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Ligand-Controlled Remarkable Regio- and Stereodivergence in Intermolecular Hydrosilylation of Internal Alkynes: Experimental and Theoretical Studies

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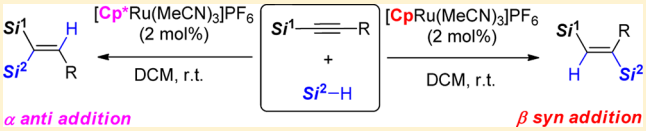
Supporting Information

ABSTRACT: The first highly efficient ligand-controlled regio- and stereodivergent intermolecular hydrosilylations of internal alkynes have been disclosed. Cationic ruthenium complexes $[Cp^*Ru(MeCN)_3]^+$ and $[CpRu(MeCN)_3]^+$ have been demonstrated to catalyze intermolecular hydrosilylations of silyl alkynes to form a range of vinyldisilanes with excellent but opposite regio- and stereoselectivity, with the former being *α anti* addition and the latter *β syn* addition. The use of a silyl masking group not only provides sufficient steric bulk for high selectivity but also leads to versatile product derivatizations toward a variety of useful building blocks. DFT calculations suggest that the reactions proceed by a mechanism that involves oxidative hydrometalation, isomerization, and reductive silyl migration. The energetics of the transition states and intermediates varies dramatically with the catalyst ligand (Cp* and Cp). Theoretical studies combined with experimental evidence confirm that steric effect plays a critical role in governing the regio- and stereoselectivity, and the interplay between the substituent in the alkyne (e.g., silyl group) and the ligand ultimately determines the observed remarkable regio- and stereodivergence.

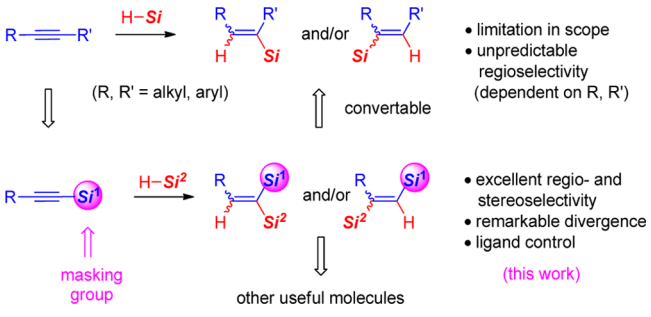


INTRODUCTION

Vinylsilanes are valuable building blocks in organic synthesis[1] not only because of their versatility in a wide range of useful organic transformations, such as Pd-catalyzed cross-coupling reactions[2] and Tamao−Fleming oxidation,[3] etc.,[4] but also due to their amenable features, including ease of handling, low cost and toxicity, and stability relative to other vinyl-metal species. Among the various synthetic methods toward vinylsilanes, hydrosilylation of alkynes represents the most straightforward and atom economical approach.[5] In the past few decades, there has been significant progress in the development of metal-catalyzed stereoselective alkyne hydrosilylation processes.[6] However, the majority of these reactions deal with terminal alkynes or symmetrical internal alkynes.[5−7] In contrast, the use of unsymmetrical internal alkynes has only met with limited success due to the increased difficulty in regio- and stereocontrol.[8] Indeed, such examples with general and excellent control in both regio- and stereoselectivity have been only limited to alkynes with a highly polarized triple bond (e.g., alkynones and alkynoates)[9] or alkynes bearing an internal directing group[10] or intramolecular hydrosilylations.[11]

While the stereoselectivity, i.e., *syn* or *anti* addition, for intermolecular hydrosilylation of internal triple bonds has been demonstrated to be well-controllable by the proper choice of catalytic systems,[12] however, the regioselectivity, i.e., *α* or *β* addition, is largely influenced by the two substituents (R and R′, Scheme 1) on the triple bond in terms of their electronic and steric difference. We were intrigued by the possibility of overcoming this intrinsic substrate limitation by an alternative approach. We hypothesized that a masking group, such as a silyl group, can be employed for temporary differentiation with the R group for potential good regio- and stereocontrol in the hydrosilylation and then can be easily converted to useful

