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Cobalt-Catalyzed Regioselective Stereoconvergent Markovnikov 1,2-Hydrosilylation of Dienes

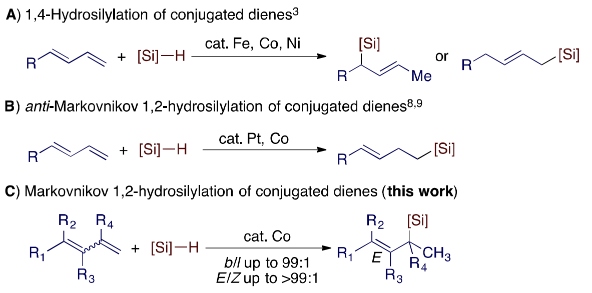
Hui Leng Sang, Songjie Yu, and Shaozhong Ge*

We report the first stereoconvergent Markovnikov 1,2-hydrosilylation of conjugated dienes using catalysts generated from bench-stable Co(acac)$_2$ and phosphine ligands. A wide range of *E*/*Z*-dienes underwent this Markovnikov 1,2-hydrosilylation in a stereoconvergent manner, affording (*E*)-allylsilanes in high isolated yields with high stereoselectivities (*E*/*Z* = >99:1) and high regioselectivities (*b*/*l* up to > 99:1). Mechanistic studies revealed that this stereoconvergence stems from a σ-π-σ isomerization of an allylcobalt species generated by 1,4-hydrometalation of *Z*-dienes. In addition, a cobalt catalyst that can only catalyze the hydrosilylation of the *E*-isomer of (*E*/*Z*)-diene was identified, which allows the separation of a (*Z*)-isomer from an isomeric mixture of (*E*/*Z*)-dienes. Furthermore, asymmetric hydrosilylation of (*E*)-1-aryl-1,3-dienes was studied with Co(acac)$_2$/(*R*)-difluorphos and good enantioselectivities (*er* up to 90:10) were obtained.

Introduction

Allylsilanes are synthetically valuable building blocks due to their non-toxicity, high stability and versatile applications in organic synthesis and material science.[1] Among the methods for allylsilane synthesis,[2] transition metal-catalyzed hydrosilylation of conjugated dienes is the most straightforward approach to prepare these synthetically valuable allylsilanes.[3] Recently, hydrosilylation of alkenes[4] and alkynes[5] has been extensively studied with cobalt catalysts,[6] particularly due to their higher abundance and lower toxicity compared to platinum catalysts for hydrosilylation reactions.[7] More importantly, recent studies indicate that cobalt catalysts can offer a precise control on regio- and stereoselectivities.[5] However, highly selective cobalt catalysts for hydrosilylation of conjugated dienes still remain rare and are under development.[3c,8]

Conjugated dienes can undergo 1,4- and 1,2-hydrosilylation and the selectivity is dependent on the catalysts employed. The majority of the catalysts based on Fe, Co, and Ni show high selectivity towards 1,4-hydrosilylation (Scheme 1A).[3] For example, Hilt reported a highly selective cobalt catalyst for 1,4-hydrosilylation of isoprene in the presence of P(*n*-Bu)$_3$,[3c] and Ritter reported a well-defined Fe(0) complex ligated by 2-iminopyridines for 1,4-hydrosilylation of 1,3-dienes.[3d] In contrast, 1,2-hydrosilylation of conjugated dienes has been barely studied, and two catalysts based on Pt and Co have been used to catalyze this 1,2-hydrosilylation.[8,9] In addition, these two catalysts show high selectivity towards *anti*-Markovnikov hydrosilylation (Scheme 1B). However, transition metal catalysts for Markovnikov 1,2-hydrosilylation of conjugated dienes, especially for stereoconvergent Markovnikov 1,2-hydrosilylation of *E*/*Z*-dienes, still remain unknown. Driven by our research interest in developing base metal catalysts for transformations of unsaturated organic molecules,[4f,5f,10] herein we report a highly selective cobalt-catalyzed stereoconvergent Markovnikov 1,2-hydrosilylation of a wide range of functionalized conjugated (*E*/*Z*)-dienes (Scheme 1C). In addition, we also identified a cobalt catalyst that selectively catalyzes the hydrosilylation of the (*E*)-isomer of an (*E*/*Z*)-diene with the (*Z*)-isomer unreacted. This discovery would represent a convenient protocol to purify (*Z*)-dienes from (*E*/*Z*)-isomeric dienes, which are generally more accessible than stereodefined (*Z*)- or (*E*)-dienes.



