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Enantioselective Si–H Insertion Reactions of Diarylcarbenes for the Synthesis of Silicon-Stereogenic Silanes

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Abstract

We report the first example of enantioselective, intermolecular diarylcarbene insertion into Si–H bonds for synthesis of silicon-stereogenic silanes. Dirhodium(II) carboxylates catalyze an Si–H insertion using carbenes derived from diazo compounds where selective formation of an enantioenriched silicon center is achieved using prochiral silanes. Fourteen prochiral silanes were evaluated with symmetrical and prochiral diazo reactants to produce a total of 25 novel silanes. Adding an ortho substituent on one phenyl ring of a prochiral diazo enhances enantioselectivity up to 95:5 er with yields up to 98 %. Using *in situ* IR spectroscopy, the impact of the off-cycle azine formation is supported based on the structural dependence for relative rates of diazo decomposition. A catalytic cycle is proposed where the Si–H insertion step is rate-determining, supported by kinetic isotope effect experiments. Transformations of an enantioenriched silane derived from this method, including selective synthesis of a novel sila-indane, are demonstrated.

The potential utility of chiral-at-silicon compounds incorporated into more complex structures has not been fully understood due to a shortage of synthetic methods. Silicon-stereogenic molecules are rare in number and diversity of structures as compared to carbon. Selected examples to generate silicon-stereogenic silanes include dehydrocouplings,[1–3] arylation,[4,5] hydrosilylation,[6–9] Si–C activation,[10,11] and reactions controlled by chiral auxillaries.[12–14] Brief explorations of the effect of silicon chirality on reaction outcome to produce more complex molecules have occurred,[15–17] yet remain limited.

The catalytic insertion of carbenes into Si–H bonds to generate organosilicon compounds has been intermittently explored since Doyle's original work in 1988.[18,19] Methods to date have focused on generation of stereogenic carbon centers using donor/acceptor carbenes (Figure 1A).[20–23] Si–H insertion to generate stereogenic silicon centers has been demonstrated by Katsuki[24] and Iwasa[25] using donor/acceptor carbenes (Figure 1A). Donor/donor carbenes (also referred to as diarylcarbenes) are less reactive, with few reports of intermolecular Si–H insertion, and one report of an enantioselective variant using functionalized alkynes as precursors (Figure 1B).[26–29]

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Donor/donor carbenes have recently emerged as useful substrates for highly selective C–H insertion reactions.[30–34] Rhodium carbene complexes demonstrate sufficient reactivity at the insertion carbon despite the presence of two aryl rings for potential stablization.[35,36] The Franz group has a long-standing interest in organosilicon chemistry and expertise synthesizing prochiral dihydridosilanes with variation of steric and electronic factors.[37–39] We envisioned that the additional aryl ring could accomplish an enantioselective intermolecular Si-H insertion process with prochiral silanes (Figure 1C). Herein, we communicate the first enantioselective diarylcarbene Si–H insertion to produce silicon-stereogenic organosilanes.

We began our studies screening metal catalysts [Ru(II), Ir(I), Fe(II), Rh(II) and Cu(II)] with diphenyldiazomethane (**2a**) and prochiral methylphenylsilane (**1a**). For all experiments, inverse addition of **2a** using a syringe pump over 1 hour increased yield of **3a** by preventing azine formation, as seen in previous studies with Si–H insertion methodologies.[21,40,41] Insertion product **4a** was only observed using dirhodium tetraacetate (Table 1, entry 1).[42] Based on this lead result, we proceeded to screen chiral dirhodium(II)-based catalysts to identify an enantioselective variant.

A screen of well-studied chiral dirhodium compounds highlighted the reactivity of dirhodium tetracarboxylates. Carboxylate ligands afforded higher yields compared to amido-containing ligands due to the increased electrophilicity of the metal center and resulting carbene (entry 2 vs. entries 4–9).[43] Of the catalysts studied, Rh_2(*S*-TCPTTL)$_4$ provided the highest levels of enantioselectivity when compared to others (entries 5–8 vs 9), which improved further using toluene (entry 10). When an insertion was tested using prochiral diazo compound **3a**, the enantioselectivity of silane product **5a** increased *from 82:18 to 93:7 er*, with a notable increase in yield (76% to 91% yield, entry 10 vs. 14). Manual slow addition of **3a** is to seen to form **5a** in comparable yield and selectivity to use of a syringe pump (81%, entry 14 vs. 15), but the use of a syringe pump was continued for further studies. Reducing the reaction temperature below 23 °C did not increase selectivity and no insertion was observed below −30 °C. With optimized conditions in hand, we investigated the effect of substituents with both symmetrical and prochiral diazo compounds.

