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Enantio- and Diastereotopos Differentiation in the Palladium(II)-Catalyzed Hydrosilylation of Bicyclo[2.2.1]alkene Scaffolds with Silicon-Stereogenic Silanes

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The palladium(II)-catalyzed hydrosilylation of *meso*-configured bicyclo[2.2.1]alkene scaffolds proved to be an invaluable model reaction for the development of reagent-controlled asymmetric transformations based on silicon-stereogenic silanes as stereoinducers. In the present investigation, the subtle structural requirements of the silane substitution pattern in enantiotopos-differentiating single hydrosilylations of a norbornene-type substrate are disclosed. Extension of this chemistry to a double hydrosilylation of norbornadiene entails a significant increase in stereochemical complexity. Although differentiation of enantiotopic positions by the chiral reagent is demanded in the first hydrosilylation, the same reagent must then differentiate diastereotopic positions in the second. Remarkably high stereocontrol was found in this double hydrosilylation with several silanes first used in the hydrosilylations of the norbornene-type system. Depending on the enantiomeric purity of the silane, C_2- and C_s-symmetric adducts, respectively, were obtained. The identity of the key quaternary silanes was revealed by crystallographic analysis. By this method, the relative and absolute configurations were also assigned, which, in turn, imply that all enantiospecific substitutions at silicon proceed with stereoretention. On the basis of these solid-state structures, we also discuss the structural implications of silane substitution for the diastereoselectivity-determining step of this palladium(II)-catalyzed hydrosilylation reaction.

Introduction

Asymmetric transformations using stereogenic silicon as the sole source of chirality constitute a largely undeveloped area in organic synthesis.[1] Aware of a number of asymmetric methods involving organosilicon compounds,[2] we were attracted by the prospect of rendering catalyst-controlled processes stereoselective by using silicon-stereogenic reagents.[3,4] From our initial efforts directed towards the preparation[5] and subsequent transformations[6] of enantiopure, asymmetrically substituted silanes, we learned that, first and foremost, the success of this chemistry will rely on a distinctive feature of silicon, its tendency to racemize by pseudorotational processes when extracoordinate.[7] As the silicon atom is both carrier of stereogenic information and reactive site in any of the envisioned silicon–element bond formation reactions, their mechanism of action must not proceed through hypervalent intermediates at any stage. Literature precedent indeed hinted that the presence of hypervalent silicon would thwart enantiospecific substitution at chiral silicon.[1,6,8–10] This fundamental aspect led us to consider unconventional transition-metal-catalyzed silicon–hydrogen bond activation of chemically and configurationally stable triorganosilanes **A** (Scheme 1).[4] The related strategies outlined in Scheme 1 are based on the silicon–hydrogen bond activation of **A** in an enantiospecific σ-bond metathesis in which hypervalent silicon might only be, if at all, present in a transition state (**D** or **E**) and not in an intermediate.

In one scenario (right, Scheme 1), a transition-metal alkyl, generated by insertion of a prochiral alkene into the silicon–metal bond of a transition-metal silyl complex, undergoes concerted silicon–hydrogen bond activation via four-centered transition state **D** (**A**→**B**).[11] Overall, this sequence facilitates diastereoselective[12] alkene hydrosilylation.[13] In another scenario (left, Scheme 1), dehydrogenative silicon–oxygen coupling[14] also makes use of an enantiospecific σ-bond metathesis. Chiral silane **A** reacts with a chiral transition-metal alkoxide via transition state **E** to form silyl ether **C** and the catalytically active metal hydride (**A**→**C**). The latter is subsequently transformed into a transition-metal alkoxide upon reaction with an alcohol accompanied by the liberation of dihydrogen. This diastereoselective silicon–oxygen coupling is a chiral recogni-

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[‡‡]X-ray crystal structure analysis of *rac*-**7a**.
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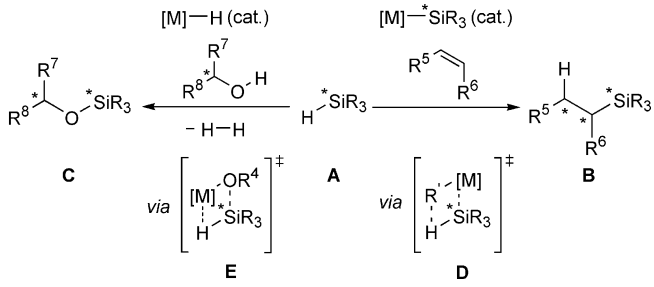
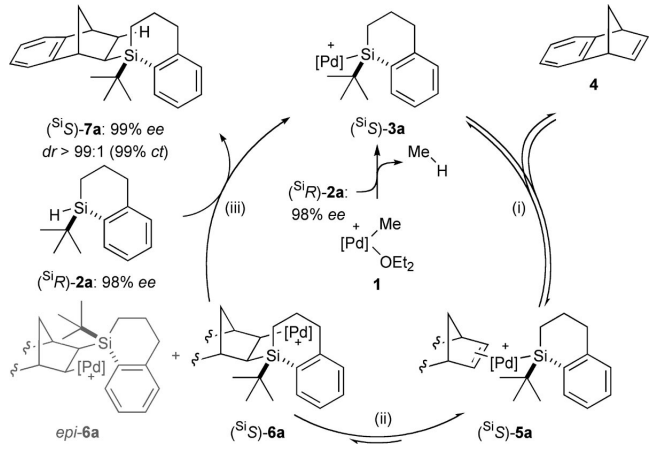
tion, that is, preferential reaction of **A** with either of the enantiomeric alcohols that inevitably leads to their kinetic resolution.[15]



Scheme 1. Synthetic strategies for silicon-stereogenic silanes based on enantiospecific σ-bond metathesis.

Within the first scenario, the utilization of a racemization-free σ-bond metathesis in stereoselective alkene hydrosilylation had set the stage for our efforts towards intermolecular chirality transfer from silicon to carbon.[3,12,16,17] Needless to say, apart from the enantiospecificity of the overall catalysis, we were mainly interested in the carbon–silicon bond formation event which must bring about a high level of stereoinduction.[3,4] For this, the substitution pattern of the chiral silane and, importantly, its role in and the nature of the diastereoselectivity-determining step emerge as crucial points.[3,4] A while ago, we accomplished the enantiospecific hydrosilylation of bicyclo[2.2.1]heptene **4** using privileged silane (^{Si}R)-**2a** with immaculate diastereocontrol [**4**→(^{Si}S)-**7a**, Scheme 2].[12]



Scheme 2. Catalytic cycle for the palladium(II)-catalyzed hydrosilylation reaction.

Subsequent mechanistic investigations revealed the intricate stereochemical features of the three-step catalytic cycle (Scheme 2).[18] Step (i): Reversible coordination of bicyclic alkene **4** to the highly electrophilic cationic silylpalladium(II) complex (^{Si}S)-**3a** [(^{Si}S)-**3a**→(^{Si}S)-**5a**]. Step (ii): Determination of the diastereoselectivity of the overall process in a reversible and thermodynamically controlled alkene insertion; this preferentially produces alkylpalladium(II) intermediate (^{Si}S)-**6a** and not the diastereomeric *epi*-**6a** [(^{Si}S)-**5a**→(^{Si}S)-**6a**]. Step (iii): σ-bond metathesis, likely to be rate-limiting,[11a] of (^{Si}S)-**6a** with the chiral silane (^{Si}R)-**2a** in a matched scenario to give the quaternary silane (^{Si}S)-**7a** [(^{Si}S)-**6a**→(^{Si}S)-**3a**]; a mismatched scenario is also possible (see below).[12,18] The diastereomeric excess corresponds to chirality transfer from the stereogenic silicon atom onto the carbon skeleton of the substrate to form three new stereocenters. We note here that the irreversible σ-bond metathesis is not diastereoselectivity- but enantioselectivity-determining. Remarkable asymmetric inductions were seen when racemic β-silylalkylpalladium(II) intermediates were treated with chiral nonracemic silanes. This situation with a fast reacting (matched case) and a slow reacting enantiomer (mismatched case) is nothing but a dynamic kinetic resolution within the catalysis, which also rationalizes the positive nonlinear effects[12] when using scalemic mixtures of the silane.[18]

So far, our research devoted to the palladium(II)-catalyzed hydrosilylation of bicyclo[2.2.1]heptenes has allowed us to gain an in-depth understanding of the mechanistic boundaries needed for the development of catalytic processes using silicon-stereogenic silanes as stereoinducers. In this full account, we present our synthetic efforts to further illuminate the structural features of the chiral silane unit essential for achieving high diastereoselectivities in the enantiotopos-differentiating hydrosilylation of **4**.[19] Moreover, extension of the substrate scope to bicyclo[2.2.1]heptadiene (norbornadiene) underlines the strong reagent control of our privileged silanes in enantio- and diastereotopos-differentiating double hydrosilylations.[20] We also provide crystallographic data of several quaternary silanes obtained by hydrosilylation, thereby allowing unambiguous assignment of the stereochemical course of the reaction pathway.

