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Stereoselective Synthesis of 4-Hydroxy-1-Silyl-1-Allenylboranes and Access to 2-Silylethynyl-1,3-Diols

Ichrak El Haj Brahim,^[a, b] Islem Ishak Dridi,^[a, b] Raoudha Abderrahim,^[b] Fabrice Chemla,^[a] Franck Ferreira,^{*[a]} Olivier Jackowski,^{*[a]} and Alejandro Pérez-Luna^[a]

The highly stereoselective *gem*-silylboration of chiral 2-substituted 1-ethynylepoxides is reported herein. The reaction involves first the deprotonation of the epoxides in the acetylenic position followed by transmetallation with Et₃SiBpin. The transient silylborane ate-complexes generated undergo the stereoselective 1,2-migration of the Et₃Si-group to the sp-hybridized terminus carbon of the ethynyl-moiety in a stereo-

specific *anti*-addition. The moisture-sensitive and thermally unstable 4-hydroxy-1-triethylsilyl-1-allenyl(pinacolato)boranes thus obtained react with aldehydes through an S_E2'-mode of addition, affording highly functionalized 2-triethylsilylethynyl-1,3-diols with a good diastereoselectivity which is rationalized by a Yamamoto-Houk type transition state model.

Introduction

Unlike allenylboranes **1**^[1] and allenylsilanes **2**,^[2] the synthesis and use of which are well-documented, only three methods of preparation of 1-silyl-1-allenylboranes **3** have been reported to date in the literature (Figure 1)

In the early 1980's, Wang first showed that chiral 1-silyl-1-allenylboranes were obtained through the deprotonation of 1-trimethylsilylhex-1-yne **4** in the propargylic position followed by the transmetalation with *B*-MeO-9-BBN/BF₃·OEt₂ to provide 1-trimethylsilyl-1-allenylborane **5** (Scheme 1, top).^[3] However, due to a rapid metallotropic equilibrium with the propargylic borane, this species could not be isolated and was immediately used in reaction with carbonyl derivatives to provide α -allenic alcohols **6** as major products via a favored S_E2'-pathway. On the other hand, homopropargylic amines **7** were predominantly obtained through the reaction of **5** with imines via a favored S_E2'-pathway. Nevertheless, in both cases no information was given on the diastereochemical outcome of the reaction.

More recently, Shimizu developed a more general method of preparation of 1-silyl-1-allenylboranes **9** based on the *gem*-

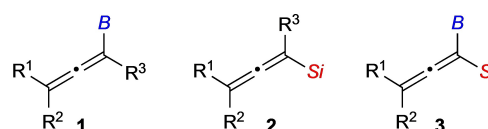


Figure 1. Allenylboranes, allenylsilanes and 1-silyl-1-allenylboranes.

silylboration of chiral propargylic electrophiles **8** (Scheme 1, middle).^[4–7] The method involves the deprotonation of **8** in the acetylenic position and the subsequent transmetalation with the use of Suginome's silylborane PhMe₂SiBpin.^[8] The protocol was amenable to asymmetric synthesis of metallotropically stable 1-phenyldimethylsilyl-1-allenylboranes **9** upon central-to-axial chirality transfer from secondary mesylates resulting from *anti*-1,2-migration of the silyl moiety. Even though the yields were good-to-excellent, the chirality transfer was modestly selective and the 1-silyl-1-allenylboranes **9** were obtained in only ~70% ee. Importantly however, the reaction of these species with cyclohexanecarboxaldehyde was shown to proceed via an S_E2'-pathway, giving the two homopropargylic alcohols **10** with a high diastereoselectivity.

