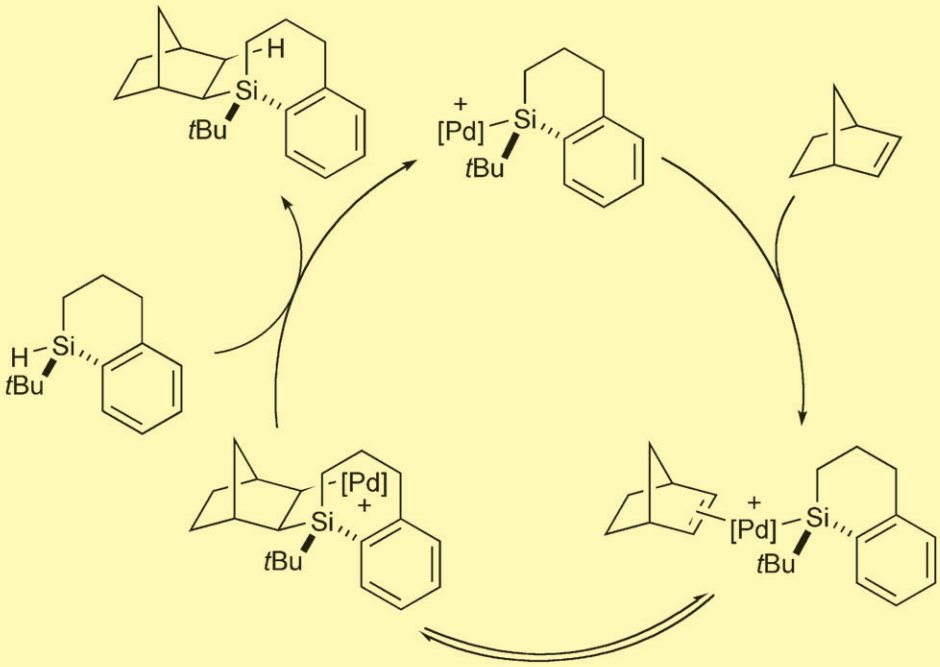
One Challenge – Two Solutions

Intermolecular Si → C Chirality Transfer



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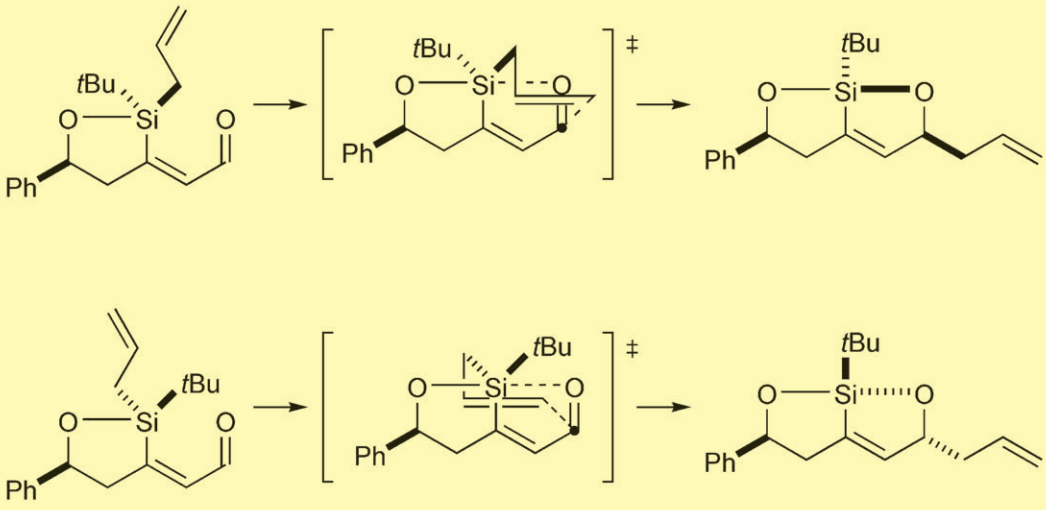

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Chirality Transfer from Silicon to Carbon

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Abstract: The exploitation of the asymmetry at silicon in stereoselective synthesis is an exceptionally challenging task. Initially, silicon-stereogenic silanes have been utilized to elucidate the stereochemical course of substitution reactions at silicon. Apart from these mechanistic investigations, only a handful of synthetic applications with an asymmetrically substituted silicon as the stereochemical controller have been reported to date. In these transformations the chiral silicon functions as a chiral auxiliary. Conversely, a direct transfer of chirality from silicon to carbon during bond formation and cleavage at silicon has remained open until its recent realization in both inter- and intramolecular reactions. In this Concept, the pivotal considerations in relation to the nature of suitable silanes as well as mechanistic prerequisites for an efficient chirality transfer will be discussed.

