ORGANIC CHEMISTRY FRONTIERS

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RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Org. Chem. Front.*, 2023, **10**, 2204

Ligand-controlled regiodivergence in cobalt-catalyzed hydrosilylation of isoprene†

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Received 12th January 2023,
Accepted 22nd March 2023

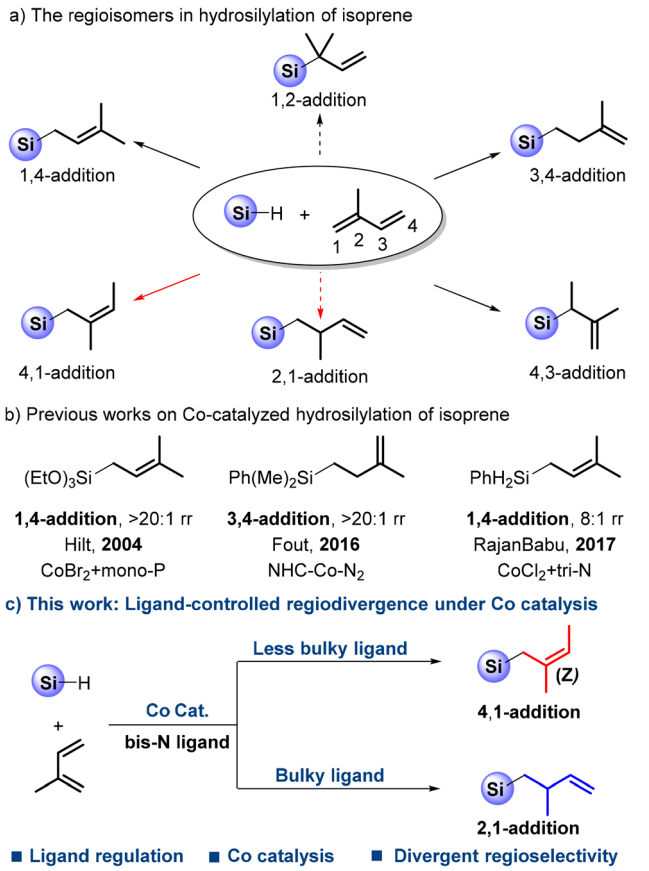
DOI: 10.1039/d3qo00041a

rsc.li/frontiers-organic

In this article, we disclose a method for the regiodivergent and stereoselective hydrosilylation of isoprene using an Earth-abundant cobalt catalyst *via* variation of ligands. With a less sterically hindered bidentate ligand, the reactions proceeded through 4,1-hydrosilylation to afford allylsilanes in excellent regio- and stereoselectivities. By switching to a bulkier ligand, the reactions were efficiently diverted to 2,1-addition products for the first time. This regiodivergent protocol provides a modular approach for the construction of structurally diverse organosilanes with high atom economy and without the formation of stoichiometric byproducts.

Owing to the abundance of silicon in the Earth's crust and the unique stability of C–Si bonds, organosilicon compounds have been extensively applied in materials science,[1] medicinal chemistry,[2] and organic synthesis.[3] During the past decades, catalytic hydrosilylation of unsaturated C–C bonds has been established as one of the most straightforward methods and atom-economical approaches for the preparation of value-added organosilanes.[4] In this context, tremendous efforts have been made toward the Markovnikov or anti-Markovnikov hydrosilylation reactions of alkenes[5] and alkynes.[6] These reactions currently are not only utilized on the laboratory scale, but also have been widely implemented in the chemical industry. In contrast, the catalytic hydrosilylation reaction of 1,3-dienes is continuously complicated by regioselectivity issues and side reactions such as olefin isomerization[7] and silane dehydrocoupling.[8] In recent years, the catalytic hydrosilylation reactions of 1-substituted 1,3-dienes are successively explored and some robust protocols have been developed.[7–9] However, few examples involved the selective addition of Si–H bonds to internally substituted dienes. Particularly, due to the weak electronic and steric effect of the methyl substituent, the regioselective hydrosilylation reaction of isoprene is an extremely challenging task (Scheme 1a).[9f,10] In most cases, the reported hydrosilylation reactions of isoprene produced a mixture of isomers with poor to moderate regioselectivity (<10 : 1 rr).[11] Very limited examples were exploited successfully with good regioselective control.[9d,12]

The cobalt-catalyzed transformations have gained ever-growing attention due to the lower cost and toxicity of cobalt in comparison with other precious transition metals.[13] In



Scheme 1 Catalytic regioselective hydrosilylation of isoprene.

