Access to stereodefined (Z)-allylsilanes and (Z)-allylic alcohols via cobalt-catalyzed regioselective hydrosilylation of allenes

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Hydrosilylation of allenes is the addition of a hydrogen atom and a silyl group to a carbon-carbon double bond of an allene molecule and represents a straightforward and atom-economical approach to prepare synthetically versatile allylsilanes and vinylsilanes. However, this reaction generally produces six possible isomeric organosilanes, and the biggest challenge in developing this reaction is to control both regioselectivity and stereoselectivity. The majorities of the developed allene hydrosilylation reactions show high selectivity towards the production of vinylsilanes or branched allylsilanes. By employing a cobalt catalyst generated from readily available and bench-stable cobalt precursor and phosphine-based ligands, here we show that this reaction proceeds under mild conditions in a regioselective and stereoselective manner, and affords synthetically challenging, but valuable linear cis-allylsilanes with excellent stereoselectivity (generally cis to trans ratios: >98:2). This cobalt-catalyzed (Z)-selective allene hydrosilylation provides a general approach to access molecules containing stereodefined (Z)-alkene units.

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Allylsilanes are a type of organosilanes with an allyl group on a silicon atom, and the stereochemistry around the allylic double bond may be E (cis) or Z (trans). Allylsilanes are synthetically valuable building blocks because of their non-toxicity, high stability and versatile applications in organic synthesis and material science. They have been employed as monomers for syntheses of silicon-containing polymers and undergo a variety of organic transformations. As such, various methods have been developed to prepare allylsilanes and the majority of these approaches produce thermodynamically more stable E-allylsilanes. However, the stereoselective synthesis of a wide range of E-allylsilanes still remains challenging and rare.

Catalytic hydrosilylation of allenes (Fig. 1a) is one of the most straightforward and atom-economical approaches to synthesize (Z)-allylsilanes, provided that catalysts and reaction conditions favoring the formation of (Z)-allylsilanes can be identified.

Allenes can undergo hydrosilylation with hydrosilanes in the presence of transition metal catalysts to produce allylsilanes or vinylsilanes (Fig. 1a). The major difficulty in allene hydrosilylation is to control the regio- and stereoselectivity because multiple vinylsilanes and allylsilane products may be generated (Fig. 1a). The majority of metal-catalyzed hydrosilylation of terminal allenes show high selectivity for β,γ-hydrosilylation, affording allylsilanes or vinylsilanes with a terminal allene group without an issue of the control over Z/E-selectivity (Fig. 1b). However, α,β-hydrosilylation of terminal allenes is more challenging because it can potentially form four isomeric Z/E-allylsilane and Z/E-vinylsilane products (Fig. 1a). Selective formation of one organosilane product out of four possible isomers is of high synthetic importance. For a recent example of molybdenum catalyst for α,β-hydrosilylation of allenes with modest Z/E selectivity at 110 °C or under UV irradiation (Fig. 1c), catalysts for selective allene α,β-hydrosilylation that can combine high catalyst activity, high Z-stereoselectivity, broad substrate scope and mild reaction conditions are conspicuously unknown.

Platinum complexes are the most frequently encountered catalysts for hydrosilylation reactions in industry. However, there is a growing interest in replacing platinum catalysts with earth-abundant base-metal catalysts for hydrosilylation. Accordingly, a tremendous development has been made in cobalt-catalyzed hydrosilylation of allenes and alkynes. The hydrosilylation of allenes has been studied with stoichiometric amounts of the cobalt complex Co₂(CO)₈, but this ligandless cobalt catalyst shows low selectivity for α,β-hydrosilylation. A Co-catalyzed allene α,β-hydrosilylation that can selectively produce (Z)-allylsilanes still remains unknown. Driven by our continuous interest in developing base-metal-catalyzed hydrofunctionalization of unsaturated organic molecules, we are interested in identifying a highly Z-selective cobalt catalyst for allene α,β-hydrosilylation. An improved Z/E-selectivity is anticipated for ligated cobalt catalysts due to a greater stereochemical communication between ligand and allene substrate from a relatively smaller cobalt center, comparing with the molybdenum catalyst Mo(CO)₆. Herein we report a cobalt-catalyzed stereo-selective α,β-hydrosilylation of terminal allenes to prepare (Z)-allylsilanes. Furthermore, we have developed a practical one-pot procedure to access synthetically challenging trisubstituted (Z)-allylic alcohols by combining this cobalt-catalyzed allene hydrosilylation and subsequent oxidation of the resulting (Z)-allylsilanes. In addition, we show that Co(acac)₂ can be reduced by PhSiH₃ in the presence of bisphosphine ligands to generate well-defined, but catalytically active, Co(I) hydride complexes.

