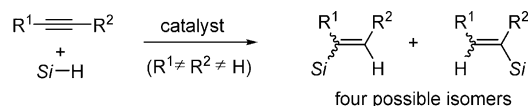


Highly Regio- and Stereoselective Hydrosilylation of Internal Thioalkynes under Mild Conditions**

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Abstract: A general and mild hydrosilylation of thioalkynes is described. With the cationic catalyst $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]^+$ and the bulky silane $(\text{TMSO})_3\text{SiH}$, a range of thioalkynes underwent smooth hydrosilylation at room temperature with excellent α regioselectivity and *syn* stereoselectivity. DFT calculations provided important insight into the mechanism, particularly the unusual *syn* selectivity with the $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]^+$ catalyst. The sulphenyl group in the substrates was found to provide important chelation stabilization to direct the reaction through a new mechanistic pathway.

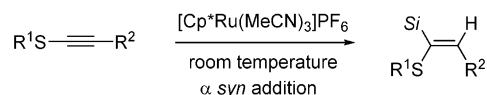
Vinyl silanes are valuable synthetic precursors to various useful small organic molecules and polymeric organosilicon materials.^[1] Consequently, the hydrosilylation of alkynes, arguably the most direct and atom-economical route to vinyl silanes, has become an area of intense investigation in the past few decades.^[2] However, despite the significant progress made, there still remain challenges (e.g., regio- and stereocontrol), particularly for unsymmetrical internal alkynes in intermolecular reactions (Scheme 1). Moreover, almost all previous studies on this topic have been focused on electron-normal^[2,3] and electron-deficient^[4] alkynes (Scheme 1a). In contrast, the hydrosilylation of electron-rich alkynes (bearing an electron-donating group (EDG) at the triple bond) remains largely unknown.^[5]



a) Background: challenge in regio- and stereocontrol

- Electron-normal: most studied (R^1, R^2 = alkyl, alkenyl, aryl, etc.)
- Electron-deficient: less studied (R^1 or R^2 = EWG, e.g., carbonyl)
- Electron-rich: largely unknown (this work) (R^1 or R^2 = EDG)

b) This work: excellent reaction with thioalkynes



- High regio- and stereoselectivity
- Unusual *syn* addition with $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]^+$ (previously all *anti* addition)
- High efficiency
- Mild conditions
- Broad scope

Scheme 1. Background to alkyne hydrosilylation. Si stands for a silyl group of the type R_3Si ; EWG = electron-withdrawing group.

In continuation of our studies on transformations of electron-rich alkynes,^[6] we report herein the first general, mild, and highly selective process of this type (Scheme 1b). Specifically, we have developed an efficient ruthenium-catalyzed intermolecular hydrosilylation of internal thioalkynes with high regio- and stereoselectivity. In this study, we also observed unprecedented *syn* addition selectivity with $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]^+$ (Cp^* = pentamethylcyclopentadienyl), a well-known catalyst for *anti* addition reactions of alkynes.^[7,8] The unusual *syn* selectivity was also rationalized by careful DFT studies.

In our initial study, we employed thioalkyne **1a** and triethoxysilane (**2a**) as model starting materials (Table 1). $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$ was chosen for initial evaluation of the transformation in view of its demonstrated catalytic capability in a range of alkyne-functionalization reactions.^[7] The reaction in CH_3CN proceeded smoothly to afford the desired vinyl silane at room temperature, albeit with only moderate regioselectivity (Table 1, entry 1). The excellent *syn* stereoselectivity observed stands in remarkable contrast to the uniform *anti* addition previously observed with this catalyst for the functionalization of alkynes.^[8] The use of other solvents did not improve the overall efficiency and selectivity of the reaction. The smaller catalyst $[\text{CpRu}(\text{MeCN})_3]\text{PF}_6$ resulted in almost no regioselectivity (Table 1, entry 2). Furthermore, previously reported Pt and Co complexes were found to be ineffective (Table 1, entries 3 and 4).^[5]

We next examined a range of silanes (Table 2). Most of them gave the product either in moderate yield or with moderate selectivity; however, tris(trimethylsiloxy)silane

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Table 1: Catalyst evaluation.

