C–H Activation

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Rhodium-Catalyzed Enantioselective Intramolecular C–H Silylation for the Syntheses of Planar-Chiral Metallocene Siloles**

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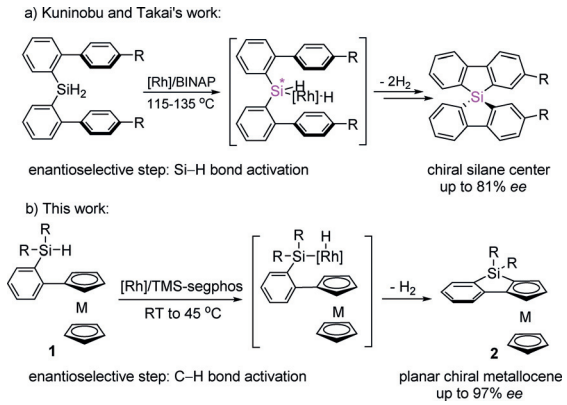
Abstract: *Reported herein is the rhodium-catalyzed enantioselective C–H bond silylation of the cyclopentadiene rings in Fe and Ru metallocenes. Thus, in the presence of (S)-TMS-Segphos, the reactions took place under very mild conditions to afford metallocene-fused siloles in good to excellent yields and with ee values of up to 97%. During this study it was observed that the steric hindrance of chiral ligands had a profound influence on the reactivity and enantioselectivity of the reaction, and might hold the key to accomplishing conventionally challenging asymmetric C–H silylations.*

Chiral metallocene derivatives have been serving as versatile ligands and catalysts in organic reactions, in addition to their many other important applications.[1,2] Among many existing methods,[3,4] catalytic direct C–H bond activation has emerged as a more efficient strategy for the asymmetric syntheses of metallocenes.[5] In 1997, the group of Schmalz disclosed a copper-catalyzed enantioselective intramolecular carbene insertion into C–H bonds of the cyclopentadiene (Cp) ring in ferrocenes.[6] In 2012 and 2013 the groups of Gu and You, respectively, developed highly enantioselective palladium-catalyzed *ortho* C–H arylation reactions directed by amine groups using amino acids as ligands.[7] Later, the groups of Cui and Wu reported the enantioselective alkenylation and acylation, respectively, of the C–H bonds of Cp rings.[8] Besides palladium catalysis, the group of Shibata employed an iridium catalyst in conjunction with chiral diene ligands for a novel enantioselective C–H alkylation directed by isoquinoline groups.[9] Remarkably, several groups (Gu and You[10], Kang and Gu[11], and Liu and Zhao[12]) have successfully accomplished C–H functionalization without the aid of a directing group. To date, enantioselective C–H functionalization of metallocenes leading to the formation of a carbon–heteroatom bond has been rarely explored.

We thus became curious about the enantioselective C–H silylation of metallocenes (Scheme 1b), given the fundamental importance of organic silicon compounds.[13] As one of the most fruitful methods to construct organic silicons, a plethora of C–H silylation protocols have been developed in the past decade. Surprisingly, with this large body of known catalysts and numerous commercial chiral ligands, enantioselective C–H silylation remains largely elusive.[14,15] Kuninobu, Takai, and co-workers have pioneered the rhodium-catalyzed dehydrogenative silylation of aryl C–H bonds, thus affording a highly efficient protocol to access silafluorenes.[16a] Later, they achieved a remarkable enantioselective variant where Rh/BINAP catalyzed the double dehydrogenative cyclization[16b] of bis(biphenyl)silanes with up to 81% *ee* (Scheme 1a), probably through desymmetric Si–H bond activation.[17] Taken together, the challenge in achieving high enantioselectivity could be seen in the fact that the reported protocols exclusively required high reaction temperatures. Very recently, Hartwig et al. accomplished an astonishing intermolecular aryl C–H silylation under milder reaction conditions (45 °C) with the aid of MeO-Biphep ligands.[14d] We therefore envisioned that the scrutiny of chiral ligands might open the door to the untamed enantioselective C–H bond silylation reactions. Herein, we report a rhodium-catalyzed C–H silylation of Fe and Ru metallocenes in the presence of (*S*)-TMS-Segphos at temperatures between room temperature and 45 °C, thus affording a diverse array of planar-chiral metallocene siloles in good yields with high to excellent enantioselectivity.[18]



Scheme 1. Proposed enantioselective C–H silylation. TMS = trimethylsilyl.

