Asymmetric Catalysis

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Rhodium(I)-Catalyzed 1,4-Silicon Shift of Unactivated Silanes from Aryl to Alkyl: Enantioselective Synthesis of Indanol Derivatives**

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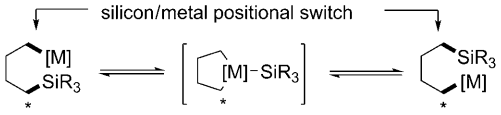
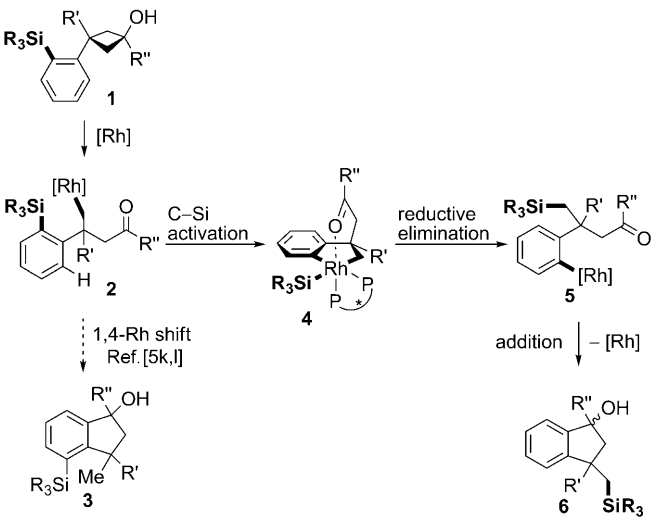
In the search for atom-economic and sustainable transformations, the selective functionalization of unactivated C–H bonds is a major topic of organometallic chemistry.[1] A specific class of such activations are 1,4-hydrogen–metal shifts which are mostly observed with organorhodium and -palladium species.[2] One major driving force for these shifts is a stabilization of the system by the formation of a stronger carbon–metal bond. Therefore, mostly migrations from C_{alkyl}-(sp^3)–M or C_{vinyl}(sp^2)–M to C_{aryl}(sp^2)–H are observed.[3] This reactivity trend can be exploited to relay organometallic species. While such tactic often leads to versatile aryl metal species, the originating position of the metal remains unfunctionalized. From a practical point of view, methods that would allow for a positional switch of two reactive functional groups are desirable. Therefore we investigated reactions involving the transfer of a synthetically versatile silyl group instead of a hydrogen atom, thus representing overall a silicon/metal swap [Eq. (1)].[4] To the best of our knowledge such a concept has not yet been explored.



(1)

β-Carbon cleavages from strained *tert*-cyclobutanols provide a suitable source to obtain the requisite alkyl organometallic species. This method has been proven to be a convenient and robust way to generate highly reactive alkylmetal species in a well defined and reagent-free manner.[5] Recently, we and Murakami demonstrated the capability of such intermediates to undergo 1,4-rhodium shifts leading to indanols.[5k,l] The metal-catalyzed activation of C–Si groups has been well established for Hiyama–Denmark cross-coupling reactions.[6] These reactions are by and large dominated by activated silyl groups such as halo- and hydrosilanes or strained silacyclobutanes. Besides reactions proceeding by discrete penta- or hexa-coordinated silicate species prior to bond cleavage, tetraorganosilanes are much less frequently used.[7] Chatani and co-workers recently reported an elegant work on rhodium(I)-catalyzed direct insertion into the Me–Si bond of aryltriorganosilanes.[8] This report corroborates the potential and the need to further develop methods allowing to capitalize on the ease of access, robustness, and versatility of tetraorganosilanes.

Herein, we report a 1,4-Rh/Si shift and a second rhodium-promoted C–Si bond cleavage of the arising products. The envisioned process is initiated by β-carbon elimination from *tert*-cyclobutanol **1** (Scheme 1). The thereof generated highly



Scheme 1. Proposed pathway of the targeted rhodium/silicon swap.

reactive alkylrhodium species **2** could undergo C_{aryl}(sp^2)–H activation giving indanol **3**.[5k,l] However, in the presence of a suitable silyl group, we hypothesized that an oxidative addition leading to presumed rhodium(III) complex **4** might become the preferred pathway.[9] In turn, this complex could reductively eliminate to give the envisioned intermediate **5**. We anticipated that the higher stability of C_{aryl}–Rh vs. C_{alkyl}–Rh bonds would drive the reaction in the desired direction.[10] Species **5**, in turn, could add across the carbonyl group, and subsequent protonation of the rhodium alkoxide formed would deliver indanol **6** and close the catalytic cycle.

