Asymmetric Catalysis | Hot Paper

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# Iron-Catalyzed Asymmetric Hydrosilylation of 1,1-Disubstituted Alkenes**

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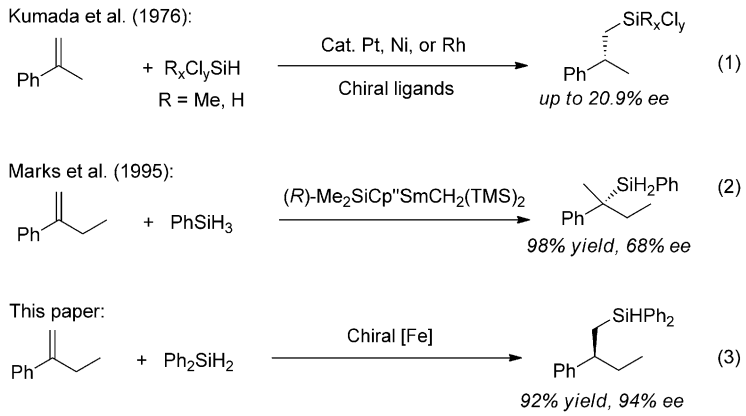
***Abstract:*** *The highly regio- and enantioselective iron-catalyzed anti-Markovnikov hydrosilylation of 1,1-disubstituted aryl alkenes was developed using iminopyridine oxazoline ligands to afford chiral organosilanes. Additional derivatization of these products lead to chiral organosilanols, cyclic silanes, phenol derivatives, and 3-substituted 2,3-dihydrobenzofurans.*

Silicon-containing chiral organic compounds are extremely useful. For instance, silasubstitution where a silicon atom substitutes a carbon atom has received increasing attention in medicinal chemistry because of their low toxicity and favorable metabolic profiles.[1] Chiral catalysts containing silicon atoms are widely used in asymmetric organic transformations.[2] Silicon-based chiral compounds are important building blocks in selective carbon–carbon bond formations.[3] Asymmetric hydrosilylation of alkenes provides direct access to constructing chiral organosilanes, however, high enantioselectivities were only achieved in the palladium- or rhodium-catalyzed Markovnikov hydrosilylation of 1-substituted or 1,2-disubstituted alkenes.[4] Because of the difficulty in differentiating two enantiotopic faces in prochiral substrates,[5] highly enantioselective hydrosilylation of 1,1-disubstituted alkenes still remains a challenge.

In 1976, Kumada reported the first catalytic asymmetric anti-Markovnikov hydrosilylation of 1,1-disubstituted alkenes. However, the enantioselectivities (0.6–20.9% *ee*) were less than ideal [Eq. (1)].[6] Although Tamao and Ito subsequently discovered the rhodium-catalyzed intramolecular asymmetric hydrosilylation of allylic alcohols to afford anti-Markovnikov products with up to 93% *ee*, the substrates were limited to di(2-propenyl)methanol and required long reaction times (11 days).[7] Bosnich and co-workers[8] also described a similar rhodium-catalyzed intramolecular asymmetric hydrosilylation of olefins with higher reactivities and a broader substrate scope, however, low enantioselectivities (0.7–60% *ee*) were observed in the cases of asymmetric hydrosilylation of 1,1-disubstituted alkenes. Marks and co-workers reported a regio- and enantioselective hydrosilylation reaction of 2-phenyl-1-butene with $PhSiH_3$, where the Markovnikov product was afforded in quantitative yield with 68% *ee* using the chiral organolanthanide precatalysts [Eq. (2); TMS = trimethylsilyl].[9] An enantioselective radical-chain hydrosilylation of alkenes using homochiral thiols as polarity-reversal catalysts was developed by Roberts and co-workers, however, their substrates were quite special and limited to cyclic vinyl lactones.[10] Although asymmetric hydrogenation,[11] dihydroxylation,[12] hydroamination,[13] and hydroboration[14] of simple 1,1-disubstituted alkenes have been recently achieved with greater than or equal to 90% *ee*, to the best of our knowledge, there have not been any reports of a general method for the highly enantioselective hydrosilylation of 1,1-disubstituted alkenes.