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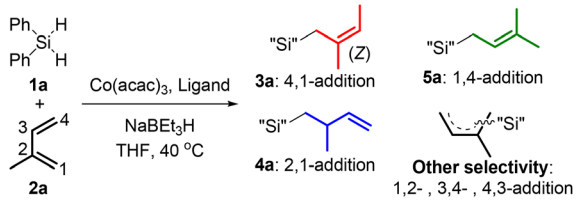
† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d3qo00041a

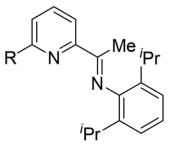
2004, Hilt's group reported an example of cobalt-catalyzed 1,4-hydrosilylation of isoprene with $(EtO)_3SiH$ using $P(^nBu)_3$ as the ligand.[12c] Later, Fout *et al.* also developed a bis(carbene) cobalt(I)-dinitrogen complex to enable an efficient 3,4-hydrosilylation reaction of isoprene.[12f] In 2017, RajanBabu and co-workers disclosed that moderate 1,4-selectivity could be achieved in a Co-catalyzed coupling reaction between phenylsilane and isoprene using the tridentate ligand PDI at −78 °C (Scheme 1b).[9d] Although these advancements were achieved, the development of regiodivergent methodologies for controllable hydrosilylation of isoprene is rather rare. Moreover, no precedents on catalytic 2,1-hydrosilylation of isoprene have been successfully realized to date. Recently, we explored an iron-catalyzed regiodivergent hydrosilylation reaction of isoprene, where the regioselectivity could be efficiently regulated by the bidentate or tridentate nitrogen ligand, respectively.[12g] As an extension of our continuous research in regiodivergent catalysis,[14] herein we report a Co-catalyzed protocol for regio-controllable 4,1- and 2,1-hydrosilylation of isoprene by modifying the substituents in bidentate nitrogen ligands (Scheme 1c).

Diphenylsilane (**1a**) and isoprene (**2a**) were initially chosen as the model substrates to test our hypothesis using $Co(acac)_3$ as the precatalyst with various pyridine imine ligands. As shown in Table 1, with a simple bidentate pyridine imine **L1**, the C–Si coupling reaction gave the hydrosilylation products in 76% yield with good 4,1-selectivity (**3a**, entry 1). To our delight, the ligand **L2** which bears a methyl group at the *ortho*-position of the pyridyl ring dramatically switched the reaction regioselectivity to 2,1-addition (**4a**, entry 2). This result encouraged us to further examine the substituent effect on ligands (**L3**–**L8**). Pleasingly, a good yield of **4a** could be obtained with the regioselectivity being maintained in the presence of *ortho*-propyl pyridine imine **L4**. Upon increasing the bulkiness of the *ortho*-substituents of the pyridyl motif on ligands, however, the reactions became comparably sluggish (entries 5–8). Moreover, replacing the isopropyl group with methyl at the *N*-phenyl ring would decrease the reactivity and selectivity of the 2,1-adduct **4a** (entry 9). Other commonly used reductants, such as $AlMe_3$, $ZnEt_2$ and PhMgBr, were also investigated. However, these employed reductants were all less effective than $NaBEt_3H$ (Table S3†). In addition, to improve the yield of **3a**, solvents were evaluated in the presence of **L1** (Table S2†). Pleasingly, the yield of **3a** was sharply improved with excellent 4,1-selectivity when the hydrosilylation reaction was conducted in *n*-hexane (entry 10).