Finally, very recently in 2021, Miura and Shishido reported the heterogeneous gold-catalyzed S_N1'-type *gem*-silylboration of propargylic methyl carbonate **11** with B₂pin₂ providing 1-trimethylsilyl-1-allenyl(pinacolato)borane **12**, albeit in achiral series (Scheme 1, bottom).^[9]

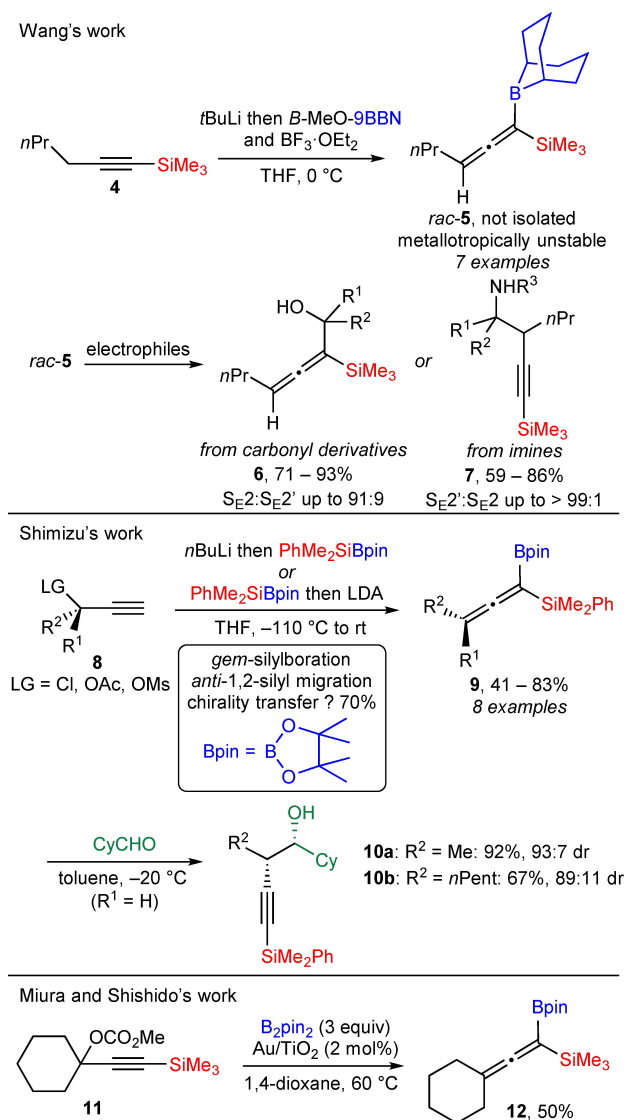
In this article, we disclose a new approach to accomplish with high diastereoselectivity the *gem*-silylboration of chiral 2-substituted 1-ethynylepoxides, thereby giving a stereoselective access to 4-hydroxy-1-silyl-1-allenylboranes (Scheme 2).^[10] The subsequent reaction of the allenylborane unit species with aldehydes is also shown to afford highly functionalized 2-silylethynyl-1,3-diols via a diastereoselective S_E2'-pathway.^[11]

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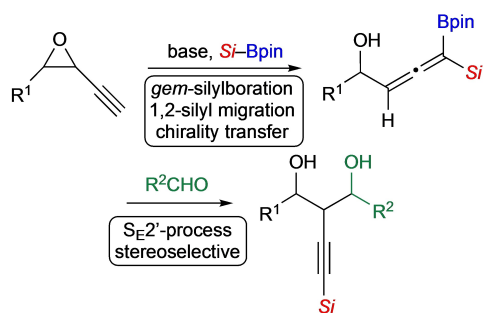
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Scheme 1. Previous works. [Correction added on 30 April 2024, after first online publication: Scheme 1 caption was updated in this version.]



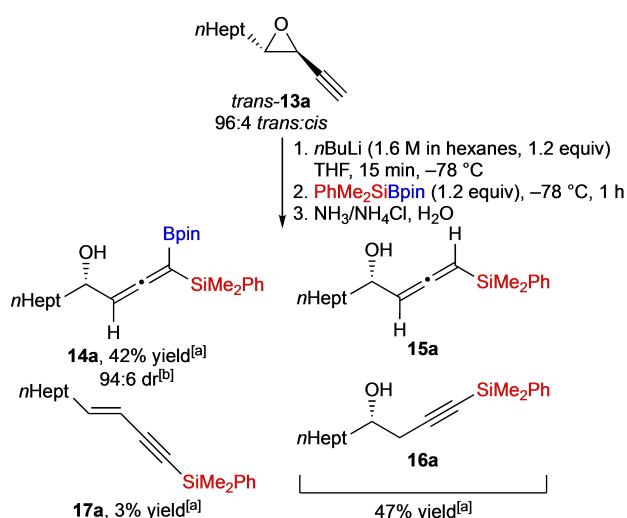
Scheme 2. This work.

