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Ligand-Regulated Regiodivergent Hydrosilylation of Isoprene under Iron Catalysis

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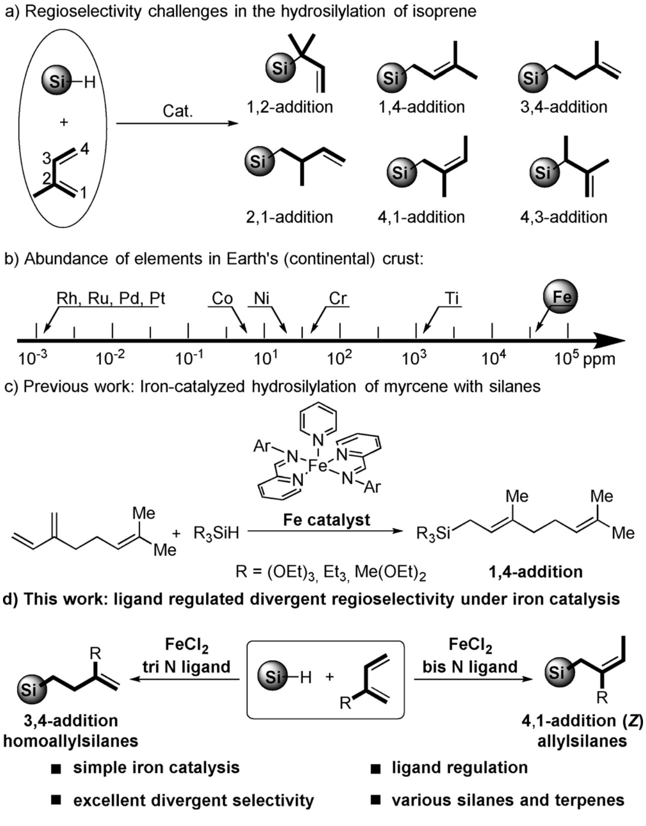
Abstract: *A method for the regiodivergent and stereoselective hydrosilylation of the basic industrial feedstock isoprene with unactivated silanes has been developed using earth-abundant iron catalysts. The manipulation of regioselectivity relies on fine modification of the coordination geometry of the iron center. While a bidentate pyridine imine ligand promoted the formation of allylic silanes through 4,1-addition, selectivity for the 3,4-adduct homoallylic silanes was observed with a tridentate nitrogen ligand. Experimental studies and analysis were carried out to elucidate the reaction mechanism and the factors enabling manipulation of the regioselectivity. This study contributes to the art of regioselectivity control in alkene hydrofunctionalization.*

Introduction

Due to the formation of one major isomer out of the possible outcomes, controlling the regioselectivity in a single reaction is a foundation of organic synthesis.[1] It is more advanced to develop a regiodivergent reaction which allows the preparation of different regioisomers just by appropriately modifying the reaction conditions or choosing the catalyst.[2] Meanwhile, these regiodivergent methodologies are becoming a practical tool in the concept of efficiency and economy for the rapid construction of molecular complexity.

The transition metal catalyzed hydrosilylation of unsaturated C–C bonds is an atom-economic approach for the preparation of value-added organosilanes, which can be further converted to useful materials such as silicon rubbers, paper releasing coatings, molding implants, and pressure-sensitive adhesives.[3] Therefore, numerous efforts have been devoted to develop efficient catalyst for the selective hydrosilylation of alkenes[2a,4] or alkynes.[4p,5] Despite huge attentions have been focused on the simple alkenes,[3d,6] the exploitation of naturally abundant isoprene[7] and their analogous terpenes in hydrosilylation remained less studied. This speculatively attributes to the regioselectivity issues arising from the differentiate of four electronically unbiased alkenyl carbon atoms of isoprene. Excluding further alkene isomerization, six potential hydrosilylation products will be expected to be observed through different addition modes (Scheme 1a). While most of the reported catalysis with precious metal (Pt, Rh, etc.)[8] or earth-abundant metal (such as Ni, Co, etc.)[9] delivered a mixture of regioisomers (low to moderate regioselectivity), very limited examples have been successfully disclosed with excellent regioselectivity.[10] Moreover, all the existing works resulted in one major isomer. Therefore, the controllable synthesis of divergent regioisomers in the hydrosilylation of isoprene with high selectivities is still a daunting task.

