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Identifying a cobalt catalyst for highly selective hydrosilylation of allenes†

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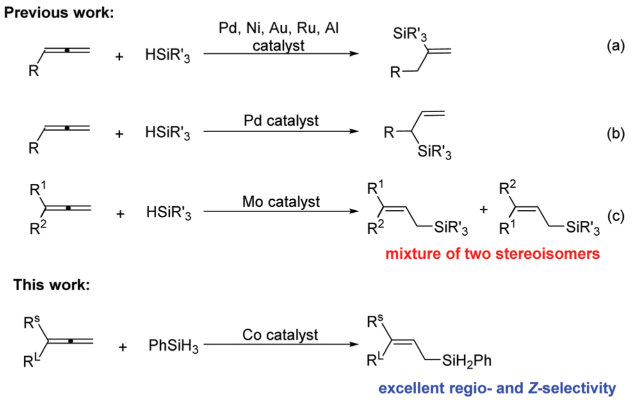
An efficient method of cobalt-catalyzed allene-hydrosilylation is developed. The reaction enjoys an excellent regio- and stereoselectivity and a broad scope affording *Z*-allylic silanes. Many synthetically useful functional groups can be tolerated. A Co(I)-species involved mechanism is proposed.

Featuring reasonable stability, low-toxicity, and ease of handling, silane reagents are valuable intermediates for synthetic transformations, such as Hiyama cross-couplings[1] and Tamao oxidation reactions to form the carbonyl group.[2] The hydrosilylation of unsaturated C–C bonds such as alkenes,[3] alkynes,[4] and dienes,[5] which is considered to be one of the most synthetically efficient approaches to organosilane compounds, has been achieved with various catalysts. However, reports on the hydrosilylation of allenes are relatively rare, partially due to the difficulty in controlling the regio- and stereoselectivity. Most of the reported allene hydrosilylations occurred at the non-terminal C=C bond, affording vinylsilanes using Pd,[6] Ni,[7] Au,[8] Ru[9] or Al[10] catalysis (Scheme 1a) or branched allylsilanes using Pd[6,7] catalysis (Scheme 1b). In 2016, Asako and Takai reported a molybdenum-catalyzed hydrosilylation at the terminal C=C bonds of allenes that yielded linear allylic silanes (Scheme 1c).[11] However, the stereoselectivity of this reaction is rather poor. To the best of our knowledge, the allene hydrosilylation catalyzed by earth-abundant base metal iron or cobalt has not been established yet. Here we report a cobalt-catalyzed hydrosilylation of allenes to form linear (*Z*)-allylsilanes, enjoying an excellent regio- and stereoselectivity.

Non-precious metal iron and cobalt catalysts in general offer lower activity than Pd and other precious metal catalysts, thus identifying that a suitable ligand is the key to achieve an efficient and selective hydrosilylation of allenes. We employed iron and cobalt complexes of phosphinite-iminopyridine[12] ($P^{O}NN$) and phosphine-iminopyridine[13] ($P^{C}NN$) ligands developed in one of our laboratories (Chart 1), which exhibited an excellent catalytic activity in the hydrosilylation of alkenes.



Scheme 1 Hydrosilylation of allenes: previous work and our observation.

We commenced the study by examining an iron catalyst generated from ($^{tBu}P^{O}NN^{iPr}$)$FeCl_2$ (**1**) and $NaBHEt_3$ for the hydrosilylation of phenyl allene (**3a**) with phenylsilane. The initial run in toluene using only 0.5 mol% of the catalyst yielded (*Z*)-phenyl(3-phenylallyl)silane *Z*-**4a** in 93% yield as determined by ^1H NMR analysis. Neither the regioisomers **4a**′ and **4a**″ nor the stereoisomer *E*-**4a** was detected. Solvent variations have a large effect on the cobalt-mediated hydrosilyl-

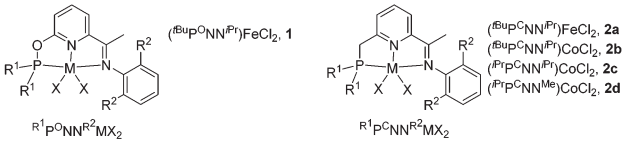


Chart 1 Fe and Co complexes with $P^{O}NN$ and $P^{C}NN$ ligands.

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† Electronic supplementary information (ESI) available: Preparation and characterisation data as well as ^1H and ^{13}C NMR spectra of all compounds. See DOI: 10.1039/c7qo00497d

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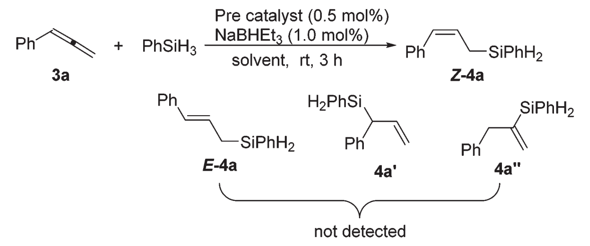
Table 1 Optimization of the reaction conditions[a]