Scheme 1. Design of Intermolecular Hydrosilylation of Silyl Alkynes



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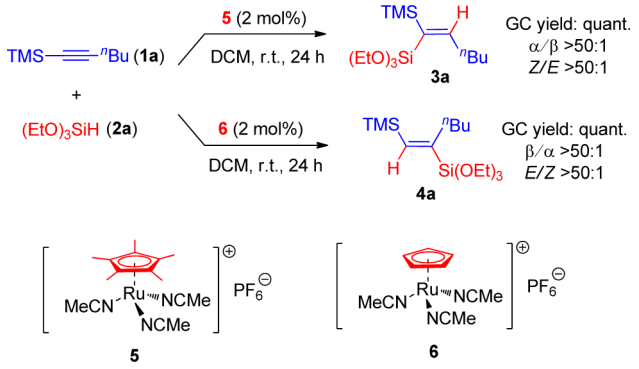
functional groups in a stereodefined fashion, thereby addressing the above limitation in an indirect but attractive way.[13] In fact, stereodefined trisubstituted vinyldisilanes, particularly with two electronically distinct silyl groups, are extremely versatile species toward various useful molecules by sequential transformations of the two silyl groups.

Herein we report highly efficient and general Ru-catalyzed intermolecular hydrosilylation reactions of internal silyl alkynes with excellent regio- and stereoselectivity. More intriguingly, with subtle variation of the ligand, we have observed unprecedentedly remarkable switch of regio- and stereoselectivity. Extensive density functional theory (DFT) calculations combined with experimental evidence provide insight into the reaction mechanism and the origin of the ligand-controlled regio- and stereodivergence.

RESULTS AND DISCUSSION

Experimental Results. We began our investigation with 1-trimethylsilyl-1-hexyne (**1a**) as the model substrate and triethoxysilane as the silylation reagent. As mentioned above, the two silyl groups in the reactants are electronically distinct, and the vinyldisilane products are expected to be particularly useful for subsequent chemoselective derivatizations. After brief survey of some potential catalytic systems (see the SI for details), we were pleased to identify that, with [Cp*Ru-$(MeCN)_3$]PF_6 (**5**) as the catalyst[14] and DCM as the solvent, the reaction proceeded smoothly at room temperature to furnish vinyldisilane **3a** in essentially quantitative yield (Scheme 2). Notably, the reaction displays not only high chemical

Scheme 2. Ligand Control in Regio- and Stereodivergent Hydrosilylations



efficiency but also excellent regio- and stereoselectivity for the Si–H bond addition, with exclusive α *anti* addition (α/β > 50:1, Z/E > 50:1). More intriguingly and surprisingly, replacement of the catalyst ligand Cp* by Cp (i.e., **6**)[14] resulted in complete switching of both regio- and stereoselectivity. Thus, under otherwise identical conditions, the reaction afforded β *syn* addition product **4a** as a single isomer in quantitative yield. It is worth noting that such a remarkable ligand-controlled divergence in both regio- and stereoselectivity is unprecedented.[15]

The unusual effect of the catalyst ligand prompted us to evaluate the generality of the phenomenon. As shown in Table 1, a wide range of different silyl alkynes and silanes can participate smoothly in the intermolecular hydrosilylation processes. More importantly, the ligand-controlled regio- and stereodivergence is indeed general, i.e., with the same pair of substrates, α *anti* addition products **3** were selectively formed with catalyst **5**, but β *syn* addition products **4** were formed with catalyst **6**. It is worth noting that Ru-catalyzed *syn* selective alkyne hydrosilylations are very scarce.[16] The mild reaction conditions can tolerate a diverse set of functional groups, such as esters, mesylates, acetals, silyl-protected alcohols, Boc-protected amines, ethers, etc. In addition to the TMS group, we also evaluated other silyl groups in the alkyne substrates (entries 10–13). The desired β *syn* addition products **4j–m** were all formed with excellent efficiency and selectivity when catalyst **6** was used. In contrast, with the bulkier catalyst **5**, the corresponding reactions proceeded with much lower conversions (**3j–m**, entries 10–13), although the levels of regio- and stereoselectivity remain high. The observed low conversions as well as slow reaction rates are presumably due to the increased steric bulk in both the alkyne silyl group and the catalyst ligand. These results suggest that steric effect plays an important role in the hydrosilylation processes. Finally, 1,7-diynes with the silyl groups at either terminal or internal positions are also effective substrates. The corresponding vinyldisilane products **3n,o** and **4n,o** from bis(hydrosilylation) were obtained with excellent efficiency and selectivity, and no cyclic products from the hypothetical hydrosilylation–cyclization cascade across the two triple bonds were observed.

