Vinylsilanes

International Edition: DOI: 10.1002/anie.201605615
German Edition: DOI: 10.1002/ange.201605615

Cobalt-Catalyzed Alkyne Hydrosilylation and Sequential Vinylsilane Hydroboration with Markovnikov Selectivity

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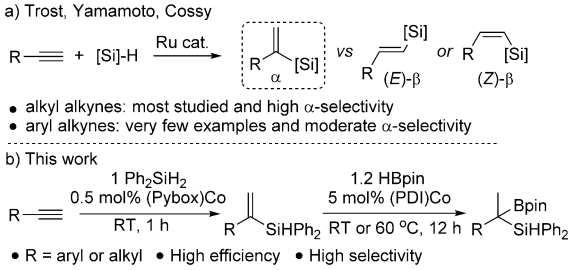
Abstract: *A pyridinebis(oxazoline) cobalt complex is a very efficient precatalyst for the hydrosilylation of terminal alkynes with Ph_2SiH_2, providing α-vinylsilanes with high (Markovnikov) regioselectivity and broad functional-group tolerance. The vinylsilane products can be further converted into geminal borosilanes through Markovnikov hydroboration with pinacolborane and a bis(imino)pyridine cobalt catalyst.*

Vinylsilanes are versatile synthetic building blocks owing to their stability, ease of handling, non-toxicity, and propensity to undergo a variety of transformations.[1] Alkyne hydrosilylation is the most atom-economic method to access such compounds.[2] One important issue in the hydrosilylation of terminal alkynes is the control of the regio- and stereochemistry because the reaction can generate (*E*)-β-, (*Z*)-β-, and α-vinylsilanes. Indeed, although many catalysts can be used for anti-Markovnikov selective hydrosilylation to form β-vinylsilanes,[3] reactions of alkynes without a directing group that proceed with Markovnikov selectivity (α-selectivity) are rare.[4] In the early 2000s, the groups of Trost[4a,b] and Yamamoto[4c] independently reported the Markovnikov hydrosilylation of terminal alkyl alkynes to form α-vinylsilanes with pentamethylcyclopentadiene ruthenium catalysts. Cossy and co-workers showed that Ru alkylidene complexes also catalyze the hydrosilylation of alkyl alkynes to form α-vinylsilanes with a high degree of regioselectivity.[4d] However, whereas these Ru catalysts gave high Markovnikov regioselectivity when alkyl alkynes were used as the substrates, α-selective hydrosilylations of terminal aryl alkynes have hardly been described (Scheme 1 a).[4,5]

The metal-catalyzed hydroboration of vinylsilanes can generate borosilanes, which are likely to be valuable synthetic intermediates for the construction of complex molecules.[6] Whereas several methods are available for the synthesis of vicinal borosilanes,[7] there are only few approaches towards geminal borosilanes,[8] and methods that provide access to derivatives with a tetrasubstituted carbon center are particularly rare.[9] Driven by our interest in developing base-metal catalysts for alkene/alkyne functionalizations,[10,11] we herein report a method for the Markovnikov hydrosilylation of terminal alkynes with a pyridinebis(oxazoline) Co catalyst. The process is highly selective for the formation of α-vinylsilanes from challenging terminal aryl alkynes. Furthermore, in the presence of a bis(imino)pyridine Co catalyst, the resulting α-vinylsilanes underwent selective Markovnikov hydroboration to produce geminal borosilanes with a tetrasubstituted carbon center (Scheme 1 b).



Scheme 1. Markovnikov hydrosilylation of terminal alkynes and hydroboration of vinylsilanes.

We commenced our study by examining Co and Fe catalysts with tridentate ligands for the hydrosilylation of phenylacetylene **1a** with Ph_2SiH_2 (Table 1). In the presence of our iminopyridine-oxazoline (IPO) cobalt complex (IPO)$CoCl_2$ (**3a**; 2 mol%)[10g] and $NaBHEt_3$ (4 mol%) as the catalyst activator in THF at room temperature, α-vinylsilane **2a** and (*E*)-β-vinylsilane (*E*)-**2a′** were formed as the major and minor product, respectively [**2a**/(*E*)-**2a′** = 81:19, 74% combined yield]. The corresponding (*Z*)-β-vinylsilane (*Z*)-**2a′** was not observed (entry 1). Switching the precatalyst to a Co complex with a PNN ligand (**4a**)[10f] resulted in a slightly improved regioselectivity for the Markovnikov product (**2a**/(*E*)-**2a′** = 87:13, 66% yield; entry 3). Whereas (IPO)Fe complex **3b** was found to be inactive (entry 2), the (PNN)Fe complex **4b** gave the three isomers **2a**, (*E*)-**2a′**, and (*Z*)-**2a′** in a 47:20:33 ratio (60% combined yield; entry 4). The bis(imino)pyridine Co and Fe complexes (PDI)$CoCl_2$ (**5a**) and (PDI)$FeBr_2$ (**5b**)[12] (2 mol%) also did not effect the desired hydrosilylation (entries 5 and 6).[13]