During our investigations we detected compounds **3** and **6**, but observed additionally silacycles **7** in significant amounts (Scheme 2). The origin of compounds **7** might be rationalized

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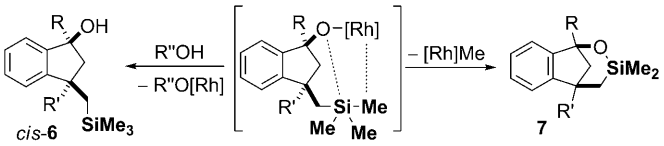
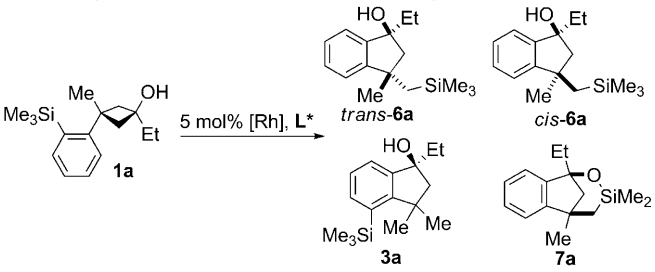


Scheme 2. Second rhodium-catalyzed C–Si bond activation.

Table 1: Optimization studies for the individual products.[a]

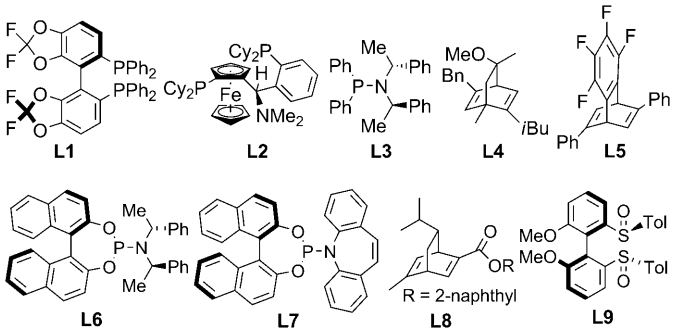


Entry	L*[b]	Solvent	Additive	*T* [°C]	*trans*-**6**/*cis*-**6**/**7**/**3**[c]	*ee* [%]
1	–	dioxane	H_2O	110	14:72:14:0	–
2[d]	–	toluene	Cs_2CO_3	130	8:4:**88**:0	–
3	**L1**	mesitylene	–	100	**72**:11:0:17	**97**[e]
4	**L2**	dioxane	H_2O	110	12:86:2:0	< 5
5[f]	**L3**	mesitylene	–	100	7:**93**:0:0	< 5
6[g]	**L4**	dioxane	H_2O	110	**78**:22:0:0	**96**[h]
7[g]	**L5**	mesitylene	–	100	29:71:0:0	18

[a] Conditions: 0.05 mmol **1a**, 0.20 M in solvent, 2.5 mol% [{Rh(OH)(cod)}$_2$], 6 mol% **L***, 1.5 equiv additive, 12 h. [b] See Scheme 3. [c] Ratio determined by ^{1}H NMR spectroscopy. [d] 0.50 M. [e] (1*S*,3*S*)-**6a**. [f] 12 mol% **L3**. [g] 2.5 mol% [{Rh(OAc)(C$_2$H$_4$)$_2$}$_2$]. [h] (1*R*,3*R*)-**6a**.

from the rhodium *tert*-alkoxide derived form *cis*-**6**.[11] Paralleling a recent report of Hiyama and co-workers who used 4-hydroxy-functionalized silanes as reagents for palladium-catalyzed methylation and alkylation of aryl halides,[12] the formation of a methyl rhodium species and the concomitant release of **7** is plausible. Liberation of methane by protonation would regenerate the active Rh^I catalyst.