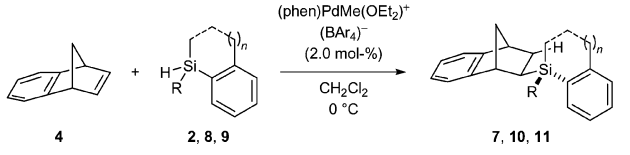
Results and Discussion

Exploration of the Silane Substitution Pattern

Initial studies using norbornene as a substrate revealed that most of the asymmetrically substituted triorganosilanes previously described are poor stereoinducers in palladium(II)-catalyzed hydrosilylation reactions.[12] From this preliminary silane screening, only 1-silatetralins decorated with a sterically demanding exocyclic alkyl substituent emerged as effective reagents for the desired chirality transfer.[3,12,18] Consequently, we surveyed this general motif in greater detail using benzannulated bicycloalkene **4**[21] as a substrate (**4**→**7**, **10**, **11**, Table 1); bicycloalkene **4** was generally preferred over its parent compound, norbornene, as it reacted cleanly without the formation of oligomeric side-products. Substrate **4** was subjected to hydrosilylation according to the protocol developed by Brookhart and coworkers.[11a] Cationic palladium(II) catalyst [(phen)PdMe(OEt$_2$)]$^+$(BAr$_4$)$^-$ [phen: 1,10-phenanthroline; Ar: 3,5-bis(trifluoromethyl)phenyl] was generated in situ by mixing the precursors [(phen)PdMe$_2$][22] and [H(OEt$_2$)$_2$]$^+$(BAr$_4$)$^-$[23] in CH_2Cl_2; the reactants were then added to this mixture. As

no detectable temperature effect on the diastereoselectivity was observed, reactions were usually performed at 0 °C with a catalyst loading of 2.0 mol-% (full conversion in 0.5–4.0 h).

Table 1. Effect of silane substitution on the hydrosilylation of **4**.[a]



4 **2, 8, 9** **7, 10, 11**

Entry	Silane[b]	Product[c]	Yield [%][d]	*dr* (*ct*)[e]	*ee* [%][b]
1	*rac*-**2a**	*rac*-**7a**	95	>99:1 (99%)	–
2	(^{Si}S)-**2a**: 98% *ee*	(^{Si}R)-**7a**	82	>99:1 (99%)	99
3	*rac*-**2b**	*rac*-**7b**	83	99:1 (98%)	–
4	(^{Si}R)-**2b**: 96% *ee*	(^{Si}R)-**7b**	85	99:1 (98%)	95
5	*rac*-**8a**	*rac*-**10a**	83	96:4 (92%)	–
6	*rac*-**8b**	*rac*-**10b**	70	95:5 (90%)	–
7	*rac*-**9**	*rac*-**11**	70	>99:1 (99%)	–

[a] All reactions were carried out in 0.1 M solutions using 1.1–1.2 equiv. of the silane until complete conversion of **4**, as monitored by ^{1}H NMR spectroscopy. [b] Enantiomeric excesses were determined by HPLC on a chiral stationary phase. [c] Relative configurations were assigned according to X-ray crystal structure analysis of *rac*-**7a** and *rac*-**11**. [d] Isolated yield of analytically pure material after flash column chromatography. [e] Diastereomeric ratios were determined by NMR spectroscopy, GLC (SE-54 column), or HPLC analysis using chiral stationary phases; chirality transfer = diastereomeric excess.

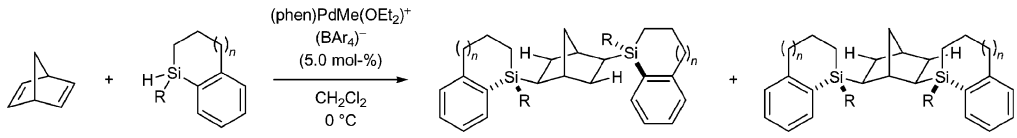
Privileged silane *rac*-**2a**[5b] decorated with an exocyclic *tert*-butyl substituent afforded perfect chirality transfer (99% *ct*, *dr* > 99:1) (Scheme 2, Table 1, entry 1). When using (^{Si}S)-**2a**[5b] in almost enantiopure form, the chiral information at the silicon was completely preserved in the product (^{Si}R)-**7a** (Table 1, entry 2). In order to evaluate the steric demands of the exocyclic substituent, we prepared the isopropyl-bearing congener *rac*-**2b** which was also available in enantioenriched form as (^{Si}R)-**2b**.[18] A slight decrease in diastereoselectivity led, for the first time, to detectable amounts of the minor diastereomer of *rac*-**7b** (*dr* = 99:1, Table 1, entry 3). As expected, enantioenriched (^{Si}R)-**2b** produced the corresponding quaternary silane (^{Si}R)-**7b** enantiospecifically (Table 1, entry 4). Impressed by this very minor effect on diastereoselectivity, we decided to assess the influence of the size of the ring in which the silicon atom is embedded. We therefore prepared the racemic strained 1-silaindane derivatives *rac*-**8a**[24] and *rac*-**8b**[25] in analogy to a previously reported procedure.[5b] Both *tert*-butyl- (*rac*-**8a**) as well as isopropyl-substituted 1-silaindanes (*rac*-**8b**) showed distinctly reduced diastereoselectivity at slightly increased reactivity[15c] (*dr* = 96:4, 92% *ct* for *rac*-**10a** and *dr* = 95:5, 90% *ct* for *rac*-**10b**, Table 1, entries 5 and 6). The structural alterations had, however, only a minor influence on the diastereoselectivity compared with the replacement of the *tert*-butyl by a phenyl group in the related norbornene hydrosilylation (*dr* > 99:1 vs. *dr* = 65:35).[12] We then directed our interests towards acyclic silane *rac*-**9**[26,27] bearing an almost identical substitution pattern to that of *rac*-**2a** and *rac*-**8a**. Corroborating the aforementioned findings, excellent chirality transfer (*dr* > 99:1, 99% *ct*) was observed (Table 1, entry 7). This outcome is particularly noteworthy: It provides further evidence for alkene insertion and not σ-bond metathesis as the diastereoselectivity-determining step (see above) because acyclic *rac*-**9** is completely ineffective (*dr* = 59:41) in the mechanistically related silicon–oxygen coupling, a σ-bond metathesis.[19]

Hydrosilylation of Norbornadiene

All the hydrosilylations of alkene **4** in Table 1 turned out to give exceptionally high chirality transfer. These promising findings encouraged us to explore the scope of this diastereoselective transformation in reactions using norbornadiene (**12**) as the substrate[20a] (**12**→**13**, **14**, Table 2). In this double hydrosilylation sequence, the silicon-stereogenic silane will have to meet a "higher level" of stereodifferentiation. After enantiotopos-differentiating hydrosilylation of the first double bond of diene **12**, which is comparable to that of alkene **4**, competition between substrate and reagent control arises in the second hydrosilylation of the chiral and thus unsymmetric (C_1) alkene intermediate **15** (cf. Scheme 3, see below).

We started our investigations of the double hydrosilylation of norbornadiene (**12**) by using a slight excess of racemic silane *rac*-**2a** (2.2 equiv.) (Table 2, entry 1). Clean conversion to products *rac*- and *meso*-**13a** was observed in the presence of 5.0 mol-% of Brookhart's palladium(II) catalyst. Analytical data obtained by NMR spectroscopy as well as GLC showed that C_2-symmetric *rac*-**13a** was formed

Table 2. Double hydrosilylation of norbornadiene (**12**).[a]



12 + **2, 8** → *rac*-**13**, *rac*-**14** + *meso*-**13**, *meso*-**14**

Entry	Silane	*ee* [%][b]	C_2 Product[c]	*ee* [%][d]	C_s Product[e]	C_2:C_s[f]	Yield [%][g]	*dr* (*ct*)[h]
1	*rac*-**2a**	–	*rac*-**13a**	–	*meso*-**13a**	46:54	78	>99:1 (99%)
2	(^{Si}S)-**2a**	97	(^{Si}R,^{Si}R)-**13a**	≥97%		98:2	91	>99:1 (99%)
3[i]	(^{Si}R)-[^{2}H]-**2a**	94	(^{Si}S,^{Si}S)-[$^2H_2$]-**13a**	>99%		97:3	74	>99:1 (99%)
4	*rac*-**2b**	–	*rac*-**13b**	–	*meso*-**13b**	59:41	87	≥98:2 (≥96%)
5	(^{Si}R)-**2b**	96	(^{Si}R,^{Si}R)-**13b**	>99%		98:2	95	99:1 (98%)
6	*rac*-**8a**	–	*rac*-**14a**	–	*meso*-**14a**	60:40	87	99:1 (98%)