Scheme 1 Transition metal-catalyzed hydrosilylation of conjugated dienes.

Results and Discussion

We chose the reaction of (*E*)-1-phenyl-1,3-butadiene with PhSiH$_3$ to evaluate reaction conditions for this Co-catalyzed hydrosilylation of conjugated dienes. We tested this reaction

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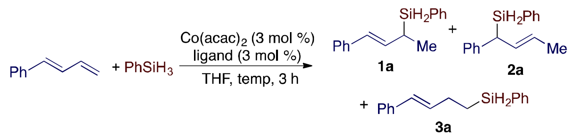
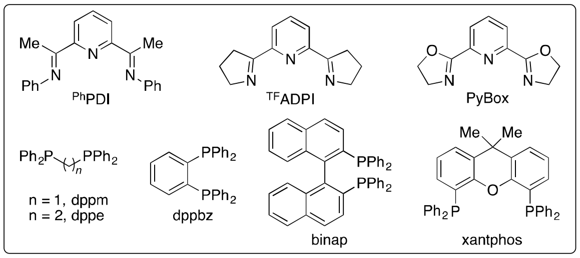
with cobalt catalysts generated from Co(acac)$_2$ and various nitrogen- and phosphine-based ligands. The selected examples of these examples are summarized in Table 1. In general, these reactions were conducted with 3 mol % of Co(acac)$_2$ and 3 mol % ligand at 50 °C for 3 h.

Table 1. Evaluation of Conditions for the Co-catalyzed Hydrosilylation of 1-Phenyl-1,3-butadiene.[a]



entry	ligand	temperature	conversion (%)[b]	yield of **1a** (%)[b]	**1a/2a/3a**[b]
1	^{Ph}PDI	50 °C	>99	27	31:-:69
2	^{TF}APDI	50 °C	>99	33	35:-:65
3	PyBox	50 °C	>99	49	56:4:40
4	dppm	50 °C	28	23	>99:-:-
5	dppe	50 °C	78	77	>99:-:-
6	dppbz	50 °C	9	5	>99:-:-
7	binap	50 °C	93	76	>99:-:-
8	xantphos	50 °C	>99	81	>99:-:-
9[c]	xantphos	rt	>99	87	>99:-:-
10[c,d]	xantphos	rt	>99	83	96:4:-



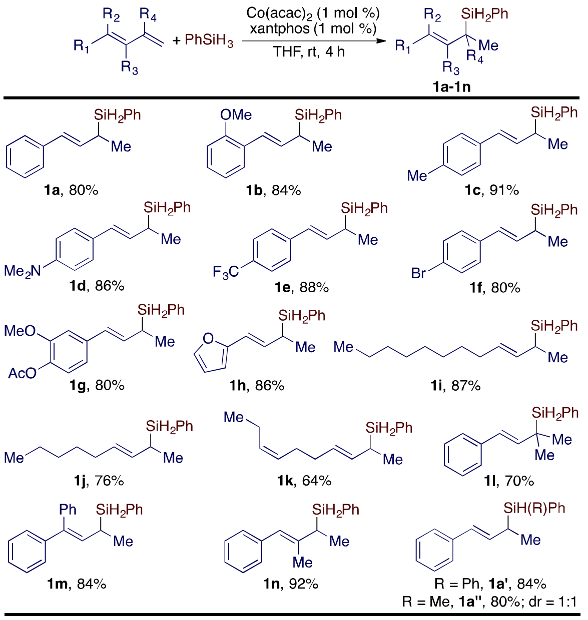
[a] Conditions: (*E*)-diene (0.400 mmol), PhSiH$_3$ (0.500 mmol), Co(acac)$_2$ (12.0 μmol), ligand (12.0 μmol), THF (1 mL), 3 h; [b] Conversion of diene, yield of **1a**, ratio of products **1a**, **2a**, and **3a** were determined by GC analysis with tridecane as the internal standard; [c] Catalyst (1 mol %); [d] A mixture of (*E*/*Z*)-1-phenyl-1,3-butadiene (*E*/*Z* = 45:55) was used.