Keywords: allylation · asymmetric synthesis · chirality · hydrosilylation · silicon

Introduction

Effecting the transfer of chirality from silicon to carbon is still a particularly demanding challenge in asymmetric chemistry. Historically, the expression "chirality transfer from silicon to carbon" has been used inconsistently to classify several categorically different stereochemical scenarios of intermolecular processes: substrate[1] and reagent[2,3] control. In the substrate-controlled transformations, the stereogenic silicon moiety is covalently bound to the substrate functioning as a chiral auxiliary while the asymmetrically substituted silicon remains untouched.[4] Conversely, a covalent bond is cleaved and formed at the chiral silicon center in reagent-controlled reactions involving functionalized silanes with silicon-centered chirality and prochiral substrates. Any induced stereoselectivity in the carbon skeleton of the reaction product originates from the chirality in the silicon reagent.[5] This scenario represents the silicon-to-carbon chirality transfer.

This concept is to be extended to intramolecular processes, which are to be assigned to substrate-controlled reactions by definition. Chirality transfer from silicon to carbon is nevertheless realized when the distinct criteria of intermolecular, reagent-controlled transformations apply to the intramolecular scenario: 1) Cleavage and formation of a covalent bond at the stereogenic silicon and 2) silicon as the sole source of stereochemical information.

A handful of investigations directed towards an intermolecular silicon-to-carbon chirality transfer was reported in the past.[5] Without exception, diastereo- or enantioselectivity emerged as notoriously difficult to control in these reactions. The discouraging findings are likely to have deterred other research groups from pursuing further work in this area. Despite this rather mediocre prospect of success, both the inter-[6] and intramolecular[7] chirality transfer were recently realized with almost perfect stereocontrol. This Concept article delineates the basic considerations and resulting strategies, which finally led to the mastery of this formidable challenge.

Intermolecular Scenario[6]

Model reaction: Out of several conceivable model reactions, we reasoned that the transition-metal-catalyzed hydrosilylation[8] of prochiral alkenes **1** with silicon-stereogenic silanes **2** is particularly attractive (**1** → **3**, Scheme 1). As the asymmetrically substituted silicon fragment will stay in the product molecule **3**, the chirality transfer is reflected in the diastereomeric ratio of **3** whereupon its quantification is expressed as the diastereomeric excess of **3**. Logically, this stereochemical coherence allows for conducting this study with racemic silanes thereby avoiding their intricate preparation in enantiopure form.

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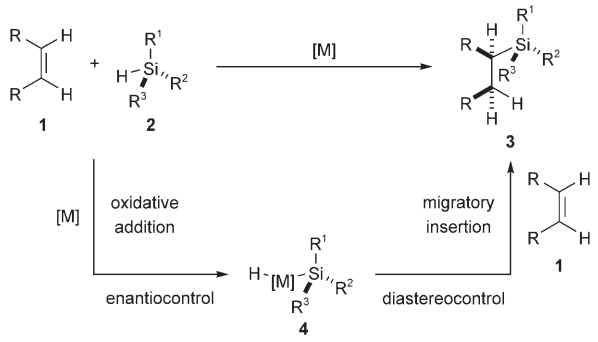


Scheme 1. Silicon-to-carbon chirality transfer in a transition-metal-catalyzed hydrosilylation ([M] = transition metal, $R^1 \neq R^2 \neq R^3$).