$n\text{BuS}-\text{C}\equiv\text{C}-n\text{Bu} \text{ (1a)} + (\text{EtO})_3\text{SiH} \text{ (2a)} \xrightarrow[\text{CH}_3\text{CN, RT, 24 h}]{\text{catalyst (2 mol\%)}} (\text{EtO})_3\text{Si}-\text{CH}=\text{CH}-n\text{Bu}$				
Entry	Catalyst	Yield [%] ^[a]	α/β ^[b]	Z/E ^[b]
1	$[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$	82	5.6:1	> 30:1
2	$[\text{CpRu}(\text{MeCN})_3]\text{PF}_6$	63	1:1	1.4:1
3	$\text{Na}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$	< 5 ^[c]	—	—
4	$\text{HO}-\text{C}(\text{Me})_2-\text{C}\equiv\text{C}-\text{CO}_2(\text{CO})_6$	< 5 ^[c]	—	—

[a] The yield was determined by GC. [b] The ratio of α/β addition and the E/Z ratio of the product were determined by ^1H NMR spectroscopy of the crude product. [c] Almost no conversion was observed.

Table 2: Evaluation of silanes for the hydrosilylation of thioalkynes.

$n\text{BuS}-\text{C}\equiv\text{C}-n\text{Bu} \text{ (1a)} + \text{Si}-\text{H} \text{ (2)} \xrightarrow[\text{CH}_3\text{CN, RT, 24 h}]{[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6 \text{ (2 mol\%)}} \text{Si}-\text{CH}=\text{CH}-n\text{Bu}$				
Entry	Silane (2)	Yield [%] ^[a]	α/β ^[b]	Z/E ^[b]
1	$(\text{MeO})_3\text{SiH} \text{ (2b)}$	54	3.6:1	> 50:1
2	$(\text{EtO})_2\text{MeSiH} \text{ (2c)}$	84	8.4:1	5.9:1
3	$(\text{EtO})\text{Me}_2\text{SiH} \text{ (2d)}$	87	14.7:1	1.1:1
4	$\text{Et}_3\text{SiH} \text{ (2e)}$	53	> 20:1	25:1
5	$\text{PhMe}_2\text{SiH} \text{ (2f)}$	91	> 20:1	1.3:1
6	$\text{BnMe}_2\text{SiH} \text{ (2g)}$	75	> 20:1	4.5:1
7	$(\text{TMSO})_3\text{SiH} \text{ (2h)}$	99	> 50:1	25:1
8	$(\text{TMS})_3\text{SiH} \text{ (2i)}$	0	—	—
9 ^[c]	$\text{Me}_2\text{SiClH} \text{ (2j)}$	79	2.1:1	—

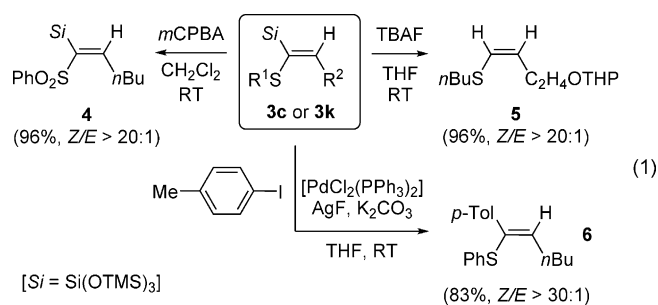
[a] Yield of the isolated product. [b] The ratio of α/β addition and the E/Z ratio of the product were determined by ^1H NMR spectroscopy of the crude product. [c] MeOH (5.0 equiv) and Et_3N were added to trap the chlorosilane product. Bn = benzyl, TMS = trimethylsilyl.

(2h) provided the product in quantitative yield with excellent selectivity (Table 2, entry 7). Notably, no reaction was observed with tris(trimethylsilyl)silane (2i).

Under the optimized conditions, a wide range of thioalkynes participated in the hydrosilylation with excellent efficiency as well as high regio- and stereoselectivity (Table 3). The mild conditions tolerate a variety of functional groups, such as acetals (THP-protected alcohols), esters, ethers, and even free alcohols.

