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Regiocontrol in the cobalt-catalyzed hydrosilylation of alkynes†

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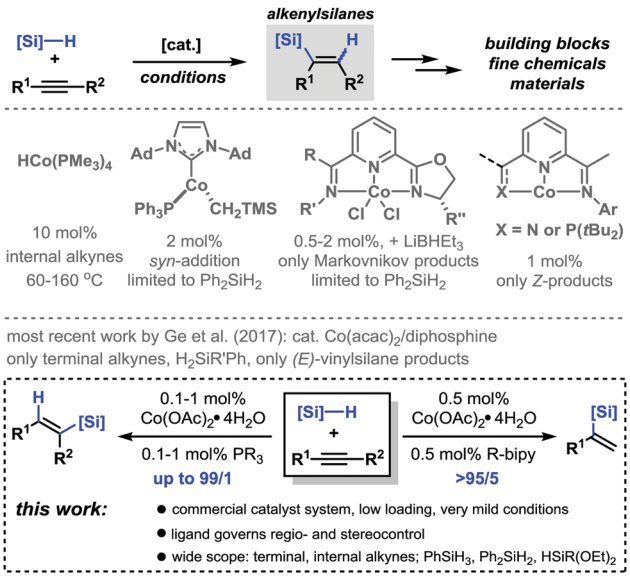
Hydrofunctionalizations of unsaturated hydrocarbons are key strategies for the synthesis of functionalized building blocks. Here, we report highly versatile cobalt-catalyzed hydrosilylations of alkynes that operate with minute amounts of the inexpensive, bench-stable pre-catalyst $Co(OAc)_2{\cdot}4H_2O$ under mild conditions (0.1–1 mol%, THF, r.t., 1 h). Near-perfect regiocontrol/stereocontrol was induced by the choice of the ligand: bidentate phosphines afforded (*E*)-β-vinylsilanes; α-vinylsilanes formed with bipyridine ligands.

Alkenylsilanes constitute versatile building blocks in the realm of fine chemicals and materials synthesis by virtue of their dense poly-functionalization.[1] The combination of a polarized alkene moiety, a Si center, and the substituents at alkene and silicon offer ample opportunities for post-synthesis manipulations. Hydro-silylations of alkynes enable a most straightforward and atom-economic synthesis of alkenylsilanes in the presence of the noble metal catalysts Ru, Rh, and Pt.[2–4] Only few protocols rely on the use of inexpensive and environmentally benign 3d base metal catalysts.[5] Despite the recent progress in the field, the precise control of regioselectivity and stereoselectivity remains a challenge of utmost importance. Cobalt catalysts were demonstrated to exhibit especially high activity and tolerance of functional groups in hydrosilylations of alkenes.[6] Much less attention has been directed towards cobalt-catalyzed hydrosilylations of alkynes which often require high catalyst loadings, complex ligands, and harsh conditions or showed poor regio/stereocontrol or a limited substrate scope with regard to alkynes and silanes (Scheme 1, top).[7–12] Very recently, Ge *et al.* reported Co-catalyzed hydrosilylations to give (*Z*)-vinylsilanes in the presence of pyridine-2,6-diimines.[13] We believed that a most user-friendly protocol would combine the following criteria: (i) high catalytic activity of a commercial catalyst system under very mild conditions; (ii) control of regioselectivity and stereoselectivity by the choice of the ligand, and (iii) a wide substrate scope involving terminal and internal alkynes and trihydrosilanes. Documented herein are the benefits of a versatile regiodivergent and stereoselective hydrosilylation of alkynes in the presence of only 0.1–1 mol% $Co(OAc)_2{\cdot}4H_2O$ and commercial phosphine or bipyridine ligands (Scheme 1, bottom).



Scheme 1 Cobalt-catalyzed hydrosilylations of alkynes.