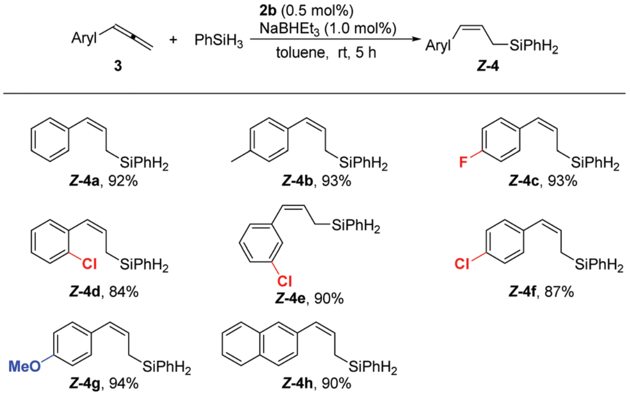


Entry	Precatalyst	Solvent	Yield of (Z)-**4a**[b] (%)	Recovery of **3a**[b] (%)
1	**1**	Toluene	93 (91)	—
2	**1**	THF	70	—
3	**1**	Hexane	81	—
4	**1**	MeCN	9	62
5	**1**	DCM	0	76
6	**1**	DMF	0	64
7	**2a**	Toluene	34	44
8	**2b**	Toluene	94 (92)	—
9	**2c**	Toluene	54	25
10	**2d**	Toluene	13	39
11	—	Toluene	0	94
12[c]	**2b**	Toluene	0	82
13	$CoCl_2$	Toluene	0	89[d]

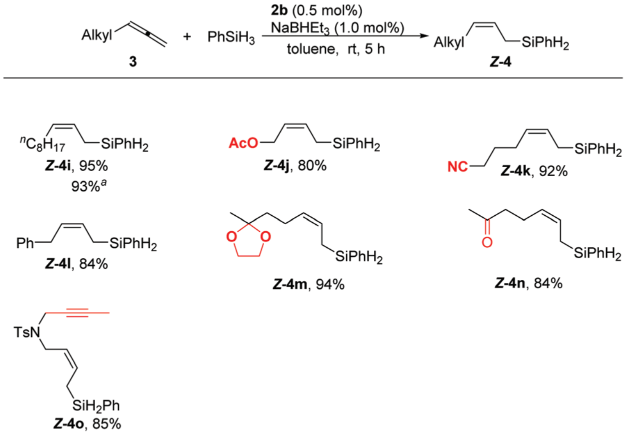
[a] Reaction conditions: **3a** (0.5 mmol), $PhSiH_3$ (0.5 mmol), 2.5 μmol of precatalyst, 5.0 μmol of $NaBHEt_3$, in solvent (0.5 mL). [b] Determined by ^1H NMR analysis with CH_3NO_2 as the internal standard. Values in parentheses are yields of the isolated products. [c] No $NaBHEt_3$ was added. [d] Isolated recovery of **3a**.

ation. The yield dropped when the reaction was conducted in THF, hexane or acetonitrile (Table 1, entries 2–4), while the reaction did not occur in dichloromethane or DMF (Table 1, entries 5 and 6). Next, we screened a series of complexes of Fe and Co ligated by P^CNN ligands (Table 1, entries 7–10) which revealed that ($^{tBu}P^CNN^{iPr}$)$CoCl_2$ (**2b**) gave the best result (Table 1, entry 8) and the steric effect of the complexes greatly affects the reaction. Lower yields were observed in the runs using the complexes with less bulky substituents on the ligands (Table 1, entries 9 and 10). No conversion was observed when running the reaction in the absence of the metal complex or $NaBHEt_3$, or replacing cobalt complexes with $CoCl_2$, indicating the important effect of the ligand on the hydrosilylation (Table 1, entries 11–13). Notably, a minor impurity was observed in the isolated product when using complex **1** as the precatalyst (entry 1), while the reaction with the precatalyst **2b** afforded the product in a very high purity (entry 8). Therefore, the parameters used in entry 8 have been chosen as the optimized reaction conditions for further study.

Next, we investigated the scope of the cobalt-catalyzed hydrosilylation with respect to the allene substrates. All the reactions of 3-aryl or alkyl substituted 1,2-dienes employed 0.5 mol% **2b** as the precatalyst, furnishing linear (*Z*)-allylsilanes in high isolated yields with an excellent (*Z*)-selectivity (Schemes 2 and 3). Aryl-substituted allenes bearing either electron-donating (**4b** and **4g**) or electron-withdrawing groups (**4c**) were hydrosilylated with high regio- and stereoselectivity, and substituents in the *ortho*, *meta*, and *para* positions of the phenyl ring are compatible with the reaction conditions (**4d–f**). The naphthyl substituent is also tolerated, giving a high yield of **4h** and no isomeric product was observed (Scheme 2).



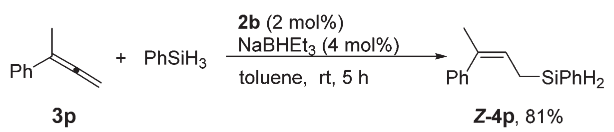
Scheme 2 Highly regio- and stereoselective hydrosilylation of aryl substituted allenes. The reaction was carried out with 1.0 mmol of **3**, 1.0 mmol of $PhSiH_3$, 5.0 μmol of **2b**, 10.0 μmol of $NaBHEt_3$, in 1 mL toluene at room temperature for 5 h. Yields of the isolated products are given.