To further improve the catalytic efficiency and the Markovnikov selectivity, a series of pyridinebis(oxazoline) Co complexes, (^{R}PyBox)$CoCl_2$ (**6a** and **6c–6g**), and one Fe complex (**6b**) were prepared (see the Supporting Information for details and Table 1 for the single-crystal structure of **6c**).[14] Among them, the Co complexes with *i*Pr (**6a**) and *t*Bu (**6c**) substituents at the oxazoline rings gave the best activity and selectivity (entries 7 and 9). The reaction proceeded to completion within one hour using only 0.5 mol% of **6c**, and furnished the desired product in 94% yield with a **2a**/(*E*)-**2a′** ratio of 93:7 (entry 10). The catalyst activator is not limited to $NaBHEt_3$ as reactions with MeLi, $TMSCH_2Li$, MeMgBr, or PhMgBr (2 equiv relative to Co) as the activator all gave the

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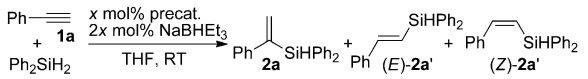
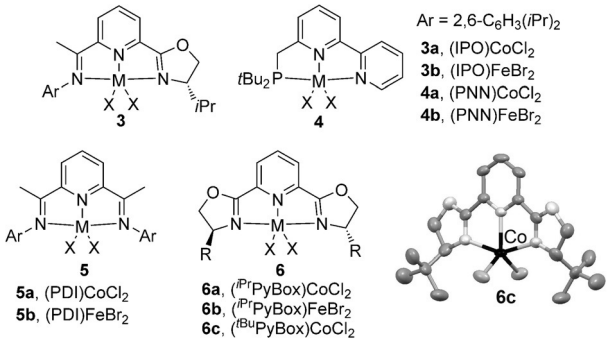
Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201605615.

Table 1: Catalyst screen for the hydrosilylation of **1a** with Ph_2SiH_2.[a]



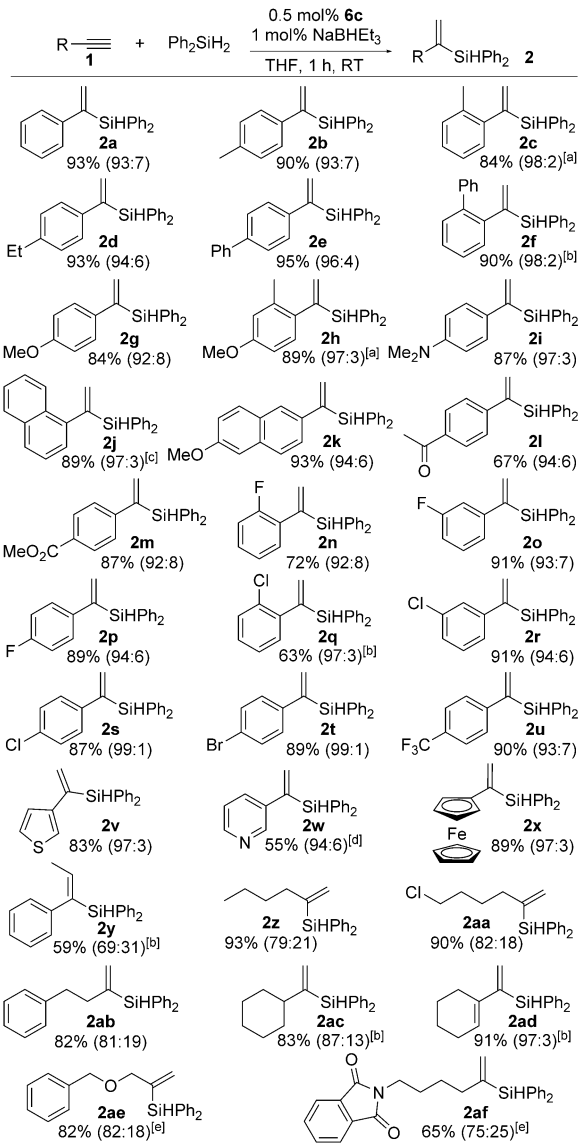
Entry	Catalyst (mol%)	*t* [h]	Yield [%]	**2a**/(*E*)-**2a′**/(*Z*)-**2a′**
1	**3a** (2)	12	74	81:19:0
2	**3b** (2)	12	< 5[b]	–
3	**4a** (2)	12	66	87:13:0
4	**4b** (2)	12	60	47:20:33
5	**5a** (2)	12	< 5[b]	–
6	**5b** (2)	12	< 5[b]	–
7	**6a** (2)	12	93	93:7:0
8	**6b** (2)	12	< 5[b]	–
9	**6c** (2)	12	92	94:6:0
10	**6c** (0.5)	1	94	93:7:0