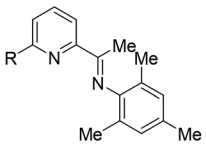
Table 1 Optimization of the reaction conditions



Entry	Ligand	Total yield[a]	Selectivity[a] 3a	4a	5a	Others
1	**L1**	76%	93	0	0	7
2	**L2**	74%	5	81	0	14
3	**L3**	89%	5	81	5	9
4	**L4**	**90%**	**4**	**92**	**0**	**4**
5	**L5**	37%	11	70	5	14
6	**L6**	65%	2	91	3	4
7	**L7**	15%	46	34	20	0
8	**L8**	30%	23	67	10	0
9	**L9**	62%	19	81	0	0
10	**L1**[b]	**86%**	**94**	**0**	**2**	**4**



L1: R = H
L2: R = Me
L3: R = Et
L4: R = ^{n}Pr
L5: R = ^{i}Pr
L6: R = Bn
L7: R = CH_2Cy
L8: R = Cy



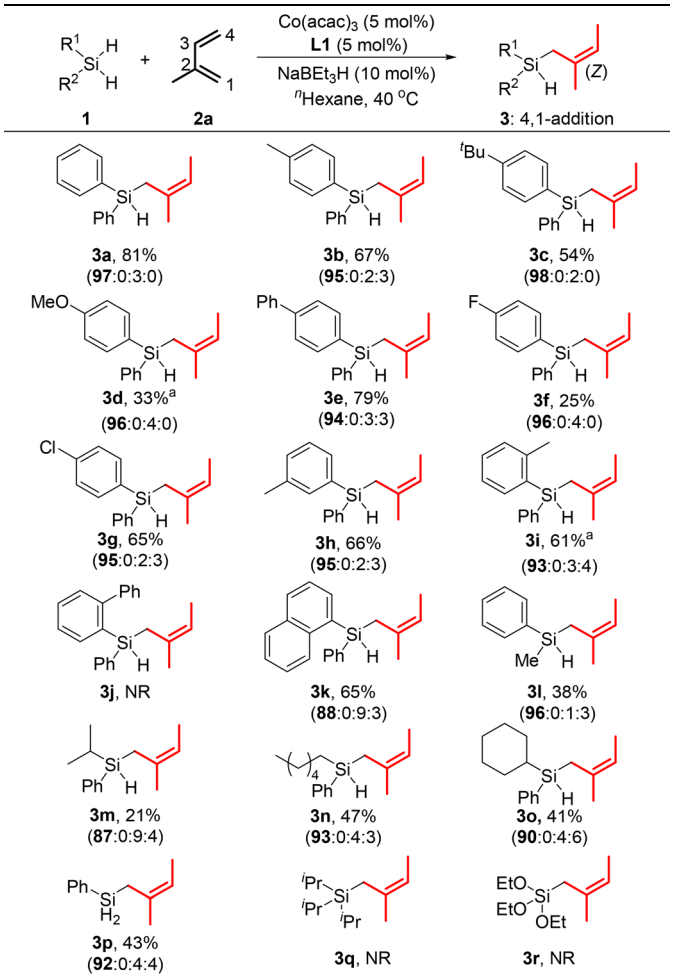
L9: R = ^{n}Pr

Conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), $Co(acac)_3$ (5 mol%), **L** (5 mol%), $NaBEt_3H$ (10 mol%), THF (0.5 mL), 40 °C, 2 h, N_2. [a] Determined by ^1H NMR with 1,3,5-trimethylbenzene as the internal standard. [b] In ^{n}hexane (0.5 mL).

