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Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes

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ABSTRACT

The search for simple and easy-to-synthesize ligands for bench stable cobalt (pre)catalysts that would ensure high activity and selectivity in alkyne hydrosilylation reactions is an interesting current challenge. Herein, we report that a cobalt(II) complex bearing pyrimidine-imine-2*H*-imidazole ligand activated by $LiHBEt_3$ exhibits not only high catalytic activity, but also unprecedented tolerance towards tertiary silanes in highly regioselective Markovnikov hydrosilylation of aliphatic and aromatic terminal alkynes to give α-vinylsilanes. In addition, a variety of 1-aryl-2-(trimethylsilyl)acetylenes have been hydrosilylated efficiently by diphenylsilane in the presence of $[Co(L)Cl_2]/LiHBEt_3$ catalytic system to yield (*E*)-1-aryl-1,2-bis(silyl)ethenes with high selectivity. Such selectivity is very rarely observed for cobalt-catalyzed hydrosilylation of silylacetylenes.

1. Introduction

Vinylsilanes are versatile reagents in organic and organometallic chemistry. Due to their stability, low toxicity and ease of handling, they have been extensively applied in organic synthesis, fine chemistry and materials science [1]. From among all the synthetic pathways for such compounds, direct addition of Si-H to alkynes is perceived as the most efficient and atom economical [2]. Initially, the field of metal-catalyzed hydrosilylation of alkynes was overwhelmed by noble metals [3] such as Ru, Pt and Ir. The reactions involving catalysts based on these metals are efficient and selective, however, the low natural abundance of such metals and increasing market demand resulted in enormous peak in price. Due to the fact that the price of noble metals determines the subsequent price of the catalyst, development of new precious metal catalysts is becoming increasingly economically questionable. To this end hydrosilylation catalysts based on earth abundant metals are more desirable from the economic and environmental points of view [4]. On the other hand, scientists should also reconsider developing multistep synthetized and complex ligands. New catalysts should bear simple and rational coordinating environment, simultaneously maintaining high efficiency and selectivity.

Cobalt catalysis offers a sustainable alternative to the commonly used noble metal catalysts [5]. In the last decade, cobalt complexes have been reported as effective catalysts in the synthesis of β-(*E*) [6], β-(*Z*) [7] and α-vinylsilanes [8]. Despite extensive research, the field of α-selective hydrosilylation of alkynes with ligand simplification has not yet been fully examined. Jin's [9] and von Wangelin's [10] groups have developed systems based on $Co(OAc)_2$ and simple, bidentate ligands. Although characterized by high conversion and selectivity, the hydrosilylation involving secondary and tertiary silanes was neither satisfactory nor accessible. Subsequently, Chen's [11] group described the complex of $CoBr_2$ with N^CNN tridentate ligand as active in the hydrosilylation of alkynes and 1,3-diynes with diphenylsilane.

Tertiary silanes are very challenging substrates in cobalt-catalyzed alkyne Markovnikov hydrosilylation (Scheme 1). Apart from noble metal catalysts, in 1999 Isobe [12] described a single example of hydrosilylation of dihydropyranyl-substituted alkyne with triethylsilane with poor selectivity (α/β = 2) in the presence of $Co_2(CO)_6/HC{\equiv}CCMe_2OH$ complex. After two decades, Deng's [13] and Park's [14] groups developed new cobalt catalysts for efficient alkyne Markovnikov hydrosilylation with tertiary silanes. Despite excellent results and impressive selectivity (α/β up to 55:1), the Deng catalyst, based on dicobalt carbonyl *N*-heterocyclic carbene complex $[(IPr)_2Co_2(CO)_6]$ (IPr = 1,3-di(2,6-diisopropylphenyl)-imidazol-2-ylidene), requires 10 mol % of cobalt loading. Park and co-workers have described the use of a cobalt hydride catalytic

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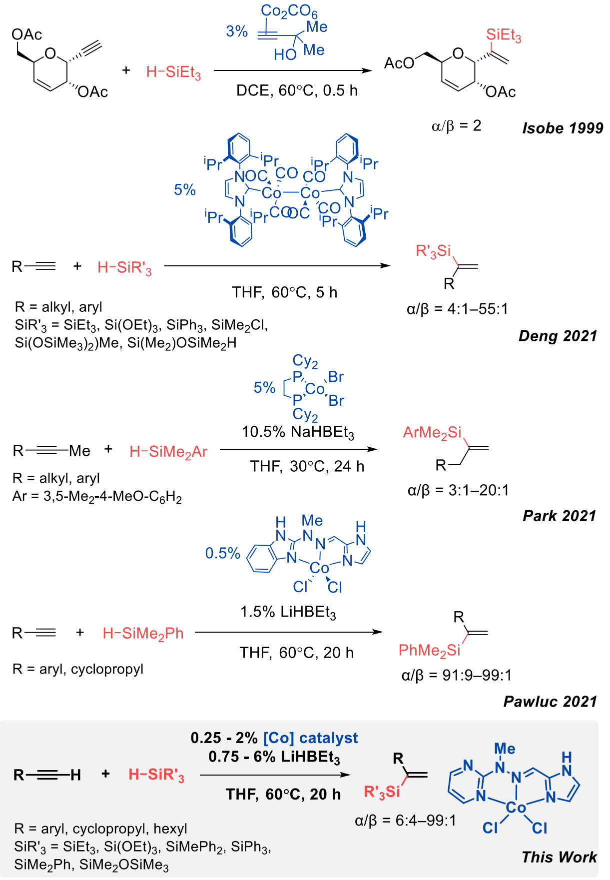


