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Stereodivergent Formation of Alkenylsilanes: *syn* or *anti* Hydrosilylation of Alkynes Catalyzed by a Cyclopentadienylcobalt(I) Chelate Bearing a Pendant Phosphane Tether

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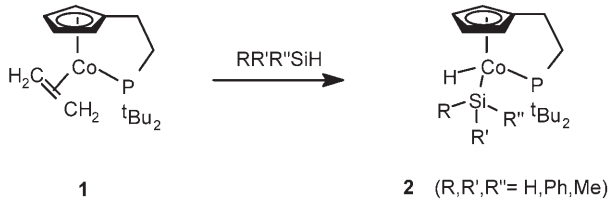
Abstract: The hydrosilylation of alkynes is catalyzed by the di-*tert*-butylphosphanylethylcyclopentadienylcobalt chelate **1**. While the reaction of internal alkynes exclusively affords *syn* hydrosilylation products with triethylsilane, the reaction with triethoxysilane shows predominant *anti* stereoselectivity. Reactions of terminal alkynes are less selective with triethylsilane and result in cyclotrimerization when triethoxysilane is used.

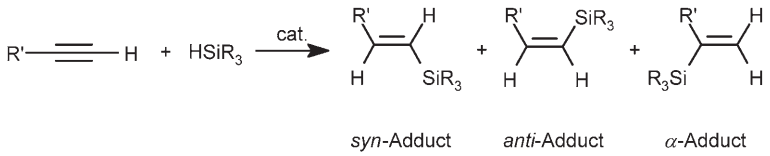
Keywords: alkynes; cobalt; hydrosilylation; P ligands; triethoxysilane; triethylsilane

The versatile and rich chemistry of alkenylsilanes has attracted considerable attention in recent years as these compounds are important building blocks in organic synthesis.[1] Alkenylsilanes are used in cross-coupling reactions with electrophiles for the stereoselective synthesis of substituted alkenes,[2] or as masked ketones through Tamao–Fleming oxidation.[3] Among the possible routes to alkenylsilanes, the most atom-economical and straightforward method is the transition metal-catalyzed hydrosilylation of alkynes.[4,5] The hydrosilylation of terminal alkynes to disubstituted alkenylsilanes has extensively been studied, and a variety of transition metal catalysts have been shown to be effective in this transformation.[6–15] Generally the reaction results in a mixture of three different isomers, *trans*, *cis*, and α-isomers, as a result of 1,2-(*syn*- and *anti*-) and 2,1-additions, respectively (Scheme 1). The distribution of the products is found to vary considerably with the nature of the catalyst, substrate and reaction conditions.[4,5,16] Significant progress has been achieved in recent years, and hydrosilylation reactions of terminal alkynes with high 1,2-*syn*,[9,17–19] 1,2-*anti*,[20–23] and 2,1 addition[24–27] selectivity were reported successively.

Because most catalysts for terminal alkynes are ineffective for internal alkynes, the preparation of trisubstituted alkenylsilanes using hydrosilylation of internal alkynes is less explored. This is even the case for the symmetrical internal alkynes. Among the catalysts reported for the hydrosilylation of internal alkynes, noble metals, such as Y,[28–30] Ru,[31,32] Pt,[32] and Rh[12,33–35] dominate. However, the success based on the less noble, cheaper first row metal catalysts remained rare.[36–39]

Recently, upon treatment of hydrosilanes with cyclopentadienylcobalt(I) chelate **1** bearing a pendant phosphane tether the cyclopentadienylhydridosilylcobalt(III)





Scheme 1. Hydrosilylation of terminal alkynes.

chelate complexes **2** were isolated as the result of an oxidative addition.[40] According to the Chalk Harrod mechanism of the metal-catalyzed hydrosilylation, the oxidative addition of silanes at vacant coordination sites of transition metals is considered as a key step.[4,41,42] This led us to examine cyclopentadienylcobalt(I) complex **1** in the catalytic hydrosilylation reaction.