A series of sterically and electronically varied silanes and symmetrical diazo compounds were evaluated to study the effects on enantioselectivity (Scheme 1, **4a**-**o**). Electron-rich diazo **2b** was less reactive than **2a** and provides lower yield for **4b** (45%, 81:19 er). Yield improved using diazo **2c** (91%) and lower enantioselectivity was observed for silane **4c** (76:24 er). Electronwithdrawing groups do not strongly affect selectivity (**4d**, 80:20 er), while electron-donating groups on the silane proved deleterious to enantioselectivity (**4e** and **4f**, 50:50 er and 74:26 er respectively). Additional steric bulk on the aryl ring of the silane generally eroded enantioselectivity (**4g-j**) but maintained fair to good yields (55–69%). Selectivity similar to **4a** (82:18) was also observed using 2-naphthyl silane **1g**, with the yield also higher compared to **4h** (69 vs 60%). A slight recovery of enantioselectivity was also observed with **4k** (52%, 82:18 er) compared to **4h** (79:21 er), and comparable to **4a**. Studies with varied alkyl substitution on the silicon center were conducted with diazo **2a**.

Isobutyl-containing **4l** provided the highest enantioselectivity observed using **2a** (86:14 er). However, neopentyl substitution led to loss of enantioselectivity (**4m**, 50:50 er), and cyclohexyl substitution reduced enantioselectivity as well (**4n**, 70:30 er). Lastly, switching to a siloxane also deleteriously affected enantioselectivity while maintaining fair yield (**40**, 0 60%, 61:39 er). We next turned our focus to insertion of prochiral diazo reactants.

The ability of the ortho substituent on one phenyl ring of the diazo compounds to control enantioselectivity was explored (Scheme 2). Electron-donating substituents lower diastereoselectivity (**5b**, 90:10 dr vs 93:7 dr), but slightly improve enantioselectivity (95:5 vs 93:7 er). With an electron-withdrawing group (**5c**), excellent yield and enantioselectivity is observed (93%, 93:7 er) and diastereoselectivity increased (98:2 vs 93:7 dr). Recent work has noted potential synergistic effects of electronics and ortho substitution on the selectivity of donor/donor carbene chemistry.[44] Substitution on both phenyl rings was able to achieve excellent yield and good selectivity in **5d** (98% yield, 90:10 dr. 89:11 er), although slightly lower compared to other substitution patterns. The steric and push-pull electronic effects combined improve enantioselectivity compared to symmetrical diazo compounds. These substrates demonstrate that the presence of any ortho-substitution may promote enantioselectivity. Replacing phenyl with a 1-naphthyl group led to decreased diastereoselectivity (**5e**, 85:15 dr) and low enantioselectivity (61:39 er), suggesting other competitive steric effects are present. We sought to explore varied substitution of silanes with prochiral diazo **3a**, given the increase in yield and enantioselectivity compared to using **2a**. Prochiral silanes were tested with diazo **3a** *and all demonstrated above 90:10 er for the major diastereomer* (Scheme 2, **5f**-**5j**). Additionally, the reaction performed with 1 gram of **3a** using <1 mol% catalyst affords excellent yield, diastereoselectivity and enantioselectivity (Scheme 2, **5a**). Overall, the data shows that diastereoselectivity is substrate controlled, while enantioselectivity is controlled by the rhodium catalyst. Notably, using a diastereoselective reaction with silane **1c** promotes enantioselectivity with **5f** (94:6 er) compared to **4e** (50:50 er). This result highlights the benefit of using prochiral **3a** to improve enantioselectivity.