Results and Discussion

We initiated our study by investigating the reaction of racemic 2-substituted 1-ethynylepoxyde *trans*-**13a** as a model substrate which was readily prepared with a high 96:4 *trans*:*cis* ratio (see

SI). In the first attempt, 1.2 equivalents of *n*BuLi (1.6 M in hexanes) were added dropwise to a THF solution of *trans*-**13a** at -78°C followed, after 15 min of stirring, by the addition of 1.2 equivalents of Suginome's silylborane $\text{PhMe}_2\text{SiBpin}$. After an additional 1 h of stirring, the mixture was quenched with an aqueous $\text{NH}_3/\text{NH}_4\text{Cl}$ solution (Scheme 3). Pleasantly, under these conditions, the formation of the desired product **14a** was observed (42% yield), accompanied by the two proto-deborylated compounds **15a** and **16a** (47% yield) and enyne **17a** (3% yield). Very interestingly, product **14a** was obtained with an excellent diastereoselectivity ($\text{dr}=94:6$) suggesting a remarkable central-to-axial chirality transfer. Both compounds **15a** and **16a** were assumed to result from hydrolysis of product **14a** by proto-deborylation with water following $\text{S}_{\text{E}2}$ - and $\text{S}_{\text{E}2'}$ -processes, respectively.^[12] In addition, product **14a** was found to be thermally unstable since after 4 h of standing at rt or 12 h at 5°C , it underwent complete degradation into enyne **17a**. It also showed instability upon purification over both silica gel (SiO_2) or neutral alumina (Al_2O_3), again leading to enyne **17a**.

This preliminary result was encouraging since it showed that compounds **15a**, **16a** and **17a** arose from the expected product **14a**, suggesting that *gem*-silylborylation efficiently occurred. We therefore undertook an intensive study to define the optimal reaction conditions (see SI). Several other lithiated bases (*n*BuLi, 2.5 M in hexanes or 3.2 M in pentane; *t*BuLi, 1.7 M in pentane; LDA, 1.7 M in pentane or 2.0 M in hexanes; MeLi, 1.5 M in Et_2O or 3.2 M in DME), at temperatures down to 0°C in coordinating or non-coordinating solvents (THF/ Et_2O mixtures, Et_2O , MTBE and pentane) were tested with $\text{PhMe}_2\text{SiBpin}$ or Et_3SiBpin by varying both the order of addition and the stoichiometry of the reagents. A large number of quenching conditions were also examined with emphasis on the use of a minimum of the proton source to avoid, or even prevent, the proto-deborylation of **14a** (solid Na_2HPO_4 and NaH_2PO_4 ; H_3PO_4 , 3.6 M in THF; HCl, 4 M in Et_2O and glacial AcOH). All these parameters were shown to have a great influence on the



Scheme 3. Preliminary study. [a] Yield calculated by ^1H NMR spectroscopy using biphenyl as internal standard on the crude material. [b] Dr determined by ^1H NMR spectroscopy on the crude material.

Table 1. Stereoselective synthesis of 4-hydroxy-1-triethylsilyl-1-allenyl(pinacolato)boranes (aS^*,S^*)-**14**.^[a]

	1. $n\text{BuLi}$ (3.2 M in pentane, 1 equiv) or MeLi (1.6 M in Et_2O , 1 equiv) THF, 45 min, $-78\text{ }^\circ\text{C}$ 2. AcOH (1 equiv), $-78\text{ }^\circ\text{C}$ to $0\text{ }^\circ\text{C}$ over 20 min		
trans-13 + Et_3SiBpin (2 equiv)		(aS^*,S^*)- 14 , up to 100% conv. ^[b] 60–90% yield ^[b] , up to 94:6 dr ^[c]	17 , 7% yield ^[b]
(aS^*,S^*)- 14a , 93% conv., 90% yield (and < 3% of enyne) 94:6 dr (from epoxide with trans:cis = 96:4)	(aS^*,S^*)- 14b , 77% conv., 70% yield (and 7% of enyne) 89:11 dr (from epoxide with trans:cis = 88:12)	(aS^*,S^*)- 14c , 100% conv., 60% yield ^[d] 88:12 dr (from epoxide with trans:cis = 82:18)	
(aS^*,S^*)- 14d , 90% conv., 85% yield (and 5% of enyne) 87:13 dr (from epoxide with trans:cis = 90:10)	14e , only traces	14f , only traces	