It is well-known that iron is the most abundant transition metal in earth's crust (Scheme 1b).[11] Therefore, iron-catalyzed hydrofunctionalization reactions have attracted significant research interests and offer complementary features with precious metal catalysis.[4d,5f,12] In 2010, Ritter and co-workers revealed an elegant work in the regioselective hydrosilylation



Scheme 1. Catalytic regioselective hydrosilylation of isoprene.

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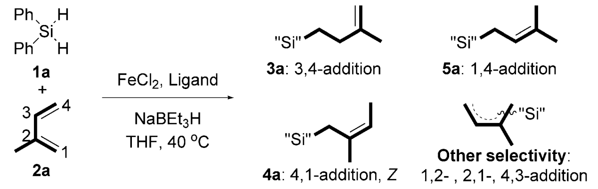
of diene with well-defined iron catalyst.[13] In their work, the reaction afforded allylic silanes in high selectivity through 1,4-hydrosilylation of myrcene rather than isoprene (Scheme 1 c). Based on our interests in catalytic functionalization of terpenes,[14] we sought to develop a regiodivergent strategy to selectively deliver other constitutional isomers in the hydrosilylation of isoprene. Herein, we reported a ligand regulated strategy for the manipulation of the regioselectivity in iron-catalyzed hydrosilylation of isoprene (Scheme 1 d). Compared with the reported iron-catalyzed protocol, the present method can controllably afford allylic silanes or homoallylic silanes with high regioselectivities via 4,1- and 3,4-hydrosilylation, respectively.

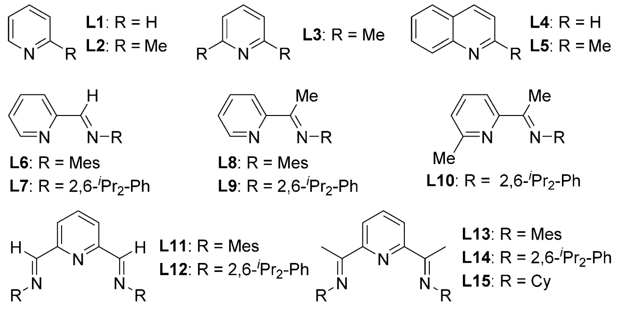
Results and Discussion

Using $FeCl_2$ (5 mol%) as precatalyst, we began the investigation by employing diphenylsilane (**1a**) and isoprene (**2a**) as the model substrates (Table 1). Pyridines and quinolines are bench-stable and commercially available chemicals and usually serve as N-based monodentate ligands in transition metal catalysis. However, these ligands all delivered **4a** and **5a** in low yields and regioselectivities (**L1**–**L5**). To our delight, a dramatic improvement in reactivity (86% yield) was observed by switching to bidentate pyridine imine ligand **L6**, but regioselectivity remained unsatisfactory (**4a**/**5a** 2:1). Through a further ligand evaluation on steric hindrance (**L6**–**L9**), an obvious enhancement in regioselectivity was achieved to produce 4,1-hydrosilylative product **4a** in good yields and excellent regioselectivities when bulky ligands (**L7** and **L9**) were employed. Blocking the *ortho*-position of pyridine with methyl group exhibited no obvious impact on the reactivity but led to a decreased selectivity (**L10**). These promising results encouraged us to divert the regioselectivity by modulating the coordination environment between iron complex and isoprene with tridentate pyridine imine ligands. Delightfully, tridentate ligand **L11** indeed produced **3a** as major product in 2:1 rr. While bulky tridentate ligands hindered the regioselectivity (**L12** and **L14**), excellent yield and selectivity were achieved when pyridine ketimine ligand **L13** was used. It should be noted that both yield and selectivity were sharply diminished in the presence of cyclohexyl substituted ligand **L15**. Eventually, a regiodivergent condition on iron-catalyzed hydrosilylation of isoprene was identified with bidentate or tridentate ligands.