A catalytic cycle for the enantioselective Si–H insertion of donor/donor carbenes is proposed (Figure 2A).[36] The Rh(II) carboxylate catalyst (**I**) reacts with the diazo compound (**2a** or **3a**) to form complex **II**, which is approached by prochiral silane **1a** to produce the silicon-stereogenic silane and regenerate catalyst. Kinetic isotope effect experiments support the rate-determining insertion step ($k_H/k_D = 1.6$), fitting closely with previous experiments of Si–H insertion with donoracceptor[20,41,45] and donor/donor carbenes.[29]. Off-cycle formation of azine (**6** or **7**) can occur when metal carbene **II** reacts with another diazo reactant. Using *in situ* IR spectroscopy, we determined that the ortho-substituted prochiral diazo **3a** has a significantly reduced rate of azine formation (vs **2a**), which accounts for higher yields of the Si–H insertion products. Relative rates of azine formation ($k_{rel} > 120$) was observed for decomposition of diazo **2a** vs **3a** with Rh_2(*S*-TCPTTL)$_4$ (in toluene) in the absence of silane (Figure 2A).[46] Increased yields of Si–H insertion products with ortho-substitution (**5a**-**i**) are attributed to steric interactions blocking the approach of diazo **3a** to **II**, which reduces off-cycle azine formation. The addition of 4Å mol sieves reduces off-cycle processes leading to formation of siloxane **8**.[42] The increase in enantioselectivity observed with prochiral donor/

donor diazo **3** is attributed to a twisting of the ortho substituted aryl ring, which blocks one face of the carbene in **II** to promote selective approach of the silane (Figure 2B).[44,47,48] There has been a recent report proposing the twisting effect to have electronic contributions similar to that of a donoracceptor carbene.[44] However, we hypothesize that the steric effect of an out-of-plane phenyl twist is more significant than the electronic effects, although the analogy is noted.

