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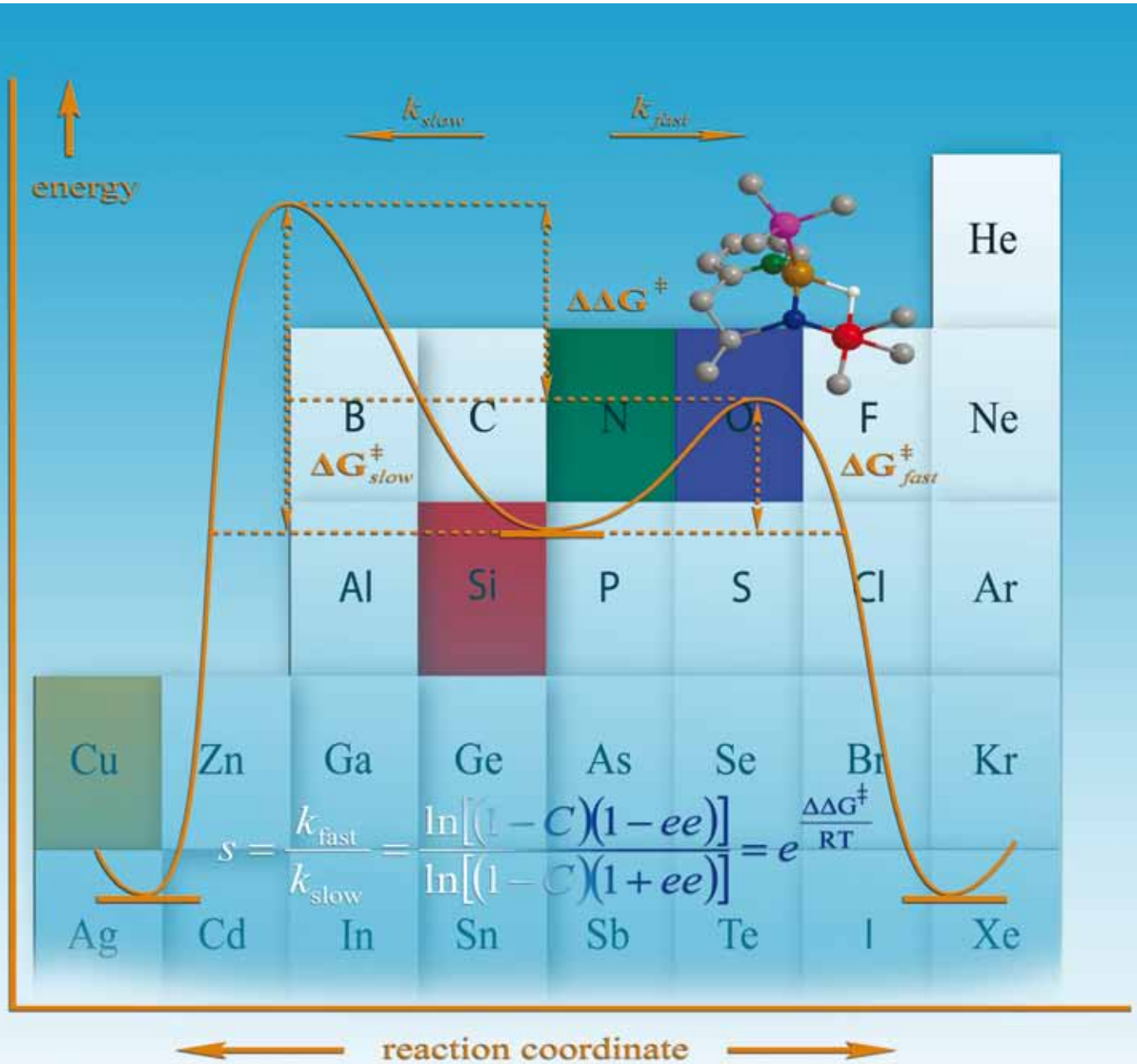

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Asymmetric Si–O coupling of alcohols

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Stereoselective Si–O couplings are auspicious processes for the synthesis of both chiral alcohols and chiral silanes. Attractive facets of this theme are currently enjoying a renaissance, and the several significant contributions are summarised in this Emerging Area.

Introduction

Chirality of life is closely connected to asymmetry at carbon, and countless synthetic methods are available to control the absolute configuration at carbon atoms. Conversely, silicon itself and, by association, stereogenicity at silicon are not integral parts of organic nature. The chemistry of silicon-stereogenic silanes might nevertheless be useful, either preparatively in the form of chiral reagents as well as mechanistic probes or as a source of inspiration for novel silicon-based methodology.[1,2] One particularly intriguing transformation, to which all of these aspects apply equally, is the stereoselective dehydrogenative Si–O coupling of Si–H and H–O bonds. The stereochemical disposition of the coupling partners will then allow for discrimination of enantiotopic groups and enantiomeric molecules, thereby accessing either silicon-stereogenic silanes or chiral alcohols. Creating stereogenicity at silicon in an Si–O bond-forming event yields valuable precursors of asymmetrically substituted silanes, as there are several protocols for subsequent stereospecific nucleophilic displacement of Si–O bonds available, and that is indeed how it all started.[2,3] In turn, making chiral non-racemic alcohols through Si–O coupling, that is the asymmetric protection of hydroxy groups, was later realised in the kinetic resolution of racemic mixtures and in the desymmetrisation of prochiral compounds.[4] This Emerging Area summarises the chronology of stereoselective dehydrogenative Si–O couplings and elaborates its evolution from substrate through reagent to finally catalyst control, not even involving chirality at the silicon atom.[5] We also establish a connection to recent catalyst-controlled Si–O bond formations of Si–X coupling partners.