The diverse mechanisms of hydrosilylation reactions have been experimentally as well as theoretically elucidated for many transition-metal catalysts.[8] In a simplified mechanistic picture, the oxidative addition (**2** → **4**) and the migratory insertion (**4** → **3**) are the stereoselectivity-determining steps of the catalytic cycle (Scheme 1). The diastereoselectivity and, hence, the chirality transfer will be determined in the latter whereas the enantioselectivity will be controlled in the former. Consequently, a detailed understanding of the diastereoselective alkene insertion might provide implications for choosing proper reactants as well as an ideal catalyst. These parameters deserve specific attention and will be discussed in separate paragraphs.

The oxidative addition of Group VII transition metals into the silicon–hydrogen bond of chiral silanes **2** proceeds stereospecifically with retention of configuration at the silicon atom.[9] In principle, our reagent-controlled hydrosilylation might also be performed in an asymmetric fashion since non-racemic **2** will afford enantiomerically enriched **3** without any loss of stereochemical information.

Pivotal considerations: The use of stereogenic silicon as a stereochemical controller in reagent- as well as substrate-controlled transformations is inherently afflicted with a fundamental flaw: A carbon–silicon single bond (187 pm) is substantially longer than a carbon–carbon single bond (153 pm).[10] This situation ultimately counteracts formation of compact transition states, which in turn might attenuate facial selectivity in stereoselectivity-determining steps. Besides this unalterable feature, the steric environment around silicon might be equally influential on stereochemical induction. This environment is determined by the steric demand of each individual substituent, which ideally allows for efficient stereofacial discrimination when interacting with a prochiral functional group.

The number of organic silicon compounds with silicon-centered chirality, which are accessible in multi-gram quantities in optically pure form, is limited.[11] Strikingly, a single asymmetrically substituted silicon precursor introduced by Sommer [(*R*)-**5**,[12] Figure 1] has served almost exclusively as the starting point for asymmetric silicon chemistry. While its facile three-step synthesis has rather randomly privileged

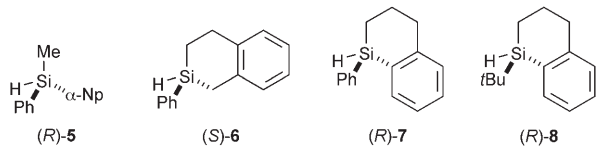


Figure 1. Silanes with silicon-centered chirality (α-Np = α-naphthyl).

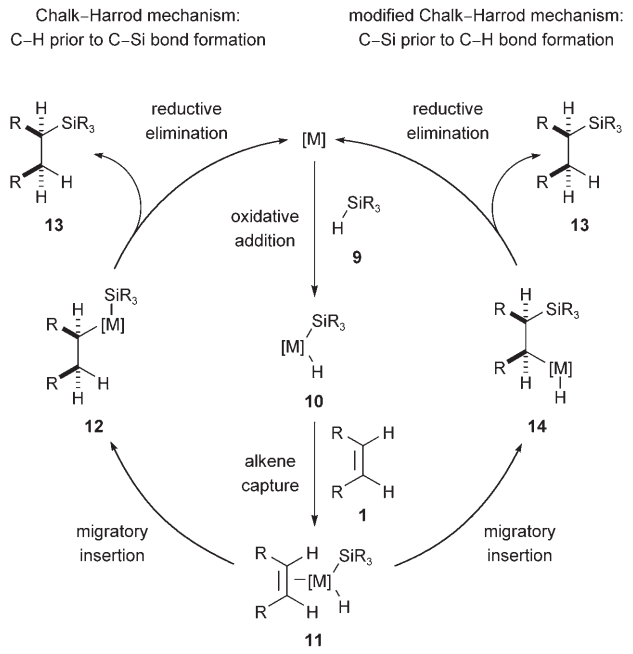
acyclic (*R*)-**5**, its structural features might, at least in part, account for the failures when probed in the chirality transfer.[1,5,13]

Within our rational yet empirical design of novel silicon-stereogenic silanes, we implemented two structural modifications, which could be particularly beneficial in chirality transfer reactions:

- In order to create rigidity, we envisioned silanes, in which the silicon center is embedded into a cyclic carbon framework [(*S*)-**6**[14] and (*R*)-**7**,[15] Figure 1]. In comparison with acyclic (*R*)-**5**, the conformational degrees of freedom around silicon are restricted, which might result in an increased level of organization in stereoselectivity-determining transition states. This would hopefully compensate for the negative effects caused by the relatively long carbon–silicon bonds.
- In acyclic silane (*R*)-**5** as well as cyclic silanes (*S*)-**6** and (*R*)-**7** (Figure 1), asymmetric induction originates from the steric differences of relatively similar substituents. We anticipated that a stereogenic silicon decorated with three substituents of distinct steric demand would be essential for efficient differentiation of stereotopic groups.