Cobalt catalysts generated from the combination of Co(acac)$_2$ and nitrogen-based ligands, such as ^{Ph}PDI, ^{TF}ADPI or PyBox, did catalyze the 1,2-hydrosilylation of (*E*)-1-phenyl-1,3-butadiene to full conversions, but these reactions produced a mixture of products **1a** and **3a** with low selectivities (entries 1–3 in Table 1).[8] The reactions conducted with the combination of Co(acac)$_2$ and bisphosphine ligands, such as dppm, dppe, or dppbz, proceeded to low to modest conversions, but with complete selectivities (>99%) to Markovnikov 1,2-hydrosilylation (entries 4–6 in Table 1). In particular, the reactions catalyzed by the combination of Co(acac)$_2$ and binap or xantphos proceeded to high or full conversions with excellent selectivities to branched allylsilane **1a** (enties 7 and 8 in Table 1). As dienes are thermally less stable and can undergo polymerization, we tested this hydrosilylation at lower temperatures. The reaction conducted with 1 mol % of Co(acac)$_2$ and 1 mol % of xantphos at room temperature proceeded to full conversion and afforded the desired allylsilane **1a** in an increased yield with an excellent Markovnikov selectivity (entry 9 in Table 1).

As (*E*/*Z*)-isomeric mixtures of dienes are synthetically more accessible than stereodefined (*E*)- or (*Z*)-dienes, we tested this hydrosilylation with a mixture of (*E*/*Z*)-isomeric 1-phenyl-1,3-butadiene to check the stereoconvergency for this reaction. To our delight, both (*Z*)- and (*E*)-1-phenyl-1,3-dienes underwent this cobalt-catalyzed Markovnikov 1,2-hydrosilylation and produced branched allylsilane **1a** in high yield with high selectivity (entry 10 in Table 1). Different from the hydrosilylation of (*E*)-1-phenyl-1,3-diene (entry 9 in Table 1), the reaction with a mixture of (*E*/*Z*)-1-phenyl-1,3-butadienes also generated a detectable amount (4%) of branched allylsilane **2a**, a product resulted from 1,4-hydrosilylation of diene.

Under the identified conditions (entry 9 in Table 1), we studied the scope of conjugated *trans*-dienes for this reaction. These results are summarized in Table 2. In general, a wide range of conjugated *trans*-dienes reacted smoothly with PhSiH$_3$ in the presence of 1 mol % of Co(acac)$_2$ and xantphos at room temperature, affording the corresponding (*E*)-allylsilanes (**1a**–**1n** in Table 2) in high yields (70%–96%) with excellent regioselectivities (*b*/*l* = >99:1). The scope of these *trans*-dienes encompassed aryl-substituted (**1a**–**1h** in Table 2), alkyl-substituted (**1i**–**1k** in Table 2), and multiply-substituted dienes (**1a**–**1h** in Table 2). The GC-MS analysis on the crude mixture of these reactions revealed that organosilane products from

Table 2. Scope of *trans*-Dienes for this Co-Catalyzed Markovnikov 1,2-Hydrosilylation[a]



[a] Conditions: (*E*)-diene (0.400 mmol), PhSiH$_3$ (0.500 mmol), Co(acac)$_2$ (12.0 μmol), ligand (12.0 μmol), THF (1 mL), 3 h; [b] Conversion of diene, yield of **1a**, ratio of products **1a**, **2a**, and **3a** were determined by GC analysis with tridecane as the internal standard; [c] Catalyst (1 mol %); [d] A mixture of (*E*/*Z*)-1-phenyl-1,3-butadiene (*E*/*Z* = 45:55) was used.