An initial evaluation of parameters in the model reaction between phenylacetylene (**1a**) and phenylsilane (**2a**) in the presence of the bench-stable and inexpensive $Co(OAc)_2{\cdot}4H_2O$ revealed very good regioselectivity and stereoselectivity toward (*E*)-styrylsilane with various commercial phosphine ligands (Table 1, entries 1–7). With only 0.1 mol% $Co(OAc)_2{\cdot}4H_2O$/dppb, an isolated yield of 86% was obtained with very high stereoselectivity (>50/1 *E*/*Z*) and regiocontrol (1/49 α/β). A complete reversal of regioselectivity was observed upon employment of bipyridine ligands (up to 25/1 α/β, entries 8–12). These results are a significant extension of previous reports with N,N,N-ligands that resulted in poor regio-selectivity with $PhSiH_3$.[12] The strict

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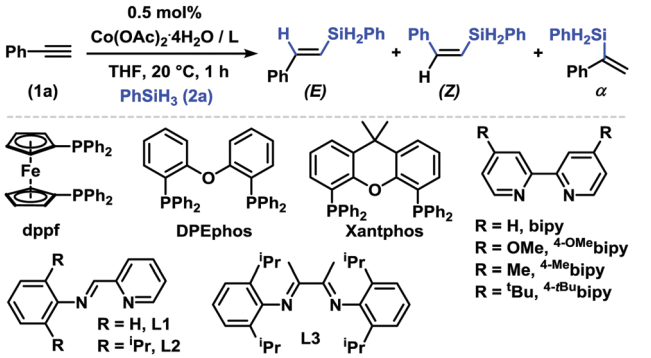
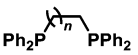
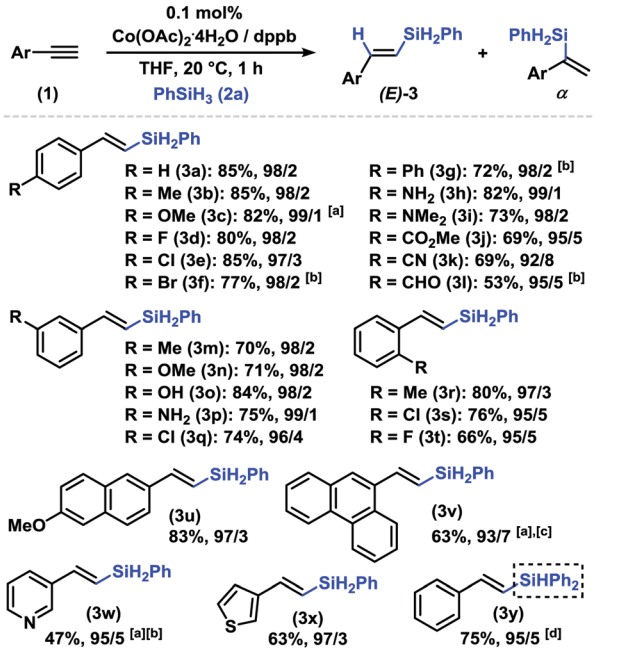
Table 1 Optimization of reaction conditions[a]



Entry	Ligand		Yield[b] [%]	$E/Z/\alpha$[b]
1		$n = 1$	72	87/0/13
2		$n = 2$	81	97/0/3
3		$n = 3$	**95**	**98/0/2**
4	Dppf		92	97/0/3
5	DPEphos		90	98/0/2
6	Xantphos		89	87/2/11
7[c]	**Dppb**		**94 (86)**[d]	**98/0/2**
8	2,2′-Bipyridine (bipy)		75	10/0/90
9	$^{4\text{-OMe}}$bipy		66	4/0/96
10	**$^{4\text{-Me}}$bipy**		**70 (60)**[d]	**5/0/95**
11	$^{4\text{-}t\text{Bu}}$bipy		64	5/0/95
12	1,10-Phenanthroline		61	10/0/90
13	L1 or L2 or L3		0	—
14	2,2′;6′,2″-Terpyridine		0	—

[a] Conditions: **1a** (0.40 mmol), **2a** (0.48 mmol), $Co(OAc)_2{\cdot}4H_2O$ (0.5 mol%), ligand (0.5 mol%), 0.5 mL THF, 20 °C, under N_2 (1 h w/PR_3, 3 h with N,N-ligands). [b] Yield and product ratios from quantitative GC-FID *vs.* internal *n*-dodecane. [c] 0.1 mol% $Co(OAc)_2{\cdot}4H_2O$ (in 10 μL methanol), 0.1 mol% dppb, 1 h. [d] Isolated yields in parentheses.