After preliminary screening to establish the optimal catalyst and solvent, [{Rh(cod)Cl}$_2$] and toluene (see the Supporting Information), respectively, we focused on the investigation of diphosphine ligands (Table 1). Importantly, no reaction took place even at 100 °C in the absence of

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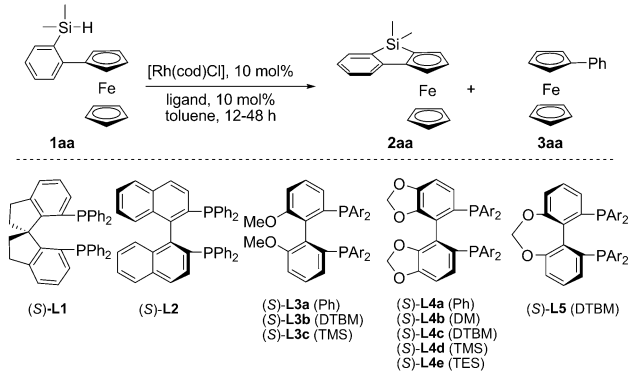
Table 1: Investigation of ligands.[a]



Entry	Ligand	*T* [°C]	Conv.[b]	**2aa/3aa**[b]	*ee* [%][d]
1	–	100	n.r.	–	–
2	(*S*)-**L1**	80	51	5:1	9
3	(*S*)-**L2**	100	97	5:1	−22
4	(*S*)-**L3a**	60	< 5	> 95:5	–
5	(*S*)-**L3b**	60	94	> 95:5	59
6	(*S*)-**L3c**	60	> 99	> 95:5	76
7	(*S*)-**L4a**	60	< 10	> 95:5	−34
8	(*S*)-**L4b**	60	50	> 95:5	4
9	(*S*)-**L4c**	60	> 99	> 95:5	77
10	(*S*)-**L4d**	40	> 99 (89)[c]	> 95:5	87
11	(±)-**L4e**	40	trace	–	–
12	(*S*)-**L5**	40	trace	–	–
13	(*S*)-**L5**	60	> 99	> 95:5	72

[a] **1aa** (0.1 mmol), [Rh(cod)Cl] (10 mol%), ligand (10 mol%), toluene (1.0 mL). [b] ^{1}H NMR analysis. [c] Yield of isolated product. [d] HPLC analysis. cod = 1,5-cyclooctadiene, DTBM: Ar = 3,5-(tBu)$_2$-4-MeOC$_6$H$_2$; DM: Ar = 3,5-Me$_2$C$_6$H$_3$; TMS: Ar = 3,5-(Me$_3$Si)$_2$C$_6$H$_3$; TES: Ar = 3,5-(Et$_3$Si)$_2$C$_6$H$_3$.

a ligand (entry 1), thus dismissing our concern about the background reaction. Overall, it was found that the steric hindrance of the ligands greatly influenced the catalytic reactivity and enantioselectivity.[19] When the less hindered Spirophos (*S*)-**L1** (Zhou)[20] was used, a low conversion (51%) and a marginal *ee* value (9%) were obtained, with a considerable amount of desilylation product (**2aa**/**3aa** = 5:1; entry 2). In the case of (*S*)-BINAP (**L2**; Kuninobu and Takai's optimal ligand),[16] the conversion was increased to 97% at 100°C but the enantioselectivity was low (−22% *ee*; entry 3). This lower enantioselectivity, compared to that reported by Kuninobu, Takai, and co-workers (81% *ee*) substantiated the mechanistic difference between these two reactions.

Additionally enhanced reactivity was observed with the MeO-Biphep ligands **L3**, which possesses a smaller dihedral angle (Table 1, entries 4–6). Notable improvements in reactivity and enantioselectivity were observed as the substituents on the phosphine atom became gradually bigger (entries 4–6). Thus, in the presence of (*S*)-**L3b** and (*S*)-**L3c** the reaction proceeded efficiently at 60°C. The good enantioselectivity obtained with the most hindered ligand (*S*)-**L3c** (76% *ee*) appeared promising. This interesting phenomenon prompted us to investigate the Segphos ligand class (**L4**), which possesses an even smaller dihedral angle.[19] Similar to **L3**, the reactivity increased from ligands (*S*)-**L4a** to (*S*)-**L4c**, as reflected by the improved conversion (< 10% to > 99%) (entries 7–9). The enantioselectivity also improved, with (*S*)-**L4a** giving an inverse enantioselectivity (−34% *ee*; entry 7). However, the highest enantioselectivity with these commercially available ligands was still unsatisfactory (77% *ee*; entry 9).