To demonstrate the utility of enantioenriched silanes, silane **5a** was transformed to silanol, dehydrocoupling, and intramolecular C–H silylation products. Silanes are useful intermediates in stereoselective synthesis, and have versatile reactivity with the remaining Si–H bond.[49] It is well know that transition metals are capable of oxidative insertion into Si–H bonds with retention of configuration.[50,51] Pd/C-catalyzed silane hydrolysis affords silanol **9** in 90% yield with 90:10 dr and 93:7 er.[38,51,52] Under attempted hydrosilylation conditions, an unexpected dehydrocoupling product **10** was isolated in good yield (62%) and 93:7 dr.[53–55] Exploiting the presence of the ortho-methyl group, diasteroenriched sila-indane **11** was accessed in 90% yield with 90:10 dr using Ir-catalyzed C–H silylation methodology developed by the Hartwig group.[56,57]

In conclusion, the first example of enantioselective diarylcarbene insertion into Si–H bonds has been accomplished with Rh_2(*S*-TCPTTL)$_4$, yielding silicon-stereogenic benzhydryl silanes. While symmetrical diazo compounds demonstrated initial enantioselectivity, using a prochiral diazo reactant dramatically improved the reaction, providing yields up to 98% with 98:2 dr and 95:5 er. A catalytic cycle is proposed and the impact of the off-cycle azine formation is supported based on the structural dependence for relative rates of diazo decomposition. Transformation of the enantioenriched silane affords access to silicon-stereogenic silanol, dehydrocoupling and intramolecular C–H silylation products.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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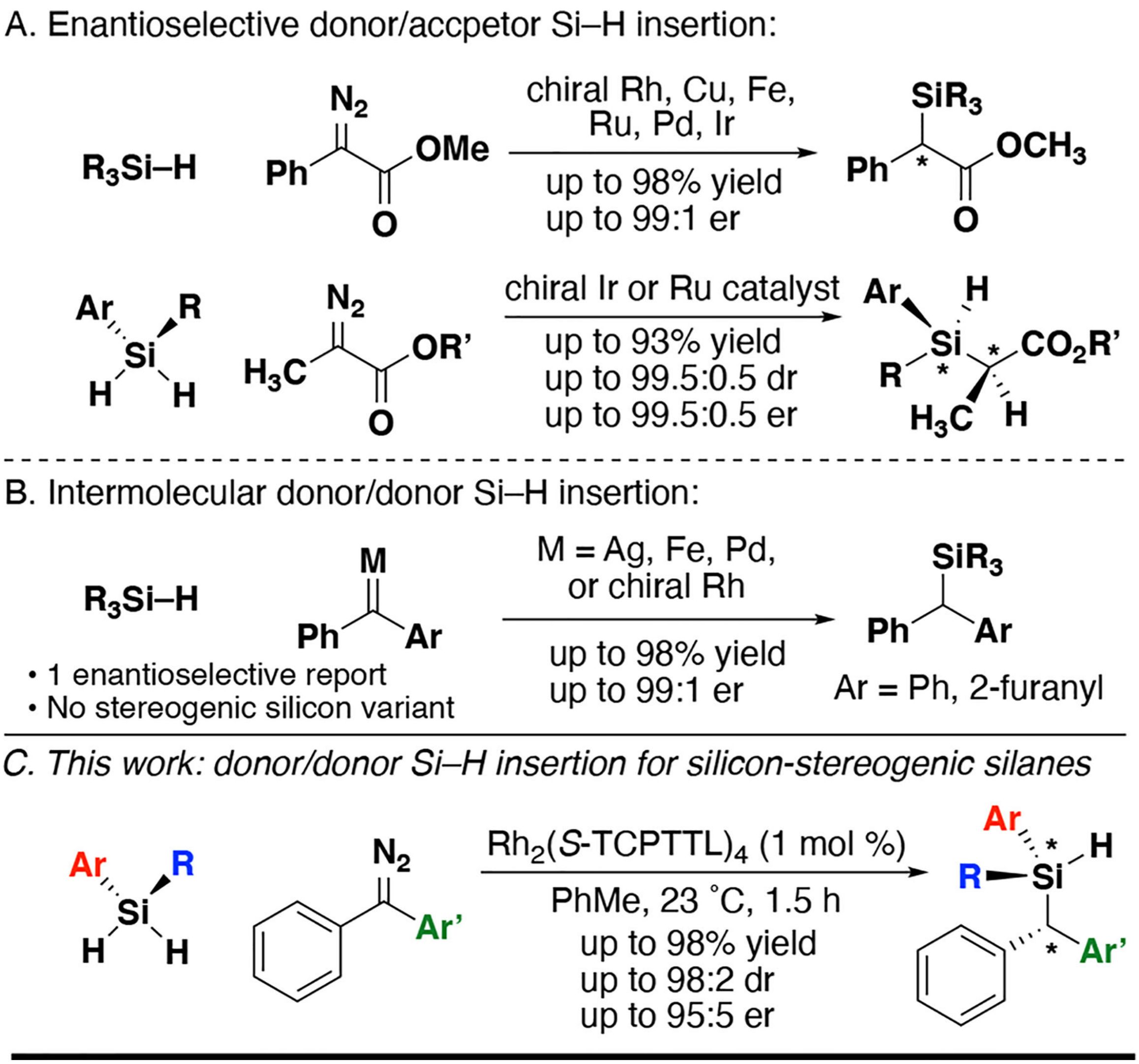


