ChemCatChem

Research Article
doi.org/10.1002/cctc.202300592

Chemistry Europe
European Chemical Societies Publishing

www.chemcatchem.org

# Co-catalyzed Selective syn-Hydrosilylation of Internal Alkynes

Hanna Stachowiak-Dłużyńska,[a] Krzysztof Kuciński,[a] Bożena Wyrzykiewicz,[a] Rhett Kempe,*[b] and Grzegorz Hreczycho*[a]

Vinylsilanes are highly appealing and convenient chemical derivatives, as evidenced by the increasing number of synthetic transformations utilizing this class of compounds. Herein, a new comprehensive cobalt-catalyzed procedure has been developed enabling selective hydrosilylation of internal aryl-, alkyl-, and silylalkynes. Cobalt complexes bearing triazine-based PNP pincer-type ligands provide exclusive *syn*-addition of primary as well as secondary silanes to C≡C bonds. As a result, (*E*)-silylalkenes and vicinal disilylalkenes were effectively obtained with excellent stereoselectivity and regioselectivity. Unlike several TM-catalyzed procedures, no external additives were required since hydrosilanes act as both substrates and activators.

## Introduction

Hydrosilylation of alkynes represents the most straightforward, atom-economical, and efficient catalytic approach for the preparation of sophisticated vinylsilanes.[1] The resulting organosilicon derivatives can be characterized as reasonably stable, low toxic, and easy-to-handle compounds with great possibilities and potential applications. These include organic/organometallic synthesis, fine chemistry, and materials science.[2–6] However, in terms of selectivity, a direct addition of a Si–H bond to an alkyne is a challenging transformation (Figure 1).[7,8] Firstly, the proper control of chemoselectivity is needed, whilst side processes including dehydrocoupling or hydrogenation reactions can occur simultaneously. Secondly, control over regio- and stereoselectivity is also required.

Among the described alkyne hydrosilylation catalysts, those containing Pt,[9–13] Pd,[14] Rh,,[15–17] Ru,[18] *etc.* have been the most extensively studied. However, due to the low availability of noble metals and rising prices of such catalysts, more and more researchers try to develop sustainable alternatives. Thus, the complexes of Ni,[19–21] Mn,,[22] Fe,[23–26] and Co[26–46] were recently intensively studied. Interestingly, for Co-catalyzed hydrosilylation of alkynes, the phenomenon of an extraordinary ligand control over the reaction pathway offers to receive all of the plausible regio- and/or stereoisomers, *e.g.*, β-(*E*)-,[26,41–44] β-(*Z*)-,[45] and α-vinylsilanes.[33,35–44] However, to the best of our knowledge, there were no protocols describing the use of the triazine-based PNP-Co catalysts in the hydrosilylation of alkynes. Please take note that these specific complexes exhibit extraordinary catalytic activity in several processes, thereby providing access to a variety of important organic molecules.[47–53]

Given our recent success in incorporating readily available and cost-effective cobalt complexes into organometallic synthesis, we hypothesized that an appropriate catalytic system could serve as a sustainable platform for producing diverse

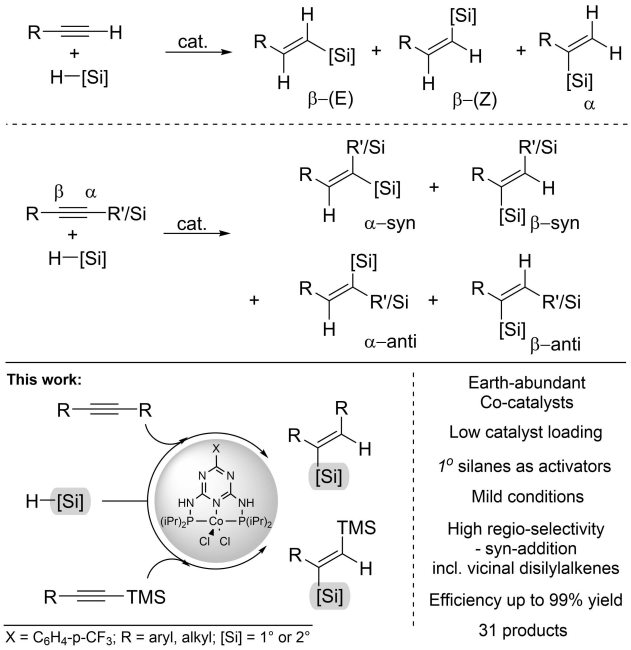



**Figure 1.** Catalytic hydrosilylation of terminal and internal alkynes.

[a] *H. Stachowiak-Dłużyńska, Dr. K. Kuciński, B. Wyrzykiewicz, Prof. Dr. G. Hreczycho*
*Faculty of Chemistry, Department of Chemistry and Technology of Silicon Compounds*
*Adam Mickiewicz University in Poznań*
*Uniwersytetu Poznańskiego St. 8, 61-614 Poznań (Poland)*
*E-mail: g.h@amu.edu.pl*
[b] *Prof. Dr. R. Kempe*
*Inorganic Chemistry II–Catalyst Design, Sustainable Chemistry Centre*
*University of Bayreuth*
*Universitätsstraße 30, 95440 Bayreuth (Germany)*
*E-mail: kempe@uni-bayreuth.de*

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.202300592

libraries of vinylsilanes.[51–53] Significantly, the subject of Co-catalyzed hydrosilylation for internal alkynes, especially symmetrical ones, was limited to a few examples up until now.[32,33,38–46] As far as we know, only four research groups have reported satisfactory results to date, specifically regarding diaryl and bis-aliphatic symmetrical internal alkynes.[34–37,39,43] Herein, we report a first example of catalytic hydrosilylation of internal alkynes triggered by the combination of PNP-Co catalyst and hydrosilanes. Remarkably, a wide range of symmetrical and silyl-substituted unsymmetrical internal alkynes undergo the addition, exclusively in *syn* stereochemistry. Excellent selectivity is not the only key feature, as the transformation can be achieved without the need for external additives, such as strong bases. Here, the activation of the pre-catalyst is achieved through the use of silanes themselves, one of the starting materials.