Scheme 1. Co complexes for α-selective hydrosilylation of alkynes with tertiary silanes.

system generated from [(bis(dicyclohexylphosphino)ethane)CoBr$_2$] complex and NaHBEt$_3$ for regioselective migratory hydrosilylation of 2-alkynes to furnish α-vinylsilanes with excellent regioselectivity (α/β up to 20:1). However, the application of.

commercially unavailable dimethyl(3,5-dimethyl-4-methoxy phenyl)silane and relatively high (pre)catalyst loading (5–7.5 mol %) somewhat limits its versatility.

Our previously reported catalytic system [15], based on cobalt (II) complex with a simple Schiff base ligand: benzimidazole-imine-2*H*-imidazole, catalyzed Markovnikov hydrosilylation of terminal alkynes with HSiMe$_2$Ph with high selectivity (91–99% of α-isomer). The hydrazone Schiff base ligand can be easily obtained in a two-step synthetic protocol from commercially available substrates. Although this is the most active catalytic system reported to date (0.5 mol % Co complex activated by 1.5 mol % LiHBEt$_3$), its further application for reactions with other tertiary silanes was unsuccessful.

Inspired by the results of the study with using Schiff bases as optimal ligands in the selective hydrosilylation of alkynes, we decided to look for a more universal coordination environment for cobalt(II) ions, which would create a catalyst tolerant to a wide variety of tertiary silanes. Herein, we describe the application of structurally simple ligands which, after coordination with cobalt (II) chloride, allow high activity and selectivity in the hydrosilylation reactions of terminal and internal alkynes to be maintained.

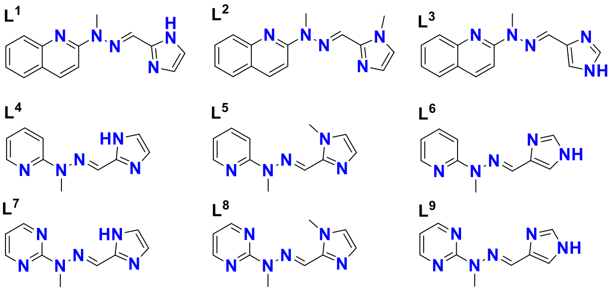
2. Results and disscusion

A series of *in situ* formed Co(II) complexes with hydrazone Schiff base ligands **L^1-L^9** (Scheme 2) were evaluated with regard to their activity and selectivity in model hydrosilylation reaction of phenylacetylene with diphenylsilane. Schiff base ligands are easily obtained through a two-step synthetic protocol (SI).

In order to check the selectivity of the hydrosilylation reaction, catalytic tests were carried out using equimolar amounts of phenylacetylene and diphenylsilane. For this purpose, anhydrous CoCl$_2$ and ligands were placed in a Schlenk flask, dried under reduced pressure and stirred in THF for an hour before the experiment. The reaction of phenylacetylene and diphenylsilane was carried out in the presence of 1 mol % of ligand (L^1-L^9), 1 mol % of anhydrous CoCl$_2$ and threefold excess of an activator (LiHBEt$_3$), at room temperature for 20hs, under argon atmosphere. The results are summarized in Table 1. The results obtained by employing the ligands with the 1Me-imidazol-2-yl motif (L^2, L^5, L^8) show diphenylsilane conversions ranging from 26% to 58% without specified selectivity. Subsequently investigated Schiff base motifs containing 1*H*-imidazol-4-yl derivatives (L^3, L^6, L^9) showed higher activity (48–87%), and selectivity towards α-selective hydrosilylation (for L^6 and L^9) products under similar reaction conditions, while the reaction in the presence of L^3 was non-selective. The efficiency and regioselectivity are mostly driven by the imidazole side of the ligand. However, the role of the activator on the activity and selectivity is not entirely clear. The borohydride seems to interact with the imidazole fragment acting as a base and deprotonating the NH groups. Further interactions with free borane can electronically and sterically stabilize the imidazole ring. The cobalt complexes containing 1*H*-imidazol-2-yl scaffold (L^1, L^4, L^7) seemed to be the most active and selective systems. Thus, the (pre)catalysts containing CoCl$_2$ and ligands **L^1**, **L^4** and **L^7** were chosen for further investigation.