Next, we examined the silane scope of the Ru-catalyzed hydrosilylation processes (Table 2). We were pleased to find that, with the smaller catalyst **6**, various silanes including trialkylsilanes and chlorosilanes are suitable reaction partners, providing the desired β *syn* addition products **4p–v** all with high efficiency and selectivity. However, these silanes exhibit different reactivity when the bulkier catalyst **5** was used. For example, alkoxysilanes **2b–d** and chlorosilane **2h** can participate in the hydrosilylation process with good chemical efficiency and excellent regio- and stereoselectivity, but the bulky tris(trimethylsiloxy)silane **2e** and the relatively electron-rich trialkylsilanes **2f,g** are unreactive (entries 4–6, conditions A). The high reactivity of alkoxysilanes and chlorosilanes relative to trialkylsilanes indicates that the reaction favors electron-deficient silanes. Unfortunately, aryl-substituted alkynes are not suitable substrates under both conditions (entries 16–17). Finally, it is noteworthy that, although the chemical efficiency varies with silanes and catalysts, the same remarkable regio- and stereodivergence with high levels of selectivity was always observed as long as these reactions proceed.

In order to gain insight into the reaction mechanism, particularly the origin of the intriguing regio- and stereodivergence controlled by ligands, we have carried out a series of theoretical and experimental mechanistic studies. We expected that these catalytic systems might have similarity with the unusual regio- and stereoselectivity of the intermolecular reactions with terminal alkynes (Markovnikov and *anti* addition) and the intramolecular reactions (endo-*dig* and *anti* addition) Trost and Ball developed.[12d–f]

Theoretical Results. Two of us, together with Trost and Ball, previously reported a DFT study and proposed a new mechanism that involves a concerted oxidative addition/hydrometalation step followed by the stereoselective C_α–C_β rotation to give a metallacyclopropene-like intermediate and then a novel reductive silyl migration.[17,18] The proposed mechanism successfully explained all the observed unusual regio- and stereochemistry Trost and Ball reported. We postulated that the present intermolecular reactions of silyl alkynes may proceed by a similar mechanism, but the energetics of the transition states and intermediates may vary due to the

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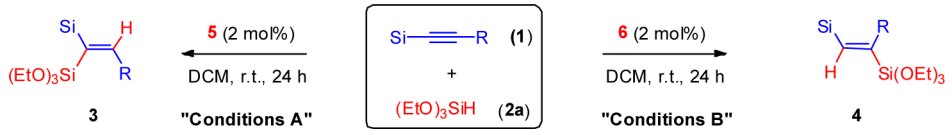
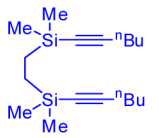
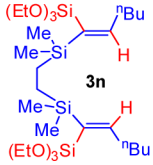
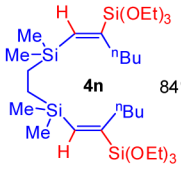
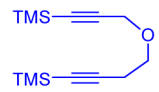
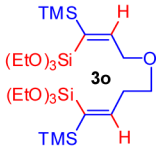
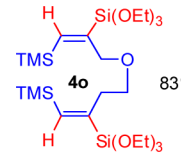
Table 1. Scope of Alkynes



