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An NNN-Pincer-Cobalt Complex Catalyzed Highly Markovnikov-Selective Alkyne Hydrosilylation

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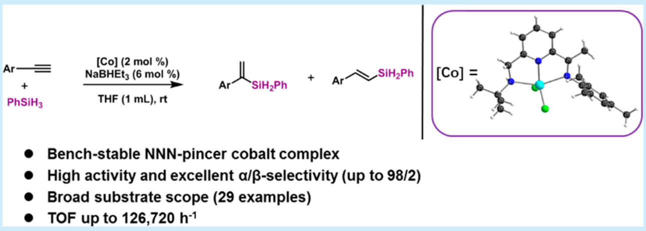
Supporting Information

ABSTRACT: A new NNN pincer (amine−pyridine−imine, API) cobalt complex, which is bench-stable and is applicable for the highly efficient and regioselective hydrosilylation of terminal alkynes, is developed. A broad set of α-vinylsilanes was successfully synthesized in good to high yields with up to 98/2 Markovnikov regioselectivity. This protocol can be readily scaled up for gram-scale synthesis and demonstrates the most efficient cobalt-catalyzed hydrosilylation of alkynes with turnover frequencies as high as 126 720 h^{-1} to date.



- Bench-stable NNN-pincer cobalt complex
- High activity and excellent α/β-selectivity (up to 98/2)
- Broad substrate scope (29 examples)
- TOF up to 126,720 h^{-1}

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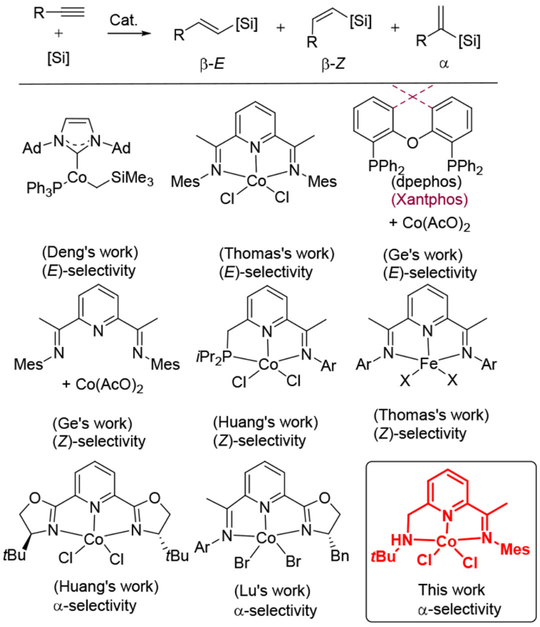
Vinylsilanes are versatile building blocks in organic synthesis and material chemistry, because of their ease of handling, nontoxicity, and utility in a broad range of transformations.[1] Among the various preparative methods for vinylsilanes, transition-metal-catalyzed hydrosilylation of alkynes has been regarded as one of the most straightforward and atom-economic approaches to obtain synthetically valuable vinylsilanes.[2] One key issue in hydrosilylation of terminal alkynes is the control of the regio- and stereo-selectivity, because the reaction usually results in a mixture of regioisomers and/or stereoisomers, e.g., β-(E)-, β-(Z)-, and α-vinylsilane isomers operated via either an *anti*-Markovnikov or Markovnikov pathway (see Scheme 1).[1e,2a]

Over the past few decades, great achievements have been made and many expensive and scarce noble-metal-catalyst systems, such as Pt,[3] Rh,[4] Ru,[5] Pd,[3g,6] and Ir,[7] for selective synthesis of vinylsilanes have been developed. However, from an economical and environmental point of view, the development of alternative catalysts based on Earth-abundant and low-toxicity non-noble metals is more desirable.[2d,8] As a consequence, several well-defined base-metal complexes (e.g., Fe,[9] Ni,[10] Mn,[11] Co,[2d,12−15]) have been reported for highly selective hydrosilylation of alkynes (Scheme 1). In this context, various cobalt complexes coordinated with structurally varying ligands generally outperformed in terms of activity and regioselectivity and stereoselectivity. For example, Deng's group explored a three-coordinated carbene-phosphane Co(I) complex, which provided high β-(E) selectivity in the hydrosilylation of terminal alkynes.[12] Research groups led by Thomas[9b] and Ge[14a] demonstrated that pyridine-2,6-diimine (PDI), as an efficient ligand, is able to promote cobalt or iron to form β-(Z)-vinylsilane isomers. Ge's group reported Co(acac)$_2$/dpephos or Co(acac)$_2$/Xantphos can selectively produce β-(E) dihydrovinylsilanes for the hydrosilylation of terminal alkynes with primary silanes.[15] In addition, Huang's and Lu's research groups have independently developed a Pybox cobalt complex and asymmetry oxazoline iminopyridine (OIP) pincer cobalt complex that exhibit excellent accessibility to α-vinylsilanes for the hydrosilylation of terminal alkynes in 2016.[13] Nonetheless, to date, the use of cobalt complexes to