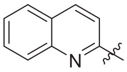
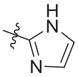
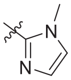
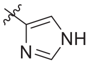
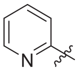
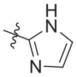
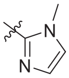
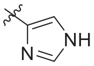
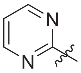
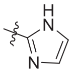
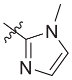
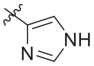
Catalytic activity and selectivity of all three systems remained unchanged when salt/ligand loadings were lowered to 0.5 mol % (Table 2, entry 1–3). Further lowering of the catalyst loading to 0.1 mol % was successful only for the CoCl$_2$ and pyrimidine ligand L^7 mixture, activated by LiHBEt$_3$ (entry 4–6). The use of the other borohydrides tested, i.e. KHBEt$_3$, NaHB(*sec*-Bu)$_3$ and NaHBEt$_3$, led to total conversion of diphenylsilane with slightly lower selectivity (entry 7–9), whereas the use of sodium *tert*-butoxide resulted in 54% of conversion of silane (entry 10). This phenomenon might be connected to the size of borohydride counterion (α/β selectivity LiHBEt$_3$ > NaHBEt$_3$ > KHBEt$_3$). Elevated temperature (40 °C) was found to be effective with a lower catalyst loading of 0.05 mol % (entry 13), which is one of the most efficient catalytic systems reported so far in the literature on cobalt-catalyzed alkyne hydrosilylation. Unfortunately, 0.01 mol % of catalyst loading, at an elevated temperature, was enough for only 58% conversion of diphenylsilane.

On the basis of these results, we synthesized a cobalt(II) complex with ligand **L^7** (synthesis and characterization is described in the Supporting Information) and we used the complex [Co(L^7)Cl$_2$], in which L^7 is (*E*)-2-(2-((1*H*-imidazol-2-yl)methylene)-1-methylhydrazinyl)pyrimidine, for further research (complex **1**). Complex **1** was air- and moisture-stable, operationally simple and easy to handle on the laboratory bench.



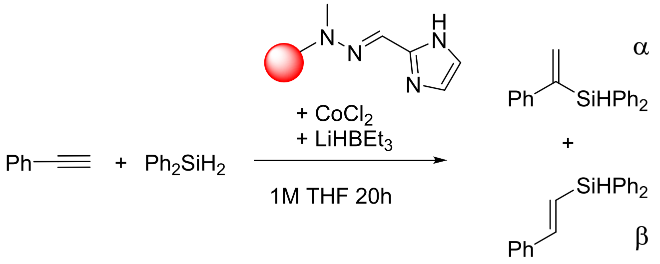
Scheme 2. Structures of Schiff base ligands.

Table 1
Hydrosilylation of phenylacetylene with diphenylsilane in the presence of $CoCl_2$/hydrazone Schiff base ligand activated by lithium triethylborohydride.

entry	🔴	🔵	Conversion of Ph_2SiH_2	α/β ratio
L^1			99	91:9
L^2			26	48:52
L^3			48	50:50
L^4			>99	89:11
L^5			58	64:36
L^6			87	85:15
L^7			**>99**	**96:4**
L^8			31	37:63
L^9			48	85:15

[a] Conditions: Phenylacetylene 1 mmol, Ph_2SiH_2 1 mmol, Schiff base ligand 1 mol %, $CoCl_2$ 1 mol %, $LiHBEt_3$ 3 mol %, 1 M solution of silane in THF, room temperature, 20 h.
[b] Calculated by GC with mesitylene (0.166 mmol) as internal standard.

Table 2
Optimization of conditions for hydrosilylation of phenylacetylene with diphenylsilane[a].



entry	$CoCl_2$ & Ligand [mol %]	Conversion of Ph_2SiH_2 [%]	α/β ratio
1	**L^1** 0.5%	98	97:3
2	**L^4** 0.5%	>99	94:6
3	**L^7** 0.5%	>99	96:4
4	**L^1** 0.1%	13	64:36
5	**L^4** 0.1%	32	72:28
6	**L^7** 0.1%	97	94:6
7[c]	**L^7** 0.1%	>99	89:11
8[d]	**L^7** 0.1%	>99	84:16
9[e]	**L^7** 0.1%	>99	95:5
10[f]	**L^7** 0.1%	54	76:24
11[g]	**L^7** 0.1%	>99	72:28
12	**L^7** 0.05%	97	98:2
13[h]	**L^7** 0,05%	>99	>99:1
14[h]	**L^7** 0,01%	58	98:1