Table 1: Optimization of the hydrosilylation of isoprene.[a]



The NO. of N coordination	The steric hindrance effect				
mono N:	**L1**	**L2**	**L3**	**L4**	**L5**
Yield[b]:	17%	24%	9%	15%	20%
(**3**:**4**:**5**:**Other**)[b]:	0:2:1:0	0:2:1:0	0:5:1:0	0:4:1:0	0:3:1:0
bis N:	**L6**	**L7**	**L8**	**L9**	**L10**
Yield[b]:	86%	85%	92%	81%	80%
(**3**:**4**:**5**:**Other**)[b]:	0:2:1:0	0:20:1:0	0:9:1:0	0:48:1:0	0:1:2:1
tri N:	**L11**	**L12**	**L13**	**L14**	**L15**
Yield[b]:	87%	85%	95%	95%	26%
(**3**:**4**:**5**:**Other**)[b]:	2:0:1:0	1:0:1:0	48:0:1:0	3:0:1:0	0:4:1:0

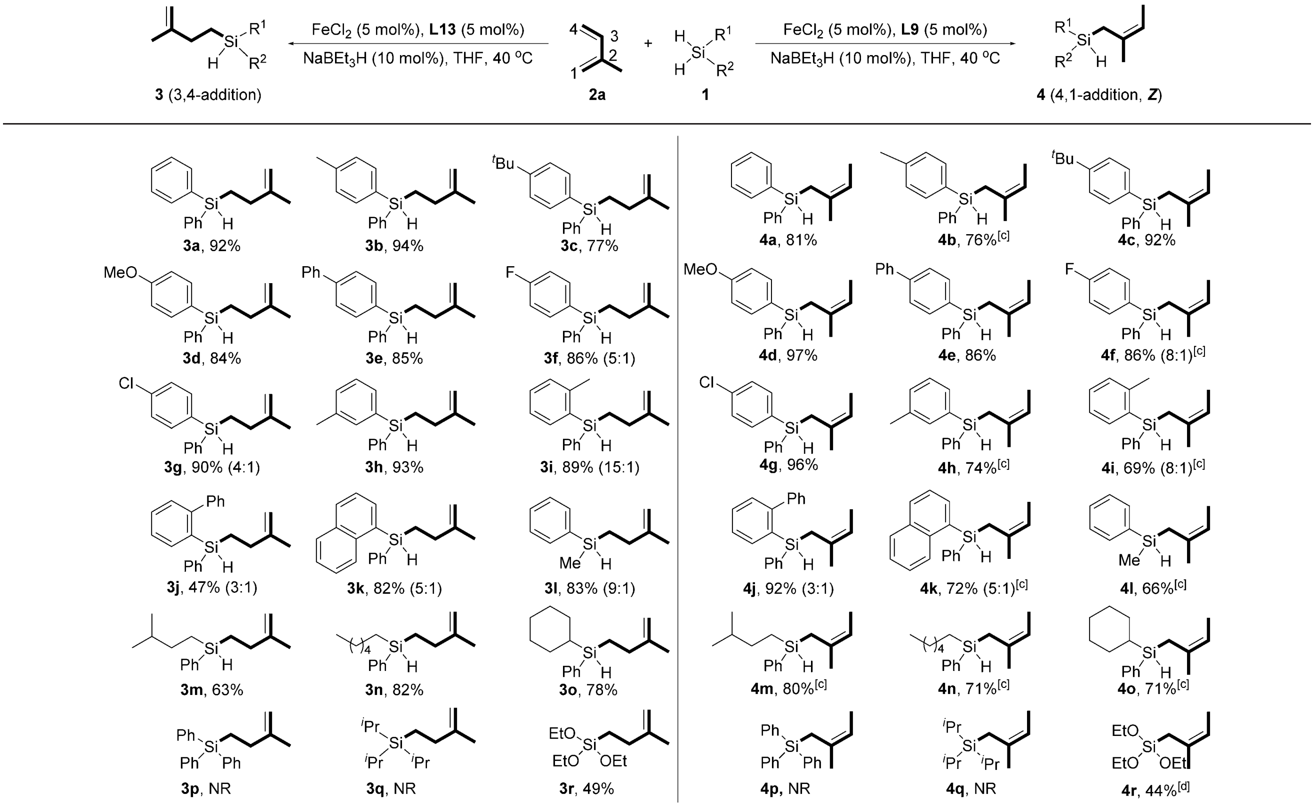


[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), $FeCl_2$ (5 mol%), ligand (5 mol%), $NaBEt_3H$ (10 mol%), THF (0.5 mL), 40 °C, 2 h, N_2. [b] Determined by ^1H NMR spectroscopy or GC-FID with 1,3,5-trimethoxybenzene as the internal standard. Cy = cyclohexyl, Mes = mesityl (2,4,6-trimethylphenyl).

