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Regio- and Stereoselective Hydrosilylation of Unsymmetrical Alkynes Catalyzed by a Well-Defined, Low-Valent Cobalt Catalyst

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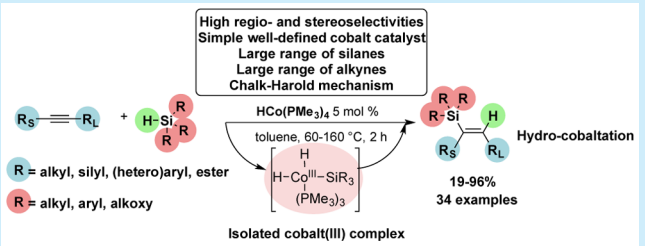
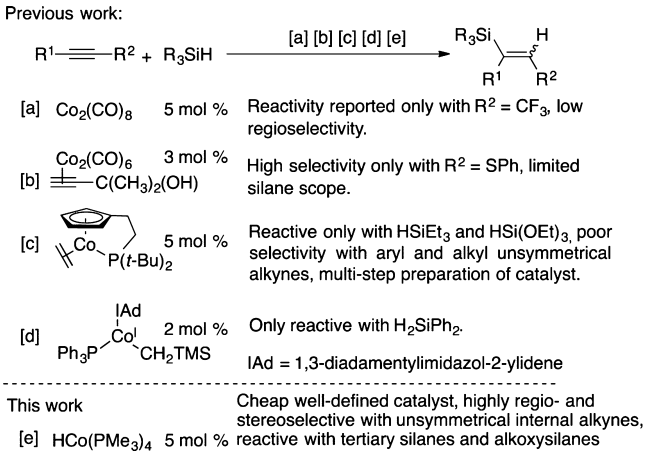
Supporting Information

ABSTRACT: Herein, the use of a well-defined low-valent cobalt(I) catalyst [$HCo(PMe_3)_4$] capable of performing the highly regio- and stereoselective hydrosilylation of internal alkynes is reported. The reaction can be applied to a variety of hydrosilanes, symmetrical and unsymmetrical alkynes, giving in many cases a single hydrosilylation isomer. Experimental and theoretical studies suggest the key step to be a hydrocobaltation and that the reaction proceeds through a classical Chalk−Harrod mechanism.



Transition metal-catalyzed hydrosilylation of alkynes represents one of the most straightforward methods to obtain synthetically valuable vinylsilanes.[1] However, a pertinent issue impeding the widespread use of this method is the difficultly in achieving regio- and stereocontrol, both of which are still currently challenging.[2] There have been several reports over the past decade on the transition-metal-catalyzed hydrosilylation of alkynes largely based on the use of noble metals (Y,[3] Ru,[4] Rh,[5] Pt).[6] In contrast, reports on the use of earth abundant metals (Fe,[7] Ni,[8] Cu)[9] have been sparse, and considering the need to develop new efficient, economic, and environmentally benign catalysts this remains an appealing area of study. Owing to its high abundancy, low cost, and rich redox chemistry, cobalt offers an attractive alternative to other transition-metal-based catalysts. While several groups using low-valent cobalt catalysis recently explored the hydrosilylation of alkenes, reports on alkynes remain rare in comparison.[10] The group of Konno demonstrated the catalytic activity of $Co_2(CO)_8$ toward the highly regio- and stereoselective hydrosilylation of fluoroalkylated alkynes with $HSiEt_3$ (Scheme 1a).[11a] Isobe initially reported the hydrosilylation of unsymmetrical alkynes which suffered from poor regioselectivity.[11b] Later, he described the *syn*-α-hydrosilylations with internal phenylthioalkynes (Scheme 1b).[11c−e] Butenschön described the hydrosilylation of a narrow range of internal alkynes using both $HSi(OEt)_3$ and $HSiEt_3$ albeit with poor control of the regioselectivity (Scheme 1c).[11f] Recently, Deng and co-workers reported the use of low-coordinated cobalt(I) complexes stabilized by a bulky N-heterocyclic carbene ligand (Scheme 1d). Such complexes have proven to be highly efficient for the regio- and stereoselective hydrosilylation of a large variety of alkynes. However, the reaction was only compatible with H_2SiPh_2; switching to a tertiary hydrosilane led to a complete shutdown of the catalytic activity.[11g]