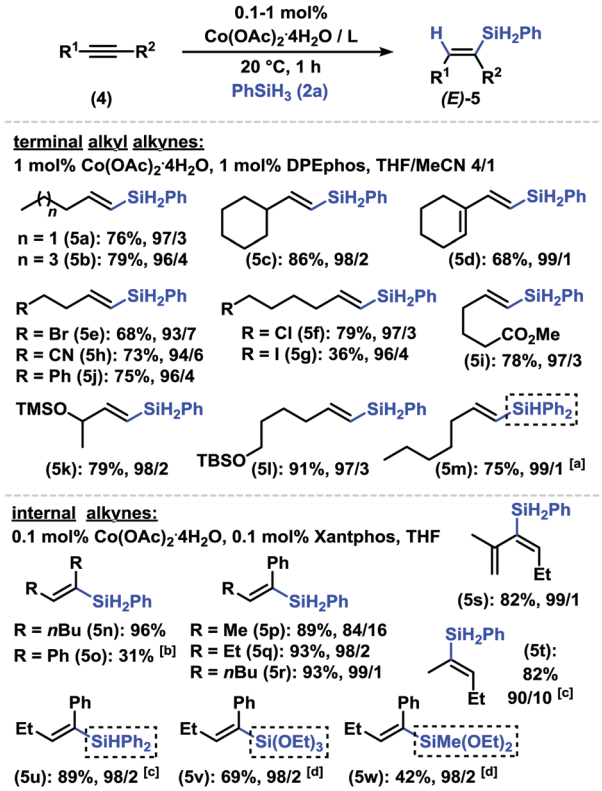
Scheme 2 Hydrosilylation of terminal aryl alkynes. Conditions: **1** (0.4 mmol), **2a** (0.48 mmol), $Co(OAc)_2{\cdot}4H_2O$ (0.1 mol%), dppb (0.1 mol%), 0.5 mL THF, 20 °C, under N_2, 1 h. Isolated yields are given. E/α ratios were determined by quantitative GC-FID *vs.* internal *n*-dodecane. [a] 3 h. [b] $Co(OAc)_2{\cdot}4H_2O$ (0.5 mol%), dppb (0.5 mol%). [c] $Co(OAc)_2{\cdot}4H_2O$ (1 mol%), dppb (1 mol%). [d] Xantphos.

ligand control of this protocol is further documented by the lack of catalytic activity in the presence of other N,N-ligands such as (pyridin-2-yl)methanimine, butane-2,3-diimine, and terpyridine (entries 13 and 14).