entry	1		Conditions A				Conditions B			
	R	Si	product	yield[b]	α/β[c]	Z/E[c]	product	yield[b]	β/α[c]	E/Z[c]
1	^{n}Bu	TMS	**3a**	96%	>50:1	>50:1	**4a**	96%	>50:1	>30:1
2	Me	TMS	**3b**	89%	>50:1	>50:1	**4b**	88%	>50:1	>30:1
3	^{n}Oct	TMS	**3c**	99%	>50:1	>50:1	**4c**	97%	>50:1	>30:1
4	CH_2OTBS	TMS	**3d**	93%	>50:1	>50:1	**4d**	94%	15:1	5:1
5	$(CH_2)_2OTBS$	TMS	**3e**	90%	>50:1	>50:1	**4e**	94%	>50:1	25:1
6	$(CH_2)_2OAc$	TMS	**3f**	90%	>50:1	>50:1	**4f**	85%	>50:1	25:1
7	$(CH_2)_2OMs$	TMS	**3g**	95%	>50:1	>50:1	**4g**	91%	12:1	25:1
8	$(CH_2)_2OTHP$	TMS	**3h**	96%	>50:1	>50:1	**4h**	75%	>50:1	>30:1
9	C_2H_4NHBoc	TMS	**3i**	84%	>50:1	>50:1	**4i**	77%	>50:1	>50:1
10	^{n}Bu	Et_3Si	**3j**	28%	>50:1	>50:1	**4j**	87%	>50:1	>50:1
11	^{n}Bu	TBS	**3k**	25%	>50:1	>50:1	**4k**	93%	15:1	>30:1
12	^{n}Bu	$PhMe_2Si$	**3l**	<5%[e]	–	–	**4l**	81%	>50:1	>50:1
13	^{n}Bu	$BnMe_2Si$	**3m**	<5%[e]	–	–	**4m**	92%	>50:1	>30:1
14[d]			 **3n**	95%	>50:1	>50:1	 **4n**	84%	>50:1	>50:1
15[d]			 **3o**	90%	>50:1	>50:1	 **4o**	83%	>50:1	>50:1
16	Ph	TMS	–	<5%[e]	–	–	–	<5%[e]	–	–
17	3-thiophenyl	TMS	–	<5%[e]	–	–	–	<5%[e]	–	–

[a]Standard conditions: A mixture of **1** (0.40 mmol), **2a** (0.80 mmol), [Ru]-catalyst (2 mol %) in DCM (3 mL) was stirred under N_2 at room temperature for 24 h. [b]Isolated yields. [c]Determined by ^{1}H NMR; [d]4 equiv of silane were used. [e]Low conversion with the starting alkyne as the mass balance.

incorporation of the silyl groups in the substrates and thus result in the observed unusual regio- and stereoselectivity. Therefore, we followed the previous computational methods (B3LYP, Lanl2dz effective core potential and basis set augmented with f functions for Ru; 6-31G* basis sets for the other atoms)[17,19−21] to study the present hydrosilylation reactions.

[CpRu(MeCN)$_3$]PF$_6$–Catalyzed β Syn Addition. Similar to the proposed mechanism,[17] the precursor complexes **A3** (**A3*α***) and **A3*β***, with different alkyne orientation but same stability) can be generated after ligand displacement of the ruthenium catalyst **A1** by the alkyne and then the silane (Figure 1). Subsequently, H−Si addition across the Ru−C bond of **A3** can occur,[22] with hydrogen migration to the substrate more favorable than silyl migration (Figure S1).[23] Regarding the regiochemistry of the favorable oxidative hydrometalation step (oxidative addition of H−Si concerted with hydrometalation), the *β*-selective pathway leading to **A6*β*** (via **A5-TS*β***) is computed to be kinetically and thermodynamically more favorable, because of the substantial steric repulsion between the Cp ring and the TMS group in **A5-TS*α*** (Figure S2).[23] In contrast to the previous calculations,[17] planar *σ*-vinyl intermediates **A6*α*/*β*** can be first formed when the internal alkyne and trimethoxysilane are used in this study. Agostic interactions between the newly formed C_β−H bond and the Ru center stabilize **A6*α*/*β***. Interestingly, a reductive elimination transition state from **A6*α*/*β*** could not be located. Instead, subsequent isomerization of **A6*α*/*β***, which involves rotation of the C_α=C_β bond, could lead to four possible ruthenacyclopropene isomers **A8**.