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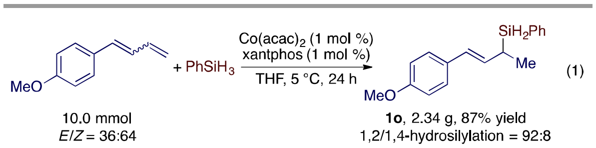
either 1,4-hydrosilylation or *anti*-Markovnikov 1,2-hydrosilylation of these *trans*-dienes were not formed during this Co-catalyzed Markovnikov 1,2-hydrosilylation. In addition, we also tested this hydrosilylation with secondary hydrosilanes (Ph_2SiH_2 and $PhMeSiH_2$), and these reactions proceeded smoothly to afford tertiary cinnamylsilanes (**1a'** and **1a"** in Table 2) in high isolated yields. However, this Co-catalyzed hydrosilylation did not occur with dialkylsilane (Et_2SiH_2) or tertiary hydrosilanes, such as $(EtO)_3SiH$ and $(EtO)_2MeSiH$.

Subsequently, we studied the scope of conjugated dienes containing a mixture of (*E*/*Z*)-isomeric 1,3-dienes for this hydrosilylation reaction, and the results are summarized in Table 3. Generally, a wide range of (*E*/*Z*)-dienes, with *E*/*Z* ratios given in the brackets in Table 3, underwent this Markovnikov 1,2-hydrosilylation in a stereoconvergent manner in full conversions, affording the corresponding (*E*)-allylsilanes (**1a**–**1z** in Table 3) in high isolated yields with high regio- and stereoselectivities (*b*/*l* = >99:1; *E*/*Z* = >99:1). The GC-MS analysis on the crude reaction mixtures indicated that these reactions also produced small amounts of 1,4-hydrosilylation products, and the ratios of these products from 1,2- and 1,4-hydrosilylation are listed in Table 3 and abbreviated as 1,2/1,4 ratios.

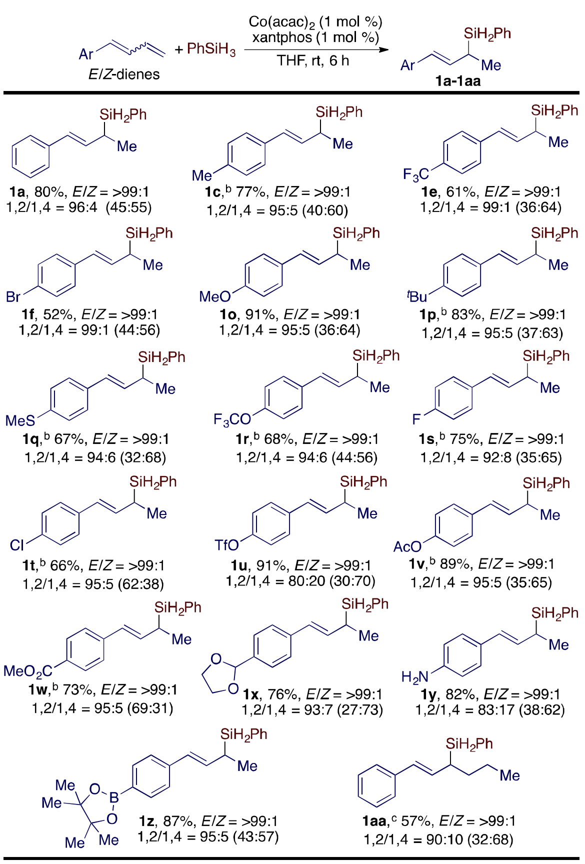
The data in Table 3 indicated that the electronic properties of the aryl substituents do not have a significant influence on the stereoconvergence and regioselectivity of these hydrosilylation reactions (e.g. **1a**, **1e**, and **1o** in Table 3). This Co-catalyzed transformation can tolerate various reactive groups, such as trifluoromethyl ether (**1r**), halogens (**1f**, **1s**, and **1t**), triflate (**1u**), ester (**1v** and **1w**), acetal (**1x**), unprotected primary aniline (**1y**), and pinacolboronic ester (**1z**). In addition, ((1*E*/*Z*,3*E*)-hexa-1,3-dien-1-yl)benzene, an internal 1,3-diene, also underwent this stereoconvergent hydrosilylation to afford allylsilane **1aa** in high isolated yield with high stereoselectivity (*E*/*Z* = >99:1).