With the optimized reaction conditions established, the substrate scope of silane was then examined (Table 2). In the presence of **L1**, the reactions with substrates bearing electron-donating substituents at the *para*-position of the phenyl ring all proceeded smoothly to produce the 4,1-addition products **3a**–**3e** in good yields and high regioselectivities. The substrates with halide groups on the phenyl unit, such as fluoro and chloro, were tolerated as well and the corresponding products **3f** and **3g** were obtained in 25% and 65% yields, respectively. Substituents with a methyl group on the *meta*- or *ortho*-position of the phenyl ring afforded the corresponding products **3h** and **3i** successfully with good selectivities. Due to steric hindrance, an erosion of reactivity was observed when the reaction was conducted with a structurally hindered substrate (**3j**). On replacing the phenyl group with the 1-naphthalenyl ring, the substrate was transformed into product **3k** in 65% yield. Alkyl-substituted silanes could be applied in the current 4,1-hydrosilylation reaction as well, albeit with decreased yields and selectivities (**3l**–**3o**). Besides dihydrosilanes, the phenylsilane was also accommodated, generating the product **3p** in 43% yield. However, the reactions with tri-substituted silanes, such as triisopropylsilane and triethoxysilane, were completely unproductive (**3q** and **3r**).

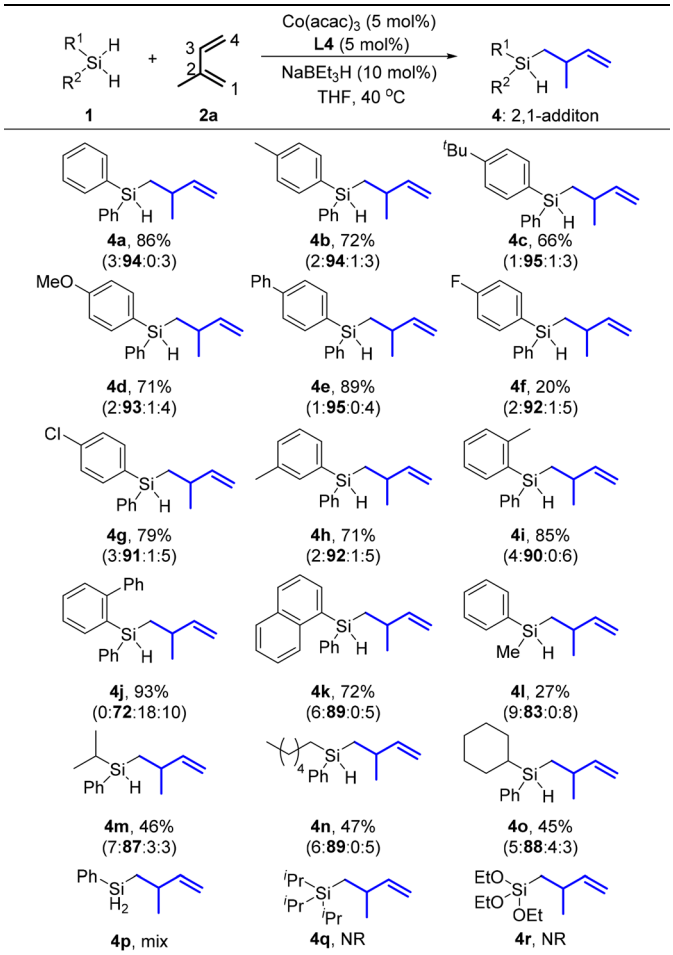
Next, we switched our attention to the substrate generality of 2,1-hydrosilylation under Co catalysis (Table 3). With the aid of Co/**L4**, diphenylsilanes with various substituents at the phenyl ring could react with isoprene and afford the corresponding 2,1-addition products (**4a**–**4j**). In most cases, substrates with either electron-donating or electron-withdrawing groups were amenable for the current transformation and delivered products in good yields and decent regioselectivities (**4a**–**4e**, **4g** and **4h**). Substrates with a fluoro group were comparably sluggish (**4f**). Delightfully, silanes with an *ortho*-substituted group on the phenyl rings could react with isoprene smoothly under the current conditions (**4i** and **4j**). 1-Naphthyl substi-

Table 2 Substrate scope for Co-catalyzed 4,1-hydrosilylation



Conditions: **1** (0.20 mmol), **2** (0.30 mmol), $Co(acac)_3$ (5 mol%), **L1** (5 mol%), $NaBEt_3H$ (10 mol%), hexane (0.5 mL), 40° C, 2 h, N_2. Isolated yields of combined regiosomers are given in all cases. The regioselectivity is given in parentheses (**3 : 4 : 5:others**). [a] Accompanied by a small amount of inseparable silane **1**, the yield of the product has been adjusted accordingly.