Scheme 1. Non-Noble Base Metal Complexes for Hydrosilylation of Terminal Alkynes



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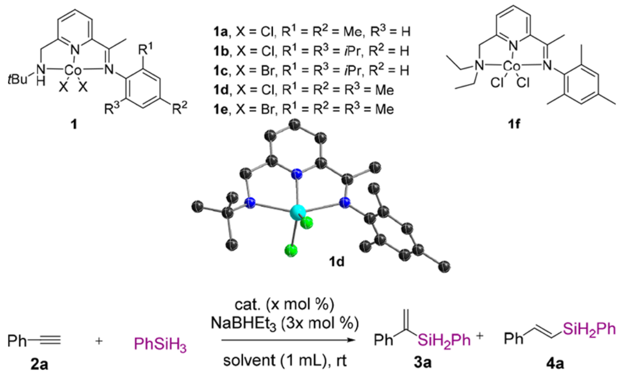
facilitate the general, highly efficient, and Markovnikov hydrosilylation of alkynes to α-vinylsilanes is still elusive and remains a challenge.

Driven by the well-defined ligand-promoted base metals for efficient and selective hydrosilylation of alkynes, we herein report a new type of NNN (amine-pyridine-imine, API) pincer ligand and its corresponding cobalt complexes (API·CoX_2) for extremely efficient and Markovnikov-selective hydrosilylation of terminal alkynes with primary silanes. A broad range of alkynes could be effectively hydrosilylated with silanes in the presence of API·CoX_2, giving α-vinylsilanes in good to high yields with excellent regioselectivity.

NNN pincer ligands could be readily synthesized from commercially available 2-acetyl-6-methylpyridine (see details in the Supporting Information). Reaction of NNN pincer ligands with CoX_2 (X = Cl or Br) in THF gave the respective API·CoX_2 complexes, which were further structurally verified by the representative crystal structure of **1d** (see Table 1). The as-synthesized complexes are air- and moisture-stable, and are operationally simple and easy to handle on the laboratory bench.

Table 1. Optimization for Alkyne Hydrosilylation[a]



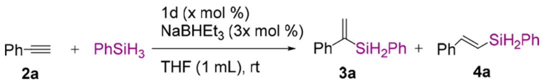
entry	catalyst	solvent	time, *t* [min]	conversion[b] [%]	yield[c] [%]	selectivity, **3a**/**4a**[b] [%]
1	**1a**	THF	5	>99	66	84/16
2	**1b**	THF	5	>99	78	90/10
3	**1c**	THF	5	>99	73	91/9
4	**1d**	THF	5	>99	90	93/7
5	**1e**	THF	5	>99	80	92/8
6	**1f**	THF	5	>99	80	93/7
7	**1d**	dioxane	5	>99	91	92/8
8	**1d**	hexane	60	30	N.D.	85/15
9	**1d**	ether	5	95	75	88/12
10	**1d**	toluene	5	98	85	92/8
11	**1d**	DCM	5	98	78	92/8

[a] Reaction conditions: phenylacetylene (0.5 mmol), $PhSiH_3$ (0.5 mmol), catalyst (2 mol %), $NaHBEt_3$ (6 mol %), solvent (1 mL), room temperature. [b] Determined by GC-FID using mesitylene as an internal standard. [c] Determined by ^1H NMR using mesitylene as an internal standard.