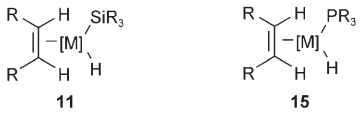
These requirements are met by sterically encumbered silane (*R*)-**8**.[6] It combines incorporation of the silicon into a cyclic framework and the desired substitution pattern at silicon (aryl versus small alkyl versus large alkyl).

Mechanistic prerequisites: The mechanism of many transition-metal-catalyzed hydrosilylation reactions is rationalized by two pathways:[8,16] Chalk–Harrod[17] (Scheme 2, left) and modified Chalk–Harrod mechanism[18] (Scheme 2, right). Both share the intermediate **11** but differ fundamentally in the order of bond-forming events. The catalysis starts with the oxidative addition of a transition metal [M] into the silicon–hydrogen bond (**9** → **10**) followed by coordination of an alkene **1** to electrophilic **10** (**10** → **11**). At this intersection, migratory insertion of the carbon–carbon double bond into both the transition-metal–hydrogen bond and the transition-metal–silicon bond are potential reaction channels for alkene–transition-metal-complex **11**. In the classic Chalk–Harrod mechanism carbon–hydrogen coupling (**11** → **12**) will occur prior to carbon–silicon bond formation (**12** → **13**). Alternatively, the reversed order of bond formations, carbon–silicon coupling (**11** → **14**) prior to carbon–hydrogen bond formation (**14** → **13**), is referred to as the modified Chalk–Harrod mechanism.



Scheme 2. Unified mechanistic overview: Classic and modified Chalk–Harrod mechanism.

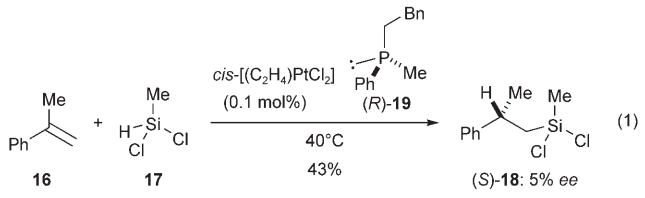
Alkene insertion as the configuration-determining step poses an interesting question: Which reaction pathway will be favorable over the other in terms of diastereoselectivity when using a chiral instead of an achiral silane? Under the circumstances of the classic Chalk–Harrod mechanism (Scheme 2, left), the alkene **1** inserts into the hydrogen–transition-metal bond (**11** → **12**). In this diastereoselectivity-determining step, the silyl group simply functions as a monodentate ligand coordinated to the transition metal. Importantly, silyl anions are isolobal to phosphines and, therefore, key intermediate **11** might formally be treated as **15** (Figure 2).



11 **15**

Figure 2. Isolobality of silyl anions (R_3Si^-) and phosphines (R_3P).[19]

When transferring this picture to asymmetrically substituted silanes, the Chalk–Harrod-type hydrosilylation becomes comparable to catalyst-controlled hydrosilylations employing monodentate phosphorus-stereogenic phosphines such as (*R*)-**19**,[19] which are known to induce low levels of enantioselection [**16** → (*S*)-**18**, Equation (1)].[20]

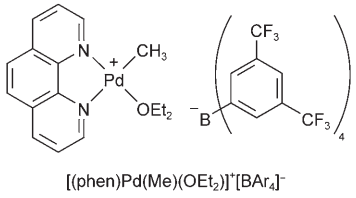


16 **17**

On the other hand, in the modified Chalk–Harrod mechanism (Scheme 2, right), the prochiral alkene **1** inserts into the silicon–transition-metal bond in the diastereoselectivity-determining step (**11** → **14**). In the course of this carbon–silicon coupling, the silicon-stereogenic silicon moiety must approach the carbon–carbon double bond in **11** from one of its diastereotopic faces and is not a remote monodentate spectator ligand.