The obtained trisubstituted vinyl silane products can be readily transformed into other useful compounds [Eq. (1); TBAF = tetrabutylammonium fluoride]. The oxidation of 3k with *m*-chloroperbenzoic acid (*m*CPBA) afforded the stereo-defined α -silyl vinyl sulfone 4 with high efficiency. Vinyl sulfones are versatile species in organic synthesis and medicinal chemistry.^[9] Furthermore, protodesilylation and Hiyama cross-coupling efficiently furnished vinyl sulfides 5 and 6, respectively. Our method provides an attractive alternative route to these molecules.^[10]

Previously, we established a new mechanism to rationalize generally observed *anti*-selective hydrosilylation with the catalyst $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]^+$.^[11] The mechanism involves the direct formation of a ruthenacyclopropene intermediate, followed by silyl migration,^[12] in this process the hydrogen atom and the silyl group of the silane are arranged on opposite sides of the ruthenacyclopropene plane.^[13] The


Table 3: Scope of the hydrosilylation of thioalkynes with $(\text{TMSO})_3\text{SiH}$.

$\text{R}^1\text{S}-\text{C}\equiv\text{C}-\text{R}^2 \text{ (1a)} + (\text{TMSO})_3\text{SiH} \text{ (2h)} \xrightarrow[\text{CH}_3\text{CN, RT, 24 h}]{[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6 \text{ (2 mol\%)}} \text{R}^1\text{S}-\text{CH}=\text{CH}-\text{R}^2 \text{ (3)}$				
Entry	R ¹	R ²	Product	Yield [%] ^[a]
1	<i>n</i> Bu	<i>n</i> Bu	3a	99
2	<i>n</i> Bu	cyclopropyl	3b	91
3	<i>n</i> Bu	$\text{C}_2\text{H}_4\text{OTHP}$	3c	97
4	<i>n</i> Bu	$\text{C}_2\text{H}_4\text{OAc}$	3d	92
5	<i>n</i> Bu	$\text{C}_2\text{H}_4\text{OBn}$	3e	87
6	<i>n</i> Bu	$\text{C}_2\text{H}_4\text{OH}$	3f	74
7	<i>n</i> Bu	Ph	3g	91 ^[b]
8	Me	<i>n</i> Bu	3h	95
9	<i>i</i> Pr	<i>n</i> Bu	3i	75
10	Bn	<i>n</i> Bu	3j	93
11	Ph	<i>n</i> Bu	3k	86
12	Ph	<i>n</i> -Oct	3l	99
13	Ph	cyclopropyl	3m	92
14	Ph	$\text{C}_2\text{H}_4\text{OTHP}$	3n	96
15	Ph	$\text{C}_2\text{H}_4\text{OAc}$	3o	84
16	Ph	$\text{C}_2\text{H}_4\text{OH}$	3p	94
17	Ph	Ph	3q	96
18	<i>p</i> -OMeC ₆ H ₄	<i>n</i> Bu	3r	98
19	<i>p</i> -ClC ₆ H ₄	<i>n</i> Bu	3s	60
20	<i>p</i> -MeC ₆ H ₄	<i>n</i> Bu	3t	97

[a] Yield of the isolated product. In all cases except for entry 7, $\alpha/\beta > 20:1$, $Z/E > 20:1$. [b] $\alpha/\beta = 5:1$, $Z/E > 20:1$. THP = 2-tetrahydropyranyl.

observed *anti* addition in the hydrogermylation, hydrostannation, hydrogenation, and hydroboration of alkynes under the catalysis of $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]^+$ has also been suggested to follow this mechanism.^[14]

Interestingly, the presence of a sulfenyl substituent leads to α selectivity and the unusual *syn* addition. Our DFT calculations suggest that the hydrometalation is the rate- and regioselectivity-determining step, and that **TS1-A** is more stable than **TS1-B** by about 2.9 kcal mol⁻¹ (Figure 1; see also Figures S1 and S3 in the Supporting Information).^[15] Also, the ruthenacyclopropene intermediate **2A** is more stable than **2B** by 5.2 kcal mol⁻¹ because the proton-like hydrogen atom^[11] preferentially attacks the more electron-rich C_β atom with the strongly π donating sulfenyl group. Moreover, the sulfenyl group stabilizes the electrophilic carbene ligand in **2A** through a conjugation effect (see resonance structure **2A₁**, Figure 1; see also Figure S2a).