[a] Reactions run with 0.5 mmol of 2-substituted 1-ethynylepoxides trans-13 . [b] Conversions and yields calculated by ^1H NMR spectroscopy on the crude materials using biphenyl as internal standard. [c] Dr determined by ^1H NMR spectroscopy on the crude materials. [d] With an unidentified side-product.

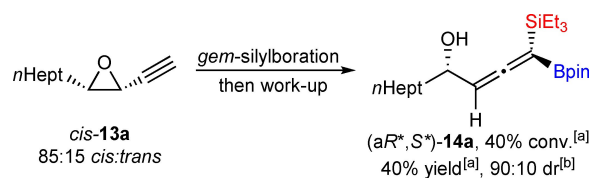
chemical outcome of the reaction. We then found that the best result was obtained when adding one equivalent of $n\text{BuLi}$ (3.6 M in pentane) or MeLi (1.6 M in Et_2O) to a 1:2 mixture of epoxide trans-13a and Et_3SiBpin ^[13] (the use of commercially available $\text{PhMe}_2\text{SiBpin}$ led to difficult-to-reproduce results) in THF at $-78\text{ }^\circ\text{C}$ for 45 min, and quenching with one equivalent of glacial acetic acid from $-78\text{ }^\circ\text{C}$ to $0\text{ }^\circ\text{C}$, over a 20 min-period (Table 1). Furthermore, in order to avoid any contact with water, the work-up was limited to drying over anhydrous Na_2SO_4 and filtration over cotton followed by concentration of the filtrate in vacuo. By following this procedure, product (aS^*,S^*)-**14a** was obtained in 90% yield with a high 94:6 dr. Except for traces of enyne **17a** (<3% yield), no other side-products were observed.

The optimal conditions in hands, we next extended the method to other epoxides trans-13 (Table 1). With epoxides trans-13b-d , bearing primary or secondary alkyl substituents, the expected products **14b-d** were obtained in good yields (60–85%) and with an excellent diastereoselectivity (dr up to 89:11) corresponding to a high central-to-axial chirality transfer. In all these cases, enynes **17** were formed in small amounts ($\leq 7\%$ yield). Conversely, these conditions proved to be ineffective with the bulky 2-*tert*-butyl-substituted and the 2-phenyl-substituted epoxides trans-13e and **13f** for which only traces of **14e** and **14f** were detected by ^1H NMR analysis.^[14] The relative (aS^*,S^*)-configuration of products **14a-e** was assigned on the basis of the *gem*-silylboration taking place via the 1,2-migration of Et_3Si in an *anti*-manner, as reported by Shimizu.^[4,15] Worthy of note, in all cases, the crude material was rapidly used in order to limit its thermal decomposition.^[16]

The reaction was next studied with epoxide cis-13a which was easily prepared with an 85:15 *cis:trans* ratio (see SI). With this epoxide, product **14a** with the (aR^*,S^*)-configuration was obtained in lower 40% conversion and yield, albeit with a

diastereomeric ratio of 90:10, suggesting again an excellent central-to-axial chirality transfer (Scheme 4).

We next envisioned to develop a straightforward access to highly functionalized chiral 2-triethylsilyl-1,3-diols **18** for which no synthesis had been reported yet. All our initial efforts to obtain product **18aa** by trapping alkoxide intermediate **Li-14a** in situ with benzaldehyde failed (Table 2). We finally manage to engage (aS^*,S^*)-**14a**, obtained following the work-up described above and without purification, in the reaction with benzaldehyde. Worthy of note, in all cases the reaction provided only two out of the four possible diastereomers. When the reaction was run at room temperature in THF, Et_2O , benzene or pentane, moderate yields ($\leq 78\%$) and poor diastereoselectivity (dr $\leq 60:40:0:0$) were obtained (Table 2, entries 1–4). Despite the complete consumption of (aS^*,S^*)-**14a**, in these four solvents, considerable degradation was observed. Using CH_2Cl_2 did not improve the yield but led to an increased diastereoselectivity, up to 77:23:0:0 (Table 1, entry 5). The best result was finally obtained in CHCl_3 with which product **18aa** was isolated in 69% yield with a satisfactory diastereoselectivity (dr = 80:20:0:0), within 4 h at room temperature (Table 2, entry 6). Lowering the temperature resulted in a slightly