Iron as a sustainable transition metal has received much attention and its applications in organic transformations,[15,16] as well as asymmetric reactions have been explored.[17] Recently, we found that an iminopyridine oxazoline iron complex catalyzed the hydroboration of 1,1-disubstituted aryl alkenes with extremely high enantioselectivity.[14d] Inspired by the iron-catalyzed racemic hydrosilylation reported by Chirik and co-workers[16d] and the asymmetric transformation using pybox ligands,[18] we report herein the first highly enantioselective iron-catalyzed anti-Markovnikov hydrosilylation of 1,1-disubtituted aryl alkenes [Eq. (3)].

In our initial experiments we chose the hydrosilylation of 2-phenyl-1-butene (**2a**) with $Ph_2SiH_2$ as the model reaction in the presence of the recently-reported iron complexes **1a–d** and $NaBHEt_3$ (Table 1). To our delight, the hydrosilylation using **1a** as a precatalyst afforded **4a** in 69% yield with high enantioselectivity (92% *ee*; entry 1). The ligand derived from

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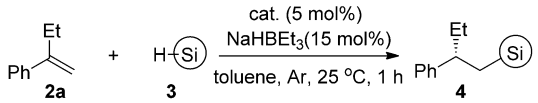
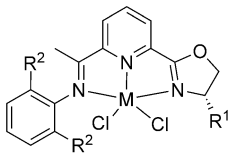
***Table 1:*** Optimization.[a]



**1a**: M = Fe, $R^1$ = Bn, $R^2$ = *i*Pr
**1b**: M = Fe, $R^1$ = *i*Pr, $R^2$ = *i*Pr
**1c**: M = Fe, $R^1$ = *t*Bu, $R^2$ = *i*Pr
**1d**: M = Fe, $R^1$ = *i*Pr, $R^2$ = Me
**1e**: M = Co, $R^1$ = *i*Pr, $R^2$ = *i*Pr

| Entry | $R^1$ | $R^2$ | RSiH | Yield [%][b] | *ee* [%][c] |
|---|---|---|---|---|---|
| 1 | Bn | *i*Pr (**1a**) | $Ph_2SiH_2$ | (69) | 92 |
| 2 | *i*Pr | *i*Pr (**1b**) | $Ph_2SiH_2$ | (69) | 94 |
| 3 | *t*Bu | *i*Pr (**1c**) | $Ph_2SiH_2$ | < 5 | – |
| 4 | *i*Pr | Me(**1d**) | $Ph_2SiH_2$ | (70) | 62 |
| 5 | *i*Pr | *i*Pr (**1e**) | $Ph_2SiH_2$ | 10 | 84 |
| 6 | *i*Pr | *i*Pr (**1b**) | $Ph_3SiH_2$ | < 5 | – |
| 7 | *i*Pr | *i*Pr (**1b**) | $PhSiH_3$ | < 5 | – |
| 8[d] | *i*Pr | *i*Pr (**1b**) | $Ph_2SiH_2$ | (92) | 94 |
| 9[e] | *i*Pr | *i*Pr (**1b**) | $Ph_2SiH_2$ | (90) | 94 |

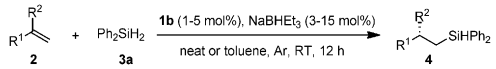
[a] The reaction was conducted using **2a** (0.6 mmol), **3** (0.5 mmol), cat. (5 mol%), $NaBHEt_3$ (15 mol%), toluene (0.5 mL) at 25 °C for 1 h. [b] Yields determined by $^1$H NMR analysis using 1,3,5-trimethylbenzene as an internal standard. Yield of the isolated product is given within parentheses. Yields and *ee* values were reported as an average of two reactions. [c] The *ee* values were determined by HPLC analysis using a chiral stationary phase. [d] Using **2a** (1.2 mmol), **3a** (1.0 mmol), 12 h. [e] Using **2a** (2.2 mmol), **3a** (2.0 mmol), **1b** (1 mmol%), $NaBHEt_3$ (3 mol%) without toluene, 5 h.