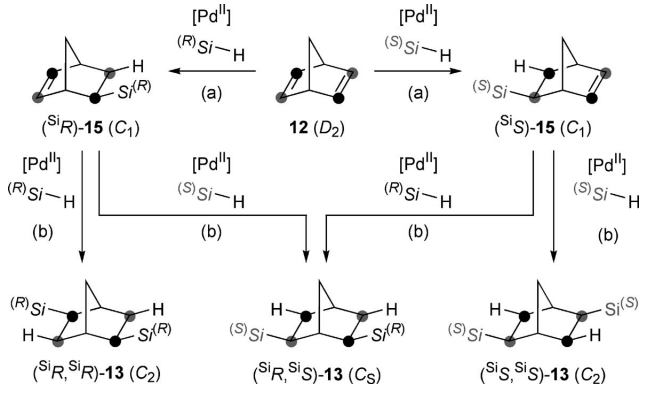
[a] All reactions were carried out in 0.1 M solutions using 2.2 equiv. of the silane until complete conversion of **12**, as determined by GLC analysis (SE-54). [b] Enantiomeric excesses of the silanes were determined by HPLC on a chiral stationary phase. [c] Relative configurations were assigned according to X-ray crystal structure analysis of (^{Si}R,^{Si}R)-**13a**. [d] Enantiomeric excesses of the products were determined by HPLC on a chiral stationary phase. [e] Relative configurations were assigned according to X-ray crystal structure analysis of *meso*-**13a**. [f] Determined by analytical GLC analysis (SE-54). [g] Isolated yield of analytically pure material after flash column chromatography. [h] Diastereomeric ratios were determined by GLC (SE-54 column) or HPLC using chiral stationary phases; chirality transfer = diastereomeric excess. [i] (^{Si}R)-[^{2}H]-**2a** (99% D) and (^{Si}S,^{Si}S)-**13a** (99% D_2) by mass spectrometry.

along with approximately equal amounts of C_s-symmetric *meso*-**13a**. Notably, no other stereoisomer was detected, which again demonstrated excellent silicon-to-carbon chirality transfer in both hydrosilylation steps (*dr* > 99:1, 99% *ct*). The C_2/C_s ratio of 46:54 indicated that the influence of substrate control was fully overridden in the second hydrosilylation step. A comparable product distribution was also observed when other racemic mixtures of chiral silanes such as *rac*-**2b** and *rac*-**8a** were converted into the corresponding hydrosilylation products *rac*-**13b**/*meso*-**13b** (C_2/C_s = 59:41) and *rac*-**14a**/*meso*-**14a** (C_2/C_s = 60:40), respectively (Table 2, entries 4 and 6). Comprehensive chromatographic (GLC and HPLC) and spectroscopic (^{1}H, ^{13}C, ^{29}Si NMR) analyses revealed almost complete chirality transfer for both 1-

silatetralin (*dr* ≥ 98:2 for **13b**) and 1-silaindane (*dr* = 99:1 for **14a**). These results compare well within experimental error with the asymmetric induction that is observed in the hydrosilylation of **4**.

Based on the product distribution of the reactions of racemic silanes, we predicted that enantiopure silanes should lead exclusively to the C_2-symmetric diastereomers. To test for this we subjected (^{Si}S)-**2a** (97% *ee*) to the same reaction conditions (Table 2, entry 2); highly enantioenriched (^{Si}R,^{Si}R)-**13a** (≥97% *ee*) with C_2 symmetry was formed with excellent diastereocontrol (C_2/C_s = 98:2). Analogously, enantioenriched deuteriosilane (^{Si}R)-[^{2}H]-**2a** (94% *ee*) gave chiral (^{Si}S,^{Si}S)-[$^2H_2$]-**13a** with the expected complete chirality transfer (Table 2, entry 3). The deuterium label in (^{Si}S,^{Si}S)-[$^2H_2$]-**13a** assisted the NMR spectroscopic verification of the *exo* selectivity. In this case, HPLC analysis using a chiral stationary phase showed that the enantiopurity of (^{Si}S,^{Si}S)-[$^2H_2$]-**13a** (>99% *ee*) was higher than that of the parent silane (^{Si}R)-[^{2}H]-**2a** (94% *ee*). The use of a slight excess of (^{Si}S)-[^{2}H]-**2a** might account for this because in the closely related hydrosilylation of norbornene (**12**) we had already detected a notable asymmetric amplification (see above).[12,28] Similar observations were made with isopropyl-substituted silane (^{Si}R)-**2b** (96% *ee*). Selective double addition yielded C_2-symmetric (^{Si}R,^{Si}R)-**13b** with excellent diastereoselectivity (*dr* = 99:1) and enantioselectivity (>99% *ee*) (Table 2, entry 5).

The observed ratio of chiral (C_2) and achiral (C_s) products can be rationalized as shown in Scheme 3.[29] After enantiotopos-differentiation (a) in the first carbon–silicon bond formation [e.g, **12**→(^{Si}R)-**15**], a second, now diastereotopos-differentiating (b) carbon–silicon bond formation [e.g., (^{Si}R)-**15**→(^{Si}R,^{Si}R)-**13**] involving an unsymmetric alkene **15** is required. If the reaction is performed with racemic silane, both enantiomeric forms of the silanes are available for step (b). Predominant reagent control consequently not only results in the formation of the C_2-symmetric product (^{Si}R,^{Si}R)-**13** (left, Scheme 3), and likewise enantiomeric (^{Si}S,^{Si}S)-**13** (right, Scheme 3), but also the C_s-symmetric diastereomer (^{Si}R,^{Si}S)-**13** (≡ *meso*-**13**, center, Scheme 3). Marginal substrate control might account for the slight experimental deviation from the expected C_2/C_s ratio of 50:50 if any substrate control is absent. If, however, enantiopure silane, for example, the ^{Si}R enantiomer (left, Scheme 3) is used, only a single enantio- and diastereomer, (^{Si}R,^{Si}R)-**13** having C_2 symmetry, is produced by double hydrosilylation, which also underlines the racemization-free overall reaction pathway. In fact, the silane is not completely enantiopure. Thus, two processes become relevant: i. A matched/mismatched scenario for σ-bond metathesis[18] may give rise to observable asymmetric amplification[12,28] and ii. minor amounts of *meso*-**13** might be formed.



Scheme 3. (a) Enantiotopos- and (b) diastereotopos-differentiating steps in the hydrosilylation of norbornadiene.[29]

X-ray Crystallographic Study

In our initial report, the relative configurations of hydrosilylation product *rac*-**7a** and the congeners thereof were assigned inconclusively by NMR measurements.[12] Our attempts to solve this issue by X-ray crystallographic analysis of quaternary silanes were hampered by their reluctance to solidify. Quite by chance, *rac*-**7a** crystallized from a solvent mixture of acetonitrile, ethanol, and water over prolonged storage at 4 °C (Figure 1). Gratifyingly, the solid-state molecular structure confirmed our NOE assignment. The relative configuration of the quaternary silane *rac*-**7a** (1*R**,2*R**,4*S**,^{Si}S*) seems to represent the thermodynamically favored product in which the sterically demanding exocyclic *tert*-butyl group is arranged in such a manner that unfavorable steric interactions are minimized. The assumption that *rac*-**7a** is the thermodynamically favored diastereomer is in agreement with the diastereoselectivity determination in step (ii) of the catalytic cycle (cf. Scheme 2) in which thermodynamic control is operative. This might be concluded if the energetic conditions of the β-silylalkylpalladium(II) intermediates (^{Si}S)-**6a** and *epi*-**6a** match those of their corresponding products after σ-bond metathesis.

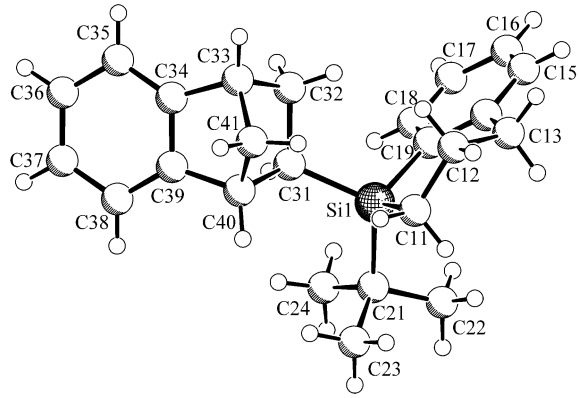


Figure 1. Molecular structure of *rac*-**7a**.