According to this argumentation, we assumed that, out of these two possible reaction modes, higher diastereoselection might be expected when carbon–silicon coupling occurs prior to carbon–hydrogen bond formation. Our hypothesis is further supported by a survey of platinum-catalyzed hydrosilylation reactions of prochiral alkenes with the silanes depicted in Figure 1. These transformations, which are known to follow the Chalk–Harrod mechanism, provided merely marginal diastereoselectivities ($dr \leq 63{:}37$).[21]

In recent years, extensive mechanistic investigations have revealed that there are several catalyst systems, which are likely to follow modified Chalk–Harrod or related mechanisms. One of these catalysts, which was introduced to hydrosilylation chemistry by Brookhart,[22] appeared to be predestined for our purposes (**20**, Figure 3). Detailed elucidation of the catalytic cycle by Brookhart[22] as well as Widenhoefer[23] disclosed that carbon–silicon coupling occurs prior to carbon–hydrogen bond formation. Moreover, cationic palladium(II) complex **20** is highly reactive and promotes hydrosilylation of disubstituted carbon–carbon double bonds with otherwise unreactive triorganosilanes under mild reaction conditions.[22]



[(phen)Pd(Me)(OEt$_2$)]$^+$[BAr$_4$]$^-$

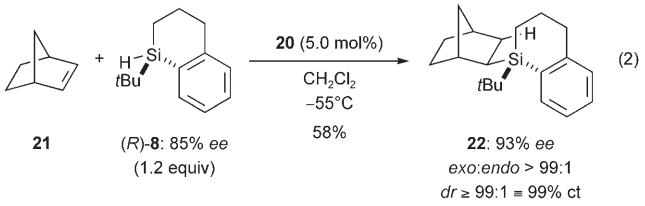
20

Figure 3. Brookhart's catalyst [phen = 1,10-phenanthroline, Ar = 3,5-bis(trifluoromethyl)phenyl].

Realization of the concept: Hydrosilylation reactions catalyzed by **20** involve the intermediacy of σ-alkylpalladium(II) complexes, which suffer fast β-hydride elimination.[22] In order to suppress this unwanted side-reaction, we selected norbornene (**21**) as the prochiral substrate. Silanes **5**–**8** (Figure 1) were used as racemic mixtures at the beginning of our study.

Acyclic silane *rac*-**5** showed almost no conversion under the standard reaction conditions [**20** (5.0 mol%), 0.1 M in CH_2Cl_2, −55 °C]. In accordance with previous results from our laboratories, cyclic silanes *rac*-**6** and *rac*-**7** were somewhat more reactive.[21] We were able to isolate the hydrosily-

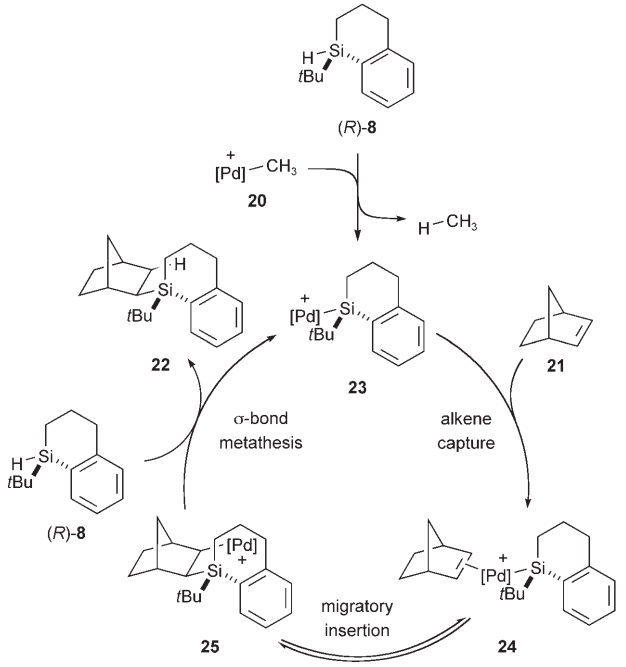
lation products in good yields but less than appreciable diastereomeric ratios (*dr* 51:49 for *rac*-**6** and *dr* 65:35 for *rac*-**7**).[6,24] The poor chirality transfer was not unexpected as none of these silanes **5**–**7** met our hypothetical constraints outlined in the pivotal considerations section. To our delight, rationally designed silane *rac*-**8** reacted with **21** in acceptable yield and with perfect diastereoselection [**21** → *rac*-**22**, Equation (2)]. This constitutes the first intermolecular silicon-to-carbon chirality transfer!