The article is arranged according to the time bar depicted in Fig. 1. The major subsections are devoted to Si–H (above) and Si–X reagents (below) as coupling partners, and we define the alcohol as the substrate in all cases. This classification allows for clearly distinguishing the origin of stereoinduction into substrate-, reagent- and catalyst-controlled protocols, including combinations thereof.

Diastereoselective transition metal-catalysed couplings of silanes and alcohols[6] began with a seminal investigation by Corriu and Moreau, in which several permutations of prochiral silanes and chiral/achiral alcohols were coupled in the presence of a chiral/achiral transition metal.[3,7,8] Leighton *et al.* later perfected the substrate- and catalyst-controlled variant on that conceptual basis.[9] It is also possible to "store" the chiral information in the silane itself, thereby rendering an Si–O coupling reagent-controlled. The resultant kinetic resolution of alcohols[10,11] was extensively investigated by ourselves over the last half decade.[12–16] In terms of synthetic applicability, catalyst control is certainly attractive, and this is where procedures based on Si–H and Si–X meet. We recently devised an enantioselective dehydrogenative Si–O coupling[17] whereas—based on a stoichiometric reaction by Ishikawa *et al.*—[18] Hoveyda and Snapper *et al.*[19–21] accomplished organocatalysed Si–O bond formation using chlorosilanes.[22]

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Marius Mewald earned his diploma degree with Martin Oestreich in Münster in 2009. As part of his training, he spent a three-months internship at F. Hoffmann-La Roche AG in Basel/Switzerland (2008). While his undergraduate project was on asymmetric Si–O coupling chemistry, his graduate research now targets the synthesis and evaluation of novel strong Lewis acids in asymmetric catalysis.

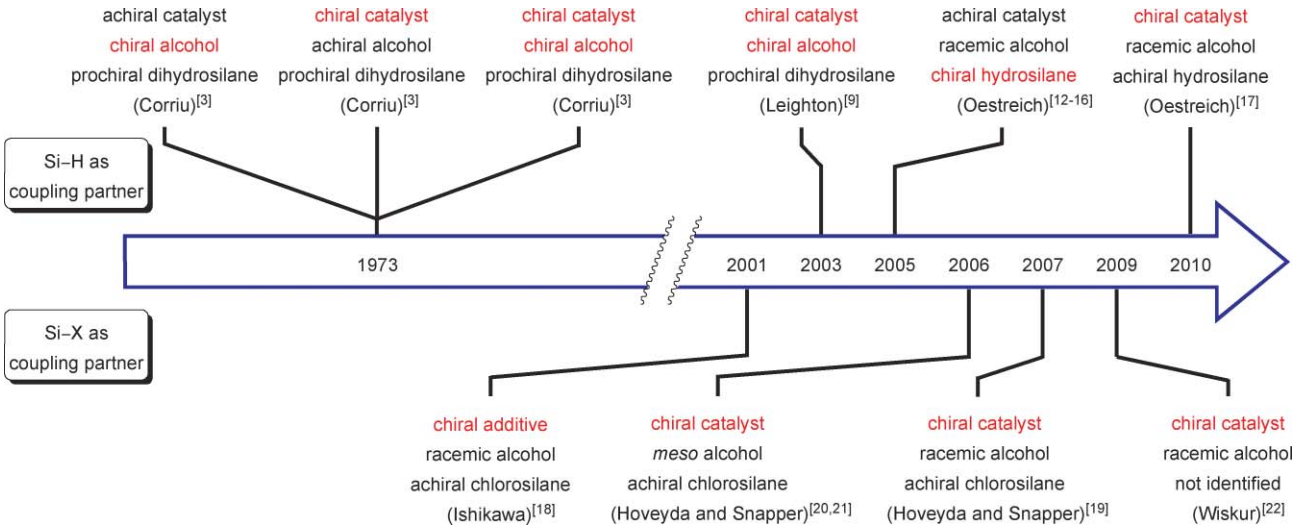


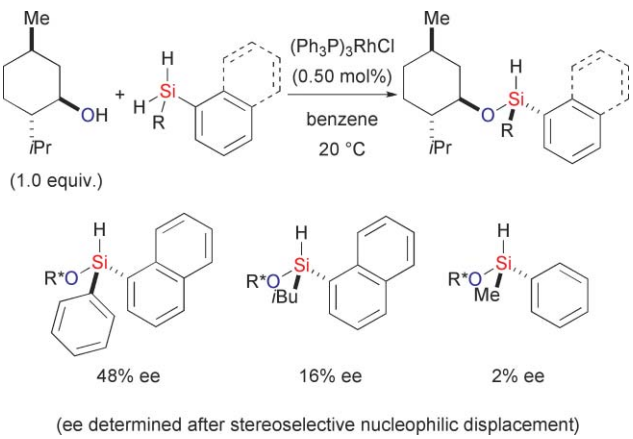
Fig. 1 Time bar of the evolution of asymmetric Si–O couplings (X = leaving group).