Scheme 1. Cobalt-Catalyzed Hydrosilylation of Alkynes



Our group has recently been interested in the application of well-defined low-valent cobalt complexes, in particular, $HCo(PMe_3)_4$ and $Co(PMe_3)_4$, toward C−H bond activation and [2 + 2 + 2] enediyne cycloadditions.[12,13] Herein, we report the highly regio- and stereoselective hydrosilylation of internal alkynes. The present study is notable for a number of features: (i) high regio- and stereoselectivities have been obtained for a large variety of unsymmetrical alkynes, (ii) the reaction is compatible with tertiary silanes and alkoxysilanes, and (iii) the one-step synthesis of catalyst is inexpensive and easy on a large

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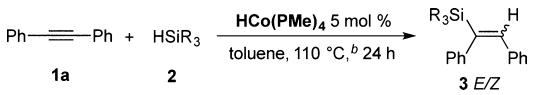
scale. To begin this study, we first examined the capacity of complex $HCo(PMe_3)_4$ to perform the hydrosilylation of diphenylacetylene **1a** with various hydrosilanes (Table 1).

Table 1. Hydrosilylation of Diphenylacetylene with Various Hydrosilanes[a]



1a 2 3 E/Z

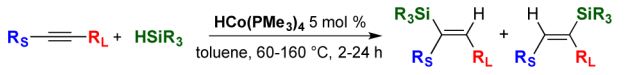
entry	silane	product	yield %[c]	E/Z
1	**2a** Ph_3SiH	**3aa**	79	96/4
2	**2b** $(EtO)_3SiH$	**3ab**	91(60)[d]	98/2
3	**2c** Et_3SiH	**3ac**	58	>98/2
4	**2d** $PhMe_2SiH$	**3ad**	94(82)[d]	>98/2
5	**2e** Ph_2MeSiH	**3ae**	86	>98/2
6	**2f** $(EtO)_2MeSiH$	**3af**	66(55)[d]	98/2
7	**2g** $(i\text{-}Pr)_2HSi{-}C{\equiv}C{-}C\text{-}SiMe_3$	**3ag**	93	>98/2

[a]Diphenylacetylene (0.5 mmol), silane (0.55 mmol). [b]Certain reactions could also be performed at lower temperatures but generally required longer reaction times and led to slightly lower yields (see the Supporting Information). [c]Isolated yields. [d]Yields obtained using $Co(PMe_3)_4$ as catalyst.

Pleasingly, we encountered a reaction amenable with an ample variety of aryl/alkyl tertiary silanes and alkoxysilanes (Table 1, entries 1–7), achieving good yields up to 94%. Notably, these reaction conditions successfully allow for the hydrosilylation of a highly functionalized and sterically demanding silane **2g** (Table 1, entry 7). In general the products of *syn*-hydrosilylation were observed as major isomers, with high (*E*/*Z*) ratios. It is worth highlighting the unique ability of this complex to carry out the hydrosilylation of alkynes with a wide variety of hydrosilanes which has not been previously described under cobalt catalysis. As shown in our previous work, terminal alkynes only afford dimerization compounds under these conditions.[13a]

We then turned out attention to the more challenging hydrosilylation of internal unsymmetrical alkynes (Table 2). Such alkynes were substituted by functional groups with different steric hindrances, described as $\mathbf{R_S}$ (smaller group) and $\mathbf{R_L}$ (larger group). The complex $HCo(PMe_3)_4$ along with the silanes $HSi(OEt)_3$ and $HSiPh_3$ were chosen due to positive preliminary results regarding the high yields and *syn* selectivity observed. Using less reactive alkynes (compared to diphenylacetylene), new optimized reactions conditions were established, i.e., toluene heated at 160 °C for 2 h (see the SI). Starting the initial scope with the silane **2a** ($HSiPh_3$), the product of hydrosilylation of 1-phenyl-1-hexyne was isolated in 92% yield (Table 2, entry 1) in favor of the *syn* adduct **3ba** (product of type **3** with the H atom positioned close to the larger substituent). Variation of the electronics on the phenyl moiety has no effect on the yield, but a better regioselectivity was observed in the presence of an electron-withdrawing group (Table 2, entries 2 and 3). Next, we examined the reactivity of TMS-protected alkynes **1e–k**. Previous reports on the hydrosilylation of these kind of alkynes indicated that both (*E*)-α,β[5d,6] or (*E*)-α,α-disilylalkenes[11g] products could be selectively obtained. Under our reaction conditions, and using $HSiPh_3$, the hydrosilylation of TMS-protected arylacetylenes **1e–i** (Table 2, entries 4–8) led exclusively to the corresponding disilylalkenes in high yields and complete