In an effort to extend this reaction in an asymmetric sense, we performed the identical hydrosilylation with enantioenriched (*R*)-**8** [**21** → **22**, Equation (2)]. We were surprised that the enantiomeric excess determined for **22** (93% *ee*) was substantially higher than the enantiomeric purity of the starting silane (*R*)-**8** (85% *ee*). This indicated a positive nonlinear effect, (+)-NLE,[25] which was later validated for several levels of enantiomeric purity of (*R*)-**8**.[6]

This asymmetric amplification in a reagent-controlled transformation provides direct experimental insight into the mechanism of hydrosilylations catalyzed by **20**. Based on the reported mechanistic investigations,[22,23] our findings are consistent with the so-called "two-silicon cycle", in which one of the partial steps involves two silicon-containing reactants (Scheme 3). The stereogenic silicon center in (*R*)-**8** functions as a stereochemical probe.

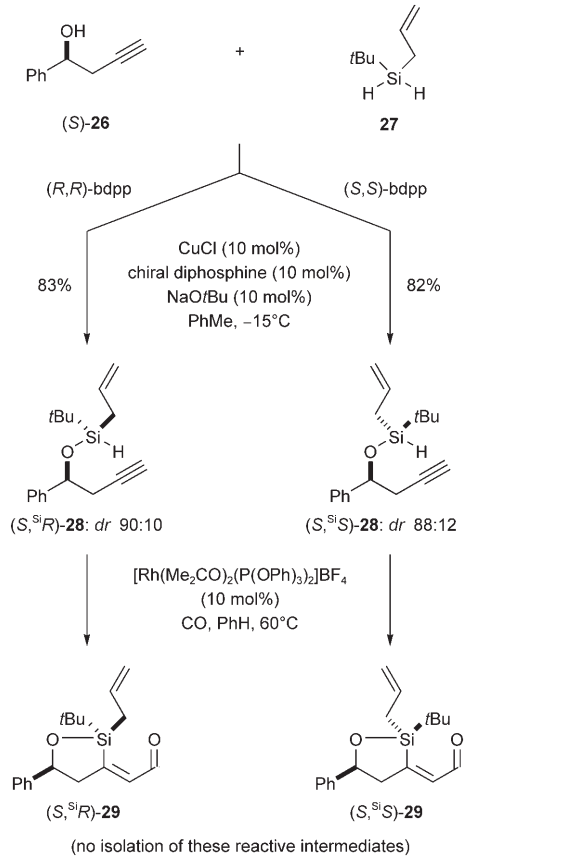
Reaction of (*R*)-**8** with in situ generated **20** furnishes cationic, mononuclear[22] silylpalladium intermediate **23** liberating methane [(*R*)-**8** → **23**].[26] Electrophilic **23** coordinates **21** thereby producing alkenepalladium complex **24**. Diastereoselective carbon–silicon coupling will take place in the subsequent migratory insertion (**24** → **25**) since there is no hydride ligand available at palladium.[27] Then, a diastereoselective σ-bond metathesis of major enantiomer (*R*)-**8** and minor enantiomer (*S*)-**8**, respectively, with enantiomerically enriched **25** is the setting for the asymmetric amplification. A matched [**25** + (*R*)-**8**] and a mismatched [**25** + (*S*)-**8**] scenario in this step are conceivable for preferential formation of one enantiomer of **22**.[26,28]



Scheme 3. Catalytic cycle: "two-silicon cycle".