## Results and Discussion

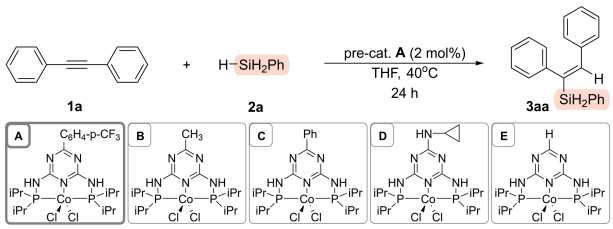
We started our investigation with the hydrosilylation of symmetrical internal alkynes, using diphenylacetylene (**1a**), and phenylsilane (**2a**) as silylating agent. This model reaction was performed in the presence of five previously synthesized PNP-Co complexes with different substituents attached to the triazine ring (**A**–**E**). Since our previous works confirmed the potential for pre-catalyst activation through hydrosilanes, no external additives were evaluated during this stage.[51–55] A summary of the results can be found in Table 1.

Initial reactions were carried out by using 2 mol% of the corresponding pre-catalysts **A**-**E** in tetrahydrofuran (THF) at 40 °C for 24 hours, under an argon atmosphere. Furthermore, a variety of commonly used solvents was examined, as well as higher temperatures, pre-catalyst loading, and the different ratio between model substrates. Additionally, experiments were conducted using the Co-complex starting material – $CoCl_2$, as well as in the absence of any Co-species.

In preliminary tests we found that all of our pre-catalysts present exclusive selectivity towards β-(*E*)-addition, and the complex A turned out to be the most promising one, affording 92% conversion of **1a** (Table 1, entries 1–5). It is worth mentioning that the same pre-catalyst showed uncommon results in the reaction of terminal silylacetylenes, leading to competitive dehydrogenative coupling selectively, while non-silylated species or silylated unsaturated alcohols gave a mixture of products and lower conversion rates, even under harsh conditions.[51] In this approach, the hydrosilanes again effectively fulfilled the dual role of reagents and activators, so no external additives were needed. Whereas the reaction in toluene, chlorobenzene, and diglyme gave deterioration in efficiency (Table 1, entries 8–10), no products were detected for $CoCl_2$ or without any catalyst, indicating the essential role of Co-complexes (Table 1, entries 6 and 7). In addition, a lower concentration of **2a** resulted in a sudden drop in the conversion of the alkyne into the corresponding vinylsilane (Table 1, entry 11). Finally, the optimized hydrosilylation of internal alkynes was settled at 3 mol% of pre-catalyst **A**, at 50 °C, in THF, and 1.5 eq. of silylating agent (**2a**). It results in almost quantitative yield of the desired product (Table 1, entry 13). Nevertheless, in the case of aliphatic Si-derivatives, *e.g.*, hexylsilane (**2b**), 5 mol% of **A** was crucial to preserve the extremely high efficiency of the entire process (Table 1, entry 17). Furthermore, the same optimization procedure was applied to hydrosilylation of 1-phenyl-1-pentyne (**1j**) with phenylsilane (**2a**). Control tests demonstrated that each of examined pre-catalysts enabled selective *syn*-addition, however, low efficiency and a mixture of two regioisomers in a moderate ratio were detected. Despite the above, experiments conducted with pre-catalyst **A** under harsh conditions succeeded in very good alkyne conversions, as well as an improvement in the ratio between resulted vinylsilanes (for more details, please see Table S1. in ESI).

With optimized conditions in hands, we explored the substrate scope on a variety of symmetrical internal alkynes (**3aa–ia, 3ab–ib, 3ac, 3cc**), as well as unsymmetrical derivatives (**3ja**, **3ka**), utilizing 3 or 5 mol% of pre-catalyst **A**, respectively for aromatic (**2a**, **2c**) and aliphatic (**2b**) hydrosilanes. In the course of our research, it turned out that a small temperature change has a significant impact on alkyne conversion in individual cases. Therefore, we decided to select this parameter for each reaction separately. Finally, the products of symmetrical internal alkyne hydrosilylation with primary silanes were synthesized in a number of 20. At this point, is worth emphasizing that dialkyl alkynes and diaryl alkynes bearing

**Table 1.** Optimization for hydrosilylation of aromatic internal alkynes with silanes.[a]




| No. | Variation from initial conditions | Conversion of **1a** [%][b] |
|---|---|---|
| 1 | No change | 92 |
| 2 | **B** instead of **A** | 55 |
| 3 | **C** instead of **A** | 84 |
| 4 | **D** instead of **A** | 8 |
| 5 | **E** instead of **A** | 55 |
| 6 | $CoCl_2$ instead of **A** | 0 |
| 7 | No catalyst | 0 |
| 8 | In toluene | 33 |
| 9 | In chlorobenzene | 33 |
| 10 | In diglyme | 88 |
| 11 | With 1.2 eq. of **2a** | 57 |
| 12 | At 50 °C | 93 |
| 13 | With 3 mol% of **A** at 50 °C | 99 (99)[c] |
| 14 | **2b** instead of **2a** with 3 mol% of **A** | 71 |
| 15 | **2b** instead of **2a** with 3 mol% of **A** at 50 °C | 74 |
| 16 | **2b** instead of **2a** with 3 mol% of **A** in toluene | 60 |
| 17 | **2b** instead of **2a** with 5 mol% of **A** | 99 (99)[c] |