With the optimized conditions in hand, we set out to explore the generalities of substrates under this divergent approach. In the presence of $FeCl_2$ and **L13**, various homoallylic silanes **3** were obtained in moderate to good yields and high selectivities via 3,4-addition (Table 2, left). For instance, diphenylsilanes with the electron-donating substituents, such as Me, ᵗBu, MeO, and Ph at the *para* position of phenyl group, all reacted smoothly under the current condition. The desired products (**3a**–**3e**) were obtained not only in good yields (77–94%) but also in excellent selectivities (> 20:1). Notably, halides such as fluoro and chloro were well tolerated and the reactions delivered corresponding products in good yields (**3f**, **3g**). Substrate bearing *meta*-substituted group also showed good performance on both reactivity and selectivity and exclusively delivered **3h** in 93% yield. Due to the steric hindrance, a decrease in regioselectivity was observed when *ortho*-substituted diphenylsilanes were employed (**3i** and **3j**). Silane bearing naphthyl group exhibited good reactivity and led to **3k** in 82% yield and 5:1 rr. Furthermore, alkyl-substituted silanes were investigated and substrates such as methyl-, isopentyl-, hexyl-, and cyclohexyl-phenylsilane gave the 3,4-adducts in moderate to good yields (63–83%) and high selectivities (in most case, > 20:1). In addition, we also examined the compatibility of trisubstituted silanes. While the triphenylsilane and triisopropylsilane were not applicable in current protocol (**1p** and **1q**), 49% yield of 3,4-additive product **3r** and 44% yield of 4,1-additive product **4r** were obtained, respectively with triethoxysilane as substrate. No subsequent intramolecular hydrosilylation of **3a** was observed even in higher temperature (100 °C) or prolonged reaction times (24 h).

Next, we shifted our attention to explore the substrate scope towards 4,1-addition (Table 2, right). Similar to the 3,4-addition reactions, substrates bearing with either electron-donating groups (**4a**–**4d**) or electron-withdrawing groups (**4e**–**4g**) were all compatible under current process and provided the corresponding products in acceptable to good yields (76–97%). Furthermore, the stereo conformation of

Table 2: Scope of the iron-catalyzed 3,4- and 4,1-hydrosilylation of isoprene with respect to the silane substrate.[a,b]



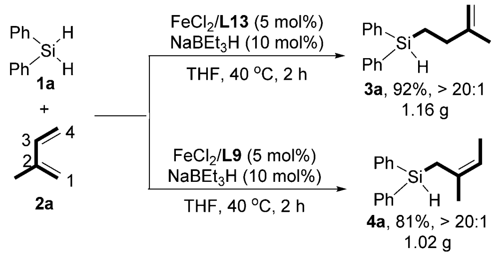
[a] Reaction conditions: **1** (0.20 mmol), **2a** (0.30 mmol), FeCl$_2$ (5 mol%), L (5 mol%), NaBEt$_3$H (10 mol%), THF (0.5 mL), 40 °C, 2 h, N$_2$. [b] Yields are for the isolated product, unless otherwise noted; selectivity > 20:1 (3,4-/1,4-addition or 4,1-/1,4-addition), as determined by ^{1}H NMR spectroscopy or GC-FID. [c] **L7** was used instead of **L9**. [d] Determined by ^{1}H NMR spectroscopy, a mixture of *trans* and *cis* isomers of **4r** was obtained.

product **4a** was determined as single *Z*-type via two-dimensional nuclear magnetic resonance (2D-NOESY). While *meta*-substituted diarylsilane performed well in both reactivity and selectivity (**4h**), the steric hindered substrates led to decreased selectivity (**4i**–**4k**). To our delight, a series of alkylarylsilanes could be successfully applied in this transformation and exclusively produced allylic isomers in 66–80% yields (**4l**–**4o**).

