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Letter

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# Cobalt-Catalyzed (*E*)-Selective *anti*-Markovnikov Hydrosilylation of Terminal Alkynes

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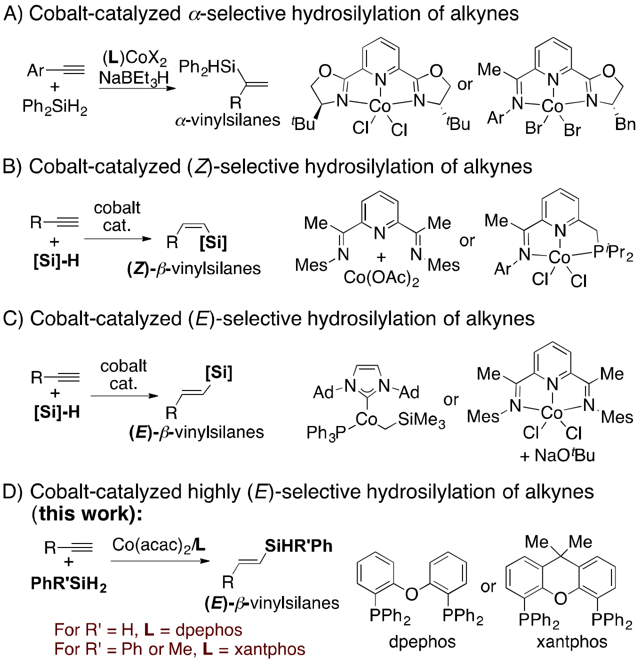
**ABSTRACT:** We report a regio- and stereoselective hydrosilylation of terminal alkynes with catalysts generated from bench-stable $Co(acac)_2$ and bisphoshpine ligands. The cobalt catalyst precursors are activated by the reaction with hydrosilanes, and air-sensitive activators, such as Grignard reagents or $NaBHEt_3$, are not required for catalyst activation. A wide range of aromatic and aliphatic terminal alkynes underwent this cobalt-catalyzed hydrosilylation, affording the corresponding *(E)*-vinylsilanes in high yields with high regio- and stereoselectivity. These reactions show good functional group compatibility and can be readily scaled up to gram-scales without using a dry box. Deuterium-labeling experiments suggest a *cis*-addition of hydrosilanes to alkynes.

KEYWORDS: *cobalt, hydrosilylation, alkynes, vinylsilanes, homogenous catalysis*

Vinylsilanes are synthetically valuable building blocks in organic synthesis due to their versatile reactivity, low toxicity, high stability, and ease for manipulations.[1] Metal-catalyzed hydrosilylation of alkynes will be one of the most atom-economic and straightforward approaches to prepare these vinylsilanes.[2] One challenge in developing the hydrosilylation reaction of alkynes is to control both regio- and stereoselectivity because this reaction can potentially produce multiple products, such as $\alpha$-, (*Z*)-$\beta$-, and (*E*)-$\beta$-vinylsilanes. Over past decades, however, a series of transition metal catalysts have been successfully developed to address these selectivity issues.[2c] The other challenge is to identify catalysts that are selective for alkyne hydrosilylation with primary silanes ($RSiH_3$) to produce dihydrovinylsilanes, which are important monomers for the synthesis of poly(silylenes).[3] However, selective transition metal catalysts that can catalyze the hydrosilylation of alkynes with primary silanes to produce stereodefined dihydrovinylsilanes are still rare.

Catalysts based on noble metals have been extensively studied for alkyne hydrosilylation with tertiary hydrosilanes $R_3SiH$ to produce $\alpha$-,[4] (*Z*)-$\beta$-,[5] or (*E*)-$\beta$-vinylsilanes[6] with high regio- and stereoselectivity. When primary silanes $RSiH_3$ are employed for the hydrosilylation of alkynes, however, these reactions tend to produce a mixture of multiple vinylsilane products, such as mono(vinyl)silanes, di(vinyl)silanes, and tri(vinyl)silanes.[7] This is because mono(vinyl)silane and di(vinyl)silane products are active enough to further react with alkynes to form higher order vinylsilanes in the presence of these noble metal catalysts.