[a] General reaction conditions: **1a** (1.0 eq.), **2a** (1.5 eq.), **A** (2 mol%), THF, under argon atmosphere, 40 °C, 24 h. [b] Conversion of **1a** determined by GC with n-dodecane as the internal standard. [c] Isolated yield.

electron-donating groups were effectively hydrosilylated by phenylsilane (**2a**) using only 3 mol% of pre-catalyst **A** (86–99% yield). In contrast, derivatives with electron-withdrawing substituents either in the *para* or *meta* positions of the aryl ring appeared to be less reactive and thus required higher catalyst loadings (5 mol% for **3ea**–**3ga**). In the case of other silanes, no further improvements were required when hexylsilane (**2b**) or p-tolylsilane (**2c**) were employed. Finally, the performance of unsymmetrical internal alkynes resulted in efficient and extremely selective β-(*E*)-addition of silanes **2a** and **2b**. The satisfactory ratio between regioisomers (given in brackets), towards attachment of silyl-motif to the aliphatic side of C–C triple bond was achieved in the case of unsymmetrical aryl-alkyl alkynes (**3ja**, **3ka**, **3la**). Analogous to the results reported by Chen and Petit, the *para*-substituted unsymmetrical diaryl derivatives brought very good isolation yields (75–85%), but poor regioselectivity (**3ma**, **3na**, **3mb**, **3nb**).[33,40] The exact conditions for each alkyne and the structures of all products are presented in Scheme 1. Moreover, to confirm the regioselectivity of the investigated hydrosilylation of internal alkynes, we decided to conduct $^{1}$H-$^{13}$C HSQC and NOESY 2D NMR experiments utilizing product **3eb**. As a result, we determined a correlation between -*Si**H**$_2$**R* and the hydrogen atom attached to the unsaturated bond, which undeniably proves the *syn* addition of the corresponding silane (**2b**) to the C≡C bond of **1e**, and provides an *E*-isomer (further details can be found in Figure S37 and S38 of the ESI).

Furthermore, we decided to expand our method on various secondary silanes in optimized reaction conditions, and the results are presented in Scheme 2. For that purpose, 6-dodecyne (**1i**) was chosen and underwent reactions giving corresponding β-(*E*)-vinylsilanes (**3id**–**3ih**) with very high efficiency (77-92% yield). It was already established, that disubstituted silanes can play a dual role as reagents and activators of our pre-catalysts. However, the utilization of phenylsilane (**2a**) as an additive resulted in better conversions of alkynes under mild reaction conditions. Due to the above, we reduced the excess of silylating agent to only 1.2 eq., considering environmental issues. Next, unsymmetrical internal alkynes were tested, and *syn*-addition products were selectively obtained. In this case, only a moderate to a good ratio of β-(*E*)-products was achieved, even under harsh reaction conditions. Noteworthy, the employment of diphenylsilane (**2d**) affected regioselectivity towards attachment of silyl-motif to the aromatic side of C–C triple bond (**3jd'**, **3kd'**, **3ld'**), in contrast to previous results with phenylsilane (**3ja**, **3ka**, **3la**).

We next investigated the hydrosilylation using various primary and secondary silanes on internal silylated alkynes. For this purpose, we carried out catalyst screening with phenylsilane (**2a**) or diphenylsilane (**2d**), and trimethyl(phenylethynyl)silane (**4a**) as model reagents. During this research we found out, that our catalytic system based on pre-catalyst **A** provides very good selectivity, resulting in vicinal species preferentially. However, poor efficiency moved us to study the reaction more comprehensively (for more details, please see Table S2 in ESI). Finally, our attempts resulted in the development of optimal conditions and the preparation of products with various substituents in the *para* or *meta* positions of the aryl ring, effectively (Scheme 3). To our knowledge, of the previously described reports utilizing Co-complexes and internal alkynes, only two have demonstrated selective hydrosilylation on TMS-blocked species to produce vicinal isomers.[31,40] As a side note, the Deng and Cui groups have recently reported the preparation of geminal disilylalkenes using catalysts based on three-coordinate cobalt(I) complex and rare-Earth elements, respectively.[43,56]