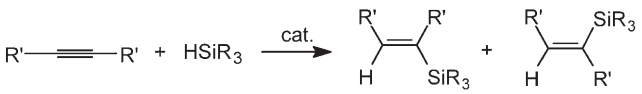
The reaction of diphenylethyne with triethylsilane was chosen as a model system to optimize the reaction conditions. After examination of the effect of solvents on the reaction we found that using THF as the solvent with 5% catalyst loading at 40 °C the reaction exclusively afforded the *syn*-adduct **3** in 60% isolated yield, neither the *anti*-adduct nor a diaddition product were obtained. Next, a variety of symmetrical internal alkynes were examined and proved amenable to this reaction (Table 1). In all cases high stereoselectivity and moderate or good yields are maintained, including examples with Lewis basic oxygen functionalities (entries 4, 5, 9). The tolerance of a cyclopropyl function towards the Co(I) catalyst is remarkable (entry 6) as cyclopropane rings frequently undergo ring opening reactions in the presence of noble transition metal complexes.[43–45] It is in accordance with our previous work that there is no impairment of the cyclopropyl group by this cobalt(I) complex.[46–48]

Remarkably, when triethoxysilane was applied instead of triethylsilane, the regioselectivity was reversed resulting in the predominant formation of *anti* adducts **4**. Transition metal-catalyzed *anti*-hydrosilylation has been observed earlier. The reaction mechanism has not been investigated in depth, however, a path *via* a *syn*-hydrosilylation followed by an isomerization has been envisaged.[49] Recently, triethoxysilane has been reported to result in an *anti*-hydrosilylation,[24] and Fürstner exploited this to devise an elegant route from cycloalkynes to (*E*)-cycloalkenes.[31]

Results concerning the hydrosilylation of unsymmetrical internal alkynes with either triethylsilane or triethoxysilane are summarized in Table 2. Substituent R is the sterically more bulky one in all cases taking into account the sp^2 hybridization of the connecting carbon atoms in the methoxycarbonyl and the phenyl substituents.

Although the yields and the regioselectivity obtained for the hydrosilylation of unsymmetrical internal alkynes are only moderate, it is interesting that exclusive *syn* hydrosilylation was observed in all cases. In contrast to the hydrosilylation of terminal alkynes with triethoxysilane no formation of a *Z* alkenylsilane was observed in the reaction of internal alkynes. The predominant formation of products **6** in the hydrosilylation with triethylsilane or with triethoxysilane suggests that the regioselectivity is not sterically controlled. Remarkably, products **6** with the sterically more bulky substituents R next to the silyl group are preferred with R′ being an electron-withdrawing methoxycarbonyl or an electron-releasing phenyl group. However, due to the moderate

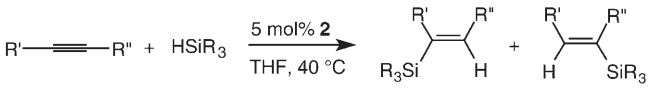
Table 1. Co(I)-catalyzed hydrosilylation of symmetrical internal alkynes.



3 **4**

	R′	R_3SiH	Product	Ratio **3**:**4**	Isolated yield [%]
1	Ph	Et_3SiH	**a**	100:0	60
2	Et	Et_3SiH	**b**	100:0	71
3	Pr	Et_3SiH	**c**	100:0	79
4	CH_2OMe	Et_3SiH	**d**	100:0	58
5	CO_2CMe_3	Et_3SiH	**e**	100:0	66
6	cyclopropyl	Et_3SiH	**f**	100:0	76
7	Ph	$(EtO)_3SiH$	**g**	9:91	69
8	Et	$(EtO)_3SiH$	**h**	8:92	77
9	CO_2CMe_3	$(EtO)_3SiH$	**i**	5:95	55

Table 2. Co(I)-catalyzed hydrosilylation of unsymmetrical internal alkynes.

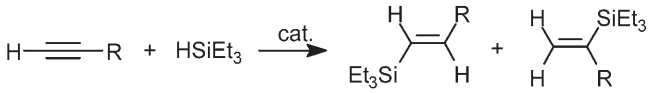


5 **6**

	R	R″	R_3SiH	Product	Ratio **5**:**6**	Isolated yield [%]
1	CO_2Me	Me	Et_3SiH	**a**	–	–[a]
2	Me	Pr	Et_3SiH	**b**	1:2	48
3	Ph	Bu	Et_3SiH	**c**	1:3	35
4	CO_2Me	Me	$(EtO)_3SiH$	**d**	1:2	10
5	Me	Pr	$(EtO)_3SiH$	**e**	1:2	65
6	Ph	Bu	$(EtO)_3SiH$	**f**	–	–[b]

[a] No reaction took place, starting material was re-isolated.
[b] The hydrosilylation products could be observed by ^1H NMR but rapidly decomposed by desilylation.