Scheme 4. Stereospecific *gem*-silylboration. [a] Conversion and yield calculated by ^1H NMR spectroscopy using biphenyl as internal standard. [b] Dr determined by ^1H NMR spectroscopy on the crude material. [Correction added on 30 April 2024, after first online publication: Scheme 4 caption was updated in this version.]

Table 2. Preliminary study for access to 2-triethylsilylethynyl-1,3-diols.^[a]

Entry	Solvent	T (°C)	t (h) ^[b]	18aa (%)	dr
1	THF	rt	48	54 ^[c,d]	53:47:0:0 ^[g]
2	Et ₂ O	rt	6	55 ^[c,d]	55:45:0:0 ^[g]
3	benzene	rt	48	78 ^[c,d]	60:40:0:0 ^[g]
4	pentane	rt	4	72 ^[c,d]	50:50:0:0 ^[g]
5	CH ₂ Cl ₂	rt	48	54 ^[c,d]	77:23:0:0 ^[g]
6	CHCl ₃	rt	4	69 ^[e] (93 ^[c])	80:20:0:0 ^[h]
7	CHCl ₃	0	24	80 ^[e]	82:18:0:0 ^[g]
8	CHCl ₃	-20	48	42 ^[e,f]	85:15:0:0 ^[h]

[a] Reactions run with 0.25 – 0.5 mmol of *trans*-13a. [b] Times required for the complete consumption of *trans*-13a by TLC. [c] Yields calculated by ¹H NMR spectroscopy using biphenyl as internal standard. [d] Important degradation. [e] Isolated yields. [f] Important formation of enyne 17a. [g] Dr determined by ¹H MNR spectroscopy on the crude materials. [h] Dr determined by ¹H MNR spectroscopy on isolated 18aa.

improved diastereoselectivity but at the expense of the yield and with a high proportion of enyne 17a at -20 °C (Table 2, entries 7 and 8).

The best reaction conditions were next applied to other aldehydes. In each case, two equivalents of the aldehyde were employed at room temperature within 4 h in CHCl₃ (Table 3). Acetaldehyde and cyclohexanecarboxaldehyde led to products 18ab and 18ac in good isolated yields (68% and 63%) with excellent diastereomeric ratios (dr=83:17:0:0 and 96:4:0:0). Crotonaldehyde and cinnamaldehyde also provided products 18ad and 18ae in satisfactory isolated yields (59% and 71%), albeit with a significantly lower diastereoselectivity (dr=63:37:0:0). By contrast, the reaction was unsuccessful with pivaldehyde, providing only enyne 17a without any trace of the desired product 18af. The same lack of reactivity was also observed with ketones. By slowing down the reaction, the steric hindrance of pivaldehyde and ketones probably gave more time to degradation of (aS*,S*)-14a into enyne 17a to occur.

All products 18 were fully characterized by ¹H and ¹³C NMR analysis and HRMS. Moreover, the relative (*anti,syn*)-configuration of the (*O,C,O*)-stereotriad of these products could be unambiguously deduced from the single crystal X-ray analysis of 18ac (Figure 2).^[17] On the other hand, the relative configuration of the minor diastereomers could not be assigned.