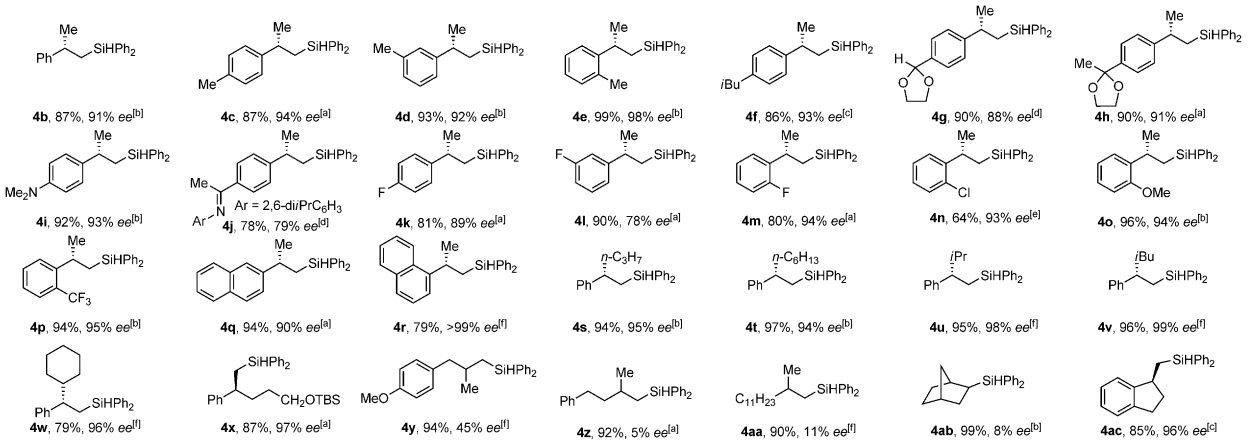
(*S*)-valine led to a slightly better enantioselectivity (94% *ee*; entry 2). The poor reactivity observed when using **1c** as a precatalyst and might be due to steric effects (entry 3). Although the less bulky precatalyst **1d** could catalyze the reaction, the enantioselectivity decreased (entry 4). By using the cobalt precatalyst **1e** instead of the iron precatalyst **1b**, both the reactivity and enantioselectivity of hydrosilylation were compromised (entry 5). Using different phenylsilanes showed no further improvement (entry 6 and 7). The reaction could be scaled up to 1 mmol and afford **4a** in 92% yield in 12 hours (entry 8). We also observed that additional solvents are not necessary, even higher reactivity was observed using THF as the sole solvent (1M) together with $NaHBEt_3$ as the reducing agent (entry 9).

The substrate scope of this method is summarized in Table 2. Hydrosilylation of electron-rich styrenes with *ortho, meta*, and *para* substitutions gave the corresponding products in good yields and excellent *ee* values (**4c–e**). The aldehyde, ketone, ester, and alcohol groups are more reactive and would react with $Ph_2SiH_2$ in our system. The acetal-protected aldehyde and ketone, amino, and imine groups were well tolerated, thus leading to the hydrosilylation products **4g–j** in 78–92% yields with 79–93% *ee*. Using 4-(prop-1-en-2-yl)benzonitrile and 2-(prop-1-en-2-yl)benzonitrile as substrates, the reactions did not occur even after increasing the temperature to 60 °C.

For electron-deficient styrenes, the position of the substituent affects the enantioselectivity. Although the yields were still good with *meta*-substituted styrenes, the enantioselectivities were slightly lower (**4k–m**, Table 2). The *ortho*-substituted styrenes which resulted in 66–84% *ee* in the iminopyridine oxazoline/iron- or cobalt-catalyzed hydroboration could undergo hydrosilylation with significantly improved enantioselectivity (≥93% *ee*; **4e** and **4m–p**). Both 1-(propen-2-yl)naphthalene and 2-(propen-2-yl)naphthalene were quite suitable for hydrosilylation to afford the product **4r** in 79% yield (>99% *ee*) and **4q** in 94% yield (90% *ee*), respectively. Other α-alkylstyrenes can also be readily catalyzed by iron with $Ph_2SiH_2$ to afford silanes (**4o–x**) in good yields and with excellent *ee* values (≥94%), including