The trend observed thus far led us to synthesize two even more hindered ligands, (*S*)-**L4d** and (±)-**L4e**.[21] To our great delight, with the 3,5-bis(trimethylsilyl)phenyl (TMS) substituted Segphos (*S*)-**L4d**, the reaction took place at 40°C and a satisfactory enantioselectivity (87% *ee*) was obtained (Table 1, entry 10). The structure and absolute configuration of (*S*)-**L4d** were confirmed by single-crystal X-ray diffraction.[22] Interestingly, the most hindered ligand (±)-**L4e**, bearing a 3,5-bis(triethylsilyl)phenyl (TES) substituent, appeared ineffective at 40°C (entry 11). Lastly, we also synthesized a new ligand, DTBM-C1-TunePhos [(*S*)-**L5**], in which a tether was introduced to further reduce the dihedral angle of the backbone.[23] Similar to (±)-**L4e**, no reaction took place at 40°C (entry 12) and an inferior enantioselectivity (72% *ee*) was obtained at 60°C. This collective nonlinear dependence of catalyst performance on the steric hindrance of the ligands echoes the bite angle effects documented in a number of earlier reactions.[24]

Using the optimized catalytic system we evaluated the effect of substituents on the silicon atom (Table 2). When the

Table 2: Effect of substituents on silicon atom.[a]

Entry	R	**2**	*T* [°C]	Yield [%][b]	*ee* [%][c]
1	Me	**2aa**	40	89	87
2	Et	**2ab**	45	90	96
3	*n*-Pr	**2ac**	45	84	97
4	$(CH_2)_4$	**2ad**	40	98	78
5	Ph	**2ae**	90	91	56
6	*i*Pr	**2af**	100	n.r.	–

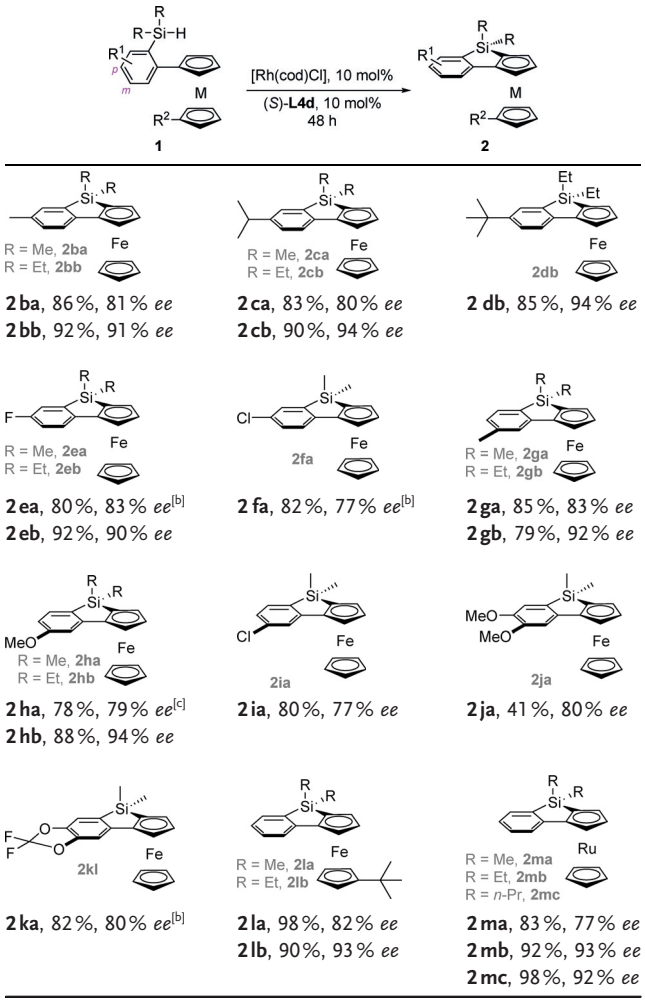
[a] **1a** (0.1 mmol), [Rh(cod)Cl] (10 mol%), ligand (10 mol%), toluene (1.0 mL). [b] Yield of isolated product. [c] HPLC analysis.