Figure 1.

Insertion of carbenes into Si–H bonds.

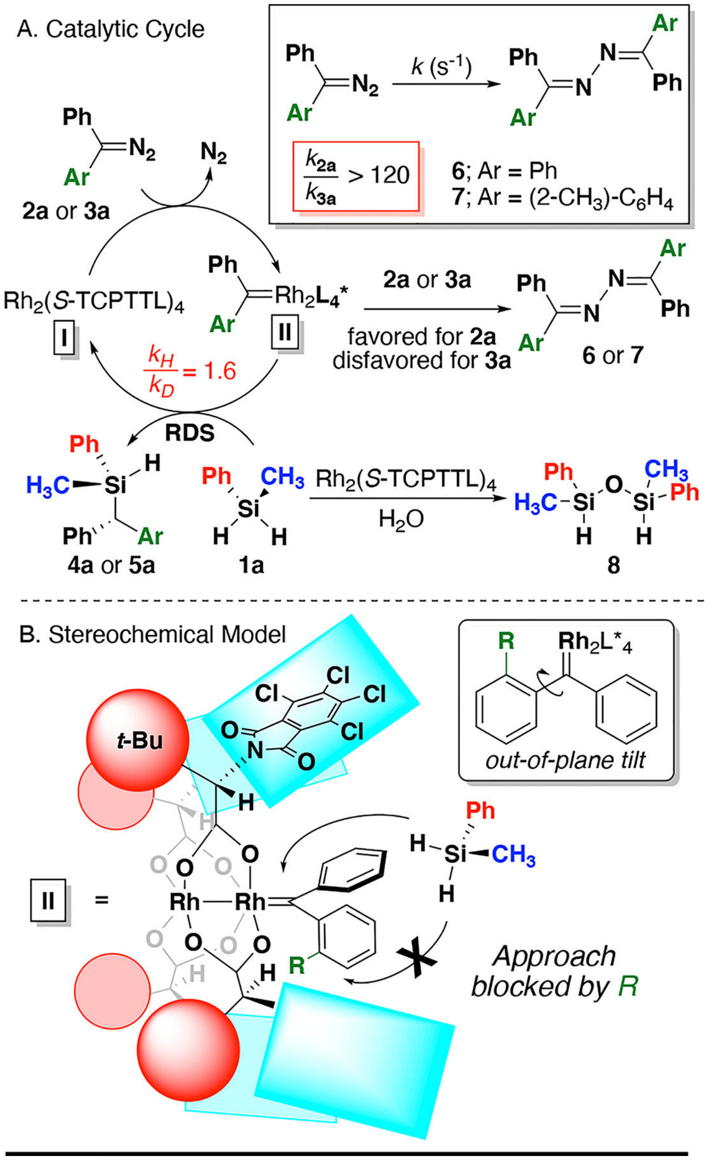
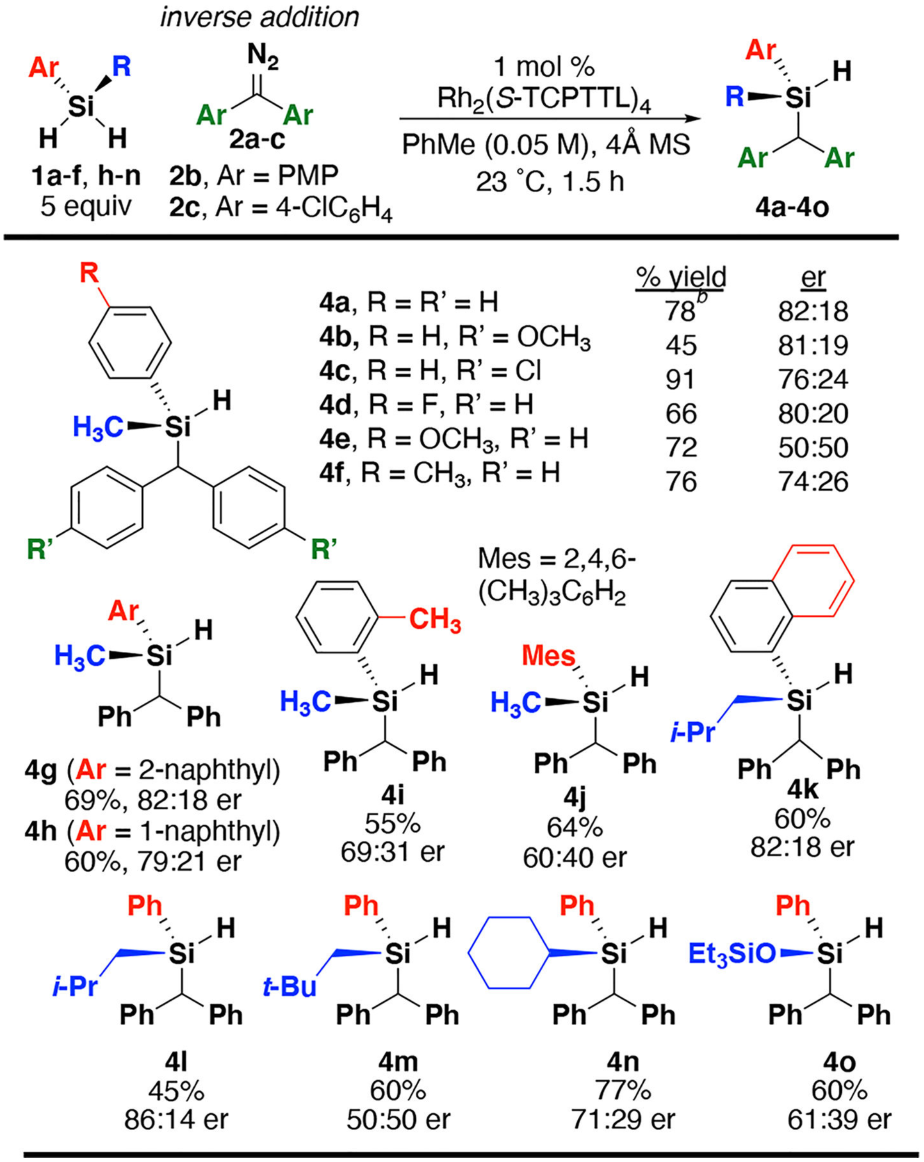


Figure 2.