Table 2. Hydrosilylation of Unsymmetrical Alkynes[a]



1 2 3 3'

entry	alkyne	R_S	R_L	silane	prod	yield %[b,c]	ratio (3/3')
1	**1b**	Ph	*n*-Bu	**2a**	**3ba**	92	79/21
2	**1c**	*p*-MeO-C_6H_4	*n*-Bu	**2a**	**3ca**	96	82/18
3	**1d**	*p*-CF_3-C_6H_4	*n*-Bu	**2a**	**3da**	94	100/0
4	**1e**	Ph	TMS	**2a**	**3ea**	88	100/0
5	**1f**	*p*-MeO-C_6H_4	TMS	**2a**	**3fa**	86	100/0
6	**1g**	*p*-CF_3-C_6H_4	TMS	**2a**	**3ga**	81	100/0
7	**1h**	3,5-dimethoxy-C_6H_3	TMS	**2a**	**3ha**	87	100/0
8	**1i**	6-methoxynaphthyl	TMS	**2a**	**3ia**	75	100/0
9	**1j**	2-pyridyl	TMS	**2a**	**3ja**	92	100/0
10	**1k**	3-pyridyl	TMS	**2a**	**3ka**	56	100/0
11	**1l**	Ph	2,6-dimethyl-C_6H_3	**2a**	**3la**	91	100/0
12	**1m**	Me	Ph	**2a**	**3ma**	19[d]	100/0
13	**1n**	Ph	*p*-MeO-C_6H_4	**2a**	**3na**	90	50/50
14	**1o**	Ph	2-pyridyl	**2a**	**3oa**	81	50/50
15	**1p**	Ph	*p*-CF_3-C_6H_4	**2a**	**3pa**	80	52/48[f]
16	**1q**	Ph	CO_2Et	**2a**	**3'qa**	78[d]	0/100
17	**1r**	*n*-Pent	CO_2Me	**2a**	**3'ra**	50[e]	0/100
18	**1b**	Ph	*n*-Bu	**2b**	**3bb**	92	100/0
19	**1c**	*p*-MeO-C_6H_4	*n*-Bu	**2b**	**3cb**	96	100/0
20	**1d**	*p*-CF_3-C_6H_4	*n*-Bu	**2b**	**3db**	94	100/0
21	**1e**	Ph	TMS	**2b**	**3eb**	95	100/0
22	**1f**	*p*-MeO-C_6H_4	TMS	**2b**	**3fb**	91	100/0
23	**1g**	*p*-CF_3-C_6H_4	TMS	**2b**	**3gb**	90	100/0
24	**1j**	2-pyridyl	TMS	**2b**	**3jb**	30	100/0
25	**1k**	3-pyridyl	TMS	**2b**	**3kb**	45	100/0
26	**1l**	Ph	2,6-dimethyl-C_6H_3	**2b**	**3lb**	61	100/0
27	**1n**	Ph	*p*-MeO-C_6H_4	**2b**	**3nb**	95	60/40

[a]Alkyne (0.5 mmol), $HSiR_3$ (0.55 mmol). [b]Isolated yields. [c]For detailed information regarding the (*E*/*Z*) and (α/β) ratios of the obtained products (see the Supporting Information). [d]Reaction was performed at 60 °C for 24 h. [e]Reaction was performed at 100 °C for 24 h. [f]Regiochemistry of the major compound was not determined.

regioselectivity toward the adducts of type **3**, i.e., (*E*)-α,β-disilylalkenes.

The catalytic system also allowed the use of heteroatoms with TMS-protected pyridylalkynes **1j–k**, isolating only the products of type **3** in moderate to good yields (Table 2, entries 9 and 10). It is worth noting that the regioselectivity oberved in our reaction with TMS-containing alkynes is opposite to the one previously reported by Deng[11g] (see below for more detailed discussion). Adding two methyl groups in the *ortho*-position on a phenyl ring generates a steric bulk on one side of the alkyne, which directs the addition of the H atom to the sterically hindered carbon to give product **3la** (Table 2, entry 11). 1-Phenylpropyne **1m** followed the same trend of steric dependence of the alkyne substituents in the formation of the final product **3ma**. The low yield is presumably due to a stability issue of the alkyne (Table 2, entry 12). On the other hand, the reaction of nonsterically differentiated unsymmetrical alkynes but bearing electronically distinct substituents (**1n**, **1o**, and **1p**) gave 50/50 mixtures of vinylsilanes of type **3** and **3′** (Table 2, entries 13–15). These latter results imply that the regio- and stereocontrol of the reaction is predominantly governed by steric factors of the starting substrates, while electronic factors have no significant effect on the outcome of