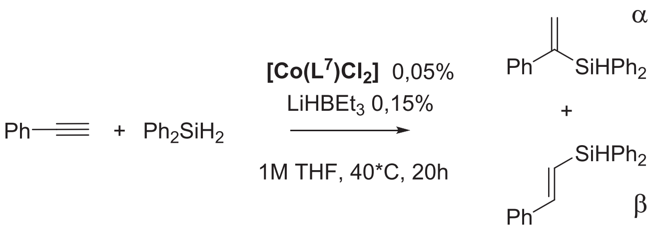
[a] Conditions: Phenylacetylene 1–5 mmol, Ph_2SiH_2 1–5 mmol, anhydrous $CoCl_2$ *n* mol %, ligand *n* mol %, $LiHBEt_3$ 3*n* mol %, 1 M solution of silane in THF, room temperature, 20 h. [b] Calculated by GC with mesitylene (0.166 mmol) as internal standard. Reactions with [c]$KHBEt_3$/[d]$NaHB(sec\text{-}Bu)_3$/[e]$NaHBEt_3$/[f]NaO^tBu/[g]Red-Al as an activator (instead of $LiHBEt_3$). [h]Reaction heated to 40 °C.

Hydrosilylation of other aliphatic and aromatic alkynes with diphenylsilane has been performed under established reaction conditions (Table 3). Application of alkyl-substituted phenylacetylenes led to the synthesis of α-vinylsilanes with good regioselectivity (**2b**-**2e**) ($\alpha/\beta > 94:6$). Halogenated aryl alkynes such as 4-fluorophenylacetylene (**2f**) or 4-bromophenylacetylene (**2 g**) were hydrosilylated effectively with good selectivity (97%) towards α-addition products.

Despite the high conversion of 2-ethynylthiophene (**2 h**), another heteroaromatic substrate – 2-ethynylpyridine (**2i**) reacted with diphenylsilane only with 23% conversion and moderate selectivity, even using a ten times higher concentration of the cobalt (pre)catalyst and activator. Reactive groups, such as amine (**2j**), dimethylamine (**2p**), methoxy (**2r**) or nitrile (**2 k**) were tolerated, affording products in good yields. Aliphatic and cycloaliphatic alkynes, such as hex-1-yne (**2 l**), ethynylcyclopropane (**2 m**), cyclohexylacetylene (**2n**) and 1-ethynylcyclohexene (**2o**) showed reactivity similar to aromatic alkynes, except for the reaction of diphenylsilane with cyclohexylacetylene, where a slightly lower selectivity ($\alpha/\beta = 84:16$) was observed. It should be noted that to achieve total conversion of substrates, the reactions with cyclohexyl-acetylene, 4-bromophenylacetylene and 4-ethynylbenzonitrile required higher catalyst loading (0.5 mol % complex **1** and 1.5 mol % $LiHBEt_3$). The reaction of phenylacetylene with an equimolar amount of diethylsilane resulted in total conversion of silane, however, a mixture of Markovnikov addition product - diethyl(1-phenylvinyl) silane, and a product of subsequent hydrosilylation of the latter - diethyldi(1-phenylvinyl)silane was detected in 87:13 ratio. Selected products were isolated and characterized using ^1H and ^{13}C NMR.

Our main target was to investigate the catalytic activity of cobalt(II) complex in the Markovnikov hydrosilylation of alkynes with tertiary silanes. For this purpose, reactions of dimethylphenylsilane with various aromatic and cycloaliphatic alkynes (Table 4) were performed. As we established in our previous work,[15] to provide complete conversion, tertiary silanes require elevated temperature (60 °C). Based on catalytic tests of the reaction of phenylacetylene with dimethylphenylsilane, we

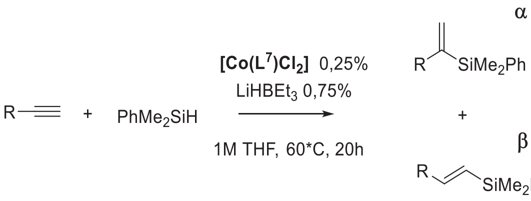
Table 3
Scope of alkynes in the hydrosilylation with secondary silanes.[a].