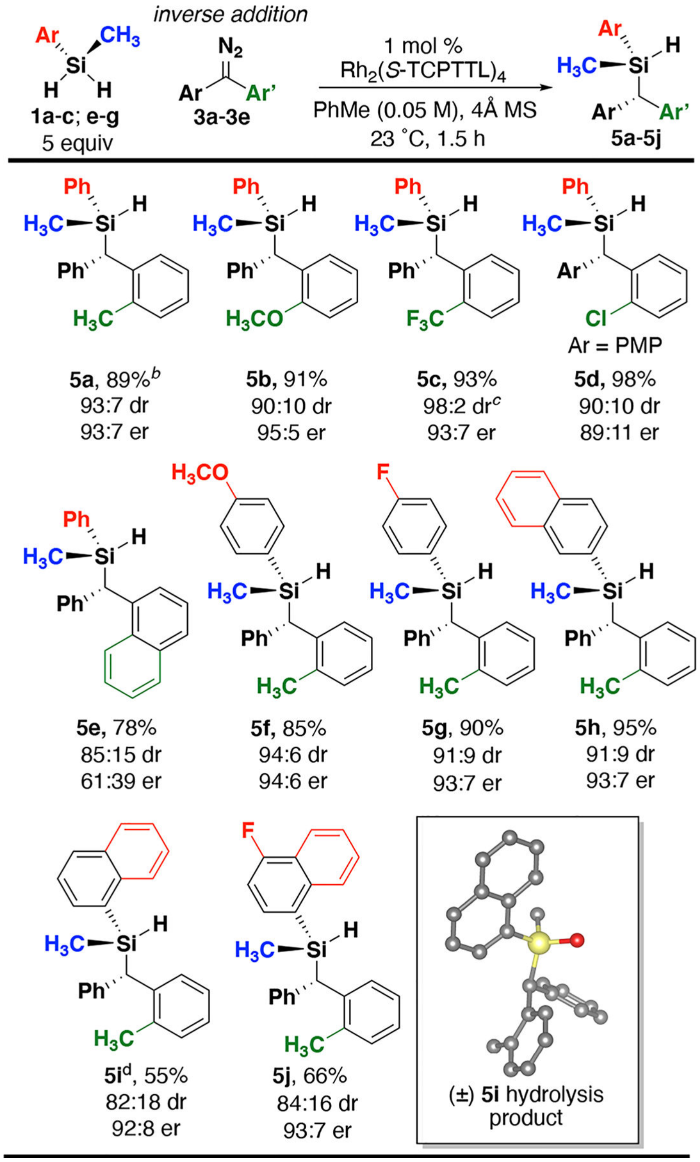
A. Proposed catalytic cycle with kinetic isotope effect; B. Diagram of proposed selectivity rationale of donor/donor insertions.



Scheme 1.

Scope of enantioselective Si–H insertion with symmetrical diazo compounds[a]