A key new feature is the isomerization of **2A** to form a more stable sulfur-chelated σ -vinyl intermediate **3A**.^[16]

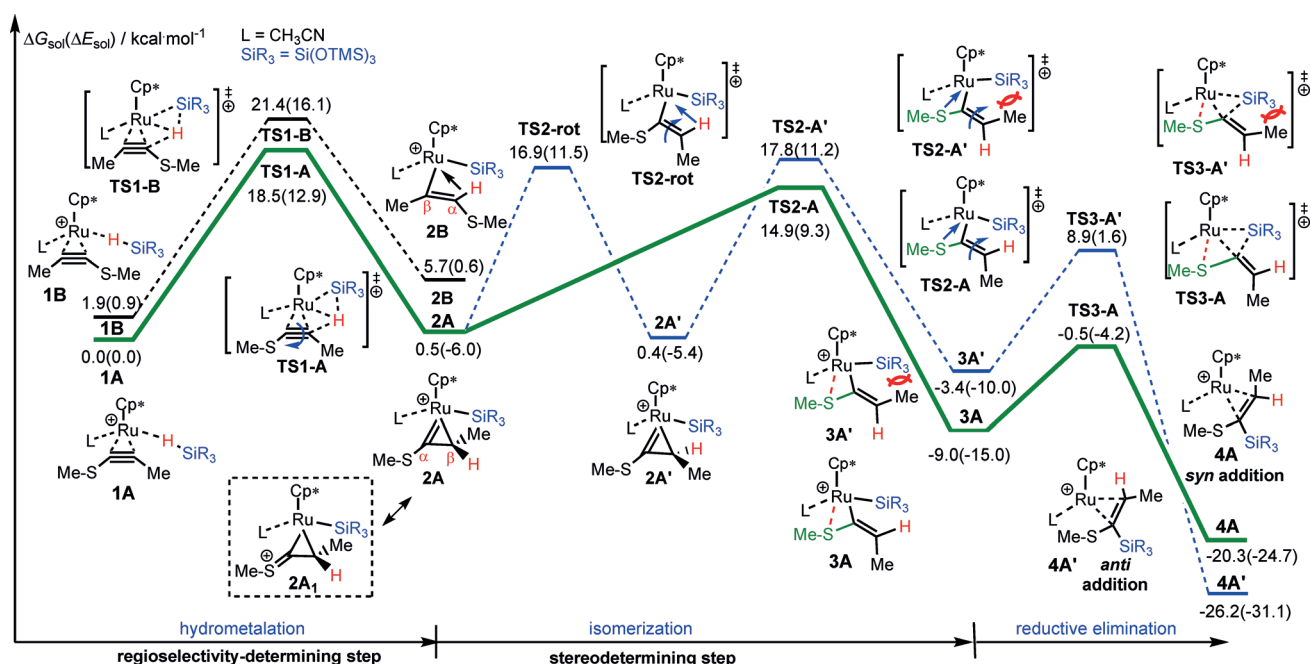


Figure 1. Energy profiles of the [Cp*Ru(MeCN)₃]⁺-catalyzed hydrosilylation of 1-methylthiopropyne. A resonance structure of **2A** is given in the dotted box.

Ring opening via **TS2-A** involves the clockwise rotation of the C_α–C_β bond to move the C_β–H bond inward with concomitant Ru–S bond formation to form the *syn* σ-vinyl intermediate **3A**. The transition state for counterclockwise rotation from **2A** to **3A'** could not be located owing to steric interactions between the methyl and bulky silyl groups. Intermediate **2A** can also undergo C_α–C_β rotation via **TS2-rot**^[17] to form **2A'**. Then clockwise rotation of the C_α–C_β bond (via **TS2-A'**) can occur to move the C_β–Me group inward to form the *anti* σ-vinyl intermediate **3A'**. **TS2-A** is calculated to be more stable than **TS2-A'** by about 2.9 kcal mol^{–1}, in agreement with the observed *syn* selectivity. This difference in stability is attributed to the steric repulsion between the C_β–Me group and the bulky silyl group in **TS2-A'** (Figure 2; see also Figures S5 and S6). The vinyl moiety in **TS2-A'** is highly distorted by the steric repulsion, as reflected by the larger Ru–C_α–C_β and Si–Ru–C_α bond angles in **TS2-A'** than those in **TS2-A** (131.6 and 103.8 versus 123.1 and 99.8°, respectively). The distortion energy attributed to the vinyl moiety in **TS2-A'** is estimated to be about 2.4 kcal mol^{–1} higher than in **TS2-A**.^[18] The steric repulsion in the *anti* form becomes more significant along the pathway, as indicated by the 5.6 kcal mol^{–1} preference for **3A** over **3A'**.