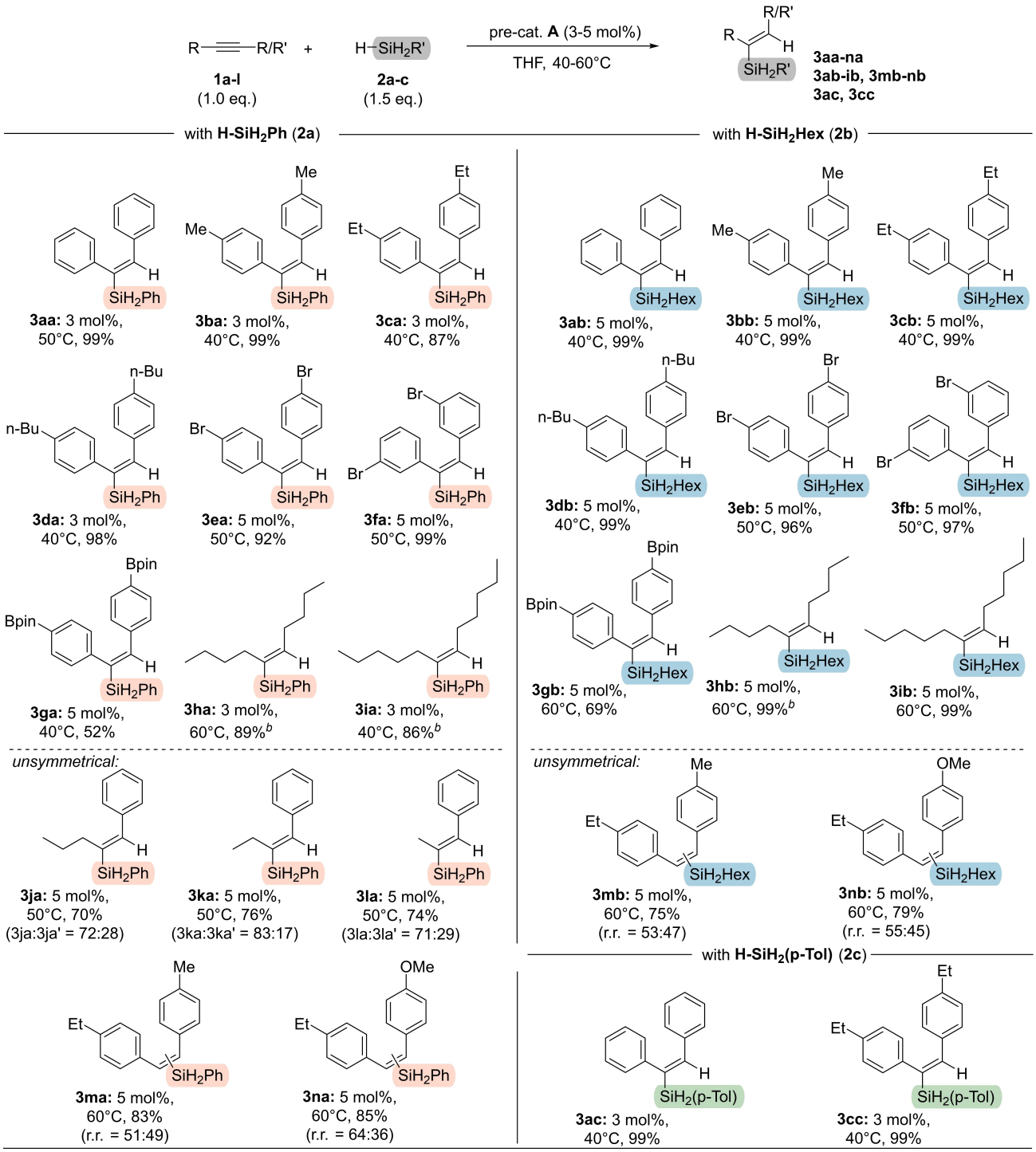
Finally, the applicable potential of produced silylalkenes was also presented in several examples, resulting in carbonyl compounds, alkenes, and silicon materials (Scheme 4.).

(E)-(1,2-Di-p-tolylvinyl)(phenyl)silane (**3ba**) was transformed into a corresponding ketone with 74% yield (**6**).[34] Highly efficient and exclusive conversion to (*Z*)-alkene was observed after treatment of **3ba** with TBAF (**7**, 99%).[57] The KHMDS-catalyzed reaction of **3ba** with t-butyldimethylsilanol yielded very complex unsymmetrical disiloxane (**8**, 82%).[58] In addition, the alkoxylation of (E)-(2-(diphenylsilyl)-2-phenylvinyl)trimethylsilane (**5ad**) with methanol using KF as catalyst was carried out under mild conditions, resulting in corresponding unsaturated alkoxysilane (**9**, 68%).

Lastly, to demonstrate preparative scale utility of our approach, the gram-scale reactions were conducted under procedurally convenient conditions (Scheme 5.).

In order to better understand the activation mode of our catalyst and the nature of its intermediates during the examined process, we conducted preliminary tests. For this purpose, complex **A** was chosen and tracked with **1a** and **2a** in THF-$d_8$ on $^{1}$H NMR. We started with the addition of 2 equiv. of the corresponding silane to 1 equiv. of catalyst **A** at room temperature, and instantly observed liberation of dihydrogen, chlorophenylsilane, as well as a mixture of [Co–H] species at −8.74 ppm (t, $J$ = 41.6 Hz) and −9.79 ppm (t, $J$ = 43.2 Hz), indicating $(PN^5P)Co^{I}H$ and $(PN^5P)Co^{III}H_2(SiH_2Ph)$ respectively.[40,59,60] Remarkably, such $Co^{I}/Co^{III}$ mechanism is compatible with our recent investigations and suggested in other Co-catalyzed processes.[40,51–54,61,62] Interestingly, a triplet at −22.87 (t, $J$ = 63.8 Hz) was also initially detected, which appears to be a short-lasting dimeric form of our activated catalyst.[63] Subsequently, increasing the amount of phenylsilane (**2a**) up to 10 equiv. resulted in fading of $(PN^5P)Co^{I}H$, and raising a broad and irregular signal in the range of −8.97 ppm to −9.96 ppm right next to previously determined [Co–H] species. Our further investigation with diphenylsilane (**2d**) instead of phenylsilane (**2a**) showed that such an entity seems to come from $(PN^5P)Co^{III}H_2(SiHPh_2)$, due to plausible redistribution of primary to secondary silane. Next, 10 equiv. of diphenylacetylene (**1a**) was added to the mixture of **A** with 10 equiv. of **2a** to generate [Co-alkenyl] species in a range of −14.25 ppm to −14.84 ppm.