We note though that asymmetric Si–O couplings of silicon-stereogenic silanes and H_2O are beyond the scope of this Emerging Area. Enantiospecific formation of chiral silanols is commonly used to distinguish between different mechanistic pathways of silane oxidation, resulting in either retention or inversion at the silicon atom.[23]

Si–H as coupling partner

Substrate control

Until today, the preparation of silicon-stereogenic silanes in virtually enantiopure form usually requires laborious separation of diastereomers with a chiral auxiliary covalently bound to the asymmetrically substituted silicon atom. In a few cases, separation of diastereomeric silicon ethers derived from (–)-menthol through crystallisation is exceptionally facile.[24–26] The demand of enantioselective approaches to chiral silanes[27–30] must have prompted Corriu *et al.* to seek alternative routes starting from prochiral silanes with enantiotopic hydrogens. For this, Corriu and Moreau reacted several prochiral silanes with chiral non-racemic alcohols under Rh(I) catalysis.[3,7] Using the example of (–)-menthol and achiral $(Ph_3P)_3RhCl$, the influence of the substitution pattern at the silicon atom on enantiotopic discrimination was investigated (Scheme 1).[3,7] Whereas the enantiomeric excesses obtained were moderate by current standards, this study had significant impact as it corroborated that stereochemical information in the alcohol backbone can induce chirality at silicon. Another important lesson might be learned from this set of acyclic silanes (Scheme 1) and from the observation that diastereocontrol is also decent with a cyclic silane (not shown): both the steric demand of substituents at the silicon atom and the rigidity of the system exert substantial influence on stereocontrol.[31] These nuances might seem trivial but it was these that enabled efficient substrate/catalyst control (*cf.* Scheme 2) as well as reagent control (*cf.* Scheme 3) several decades later.

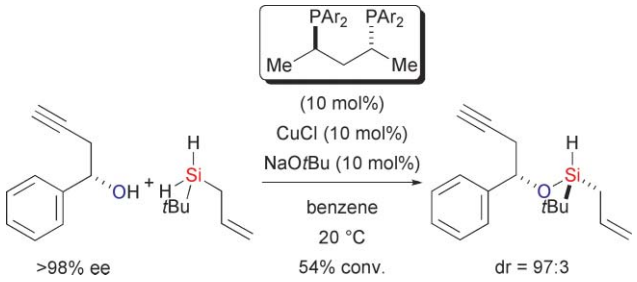


Scheme 1 Substrate-controlled Si–O coupling developed by Corriu.

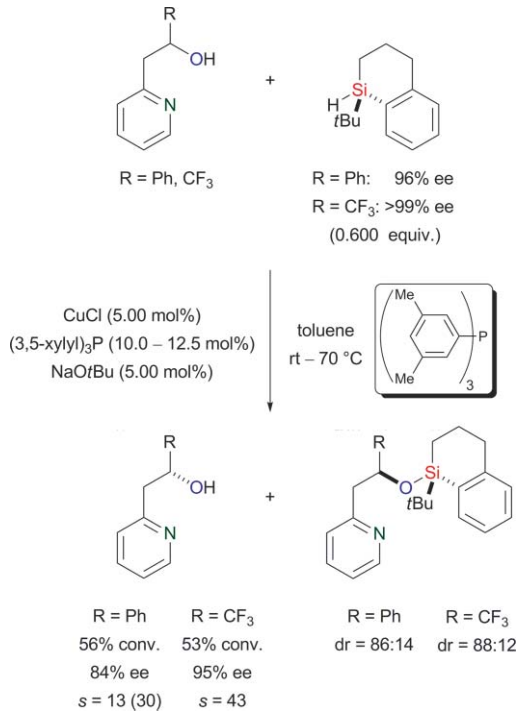
In the above setup, (achiral) Wilkinson's catalyst and chiral alcohols were combined. Corriu and Moreau also tested a catalyst-controlled version, using chiral catalysts and achiral alcohols.[3] The

Martin Oestreich

Martin Oestreich is Professor of Organic Chemistry at the Westfälische Wilhelms-Universität Münster. He received his diploma degree with Paul Knochel (Marburg, 1996) and his doctoral degree with Dieter Hoppe (Münster, 1999). After a two-year postdoctoral stint with Larry E. Overman (Irvine, 2001), he initiated an independent research program and completed his habilitation with Reinhard Brückner (Freiburg, 2005). His current research interests span areas of organoelement chemistry, understanding reaction mechanisms, and asymmetric catalysis.



Scheme 2 Joining substrate and catalyst control in an Si–O coupling developed by Leighton (Ar = 3,5-$F_2C_6H_3$).