Recently, there has been a growing interest in replacing noble metal catalysts with base metal catalysts due to increasing concerns on long-term sustainability.[8] With its low cost, high natural abundance, and low toxicity, cobalt is a particularly appealing alternative.[9] Accordingly, the development of cobalt-catalyzed hydrosilylation reactions of unsaturated organic molecules is undergoing an explosive growth.[10] Particularly, cobalt catalysts for selective production of $\alpha$-, (*Z*)-$\beta$-, and (*E*)-$\beta$-vinylsilanes have been identified for hydrosilylation reactions of alkynes (Scheme 1).



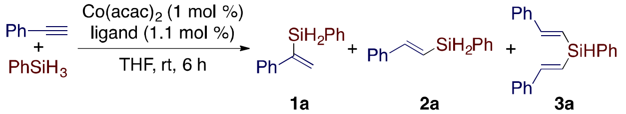
**Scheme 1. Regio- and Stereoselective Co-Catalyzed Hydrosilylation of Terminal Alkynes**

In 2016, Lu and Huang independently developed a highly selective cobalt-catalyzed Markovnikov hydrosilylation of alkynes with $Ph_2SiH_2$ to access α-vinylsilanes (Scheme 1A).[11] In addition, highly *Z*-selective Co-catalyzed hydrosilylation of alkynes has also been developed, and both primary and secondary hydrosilanes could be used for this transformation (Scheme 1B).[12] In 2014, Deng reported a highly (*E*)-selective hydrosilylation of alkynes with $Ph_2SiH_2$ using a carbene-supported cobalt alkyl complex (Scheme 1C).[13] However, this

Co-catalyzed hydrosilylation of alkynes proceeds with low selectivity when primary hydrosilane $PhSiH_3$ is used, and produces a mixture of $\alpha$-, (*Z*)-$\beta$-, and (*E*)-$\beta$-vinylsilanes. In 2017, Thomas reported the hydrodrosilylation of 1-octyne with $PhSiH_3$ using ($^{mes}$PDI)$CoCl_2$/NaO$^t$Bu, and this reaction produces a mixture of (*Z*)-$\beta$- and (*E*)-$\beta$-vinylsilanes with a modest *E*-selectivity (Scheme 1C).[14] Therefore, it still remains a challenge to develop catalytic hydrosilylation of alkynes with a primary hydrosilane. Driven by our continuous interest in developing selective base metal catalysis,[10i,j,m,12a,15] we herein report a Co-catalyzed highly regio- and stereoselective hydrosilylation of terminal alkynes with both primary and secondary hydrosilanes PhR'$SiH_2$ (R' = H, Me, Ph) to prepare (*E*)-vinylsilanes (Scheme 1D).

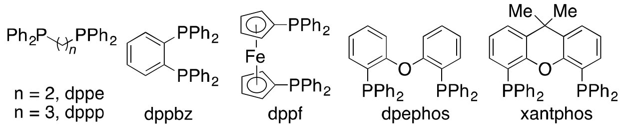
We started this cobalt-catalyzed hydrosilylation of alkynes by evaluating the conditions for the reaction between phenylacetylene and $PhSiH_3$. Cobalt catalysts are generated from bench-stable Co(acac)$_2$ and bisphosphine ligands and activated by the reaction with $PhSiH_3$. These reactions were conducted with 1 mol % cobalt catalyst at room temperature for 6 h, and the selected examples are summarized in Table 1. In general, these reactions occurred to full conversion of phenylacetylene and afforded three products (**1a**, **2a**, and **3a**) with varied ratios, and product **3a** was generated by hydrosilylation of phenylacetylene with vinylsilane **2a**.