Scheme 3 Highly regio- and stereoselective hydrosilylation of alkyl substituted allenes. The reaction was carried out with 1.0 mmol of **3**, 1.0 mmol of $PhSiH_3$, 5.0 μmol of **2b**, 10.0 μmol of $NaBHEt_3$, in 1 mL toluene at room temperature for 5 h. Yields of the isolated products are given. [a] The reaction was carried out with 5 mmol of **3i** to afford 1.2 g of *Z*-**4i**.

Alkyl substituted allenes also reacted with phenylsilane smoothly under the standard reaction conditions. Synthetically useful functional groups such as acetoxy (**4j**), cyano (**4k**), benzyl (**4l**), and ketal (**4m**) could be tolerated. Notably, even the reactive acetyl (**4n**) could be accommodated in this hydrosilylation reaction. Furthermore, the allene showed a higher reactivity than the internal alkyne as demonstrated by the isolation of **4o** in a high yield with an exclusive chemoselectivity towards the allene unit. No side-products resulting from the hydrosilylation of the acetyl and internal alkyne groups were observed in these reactions. Moreover, these reactions could be carried out on a one-gram scale, affording **4i** in 93% yield.

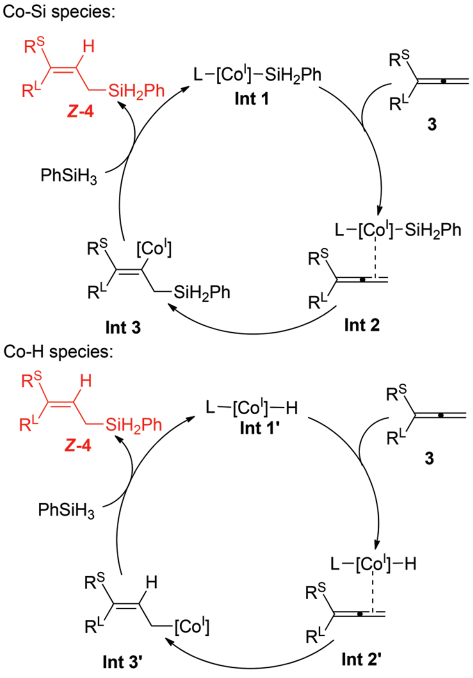
The reaction of unsymmetric 1,1-disubstituted allene **3p** also proceeded smoothly to afford linear allylsilanes *Z*-**4p** in a decent yield (Scheme 4). Significantly, only the *Z*-isomer was formed, demonstrating the capability of the cobalt catalyst to discriminate between Me and a larger substituent in the 1,1-disubstituted allene substrate.



Scheme 4 Highly regio- and stereoselective hydrosilylation of 1,1-disubstituted allenes.

Other silanes such as Ph_2SiH_2, Et_2SiH_2, and Et_3SiH were also tried for this reaction but only complicated mixtures were obtained.

We propose a rationale for the cobalt-catalyzed hydrosilylation of allenes on the basis of the precedents of the relevant (P^CNN)Co-catalyzed alkene and alkyne hydrosilylations[13,14] (Scheme 5). The hydrosilylation process starts with the activation of **2b** by using $NaBHEt_3$, followed by the reaction with $PhSiH_3$ to form a cobalt(I) silyl intermediate **Int-1**.[15] Most likely due to the steric repulsion between the P^CNN ligand and the substituent groups of the allenes, the terminal C═C double bond of substrate **3** coordinates to the metal center of **Int-1** from the less hindered side, resulting in the generation of the allene adduct **Int-2**. The subsequent insertion of the C═C double bond into the Co–Si bond would afford the vinyl cobalt intermediate **Int-3** with the Co center located at the *cis* position relative to the small substituent due to the steric effect. The vinyl complex **Int-3** then reacts with $PhSiH_3$, *via* either sigma-bond metathesis or a silane oxidative addition/reductive elimination pathway, to deliver the hydrosilylation product and regenerate **Int-1**. Alternatively, the catalytic process may involve a cobalt(I) hydride intermediate **Int-1′**.[16] The corresponding allene adduct **Int-2′** then undergoes insertion to form the allyl cobalt intermediate **Int-3′**, which further reacts with $PhSiH_3$ to form the desired product and regenerate the cobalt(I) hydride. Further detailed mechanistic studies are ongoing to establish unambiguously the real mechanistic nature of the reaction.



Scheme 5 Proposed mechanisms.

In conclusion, we have developed a highly regio- and stereoselective cobalt-catalyzed allene-hydrosilylation method for the synthesis of linear (*Z*)-allylsilanes. Both mono and 1,1-disubstituted allenes are applicable for this transformation and a variety of synthetically useful functional groups could be tolerated. Further investigations including mechanistic studies and synthetic applications of the allylsilane products have been pursued in this laboratory.

Acknowledgements

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