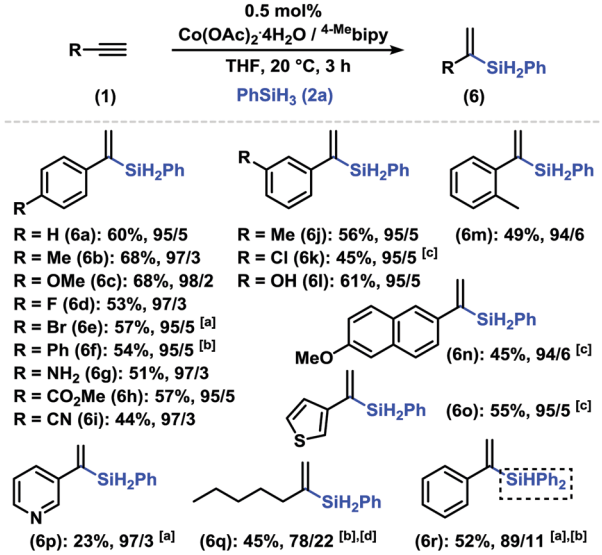
Various arylacetylenes underwent clean formation of (*E*)-alkenyl-silanes in good yields, very high stereoselectivities (>50/1 *E*/*Z*) and regioselectivities (>18/1 *β*/*α*) with only 0.1 mol% $Co(OAc)_2{\cdot}4H_2O$ and dppb at r.t. (Scheme 2). Diverse substitution patterns (incl. *ortho*-substituents) and functional groups (OH, NH_2, nitrile, ester, aldehyde, thiophene, and pyridine) were tolerated. No dehalogenation was observed with halides (Br, Cl, and F). The same conditions were successfully applied to hydrosilylations with monohydrosilanes and dihydrosilanes (*i.e.* $(EtO)_3SiH$ and Ph_2SiH_2). An extension of the methodology to terminal and internal alkyl alkynes was realized with cobalt/diphosphine catalyst systems (entries 5 and 6 in Table 1 and ESI†). Terminal alkynes exhibited the highest reactivities, very high stereoselectivities (>50/1 *E*/*Z*), and very high regioselectivities (up to 99/1 *β*/*α*) toward (*E*)-alkenyl-silanes in the presence of 1 mol% $Co(OAc)_2{\cdot}4H_2O$ and DPEphos (Scheme 3, top). Silylethers, halides, nitriles, and ester moieties were tolerated. Free OH groups inhibited the conversion. The protocol was also applied to hydrosilylation with diphenylsilane (**5m**).

Internal alkynes successfully reacted under slightly modified conditions with Xantphos as a ligand (Scheme 3, bottom). Highly selective *syn*-hydrosilylation was operative with all substrates. Unsymmetrical alkynes engaged in the regioselective addition of the silyl moiety to the less bulky C atom (Ph, i-Pr *vs.* alkyl; alkyl *vs.* Me). This is also manifested in the series of 2-alkyl phenylacetylenes with increasing regioselectivities in the order Me < Et < *n*Bu (**5p**, **5q**, and **5r**). The conjugated enyne 2-methylhex-1-ene-3-yne cleanly afforded the desired 3-silyl product **5s**. The hydrosilylation of the sterically rather unbiased 2-pentyne gave impressive regio-selectivity (9/1) and stereoselectivity. Ph_2SiH_2, $HSi(OEt)_3$, and $HSiMe(OEt)_2$ fared equally well. Steric silanes ($HSiEt_3$ and $HSi(OiPr)Me_2$) gave complex product mixtures, possibly from rapid alkyne (cyclo)oligomerizations. We further explored the regioselective α-silylation of terminal alkynes (entries 8–12, Table 1). The Co/2,2′-bipyridine catalysts enabled a reversal of regio-selectivity to cleanly afford 1-phenylvinyl silanes which constitute important synthetic building blocks (Scheme 4).[1] The reaction displayed compatibility with Br, NH_2, ester, nitrile, and free OH functional groups. 2-Ethynyl-6-methoxynaphthalene, 3-ethynylthiophene, and 3-ethynylpyridine gave slightly lower conversions (**6n**, **6o**, and **6p**). Internal alkynes reacted poorly (~10% yield, low regiocontrol).

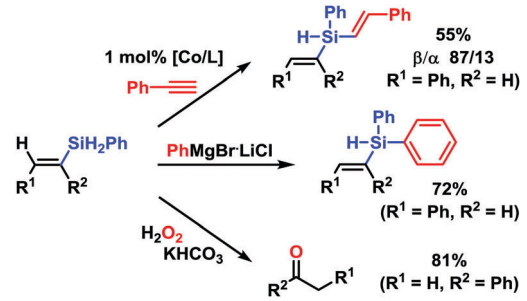
The versatility of the derived alkenylsilanes for further manipulations is exemplified in Scheme 5. Sequential hydro-silylations afforded a divinylsilane (87/13 *β*/*α*) *via* the alkenyl-silane **3a**. Substitution of the hydride at Si with Grignard reagents is a robust method of silane functionalization. With PhMgBr, tertiary silane **3a** was obtained in 74% yield. Tamao oxidation of vinylsilane **6a** gave the corresponding phenone in 81% yield. Further alkenylsilane reactions of high utility include electrophilic and nucleophilic olefin additions, silyl substitutions, oxidations, cross-couplings, hydro-functionalizations and polymerizations.[1]