For the silyl group transfer, we initially investigated conditions controlling the C–Si vs. C–H activation ratio and the diastereo- as well as enantioselectivity of the process.[13] In addition, we tried to promote selectively the C–Si bond activation leading to tricycle **7**. When [{Rh(cod)OH}$_2$] was used as rhodium source in the absence of phosphine ligands, *cis*-**6** was obtained as the major product (Table 1, entry 1). Increasing the concentration to 0.5 M M and the reaction temperature to 130 °C, as well as adding cesium carbonate, **7** becomes the dominant product (entry 2). Difluorphos (**L1;** Scheme 3) showed the highest selectivity for the formation of *trans*-**6a** and the use of mesitylene as solvent mitigated concurrent C–H activation (entry 3).[14,15] Contrasting these findings, taniaphos (**L2**) and simplephos (**L3**)[16] displayed both a high selectivity for the

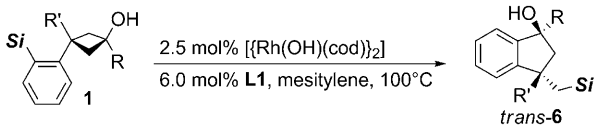


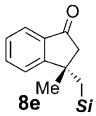
Scheme 3. Employed ligands.

isomer *cis*-**6a**, although it was formed virtually racemic (entries 4 and 5). However, even in the presence of cesium carbonate at high reaction temperatures, no tricyclic product **7** was detected. Led by the high *cis* selectivity of [{Rh(cod)OH}$_2$] in the absence of phosphine ligands, we evaluated chiral dienes for the synthesis of **7**. Dolefin (**L4**), developed by Carreira et al.,[17] induced high enantioselectivity, albeit it displayed the inverse diastereoselectivity, favoring *trans*-**6a** over *cis*-**6a** (entry 6). On the other hand, diene **L5**, reported by Hayashi et al.,[18] showed the desired *cis* selectivity, but the enantioselectivity and its potential for the second C–Si activation are low (entry 7).

Under the optimized conditions of entry 3, we explored the scope of the reaction with special focus on different silyl groups (Table 2). The substituents R and R′ can be varied

Table 2: Scope and limitation of the C–Si activation.[a]



Entry	R	R′	*Si*	*trans*-**6**	d.r.[b]	yield [%][c]	*ee* [%]
1	Et	Me	$SiMe_3$	**6a**	6:1	82	97
2	*t*Bu	Me	$SiMe_3$	**6b**	20:1	82	96
3	*p*-ClC_6H_4	Me	$SiMe_3$	**6c**	10:1	80	96
4	*p*-ClC_6H_4	CH_2OBn	$SiMe_3$	**6d**	8:1	93	99
5[d]		Me	$SiMe_3$	 **8e**	–	70	85
6	Et	Me	$SiMe_2Bn$	**6f**	9:1	61	97
7	Et	Me	$SiMe_2Ph$	**6g**	9:1	72	97
8	Et	Ph	$SiMe_2Ph$	**6h**	9:1	72	82
9	Et	Me	$SiMe_2(HC{=}CH_2)$	**6i**	8:1	90	96
10	$HC{=}CH_2$	Me	$SiMe_2(HC{=}CH_2)$	**6j**	19:1	75	99
11	Et	Me	$SiMe_2(H_2CCH{=}CH_2)$	**6k**	13:1	75	98
12	Et	Me	$SiEt_3$	**6l**	1.2:1	22	86

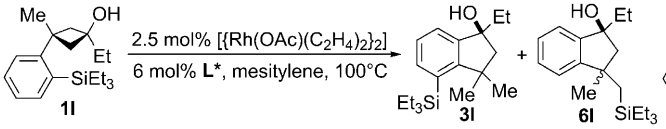
[a] Conditions: 0.10 mmol **1**, 0.20 M in mesitylene, 2.5 mol% [{Rh(OH)(cod)}$_2$], 6.0 mol% **L1**, 100 °C, 12 h. [b] Ratio determined by ^{1}H NMR spectroscopy. [c] Yield of isolated product **6**.[19] [d] With *cis*-**1e**.

without affecting the outcome of the reaction, providing **6a**–**6d** in good yields and with high enantioselectivities (entries 1–4). Notably, with a 2-thienyl group, indanone **8e** is formed instead of **6e** (entry 5).[5p] Silyl groups possessing another potentially reactive insertion site, like $SiMe_2Bn$, $SiMe_2Ph$, $SiMe_2(HC{=}CH_2)$, and $SiMe_2(H_2CCH{=}CH_2)$, are cleaved exclusively at the reported positions (entries 6–11). This selectivity can be rationalized by a more favorable five-membered rhodacycle **4** compared to a hypothetical six-membered rhodacycle that would arise from the alternative insertion positions. The triethylsilyl group proved to be more reluctant and the C–Si cleavage proceeded only in modest yields, whereas the concurrent C–H activation pathway became dominant (entry 12).