As it turned out, *rac*-**11** derived from the acyclic silane *rac*-**9** is a white solid that was recrystallized from hexanes at 4 °C to yield single crystals suitable for X-ray diffraction (Figure 2). Strikingly, the conformations around the newly formed carbon–silicon bonds in *rac*-**7a** and *rac*-**11** are almost identical in the solid state. This is exemplified by their respective dihedral angles of 78.5° for C21–Si1–C31–C40 in *rac*-**7a** compared to 71.1° for C1b–Si–C2–C1 in *rac*-**11**.

Having a similar β-silylalkylpalladium(II) intermediate in mind, this might also explain the equally high chirality transfer using acyclic silane *rac*-**9**.

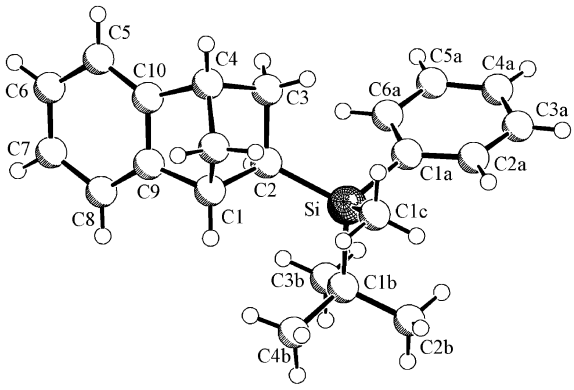


Figure 2. Molecular structure of *rac*-**11**.

Enantiomerically enriched samples of **7**, **10**, and **11** failed to afford single crystals of sufficient quality to assign their absolute configurations. Conversely, this problem did not arise in the double addition of virtually enantiopure (^{Si}S)-**2a** to **12**. High-molecular-weight compound (^{Si}R,^{Si}R)-**13a** readily solidified. Single crystals were obtained by recrystallization at room temperature using a mixture of acetonitrile, ethanol, and water as solvent (Figure 3). As determined by NMR spectroscopy, the two-fold *exo* addition indeed delivered the C_2-symmetric product (^{Si}R,^{Si}R)-**13a**. The third-row element silicon also enabled the absolute configuration to be assigned based on anomalous dispersion.[30] As the absolute configuration of the starting silane (^{Si}S)-**2a** is known from previous work by correlation with its precursor, the (–)-menthyl ether,[5b] retention of configuration for this hydrosilylation is proved.[31] The enantiospecific silicon–hydrogen bond activation with retention of configuration at silicon coincides with literature precedent for homogeneous transition-metal-catalyzed hydrosilylations.[32] Finally, X-ray diffraction also delivered structural proof of the achiral *meso*-**13a** (Figure 4). Single crystals were again obtained by recrystallization from ethanol, acetonitrile, and water at room temperature. The structural representation of *meso*-**13a** shows C_s symmetry after two-fold *exo*-selective, highly diastereoselective addition of two different enantiomers of silane **2a**.

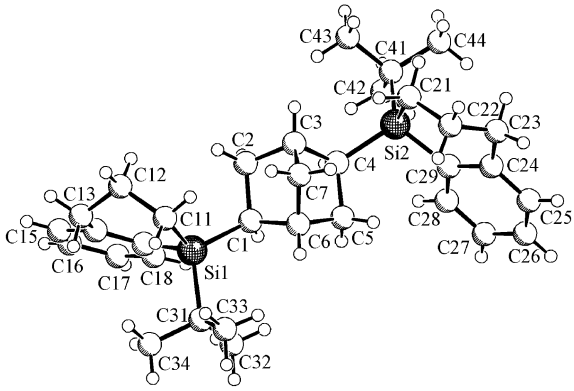


Figure 3. Molecular structure of (^{Si}R,^{Si}R)-**13a**.

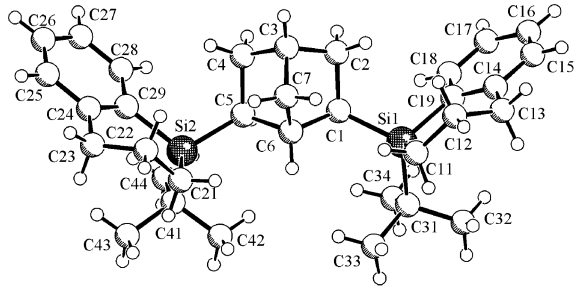


Figure 4. Molecular structure of *meso*-**13a**.

Conclusions

In this synthetic and X-ray crystallographic study, we explored the structural requirements for the intermolecular chirality transfer from silicon to carbon in a palladium(II)-catalyzed enantiotopos-differentiating hydrosilylation of a bicyclo[2.2.1]alkene, namely, benzannulated alkene **4**. These investigations demonstrate that structural alteration around the silicon atom is tolerated to some extent without affecting the diastereoselectivity. It has been demonstrated that the steric differences of the three substituents at silicon are crucial to obtain high diastereoselectivity,[12] whereas integration of the silicon atom into a rigid cyclic framework is not essential. The subsequent extension of this methodology to the double hydrosilylation of norbornadiene (**12**) has provided an insight into the unusually pronounced reagent control of our privileged silanes. Equally high chirality transfer was seen in both steps, the enantiotopos-differentiating followed by the diastereotopos-differentiating hydrosilylation.

X-ray crystallographic data of several quaternary silanes obtained from these hydrosilylations has allowed the unambiguous verification of their relative and absolute configurations. The structurally closely related products seem to represent the thermodynamically favored diastereomers, which is in agreement with the thermodynamically controlled alkene insertion step being diastereoselectivity-determining.

In summary, these studies complement previously reported research on intermolecular chirality transfer from silicon to carbon. Our investigations of the palladium(II)-catalyzed hydrosilylation reaction provide both a mechanistic and a synthetic basis for future developments in the still underrated chemistry of silicon-stereogenic reagents.

Experimental Section

General Information: [(phen)$PdMe_2$],[22] $[H(OEt_2)_2]^+(BAr)_4^-$,[23] *rac*-**2a**, (^{Si}S)-**2a**,[5b] (^{Si}R)-[^{2}H]-**2a**, *rac*-**2b**, (^{Si}R)-**2b**,[18] **4**,[21] *rac*-**8a**,[24] and *rac*-**9**[26] were prepared according to known procedures. All reactions were performed in flame-dried Schlenk tubes under a static

pressure of argon. Liquids and solutions were transferred with syringes. CH_2Cl_2 was dried by continuous distillation from CaH_2 prior to use. Melting points were determined using a Stuart Scientific SMP3 melting point apparatus (uncorrected values). Analytical thin-layer chromatography (TLC) was performed on silica gel SIL G-25 glass plates (Macherey–Nagel, Germany). Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM, Merck, Germany) with cyclohexane as solvent. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded in $CDCl_3$ with Bruker AV 400, Varian INOVA 500, and Varian Unity plus 600 spectrometers. GLC analyses were performed using a Shimadzu GC-17A instrument equipped with a SE-54 capillary column (30 m × 0.32 mm, 0.25 μm, N_2 carrier gas, 250 °C injection temperature, detector temperature 300 °C; temperature program: start temperature 40 °C for 1 min, heating rate 10 °C min^{-1}, 300 °C end temperature for 25 min). HPLC analyses were performed with an Agilent 1200 instrument on a chiral stationary phase using a Daicel Chiralcel OD-RH column (MeCN/H_2O mixtures as solvent). Mass spectra were recorded with a Waters Micromass MAT 8200 GC-TOF (EI/HRMS) instrument. IR spectra were recorded with a Varian 3100 FT-IR instrument equipped with an ATR unit. Optical rotations were measured in a 1 dm cuvette with a Perkin-Elmer 341 polarimeter. Elemental analyses were conducted with a Vario EL III instrument from Elementaranalysensysteme GmbH. Analytical data for quaternary silanes *rac*-**7a**, (^{Si}R)-**7a**, *rac*-**7b**, (^{Si}R)-**7b**, and *rac*-**11** were included in preliminary reports.[12,18,19]

General Procedure for the Hydrosilylation of 4 (GP 1): A Schlenk tube was charged with a mixture of [(phen)$PdMe_2$] (0.02 equiv.) and $[H(OEt_2)_2]^+(BAr_4)^-$ (0.02 equiv.) under argon. The solids were dissolved in anhydrous degassed CH_2Cl_2 at 0 °C forming a pale-yellow solution. At this temperature, a solution of bicyclic alkene **4** (1.00 equiv.) and silane (**2**, **8**, or **9**) (1.20 equiv.) in CH_2Cl_2 was added in one portion by syringe. The resulting bright-yellow solution (0.1 M in **4**) was maintained at 0 °C until complete consumption of the reactants (0.5–4 h) as monitored by ^1H NMR analysis. After addition of cyclohexane (10 mL) and a small portion of silica gel the solvents were evaporated. Purification by flash column chromatography on silica gel (cyclohexane) afforded the analytically pure products (**7**, **10**, or **11**) as colorless, highly viscous oils.