Results

Evaluation of reaction conditions. We initiated our studies of Co-catalyzed hydrosilylation of allenes by evaluating reaction conditions for the reaction of cyclohexylallene with phenylsilane. This reaction can potentially produce six organosilanes from either 1,2-hydrosilylation (E)-1a, (Z)-1a, (E)-1a, and (Z)-1a or 2,3-hydrosilylation (1a and 1a”), as depicted in Table 1. We tested this reaction with various cobalt catalysts that were generated in situ from bench-stable Co(acac)₂ and phosphine ligands. In general, these experiments were conducted with 2 mol % cobalt catalysts in THF at room temperature for 18 h. The results of these experiments are summarized in Table 1. The reactions catalyzed by the combination of Co(acac)₂ and monophosphine ligands, such as PPh₃ and PCy₃, proceeded to low conversions of cyclohexylallene and produced a mixture of six products with low selectivities for (Z)-1a (Table 1, entries 1 and 2). Improved conversions and selectivities to (Z)-1a (83–91%) were achieved for reactions that were conducted with the combination of Co(acac)₂ and biphosphine ligands, such as dppe, bpp, dpb, dpe or dppf (Table 1, entries 3–7). In particular, the reaction with the catalyst generated from Co(acac)₂ and rac-binap occurred to full conversion with excellent selectivity (98%) for (Z)-1a (Table 1, entry 8). Similarly high

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Fig. 1 Hydrosilylation of allenes. a Overview of hydrosilylation of allenes. b Metal-catalyzed β,γ-hydrosilylation of allenes. c Metal-catalyzed α,β-hydrosilylation of allenes
selectivity for (Z)-1a was obtained for the reaction catalyzed by Co(acac)2 and xanthos, but this reaction produced a significant amount of bis((Z)-3-cyclohexylallyl)(phenyl)silane 2 (Table 1, entry 9), which was generated by the hydrosilylation of cyclohexylallene with (Z)-1a as a hydrosilylating reagent (Table 1, entry 9). The result of entry 9 indicates that the hydrosilylation of cyclohexylallene with secondary silanes is likely feasible. Indeed, cyclohexylallene reacted with secondary silanes Ph2SiH2 and MePhSiH2 in the presence of 1 mol% Co(acac)2 and 1 mol % xanthos, affording the corresponding (Z)-allylsilanes 1b and 1c in high yields with excellent stereoselectivities (Fig. 2b, c)\(^{11}\). In addition, we tested a nitrogen-based ligand \(^{\text{mepDI}}\) for this transformation, and the reaction afforded a mixture of (Z)-1a, (E)-1a and (E)-1a with low regio- and stereoselectivity (Table 1, entry 10). Furthermore, we also tested various solvents for this hydrosilylation catalyzed by Co(acac)2/binap (Table 1, entries 11–14). The reactions conducted in toluene, diethyl ether and tert-butylmethylether proceeded to full conversions of cyclohexylallene with low regio- and stereoselectivity (Table 1, entry 14). The reactions conducted in toluene, diethyl ether and tert-butylmethylether proceeded to full conversions of cyclohexylallene with excellent selectivity for (Z)-1a (Table 1, entries 11, 13 and 14), but the reaction did not occur in hexane, likely due to the poor solubility of the cobalt catalyst in hexane (Table 1, entry 12). In addition, this reaction occurred smoothly in the absence of any solvent and afforded the desired product (Z)-1a in 85% isolated yield with Z/E of 99:1 (Table 1, entry 15).

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### Table 1 Evaluation of conditions for cobalt-catalyzed hydrosilylation of cyclohexylallene