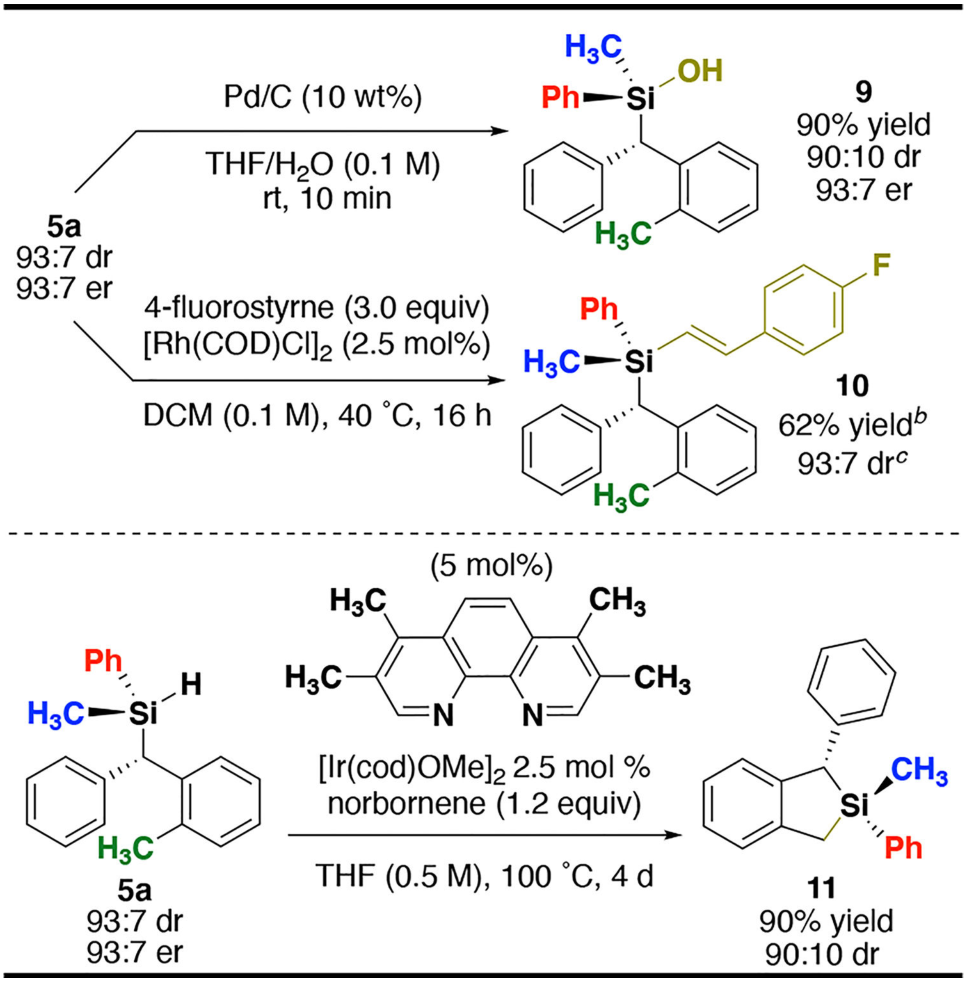
[a] isolated yields; er determined using ^{1}H NMR spectroscopy; er Determined using CSP-HPLC analysis of silanol obtained from Pd/C hydrolysis. [b]Reaction performed using 1.00 g of **3a** and 0.05 mol % catalyst, at 0.1 M in toluene. [c]dr was determined using ^{19}F NMR spectroscopy. [d]Relative configuration assigned by X-ray analysis.



Scheme 2.

Scope of enantioselective Si–H insertion with prochiral diazo reagents[a]

[a] Isolated yields; dr determined using ^{1}H NMR spectroscopy; er Determined using CSP-HPLC analysis of silanol obtained from Pd/C hydrolysis. [b]Reaction performed using 1.00 g of **3a** and 0.05 mol % catalyst, at 0.1 M in toluene. [c]dr was determined using ^{19}F NMR spectroscopy. [d]Relative configuration assigned by X-ray analysis.



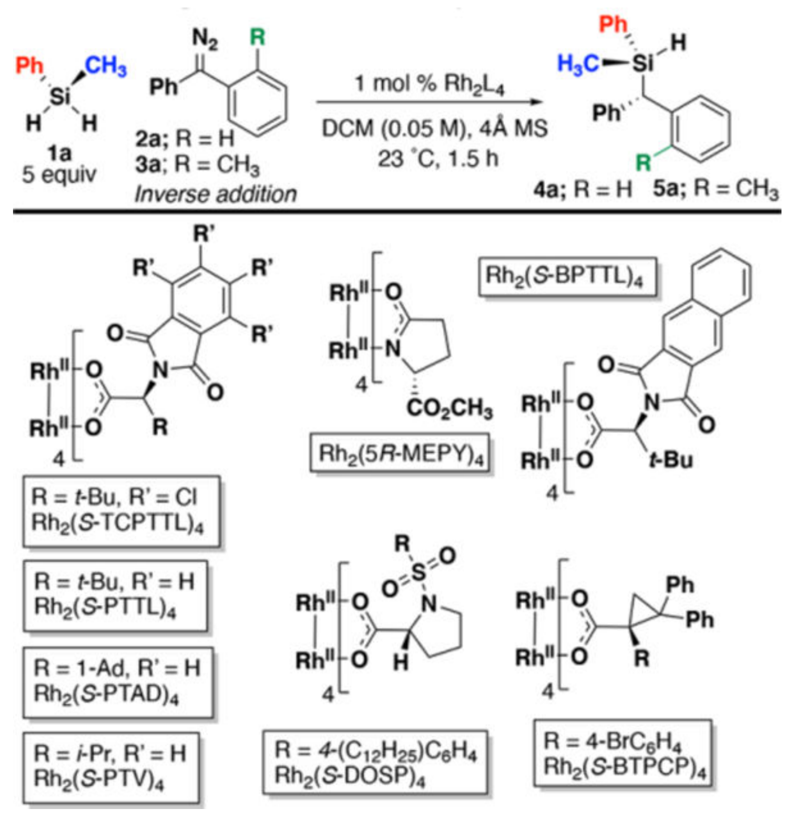
Scheme 3.