(1*R,2*R**,4*S**,^{Si}*S**)-1-*tert*-Butyl-1-(1,2,3,4-tetrahydro-1,4-methano-2-naphthyl)silatetralin (*rac*-7a):** See Table 1, Entry 1.[12] According to GP 1, starting from **4** (71.1 mg, 0.500 mmol), *rac*-**2a** (112 mg, 0.550 mmol), [(phen)$PdMe_2$] (3.2 mg, 0.010 mmol), and $[H(OEt_2)_2]^+(BAr_4)^-$ (10 mg, 0.010 mmol), compound *rac*-**7a** (165 mg, 95%, *dr* > 99:1 by HPLC, *exo*/*endo* > 99:1 by HPLC) was obtained as a colorless oil that solidified upon prolonged storage at 4 °C.

X-ray Crystal Structure Analysis for *rac*-7a: Formula $C_{24}H_{30}Si$, M = 346.57, colorless crystal, 0.20 × 0.15 × 0.15 mm, a = 8.1125(2), b = 10.6360(4), c = 22.9921(8) Å, $\alpha = \beta = \gamma = 90°$, V = 1983.86(11) Å^3, $\rho_{calcd.}$ = 1.160 g cm^{-3}, μ = 1.031 mm^{-1}, semi-empirical absorption correction ($0.917 \le T \le 0.983$), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 0.71073 Å, T = 100(2) K, ω and ϕ scans, 14742 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.67 Å^{-1}, 2831 independent (R_{merge} = 0.0568) and 2394 observed reflections [$I \ge 2\sigma(I)$], 229 refined parameters, R = 0.0350, wR_2 = 0.0838, max./min. residual electron density: 0.283/–0.418 e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(1*R,2*R**,4*S**,^{Si}*S**)-1-*tert*-Butyl-1-(1,2,3,4-tetrahydro-1,4-methano-2-naphthyl)-1-silaindane (*rac*-10a):** See Table 1, Entry 5. According to GP 1, starting from **4** (142 mg, 1.00 mmol), *rac*-**8a** (228 mg, 1.20 mmol), [(phen)$PdMe_2$] (6.3 mg, 0.020 mmol), and $[H(OEt_2)_2]^+(BAr_4)^-$ (20 mg, 0.020 mmol), compound *rac*-**10a** (277 mg, 83%, *dr* = 96:4 by GLC, *exo*/*endo* > 99:1 by GLC) was obtained as a colorless, highly viscous oil. R_f = 0.35 (cyclohexane); GLC (SE-54): t_R = 22.8 (minor diastereomer), 23.5 min (major diastereomer). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.98–1.07 (m, 1 H), 1.01 (s, 9 H), 1.10–1.28 (m, 3 H), 1.43–1.49 (m, 2 H), 2.06 (ddd, J = 11.7, J = 6.5, J = 3.8 Hz, 1 H), 3.18 (m_c, 2 H), 3.32–3.37 (m, 2 H), 7.07–7.13 (m, 2 H), 7.17–7.23 (m, 3 H), 7.29 (br. d, J = 7.7 Hz, 1 H), 7.33 (ddd, J = 7.3, J = 7.3, J = 1.3 Hz, 1 H), 7.58 (br. d, J = 7.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.9, 18.4, 23.4, 27.4, 30.8, 32.5, 44.6, 45.8, 48.1, 119.1, 121.0, 125.3, 125.5, 125.6, 125.8, 129.3, 133.6, 136.9, 147.2, 150.8, 154.3 ppm. ^{29}Si NMR (99.3 MHz, $CDCl_3$): δ = 25.3 (minor), 25.7 (major) ppm. IR (ATR): $\tilde{\nu}$ = 3053 (m), 2949 (s), 2926 (s), 2854 (s), 1590 (w), 1559 (w), 1469 (s), 1440 (s), 1389 (w), 1361 (m), 1312 (m), 1261 (m), 1195 (w), 1155 (w), 1118 (s), 1064 (m), 1012 (m), 975 (s), 940 (m), 909 (s), 885 (m), 822 (s), 792 (w), 753 (s), 742 (s), 724 (s), 694 (m), 674 (m), 633 (m), 556 (w), 515 (m) cm^{-1}. HRMS (EI): calcd. for $C_{23}H_{28}Si$ [M – C_4H_9]$^+$ 275.1256; found 275.1239. $C_{23}H_{28}Si$ (332.6): calcd. C 83.07, H 8.49; found C 82.98, H 8.39.

(1*R,2*R**,4*S**,^{Si}*R**)-1-Isopropyl-1-(1,2,3,4-tetrahydro-1,4-methano-2-naphthyl)-1-silaindane (*rac*-10b):** See Table 1, Entry 6. According to GP 1, starting from **4** (142 mg, 1.00 mmol), *rac*-**8b** (199 mg, 1.13 mmol), [(phen)$PdMe_2$] (6.3 mg, 0.020 mmol), and $[H(OEt_2)_2]^+(BAr_4)^-$ (20 mg, 0.020 mmol), compound *rac*-**10b** (223 mg, 70%, *dr* = 95:5 by GLC, *exo*/*endo* = 99:1 by GLC) was obtained as a colorless, highly viscous oil. R_f = 0.38 (cyclohexane); GLC (SE-54): t_R = 22.2 (*endo* isomer), 22.5 (minor diastereomer), 23.2 min (major diastereomer). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.99 (ddd, J = 9.7, J = 6.5, J = 1.7 Hz, 1 H), 1.05 (d, J = 7.2 Hz, 3 H), 1.06 (d, J = 7.2 Hz, 3 H), 1.08–1.15 (m, 1 H), 1.16–1.25 (m, 2 H), 1.30 (ddd, J = 8.9, 2× J = 1.4 Hz, 1 H), 1.42 (ddd, J = 11.6, J = 9.7, J = 1.8 Hz, 1 H), 1.51 (ddddd, J = 8.7, 4× J = 1.9 Hz, 1 H), 2.01 (ddd, J = 11.6, J = 6.6, J = 3.3 Hz, 1 H), 3.18 (m_c, 2 H), 3.31 (br. s, 1 H), 3.39 (br. d, J = 2.6 Hz, 1 H), 7.06–7.13 (m, 2 H), 7.16–7.22 (m, 3 H), 7.29 (br. d, J = 7.7 Hz, 1 H), 7.33 (ddd, 2× J = 7.4, J = 1.3 Hz, 1 H), 7.56 (d, J = 7.0 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 6.4, 13.2, 18.2, 18.3, 24.2, 30.0, 32.5, 44.5, 45.3, 48.1, 119.0, 121.0, 125.2, 125.5, 125.6, 125.8, 129.4, 133.4, 137.0, 147.2, 150.8, 154.2 ppm. ^{29}Si NMR (99.3 MHz, $CDCl_3$): δ = 23.7 (minor), 23.3 (major) ppm. IR (ATR): $\tilde{\nu}$ = 3052 (m), 2950 (s), 2862 (s), 1590 (w), 1460 (s), 1440 (s), 1261 (m), 1195 (w), 1118 (s), 1063 (w), 995 (w), 974 (w), 942 (m), 909 (s), 881 (s), 792 (w), 726 (s), 699 (m), 674 (w), 638 (s), 557 (w), 518 (m) cm^{-1}. HRMS (EI): calcd. for $C_{22}H_{26}Si$ [M]$^+$ 318.1804; found 318.1782. $C_{22}H_{26}Si$ (318.5): calcd. C 82.96, H 8.23; found C 82.82, H 8.23.

(1*R,2*R**,4*S**,^{Si}*S**)-(*tert*-Butyl)(methyl)(phenyl)(1,2,3,4-tetrahydro-1,4-methano-2-naphthyl)silane (*rac*-11):** See Table 1, Entry 7.[19] According to GP 1, starting from **4** (99.5 mg, 0.700 mmol), *rac*-**9** (137 mg, 1.10 mmol), [(phen)$PdMe_2$] (6.7 mg, 0.021 mmol), and $[H(OEt_2)_2]^+(BAr_4)^-$ (21 mg, 0.021 mmol), compound *rac*-**11** (157 mg, 70%, *dr* > 99:1 by NMR, *exo*/*endo* > 99:1 by NMR) was obtained as a white solid; m.p. 69 °C (cyclohexane).