**Table 1. Evaluation of the Reaction Conditions for Hydrosilylation of Phenylacetylene with $PhSiH_3$[a]**



**1a** **2a** **3a**

| entry | ligand | equiv. ($PhSiH_3$) | conv. (%)[b] | ratio (**1a**:**2a**/**3a**)[b] | yield of **2a** (%)[b] |
|---|---|---|---|---|---|
| 1 | dppe | 1.0 | >99 | 9:69:22 | 63 |
| 2 | dppp | 1.0 | >99 | 2:68:30 | 61 |
| 3 | dppbz | 1.0 | >99 | 16:72:12 | 67 |
| 4 | dppf | 1.0 | >99 | 2:91:8 | 84 |
| 5 | xantphos | 1.0 | >99 | 4:41:55 | 33 |
| 6 | dpephos | 1.0 | >99 | 3:83:14 | 77 |
| **7** | **dpephos** | **1.5** | **>99** | **1:98:1** | **90 (83[c])** |
| 8 | dpephos | 2.0 | >99 | 2:98:-- | 94 |
| 9 | dpephos | 0.5 | 93 | --:--:>99 | -- (84[d]) |
| 10 | xantphos | 0.5 | 97 | --:--:>99 | -- (78[d]) |

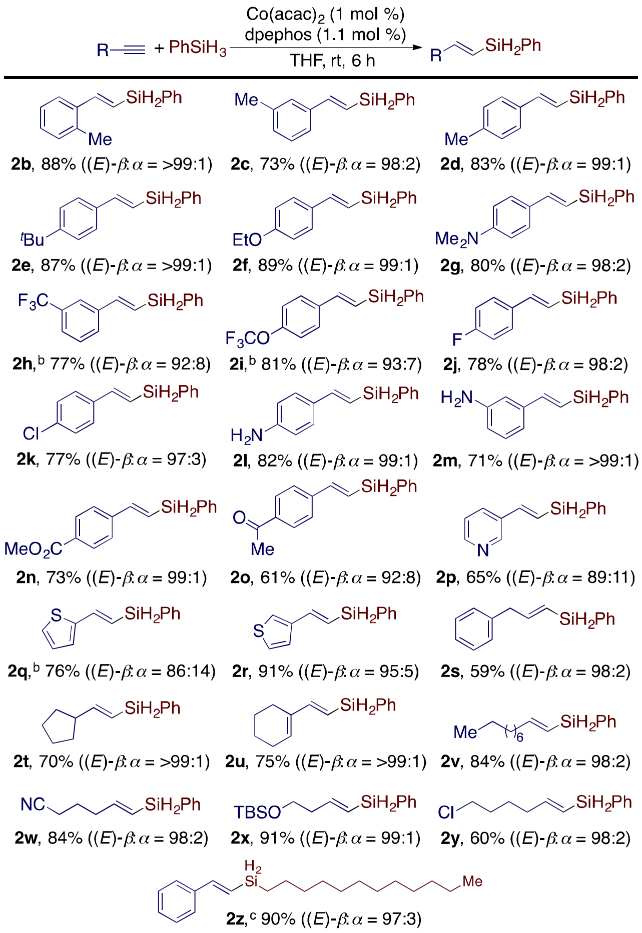


[a] Conditions: phenylacetylene (0.500 mmol), $PhSiH_3$ (0.500-1.00 mmol), Co(acac)$_2$ (5.0 μmol), ligand (5.5 μmol), THF (1 mL), room temperature, 6 h; [b] Determined by GC analysis with dodecane as the internal standard; [c] Isolated yield of **2a**; [d] Isolated yield of **3a**.