Finally, reductive elimination from **3A** involving sulfur chelation completes the reaction via **TS3-A**. The bulky silyl

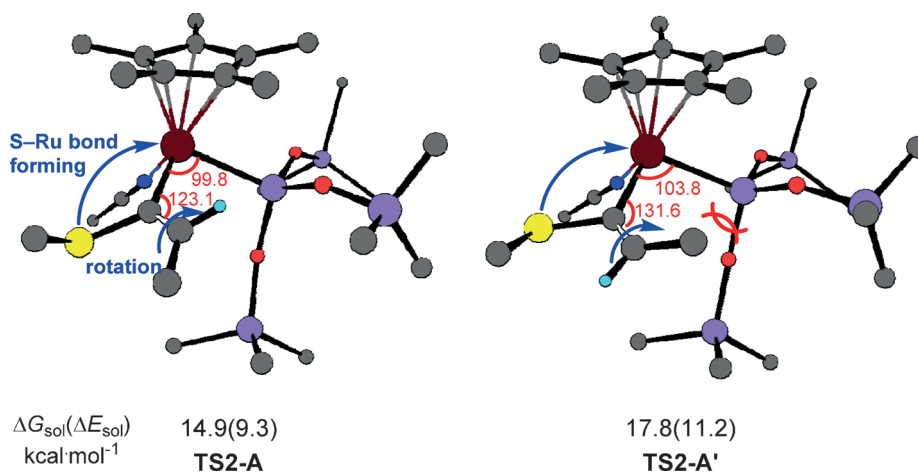


Figure 2. Optimized structures of the transition states of the stereodetermining isomerization (with key bond angles).

group approaches the less hindered side of the alkene in **TS3-A** (the *syn* form), and thus has a lower barrier of 8.5 kcal mol^{–1} to give the observed product of *α syn* addition, rather than the *anti*-addition product via **TS3-A'** (see Figure S7).^[7,11] Overall, the *syn* addition stereoselectivity is determined in the ring-opening/isomerization process (the proposed catalytic cycle is summarized in Scheme S1 of the Supporting Information).^[19] Notably, Ru–S chelation and steric effects play important roles in dictating the excellent and uncommon regio- and stereoselectivity.

In conclusion, we have developed the first general and mild hydrosilylation of thioalkynes. With [Cp*Ru(MeCN)₃]⁺ as the catalyst, a range of thioalkynes participated in the efficient hydrosilylation at room temperature with excellent regio- and stereoselectivity. The stereodefined vinyl sulfide

products are useful precursors to other valuable compounds. Particularly noteworthy is the unusual *syn* addition selectivity with the $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]^+$ catalyst. The unusual selectivity has been rationalized by DFT calculations. In the distinct mechanistic scenario, the sulfonyl group plays a key role by providing additional stabilization through S–Ru chelation. The bulky silane $(\text{TMSO})_3\text{SiH}$ also contributes to the enhanced selectivity by a steric effect. Further studies of the highly selective functionalization of electron-rich alkynes are under way.

Keywords: electron-rich alkynes · homogeneous catalysis · hydrosilylation · ruthenium · stereoselectivity

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- [17] Unlike **TS2-A**, **TS2-rot** does not involve the formation of a Ru–S bond.
- [18] The difference in the distortion energy for the remaining parts of the transition state is 0.8 kcal mol^{−1}.
- [19] The poor regioselectivity, stereoselectivity, or reactivity observed with various silanes (compounds **2b,d,i**) was mainly attributed to steric effects (see Tables S1–S3 and Figures S9–S11).

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