X-ray Crystal Structure Analysis for *rac*-11: Formula $C_{22}H_{28}Si$, M = 320.53, colorless crystal, 0.35 × 0.35 × 0.30 mm, a = 14.799(1), b = 7.776(1), c = 18.138(1) Å, β = 112.56(1)°, V = 1927.5(3) Å^3, $\rho_{calcd.}$ = 1.105 g cm^{-3}, μ = 1.031 mm^{-1}, empirical absorption correction ($0.714 \le T \le 0.747$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 13632 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 3384 independent (R_{merge} = 0.031) and 3241 observed reflections [$I \ge 2\sigma(I)$], 212 refined parameters, R = 0.044, wR_2 = 0.124, max. (min.) residual electron density: 0.37 (–0.19) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

General Procedure for the Hydrosilylation of 12 (GP 2): A Schlenk tube was charged with a mixture of [(phen)$PdMe_2$] (0.05 equiv.) and $[H(OEt_2)_2]^+(BAr_4)^-$ (0.05 equiv.) under argon. The solids were dissolved in anhydrous degassed CH_2Cl_2 at 0 °C forming a pale-yellow solution. At this temperature, a solution of bicyclic diene **12** (1.00 equiv.) and silane (**2** or **8**) (2.20 equiv.) in CH_2Cl_2 was added in one portion by syringe. The resulting bright-yellow solution (0.1 M in **12**) was maintained at 0 °C until complete consumption of the reactants (4–8 h), as monitored by GLC analysis. After addition of cyclohexane (10 mL) and a small portion of silica gel the solvents were evaporated. Purification by flash column chromatography on silica gel (cyclohexane) afforded the analytically pure products (**13** or **14**) as colorless, highly viscous oils.

(1*R,2*S**,4*R**,5*S**)-2,5-Bis[(^{Si}*R**)-1-*tert*-butyl-1-silatetralin-1-yl]-bicyclo[2.2.1]heptane (*rac*-13a) and (2*R*,6*S*)-2-[(^{Si}*S*)-1-*tert*-Butyl-1-silatetralin-1-yl]-6-[(^{Si}*R*)-1-*tert*-butyl-1-silatetralin-1-yl]bicyclo-[2.2.1]heptane (*meso*-13a):** See Table 2, Entry 1. According to GP 2, starting from **12** (36.9 mg, 0.400 mmol), *rac*-**2a** (180 mg, 0.880 mmol), [(phen)$PdMe_2$] (6.3 mg, 0.020 mmol), and $[H(OEt_2)_2]^+(BAr_4)^-$ (20 mg, 0.020 mmol), a mixture of compounds *rac*-**13a** and *meso*-**13a** (156 mg, 78%, C_2/C_s = 46:54 by GLC, *dr* > 99:1 by GLC, *exo*/*endo* > 99:1 by GLC) was obtained as a white solid. Repeated flash chromatography on silica gel (cyclohexane) furnished separate fractions of *rac*-**13a** (56 mg, 28%, C_2/C_s = 99:1) and *meso*-**13a** (34 mg, 17%, C_2/C_s = 2:98). GLC (SE-54): t_R = 37.1 (*meso*-**13a**), 39.3 min (*rac*-**13a**); HPLC (Daicel Chiralcel OD-RH, 20 °C, MeCN/H_2O, 90:10, flow rate = 0.80 mL min^{-1}, λ = 230 nm): t_R = 9.8 [(^{Si}*S*,^{Si}*S*)-**13a**], 10.0 (*meso*-**13a**), 11.8 min [(^{Si}*R*,^{Si}*R*)-**13a**]; no separation of (^{Si}*S*,^{Si}*S*)-**13a** and *meso*-**13a**.

Analytical Data for *rac*-13a: R_f = 0.44 (cyclohexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92–1.10 (m, 2 H), 1.01 (s, 18 H), 0.94–1.03 (m, 2 H), 1.09 (br. s, 2 H), 1.14 (dd, 2× *J* = 8.7 Hz, 2 H), 1.39–1.45 (m, 4 H), 1.71 (m_c, 2 H), 2.04 (m, 2 H), 2.29 (s, 2 H), 2.66 (ddd, *J* = 15.7, *J* = 10.1, *J* = 2.8 Hz, 2 H), 2.72 (ddd, *J* = 15.5, *J* = 6.3, *J* = 2.8 Hz, 2 H), 7.08 (br. d, *J* = 7.4 Hz, 2 H), 7.15 (br. dd, 2× *J* = 7.2 Hz, 2 H), 7.23 (ddd, 2× *J* = 7.5, *J* = 1.7 Hz, 2 H), 7.47 (dd, *J* = 7.2, *J* = 1.4 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.2, 18.5, 23.9, 24.3, 27.7, 36.0, 38.4, 36.8, 39.0, 124.8, 128.4, 128.5, 132.8, 135.5, 150.1 ppm. ^{29}Si NMR (99.3 MHz, $CDCl_3$): δ = –5.51 ppm. IR (ATR): $\tilde{\nu}$ = 3055 (w), 2999 (w), 2926 (s), 2855 (s), 1471 (s), 1435 (s), 1361 (m), 1293 (w), 1264 (w), 1216 (m), 1142 (m), 1127 (m), 1074 (m), 1007 (w), 973 (w), 865 (m), 820 (s), 754 (s), 738 (w), 693 (m), 674 (m), 645 (w), 608 (m) cm^{-1}. HRMS (EI): calcd. for $C_{33}H_{48}Si_2$ [M – C_4H_9]$^+$ 443.2590; found 443.2632. $C_{33}H_{48}Si_2$ (500.9): calcd. C 79.13, H 9.66; found C 78.88, H 9.71.

Analytical Data for *meso*-13a: M.p. 110 °C (cyclohexane). R_f = 0.35 (cyclohexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–1.10 (m, 6 H), 0.96 (s, 18 H), 1.27 (dd, *J* = 9.5, *J* = 6.8 Hz, 2 H), 1.42–1.55 (m, 4 H), 1.75 (m_c, 2 H), 2.08 (m_c, 2 H), 2.14 (br. t, *J* = 3.7 Hz, 1 H), 2.59 (br. s, 1 H), 2.68 (ddd, *J* = 15.8, *J* = 10.7, *J* = 3.0 Hz, 2 H), 2.75 (ddd, *J* = 16.0, *J* = 6.8, *J* = 2.8 Hz, 2 H), 7.10 (dd, *J* = 7.5, *J* = 0.7 Hz, 2 H), 7.16 (ddd, 2× *J* = 7.5, *J* = 1.5 Hz, 2 H), 7.24 (ddd, 2× *J* = 7.5, *J* = 1.5 Hz, 2 H), 7.49 (dd, *J* = 7.3, *J* = 1.4 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.9, 18.5, 23.9, 27.7, 31.9, 34.0, 36.0, 37.3, 38.0, 41.4, 124.8, 128.4, 128.6, 132.8, 135.6, 150.1 ppm. ^{29}Si NMR (99.3 MHz, $CDCl_3$): δ = –7.24 ppm. IR (ATR): $\tilde{\nu}$ = 3051 (w), 2995 (w), 2925 (s), 2876 (m), 2855 (s), 1470 (s), 1435 (s), 1360 (m), 1292 (w), 1267 (w), 1185 (w), 1140 (m), 1128 (m), 1074 (m), 1031 (w), 971 (w), 937 (m), 866 (m), 822 (s), 781 (w), 738 (s), 699 (s), 649 (w), 605 (m), 574 (w) cm^{-1}. HRMS (EI): calcd. for $C_{33}H_{48}Si_2$ [M – C_4H_9]$^+$ 443.2590; found 443.2609.

X-ray Crystal Structure Analysis for *meso*-13a: Formula $C_{33}H_{48}Si_2$, *M* = 500.89, colorless crystal, 0.25 × 0.15 × 0.03 mm, *a* = 25.4207(9), *b* = 7.6862(2), *c* = 15.8275(5) Å, β = 105.177(2)°, *V* = 2984.65(16) Å^3, $\rho_{calcd.}$ = 1.115 g cm^{-3}, μ = 1.198 mm^{-1}, empirical absorption correction 0.754 ≤ *T* ≤ 0.965, *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, *T* = 223 K, ω and ϕ scans, 26089 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 5220 independent (R_{merge} = 0.111) and 3369 observed reflections [$I \geq 2\sigma(I)$], 322 refined parameters, *R* = 0.066, wR_2 = 0.154, max. (min.) residual electron density: 0.26 (–0.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(1*R*,2*S*,4*R*,5*S*)-2,5-Bis[(^{Si}*R*)-1-*tert*-butyl-1-silatetralin-1-yl]bicyclo-[2.2.1]heptane [(^{Si}*R*,^{Si}*R*)-13a]: See Table 2, Entry 2. According to GP 2, starting from **12** (27.6 mg, 0.300 mmol), (^{Si}*S*)-**2a** (135 mg, 0.660 mmol, 97% *ee*), [(phen)$PdMe_2$] (4.8 mg, 0.015 mmol), and $[H(OEt_2)_2]^+(BAr_4)^-$ (15 mg, 0.015 mmol), compound (^{Si}*R*,^{Si}*R*)-**13a** (137 mg, 91%, C_2/C_s = 98:2 by GLC, *dr* > 99:1 by GLC, *exo*/*endo* > 99:1 by GLC, ≥97% *ee* by HPLC) was obtained as a white solid; m.p. 134 °C (cyclohexane). $[\alpha]_D^{20}$ = –6.15 (*c* = 0.585, $CHCl_3$), $[\alpha]_{578}^{20}$ = –6.84, $[\alpha]_{546}^{20}$ = –8.03, $[\alpha]_{436}^{20}$ = –14.9, $[\alpha]_{365}^{20}$ = –24.1. HPLC analysis on a chiral stationary phase (see above) did not allow separation of *meso*-**13a** and the minor enantiomer (^{Si}*S*,^{Si}*S*)-**13a** (integration of this peak: 1.5%). According to GLC data (C_2/C_s = 98:2, see above) this minor peak should exclusively consist of *meso*-**13a**. Thus, >99% *ee* emerges for (^{Si}*R*,^{Si}*R*)-**13a**.