The reactions conducted with the combination of Co(acac)$_2$ and various bisphosphine ligands afforded a mixture of three vinylsilane products **1a**–**3a** when a 1:1 ratio of phenylacetylene and $PhSiH_3$ was used (entries 1–6 in Table 1). Monitoring these reactions with GC-MS analysis revealed that product **3a** was generated only in the late stage of these reactions. Based on these analyses, we rationalized that increasing the amounts of $PhSiH_3$ could improve the selectivity for product **2a** because $PhSiH_3$ can compete with hydrosilane **2a** for the reaction with phenylacetylene. Subsequently, we tested the hydrosilylation of phenylacetylene with varied amounts of $PhSiH_3$ in the presence of 1 mol % of Co(acac)$_2$ and dpephos (entries 6−8 in Table 1). As expected, reactions with 1.5 or 2 equivalents of $PhSiH_3$, relative to phenylacetylene, afforded the product **2a** with excellent selectivity (entries 7 and 8 in Table 1). In addition, we also tested the reactions with a 2:1 ratio of phenylacetylene and $PhSiH_3$, and these reactions afforded the product **3a** with a complete selectivity (entries 9 and 10 in Table 1).

Under the identified conditions (entry 7 in Table 1), we studied the scope of terminal alkynes that undergo this cobalt-catalyzed *E*-selective hydrosilylation and the results are summarized in Table 2. In general, a wide range of terminal alkynes containing electronically varied aromatic (**1b**–**1r**) and aliphatic (**1s**–**1y**) substituents reacted smoothly with 1 mol % Co(acac)$_2$/dpephos at room temperature, yielding the corresponding (*E*)-vinylsilanes (**2b**–**2y**) in high yields (59–91%) with high regioselectivity ((*E*)-$\beta$:$\alpha$ up to >99:1). The GC-MS analysis on the crude mixtures of these reactions indicated the formation of trace amounts (< 3%) of the corresponding bis(vinyl)silanes.

**Table 2. The Scope of Terminal Alkynes for Hydrosilylation Reactions with $PhSiH_3$[a]**



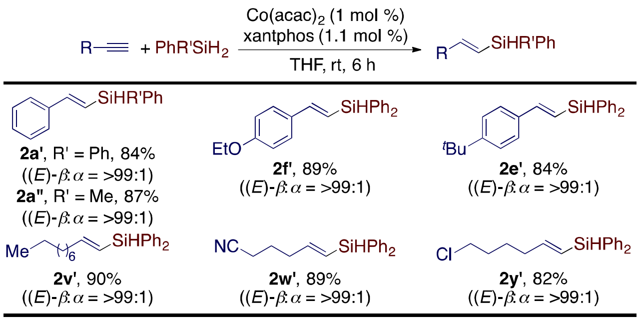
**2b**, 88% ((*E*)-$\beta$:$\alpha$ = >99:1)
**2c**, 73% ((*E*)-$\beta$:$\alpha$ = 98:2)
**2d**, 83% ((*E*)-$\beta$:$\alpha$ = 99:1)
**2e**, 87% ((*E*)-$\beta$:$\alpha$ = >99:1)
**2f**, 89% ((*E*)-$\beta$:$\alpha$ = 99:1)
**2g**, 80% ((*E*)-$\beta$:$\alpha$ = 98:2)
**2h**,[b] 77% ((*E*)-$\beta$:$\alpha$ = 92:8)
**2i**,[b] 81% ((*E*)-$\beta$:$\alpha$ = 93:7)
**2j**, 78% ((*E*)-$\beta$:$\alpha$ = 98:2)
**2k**, 77% ((*E*)-$\beta$:$\alpha$ = 97:3)
**2l**, 82% ((*E*)-$\beta$:$\alpha$ = 99:1)
**2m**, 71% ((*E*)-$\beta$:$\alpha$ = >99:1)
**2n**, 73% ((*E*)-$\beta$:$\alpha$ = 99:1)
**2o**, 61% ((*E*)-$\beta$:$\alpha$ = 92:8)
**2p**, 65% ((*E*)-$\beta$:$\alpha$ = 89:11)
**2q**,[b] 76% ((*E*)-$\beta$:$\alpha$ = 86:14)
**2r**, 91% ((*E*)-$\beta$:$\alpha$ = 95:5)
**2s**, 59% ((*E*)-$\beta$:$\alpha$ = 98:2)
**2t**, 70% ((*E*)-$\beta$:$\alpha$ = >99:1)
**2u**, 75% ((*E*)-$\beta$:$\alpha$ = >99:1)
**2v**, 84% ((*E*)-$\beta$:$\alpha$ = 98:2)
**2w**, 84% ((*E*)-$\beta$:$\alpha$ = 98:2)
**2x**, 91% ((*E*)-$\beta$:$\alpha$ = 99:1)
**2y**, 60% ((*E*)-$\beta$:$\alpha$ = 98:2)
**2z**,[c] 90% ((*E*)-$\beta$:$\alpha$ = 97:3)