Table 3 Substrate scope for Co-catalyzed 2,1-hydrosilylation

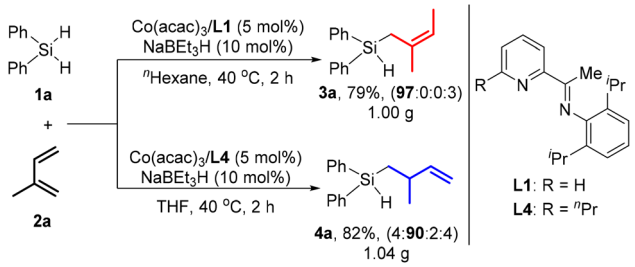


Conditions: **1** (0.20 mmol), **2a** (0.30 mmol), $Co(acac)_3$ (5 mol%), **L4** (5 mol%), $NaBEt_3H$ (10 mol%), THF (0.5 mL), 40 °C, 2 h, N_2. Isolated yields of combined regioisomers are given in all cases. The regioselectivity is given in parentheses (**3 : 4 : 5:others**). If applicable, products were all obtained in 1 : 1 dr.

tuted silane exhibited good reactivity and led to **4k** in 72% yield. The reactions with alkylphenylsilanes could produce 2,1-hydrosilylation products with decreases in yields (**4l–4o**). While the reaction with phenylsilane resulted in a complicated mixture of isomers (**4p**), triisopropylsilane and triethoxysilane were not reactive under the current conditions (**4q** and **4r**).

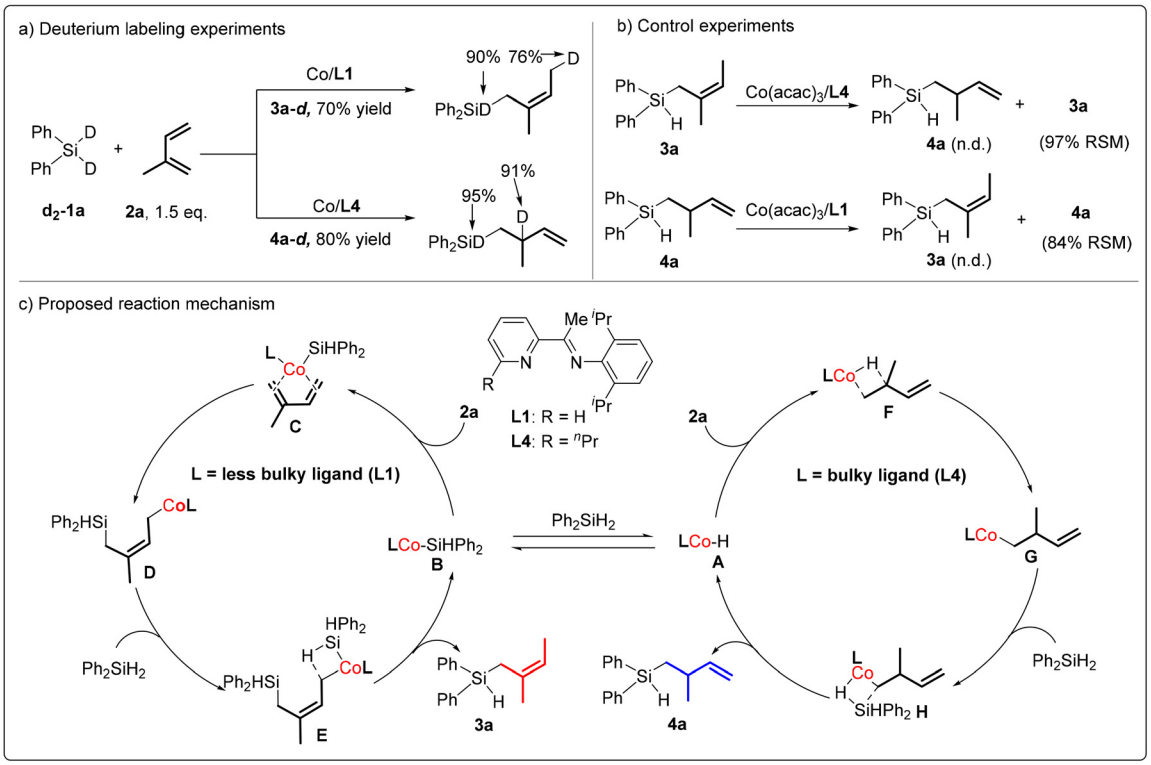
To demonstrate the utility of our methods, gram-scale reactions were carried out (Scheme 2). Under the optimal conditions, 4,1-addition and 2,1-addition products could be afforded in 1.00 g with 79% yield (**3a**) and 1.04 g with 82% yield (**4a**), respectively. And both regioselectivities were maintained well on the gram-scale.