Scheme 3 Hydrosilylation of alkynes. Conditions: **4** (0.4 mmol), **2a** (0.48 mmol), $Co(OAc)_2{\cdot}4H_2O$ (0.1 or 1 mol%), ligand (0.1 or 1 mol%), 0.5 mL solvent, 1 h, under N_2. Isolated yields are given. Product ratios *E*/α were determined by quantitative GC-FID *vs.* internal *n*-dodecane. [a] Xantphos. [b] $Co(OAc)_2{\cdot}4H_2O$ (0.5 mol%). [c] $Co(OAc)_2{\cdot}4H_2O$ (1 mol%). [d] $Co(OAc)_2{\cdot}4H_2O$ (0.5 mol%), 0.5 mL MeCN, 60 °C, 2 h.

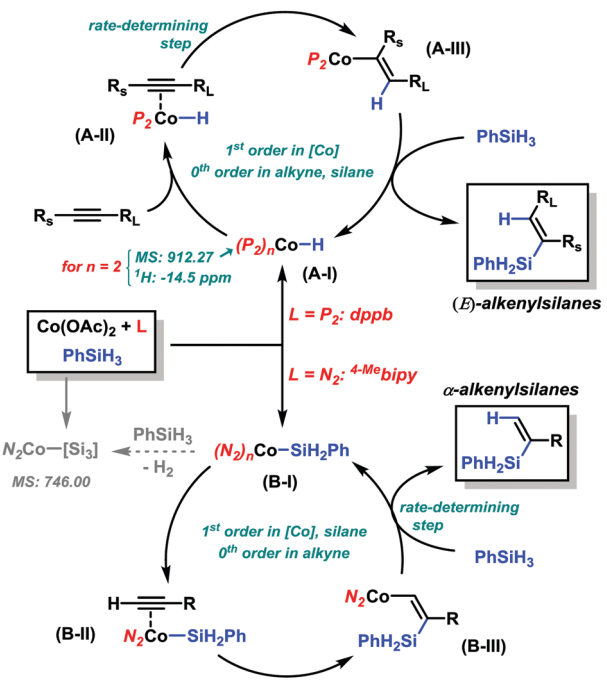


Scheme 4 Markovnikov hydrosilylation of arylacetylenes. Conditions: **1** (0.4 mmol), **2a** (0.48 mmol), $Co(OAc)_2{\cdot}4H_2O$ (0.1 or 1 mol%), ligand (0.1 or 1 mol%), 0.5 mL solvent for 1 h under N_2. Isolated yields are given. The product ratios [α/*E*] were determined by GC analysis. [a] 50 °C. [b] 6 h. [c] **2a** (1.5 equiv.). [d] $^{4\text{-OMe}}$bipy as a ligand (0.5 mol%).



Scheme 5 Post-synthesis manipulations of (*E*)-alkenyl silanes.