[a] Conditions: alkyne (0.500 mmol), $PhSiH_3$ (0.750 mmol), Co(acac)$_2$ (5.0 μmol), dpephos (5.5 μmol), THF (1 mL), room temperature, 6 h, and isolated yields after column chromatography. [b] dppf ligand was used instead of dpephos ligand. [c] *n*-$C_{12}H_{25}SiH_3$ was used instead of $PhSiH_3$.

The data in Table 2 indicate that aliphatic alkynes reacted with excellent regioselectivities ((*E*)-$\beta$:$\alpha$ > 98:2) to afford the corresponding (*E*)-vinylsilanes in good yields (**2s**–**2y**). However, the electronic properties of aryl groups in aromatic alkynes have noticeable effects on the regioselectivity of this hydrosilylation reaction. For example, aromatic alkynes containing electro-rich aryl groups (**2b**–**2g**) reacted with higher regioselectivities than those containing electro-deficient aryl groups (**2h**, **2o** and **2p**). This Co-catalyzed hydrosilylation of alkynes tolerates a range of functionalities, including ether (**2f**), tertiary amine (**2g**), trifluoromethylether (**2i**), chloro (**2k** and **2y**), primary aniline (**2l** and **2m**), carboxylic ester (**2n**), ketone (**2o**), cyano (**2w**), and siloxy (**2x**) moieties. In addition, nitrogen- and sulfur-containing heteroaromatic alkynes reacted with high yields and high regio- and stereoselectivity (**2p**–**2r**). Primary alkylsilanes also reacted termianl alkynes under the identified conditions. For example, the hydrosilylation of phenylacetylene with *n*-dodecylsilane afforded the desired (E)-vinylsilane **2z** in 90% isolated yield with high regioselectivity.

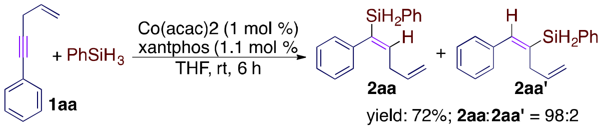
We also tested this Co-catalyzed hydrosilylation with a secondary hydrosilane $Ph_2SiH_2$, and the reactions did not proceed when conducted with the catalyst generated from $Co(acac)_2$ and dpephos. However, when catalyzed by the combination of $Co(acac)_2$/xantphos, these reactions occurred smoothly at room temperature in the presence of 1 mol % cobalt catalyst. We chose several alkynes from Table 2 to study the scope of this hydrosilylation with $Ph_2SiH_2$ and these examples are listed in Table 3. Both aromatic and aliphatic alkynes reacted to afford the corresponding (*E*)-vinylsilanes in high isolated yields and with excellent regioselectivity.

**Table 3. Co-Catalyzed Hydrosilylation of Terminal Alkynes with $Ph_2SiH_2$[a]**



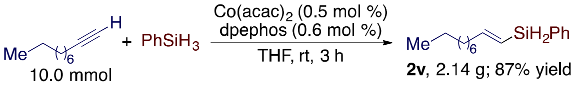
[a] Conditions: alkyne (0.500 mmol), $Ph_2SiH_2$ (0.550 mmol), $Co(acac)_2$ (5.0 μmol), dpephos (5.5 μmol), THF (1 mL), room temperature, 6 h, and isolated yields after column chromatography.