We started our investigations by testing the hydrosilylation of phenylacetylene (**2a**) with $PhSiH_3$ as a benchmark reaction. The reaction was initially performed in the presence of 2 mol % of cobalt precatalyst **1a** and 6 mol % of $NaBHEt_3$ as an activator in tetrahydrofuran (THF) at room temperature. We found that **1a** demonstrates high activity and the reaction is rapidly completed within 5 min to afford a mixture of (α + β-(*E*))-vinylsilanes (**3a**/**4a** = 84/16) with α-vinylsilane **3a** as the major isomer, while only 66% NMR yield to α-vinylsilane was achieved (see Table 1, entry 1). Based on this finding, a variety of API·CoX_2 (**1a**–**1f**) with different substitutes at either amine fragment or imines fragment in the API skeleton were subjected to the reaction conditions. We were pleased to find that the 1,3,5-trimethyl imine-derived ligands cobalt chloride complex (**1d**) affords maximum regioselectivity (up to 93:7) while the NMR yield was improved to 90% (entry 4). The use of more sterically hindered 2,6-diisopropyl imine (**1b** and **1c**) or diethyl-substituted-NH_2 (**1f**) did not give any improvement in the yield and regioselectivity to the desired vinylsilane. Comparatively, the cobalt bromide complexes were inferior to their chloride counterpart (entries 3 and 5 in Table 1) under identical conditions. Subsequently, various solvents were screened to improve the reaction efficiency (Table 1, entries 7–11). It turns out that 1,4-dioxane showed roughly equal reactivity and regioselectivity to that in THF, while toluene, dichloromethane, ether, and hexane all gave relatively poorer outcomes.

Further studies show that the catalyst loading (**1d**) can be reduced to 0.5 mol % (see Table 2). In this case, the reaction could complete instantaneously in 5 s to produce the silylated products in 88% yield with excellent regioselectivity (**3a**/**4a** = 90/10), in which the turnover frequency is as high as 126 720 h^{-1}. To the best of our knowledge, this is the most efficient cobalt catalysis system for alkyne hydrosilylation so far.[13b] A further decrease of the catalyst loading results in relatively lower regioselectivity (**3a**/**4a** = 84/16) (see Table 2). In addition, the hydrosilylation did not proceed at all in the absence of either **1d** or $NaBHEt_3$, albeit with prolonging reaction times (see entries 4 and 5 in Table S1 in the Supporting Information), indicating the essential role of **1d** and activator for the reaction.

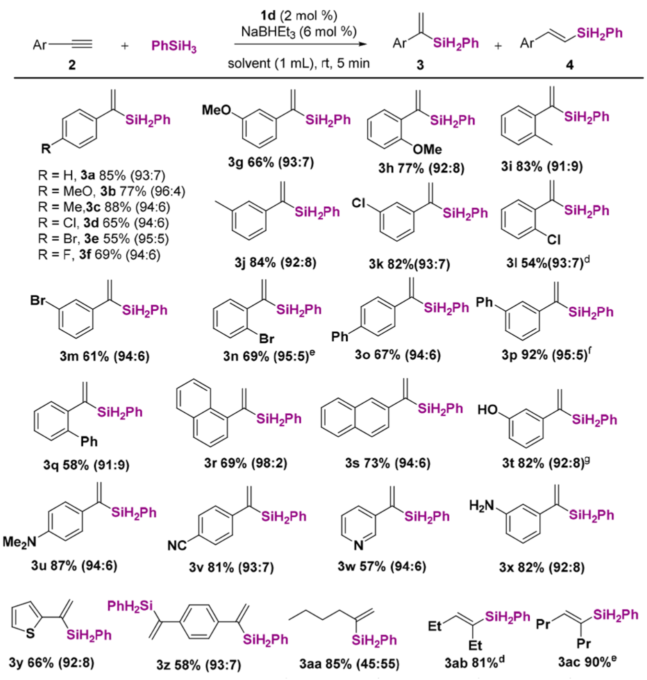
Table 2. Catalytic Performance with Lower Catalyst Loading under Optimized Conditions



x [mol %]	time, *t* [s]	conversion [%]	GC yield [%]	selectivity, **3a**/**4a** [%]	TOF [h^{-1}]
0.5	5	>99	88	90/10	126720
0.085	5	17	15	92/8	127059
0.085	30	65	62	88/12	87529
0.085	60	98	86	84/16	60706

To explore the general applicability of this protocol, a variety of alkynes were subjected to the optimized conditions for selective hydrosilylation, and the results are summarized in Scheme 2. Overall, a wide range of alkynes bearing electron-donating or electron-withdrawing substituents on the phenyl ring reacts with $PhSiH_3$ smoothly to afford the corresponding α-vinylsilanes (**3a**–**3x**) in moderate to good yields and excellent regioselectivities. The substituents in the *para*, *meta*, and *ortho* of the phenyl ring are compatible with the reaction conditions. The substrates with the *ortho* position appeared to be less reactive than their *para*- or *meta*-substituted analogues; therefore, prolonging the reaction time or increasing the catalyst loading is demanded for full conversion (**2l** and **2n**). Moreover, the *ortho*-substituted alkynes gave relatively lower α-selectivity, compared with *para*- or *meta*-substituted