Based on our research and previous literature, we proposed an activation step and catalytic cycle for Co-catalyzed hydrosilylation of internal alkynes in Scheme 6. The treatment of complex $(PN^5P)Co^{I}H$ with hydrosilane resulted in oxidative addition and formation of $(PN^5P)Co^{III}(SiH_2Ph)$ entity. Afterward, the $Co^{III}$ specie undergoes ligand replacement with the alkyne molecule to create the plausible [Co-alkenyl] complexes.[40]



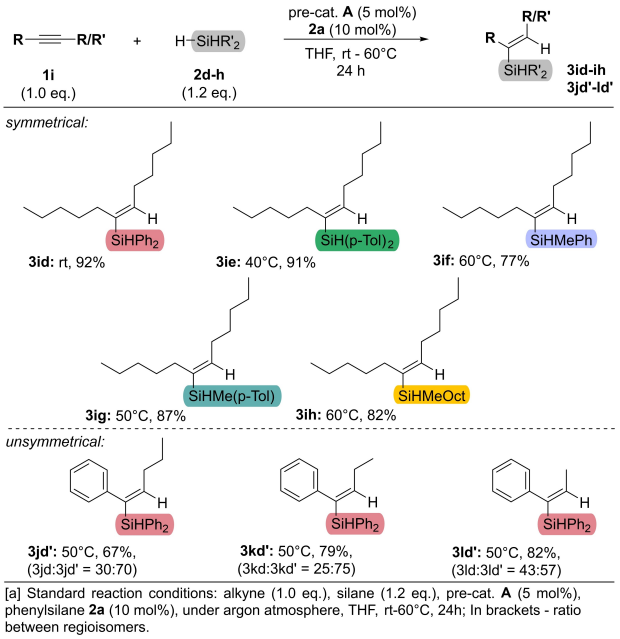

[a] Standard reaction conditions: alkyne (1.0 eq.), silane (1.5 eq.), pre-cat. **A** (3-5 mol%), under argon atmosphere, THF, 40-60°C, 24h;
[b] in toluene; In brackets - ratio between regioisomers.

**Scheme 1.** Products scope for hydrosilylation of internal alkynes with primary silanes.[a]

Finally, the corresponding product is liberated after reductive elimination, and the [Co–H] active form regenerates.

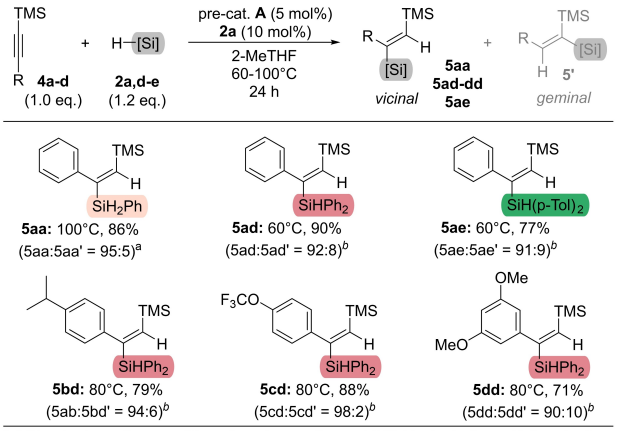
## Conclusions

To summarize, we have established a novel method for the Co-catalyzed hydrosilylation of a wide range of symmetrical alkynes and their TMS-blocked derivatives. The cobalt complexes studied in this work are equipped with readily available and



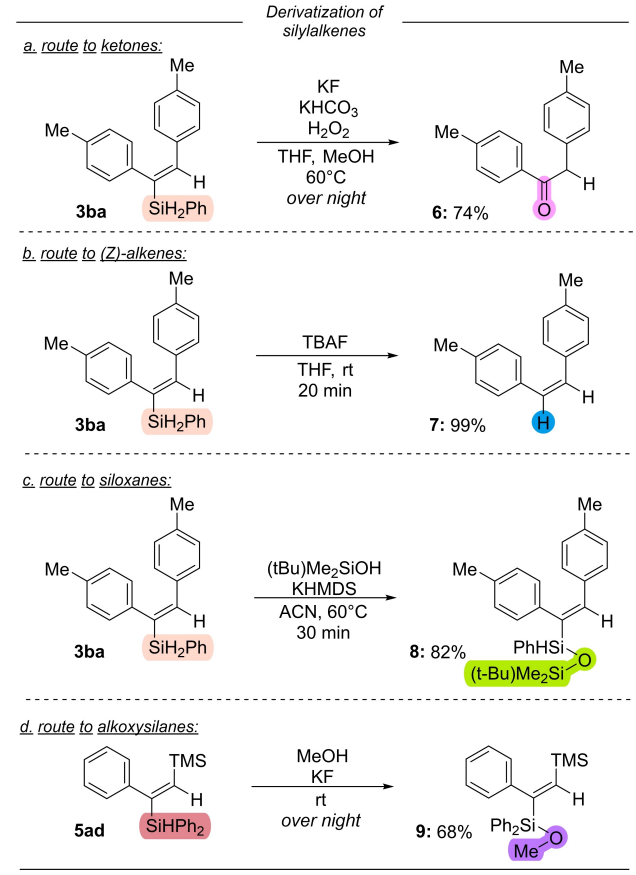

[a] Standard reaction conditions: alkyne (1.0 eq.), silane (1.2 eq.), pre-cat. **A** (5 mol%), phenylsilane **2a** (10 mol%), under argon atmosphere, THF, rt-60°C, 24h; In brackets - ratio between regioisomers.