This outcome with bulkier silyl groups prompted us to re-evaluate the decisive variables governing C–Si vs. C–H activation (Table 3).[20] Whereas phosphorus containing ligands displayed a high preference for the C–H pathway forming **3l** (entries 1 and 2), diene ligands promoted virtually exclusively C–Si activation, though with varying enantio- and diastereoselectivity of the product **6l** (entries 4–7). **L4** worked best and provided *ent*-**6l** in 90% *ee* (entry 5). Notably, P-olefin ligand **L7** (entry 3) gave selectively **6l** and bis-sulfoxide **L9** did not catalyze the reaction (entry 8).

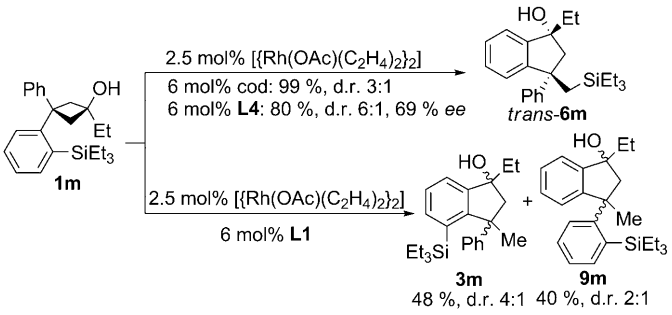
The influence of the ligand is even more striking with substrate **1m** possessing three potential C–H insertion positions. Diene ligands (cod and **L4**) cleanly provided the silyl-transfer product *trans*-**6m**, whereas the use of phosphine ligand **L1** led to a mixture of the isomers of **3m** and **9m** (Scheme 4).

Table 3: C–Si vs. C–H bond activation.[a]



Entry	L*[b]	3l/6l[c]	Entry	L*	3l/6l[c]
1	**L1**	78:22[d]	5	**L4**	<5:95[g]
2[e]	**L6**	98:2	6	**L5**	<5:95
3	**L7**	<5:95	7	**L8**	<5:95
4[f]	–	<5:95	8	**L9**	–[h]

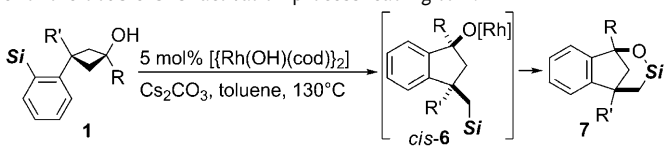
[a] Conditions: 0.05 mmol **1l**, 0.20 M in mesitylene, 12 h for full conversion. [b] See Scheme 3. [c] Ratio determined by ^{1}H NMR spectroscopy. [d] 72% **3k**, 86% *ee*. [e] 12 mol% **L6**. [f] [{Rh(OH)(cod)}$_2$]. [g] 89% **6l**, d.r. = 2:1 (*trans*-**6l**), 90% *ee*. [h] No reaction.

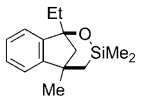
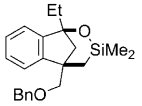
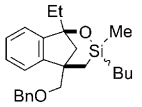
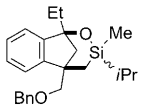
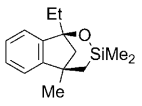
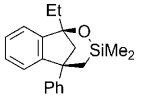


Scheme 4. **L4** enables selective C–Si activation of **1m**.

We next examined the second C–Si bond activation under phosphine-free conditions leading to tricyclic products **7** (Table 4). For a trimethylsilyl group, the reaction yielded, independent of the substitution of the 3-position of the cyclobutanol, the silacycle (**7a** and **7n**, entries 1 and 2). Furthermore, a Si–Me bond was selectively cleaved over a Si–Bu bond (entry 3). However, we observed no diastereoselec-

Table 4: Scope for the double C–Si activation process leading to **7**.[a]