The relative (*anti,syn*)-configuration of 2-triethylsilylethynyl-1,3-diols 18 was rationalized by the S₂'-nucleophilic addition of (aS*,S*)-14 to aldehydes occurring through chair-like Yamamoto-Houk^[18,19] type transition state model M1 (Scheme 5). In this model, the electrophilicity of the aldehyde is enhanced by the coordination of the boron atom of (aS*,S*)-14 on the oxygen of

Table 3. Stereoselective synthesis of 2-triethylsilylethynyl-1,3-diols (*anti,syn*)-18.^[a]

[a] Reactions carried out with 0.25 – 0.5 mmol of epoxide *trans*-13a. [b] Isolated yields over two steps. [c] Dr determined by ¹H MNR spectroscopy on isolated products (*anti,syn*)-18aa-ae. [d] Degradation into enyne 17a.

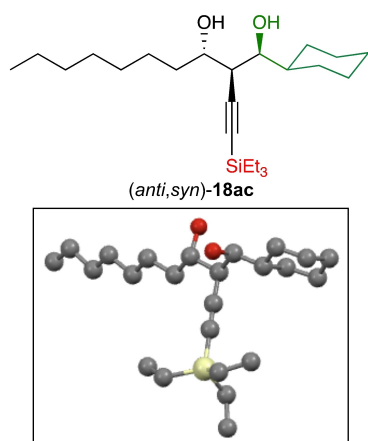


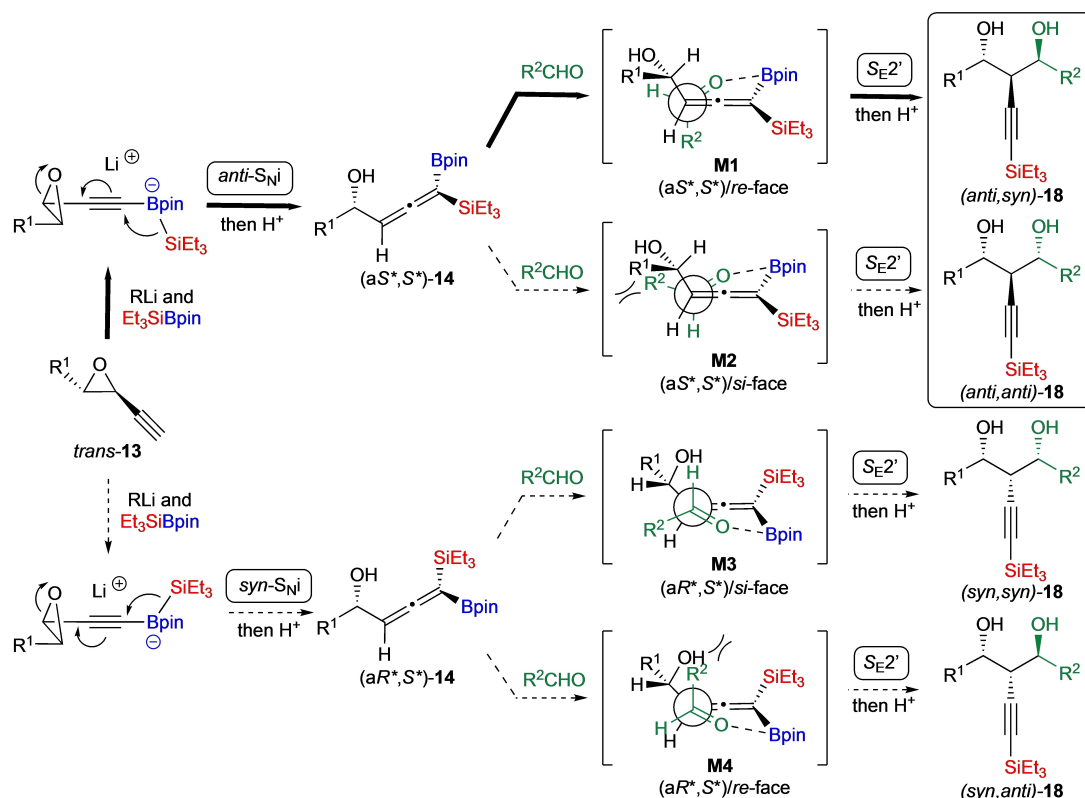
Figure 2. Single crystal X-ray analysis of (*anti,syn*)-**18ac**. Hydrogen atoms have been omitted for clarity.