Internal alkynes were also studied for this cobalt-catalyzed hydrosilylation. For example, pent-4-en-1-yn-1-ylbenzene (**1aa**), a 1,4-enyne containing an internal alkyne group, smoothly reacted with $PhSiH_3$ in the presence of 1 mol % $Co(acac)_2$ and xantphos at room temperature, affording a 1,4-dienylsilane product **2aa** in 72% isolated yield with an excellent regioselectivity (eq. 1).

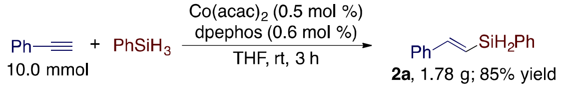


(1)

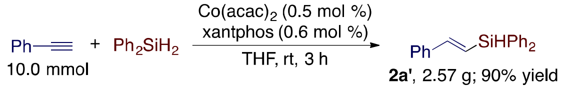
To highlight the utility of this practical protocol for the synthesis of (*E*)-vinylsilane, we conducted gram-scale reactions without using a dry box because both $Co(acac)_2$ and phosphine ligands are bench-stable (See the Supporting Information for the detailed procedure). The reactions of 1-octyne or phenylacetylene and $PhSiH_3$ on a 10 mmol scale in the presence of 0.5 mol % $Co(acac)_2$ and dpephos proceeded to full conversion at room temperature in 3 h and afforded the corresponding (*E*)-vinylsilanes **2v** and **2a** in 87% and 85% isolated yields, respectively (eqs. 2 and 3). Similarly, a 10 mmol scale reaction of phenylacetylene with secondary hydrosilane $Ph_2SiH_2$ catalyzed by 0.5 mol % $Co(acac)_2$ and xantphos produced **2a'** in a 90% isolated yield (eq. 4). In addition, we also showed that the tertiary (*E*)-vinylsilane **2v'** smoothly underwent a Pd-catalyzed cross-coupling with 4'-iodoacetophenone at room temperature, affording the internal (*E*)-vinylarene **4** in a 85% isolated yield (eq. 5).



(2)



(3)



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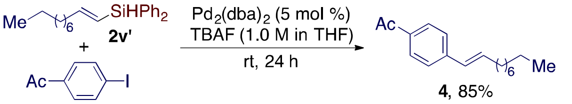

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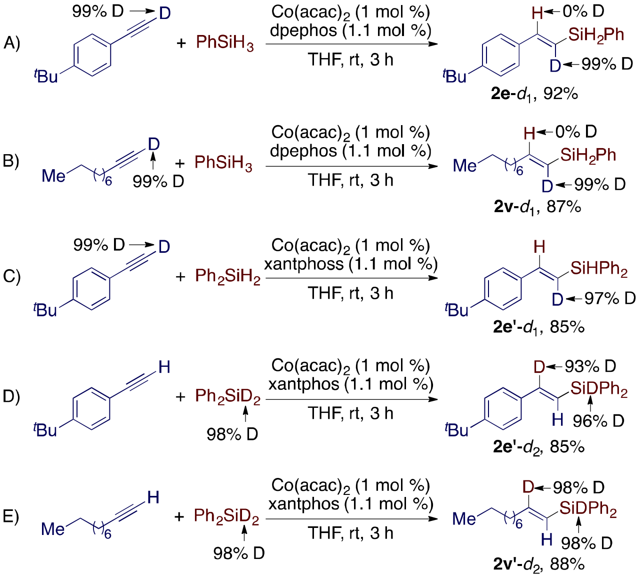
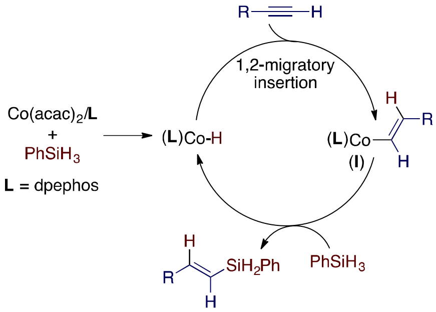