Transformations of Si–H insertion products[a]

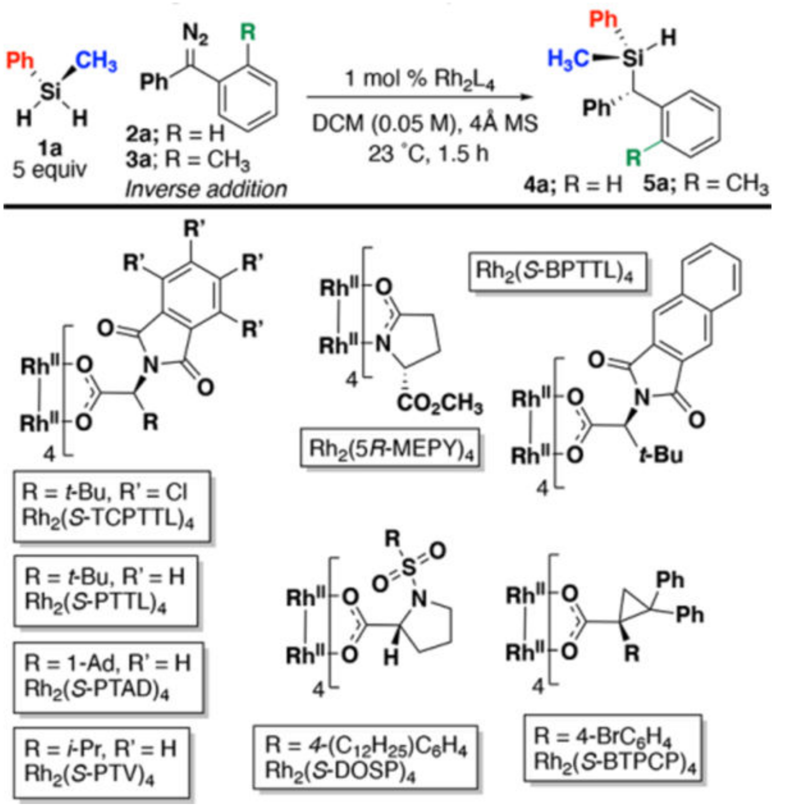
[a] Isolated yields; dr determined using ^{1}H NMR spectroscopy; er determined using CSP-HPLC. [b]Isolated as a 85:15 (major) mixture with the hydrosilylation product. See SI for more information. [c]dr determined using ^{19}F NMR spectroscopy.

Table 1.

Optimization of donor/donor Si–H insertion



entry	R	Rh_2L_4	% yield[a]	dr[b]	er[c]
1	H	$Rh_2(OAc)_4$	34	-	50:50
2	H	Rh$_2$(5*R*-MEPY]$_4$	<5	-	ND
3	H	Rh$_2$(*S*-BTPCP)$_4$	<5	-	ND
4	H	Rh$_2$(S-DOSP)$_4$	65	-	55:45
5	H	Rh$_2$(*R*-PTAD)$_4$	67	-	61:39
6	H	Rh$_2$(S-PTTL)$_4$	62	-	64:36
7	H	Rh$_2$(S-BPTTL)$_4$	62	-	64:36
8	H	Rh$_2$(S-PTV)$_4$	67	-	59:41
9	H	Rh$_2$(S-TCPTTL)$_4$	76	-	76:24
10	**H**	**Rh$_2$(S-TCPTTL)$_4$**[d]	**78**	**-**	**82:18**
11	CH_3	$Rh_2(OAc)_4$	45	55:45	50:50
12	CH_3	Rh$_2$(*R*-PTAD)$_4$	72	60:40	ND
13	CH_3	Rh$_2$(S-DOSP)$_4$	75	61:39	ND
14	**CH_3**	**Rh$_2$(S-TCPTTL)$_4$**[d]	**91**	**93:7**	**93:7**



entry	R	Rh_2L_4	% yield[a]	dr[b]	er[c]
15[e]	CH3	Rh_2(S-TCPTTL)$_4$[d]	81	93:7	93:7

[a] NMR yield using Ph-TMS as an internal standard.

[b] Determined using 1H NMR Spectroscopy.

[c] Determined using CSP-HPLC analysis of silanol obtained from Pd/C hydrolysis; major diastereomer if relevant.

[d] Toluene used as a solvent.

[e] Diazo added via syringe over five minutes.