Intramolecular Scenario[7]

General comments: Silicon-to-carbon chirality transfer in intramolecular transformations requires covalent linkage of the silicon-based stereochemical controller to the carbon framework. Apart from this requirement, the tetravalent silicon must at least bear another functional group, which will be displaced upon carbon–silicon coupling. Therefore, the



Scheme 4. Two-step in-situ-generation of chiral allylic silanes **29** [bdpp = 2,4-bis(diphenylphosphino)pentane].

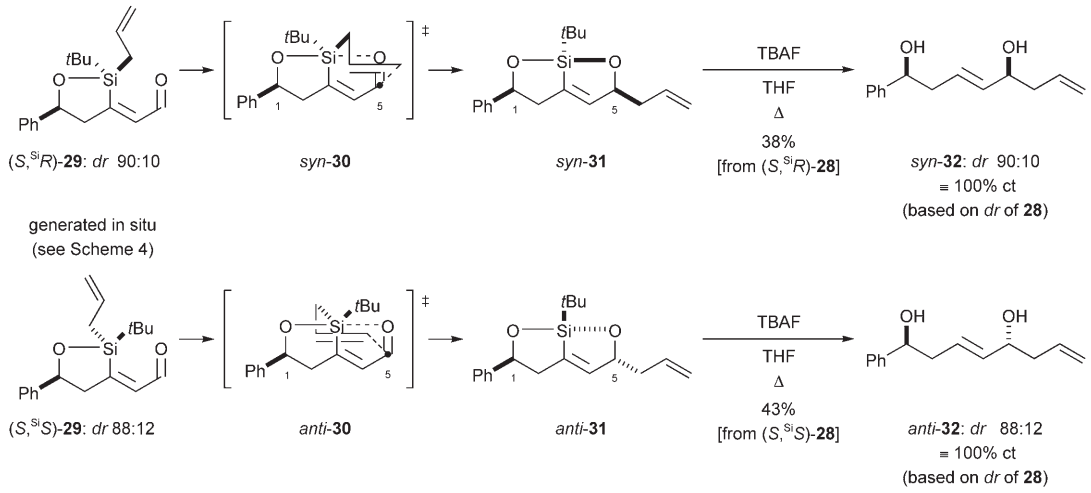
substitution pattern at silicon might not be as arbitrary as in the intermolecular case. In return, intramolecular carbon–silicon bond formation is likely to involve structurally more biased intermediates and transition states thereby enhancing diastereoselection.

Realization of the concept: In a system devised by Leighton,[7] a silicon-stereogenic allylic silane is supposed to intramolecularly transfer its allyl group onto an aldehyde. The requisite allylic silanes containing an asymmetrically substituted silicon (and carbon atom) were elegantly accessed in two synthetic operations (Scheme 4): Diastereoselective, dehydrogenative etherification[7,29] of alcohol (*S*)-**26** with prochiral **27** (**26** → **28**) and subsequent diastereospecific silylformylation[7,30] (**28** → **29**). By this, both reactive intermediates (*S*,^{Si}*R*)-**29** and (*S*,^{Si}*S*)-**29** were obtained in enantiomerically pure form and good diastereoselectivity.