Entry	R	Silane	Silane Conver-sion [%][b]	Selecti-vity α/β
2a	Phenyl	Ph_2SiH_2	>99 (95)	100:0
2b	(4-Me)C_6H_4		>99	96:4
2c	(2-Me)C_6H_4		99	99:1
2d	(3-Me)C_6H_4		99	94:6
2e	(4-*t*Bu)C_6H_4		>99 (92)	99:1
2f	(4-F)C_6H_4		>99 (96)	97:3
2g[c]	(4-Br)C_6H_4		99	97:3
2 h	2-thienyl		>99	100:0
2i[c]	2-pyridyl		23	69:31
2j	(4-NH_2)C_6H_4		>99	100:0
2k[c]	(4-CN)C_6H_4		69	97:3
2 l	*n*-hexyl		>99	93:7
2 *m*	cyclopropyl		>99	100:0
2n[c]	cyclohexyl		95	84:16
2o	cyclohexen-1-yl		>99	92:8
2p	(4-NMe_2)C_6H_4		>99 (98)	95:5
2r	(4-MeO)C_6H_4		>99 (96)	100:0
2s[e]	Phenyl	Et_2SiH_2	>99	100:0[d]

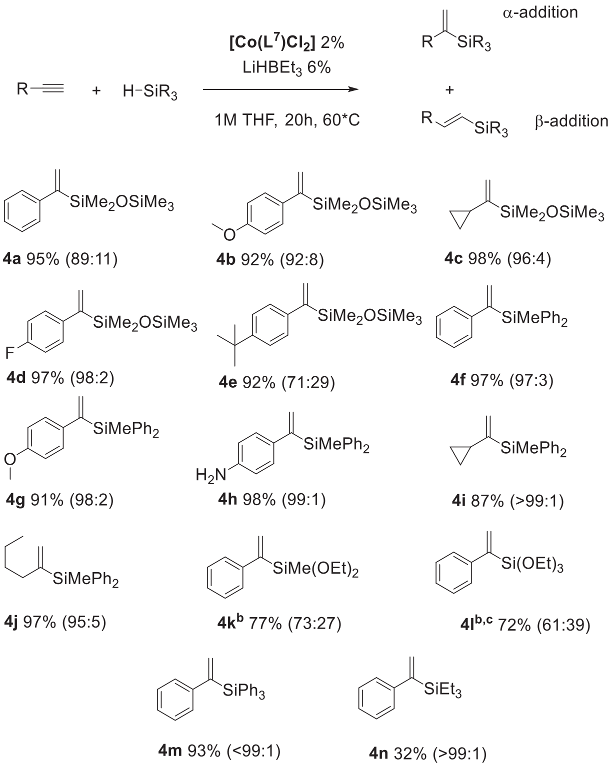
[a] Conditions: Alkyne 0.5 mmol, silane 0.5 mmol, 0.05 mol % of complex **1**, 0.015 mol % $LiHBEt_3$, 1 M solution of silane in THF, 40 °C, 20 h. [b]Calculated by GC with mesitylene (0.166 mmol) as internal standard. [c]0.5 mol % of complex **1**, 1.5 mol % $LiHBEt_3$, 60 °C. Isolated yields of the reaction products are given in parentheses. [d]Mixture of diethyl(1-phenylvinyl)silane and diethyldi(1-phenylvinyl)silane in 87:13 ratio. [e]2 mol % of complex **1**.

Table 4
Scope of alkynes in the hydrosilylation with dimethylphenylsilane[a].



Entry	R	Silane Conversion [%]	Selectivity α/β
3a	Phenyl	98	96:4
3b	(4-Me)C_6H_4	98	94:6
3c	(4-*t*Bu)C_6H_4	78	93:7
3d	(2-Me)C_6H_4	89	98:2
3e	(3-Me)C_6H_4	94	93:7
3f	(4-MeO)C_6H_4	97	94:6
3 g	(4-NH_2)C_6H_4	88	96:4
3 h	(4-NMe_2)C_6H_4	>99 (95)	99:1
3i	(4-F)C_6H_4	>99 (98)	97:3
3j	cyclopropyl	100	98:2
3 k	cyclohexen-1-yl	100	88:12
3 l	2-thienyl	30	85:15

[a] Conditions: Alkyne 0.5 mmol, $PhMe_2SiH$ 0.5 mmol, 0.25 mol % of complex **1**, 0.75 mol % $LiHBEt_3$, 1 M solution of silane in THF, 60 °C, 20 h. [b]Calculated by GC with mesitylene (0.166 mmol) as internal standard. Isolated yields of the selected reaction products are given in parentheses.



Scheme 3. Reactivity of tertiary silanes in the reactions with terminal alkynes.[a]. [a]Conditions: Alkyne 0.5 mmol, silane 0.5 mmol, 2 mol % of complex **1**, 6 mol % $LiHBEt_3$, 1 M solution of silane in THF, 60 °C, 20 h. Ratio of α- to β-addition products in parentheses, determined by ^1H NMR. Isolation yields. [b]Not isolated, conversions calculated by GC with mesitylene as internal standard. [c]Reaction with twofold excess of silane.