**Scheme 2.** Products scope for hydrosilylation of internal alkynes with secondary silanes.[a]

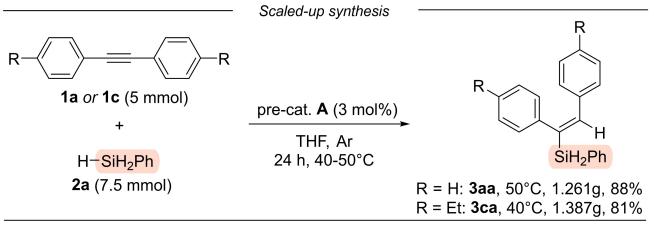



[a] Standard reaction conditions for primary silanes: TMS-blocked alkyne (1.0 eq.), silane (1.5 eq.), pre-cat. **A** (5 mol%), under argon atmosphere, 2-MeTHF, 100°C, 24h. [b] Standard reaction conditions for secondary silanes: TMS-blocked alkyne (1.0 eq.), silane (1.2 eq.), phenylsilane **2a** (10 mol%), under argon atmosphere, 2-MeTHF, 60-80°C, 24h.

**Scheme 3.** Products scope for hydrosilylation of internal TMS-blocked alkynes with primary[a] and secondary silanes.[b]




**Scheme 4.** Derivatization of silylalkenes.

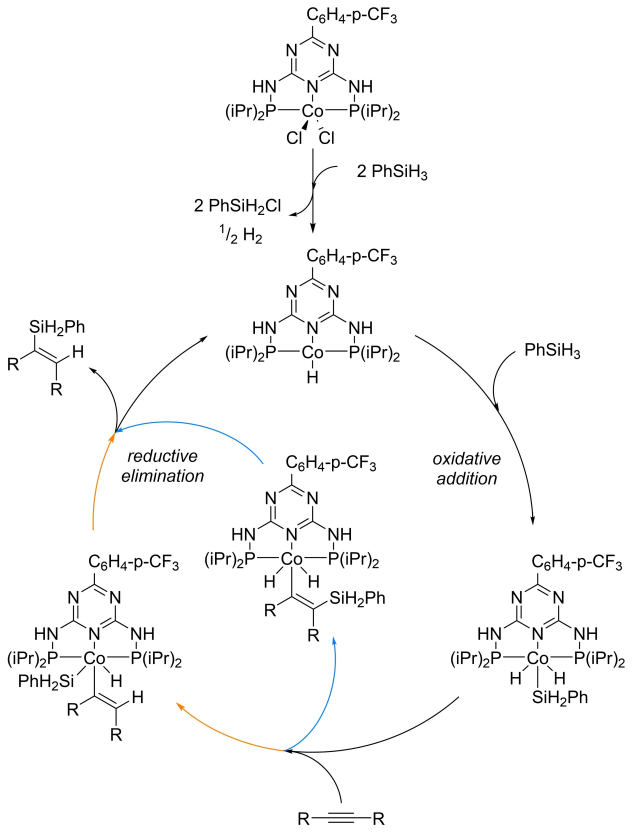



**Scheme 5.** Scaled-up synthesis of **3 aa** and **3 ca**.

inexpensive PNP pincer-type ligands, which allow for exclusive *syn*-addition to unsaturated triple bonds using different primary and secondary silanes. As a result, valuable silylalkenes and vicinal disilylalkenes were synthesized respectively, and isolated with very good to excellent yields. Moreover, our approach can be utilized for both aliphatic and aromatic acetylenes in a comprehensive way, encompassing aryl rings having both electron-donating and electron-withdrawing groups. Furthermore, the great utility potential of received products was demonstrated on several essential transformations from organic and organometallic points of view. It is worth noting that our approach was designed to minimize the use of external additives, allowing hydrosilanes to play a dual role as reagents and pre-catalyst activators. This reduces costs and has a lower environmental impact.

## Experimental Section

*General procedure for the hydrosilylation of internal alkynes:* In a 12 mL vial equipped with a magnetic stirring bar, a 0.03 M solution of pre-catalyst A (3 or 5 mol%) in THF or toluene was added, along with silane (0.75 mmol, 1.5 eq. of primary silane, or 0.6 mmol, 1.2 eq. of secondary silane and 10 mol% of phenylsilane), and acetylene (0.5 mmol, 1.0 eq.), under an inert gas atmosphere in a glove box. The reaction mixture was then stirred at the specified temperature for 24 hours. After this time, the solvent and volatile




**Scheme 6.** Plausible activation of precatalyst and catalytic cycle.

residues were evaporated under high vacuum. Next, the catalyst was precipitated by adding pentane or hexane (1 mL), and the resulting solution was filtered through a pad of silica gel. Finally, the crude products were separated by bulb-to-bulb distillation. The pure products were identified using $^{1}H$, $^{13}C$, and $^{29}Si$ NMR spectroscopy, as well as MS spectrometry.

*General procedure for the hydrosilylation of silylacetylenes:* Vicinal disilylalkenes were prepared and isolated similarly to (E)-silylalkenes, using 2-MeTHF as the solvent.