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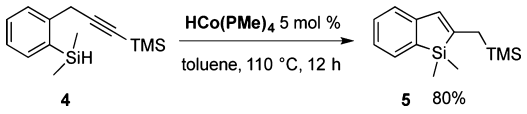
Org. Lett. XXXX, XXX, XXX–XXX

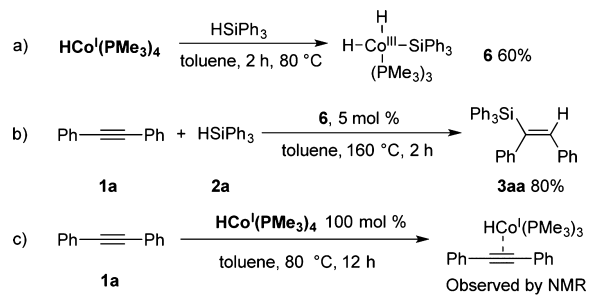
the reaction. Finally, the use of ester-substituted substrates **1q** and **1r** in the hydrosilylation with $HSiPh_3$ yields solely the product of type **3′**, presumably due to the chelating effect of the ester which appears to overcome the steric control (Table 2, entries 16 and 17).[12,14] We obtained analogous results when we addressed the hydrosilylation of unsymmetrical internal alkynes using the silane $HSi(OEt)_3$ **2b**, which again gave almost exclusively the *syn*-adducts of type **3** (Table 2, entries 18−27). This time, products **3bb** and **3cb** showed complete regioselectivity, presumably due to the larger steric bulk provided by the triethoxy moieties in the silane (Table 2, entries 18 and 19). Further exploration into the scope of the current reaction showed identical results by employing TMS-protected arylacetylenes, with complete selectivity toward the corresponding (*E*)-*α*,*β*-disilylalkenes of type **3** and regardless of the aromatic group linked to the alkyne. Again, alkynes **1l** and **1n** gave similar regioselectivities as previously observed with triphenylsilane (Table 2, entries 26 and 27). Extension of this methodology to an intramolecular version was also possible, which provides an alternative route to benzosilole derivatives via a hydrosilylation/double migration sequence (Scheme 2).[15]

Scheme 2. Intramolecular Hydrosilylation



Focusing our attention now on the reaction mechanism, we studied the stoichiometric reaction of hydridocobalt complex $HCo(PMe_3)_4$ and triphenylsilane (Scheme 3a). Having

Scheme 3. Reaction of $HCo(PMe_3)_4$ with $HSiPh_3$



successfully isolated the dihydrocobalt(III) complex **6**, we began to explore its catalytic activity.[16,17] To this end, the reaction of diphenylacetlyene and triphenylsilane in the presence of 5 mol % of **6** afforded the desired hydrosilylation product **3aa** in good yields and the same selectivity as that observed with $HCo(PMe_3)_4$ (Scheme 3b). This result suggests a potential participation of the dihydrodocobalt(III) complex to trigger the catalytic process. Moreover, the stoichiometric reaction of diphenylacetylene with $HCo(PMe_3)_4$ shows only a ligand exchange and no evidence of hydrocobaltation (Scheme 3c).

To gain deeper insight into the mechanistic details, DFT (density functional theory) calculations were performed on a system based on complex **6** in conjunction with 1-phenylpropyne and $HSi(OMe)_3$. Following our previous studies,[13] parameters were set as functional B3LYP and basis set SVP, while all the DFT calculations were performed with Gaussian09. We present the conformation, which led to the smallest activation barrier, shown in Figure S1 (see the SI). The main question addressed is whether the alkyne insertion initially occurs into the Co−H bond (hydrocobaltation) or into the Co−Si bond (silacobaltation). According to the results, the barrier for the hydro-obaltation process is 3.18 kcal/mol, while the silacobaltation barrier is 19.42 kcal/mol. Thus, our cobalt catalyst would follow the classical Chalk−Harrod mechanism.[18] Another important question addressed by the DFT calculations was that, despite the use of a hydridocobalt catalyst with a silane, no H_2 evolution was experimentally observed. This could be explained since starting from the cobalt complex **6** bearing two hydrogen atoms the reductive elimination of H_2 is an endothermic process with a transition state residing above by 3.36 kcal/mol, while the reverse barrier (i.e., H_2 addition on the cobalt center) is very small (0.47 kcal/mol). Thus, even if H_2 is produced during the catalytic process, it will quickly rebound and split onto the cobalt center to regenerate the active species (Figure S2, SI).