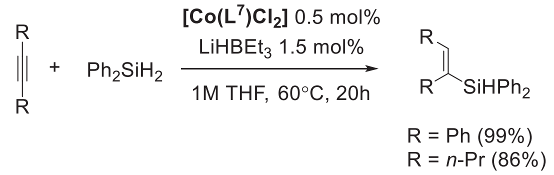
determined the optimal catalyst loading as 0.25 mol % of complex **1**, which is not achievable for previously reported cobalt-based catalysts. Phenylacetylene and its alkyl-substituted derivatives (**3a**-**e**) reacted with excellent selectivity and good yields. However, slightly worse selectivity in the reaction with 3-ethynyltoluene was observed. Methoxy, amino, dimethylamino, and fluoro substituents (**3f**-**3i**) were tolerated and functionalized aryl acetylenes reacted with good conversion and with selectivity α/β not less than 94:6. Cycloaliphatic alkynes such as cyclopropylacetylene (**3j**) and 1-ethynylcyclohexene (**3 k**) were smoothly hydrosilylated under the given conditions, however, the reaction with the latter resulted in generation of an increased amount of β-(*E*) addition product (α/β = 88:12). The reaction with 2-ethynylthiophene (**3 l**) was less successful in terms of substrate conversion and reaction selectivity.

We broadened the reaction scope by applying various tertiary silanes (Scheme 3) such as triethylsilane, triethoxysilane, methyldiphenylsilane, triphenylsilane, diethoxymethylsilane and pentamethyldisiloxane (**4a-n**), from which α-vinylsilanes bearing different silyl groups were synthesized in moderate to good yields. The best results were achieved by applying 2 mol% of complex **1**, at 60 °C for 20 h. Outstanding selectivities were obtained in the reactions of both aromatic and aliphatic alkynes with methyldiphenylsilane and triphenylsilane (**4f**-**4i**, **4 m**) (α/β > 97:3). Triethylsilane reacted with phenylacetylene affording only one product (**4n**). Although the obtained selectivity was excellent, the conversion of silane was only 32%. Triethoxysilane and diethoxymethylsilane reacted with moderate conversions (**4 k**, **4 l**) and selectivities lower than that obtained using the other silanes. The decreased Markovnikov selectivity observed for the reactions of alkoxysilanes can be attributed to the steric, less demanding nature of ethoxylsilyl groups. Unsurprisingly, the Si-O bond cleavages with simultaneous formation of cyclic siloxanes were observed under the applied conditions. This phenomenon is a common issue in the reaction of alkoxysilanes in the presence of strong bases and nucleophiles [16]. Contrary to alkoxysilanes, pentamethyldisiloxane proved to be an effective partner for the catalytic hydrosilylation of aromatic and aliphatic alkynes (**4a-4e**), however, the Markovnikov selectivity was strictly dependent on the alkyne used and varied within the range 71–98%.

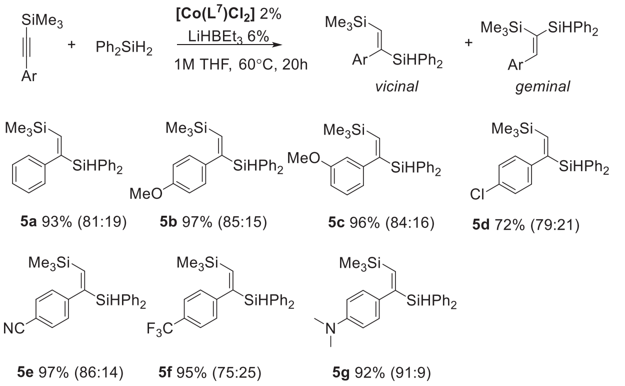
The reaction of D_1-phenylacetylene and diphenylsilane afforded *syn*-addition product, and no anti-addition products were observed (SI). On the basis of deuterium labeling experiments and the previously reported data[5b] we assume that the hydrosilylation of alkynes catalyzed by complex **1** in the presence of $LiHBEt_3$ proceed *via* cobalt(I)-silyl intermediate. Alternatively, Co(0) pathway of Markovnikov-selective hydrosilylation, recently proposed for 3 *N* pincer cobalt complex on the basis of DFT calculations can be considered [17].

Internal alkynes could also be hydrosilylated under our cobalt-catalyzed conditions. Symmetrical internal alkynes: oct-4-yne and diphenylacetylene underwent hydrosilylation with diphenylsilane with good yield (86–99%), selectively giving the corresponding (*E*)-silylalkenes (Scheme 4). The reaction occurred with 0.5 mol % complex **1** and 1.5 mol% $LiHBEt_3$ at 60 °C for 20 h. Unfortunately, increasing the reaction temperature, time and the precatalyst loading did not afford positive results for the reaction with tertiary silanes.