## Supporting Information

The authors have cited additional references within the Supporting Information.[64–68]

## Acknowledgements

*This work was supported by a National Science Centre Grant UMO-2018/30/E/ST5/00045 (G.H.) and by grant no. POWR.03.02.00-00-I020/17 (H.S.-D.) co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education Development. Open Access funding enabled and organized by Projekt DEAL.*

## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** alkynes · alkynylsilanes · cobalt · hydrosilylation · vinylsilanes

[1] L. D. De Almeida, H. Wang, K. Junge, X. Cui, M. Beller, *Angew. Chem. Int. Ed.* **2021**, *60*, 550–565.
[2] L. Cornelissen, V. Cirriez, S. Vercruysse, O. Riant, *Chem. Commun.* **2014**, *50*, 8018–8020.
[3] E. Langkopf, D. Schinzer, *Chem. Rev.* **1995**, *95*, 1375–1408.
[4] T. H. Chan, K. Koumaglo, *Tetrahedron Lett.* **1986**, *27*, 883–886.
[5] C. J. Flann, L. E. Overman, *J. Am. Chem. Soc.* **1987**, *109*, 6115–6118.
[6] G. Stork, M. E. Jung, *J. Am. Chem. Soc.* **1974**, *96*, 3682–3684.
[7] P. He, M.-Y. Hu, X.-Y. Zhang, S.-F. Zhu, *Synthesis (Stuttg).* **2022**, *54*, 49–66.
[8] J.-W. Park, *Chem. Commun.* **2022**, *58*, 491–504.
[9] A. Naka, T. Mihara, M. Ishikawa, *J. Organomet. Chem.* **2019**, *879*, 1–6.
[10] A. Franczyk, K. Stefanowska, M. Dutkiewicz, B. Marciniec, *Dalton Trans.* **2017**, *46*, 158–164.
[11] P. Żak, M. Bołt, M. Kubicki, C. Pietraszuk, *Dalton Trans.* **2018**, *47*, 1903–1910.
[12] S. Dierick, E. Vercruysse, G. Berthon-Gelloz, I.E. Markó, *Chem. Eur. J.* **2015**, *21*, 17073–17078.
[13] K. Stefanowska, A. Franczyk, J. Szyling, M. Pyziak, P. Pawluc, J. Walkowiak, *Chem. Asian J.* **2018**, *13*, 2101–2108.
[14] M. Planellas, W. Guo, F. Alonso, M. Yus, A. Shafir, R. Pleixats, T. Parella, *Adv. Synth. Catal.* **2014**, *356*, 179–188.
[15] E. Van Vuuren, F. P. Malan, W. Cordier, M. Nell, M. Landman, *Organometallics* **2022**, *41*, 187–200.
[16] T. Sanada, T. Kato, M. Mitani, A. Mori, *Adv. Synth. Catal.* **2006**, *348*, 51–54.
[17] P. K. R. Panyam, B. Atwi, F. Ziegler, W. Frey, M. Nowakowski, M. Bauer, M. R. Buchmeiser, *Chem. Eur. J.* **2021**, *27*, 17220–17229.
[18] B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2005**, *127*, 17644–17655.
[19] V. Srinivas, Y. Nakajima, W. Ando, K. Sato, S. Shimada, *J. Organomet. Chem.* **2016**, *809*, 57–62.
[20] P. M. Keil, T. J. Hadlington, *Angew. Chem. Int. Ed.* **2022**, *61*, e202114143.
[21] M. Tanabe, R. Yumoto, K. Osakada, T. Sanji, M. Tanaka, *Organometallics* **2012**, *31*, 6787–6795.
[22] C. Wang, X. Yang, *Angew. Chem. Int. Ed.* **2018**, *57*, 923–928.
[23] M. Hu, P. He, T. Qiao, W. Sun, W. Li, J. Lian, J. Li, S. Zhu, *J. Am. Chem. Soc.* **2020**, *142*, 16894–16902.
[24] C. Belger, B. Plietker, *Chem. Commun.* **2012**, *48*, 5419–5421.
[25] M. D. Greenhalgh, D. J. Frank, S. P. Thomas, *Adv. Synth. Catal.* **2014**, *356*, 584–590.
[26] J. H. Docherty, J. Peng, A. P. Dominey, S. P. Thomas, *Nat. Chem.* **2017**, *9*, 595–600.
[27] K. Chen, H. Zhu, Y. Li, Q. Peng, Y. Guo, X. Wang, *ACS Catal.* **2021**, *11*, 13696–13705.
[28] M. K. Sahoo, D. Kim, S. Chang, J. Park, *ACS Catal.* **2021**, *11*, 12777–12784.
[29] M. Skrodzki, V. Patroniak, P. Pawluc, *Org. Lett.* **2021**, *23*, 663–667.
[30] J. Guo, Z. Lu, *Angew. Chem. Int. Ed.* **2016**, *128*, 10993–10996.
[31] M. Skrodzki, V. O. Garrido, A. G. Csaky, P. Pawluc, *J. Catal.* **2022**, *411*, 116–121.
[32] Z. Zong, Q. Yu, N. Sun, B. Hu, Z. Shen, X. Hu, L. Jin, *Org. Lett.* **2019**, *21*, 5767–5772.
[33] D. Kong, B. Hu, D. Chen, *Chem. Asian J.* **2019**, *14*, 2694–2703.
[34] Z. Zuo, J. Yang, Z. Huang, *Angew. Chem. Int. Ed.* **2016**, *55*, 10839–10843.
[35] S. Zhang, J. J. Ibrahim, Y. Yang, *Org. Lett.* **2018**, *20*, 6265–6269.
[36] M. Bołt, P. Żak, *Catalysts* **2023**, *13*, 510.
[37] L. Yong, K. Kirleis, H. Butenschon, *Adv. Synth. Catal.* **2006**, *348*, 833–836.