[a] Reaction conditions: **1a** (0.5 mmol), $PhSiH_3$ (0.5 mmol), THF (1 mL). Yields of isolated products are given unless otherwise noted. The product ratios were determined by GC analysis. [b] Determined by GC analysis.



desired product in high yield and selectivity (see the Supporting Information). The Fe analogue (^{iPr}PyBox)FeBr (**6b**), however, gave only a trace amount of the hydrosilylation product (entry 8).

Utilizing the (PyBox)Co complex **6c** as the precatalyst, we examined the alkyne substrate scope of the Markovnikov hydrosilylation (Scheme 2). The catalyst enabled the hydrosilylation of a diverse array of terminal aryl alkynes with Ph_2SiH_2, providing the corresponding α-vinylsilanes with high regioselectivities [α/(*E*)-β ratios of 92:8 to 99:1]; the (*Z*)-β isomers were never observed. Aryl alkynes bearing either electron-donating or electron-withdrawing groups were effectively hydrosilylated, and substituents in the *para*, *meta*, and *ortho* positions of the aryl ring are compatible with the reaction conditions. However, substrates with *ortho* substituents appeared to be less reactive than their *para*- or *meta*-substituted analogues, and thus required longer reaction times (2 h for **2c** and **2h**) or higher catalyst loadings (2 mol% for **2f** and **2q**). On the other hand, *ortho*-substituted alkynes generally gave higher α-selectivities than the sterically less demanding *para*- or *meta*-substituted analogues (e.g., **2c**: 98:2 vs. **2b**: 93:7; **2h**: 97:3 vs. **2g**: 92:8), but the reasons for this "*ortho* effect" on the selectivity remain to be elucidated. Halogen-substituted aryl alkynes, including the *para*-bromo-substituted one, underwent Markovnikov hydrosilylation in high yields, and dehalogenation products were not observed. Tertiary amine (**2i**), ether (**2g**, **2h**, **2k**), ester (**2m**), and even



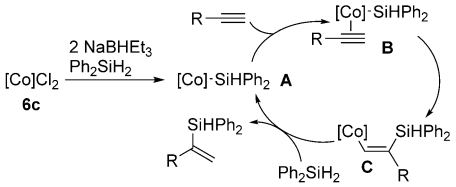
Scheme 2. Markovnikov hydrosilylation of various alkynes. Reaction conditions: **1** (0.5 mmol), Ph_2SiH_2 (0.5 mmol), **6c** (0.5 mol%), $NaBHEt_3$ (1 mol%), THF (2 mL), RT, 1 h. Yields of isolated products are given. The product ratios [α/(*E*)-β] were determined by GC analysis. [a] 2 h. [b] With 2 mol% **6c** for 10 h. [c] With 1 mol% **6c**. [d] With 3 mol% **6c** for 12 h. [e] With 1 mol% **6c** for 5 h. Product ratio determined by ^{1}H NMR spectroscopy.

ketone (**2l**) functional groups were also tolerated. Heteroaromatic alkynes, such as 3-ethynylthiophene and 3-ethynylpyridine, gave the corresponding products (**2v** and **2w**) with high site selectivity. Ferrocenyl alkyne provided the desired product **2x** in 89% yield with 97:3 selectivity. The reaction of an internal aryl alkyne, 1-phenyl-2-methylacetylene, exclusively provided the *syn* addition product **2y**, but the regioselectivity was moderate (69:31).