Table 3. Co(I)-catalyzed hydrosilylation of terminal alkynes with Et_3SiH.



7 **8**

	R	Product	Ratio **7**:**8**	Isolated yield [%]
1	Ph	**a**	54:46	71
2	$CH_2CH_2CH_2CN$	**b**	55:45	73
3	CO_2Et	**c**	55:45	57
4	$CH_2OCH_2CH{=}CH_2$	**d**	53:47	26

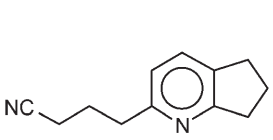
yields of the reaction the evidence of this interpretation remains limited.

The stereoselectivity of the hydrosilylation of *terminal* alkynes with triethylsilane (Table 3) is also very high, but the reaction suffered from the poor regioselectivity. 1:1 mixtures of *syn*-adduct and α-adduct were obtained, no *trans*-adducts were detected. For an enyne substrate full chemoselectivity for the monohydrosilylation of the alkyne group was observed. Neither a C–N triple bond nor an ester carbonyl group interfere with the alkyne hydrosilylation. In no case was a double hydrosilylation observed. Due to both the higher reaction activity and ready cyclotrimerization of terminal alkynes,[50] the hydrosilylation reaction of terminal alkynes was carried out at room temperature with dropwise addition of 1.4 equivalents of terminal alkynes in 2 mL of THF over 20 minutes.

The reaction of some terminal alkynes was also tested with triethoxysilane instead of triethylsilane under otherwise unchanged reaction conditions. However, these reactions did not yield hydrosilylation products but resulted in cyclotrimerization products **9**–**13** instead. The new pyridine **9** was obtained along with an equivalent amount of its regioisomer in 34% yield [60% yield in the absence of $(EtO)_3SiH$], while ethyl propynoate gave regioisomers **10** and **11** in 70% yield as a 8:1 mixture. Compounds **12** and **13** were obtained from 1-hexyne in only 25% yield as a 13:7 mixture. The known cyclization products were characterized by comparison of their spectroscopic data with published data.[51,52] Alkyne cyclotrimerizations were earlier observed to be catalyzed by **1**.[50]

Concerning the hydrosilylation reactions catalyzed by cyclopentadienylcobalt chelate **1**, we believe that in the first step an oxidative addition of the hydrosilane with formation of complexes **2** takes place. According to the accepted mechanism of the hydrosilylation,[4,5,41,42] the decomplexation of the hemilable phosphane tether delivers a vacant coordination site, which is occupied by the alkyne. Insertion of the alkyne into the Co–Si or into the Co–H bond followed by reductive elimination accounts for product formation and catalyst regeneration. The catalyst might be stabilized by re-coordination of the phosphane tether, a feature much less easily to achieve with usual decoordinated phosphane ligands.

In summary, a highly selective, stereodivergent hydrosilylation of internal alkynes catalyzed by an inexpensive cyclopentadienylcobalt complex with a pendant phosphane donor is reported. Due to the hemilabile phosphane tether in the catalyst, the hydrosilylation reaction can proceed smoothly under mild reaction conditions. The reaction using triethylsilane resulted in a *syn* hydrosilylation exclusively, while triethoxysilane caused the reaction to display good *anti* selectivity. Thus, it opens a door to *E* or *Z* trisubstituted alkenylsilanes using the same catalyst only by variation of the hydrosilane. Further investigations of this catalytic reaction regarding the mechanism and new applications are currently under way.



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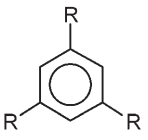
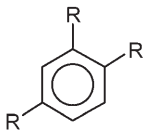


10: R = CO_2Et
12: R = Bu



11: R = CO_2Et
13: R = Bu

Experimental Section

General Experimental Procedure

In a Schlenk flask 0.05 mmol of 1, 1.0 mmol of the hydrosilane, and 1.2 mmol of the internal alkyne (for terminal alkynes: 1.4 mmol) in 20 mL of THF are stirred at 40 °C (for terminal alkynes: 25 °C) for 10 h. After concentration and extraction with diethyl ether the product is isolated by column chromatography (petroleum ether/ethyl acetate 15–100:1).

Characterization data of the isolated compounds are given in the Supporting Information.

Acknowledgements

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