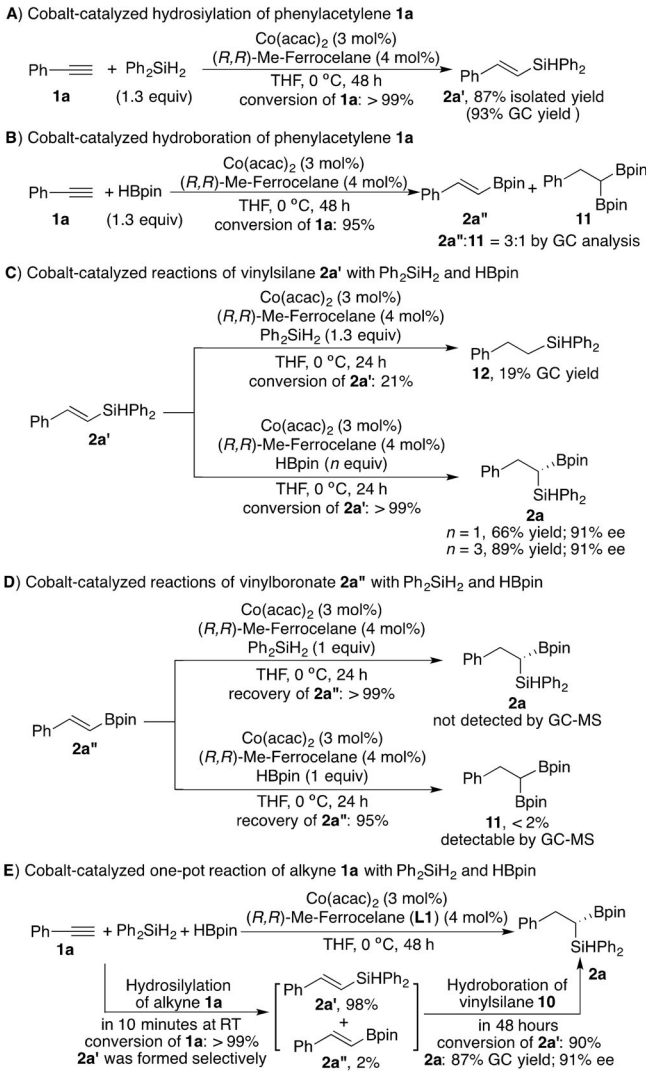
Based on the results of the above control experiments and the precedent for cobalt-catalyzed hydrosilylation and hydroboration of alkynes,[8,14] we proposed plausible catalytic pathways, which consist of a hydrosilylation cycle and a hydroboration cycle, for this cobalt-catalyzed synthesis of *gem*-(borylsilyl)alkanes (Scheme 5). The activation of Co-



Scheme 5. Proposed catalytic cycles for this cobalt-catalyzed asymmetric tandem hydrosilylation and hydroboration of terminal alkynes.

$(acac)_2$ with HBpin in the presence of chiral ligand (**L***) generates a cobalt hydride intermediate (**L***)CoH. The migratory insertion of alkyne **1a** into this Co-H species affords a vinylcobalt intermediate (**A**), which reacts with Ph_2SiH_2 to form (*E*)-vinylsilane **2a′**. The insertion of this vinylsilane intermediate into (**L***)Co-H generates an alkylcobalt species (**B**). This cobalt intermediate then reacts with HBpin to form *gem*-(borylsilyl)alkane **2a** and regenerates the catalytically active species (**L***)Co-H.

In summary, we have developed an enantioselective protocol to synthesize chiral *gem*-(borylsilyl)alkanes by a one-pot tandem reaction combining cobalt-catalyzed (*E*)-selective hydrosilylation of terminal alkynes and asymmetric hydroboration of the resulting (*E*)-vinylsilane intermediates. A series of terminal alkynes undergo this asymmetric reaction with high enantioselectivity in the presence of a chiral catalyst generated from $Co(acac)_2$ and (*R*,*R*)-Me-Ferrocelane. The chiral *gem*-(borylsilyl)alkane products from these asymmetric reactions can be readily converted to other chiral molecules by standard functional group manipulations. This protocol



Scheme 4. Control experiments.

provides a convenient and practical approach to prepare synthetically useful enantioenriched *gem*-(borylsilyl)alkanes from simple starting materials with one readily available cobalt catalyst.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: chiral *gem*-borylsilylalkanes · cobalt · hydroboration · hydrosilylation · terminal alkynes

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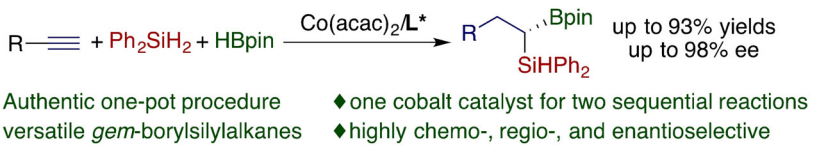
Communications

Asymmetric Catalysis

Y.'e. You, S. Ge* _____ ■■■■–■■■■

Cobalt-Catalyzed One-Pot Asymmetric Difunctionalization of Alkynes to Access Chiral *gem*-(Borylsilyl)alkanes



Enantioselective cobalt-catalyzed sequential hydrosilylation/hydroboration of alkynes is developed to access synthetically versatile chiral *gem*-(borylsilyl)alkanes with $Co(acac)_2$ and (*R*,*R*)-Me-Ferrocelane. A range of terminal alkynes react to afford the corresponding *gem*-(borylsilyl)alkanes with excellent enantioselectivity.