In extension of literature precedents and our own preliminary mechanistic data derived from the optimization experiments, substrate scope, and regiochemical and stereochemical course of the cobalt-catalyzed hydrosilylation reactions, we performed key mechanistic studies on the nature of catalytic intermediates (Scheme 6).[6,10–15] In full accord with the literature,[6g] the reduction of $Co(OAc)_2$ by the silane in the presence of diphosphine ligands (L = P_2) was observed by MS and NMR. We postulate the formation of the monohydrido species L_nCoH (A-I). Indeed, the penta-coordinate complex $(dppb)_2CoH$ was observed in LIFDI-MS spectra (*m*/*z* 912.27) and showed a characteristic ^{1}H NMR resonance at −14.5 ppm (see the ESI† for details). Coordination of the alkyne (A-II) and migratory insertion into the Co–H bond constitute the elemental steps that govern the regioselectivity and stereoselectivity of the reaction. The preferential addition of the cobalt complex to the less hindered side of the alkyne bearing the smaller substituent R_s affords the more stable alkenylcobalt species A-III. Formal trans-metalation to Si results in the formation of the (*E*)-alkenylsilane and regeneration of the active species A-I. The reaction is first order in



Scheme 6 Proposed reaction mechanisms of hydrosilylation catalysed by (diphosphine)cobalt complexes (top) and (bipy)cobalt complexes (bottom).

the cobalt catalyst and zero order in phenylacetylene and silane (see the ESI†), which suggests that the alkyne insertion into Co–H is rate-determining. A different mechanistic scenario appears to be operative with bipy ligands (L = N_2, Scheme 6, bottom). The reductive formation of a silylcobalt complex LCo-Si (B-I) is in full agreement with the literature.[6c,6f,11] ^{1}H NMR spectra of the reaction of $Co(OAc)_2{\cdot}4H_2O$/^{4Me}bipy with $PhSiH_3$ (1 : 1 : 10) documented the anticipated formation of a paramagnetic species. The presence of silylcobalt complexes was suggested by LIFDI-MS measurements of the catalyst mixture which exhibited the trisilyl complex (^{4Me}bipy)$_2$-Co(SiHPhSiHPhSiH$_2$Ph) (*m*/*z* 746.00). Such oligosilane complexes constitute key intermediates in silane dehydro-coupling and oligomerization reactions and were also observed with other metals.[15] The same paramagnetic oligosilyl complex was independently formed by the reaction of equimolar $Co(OAc)_2{\cdot}4H_2O$ and $^{4\text{-}Me}$bipy with 5 equiv. of $PhSiH_3$. The dehydrocoupling could be reversed by the addition of $LiAlH_4$ (2.5 equiv. per [Co]) which resulted in the generation of $PhSiH_3$ (see the ESI† for details). The silylcobalt complex B-I is postulated to engage in alkyne coordination followed by regioselective and stereo-selective 1,2-*syn*-insertion. The resultant *syn*-alkenylcobalt complex B-III releases α-alkenylsilane upon reaction with $PhSiH_3$. This hydrosilylation reaction is first order in [Co] and silane and zero order in phenylacetylene (see the ESI†). This indicates a rate limitation by the product release step.

In conclusion, a highly versatile cobalt-catalyzed hydrosilylation has been developed that enables precise regiocontrol by the choice of the ligand. The catalysts exhibit superior activity over the current state-of-the-art, operating under very mild conditions (20 °C, 1 h) with only 0.1–1 mol% catalyst loading. The catalysts are based on commercial and inexpensive components: the bench-stable $Co(OAc)_2{\cdot}4H_2O$ and the ligand dppb or $^{4\text{-}Me}$bipy. The mild conditions allow a wide substrate scope (terminal and internal alkynes, various silanes) and the tolerance of sensitive functional groups (halides, aldehydes, esters, nitriles, NH_2, and OH). Key mechanistic studies support the notion of a mechanistic dichotomy: the ligand dppb enables highly selective formation of (*E*)-alkenyl-silanes *via* anti-Markovnikov hydrosilylation. A full regiochemical switch is effected by the ligand $^{4\text{-}Me}$bipy which selectively delivers Markovnikov products. The former pathway involves the formation of hydridocobalt catalyst species, while the latter mode of reactivity is most likely based on silylcobalt species. The high functional group tolerance and mild reaction conditions make these protocol highly attractive for complex molecule synthesis with great utility for medicinal and materials chemistry endeavours.

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Conflicts of interest

There are no conflicts to declare.

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