The scope of dienes was then explored under current regiodivergent strategy (Table 3). Terpenes bearing two isoprene units, such as myrcene (**2b**) and its derivatives (**2c**, **2d**) proceeded smoothly to deliver the homoallylic product (**3s**–**3u**) in good yields (74–94%) and excellent selectivities (> 20:1). Under FeCl$_2$/**L9** condition, these substrates also reacted well and gave the regiospecific silanes (**4s**–**4u**) in slightly decreased yields (52–66%). With the aid of **L13**, diterpene phytadiene was also well tolerated and produced corresponding homoallylic silane **3v** in acceptable yield and excellent regioselectivity (> 20:1). A switch of regioselectivity was observed through the alteration of ligand (**L13** vs. **L9**) and allylic silane **4v** with long alkyl chain was obtained. No desirable hydrosilylation products were detected with polyene (retinol) as substrate. Although no homoallylic product could be observed with the internal 1,3-dienes **2f** as the substrate with the aid of **L13**, 51% yield of product **3w** could be obtained in the presence of ligand **L9**.

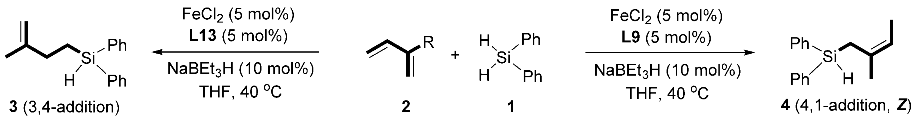
To verify the practical utility of our protocol, gram scale experiments were carried out (Scheme 2). Diphenylsilane **1a** reacted smoothly under two standard reaction conditions and delivered corresponding products **3a** and **4a** in good yields (92%, 81%, respectively). It should be noted that the selectivities were well maintained in the gram scale reactions for both 3,4-addition and 4,1-addition.

Next, several deuterium labeling experiments have been conducted to explore the mechanism. When deuterated silane (Ph$_2$SiD$_2$, ***d*$_2$-1a**) and one equivalent of isoprene **2a** were employed in two selective standard conditions, the corresponding hydrosilylative products (**3a-*d*** and **4a-*d***) were obtained without obvious deuterium scrambling (Scheme 3a, left). However, only 70% of deuterium at Si atom and 65% of deuterium at allylic position were detected in product **3a-d**.

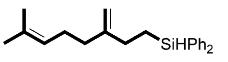
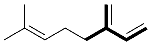
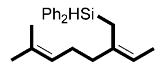
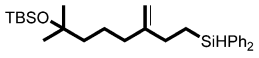
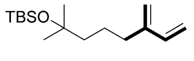
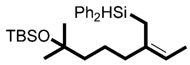
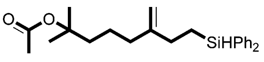
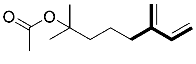
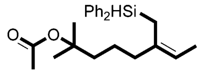
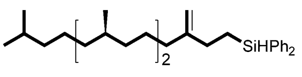
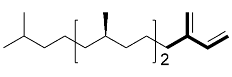
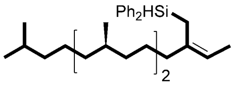
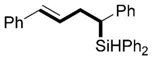
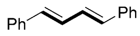
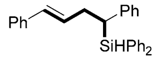


Scheme 2. Gram-scale reactions for the regiodivergent hydrosilylation of isoprene.

Table 3: Scope of the reaction with respect to the diene substrate.[a]



3 (3,4-addition) 2 1 4 (4,1-addition, *Z*)