In general, isomerization via counterclockwise rotation (e.g., **A7-TS*α*-anti** and **A7-TS*β*-anti**) requires a lower barrier than that via clockwise rotation (e.g., **A7-TS*α*-syn** and **A7-TS*β*-syn**), because a relatively large group (e.g., TMS in **A6*β*** and Me in

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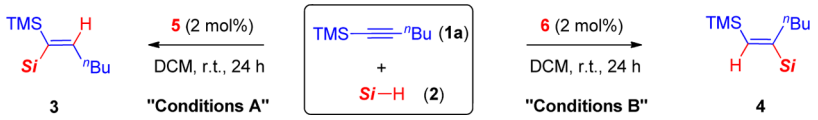
Table 2. Scope of Silanes



		conditions A				conditions B			
entry	Si–H (2)	product	yield[b]	α/β[c]	Z/E[c]	product	yield[b]	β/α[c]	E/Z[c]
1	$(EtO)_2MeSiH$ (**2b**)	**3p**	66%	>50:1	>50:1	**4p**	85%	>50:1	50:1
2	$(EtO)Me_2SiH$ (**2c**)	**3q**	88%	>50:1	>50:1	**4q**	59%	>50:1	>50:1
3	$(MeO)_3SiH$ (**2d**)	**3r**	85%	>50:1	>50:1	**4r**	58%	>50:1	25:1
4	$(TMSO)_3SiH$ (**2e**)	**3s**	<10%	–	–	**4s**	99%	20:1	>50:1
5	Et_3SiH (**2f**)	**3t**	<10%	–	–	**4t**	93%	16:1	>50:1
6	$BnMe_2SiH$ (**2g**)	**3u**	<10%	–	–	**4u**	94%	25:1	>50:1
7	Me_2SiClH (**2h**)	**3v**	74%[d]	>50:1	>50:1	**4v**	80%[d]	14:1	>30:1

[a]Standard conditions: Mixture of **1a** (0.40 mmol), **2a** (0.80 mmol), [Ru]-catalyst (2 mol %) in DCM (3 mL) was stirred under N_2 at rt for 24 h. [b]Isolated yield. [c]Determined by ^1H NMR. [d]Reaction was quenched by Et_3N (3.0 equiv) and MeOH (3.0 equiv), and the corresponding methyl silyl ether derivative was obtained.