Based on the experimental and theoretical information (see also Tables S2 and S3 in the SI), we propose the following catalytic cycle (Figure 1). Initial oxidative addition of the silane

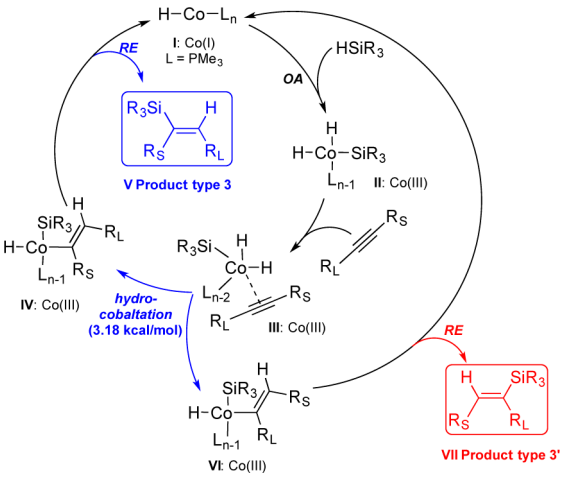


Figure 1. Proposed mechanism.

to the cobalt center, followed by coordination of the alkyne, gives the dihydridocobalt(III) intermediate **III**, which undergoes alkyne insertion into a Co−H bond to furnish the vinyl organometallic **IV**. At this point, the H atom is directed toward the more bulky substituent in order to place the cobalt moiety in the less hindered plane of the molecule. Direct reductive elimination releases the vinylsilane **V** as the major product with the observed regioselectivity and regenerates the catalytically active species **I**. To a much lesser extent, an opposite migratory insertion would yield the adduct isomer **VI**, which eventually results in the unfavored product **VII**.

A model to compare the regioselectivity between our results and Deng's[11g] is shown in Scheme 4. In the model proposed by Deng, the sila-cobaltation step is controlled by the very bulky ligand IAd (1,3-diadamantylimidazol-2-ylidene), and this determines the regioselectivity of the reaction. For unsymmetrical internal alkynes, this control based on a bulky ligand is efficient when the steric differentiation between the two substituents is significant. Otherwise, it leads to low selectivity as shown by Deng using 1-phenylpropyne which yielded a 50/50 mixture of regioisomers. In our system, we proposed that a hydrocobaltation step controls the selectivity. In this process

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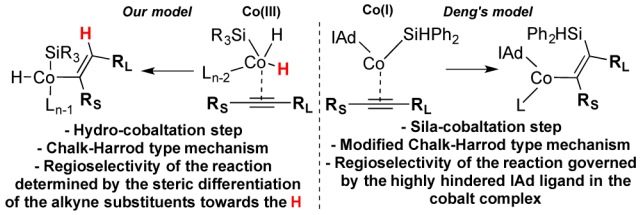
Scheme 4. Comparison between Regioselectivity-Determining Steps



the steric differentiation between the silylcobalt moiety and the hydrogen atom is very important. Thus, the regioselectivity is less affected by a change of the silane and by a small steric differentiation between $\mathbf{R_L}$ and $\mathbf{R_S}$ (Scheme 4).

In summary, a highly regio- and stereoselective hydrosilylation of a wide variety of internal alkynes catalyzed by the inexpensive and versatile low-valent cobalt(I) $HCo(PMe_3)_4$ is reported. The analysis of data obtained from NMR and computational studies revealed the direct correlation of steric effects in the outcome of the hydrosilylation products toward a *syn*-regioselective reaction. Based on our initial investigations, we proposed a mechanism via a hydrocobaltation pathway. Further studies on complex **6** are underway to determine its exact structure as a dihydrogen or a dihydride cobalt complex and to confirm the mechanism.[19]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01987.

Experimental procedures and analytical data (PDF)
Crystallographic data for **3ha**, **3ia**, and **3la** (CIF)

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Notes

The authors declare no competing financial interest.

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