methyl group was replaced by ethyl (**1ab**), the enantioselectivity increased from 87 to 96% *ee* (entry 1 versus 2). In striking contrast, the silolane **1ad**, which closely resembles substrate **1ab**, only gave 78% *ee* (entry 4). Excellent enantioselectivity (97% *ee*) was obtained on the di-*n*-propyl substituted substrate **1ac**. The lower yield (84%) in this case was a result of a lower conversion (entry 3). The diphenyl substrate **1ae** required a higher temperature (80°C) to achieve full conversion, thus affording 56% *ee* (entry 5). The substrate **1af** with a diisopropyl group did not react even at 100°C (entry 6). These results indicated that the steric hindrance on the silicon atom also plays a key role in determining the reactivity and enantioselectivity. It is unclear

at this point how the steric hindrance of the substrate and the ligands influences the reaction. Detailed mechanistic studies are necessary to uncover the rate-limiting and asymmetry-inducing steps.

The reaction scope was demonstrated using substrates bearing dimethyl and diethyl groups on the silicon atom (Table 3). In all cases, diethyl substrates gave excellent enantioselectivity (90–97% *ee*), while dimethyl substrates gave good results (77–87% *ee*). Substituents of different sizes on the *para*-position of the phenyl ring, that is, methyl (**1ba**, **1bb**), isopropyl (**1ca**, **1cb**), and *tert*-butyl groups (**1db**), reacted smoothly to afford the desired products in high yields (83–92%) with good to excellent enantioselectivity (81–94% *ee*). The reaction rate decreased on the order of **1bb**, **1cb**, and **1db**, thus suggesting that a bulky group might disfavor C–H silylation. Substrates bearing electron-withdrawing halogen atoms on the *para* position of the phenyl ring (**1ea**, **1eb**, **1fa**) appeared to be more reactive, such that the reaction took place at room temperature. In these cases, comparable yields (77–92%) and enantioselectivity (77–90% *ee*) were obtained.

Table 3: Substrate scope.[a]



[a] 40 °C for dimethyl substrates and 45 °C for diethyl ones unless noted. [b] At RT. [c] (*R*)-**L4d** as ligand, opposite *ee*.

Electron-neutral (**1ga**, **1gb**), electron-donating (**1ha**, **1hb**), and electron-withdrawing groups (**1ia**) on the *meta* position of the phenyl ring did not significantly affect the performance. However, the electronic effect became pronounced in the cases of **1ja** and **1ka**: while the 3,4-dimethoxyl substrate **1ja** required a prolonged time and gave a poor yield, the close analogue **1ka** underwent smooth reaction at room temperature with good efficiency (82% yield). Substituents on the Cp ring were also tested. Under standard reaction conditions, the *tert*-butyl group had little effect on the reaction rate regardless of the substitutions on the silicon atom (**1la** and **1lb**). The yields (98 and 82%) and enantioselectivity (82 and 93% *ee*) were comparable to those of the unsubstituted substrates **1aa** and **1ab**. Ruthenocenes were also capable substrates, and the methyl (**1ma**), ethyl (**1mb**), and *n*-propyl (**1mc**) substituents on the silicon atom were well tolerated. The corresponding ruthenocene siloles were obtained in 83–98% yields with 77–93% *ee*. Finally, the absolute configuration of **2ab** was unambiguously determined to be S_p by single-crystal X-ray analysis.[22]

In conclusion, through systemic investigation of chiral diphosphine ligands we identified that (*S*)-TMS-Segphos could effect rhodium-catalyzed enantioselective C–H bond silylation reaction of metallocenes under much milder reaction conditions. Owing to this novel chiral ligand, various planar-chiral ferrocene and ruthenocene siloles were prepared in good yields with high enantioselectivity. As one of the few enantioselective variants, the present results provide valuable information for the quest of other asymmetric C–H bond silylation reactions. Such studies as well as employing enantioselective C–H silylation to construct chiral silicon centers are currently ongoing in our laboratory.

Experimental Section

1 (0.1 mmol), [Rh(cod)Cl] (10 mol%, 2.5 mg), (*S*)-**L4d** (10 mol%, 12.0 mg), and degassed toluene (1 mL) were added to a screw-caped tube in a N_2 flushed glove box. The tube was capped, removed from the glove box. The system was stirred at the indicated temperature and concentrated under vacuum after completion. The residue was purified on silica gel to afford the desired product.

Keywords: chirality · ligand effects · metallocenes · rhodium · silicon

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