Scheme 3 Reagent-controlled Si–O coupling in the Cu(I)-catalysed kinetic resolution developed by Oestreich (for R = CF_3, absolute configurations are inverted).

reaction of cyclohexanol and 1-NpPhSiH_2 in the presence of a chirally modified Rh(I) catalyst indeed yielded the corresponding silicon ether in 17% ee (not shown). Although the enantiomeric excess was low, it again showed that it is possible to introduce silicon-centred chirality in a transition metal-catalysed Si–O coupling.

To our surprise, this chemistry was then abandoned by Corriu *et al.* and not revived by other research groups for nearly three decades. Leighton *et al.* were the first to realise its potential.[9,32] Joining substrate and catalyst control, these authors elaborated the enantioselective synthesis of a single silane (Scheme 2). Their catalytic system is based on a report by Lorenz and Schubert,[33] in which phosphine-stabilised hexameric copper(I) hydride [(Ph_3P)CuH]$_6$[34]—Stryker's reagent, a "Cu–H" complex—is shown to effectively promote dehydrogenative Si–O couplings. According to a method introduced by Buchwald *et al.*,[35] a Cu–H complex is also generated *in situ* from CuCl, a phosphine ligand and NaO*t*Bu. Consistent with the observations made by Corriu and Moreau,[3,7] a sterically demanding substituent at the silicon atom is also crucial in Leighton's system, and a *t*Bu group emerged as optimal. An extensive screening of both chiral bidentate phosphine ligands and chiral alcohols eventually produced a synthetically useful level of enantiotopic discrimination (Scheme 2). This methodology has not been extended to other silane–alcohol combinations yet.

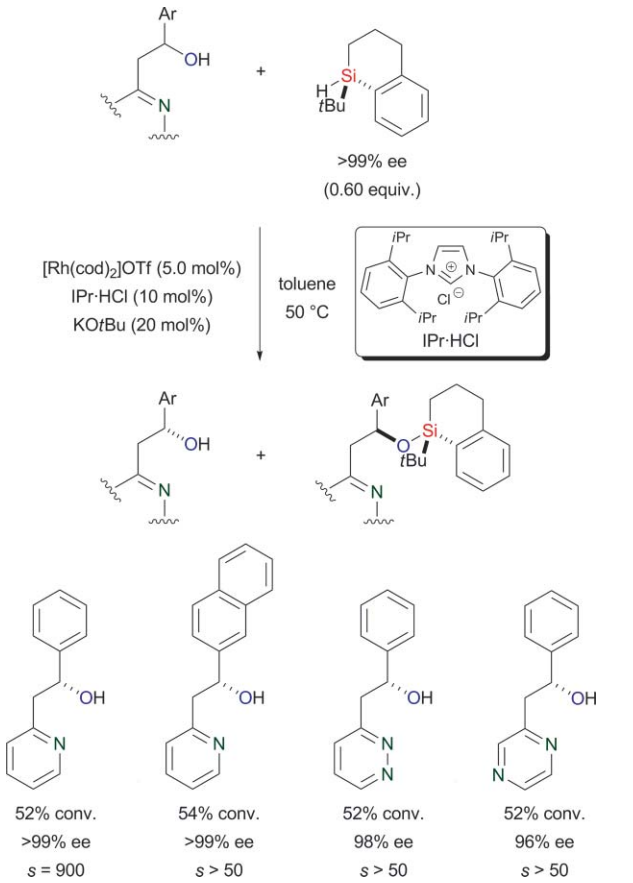
Reagent control

When we entered the field of asymmetric Si–O coupling half a decade ago, we were asking ourselves whether a reagent-controlled strategy complementary to previous ones (*cf.* Schemes 1 and 2)[3,7–9] would also be viable. To perform an Si–O coupling with an enantiopure silicon-stereogenic silane and a racemic mixture of an alcohol corresponds to a kinetic resolution, in which the chiral silane kinetically selects one of the two enantiomeric alcohols. Such a process is conceptually attractive because silanes are standard protecting groups,[36] and kinetic resolution and alcohol protection would be merged into a single synthetic operation.

