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-couplings1 and Tamao oxidation reactions to form the carbonyl group.2 The hydrosilylation of unsaturated C–C bonds such as allenes,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 Ru9 or Al10 catalysis (Scheme 1a) or branched allylsilanes using Pd6,7 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-iminopyridine12 (P3NN) and phosphine-iminopyridine13 (P2NN) ligands developed in one of our laboratories (Chart 1), which exhibited an excellent catalytic activity in the hydrosilylation of allenes.

We commenced the study by examining an iron catalyst generated from (tBuPONNiPr)FeCl2 (1) and NaBH4 for the hydrosilylation of phenyl allene (3a) with phenylsilane. The initial run in toluene using only 0.5 mol% of the catalyst yielded linear (Z)-phenyl(3-phenylallyl)silane (4a) in 93% yield as determined by 1H NMR analysis. Neither the regioisomers 4a′ nor the stereoisomer E-4a was detected. Solvent variations have a large effect on the cobalt-mediated hydrosilyl-
Highly regio- and stereoselective hydrosilylation of alkyl substituted allenes. The reaction was carried out with 1.0 mmol of Scheme 2. Highly regio- and stereoselective hydrosilylation of alkyl substituted allenes. The reaction was carried out with 1.0 mmol of 3a, 1.0 mmol of PhSiH₃, 5.0 μmol of 2b, 10.0 μmol of NaBHEt₃, in 1 mL toluene at room temperature for 5 h. Yields of the isolated products are given. The reaction was carried out with 5 mmol of 3i to afford 1.2 g of Z-4i.

Highly regio- and stereoselective hydrosilylation of 4 alkyl substituted allenes. The reaction was carried out with 1.0 mmol of Scheme 3. Highly regio- and stereoselective hydrosilylation of 4 alkyl substituted allenes. The reaction was carried out with 1.0 mmol of 3a, 1.0 mmol of PhSiH₃, 5.0 μmol of 2b, 10.0 μmol of NaBHEt₃, in 1 mL toluene at room temperature for 5 h. Yields of the isolated products are given. 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 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).

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 (4e) 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).

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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 Ph₃SiH₂, Et₂SiH₂, and Et₃SiH 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 precedence of the relevant [(P²NN)Co]-catalyzed alkene and alkyne hydrosilylations.13,14 (Scheme 5). The hydrosilylation process starts with the activation of 2b by using NaBH₄, followed by the reaction with PhSiH₃ to form a cobalt(i) silyl intermediate Int-1.15 Most likely due to the steric repulsion between the P²NN 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 PhSiH₃, 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 PhSiH₃ 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.

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.

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