To emphasize the applicability of our catalytic system, we investigated the hydrosilylation of 1-phenyl-2-(trimethylsilyl)acetylenes (Scheme 5). The most common approach to the hydrosilylation of silylacetylenes involves ruthenium catalysts [18]. Silylacetylenes are challenging substrates for cobalt complex-catalyzed hydrosilylation. So far, only few catalytic systems have been reported for the hydrosilylation of terminal [8b] and internal silylacetylenes [6g], most of which promoted the formation of geminal bis(silyl)alkene products. The application of our catalytic system $[Co(L^7)Cl_2]/LiHBEt_3$ indicated formation of isomeric (bis) silylated products - (*E*)-1-aryl-1,2-bis(silyl)ethenes in good yields (72–97%), which constitute a group of useful synthons [19]. To the best of our knowledge, there is only one example in the literature of cobalt-catalyzed alkyne hydrosilylation leading to such products [20]. 1-Phenyl-2-(trimethylsilyl)acetylene and its derivatives were reacted with diphenylsilane in the presence of 2 mol% of complex **1** over 20 h at 60 °C. The reaction of diphenylsilane with 1-phenyl-2-(trimethylsilyl)acetylene led to (*E*)-1-phenyl-1-diphenylsilyl-2-(trimethylsilyl)ethene (**5a**) as a predominant product with 93% yield (selectivity 81:19 of *1,2- (vicinal)* to *1,1-* (*geminal*) product). A similar selectivity was observed for *p*- and *m*-substituted derivatives on the phenyl ring, irrespective of the nature of the substituents (**5b**-**5 g**). The highest selectivity was achieved for an electron donating dimethylamino group (*vic*: *gem* = 91:9), and the lowest for an electron withdrawing *p*-trifluoromethyl substituent (*vic*: *gem* = 75:25).



Scheme 4. Hydrosilylation of symmetrical internal alkynes with diphenylsilane.



Scheme 5. Hydrosilylation of 1-aryl-2-(trimethylsilyl)ethynes with diphenylsilane. [a]Conditions: Alkyne 0.5 mmol, Ph_2SiH_2 0.5 mmol, 2 mol % of complex **1**, 6 mol % $LiHBEt_3$, 1 M solution of silane in THF, 60 °C, 20 h. Ratio of *vicinal* to *geminal* products determined by ^1H NMR. Isolated yields.

3. Conclusions

In summary, a new bench stable and easily synthesized (pre)-catalyst for cobalt-catalyzed Markovnikov hydrosilylation of alkynes has been developed. A pentacoordinated cobalt(II) chloride complex with pyrimidine/2*H*-imidazole-based ligand, activated by lithium triethylborohydride, has been found to act as a good catalyst for regioselective hydrosilylation of terminal alkynes by secondary and tertiary silanes as well as internal alkynes by diphenylsilane. The catalytic system is applicable to both alkyl- and aryl-substituted alkynes showing good functional group compatibility (amine, halide, ether, nitrile etc.) and broad scope on tertiary silanes. Low catalyst loading (0.05–2 mol %) and high selectivity towards α-hydrosilylation products make it more universal than the previously reported catalytic systems based on cobalt complexes with 3 *N*-donor ligands.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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We would like to dedicate our article to professor Pierre Dixneuf in recognition of his outstanding achievements in the field of homogeneous catalysis.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2022.05.002.

References

[1] (a) J. Szudkowska-Frątczak, G. Hreczycho, P. Pawluć, Org. Chem. Front. 2 (2015) 730–738;
(b) I. Fleming, A. Barbero, D. Walter, Chem. Rev. 97 (1997) 2063–2192;
(c) D.S.W. Lim, E.A. Anderson, Synthesis 44 (2012) 983–1010.

[2] (a) B. Marciniec, C. Pietraszuk, P. Pawluć, H. Maciejewski, Chem. Rev. 122 (2022) 3996–4090;
(b) M.D. Greenhalgh, A.S. Jones, S.P. Thomas, ChemCatChem 7 (2015) 190–222;
(c) J. Chen, J. Guo, Z. Lu, Chin. J. Chem. 36 (2018) 1075–1109.

[3] (a) B.M. Trost, Z.T. Ball, Synthesis 6 (2005) 853–887;
(b) M. Zaranek, B. Marciniec, P. Pawluć, Org. Chem. Front 3 (2016) 1337–1344;
(c) W. Gao, S. Ding, Synthesis 52 (2020) 3549–3563;
(d) P. He, M.-Y. Hu, X.-Y. Zhang, S.-F. Zhu, Synthesis 54 (2022) 49–66.