Terminal alkyl alkynes also underwent the hydrosilylation reaction under the optimized conditions to afford the products in good yields. The Markovnikov products were obtained as the major products, although the regioselectivity (ca. 4:1) was relatively low compared to that achieved with

terminal aryl alkynes (see above). Chloride, ether, and phthalimide moieties in the alkyl chains were tolerated as demonstrated by the formation of **2aa, 2ae**, and **2af**. The hydrosilylation of 1-ethynylcyclohexene provided the desired α-vinylsilane **2ad** in high yield with very high regioselectivity (97:3), whereas 1-ethynylcyclohexane only reacted with 87:13 selectivity (**2ac**). The preliminary data, together with the results obtained with aryl-substituted alkynes, suggest that the presence of a C=C bond in conjugation with the alkyne may have an advantageous effect on the Markovnikov selectivity.

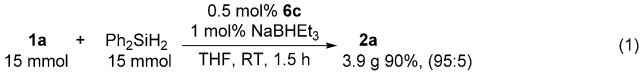
On the basis of the data of selective *syn* H/Si addition to internal alkynes (**2y**, Scheme 2) and precedents regarding relevant Co-catalyzed alkene and alkyne hydrosilylation reactions,[3k,10a,15] we propose a silyl migration mechanism involving Co^{I} silyl intermediate **A**[16] (Scheme 3). Most likely



Scheme 3. Proposed mechanism for the Co-catalyzed Markovnikov alkyne hydrosilylation.

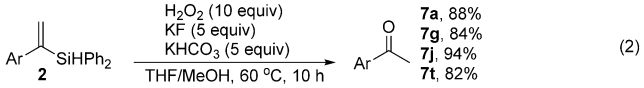
for steric reasons, the alkyne undergoes selective 1,2-insertion into the Co–Si bond to form Co alkenyl species **C**, which then reacts with Ph_2SiH_2 to form the Markovnikov product and regenerate **A**.

Using the standard reaction conditions, we developed procedures to perform the reaction on gram scale. The hydrosilylation of **1a** (15 mmol) with 1 equiv of Ph_2SiH_2 afforded 3.9 g of the hydrosilylation product (90% yield of isolated product) with 95:5 α/β selectivity [Eq. (1)]. The



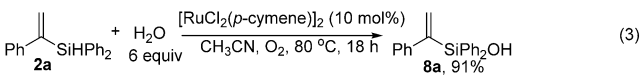
(1)

vinylsilane products can undergo various transformations. Tamao oxidation, for example, gave the corresponding ketones (**7**) in high yields [Eq. (2)]. In the presence of a Ru



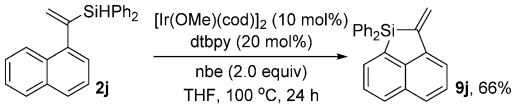
(2)

catalyst,[17] the Si–H bond in **2a** was successfully converted into a Si–OH bond, enabling the isolation of silanol **8a** in 91% yield [Eq. (3)]. Furthermore, intramolecular dehydro-



(3)

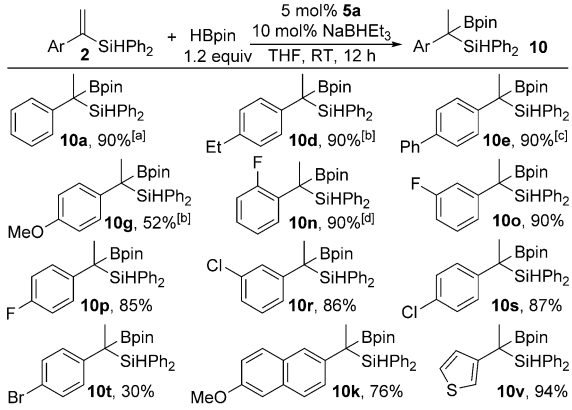
genative silylation of **2j** in the presence of an Ir catalyst[18] gave sila-acenaphthene **9j** in useful yield [Eq. (4); dtbpy = 4,4'-di-*tert*-butyl-2,2'-dipyridyl, nbe = norbornene].