To gain insight into the mechanism, we conducted deuterium-labeled experiments (Scheme 3a). Using deuterated silane (Ph_2SiD_2, **d_2-1a**) as the substrate, 4,1- and 2,1-hydrosilylation reactions were performed under the standard conditions. For the 4,1-addition reaction, 70% yield of the product was



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

obtained without obvious deuterium scrambling (90% of deuterium at Si and 76% of deuterium at the terminal allylic position in **3a–d**). Similarly, deuterium incorporation was only observed at the allylic position of **4a–d**. These observations indicate that the alkene insertion step was highly regiospecific. In addition, the mutual transformation reactions between **3a**



Scheme 3 Proposed mechanism for regioselectivity.

and **4a** showed that these products remained intact under the standard conditions, suggesting that the formation of hydrosilylation products should be irreversible (Scheme 3b).

Based on the above results and previous reports,[15] a plausible reaction mechanism is proposed (Scheme 3c). In the presence of $NaBEt_3H$, cobalt(I) hydride species **A** may be initially delivered. When reactions were performed with the less bulky ligand **L1**, the hydride species **A** may interact with Ph_2SiH_2 to form the silylcobalt(I) intermediate **B**. Moreover, the smaller ligand **L1** may also favor the formation of the bis-coordination intermediate **C** with isoprene **2a**. After that, the 4,1-insertion of the Co–Si bond occurs and produces the intermediate **D**. Next, the four-centered transient complex **E** leads to the 4,1-hydrosilylation product **3a** and regenerates the silylcobalt(I) species **B**. On the other hand, in the presence of the bulky ligand **L4**, the intermediate **B** may be unfavorable due to steric hindrance. Instead, the reaction may initiate with Co–H insertion between the cobalt(I) hydride species **A** and isoprene (*via* Int **F**). Considering that the methyl group is an electron-donating substituent that can make the di-substituted double bond electron richer, the cobalt(I) hydride **A** may preferentially coordinate with the methyl-substituted double bond of isoprene and lead to 2,1-selectivity. Subsequently, a homoallylcobalt intermediate **G** is yielded and followed through a four-centered transient complex **H** to produce the 2,1-hydrosilylation product **4a** and release the cobalt(I) hydride species **A**.

In conclusion, we have developed a cobalt-catalyzed method to achieve regiodivergent selectivities in isoprene hydrosilylation reactions by ligand regulation. The use of a simple bidentate imine ligand **L1** efficiently promoted the formation of 4,1-hydrosilylation products, whereas the presence of a bulkier bidentate nitrogen ligand **L4** diverted the regioselectivity toward 2,1-hydrosilylation which was reported first. This protocol also features high atom economy without stoichiometric byproduct formation. Further applications of this ligand-controlled regiodivergence in olefin hydrofunctionalization are currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the Dalian Outstanding Young Scientific Talent Program (2020RJ05) and the National Natural Science Foundation of China (22071239) is acknowledged.

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