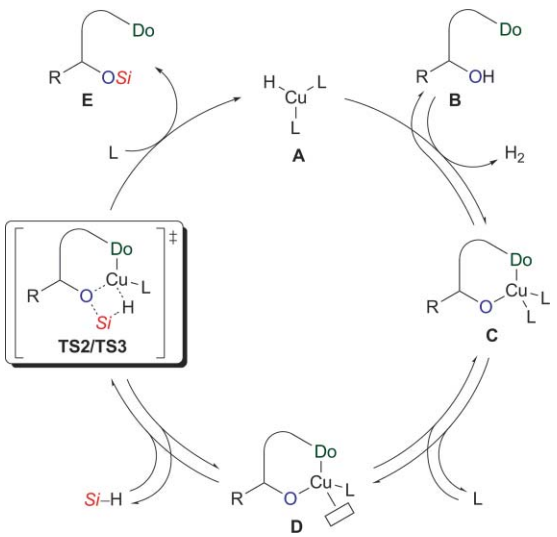
We then chose the CuCl–phosphine–NaO*t*Bu system (*vide supra*) and reacted a donor-functionalised alcohol with our cyclic silane (Scheme 3).[12,13] The design of this and related silanes from our laboratory[25,26] was guided by the above-discussed parameters[3,7] and experiences from other projects.[31,37] Again, the steric hindrance imposed by the *t*Bu group and the rigidity imparted by the cyclic skeleton were pivotal factors for efficient stereoselection. Thus, we were able to isolate the slow-reacting alcohol enantiomer with 84% ee and the silicon ether of the fast-reacting alcohol with dr = 86 : 14 at 56% conversion (Scheme 3).[12] The selectivity factor *s* was determined to be 30 (based on enantiopure silane). By this methodology, we were able to resolve a number of chiral carbinols with different azine donors (not shown),[13] including a series of CF_3-substituted alcohols with improved selectivity factors (*e.g.*, *s* = 43, Scheme 3).[14] In contrast to the work of Leighton *et al.* (*cf.* Scheme 2), our system required the use of monodentate phosphine ligands, which is logically rationalised by our mechanistic picture (*vide infra*). A donor, usually an N(sp^2) atom, is also needed to secure turnover and stereoselection, an obvious limitation that will have to be addressed in the near future.

Inspired by the Corriu and Moreau papers,[3,7] we had also tested Rh(I)-based catalytic systems and we discovered that a Rh(I)–carbene complex enables the resolution of our model alcohols with near perfect selectivities (Scheme 4).[16] In a single example, we rigorously determined the selectivity factor, peaking at a "world record" for non-enzymatic kinetic resolution of *s* = 900. The mechanism of this Rh(I) catalysis is unclear at this stage but it might be similar to that of the Cu(I)- or Cu–H-catalysed process (*cf.* Scheme 5).

Tertiary alcohols are by far the most challenging substrates for kinetic resolution and merely a handful of examples are known.[15] Attempts to subject these to our diastereoselective Si–O coupling protocols initially failed since the *t*Bu-substituted, six-membered ring silane was simply too unreactive. Conversely, the cognate five-membered ring silane with its unique strain-induced Lewis acidity displayed sufficient reactivity (Scheme 6).[15] Due to difficulties to obtain the silane in enantiopure form, the experimental *s* values are lower than those expected for the genuine reagent (those are available from the dr in the racemic series and reported in parentheses).

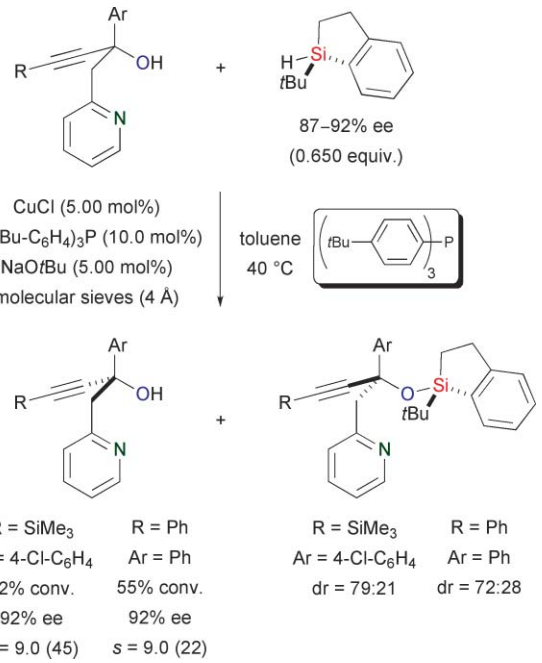


Scheme 4 Reagent-controlled Si–O coupling in the Rh(I)-catalysed kinetic resolution developed by Oestreich.



Scheme 5 Mechanistic rationale for the Cu(I)-catalysed dehydrogenative Si–O coupling of donor-functionalised alcohols (Do = donor).

Supported by experimental data and quantum-chemical calculations, we proposed a mechanism of the Cu–H-catalysed Si–O coupling (Scheme 5).[13,38] The Cu(I) hydride **A**, likely to be stabilised by two monodentate phosphine ligands, is the



Scheme 6 Diastereoselective Si–O coupling of tertiary alcohols with a strained cyclic silane developed by Oestreich.

(*in situ*-generated) catalytically active complex. The cycle then commences with a H_2-releasing proton–hydride reaction of the hydroxy group in **B** and Cu–H complex **A** as well as coordination of the donor in **B** to the Cu(I) centre (**A** → **C**). In **C**, the Cu(I) atom is coordinatively saturated, which is why one phosphine ligand must dissociate to make room for the silane to coordinate (**C** → **D**), and this step is presumably rate-determining. Coordinatively unsaturated **D** is now disposed to silane coordination, followed by Si–O bond formation in an irreversible σ-bond metathesis (**D** → **TS2/TS3** → **E**). This silane coordination–σ-bond metathesis sequence is the stereochemistry-determining step of this catalysis. **TS2/TS3** might also be viewed as a transient intermediate[13] with concerted reorganisation of bonds. However, no racemization is seen with silicon-stereogenic silanes, which clearly demonstrates that **TS2/TS3** is not a hypervalent intermediate, otherwise prone to racemization through pseudorotation. The σ-bond metathesis transforms bidentate alcohol **B** into monodentate **E**, which dissociates from Cu(I) to reform active catalyst **A** (**TS2/TS3** → **A**).