Scheme 2. Scope of Alkynes[a]



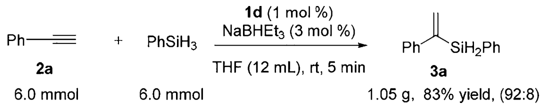
[a]Reaction conditions: alkyne (0.5 mmol), $PhSiH_3$ (0.5 mmol), **1d** (2 mol %), $NaBHEt_3$ (6 mol %), THF (1 mL), room temperature. [b]1 h. [c]**1d** (5 mol %), 2.5 h. [d]1 mL 1,4-dioxane instead of THF. [e]The ratio of **3t**/**4t** determined by ^1H NMR. Parentheses represents the ratio of **3**/**4** determined by GC-FID. Yields of isolated product are given.

analogues (**2h**, **2i**, and **2q**). These outcomes indicate the *ortho*-substituted groups have a negative influence on the reaction efficiency, in terms of activity and regioselectivity, most likely due to the steric effect. A broad range of functional groups are tolerated to give high activity and excellent regioselectivity, showcasing good functionalities of this catalysis system. Halogen-substituted phenyl alkynes gave the Markovnikov hydrosilylation product smoothly in high regioselectivity and no observation of dehalogenation products (**2k**, **2l**, **2m**, and **2n**). Other functional groups, such as $-NH_2$ (**2x**), $-N(CH_3)_2$ (**2u**), $-CN$ (**2v**), $-OH$ (**2t**) are compatible with the present conditions to afford their corresponding α-vinylsilanes in high yields. In addition, heteroaromatic alkynes, such as 3-ethynylpyridine (**2w**) and 2-ethynylthiophene (**2y**), proceed smoothly to deliver the corresponding α-vinylsilanes products in satisfactory yield with high regioselectivity. The 1,4-diethynylbenzene (**2z**) can also react with $PhSiH_3$ smoothly to form the divinylsilane compound in moderate yield with excellent regioselectivity. Note that the internal alkynes (**2ab** and **2ac**) efficiently underwent the hydrosilylation reaction under the optimized conditions too, affording the *syn*-addition products in good yield. However, when the terminal alkyl alkyne (**2aa**) was subjected to the standard conditions, a mixture of Markovnikov and *anti*- Markovnikov vinylsilanes (α:β ratio = 45:55) was obtained, albeit in high yield.

Primary, secondary, and tertiary hydrosilanes are also suitable for the hydrosilylation reaction with phenylacetylene to afford their corresponding α-vinylsilanes in appreciable yields (Table S1, entries 13–16). However, the reaction efficiency and regioselectivity are highly hydrosilane substrate-dependent. Longer reaction times, in particular, are necessary for the tertiary hydrosilane to achieve good results. Note that no reaction occurs for Ph_3SiH with more steric hindrance, albeit with a prolonging reaction time.

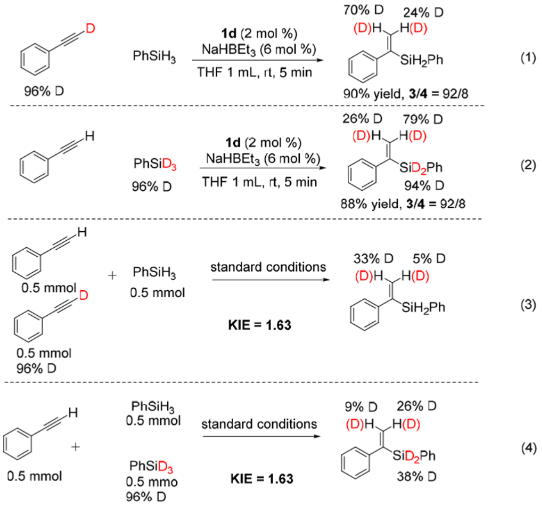
To highlight the practical utility of this procedure for the synthesis of α-vinylsilane, we conducted the reaction on gram-scale under the standard conditions. The hydrosilylation of **2a** (6 mmol) with $PhSiH_3$ in the presence of 1 mol % **1d** afforded 1.05 g of **3a** in 83% isolated yield with 92:8 α/β selectivity (Scheme 3).