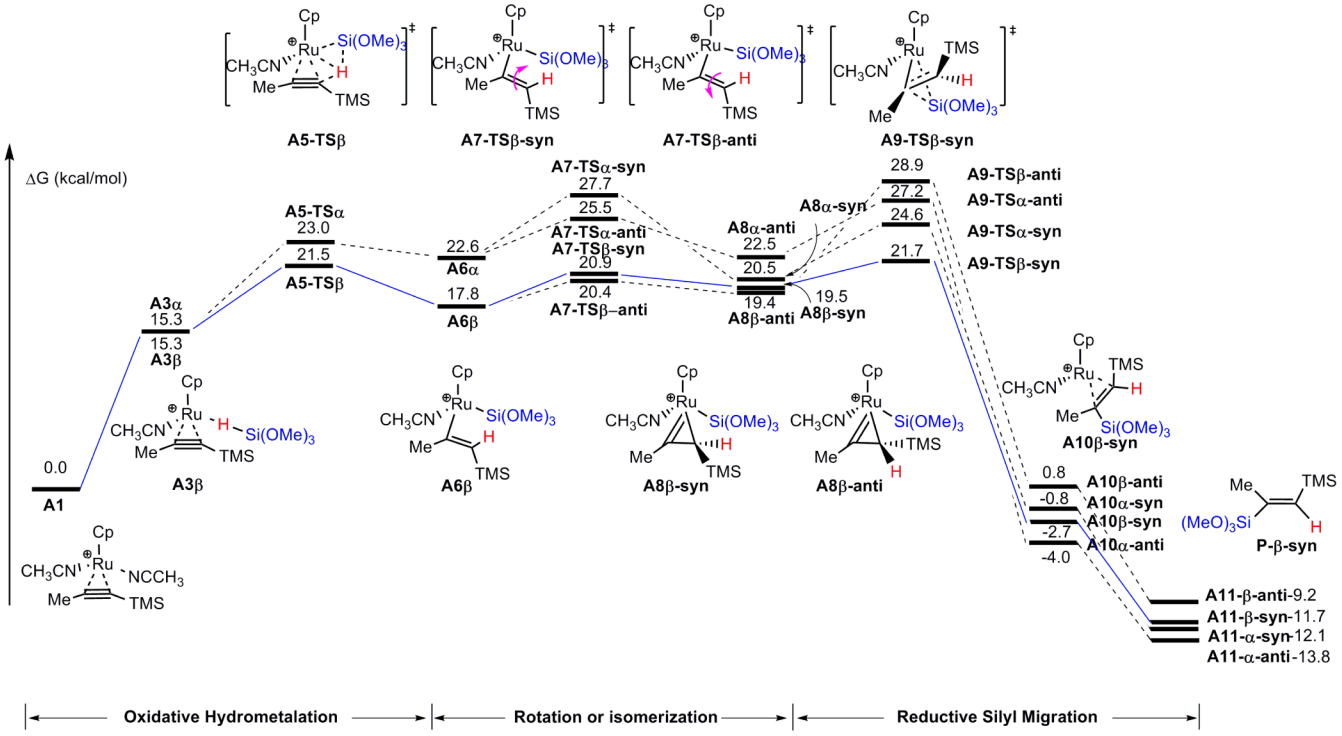


Figure 1. Free energy profile of the $[CpRu(MeCN)_3]PF_6$-catalyzed hydrosilylation. The favorable pathway is shown with solid blue line.

A6*α*) moves toward the bulky Cp moiety in the latter case (Figure S3).[23] Finally, reductive silyl migration delivers the corresponding complexes **A10**, leading to the hydrosilylation product and the active catalytic species **A1** for the next catalytic cycle. The bulky silyl group is more favored to migrate when the small hydrogen atom at C_β is placed on the same side of the metallacyclopropene plane (Figure S4): **A9-TS*α*-syn** (24.6 kcal/mol) and **A9-TS*β*-syn** (21.7 kcal/mol) are lower in free energy than **A9-TS*α*-anti** (27.2 kcal/mol) and **A9-TS*β*-anti** (28.9 kcal/mol).[23]

Overall, the most favorable pathway leading to the observed *β syn* addition product (**A10*β*-syn**) occurs through **A9-TS*β*-syn**, because the migrating silyl group approaches the less bulky carbon. As shown in Figure 1, the *β* regioselectivity and *syn* stereoselectivity are primarily determined in the initial oxidative hydrometalation step and the final silyl migration step, respectively. The computational results are fully consistent with the observed experimental outcomes with $[CpRu(MeCN)_3]PF_6$ as the catalyst.

$[Cp^*Ru(MeCN)_3]PF_6$-Catalyzed α Anti Addition. The above computational findings indicate that hydrosilylation of internal silyl alkynes, in contrast to terminal alkynes,[17] can be significantly influenced by steric effect. As a result, the Cp* ligand is expected to have a more pronounced steric effect. Indeed, as shown in Figure 2, in the oxidative hydrometalation step, the energy gap between *α* addition (**B5-TS*α***) and *β* addition (**B5-TS*β***) is larger (2.4 kcal/mol) with the Cp* ligand than that with the Cp ligand (1.5 kcal/mol), supporting a stronger repulsion between the Cp* ligand and the TMS substituent.

In the isomerization step, the counterclockwise rotation is again found to have a much lower barrier than the clockwise