As both $Co(acac)_2$ and xantphos used for this hydrosilylation reaction are bench-stable, we tested the hydrosilylation of 1-(buta-1,3-dien-1-yl)-4-methoxybenzene with $PhSiH_3$ on a 10 mmol scale with 1 mol % of $Co(acac)_2$/xantphos weighed on the benchtop without using a dry box. This reaction proceeded to full conversion of the diene substrate and afforded **1o** in 87% isolated yield (eq 1).



To understand the stereoconvergence of this hydrosilylation of (*E*/*Z*)-dienes, we analyzed the reaction of (*E*/*Z*)-1-phenyl-1,3-butadiene and found that the (*E*)-isomer was consumed at a significantly higher rate than (*Z*)-isomer.[11] In addition, the hydrosilylation of (*Z*)-1-phenyl-1,3-butadiene was studied, and this reaction afforded 1,2-hydrosilylation product **1a** together with a significant amount of 1,4-hydrosilylation product **2a** (**1a**:**2a** = 74:26, Scheme 2A). The results of this reaction and the reactions of the *E*-isomer (entry 9 in Table 1) and the mixture of the (*E*/*Z*)-isomers (entry 10 in Table 1) suggest that allylsilane **2a** was formed by 1,4-hydrosilylation of the (*Z*)-

Table 3. Scope of (*E*/*Z*)-Dienes for Stereoconvergent Hydrosilylation Reactions[a]



1a, 80%, *E*/*Z* = >99:1
1,2/1,4 = 96:4 (45:55)

1c,[b] 77%, *E*/*Z* = >99:1
1,2/1,4 = 95:5 (40:60)

1e, 61%, *E*/*Z* = >99:1
1,2/1,4 = 99:1 (36:64)

1f, 52%, *E*/*Z* = >99:1
1,2/1,4 = 99:1 (44:56)

1o, 91%, *E*/*Z* = >99:1
1,2/1,4 = 95:5 (36:64)

1p,[b] 83%, *E*/*Z* = >99:1
1,2/1,4 = 95:5 (37:63)

1q,[b] 67%, *E*/*Z* = >99:1
1,2/1,4 = 94:6 (32:68)

1r,[b] 68%, *E*/*Z* = >99:1
1,2/1,4 = 94:6 (44:56)

1s,[b] 75%, *E*/*Z* = >99:1
1,2/1,4 = 92:8 (35:65)

1t,[b] 66%, *E*/*Z* = >99:1
1,2/1,4 = 95:5 (62:38)

1u, 91%, *E*/*Z* = >99:1
1,2/1,4 = 80:20 (30:70)

1v,[b] 89%, *E*/*Z* = >99:1
1,2/1,4 = 95:5 (35:65)

1w,[b] 73%, *E*/*Z* = >99:1
1,2/1,4 = 95:5 (69:31)

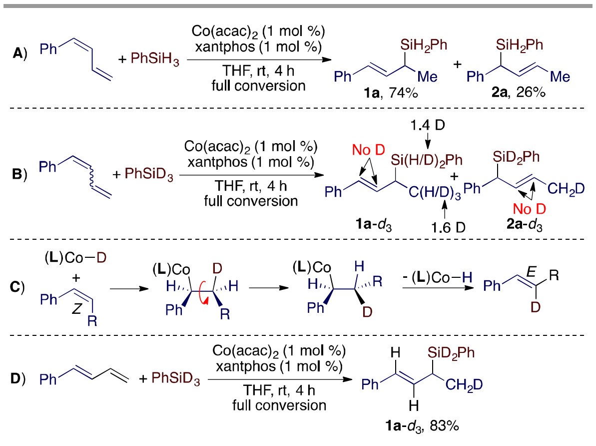
1x, 76%, *E*/*Z* = >99:1
1,2/1,4 = 93:7 (27:73)

1y, 82%, *E*/*Z* = >99:1
1,2/1,4 = 83:17 (38:62)

1z, 87%, *E*/*Z* = >99:1
1,2/1,4 = 95:5 (43:57)

1aa,[c] 57%, *E*/*Z* = >99:1
1,2/1,4 = 90:10 (32:68)

[a] Conditions: (*E*/*Z*)-Diene (0.400 mmol), $PhSiH_3$ (0.500 mmol), $Co(acac)_2$ (5.0 μmol), xantphos (5.0 μmol), THF (1 mL), rt, 6 h; yield of isolated product; 1,2/1,4 ratios refer to 1,2-/1,4-hydrosilylation, ratios in brackets are *E*/*Z* ratios of conjugated butadiene reagents. [b] Reactions were conducted at 5 °C for 24 h. [c] 3 mol % catalyst, rt, and 48 h.