X-ray Crystal Structure Analysis for (^{Si}*R*,^{Si}*R*)-13a: Formula $C_{33}H_{48}Si_2$, *M* = 500.89, colorless crystal, 0.30 × 0.15 × 0.05 mm, *a* = 8.1786(1), *b* = 14.4813(2), *c* = 13.2245(2) Å, β = 103.588(1)°, *V* = 1522.43(4) Å^3, $\rho_{calcd.}$ = 1.093 g cm^{-3}, μ = 1.174 mm^{-1}, empirical absorption correction (0.720 ≤ *T* ≤ 0.944), *Z* = 2, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, *T* = 223 K, ω and ϕ scans, 12632 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 4906 independent (R_{merge} = 0.050) and 4620 observed reflections [$I \geq 2\sigma(I)$], 322 refined parameters, *R* = 0.045, wR_2 = 0.109, Flack parameter = 0.02(3), max. (min.) residual electron density: 0.21 (–0.19) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(1*S*,2*R*,4*S*,5*R*)-[3,6-$^2H_2$]-2,5-Bis[(^{Si}*S*)-1-*tert*-butyl-1-silatetralin-1-yl]-bicyclo[2.2.1]heptane [(^{Si}*S*,^{Si}*S*)-[$^2H_2$]-13a]: See Table 2, Entry 3. According to GP 2, starting from **12** (27.6 mg, 0.300 mmol), (^{Si}*S*)-**2a** (136 mg, 0.660 mmol, 99% D, 94% *ee*), [(phen)$PdMe_2$] (4.8 mg, 0.015 mmol), and $[H(OEt_2)_2]^+(BAr_4)^-$ (15 mg, 0.015 mmol), compound (^{Si}*S*,^{Si}*S*)-[$^2H_2$]-**13a** (112 mg, 74%, 99% D by MS, C_2/C_s = 97:3 by GLC, *dr* > 99:1 by GLC, *exo*/*endo* > 99:1 by GLC, ≥99% *ee* by HPLC) was obtained as a white solid; m.p. 132 °C (cyclohexane); R_f = 0.44 (cyclohexane). $[\alpha]_D^{20}$ = +5.36 (*c* = 0.560, $CHCl_3$), $[\alpha]_{578}^{20}$ = +5.54, $[\alpha]_{546}^{20}$ = +6.43, $[\alpha]_{436}^{20}$ = +10.4, $[\alpha]_{365}^{20}$ = +15.9. HPLC analysis on a chiral stationary phase (as for unlabeled **13a**, see above) did not allow separation of *meso*-**13a** and the major enantiomer (^{Si}*S*,^{Si}*S*)-[$^2H_2$]-**13a**. As no minor enantiomer was detectable, >99% *ee* emerges for (^{Si}*S*,^{Si}*S*)-[$^2H_2$]-**13a**. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.93 (m, 2 H), 0.94–1.03 (m, 2 H), 0.95 (s, 18 H), 1.08 (br. s, 2 H), 1.13 (br. d, *J* = 9.5 Hz, 2 H), 1.39 (br. d, *J* = 9.5 Hz, 2 H), 1.71 (m_c, 2 H), 2.04 (m_c, 2 H), 2.28 (s, 2 H), 2.65 (ddd, *J* = 15.5, *J* = 10.2, *J* = 2.8 Hz, 2 H), 2.71 (ddd, *J* = 15.5, *J* = 6.5, *J* = 2.8 Hz, 2 H), 7.08 (br. d, *J* = 7.5 Hz, 2 H), 7.15 (ddd, 2× *J* = 7.3, *J* = 1.2 Hz, 2 H), 7.23 (ddd, 2× *J* = 7.4, *J* = 1.6 Hz, 2 H), 7.47 (dd, *J* = 7.3, *J* = 1.6 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.2, 18.5, 23.9, 24.2, 27.7, 36.0, 38.3, 38.7 (t, $^1J_{C,D}$ = 19 Hz), 38.7, 124.8, 128.4, 128.5, 132.8, 135.5, 150.1 ppm. ^{29}Si NMR (99.3 MHz, $CDCl_3$): δ = –5.60 ppm. IR (ATR): $\tilde{\nu}$ = 3054 (w), 2925 (s), 2854 (s), 2127 (w) (C–D), 1589 (w), 1466 (s), 1434 (s), 1407 (w), 1389 (w), 1361 (m), 1293 (w), 1264 (m), 1216 (m),

1179 (w), 1141 (m), 1127 (m), 1074 (m), 1008 (w), 974 (m), 865 (m), 820 (s), 755 (s), 763 (s), 727 (m), 712 (m), 693 (m), 674 (m), 671 (m), 643 (w), 608 (m), 575 (w) cm^{-1}. HRMS (EI): calcd. for $C_{33}H_{46}D_2Si_2$ [M – C_4H_9]$^+$] 445.2716; found 445.2719.

(1*R,2*S**,4*R**,5*S**)-2,5-Bis[(^{Si}*S**)-1-isopropyl-1-silatetralin-1-yl]-bicyclo[2.2.1]heptane (*rac*-13b) and (2*R*,6*S*)-2-[(^{Si}*R*)-1-Isopropyl-1-silatetralin-1-yl]-6-[(^{Si}*S*)-1-isopropyl-1-silatetralin-1-yl]bicyclo-[2.2.1]heptane (*meso*-13b):** See Table 2, Entry 4. According to GP 2, starting from **12** (27.6 mg, 0.300 mmol), *rac*-**2b** (126 mg, 0.660 mmol), [(phen)$PdMe_2$] (4.8 mg, 0.015 mmol), and $[H(OEt_2)_2]^+$-$(BAr_4)^-$ (15 mg, 0.015 mmol), a mixture of compounds *rac*-**13b** and *meso*-**13b** (124 mg, 87%, C_2/C_s = 59:41 by GLC, *dr* ≥ 98:2 by GLC, *exo*/*endo* > 99:1 by GLC) was obtained as a colorless, highly viscous oil that was inseparable by flash chromatography. R_f = 0.46 (cyclohexane); GLC (SE-54): t_R = 33.2 (minor diastereomer), 34.1 (*meso*-**13b**), 37.1 min (*rac*-**13b**); HPLC (Daicel Chiralcel OD-RH, 20 °C, MeCN/H_2O, 85:15, flow rate = 0.80 mL min^{-1}, λ = 230 nm): t_R = 18.7 (*meso*-**13b**), 20.2 [(^{Si}R,^{Si}R)-**13b**], 23.2 (minor diastereomer), 24.7 (minor diastereomer), 28.6 min [(^{Si}S,^{Si}S)-**13b**]. IR (ATR): $\tilde{\nu}$ = 3053 (w), 2995 (w), 2921 (s), 2860 (s), 1589 (w), 1463 (s), 1434 (s), 1293 (w), 1266 (w), 1216 (m), 1141 (m), 1127 (m), 1074 (m), 995 (m), 972 (m), 908 (s), 881 (s), 781 (m), 754 (s), 707 (s), 685 (m), 650 (m), 624 (s), 609 (s) cm^{-1}. $C_{31}H_{44}Si_2$ (472.9): calcd. C 78.74, H 9.38; found C 78.51, H 9.67.