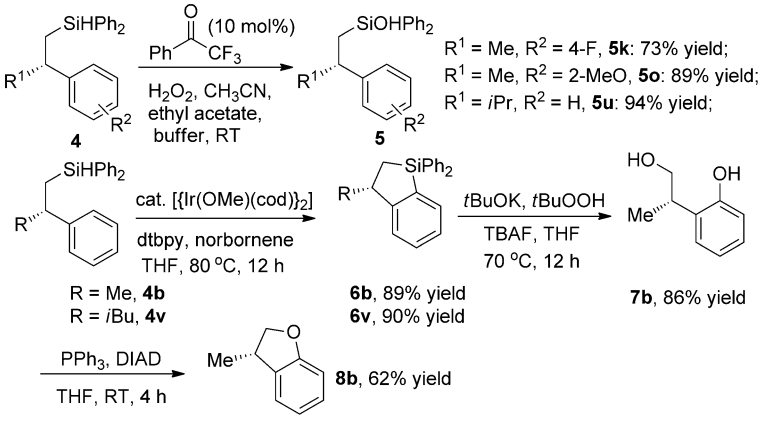
***Table 2:*** Substrate scope.




[a] Standard conditions A: alkenes (1.2 mmol), $Ph_2SiH_2$ (1.0 mmol), **1b** (0.05 mmol), $NaBHEt_3$ (0.15 mmol) in 1 mL of toluene at RT under argon for 12 h. [b] Standard conditions B: alkenes (2.2 mmol), $Ph_2SiH_2$ (2.0 mmol), **1b** (0.02 mmol), $NaBHEt_3$ (0.06 mmol) at RT under argon for 12 h. [c] Conditions B with **1b** (2.5 mol%). [d] Conditions A with **1a** (5 mol%). [e] Conditions B with **1b** (5 mol%), 60 °C, 36 h. [f] Conditions B with **1b** (5 mol%). TBS = *tert*-butyldimethylsilyl.




***Scheme 1.*** Further functionalizations. cod = 1,5-cyclooctadiene, DIAD = diisopropyl azodicarboxylate, dtbpy = di-*tert*-butyldipyridine, TBAF = tetra-*n*-butylammonium fluoride, THF = tetrahydrofuran.

bulky substitutions, such as isopropyl, isobutyl, cyclohexyl, and the TBS-protected alcohol. Aliphatic 1,1-disubstituted olefins (**2y**–**aa**) and 1,2-disubstituted olefins (**2ab**) showed similarly good reactivities, but the enantioselectivity was compromised. Finally, the cyclic hydrosilylation product **4ac** was obtained in 85% yield with 96% *ee*.

The oxidation of silanes (**4**) using reported reaction conditions[19] easily afforded the corresponding silanols **5** in 73–94% yields (Scheme 1).[20] The silanes **4** were additionally functionalized to form chiral five-membered silyl rings (**6**) without loss of enantioselectivity using iridium-catalyzed intramolecular dehydrogenation.[21] We determined the absolute configuration of hydrosilylation products by X-ray analysis of the compounds **6b** and **6v**.[22] The phenol derivatives with chiral motifs at the *ortho*-position are also core structures and useful precursors[23] for bioactive natural products,[24] and **7b** was obtained in 86% yield by oxidative hydrolysis[20] of the cyclic silane **6b**. Chiral 3-substituted 2,3-dihydrobenzofurans[25] are precursors for the anticancer active (−)-thespesone[26] or single-stranded abiotic metallofoldamers.[27] (*S*)-(+)-3-Methyl dihydrobenzofuran (**8b**) was obtained through an intramolecular Mitsunobu reaction[20] of **7b** in 62% yield (the product was highly volatile). Compared to the known method for synthesis of stereochemistry-confirmed **8b** [four steps from 2-bromophenylacetyl chloride with stoichiometrical (*S*)-4-phenyloxazolidinone, 19% yield],[26a] our protocol is more efficient (4 steps, 41% total yield). A primary model to predict the stereochemical outcome of this reaction is shown in Figure S1 in the Supporting Information. More in-depth mechanistic studies are required and are currently underway.

In conclusion, we have developed the first highly regio- and enantioselective iron-catalyzed anti-Markovnikov hydrosilylation reactions of 1,1-disubstituted aryl alkenes. A series of chiral organosilanes and organosilanols can be easily constructed from the simple alkenes without a directing group. Chiral phenol derivatives and chiral 2,3-dihydrobenzofurans can be obtained by further functionalization of the hydrosilylation products. Efforts to develop new types of asymmetric iron-catalyzed reactions are undergoing in our laboratory.

**Keywords:** arenes · asymmetric catalysis · iron · silicon · synthetic methods

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