(4)

More interestingly, the α-vinylsilanes react with pinacolborane (HBpin) to form geminal borosilanes **10** with excellent regioselectivity. The formation of the sterically crowded tetrasubstituted carbon center through Markovnikov hydroboration is remarkable because Lu and co-workers[19] and our group[10g] previously demonstrated that IPO Co precatalyst **3a** gave exclusively the anti-Markovnikov hydroboration products when 1,1-disubstituted aryl alkyl alkenes were used as the substrates. In contrast, a catalyst screen revealed that the Co and Fe complexes of IPO (**3a**, **3b**), PDI (**5a**, **5b**), and Pybox (**6a**, **6b**) were all selective for the formation of geminal borosilane **10a** in the reaction of **2a** with HBpin (see the Supporting Information). Among them, PDI Co complex **5a** was most effective; in the presence of this precatalyst (2 mol%) and $NaBHEt_3$ (4 mol%), **10a** was formed in 90% yield. For comparison, the reaction of α-methylstyrene with HBpin catalyzed by **5a** gave a trace amount of the anti-Markovnikov product (< 5%), but no Markovnikov product. These results indicate that substitution of the alkyl group in 1,1-disubstituted styrenes with a silyl moiety leads to an inversion of the site selectivity in the hydroboration with HBpin.

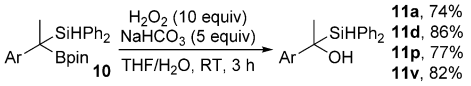
To delineate the scope of the method, we studied the hydroboration of various α-vinylsilanes with **5a** as the precatalyst (Scheme 4). All reactions were selective for the generation of the geminal borosilane, and the vicinal borosilanes were never detected.[20] Most reactions proceeded to high conversion within 12 hours at room temperature using



Scheme 4. Markovnikov hydroboration of various α-vinylsilanes. Reaction conditions: **2** (0.2 mmol), HBpin (0.24 mmol), **5a** (5 mol%), $NaBHEt_3$ (10 mol%), THF (1 mL), RT, 12 h. Yields of isolated products are given. [a] With 2 mol% **3a**. [b] At 60°C. [c] With 5 mol% (^{Mes}PDI)$CoCl_2$ as the precatalyst (^{Mes}PDI = 2,4,6-$Me_3C_6H_2N$=$CMe]_2C_5H_3N$). [d] With 10 mol% **5a**.

5 mol% of the catalyst. However, the method works more efficiently for 1,1-disubstituted aryl silyl alkenes with electron-withdrawing groups than for those bearing electron-donating groups. For instance, the reaction of a *para*-methoxy-substituted vinylsilane required an elevated temperature (60 °C) and gave product **10g** in 52% yield over 12 h, whereas the reactions of substrates with a fluoro or chloro substituent in *para* position proceeded at 25 °C to form the desired products in high yields (**10p**: 85%, **10s**: 87%) within the same time frame. Fluorine substitution of the *meta* and *ortho* positions of the aromatic ring was tolerated (**10n**: 90%, **10o**: 90%). However, the *para*-bromo-substituted vinylsilane gave the desired product **10t** in low yield (30%). Finally, substrates bearing 2-naphthyl and 3-thiophenyl substituents afforded the corresponding products in good yields (**10k**: 76%, **10v**: 94%).

The geminal borosilanes may find application in the synthesis of multifunctionalized molecules.[6] To our delight, preliminary studies showed that treatment of borosilanes **10** with H_2O_2 and $NaHCO_3$ at room temperature resulted in the selective conversion of the C–B bond into a C–OH bond while the silyl group remained intact during the oxidation process [Eq. (5)]. This method provides a convenient route to α-silyl-substituted tertiary alcohols **11** from alkynes.



(5)

In summary, we have demonstrated that synthetically valuable α-vinylsilanes can be selectively prepared from terminal alkynes by Co-catalyzed Markovnikov hydrosilylation. These α-vinylsilanes were also used as substrates for a Co-catalyzed Markovnikov hydroboration to generate novel geminal borosilanes, which are difficult to access by other means. Both processes use sustainable, inexpensive Co catalysts with commercially available ligands. To the best of our knowledge, this method represents the first approach towards geminal borosilanes with tetrasubstituted carbon centers from simple alkynes.

Acknowledgements

Financial support was provided by the National Basic Research Program of China (2015CB856600) and the National Natural Science Foundation of China (21422209, 21432011, 21272255, and 21421091).

Keywords: alkynes · cobalt · hydroboration · hydrosilylation · vinylsilanes

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 10839–10843
Angew. Chem. **2016**, *128*, 10997–11001

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Received: June 9, 2016
Revised: July 12, 2016
Published online: August 1, 2016