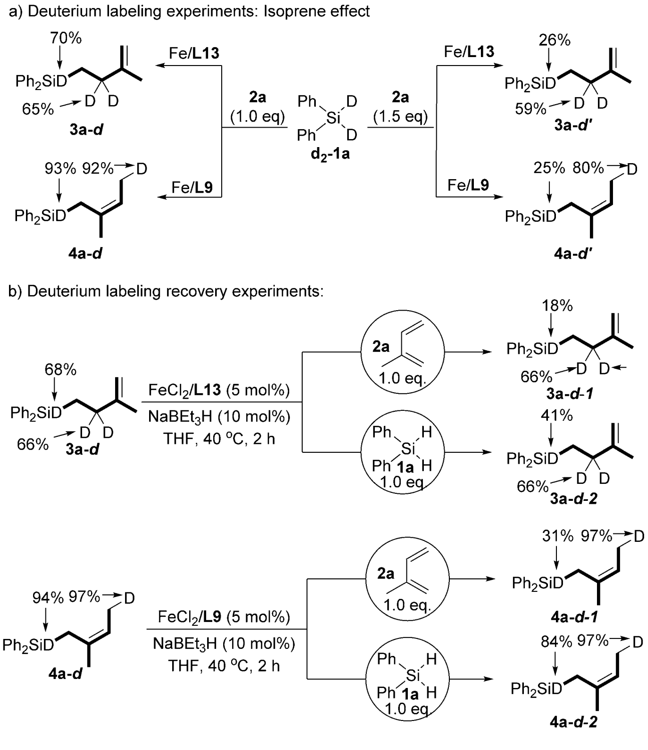
Product (3)	Diene 2	Product (4)
 **3s**, 94%	 **2b**, Myrcene	 **4s**, 62%[b]
 **3t**, 77%	 **2c**	 **4t**, 66%[b]
 **3u**, 74%	 **2d**	 **4u**, 52%
 **3v**, 58%	 **2e**, Phytadiene	 **4v**, 74%, 7:1 *rr*
 **3w**, NR	 **2f**	 **3w**, 51%[c]

[a] Reaction conditions: **1a** (0.20 mmol), **2** (0.30 mmol), $FeCl_2$ (5 mol%), ligand (5 mol%), $NaBEt_3H$ (10 mol%), THF (0.5 mL), 40 °C, 2 h, N_2. Isolated yield of all isomers. Unless otherwise noted, selectivity > 20:1 (3,4-/1,4-addition or 4,1-/1,4-addition), as determined by ^1H NMR spectroscopy or GC-FID. [b] **L7** was used instead of **L9**. [c] **3w**/**4w** (2,1/1,4-addition) = 11:1.

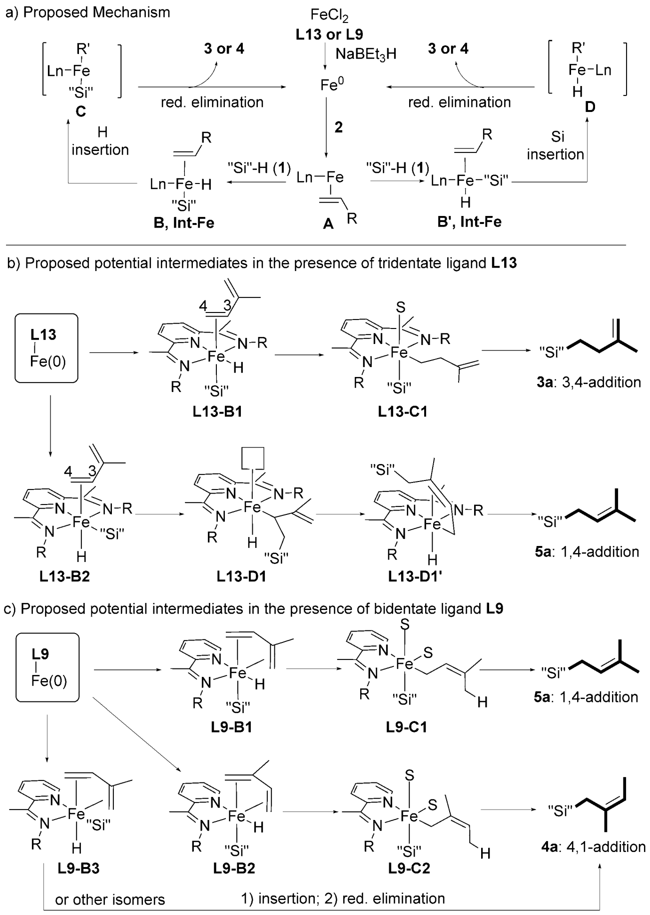
This observation made us wonder if H–D exchange occurred between Si–H/D and isoprene. To testify this proposal, we conducted the reactions with excess isoprene (Scheme 3a, right) and a significant loss of deuterium was observed for both **3a-d′** and **4a-d′** products. Furthermore, deuterium labeling recovery experiments also showed remarkable loss of deuterium at Si atom when deuterated **3a-d** and **4a-d** were treated with one equivalent of isoprene under standard conditions, respectively (Scheme 3b). In comparison, only slight D–H exchange on silicon atom was observed when deuterated **3a-d** and **4a-d** were treated with one equivalent of diphenylsilane **1a**. These observations support that a reversible migratory insertion between the isoprene and Fe–hydride is involved in the catalytic cycle.