| entry | ligand | solvent | conversion | yield | product distribution | (E)-1a | (Z)-1a | (E)-1a’ | (Z)-1a’ | 1a'' | 1a’’’ |
|-------|--------|---------|------------|-------|----------------------|--------|--------|--------|--------|------|-------|
| 1     | PPh3\(^{\text{a}}\) | THF     | 73%        | 65%   | 2.6% 60.0% 9.7% 11.8% 2.0% 16.9% |
| 2     | PCy\(^{\text{a}}\) | THF     | 15%        | <10%  | 2.9% 12.2% 15.0% 38.6% 5.7% 25.7% |
| 3     | dppe   | THF     | 73%        | 51%   | 5.6% 83.6% 7.1% 0.9% 2.8% |
| 4     | dppp   | THF     | >99%       | 80%   | 10.1% 83.0% 2.8% 4.1% |
| 5     | dppb   | THF     | >99%       | 79%   | 3.3% 90.9% 2.0% 3.8% |
| 6     | dcpe   | THF     | >99%       | 81%   | 5.5% 88.7% 4.0% 0.3% 1.5% |
| 7     | dppf   | THF     | >99%       | 87%   | 2.5% 91.0% 3.5% 0.2% 0.2% 1.5% |
| 8     | rac-binap | THF     | >99%       | 91%   | 0.7% 97.7% 1.0% 0.1% |
| 9     | xanthos | THF     | >99%       | 23%   | 2.3% 94.7% 3.0% |
| 10    | \(^{\text{mepDI}}\) | THF     | >99%       | 57%   | 13.3% 29.6% 57.1% |
| 11    | binap   | toluene | >94%       | 86%   | 0.8% 94.8% 2.3% 1.4% |
| 12    | binap   | hexane  | <5         | -     | - 0.2% 1.3% |
| 13    | binap   | \(\text{Et}_2\text{O}\) | >99% | 91% | 0.8% 94.6% 2.6% 0.2% |
| 14    | binap   | \(\text{BuOMe}\) | >99% | 87% | 0.8% 99.1% 0.2% |
| 15    | -      | -       | 92%        | 85%   | 0.8% 92.6% 3.5% 0.2% 1.6% |

Reaction conditions: cyclohexylallene (0.500 mmol), PhSiH3 (0.550 mmol), Co(acac)2 (10.0 mmol), ligand (10.0 mmol), solvent (1 mL), room temperature, 18 h. Cy cyclohexyl; acac acetylacetonate; THF tetrahydrofuran.

\(^{\text{a}}\)Overall yield of six products and product distribution determined by GC analysis with dodecane as the internal standard.

\(^{\text{b}}\)The loading of ligand was 4 mol%.

\(^{\text{c}}\)This reaction afforded bis((Z)-3-cyclohexylallyl)(phenyl)silane 2 in 35% yield.

\(^{\text{d}}\)This reaction was conducted on 1.0 mmol scale without any solvent and affordeds the desired product (Z)-1a in 85% isolated yield with Z/E of 99:1.
Substrate scope of allenes. Under the identified conditions (Table 1, entry 8), we studied the scope of monosubstituted allenes for this reaction. These results are summarized in Fig. 3. In general, a variety of monosubstituted allenes reacted to produce the desired disubstituted (Z)-allylsilanes (1a−1q) in high yields (74−92%) with excellent stereoselectivities (Z/E = 99:1). This reaction shows good functional group tolerance and a range of reactive groups, such as chloro (1g), bromo (1h and 1p), iodo (1i), siloxy (1j), ester (1k), pinacol boronic ester (1l), and imide (1m), are compatible with the reaction conditions. Under the identified conditions, the bromine- and iodine-containing allenes (1h, 1p and 1i) were not fully consumed and this accounts for the relatively lower yields of 1h, 1p and 1i compared with other entries.

Similarly, disubstituted terminal allenes also reacted with PhSiH3 under the conditions identified for hydrosilylation of monosubstituted allenes (Fig. 3). For example, the reaction between 1-methyl-1-phenylallene and PhSiH3 proceeded to full conversion in 24 h in the presence of 2 mol% Co(acac)2 and rac-binap. However, the same reaction conducted with 1 mol% Co(acac)2/xantphos proceeded to full conversion in only 3 h, affording (Z)-allylsilane 3a in 94% isolated yield with excellent stereoselectivity. Therefore, we chose Co(acac)2/xantphos to study the scope of disubstituted terminal allenes and the results are...
listed in Fig. 4. A series of disubstituted terminal allenes containing aromatic or aliphatic groups readily reacted with PhSiH3 in the presence of 1 mol% Co(acac)2/xantphos at room temperature for 3 h, affording the desired (Z)-allylsilanes (3b–3s) in high yields (74–95%) with excellent stereoselectivities (Z/E = 99:1). Decreased Z/E ratio (88:12) was obtained for allene with decreased steric difference between R and R’ (3q). A variety of reactive groups, such as siloxy (3f), chloro (3g and 3n), bromo (3h), ester (3i), and acetal (3j), are tolerated under the reaction conditions. In addition, this allene hydrosilylation was tested with secondary hydrosilanes (Ph2SiH2, Ph(Me)SiH2, and Et2SiH2), and these reactions produced the corresponding (Z)-allylsilanes (3s–3v) in high yields with high stereoselectivities. However, this hydrosilylation of allene did not occur when tertiary hydrosilanes, such as (EtO)3SiH and (Me3SiO)2MeSiH, were used.