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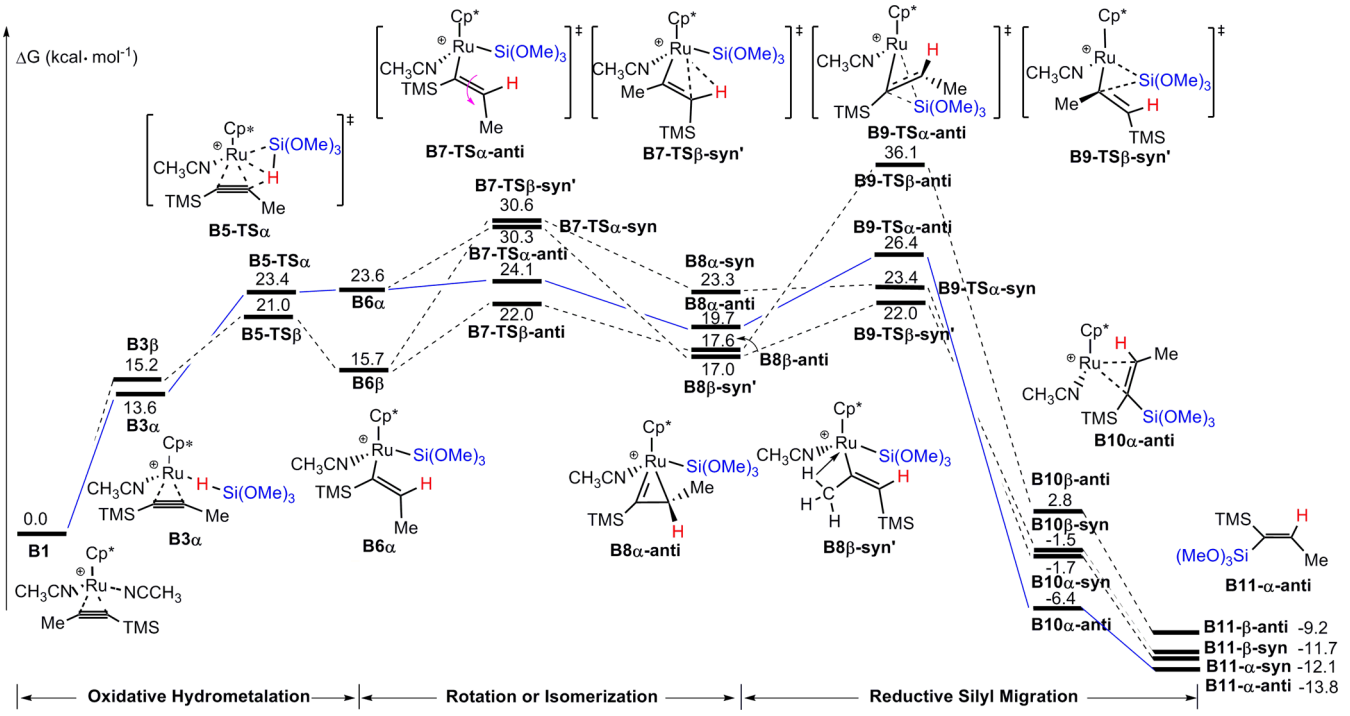

Figure 2. Free energy profile of the $[Cp^*Ru(MeCN)_3]PF_6$-catalyzed hydrosilylation. The favorable pathway is shown with solid blue line.

rotation (Figure S5).[23] Importantly, for α additions, more severe steric repulsion results in a larger energy difference between the counterclockwise and clockwise rotation transition states with Cp* (6.2 kcal/mol, calculated from **B7-TS*α*-syn** and **B7-TS*α*-anti**) than that with Cp (2.2 kcal/mol, calculated from **A7-TS*α*-syn** and **A7-TS*α*-anti**, Figure 1).

Although the oxidative hydrometalation (via **B5-TS*β***) and isomerization steps (via **B7-TS*β*-anti**) for β additions are energetically more favorable, the reaction barrier of the final silyl migration step via **B9-TS*β*-anti** is too high (36.1 kcal/mol) to be accessed,[24] because of the steric repulsion between TMS and the Cp* ligand (H···H: 2.08 Å, Figure S6).[23] Also, the rate-determining isomerization step via **B7-TS*β*-syn′**, which lacks stabilization by either formation of three-membered ring or an agostic interaction, has a very high barrier (30.6 kcal/mol). Therefore, the β addition paths are strongly destabilized with the bulky Cp* ligand. In this respect, the transition states for α *anti* and α *syn* additions have much lower barriers (26.4 and 23.4 kcal/mol for **B9-TS*α*-anti** and **B9-TS*α*-syn**, respectively), since a relatively small group (Me or H) is on the same side of the silyl migration. However, a high isomerization barrier (30.3 kcal/mol) via **B7-TS*α*-syn** (H···H: 2.22 Å, Figure S6)[23] prevents α *syn* addition. Therefore, the energetically most favorable pathway for hydrosilylation catalyzed by **6** is α *anti* addition via intermediates **B6*α*** and **B8*α*-anti** as well as transition states **B5-TS*α***, **B7-TS*α*-anti**, and irreversible **B9-TS*α*-anti**. The computed regio- and stereoselectivity are also consistent with the experimental results.