It is reasonable to assume a similar mechanism for the substrate- and catalyst-controlled catalysis developed by Leighton *et al.*[9] (*cf.* Scheme 2). The corresponding transition state **TS1** now accommodates a monodentate alcohol and a bidentate phosphine ligand (Fig. 2). These transition-state models **TS2** and **TS1** help to understand the experimental observation that either mono- or bidentate ligands are superior. By looking at these stereochemical scenarios, a third option emerges: while chirality resides in the alcohol or the silane in **TS1** and **TS2**, respectively, a purely catalyst-controlled process with a chiral ligand is possible (**TS3**, Fig. 2). In turn, such a scenario is particularly challenging as asymmetric induction will have to originate from a single monodentate ligand. By this, we could replace our *chiral* silane by an *achiral* silane, thereby rendering our diastereoselective Si–O coupling enantioselective (**TS2** *vs.* **TS3**, Fig. 2).

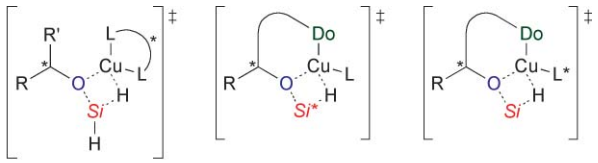


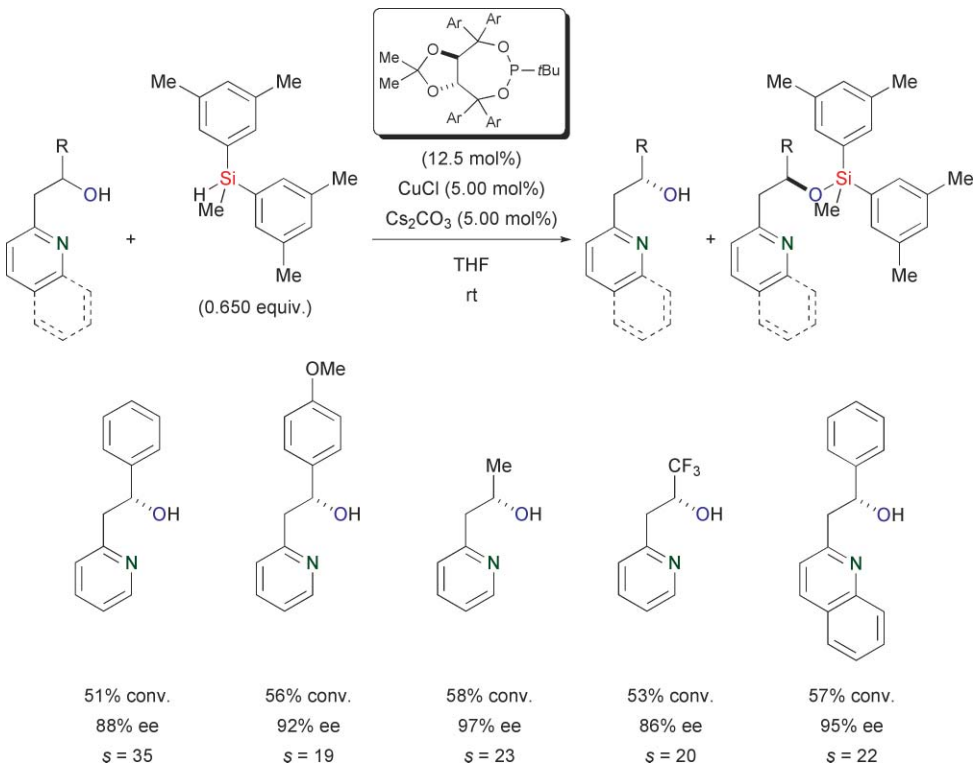
Fig. 2 Transition states in substrate, reagent and catalyst control.

Before moving on to the next section, we would like to note that, in principle, it is also possible to "reverse" the diastereoselective Si–O coupling. In other words, the kinetic resolution of racemic silicon-stereogenic silanes with enantiopure alcohols as resolving reagents also works.[26] For example, reaction of a virtually enantiopure donor-functionalised alcohol with a racemic mixture of our six-membered ring silane afforded a moderate selectivity factor of 4.9.