**Scheme 2. Deuterium-Labeling Experiments**

To get some insights on this Co-catalyzed (*E*)-selective hydrosilylation of alkynes, we conducted a series of deuterium-labeling experiments, and the results are summarized in Scheme 2. The hydrosilylation of 4-*tert*-butylphenylacetylene-$d_1$ or 1-decyne-$d_1$ with $PhSiH_3$ under the standard conditions produced **2e**-$d_1$ or **2v**-$d_1$ with high *E*-selectivity, and the deuterium atoms of these two vinylsilanes were exclusively located at the $\beta$-vinylic carbon (Scheme 2A and 2B). Similar results were obtained for the hydrosilylation reaction of 4-*tert*-butylphenylacetylene-$d_1$ with $Ph_2SiH_2$ (Scheme 2C). We also studied the hydrosilylation of 4-*tert*-butylphenylacetylene or 1-decyne with $Ph_2SiD_2$ under the standard conditions. These reactions afforded vinylsilanes **2e'**-$d_2$ and **2v'**-$d_2$ in high isolated yields with excellent *E*-selectivity ((*E*)-$\beta$:$\alpha$ = 99:1), and the deuterium atoms of **2e'**-$d_2$ and **2v'**-$d_2$ are located at the α-vinylic carbon and silicon of these vinylsilanes (Scheme 2D and 2E). The results of these deuterium-labeling experiments suggest that this Co-catalyzed hydrosilylation of alkynes proceed through a *cis*-addition of Si-H to an alkyne group.

Based on the precedent of cobalt-catalyzed hydrosilylation of unsaturated molecules[9c,10i], and the results of the series of deuterium labeling experiments, we propose a catalytic cycle depicted in Scheme **3** for this Co-catalyzed alkyne hydrosilylation.[16] The activation of Co(acac)$_2$ with hydrosilane in the presence of dpephos generates a cobalt hydride species (**L**)Co-H. 1,2-Migratory insertion of alkynes into this Co-H intermediate produces a vinylcobalt species (**I**), which turns over with hydrosilane to afford the *(E)*-vinylsilane products and regenerate the catalytically active cobalt hydride (**L**)Co-H.



**Scheme 3. The Proposed Catalytic Cycle for this Co-Catalyzed Hydrosilylation of Alkynes**

In summary, we have developed a convenient and effective protocol for the synthesis of (*E*)-vinylsilanes through a cobalt catalyzed *anti*-Markovnikov hydrosilylation of terminal alkynes. The cobalt catalysts are generated in situ from bench stable Co(acac)$_2$ and dpephos or xantphos ligands, and are activated by the reaction with hydrosilane substrates. A broad range of alkynes containing either aromatic or aliphatic substituents underwent this hydrosilylation reaction to afford *(E)*-vinylsilanes in high isolated yields with high regio- and stereoselectivity. In addition, this reaction could be conducted on a gram scale without the loss of selectivity with a reduced catalyst loading (0.5 mol %). Thus, this Co-catalyzed hydrosilylation provides a general and practical approach to prepare functionalized (*E*)-vinylsilanes with commercially available abundant base-metal catalysts.

## ASSOCIATED CONTENT

### Supporting Information

Experimental details, characterization data, and copies of NMR spectra of all compounds. This material is available free of charge on the ACS Publications website at http://pubs.acs.org.

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### Note

The authors declare no competing financial interest.

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(16) For a discussion on an alternative mechanism involving a cobalt-silyl intermediate, see the Supporting Information.

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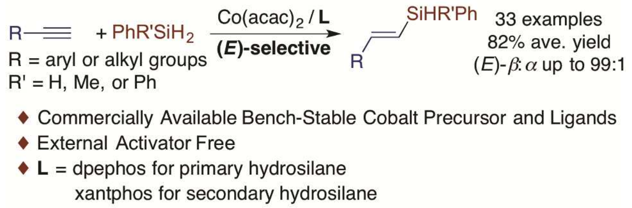

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