the carbonyl function. In addition, (*aS**,*S**)-**14** adopts a conformation such that the hydrogen of the α -allenyl stereocenter eclipses the allenyl moiety while the electron-donating substituent R^1 reinforces the nucleophilicity of (*aS**,*S**)-**14** by the $\sigma_{(C-C)}/\pi_{(C=C)}$ overlap. In order to minimize steric interactions, the nucleophilic attack thus takes place on the *re*-face of the aldehyde and opposite to the R^1 substituent. The analogous competitive model **M2**, in which the nucleophilic addition of (*aS**,*S**)-**14** takes place on the *si*-face of the aldehyde, is more sterically demanding because of non-bonding interactions

between the R^2 substituent of the aldehyde and the γ -substituent of (*aS**,*S**)-**14**. Model **M2** is therefore less favorable than model **M1** and can be invoked in the formation of the minor diastereomers of products **18**, for which the relative (*anti,anti*)-configuration can reasonably be assigned. The two other possible Yamamoto-Houk type transition state models, **M3** and **M4**, which correspond to the nucleophilic addition of (*aR**,*S**)-**14** on the *si*- and *re*-face of the aldehyde respectively, lead to the two remaining (*syn,syn*)- and (*syn,anti*)-diastereomers. From these four possible models, the formation of products **18** with the relative (*anti,syn*)-configuration allows us to confirm the relative (*aS**,*S**)-configuration of products **14** and to assert with certainty that the *gem*-silylboration of 2-substituted 1-ethynylepoxides *trans*-**13** proceeds by an *anti*- S_Ni through the 1,2-migration of the silyl group.

Conclusions

To sum up, we have unveiled the highly stereoselective *gem*-silylboration of chiral 2-substituted 1-ethynylepoxides by deprotonation and subsequent transmetalation with $Et_3SiBpin$. The reaction was shown to proceed through an *anti*- S_Ni with the 1,2-migration of the Et_3Si -group from the in situ generated silylborane ate-complexes and gave 4-hydroxy-1-triethylsilyl-1-allenyl(pinacolato)boranes in a remarkable stereoselective and stereospecific manner. These chiral *gem*-bimetallic species further reacted with aldehydes to afford highly functionalized



Scheme 5. Rationalization of the stereoselectivity.

2-triethylsilylethynyl-1,3-diols with a good diastereoselectivity. Similar S_E2' -substitution reactions with other electrophiles are currently being investigated in our group.

Supporting Information

The authors have cited additional references within the Supporting Information. [Correction added on 30 April 2024, after first online publication: Citation for references 20-24 were removed in this version.]

Experimental Section

Representative procedure for the synthesis of compounds 14. Under argon atmosphere, to a solution of epoxide **13** (0.50 mmol) and Et_3SiBpin (242 mg, 1.00 mmol) in THF (5 mL), $n\text{BuLi}$ (3.2 M in pentane from the dilution of an 11 M commercial solution, 0.16 mL, 0.50 mmol) or MeLi (1.6 M in Et_2O , 0.31 mL, 0.50 mmol) was added dropwise at -78°C . The solution was stirred for 45 min at -78°C at which time Et_2O (5 mL) and glacial AcOH (29 μL , 1.00 mmol) were successively added. The resulting mixture was gently warmed to 0°C , over a 20 min-period. It was then dried over anhydrous Na_2SO_4 , filtered through cotton and concentrated in vacuo to afford **14**, as a pale-yellow oil, which was immediately used without purification or stored in the fridge before use as soon as possible.

Representative procedure for the synthesis of compounds (anti,syn)-18. Under argon atmosphere, to a 0.25 M solution of freshly prepared crude (aS^*,S^*)-**14** in CHCl_3 , the aldehyde (2 equiv) was added dropwise at room temperature. The mixture was stirred for 4 h and hydrolyzed with a 0.1 M aqueous HCl solution (5 mL). After addition of CH_2Cl_2 (5 mL), the layers were separated and the aqueous one was extracted with CH_2Cl_2 (3 \times). The combined organic layers were successively washed with brine and water, dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by flash column chromatography over silica gel (pentane/ Et_2O =100/0 to 40/60 gradient, v/v) afforded (*anti,syn*)-**18**.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: allenylboranes · allenylsilanes · silylboration · stereoselectivity · synthesis

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