Scheme 2 Hydrosilylation of stereodefined diene by $Co(acac)_2$/xantphos

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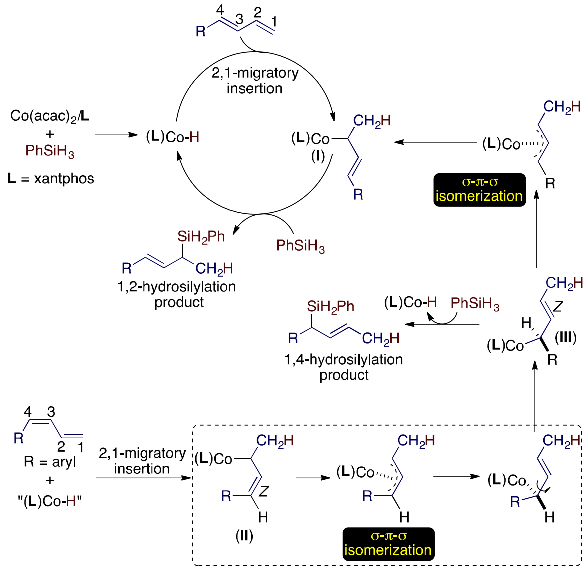
isomer. To provide insight into the isomerization of the internal *Z*-alkene in the diene to the *E*-alkene in product **1a**, we subsequently conducted a deuterium-labelling experiment using the (*E*/*Z*)-isomers and $PhSiD_3$ (Scheme 2B) and found that deuterium was solely incorporated onto the methyl group of **1a** and **2a**. This lack of deuterium incorporation into the internal vinylic carbons suggests that this *E*/*Z*-isomerization through migratory insertion of *Z*-alkene into a Co-H species followed by β-H elimination,[12] as indicated in Scheme 2C, is unlikely. Furthermore, we also tested the reaction of (*E*)-isomer with $PhSiD_3$ and the same deuterium incorporation was observed (Scheme 2D).

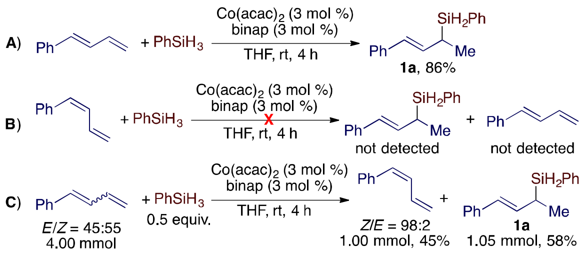
Based on the results of experiments in Scheme 2 and the precedent of Co-catalyzed hydrosilylation of alkenes,[4f,6] we proposed a hydrometalation pathway with a Co(I)-H intermediate for this Co-catalyzed Markovnikov hydrosilylation of conjugated dienes (Scheme 3). 2,1-Migratory insertion of (*E*)-diene into a Co-H species forms an allylcobalt intermediate **I**, which turns over with $PhSiH_3$ to release the allylsilane product and to regenerate the Co-H species.



Scheme 3 Proposed Catalytic Pathways for this Co-Catalyzed Stereoconvergent Markovnikov Hydrosilylation of Dienes

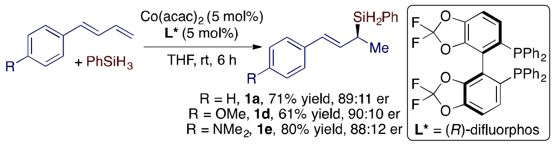
For the hydrosilylation of (*Z*)-dienes, 2,1-migratory insert of (*Z*)-dienes occurs to generate an allylcobalt species **II**, which undergoes σ-π-σ isomerization to form the allylcobalt intermediate **III**.[13] This allylcobalt species reacts with $PhSiH_3$ to give a 1,4-hydrosilylation product. In addition, the allylcobalt species **III** also undergoes σ-π-σ isomerization to generate the allylcobalt intermediate **I**. and this explains the observed stereoconvergency of (*Z*/*E*)-diene hydrosilylation. Both allylcobalt species **I** and **III** can react with $PhSiH_3$ to generate allylsilane products and the difference in the sterics around the Co-C bonds in these two allylcobalt specis may account for the product ratio observed for the reaction listed in Scheme 2A.