[38] Z. Cheng, M. Li, X.-Y. Zhang, Y. Sun, Q.-L. Yu, X.-H. Zhang, Z. Lu, *Angew. Chem. Int. Ed.* **2023**, *62*, e202215029.
[39] W. Bai, J. Sun, D. Wang, S.-D. Bai, L. Deng, *Appl. Organomet. Chem.* **2022**, *36*, e6694.
[40] A. Rivera-Hernandez, B. J. Fallon, S. Ventre, S. Cedric, M.-H. Tremblay, G. Gontard, E. Derat, M. Amatore, C. Aubert, M. Petit, *Org. Lett.* **2016**, *18*, 4242–4245.
[41] C. Wu, W. J. Teo, S. Ge, *ACS Catal.* **2018**, *8*, 5896–5900.
[42] H. Li, C. Yang, D. Wang, L. Deng, *Organometallics* **2023**, DOI 10.1021/acs.organomet.2c00563.
[43] Z. Mo, J. Xiao, Y. Gao, L. Deng, *J. Am. Chem. Soc.* **2014**, *136*, 17414–17417.
[44] G. Wu, U. Chakraborty, A. Jacobi von Wangelin, *Chem. Commun.* **2018**, *54*, 12322–12325.
[45] W. J. Teo, C. Wang, Y. W. Tan, S. Ge, *Angew. Chem. Int. Ed.* **2017**, *56*, 4328–4332.
[46] D. Wang, Y. Lai, P. Wang, X. Leng, J. Xiao, L. Deng, *J. Am. Chem. Soc.* **2021**, *143*, 12847–12856.
[47] S. Rösler, J. Obenauf, R. Kempe, *J. Am. Chem. Soc.* **2015**, *137*, 7998–8001.
[48] N. Deibl, R. Kempe, *J. Am. Chem. Soc.* **2016**, *138*, 10786–10789.
[49] S. Rösler, M. Ertl, T. Irrgang, R. Kempe, *Angew. Chem. Int. Ed.* **2015**, *54*, 15046–15050.
[50] F. Freitag, T. Irrgang, R. Kempe, *Chem. Eur. J.* **2017**, *23*, 12110–12113.
[51] H. Stachowiak, K. Kuciński, F. Kallmeier, R. Kempe, G. Hreczycho, *Chem. Eur. J.* **2022**, *28*, e202103629.
[52] D. Lewandowski, T. Cytlak, R. Kempe, G. Hreczycho, *J. Catal.* **2022**, *413*, 728–734.
[53] E. Szafoni, K. Kuciński, G. Hreczycho, *Green Chem. Lett. Rev.* **2022**, *15*, 757–764.
[54] E. Szafoni, K. Kuciński, G. Hreczycho, *J. Catal.* **2023**, *423*, 1–9.
[55] D. Lewandowski, G. Hreczycho, *Inorg. Chem. Front.* **2023**, *10*, 3656–3663.
[56] X. Xu, A. Gao, W. Chen, X. Xu, J. Li, C. Cui, *ACS Catal.* **2023**, *13*, 3743–3748.
[57] K. Itami, T. Nokami, Y. Ishimura, K. Mitsudo, T. Kamei, J. Yoshida, *J. Am. Chem. Soc.* **2001**, *123*, 11577–11585.
[58] K. Kuciński, H. Stachowiak, G. Hreczycho, *Inorg. Chem. Front.* **2020**, *7*, 4190–4196.
[59] X. Du, Y. Zhang, D. Peng, Z. Huang, *Angew. Chem.* **2016**, *128*, 6783–6787.
[60] H. H. Cramer, S. Ye, F. Neese, C. Werl, W. Leitner, *JACS Au* **2021**, *1*, 2058–2069.
[61] J. V. Obligacion, S. P. Semproni, I. Pappas, P. J. Chirik, *J. Am. Chem. Soc.* **2016**, *138*, 10645–10653.
[62] S. P. Semproni, C. C. H. Atienza, P. J. Chirik, *Chem. Sci.* **2014**, *5*, 1956–1960.
[63] Y. B. Kim, D. Kim, S. U. Dighe, S. Chang, J.-W. Park, *ACS Catal.* **2021**, *11*, 1548–1553.
[64] K. Kuciński, G. Hreczycho, *ChemCatChem* **2022**, *14*, e202200794.
[65] H. Wang, Y. Huang, X. Wang, X. Cui, F. Shi, *Org. Biomol. Chem.* **2020**, *18*, 7554–7558.
[66] J. Yu, S. Mao, Y. Wang, *Tetrahedron Lett.* **2015**, *56*, 1575–1580.
[67] J. Xu, N. Liu, H. Lv, C. He, Z. Liu, X. Shen, F. Cheng, B. Fan, *Green Chem.* **2020**, *22*, 2739–2743.
[68] M. Ishikawa, H. Sugisawa, T. Fuchikami, M. Kumada, *J. Am. Chem. Soc.* **1982**, *104*, 2872–2878.

Manuscript received: April 28, 2023
Revised manuscript received: May 27, 2023
Accepted manuscript online: May 30, 2023
Version of record online: June 30, 2023