[4] (a) Almeida, L. D.; Wang, H.; Junge, K.; Cui, X; Beller, M. *Angew. Chem. Int. Ed.* **2021**, *60*, 550–565. (b) Obligacion, J. V.; P. J. Chirik P. J., *Nat. Rev*. Chem. **2018**, *2*, 15–34. (c) Wen, H. A.; Liu, G. X.; Huang, Z. *Coord. Chem. Rev*. **2019**, *386*, 138–153.

[5] (a) J. Sun, L. Deng, ACS Catalysis 6 (2016) 290–300;
(b) J.-W. Park, Chem. Commun. 58 (2022) 491–504.

[6] (a) J. Chen, J. Guo, Z. Lu, Chin. J. Chem. 36 (2018) 1075–1109;
(b) Z. Mo, J. Xiao, Y. Gao, L. Deng, J. Am. Chem. Soc. 136 (2014) 17414;
(c) C. Wu, W.J. Teo, S. Ge, ACS Catal. 8 (2018) 5896;
(d) B. Raya, S. Jing, V. Balasanthiran, T.V. RajanBabu, ACS Catal. 7 (2017) 2275;
(e) C. Belger, B. Plietker, Chem. Commun. 48 (2012) 5419;
(f) J.H. Docherty, J. Peng, A.P. Dominey, S.P. Thomas, Nat. Chem. 9 (2017) 595–600;
(g) Z. Mo, J. Xiao, Y. Gao, L. Deng, J. Am. Chem. Soc. 136 (50) (2014) 17414–17417.

[7] W.J. Teo, C. Wang, Y.W. Tan, S. Ge, Angew. Chem. Int. Ed. 56 (2017) 4328–4332.

[8] (a) Z. Zuo, J. Yang, H.Z. Angew, Chem. Int. Ed. 55 (2016) 10839–10843;
(b) J. Guo, Z. Lu, Angew. Chem., Int. Ed. 55 (2016) 10835–10838;
(c) S. Zhang, J.J. Ibrahim, Y. Yang, Org. Lett. 20 (2018) 6265–6269;
(d) J.-S. Jia, Y. Cao, T.-X. Wu, Y. Tao, Y.-M. Pan, P.-F. Huang, H.-T. Tang, ACS Catal. 11 (2021) 6944–6950.

[9] Z. Zong, Q. Yu, N. Sun, B. Hu, Z. Shen, X. Hu, L. Jin, Org. Lett. 21 (2019) 5767–5772.

[10] G. Wu, U. Chakraborty, A.J. von Wangelin, A. J. Chem. Commun. 54 (2018) 12322–12325.

[11] (a) D. Kong, B. Hu, M. Yang, D. Chen, H. Xia, Organometallics 38 (2019) 4341–4350;
(b) D. Kong, B. Hu, D. Chen, Chem. Asian J. 14 (2019) 2694–2703.

[12] M. Isobe, R. Nishizawa, T. Nishikawa, K. Yoza, Tetrahedron 40 (1999) 6927–6932.

[13] D. Wang, Y. Lai, P. Wang, X. Leng, J. Xiao, L. Deng, J. Am. Chem. Soc. 143 (2021) 12847–12856.

[14] M.K. Sahoo, D. Kim, S. Chang, J.-W. Park, ACS Catal. 11 (2021) 12777–12784.

[15] M. Skrodzki, V. Patroniak, P. Pawluć, Org. Lett. 23 (2021) 663–667.

[16] C.L. Chang, H.S.J. Lee, C.K. Chen, J. Polym. Res. 12 (2005) 433–438.

[17] M. Yumiao, H. Zongchang, J. Org. Chem. 83 (2018) 14646–14657.

[18] (a) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726–12727. (b) Ding, S.; Song, L-J.; Chung, L.W.; Zhang X.; Sun, J.; Wu Y-D. *J. Am. Chem. Soc.* **2013**, *135*, 13835–13842. (c) Zhang, X.; J, X.; Xie, X.; Ding, S. *Chem. Commun*., **2018**, *54*, 12958–12961.

[19] (a) A. Inoue, J. Kondo, H. Shinokubo, K. Oshima, Chem. Commun. (2002) 114–115;
(b) K. Karabelas, A. Hallberg, J. Org. Chem. 54 (1989) 1773–1776;
(c) P. Pawluc, G. Hreczycho, J. Szudkowska, A. Franczyk, B. Marciniec, Appl. Organometal. Chem. 24 (2010) 853–857.

[20] A. Rivera-Hernández, B.J. Fallon, S. Ventre, C. Simon, M.H. Tremblay, G. Gontard, E. Derat, M. Amatore, C. Aubert, M. Petit, Org. Lett. 18 (2016) 4242–4245.