Catalyst control

As illustrated by the stereochemistry-determining transition state **TS3** (Fig. 2), chirality arises from a single monodentate chiral ligand in the Cu–H-catalysed enantioselective Si–O coupling. Such a stereochemical situation is not unprecedented but it is nevertheless challenging. In our approach to that, we chose easy-to-make binol- and taddol-based phosphoramidites and phosphonites and simple achiral silanes.[17] After considerable experimentation and screening of dozens of ligand–silane combinations, we had identified a suitable reaction setup, consisting of a taddol-based, *t*Bu-substituted phosphonite and xylyl-substituted silane (Scheme 7). In contrast to previous catalytic systems (*cf.* Schemes 3 and 6),[12–15] we had to change the solvent (toluene to THF) and, as a consequence of that, the base (NaO*t*Bu to Cs_2CO_3). By this, we were able to suppress the unexpected *tert*-butoxide-catalysed background reaction in THF.[39] Several donor-functionalised alcohols were kinetically resolved with good to excellent selectivities. Control experiments[17] (not shown) provided strong evidence for the catalysis to pass through transition state **TS3** (Fig. 2). A recent report by Dagorne and Bellemin-Laponnaz *et al.* seems to further support our results.[40] These authors showed that combinations of chiral bidentate ligands and monodentate (not donor-functionalised) alcohols give modest values of *s* in Cu–H-catalysed kinetic resolutions.

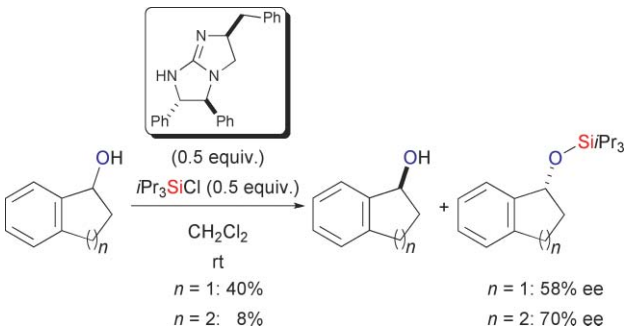
While the focus of this Emerging Area is on the Si–O coupling of alcohols, there is another approach to enantioselectively form an Si–O bond, that is the catalytic asymmetric hydrosilylation of ketones.[5,41] One rare variation of that is the catalyst-controlled reduction using prochiral silanes, and here we briefly mention the seminal contributions to that area. It was again Corriu and Moreau who considered this chemistry as an entry into chiral silanes, and achieved promising 55% ee in an enantioselective Rh(I)-catalysed ketone reduction with prochiral 1-NpPhSiH$_2$.[28] At the same time, Kumada *et al.* reported a similar example albeit with 28% ee (due to an enantioimpure chiral ligand).[29] Two decades later, Takaya *et al.* brought this Rh(I) catalysis to perfection, culminating in >99% ee in the reaction with a symmetric ketone.[30]



Scheme 7 Cu(I)-catalysed, enantioselective Si–O coupling developed by Oestreich (Ar = 2-naphthyl).

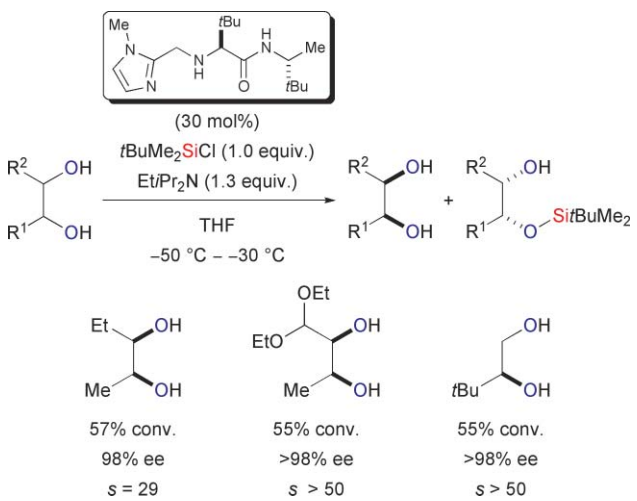
Si–X as a coupling partner

The previous section ended with the catalyst-controlled Si–O coupling using silanes as coupling partners. There is however a complementary strategy for enantioselective Si–O bond formation of alcohols, namely the kinetic resolution or desymmetrisation of alcohols using chlorosilanes (Si–X = Si–Cl). The idea was introduced by Ishikawa *et al.* but stoichiometric amounts of a chiral guanidine base were necessary (Scheme 8).[18] Moderate enantiomeric excesses were obtained for both 1-indanol and 1-tetralol in the silylation with iPr$_3$SiCl.



Scheme 8 Kinetic resolution of alcohols mediated by a chiral base developed by Ishikawa.