On the basis of these observations and previous reports, a plausible mechanism for the divergent selectivity manipulation was proposed (Scheme 4a). The reduction of the iron complex with $NaEt_3BH$ directly gives the corresponding Fe^0 species, which undergoes coordination with isoprene to generate Fe complex **A**. Subsequently, the oxidative addition of silane **1** with **A** yields an Fe^{II}–hydride intermediate **B** or **B′**. Depending on the coordination geometry of iron complex **B** or **B′** with different ligands, two possible migratory insertions will occur. An iron(II)–silicon intermediate **C** could be formed via the insertion of isoprene **1a** into the Fe^{II}–H bond. On the contrary, a migratory insertion of isoprene **1a** into the Fe^{II}–Si bond generates Fe^{II}–H **D**. The final reductive elimination of intermediate **C** or **D** delivers the hydrosilylation product and regenerates Fe^0 catalyst.

Based on the analysis of coordination geometry of iron complex, we proposed the potential intermediates for the elucidation of regioselective manipulation (Scheme 4b,c). In the presence of tridentate ligand **L13**, coordinatively saturated (18 electron) Fe^{II}–H **L13-B1** and **L13-B2** could be formed as two major species via oxidative addition during the hydrosilylation. Given the obtained result from deuterium labeling studies, migratory insertions of alkene into Fe^{II}–H (**L13-B1** to **L13-C1**) is favored and delivers **3a** as major product. Minor isomer **5a** could be formed via the insertion of alkene into Fe^{II}–Si (**L13-B2** to **L13-D1**) and subsequent allylic isomerization (**L13-D1** to **L13-D1′**), reductive elimination. Switching to bidentate ligand **L9**, one extra coordination site is spared to facilitate the coordination of isoprene to iron in a chelated form. Therefore, both major product **4a** and minor product **5a** are formed via 1,4 insertion of isoprene into Fe^{II}–H (**L9-B1** to **L9-C1**, **L9-B2** to **L9-C2**, etc.). The presence of methyl group on isoprene makes C1 position more electron rich than C4 position. Therefore, hydride prefers to undergo



Scheme 3. Deuterium labeling studies.



Scheme 4. Proposed mechanism for regioselectivity. S = solvent or substrate.

addition into isoprene on the relatively electron-deficient C4 position (**L9-B2** to **L9-C2**) to form **4a** other than **5a** as major product.

Conclusion

In conclusion, we have developed an iron-catalyzed regiodivergent and stereoselective hydrosilylation of terpenes through ligand regulation. In the presence of iron catalyst, the use of bidentate nitrogen ligand **L9** delivered allylic silanes as 4,1-hydrosilylation products. A switch of regioselectivity to 3,4-hydrosilylation was obtained by using tridentate nitrogen ligand **L13**. Experimental studies and analysis have been performed to interpret the regioselective manipulation. Further studies on the other regioselective functionalizations of terpenes are currently underway in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: divergent regioselectivity · hydrosilylation · iron · isoprene · terpenoids

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Research Articles

Hydrosilylation

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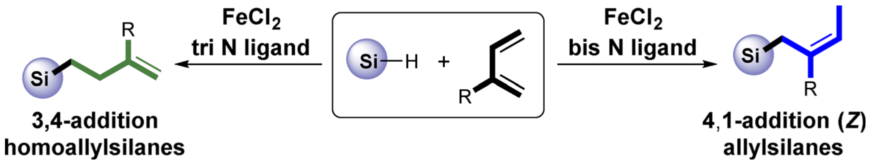
Y. C. Hu, Q. A. Chen* ______ ▮▮▮▮–▮▮▮▮

Ligand-Regulated Regiodivergent Hydrosilylation of Isoprene under Iron Catalysis



A ligand-regulated regiodivergent and stereoselective hydrosilylation of terpenes has been developed using earth-abundant iron catalysts. Various silanes and terpenes were transformed with excellent selectivity into the corresponding allylic silanes and homoallylic silanes through 4,1- and 3,4-addition, respectively.