**Synthetic potential.** As both Co(acac)2 and the xantphos ligand employed in this transformation are bench-stable, we tested the reaction between 1-methyl-1-phenyllene and PhSiH3 or Ph2SiH2 on a 10 mmol scale in the presence of 0.5 mol% of Co(acac)2 and xantphos that were weighed on the benchtop without using a drybox. These reactions afforded (Z)-allylsilanes 3a and 3s in high isolated yield with Z/E of 99:1 (Fig. 5a). In addition, we demonstrated that (Z)-allylsilane 3v underwent Ir-catalyzed intramolecular dehydrogenative silylation to afford a six-membered silacyclic compound 4 in 51% isolated yield (Fig. 5b); [dtbpy = 4,4′-di-tert-butyl-2,2′-bipyridyl, nbe = norbornene].

Allylic alcohols are synthetically valuable intermediates in various organic transformations. The synthesis of stereodefined allylic alcohols, particularly ones containing a trisubstituted Z-alkene unit, is a persisting challenge in synthetic chemistry. Here we developed a one-pot procedure to synthesize (Z)-allylic alcohols containing disubstituted or trisubstituted allenes by combining the cobalt-catalyzed allene hydrosilylation and the subsequent oxidation of the resulting (Z)-allylsilanes with H2O2 under basic conditions. A series of (Z)-allylic alcohols (5a–5h) can be prepared in good isolated yields using this one-pot procedure (Fig. 5c, see Supplementary Methods for the detailed procedure).

**Discussion**

(Z)-allylsilanes are thermodynamically less stable than (E)-allylsilanes and are susceptible to Z/E-isomerization to form the thermodynamically more stable (E)-allylsilanes in the presence of a Co-H species. The high Z-selectivities obtained for
Hydrosilylation of cyclohexylallene with Ph₂SiH₂ conducted for 48 h.

Conditions A or B: Co(acac)₂ (2 mol%), binap (2 mol%), PhSiH₃ (1 equiv.)
Conditions C or D: Co(acac)₂ (1 mol%), xantphos (1 mol%), PhSiH₃ (1 equiv.)

**Fig. 5** Synthetic potential. a A concentration of 10 mmol scale reactions. b Ir-catalyzed dehydrogenative silylation of (Z)-allylsilane 3v. c One-pot synthesis of (Z)-allylic alcohols; The Z/E ratios were determined with gas chromatography (GC) analysis on crude reaction mixtures.

**Fig. 6** Isomerization of (Z)-allylsilanes. a, b Isomerization of a disubstituted (Z)-allylsilane (Z)-1l. c, d Isomerization of a trisubstituted (Z)-allylsilane (Z)-3a. e Hydrosilylation of cyclohexyllallene with Ph₂SiH₂ conducted for 48 h.

Reactions listed in Fig. 2 suggest that the cobalt catalyst generated from Co(acac)₂ and binap does not catalyze the Z/E-isomerization of these Z-allylsilanes. Indeed, the isolated (Z)-allylsilane (Z)-1l does not undergo Z/E-isomerization in the presence of 2 mol % Co(acac)₂/binap and 1 equivalent of PhSiH₃ (Fig. 6a). However, (Z)-allylsilane (Z)-1l was isomerized to (E)-1l at room temperature in 24 h in the presence of 1 mol % Co(acac)₂/xantphos and 1 equivalent of PhSiH₃ (Fig. 6a). We also tested these isomerization
The cobalt-catalyzed allene hydrosilylation is achieved through a deuterium-labeling reaction, which confirms the hydrofunctionalization of alkenes. The mechanism involves the formation of a Co(I)-H complex followed by migratory insertion of the allene substrate into a Co(III) hydride intermediate, leading to the formation of a terminal allene hydrosilation product.

**Methods**

**General procedure for cobalt-catalyzed allene hydrosilylation.** An argon-filled dry box, Co(acac)₂, phosphine ligand, THF (1 mL) and a magnetic stirring bar were added to a 4-mL screw-capped vial and the mixture was stirred for 5 min. Then terminal allenes (0.500 mmol) and silane (1.1 equiv, 0.550 mmol) were added to a 4-mL screw-capped vial and the mixture was stirred for 5 min. The vial was sealed with a cap containing a PTFE septum and removed from the dry box. The reaction mixture was warmed to 80 °C for 18 h (Fig. 3) or 3 h (Fig. 4) and the resulting solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and hexane as eluent.
Data availability. The authors declare that all the data supporting the findings of this study are available within the article and Supplementary Information files, and also are available from the corresponding author upon reasonable request.

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C.W. planned and conducted most of the experiments; C.W. and W.J.T. prepared substrates for the reaction scope evaluation; S.G. directed the projects and S.G. and C.W. co-wrote the manuscript. All authors contributed to the discussion.

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