Analytical Data for *rac*-13b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82–0.94 (m, 2 H), 0.90 (br. s, 2 H), 0.96 (d, *J* = 7.2 Hz, 6 H), 1.03 (d, *J* = 7.2 Hz, 6 H), 0.98–1.04 (m, 4 H), 1.06–1.14 (m, 2 H), 1.42 (br. dd, *J* = 10.9, *J* = 8.5 Hz, 2 H), 1.52 (ddd, *J* = 11.8, *J* = 7.9, *J* = 3.2 Hz, 2 H), 1.79–1.87 (m, 2 H), 1.88–1.96 (m, 2 H), 2.23 (br. d, *J* = 2.8 Hz, 2 H), 2.65–2.75 (m, 4 H), 7.08 (dd, *J* = 7.5, *J* = 0.6 Hz, 2 H), 7.14 (ddd, 2× *J* = 7.3, *J* = 1.0 Hz, 2 H), 7.22 (ddd, 2× *J* = 7.5, *J* = 1.4 Hz, 2 H), 7.42 (dd, *J* = 7.2, *J* = 1.2 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.3, 12.9, 18.1, 18.3, 23.6, 25.8, 35.9, 37.6, 37.8, 38.6, 125.0, 128.5, 132.9, 135.0, 149.9 ppm. ^{29}Si NMR (99.3 MHz, $CDCl_3$): δ = –7.07 ppm. HRMS (EI): calcd. for $C_{31}H_{44}Si_2$ [M – C_3H_7]$^+$ 429.2434; found 429.2394.

Analytical Data for *meso*-13b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–1.16 (m, 22 H), 1.38–1.46 (m, 2 H), 1.49–1.53 (m, 2 H), 1.79–1.96 (m, 4 H), 2.17 (br. t, *J* = 3.6 Hz, 1 H), 2.43 (s, 1 H), 2.66–2.74 (m, 4 H), 7.06–7.10 (m, 2 H), 7.12–7.17 (m, 2 H), 7.20–7.25 (m, 2 H), 7.40–7.45 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.6, 13.0, 18.2, 18.4, 23.6, 32.7, 33.0, 35.9, 37.4, 37.5, 40.4, 125.0, 128.5, 133.0, 135.1, 149.9 ppm. ^{29}Si NMR (99.3 MHz, $CDCl_3$): δ = –8.51 ppm. HRMS (EI): calcd. for $C_{31}H_{44}Si_2$ [M – C_3H_7]$^+$ 429.2434; found 429.2451.

(1*S*,2*R*,4*S*,5*R*)-2,5-Bis[(^{Si}*R*)-1-isopropyl-1-silatetralin-1-yl]bicyclo-[2.2.1]heptane [(^{Si}*R*,^{Si}*R*)-13b]: See Table 2, Entry 5). According to GP 2, starting from **12** (29.5 mg, 0.320 mmol), (^{Si}*R*)-**2b** (133 mg, 0.700 mmol, 96% *ee*), [(phen)$PdMe_2$] (5.1 mg, 0.016 mmol), and $[H(OEt_2)_2]^+(BAr_4)^-$ (16 mg, 0.016 mmol), compound (^{Si}*R*,^{Si}*R*)-**13b** (143 mg, 95%, C_2/C_s = 98:2 by GLC, *dr* = 99:1 by GLC, *exo*/*endo* > 99:1 by GLC, ≥99% *ee* by HPLC) was obtained as a colorless, highly viscous oil. $[\alpha]_D^{20}$ = –33.2 (*c* = 0.600, $CHCl_3$), $[\alpha]_{578}^{20}$ = –34.7, $[\alpha]_{546}^{20}$ = –39.7, $[\alpha]_{436}^{20}$ = –71.3, $[\alpha]_{365}^{20}$ = –121. The minor enantiomer (^{Si}*S*,^{Si}*S*)-**13b** was not detected by HPLC analysis on a chiral stationary phase (see above). Thus, >99% *ee* emerges for (^{Si}*R*,^{Si}*R*)-**13a**. IR (ATR): $\tilde{\nu}$ = 3054 (w), 2996 (w), 2921 (s), 2859 (s), 1589 (w), 1463 (s), 1434 (s), 1406 (w), 1293 (w), 1264 (m), 1216 (m), 1158 (w), 1141 (m), 1127 (m), 1074 (m), 993 (m), 972 (m), 912 (s), 880 (s), 804 (m), 781 (m), 755 (s), 738 (s), 7.26 (s), 706 (s), 680 (m), 628 (s), 597 (m), 562 (m), 518 (m) cm^{-1}.

(1*R,2*S**,4*R**,5*S**)-2,5-Bis[(^{Si}*R**)-1-*tert*-butyl-1-silaindan-1-yl]bicyclo[2.2.1]heptane (*rac*-14a) and (2*R*,6*S*)-2-[(^{Si}*S*)-1-*tert*-Butyl-1-silaindan-1-yl]-6-[(^{Si}*R*)-1-*tert*-butyl-1-silatetralin-1-yl]bicyclo[2.2.1]-heptane (*meso*-14a):** See Table 2, Entry 6. According to GP 2, starting from **12** (27.6 mg, 0.300 mmol), *rac*-**8a** (126 mg, 0.660 mmol), [(phen)$PdMe_2$] (4.8 mg, 0.015 mmol), and $[H(OEt_2)_2]^+(BAr_4)^-$ (15 mg, 0.015 mmol), a mixture of compounds *rac*-**14a** and *meso*-**14a** (124 mg, 87%, C_2/C_s = 60:40 by GLC, *dr* = 99:1 by GLC, *exo*/*endo* > 99:1 by GLC) was obtained as a white solid that was inseparable by flash chromatography; m.p. 114 °C (cyclohexane); R_f = 0.46 (cyclohexane); GLC (SE-54): t_R = 29.8 (minor diastereomer), 30.3 (*meso*-**14a**), 32.2 min (*rac*-**14a**). IR (ATR): $\tilde{\nu}$ = 3055 (w), 2995 (w), 2926 (s), 2854 (s), 1591 (w), 1470 (s), 1440 (s), 1388 (w), 1361 (m), 1312 (w), 1185 (w), 1159 (w), 1117 (s), 1058 (w), 1030 (w), 1007 (w), 962 (w), 908 (s), 735 (s), 678 (m), 619 (m), 570 (w) cm^{-1}. $C_{31}H_{44}Si_2$ (472.9): calcd. C 78.74, H 9.38; found C 78.45, H 9.21.

Analytical Data for *rac*-14a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.70 (br. s, 2 H), 0.94–1.03 (m, 4 H), 0.97 (s, 18 H), 1.10 (dd, 2× *J* = 8.6 Hz, 2 H), 1.50–1.65 (m, 4 H), 2.19 (br. d, *J* = 2.4 Hz, 2 H), 3.00–3.07 (m, 4 H), 7.10–7.16 (m, 2 H), 7.17–7.23 (m, 2 H), 7.23–7.29 (m, 2 H), 7.48 (d, *J* = 7.3 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 5.6, 18.4, 24.5, 27.4, 32.4, 37.6, 38.1, 39.5, 125.2, 125.6, 133.5, 137.0, 154.4 ppm. ^{29}Si NMR (99.3 MHz, $CDCl_3$): δ = 24.27 ppm. HRMS (EI): calcd. for $C_{31}H_{44}Si_2$ [M – C_4H_9]$^+$ 415.2277; found 415.2308.

Analytical Data for *meso*-14a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.74 (br. s, 2 H), 0.94–1.03 (m, 4 H), 0.99 (s, 18 H), 1.20 (dd, *J* = 9.5, *J* = 6.3 Hz, 2 H), 1.50–1.65 (m, 4 H), 2.12 (br. t, *J* = 3.5 Hz, 1 H), 2.37 (br. s, 1 H), 3.00–3.07 (m, 4 H), 7.10–7.16 (m, 2 H), 7.17–7.23 (m, 2 H), 7.23–7.29 (m, 2 H), 7.48 (d, *J* = 7.3 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 5.7, 18.4, 27.5, 31.1, 32.5, 33.3, 37.4, 38.0, 41.5, 125.3, 125.6, 129.1, 133.4, 137.2, 154.2 ppm. ^{29}Si NMR (99.3 MHz, $CDCl_3$): δ = 22.90 ppm. HRMS (EI): calcd. for $C_{31}H_{44}Si_2$ [M – C_4H_9]$^+$ 415.2277; found 415.2287.

Crystallographic Data: Data sets were collected with a Nonius-KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[33] absorption correction Denzo,[34] structure solution SHELXS-97,[35] structure refinement SHELXL-97,[36] graphics SCHAKAL.[37] CCDC-667979 (for *rac*-**7a**), -668281 (for *rac*-**11**), -668282 (for *meso*-**13a**), and -668283 [for (^{Si}*R*,^{Si}*R*)-**13a** or *rac*-**13a**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Copies of NMR spectroscopic data, HPLC and GLC (if any) traces of new compounds, and experimental details for the preparation of *rac*-**8b**.

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