Scheme 3. Gram-Scale Synthesis of 3a



Deuterium-labeling experiments[16] (Scheme 4) were conducted to gain insight into the Co-catalyzed Markovnikov hydrosilylation of alkynes. Both the reaction of deuterated **2a**/$PhSiH_3$ (eq 1 in Scheme 4) and **2a**/$PhSiD_3$ (eq 2 in Scheme 4) afforded deuterated **3a** with high yield and α-selectivity (92:8). Furthermore, the deuterium ratio in **3a** showed that both *syn*- and *anti*-addition pathways of $PhSiH_3$ to alkyne occur in the reaction process, indicating that more than one intermediate exists during the alkyne addition, which is consistent with the previous report.[17] However, a direct D/H exchange pathway could not be excluded at this point.[18]

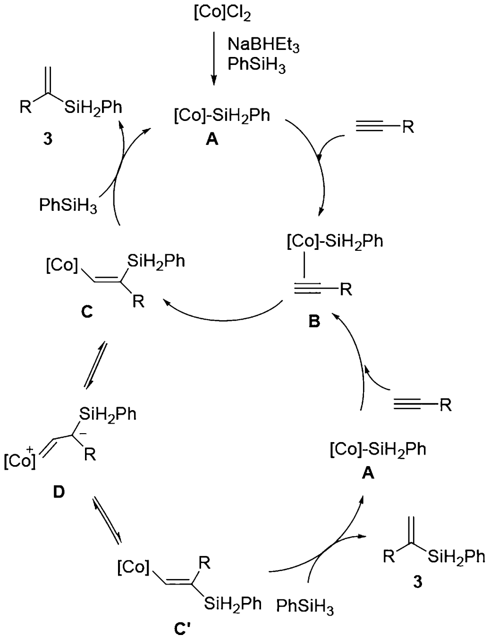
Scheme 4. Deuterium-Labelling Experiments



In addition, two competing reactions (Scheme 4, eqs 3 and 4) were conducted to investigate kinetic isotope effect (KIE) of Co-catalyzed hydrosilylation of alkynes. A typical secondary KIE value (k_H/k_D = 1.63) was detected for the reaction of phenylacetylene (1.0 equiv) with $PhSiH_3$ (1.0 equiv) and $PhSiD_3$ (1.0 equiv) (eq 4 in Scheme 4), suggesting that the oxidative addition of hydrosilane is not involved in the rate-determining step. Alternatively, for the reaction of phenylacetylene (1.0 equiv) and D-phenylacetylene (1.0 equiv) with $PhSiH_3$ (1.0 equiv) (eq 3), an equal KIE value (k_H/k_D = 1.63) was determined. The deuterated products in two reactions showed that the *syn*-addition of the silane to alkyne is a more favorable pathway than the *anti*-addition.

Based on the results of the deuterium labeling experiments and the precedent of cobalt-catalyzed hydrosilylation of unsaturated compounds,[2d,19] a mechanism accounting for the formation of α-vinylsilane is presented in Scheme 5. We propose that a low-valent cobalt(I) silyl intermediate (**A**)[2d,20] was generated by a precatalyst with $NaBHEt_3$ and $PhSiH_3$, which can further coordinate to the C−C triple bond of alkynes to form the intermediate (**B**). The insertion of alkynes into a Co−Si intermediate produces a vinylcobalt species (**C**), which can undergo Crabtree−Ojima-type[21] isomerization to form intermediates **D** and **C′**. Both intermediate **C** and **C′** can afford α-vinysilane **3** by hydrosilane and regenerate the catalytically active cobalt silyl species (**A**).

Scheme 5. Proposed Mechanism



In summary, we have developed a new type of amine-pyridine-imine (API) pincer and its corresponding air-stable cobalt complexes for highly Markovnikov-selective hydrosilylation of alkynes with primary silane $PhSiH_3$. A broad set of alkynes could be efficiently converted to their respective α-vinylsilanes in good to high yields with excellent regioselectivities. Various functional groups, including halides, amine, hydroxyl and nitriles, are well-tolerated. This operationally simple and atom-economic protocol could be easily scaled-up for gram-scale synthesis. To the best of our knowledge, this is the most efficient cobalt catalysis system for the hydrosilylation of alkyne to date and turnover frequency is as high as 126 720 h^{-1}. Further mechanistic investigations and applications of this type API pincer are underway in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02746.

Detailed experimental procedures and spectral data for all products; experimental details and characterization data (PDF)

Accession Codes

CCDC 1860603−1860604 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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