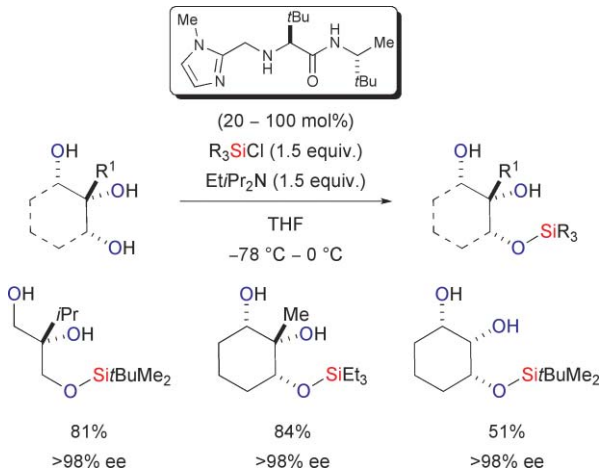
The major drawback of that process is that it is not catalytic in nucleophilic reagent. A catalytic version in the presence of stoichiometric amounts of Et$_3$N only produced racemic material. This outcome might be understood by comparison of the pK_a values[42] of both protonated Et$_3$N (pK_a ≈ 10.0) and protonated guanidine (pK_a ≈ 13.5). It reveals that the nucleophilic mediator is much more basic than Et$_3$N, and that makes catalytic turnover unlikely.[4] This limitation was finally overcome by Hoveyda and Snapper *et al.* using a chiral imidazole, well-adapted for catalytic activation of chlorosilanes (Scheme 9).[19] Imidazole (pK_a ≈ 7.1 of conjugate acid) is less basic than EtiPr$_2$N, thereby facilitating turnover in the kinetic resolution of racemic 1,2-diols. Again, a tethered donor, here another hydroxy group, is crucial for excellent enantioselection.



Scheme 9 Kinetic resolution of acyclic 1,2-diols developed by Hoveyda and Snapper.

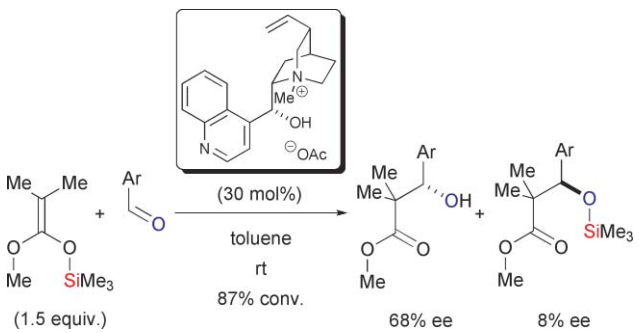
The reaction is truly remarkable in that the peptide-like catalyst is not only able to discriminate between the two enantiomers but also between the two regioisomers (one out of four isomers). Even two contiguous 2° hydroxy groups were differentiated with outstanding selectivities (Scheme 9).

Moreover, Hoveyda and Snapper *et al.* extended their methodology to another important class of substrates, *i.e.*, diols (not shown)[20] and triols[21] (Scheme 10) with *meso* configuration. The desymmetrisation of such triols is particularly challenging as the chiral imidazole–chlorosilane adduct must differentiate three (!) hydroxy groups. The Hoveyda–Snapper desymmetrisation yields fantastic levels of enantioselection for very demanding substrates.[20,21]



Scheme 10 Desymmetrisation through enantioselective Si–O coupling developed by Hoveyda and Snapper.

Recently, Wiskur and Patel reported an unexpected organocatalysed approach to kinetic resolution through Si–O coupling.[22] A Mukaiyama aldol reaction was found to deliver the alcohol in enantioenriched form along with its almost racemic silicon ether of opposite absolute configuration (Scheme 11).



Scheme 11 Assumed kinetic resolution in a Mukaiyama aldol reaction developed by Wiskur.

Enantioinduction is believed not to originate from the aldol addition itself but from a subsequent Si–O coupling of the intermediate racemic alkoxide and remaining silyl ketene acetal (not shown). The authors speculate that the racemic alkoxide forms a contact ion pair with the enantiopure quaternary ammonium

ion. The thus-formed diastereomers are likely to react with an achiral Si–X reagent at different reaction rates, thereby resulting in a kinetic resolution. A few test experiments were performed in support of this mechanism but the available data is not yet fully convincing. One of the more obvious issues is the nature of the silyl transfer reagent: *in situ*-generated Me_3SiOAc might also release the Me_3Si group, and the role of the unprotected hydroxy group in the cinchona alkaloid remained vague as well.

Conclusions

The past decade witnessed the revival of asymmetric Si–O couplings (Fig. 1). Based on the seminal investigation(s) by Corriu and Moreau dating back almost forty years,[3,7,8a] the recent developments in reagent- and catalyst-controlled Si–O bond formation were major leaps in organosilicon chemistry…if not in stereoselective catalysis. The work of Leighton *et al.* is a wonderful case of enantiotopic discrimination to create chirality at a silicon atom (Scheme 2)[9] whereas parts of our work are intriguing examples of enantiomeric discrimination using chirality at a silicon atom (Schemes 3, 4 and 6).[12–16] These strategies might fall into the category of "academic playground". Conversely, the enantioselective Si–O couplings by us[17] and, first and foremost, by Hoveyda and Snapper *et al.*[19–21] are now synthetically useful, and the latter will certainly find its way into complex molecule synthesis.[21]

Several aspects of these contributions are likely to have impact on modern organic chemistry. For example, a recent attempt to effect kinetic resolution by enantioselective Si–O bond cleavage might have been motivated by the asymmetric Si–O coupling.[43,44] Lee, Chi and Song *et al.* devised a chiral fluoride source that mediates the enantioselective deprotection of an Si–O linkage.[43] This simple-looking transformation, while not yet catalytic, certainly opens up a whole new area of research, the stereoselective deprotection of alcohols.

Acknowledgements

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