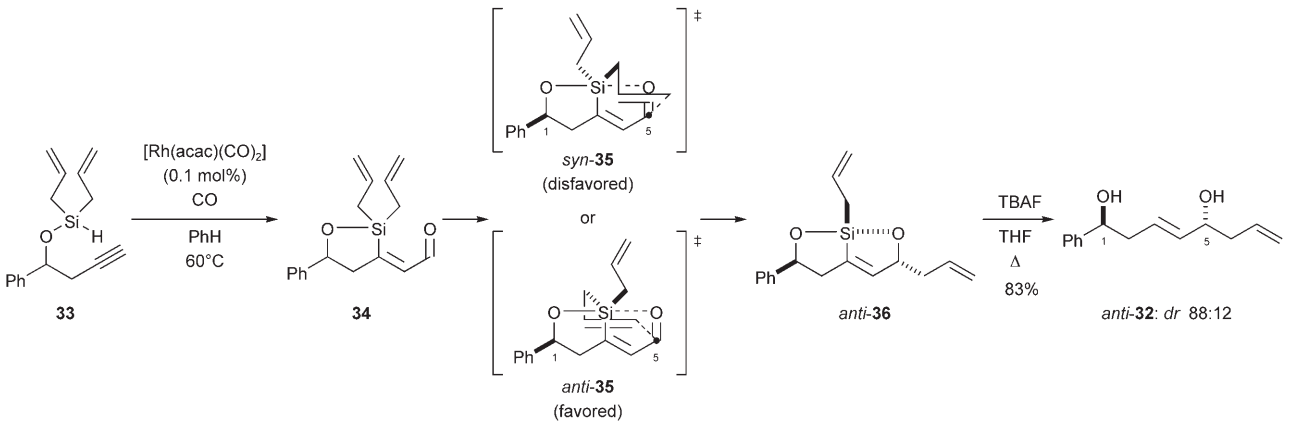
These strained five-membered silacycles[31] were sufficiently Lewis-acidic to bind the Lewis-basic carbonyl oxygen (**29** → **30**, Scheme 5). The configuration at C-5 is set diastereospecifically in the following spontaneous allylation, which proceeds through six-membered transition states (**30**, Scheme 5).[32] Dependent on the configuration at silicon and independent of the configuration at C-1 in **29**, the primary products **31** were formed diastereoselectively with *syn* [(*S*,^{Si}*R*)-**29** → *syn*-**31**)] and *anti* [(*S*,^{Si}*S*)-**29** → *anti*-**31**] 1,5-relative configurations, respectively. Exhaustive cleavage of all linkages to silicon afforded the deprotected 1,5-diol (**31** → **32**).

In this case, the silicon-to-carbon chirality transfer is calculated from the diastereomeric ratios of substrate **29** and product **32** [ct = 100 × *de* (**32**)/*de* (**29**)]. The asymmetry at C-1 has no effect on the stereochemical course of the allylsilylation and might be regarded as a stereochemical reference point. This transformation is diastereospecific because of an immaculate chirality transfer (100 % ct) for the pair (*S*,^{Si}*R*)-**29** and (*S*,^{Si}*S*)-**29**. Since the stereochemical outcome is solely governed by the stereogenic silicon center, this constitutes the first intramolecular silicon-to-carbon chirality transfer.

Leighton also demonstrated that the pronounced induction of the stereogenic silicon (**30** → **31**, Scheme 5) over-



Scheme 5. Silicon-to-carbon chirality transfer in an intramolecular allylation.



Scheme 6. Remote 1,5-induction in a diastereoselective allylation.

rides strong induction of C-1 (Scheme 6).[33] Intramolecular silylformylation[30] of **33** provided silacycle **34** with two diastereotopic allyl groups at silicon. In the resulting Lewis-acid/Lewis-base complexes formed (**34** → **35**), one of the diastereotopic allyl groups is preferentially transferred (**35** → **36**).[32] Intermediate *anti*-**35** is favored over *syn*-**35** and, after complete desilylation (*anti*-**36** → *anti*-**32**), the 1,5-diol *anti*-**32** was isolated in good diastereoselectivity. Consequently, in the absence of asymmetric substitution at silicon, rare 1,5-induction controls the stereochemical outcome.

Perspectives

For the first time, the reagent-controlled hydrosilylation clearly illustrates that under certain circumstances it is possible to transfer chirality from silicon to carbon in an intermolecular transformation.[6] Our current understanding has led to cyclic silane **8** decorated with three different substituents (Figure 1). While **8** appears to be privileged[34] with regard to chirality transfer, synthetic applicability will require the elaboration of new protocols for the difficult oxidative degradation of sterically hindered silanes. Hence, the present work rather aims at the utilization of stereogenic silanes as a stereochemical probe in transition-metal catalysis.

On the other hand, the intramolecular silicon-to-carbon chirality transfer developed by Leighton is synthetically useful.[7] It allows for the stereoselective access of the *syn*- and *anti*-1,5-diol motif, which is found in several attractive natural products. Leighton has nicely included this diastereoselective allylation in a fragment synthesis of the dolabelide family.[35]

The novel concepts described herein might pave the way for further activities in asymmetric organosilicon chemistry.

Acknowledgements

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