After developing this stereoconvergent hydrosilylation reaction, we rationalized that the separation of a (*Z*)-diene from *Z*/*E*-diene mixtures could be achieved if we could identify a cobalt catalyst that can convert only the (*E*)-isomer of dienes. We tested various cobalt catalysts generated from the combination of $Co(acac)_2$ and bisphosphine ligands for this purpose. To our delight, we found that the cobalt complex from $Co(acac)_2$/binap was active for Markovnikov 1,2-hydrosilylation of (*E*)-1-phenyl-1,3-diene (Scheme 4A) but did not catalyze the hydrosilylation or the isomerization of (*Z*)-1-phenyl-1,3-diene (Scheme 4B). Then we conducted this hydrosilylation reaction with a *E*/*Z*-mixture of 1-phenyl-1,3-diene (Scheme 4C). As expected, this reaction afforded (*E*)-allylsilane **1a** in 58% isolated yield and (*Z*)-1-phenyl-1,3-diene was recovered in 45% isolated yield with *Z*/*E* ratio of 98:2.



Scheme 4 Hydrosilylation of *E*/*Z*-mixture of dienes by $Co(acac)_2$/binap

We subsequently studied cobalt catalysts generated from $Co(acac)_2$ and chiral bisphosphine ligands in order to develop an asymmetric Markovnikov 1,2-hydrosilylation of conjugated dienes.[14] After evaluating various chiral phosphine ligands (see ESI for the details), we found that the hydrosilylation of *trans*-diene with $PhSiH_3$ conducted with $Co(acac)_2$ and (*R*)-difluorphos proceeded smoothly to afford the corresponding allylsilanes in good yield and good *er* (eq 2).



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Conclusions

In summary, we have developed the first Co-catalyzed Markovnikov 1,2-hydrosilylation of conjugated dienes with the catalyst generated from $Co(acac)_2$ and xantphos. A broad scope of *trans*-dienes underwent this Markovnikov hydrosilylation to afford (*E*)-allylsilanes in high isolated yields and excellent regioselectivities (*b*/*l* = >99:1). In addition, (*E*/*Z*)-isomeric 1,3-dienes reacted in a stereoconvergent manner to form (*E*)-allkylsilanes with good to excellent regioselectivity (ratio of 1,2/1,4-hydrosilylation up to 99:1). This stereoconvergence was resulted from a σ-π-σ isomerization of the allkylcobalt intermediate. In particular, we also identified a cobalt catalyst, $Co(acac)_2$/binap, for selectively converting the

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(*E*)-isomer of a mixture of (*E*/*Z*)-isomers, and this allows the separation of (*Z*)-dienes from a mixture of (*E*/*Z*)-dienes.

Experimental Details

General Procedures for Stereoconvergent Hydrosilylation of (*E*/*Z*)-Dienes

In an Ar-filled glovebox, a mixture of Co(acac)$_2$ (5.0 μmol) and xantphos (5.0 μmol) in THF (1 mL) was added into a 4 mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 mins prior adding phenylsilane (0.500 mmol) and (*E/Z*)-1,3-dienes (0.400 mmol) successively. The vial was removed from the glove box, and the mixture was stirred at room temperature for 6 hours. After that, the crude reaction mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of ethyl acetate and hexane as eluent. The conditions for flash chromatography and data for characterization of the products are listed in the ESI.

Acknowledgement

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The first transition metal-catalyzed stereoconvergent Markovnikov 1,2-hydrosilylaiton of (*E*/*Z*)-dienes was effectively achieved with excellent *E*-selectivities using a cobalt catalyst.