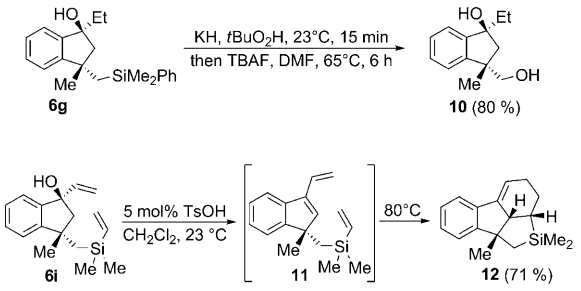


Entry	1	*Si*	7		yield [%][c]	*ee* [%][d]
1	*trans*-**1a**	$SiMe_3$		**7a**	80	–
2	*trans*-**1n**	$SiMe_3$		**7n**	71	–
3	*trans*-**1o**	$SiMe_2Bu$		**7o**	72 (d.r. 1:1)	–
4	*trans*-**1p**	$SiMe_2iPr$		**7p**	28 (d.r. 2:1)	–
5[b]	*cis*-**1a**	$SiMe_3$		(*S,R*)-**7a**	57	96
6[b]	*cis*-**1q**	$SiMe_3$		(*S,S*)-**7q**	35	82

[a] Reaction conditions: 0.10 mmol **1**, 0.3 M in toluene, 5 mol% [{Rh(OH)(cod)}$_2$], 3.0 equiv Cs_2CO_3, 130°C, 8 h. [b] 0.2 M in mesitylene, 2.5 mol% [{Rh(OH)(cod)}$_2$], 6.0 mol% **L1**, , 100°C, 5 h, then 3.0 equiv Cs_2CO_3, 5 mol% [{Rh(OH)(cod)}$_2$], 130°C, 8 h. [c] Of isolated product. [d] Determined on an aliquot of *cis*-**6**.

tion of the two methyl groups of intermediate *cis*-**6o**, thus **7o** was formed as a 1:1 mixture of diastereomers at the silicon stereogenic center. A moderate diastereoselectivity of 2:1 could be obtained by replacing the butyl group by the bulkier isopropyl group (**7p**, entry 4). Additionally, optically active silacycles were accessible by a sequential procedure in moderate yields: First, enantioenriched indanols *cis*-**6a** and *cis*-**6q** were prepared selectively with **L1** from cyclobutanols *cis*-**1a** and *cis*-**1q**, respectively.[21] After complete conversion, 5 mol% of [{Rh(OH)(cod)}$_2$] were added and the Si–Me bond cleavage was induced at 130°C giving (*R*,*S*)-**7a** and (*S*,*S*)-**7o** in 96% and 82% *ee*, respectively.

To illustrate the versatility of the silyl group transfer, compound **6g** containing a dimethylphenylsilyl group was converted by the Woerpel modification[22] of the Tamao–Fleming oxidation into the corresponding diol **10** in 80% yield (Scheme 5). Other functionalized silanes are as well



Scheme 5. Transformations of indanols **6**. TBAF: tetrabutylammonium fluoride, DMF: dimethylformamide.

suited for further reactions. For instance, treating bis vinyl-substituted indanol **6i** with 10 mol% of toluenesulfonic acid (TsOH) resulted in a smooth dehydration to diene **11** which underwent upon heating to 80°C a Diels–Alder reaction to give tetracycle **12** in 71% yield as a single diastereomer.

In summary, we reported a rhodium(I)-promoted activation and 1,4-positional swap of unactivated tetraorganosilanes. As an extension to this process, a second Si–C bond activation is initiated by rhodium *tert*-alkoxides. Both reactivities underline the potential of rhodium(I) species to undergo unexplored reactivity leading to reorganizations of the molecular framework. Ongoing research focuses on a further understanding of the decisive factors of the individual activation modes and their exploitation for synthetic applications.

Experimental Section

Cyclobutanol **1a** (26.2 mg, 0.10 mmol), [{Rh(cod)(OH)}$_2$] (1.14 mg, 2.50 μmol), and (*R*)-difluorphos (**L1**) (4.10 mg, 6.00 μmol) were weighed into an oven-dried vial equipped with a magnetic stir bar, sealed with a rubber septum, and flushed with nitrogen. After the addition of 0.5 mL of mesitylene, the reaction mixture was degassed by three freeze–pump–thaw cycles, stirred for 5 min at 23°C, and subsequently immersed into a preheated oil bath (100°C) for 5 h. After thin layer chromatography showed the complete conversion, the reaction mixture was cooled to 23°C and directly purified on silica gel (pentane/EtOAc 15:1, $R_f = 0.19$) giving 21.6 mg (82%, d.r. = 6:1, 97% *ee*) of indanol (1*S*,3*S*)-**6a** as a colorless oil.

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