Proposed Mechanisms and Theoretical Prediction for t-Butyl-Substituted Alkynes. The above computational results have clearly explained the experimentally observed regio- and stereodivergence. Traditional Chalk−Harrod mechanism and its variant,[25] which typically refer to the Pd-catalyzed hydrosilylations of terminal alkynes, proved inapplicable to the cationic Ru-catalyzed hydrosilylations. Instead, our calculations demonstrated that the current mechanism is similar to that proposed by Wu and Trost.[17] The major difference is that the planar σ-vinylruthenium complexes here are obtained to be intermediates, rather than transition states in the previous mechanism. The formation of these intermediates and their subsequent isomerization affects the regio- and stereoselectivity. Additionally, due to significant steric effect, the rate-determining step also depends on the isomerization and reductive silyl migration steps. In contrast, electronic effect is dominant in the previously proposed mechanism of the hydrosilylation of terminal alkynes.[17c]

We have summarized the two catalytic cycles that lead to the selective formation of α *anti* and β *syn* products with catalysts **5** and **6**, respectively (Scheme 3). For both catalytic cycles, the reaction starts with replacement of the two MeCN ligands by the alkyne and the silane. Next, oxidative hydrometalation forms the planar σ-vinyl intermediate (e.g., **A6*β*** and **B6*α***), which can rotate to form a metallacyclopropene-like intermediate (e.g., **A8*β*-syn** and **B8*α*-anti**). The more favorable rotation leads the β-substituent to be opposite to Cp (or Cp*) to avoid steric repulsion (i.e., *syn* configuration). The final step is silyl migration to the carbene carbon center. In both catalytic cycles, the reductive silyl migration is principally the rate-determining step. In the case of Cp, the rate-determining step (via **A9-TS*β*-syn**) is most favorable among the four possible pathways, thereby leading to the formation of β *syn* addition products. The mechanistic pathway is more complicated for the case of Cp*. Although the β pathway is more favorable in the oxidative hydrometalation step, it is suppressed by a very high barrier in the isomerization step (**B7-TS*β*-syn′**) or the silyl migration step (**B9-TS*β*-anti**). Instead, the α *anti* pathway has the overall lowest activation barrier (**B9-TS*α*-anti**), thus leading to the observed α *anti* addition product.

On the basis of the above calculation results, we conclude that the dominant factor for the highly selective reactions is steric effect, rather than electronic effect, which explains that the steric bulk of the catalyst ligand and silyl group in the

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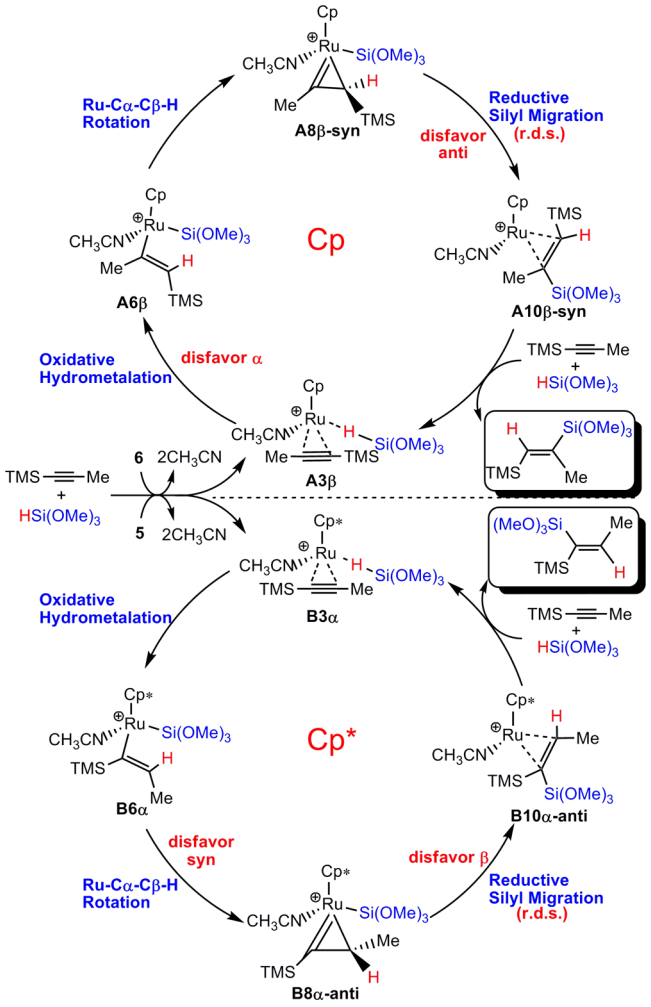
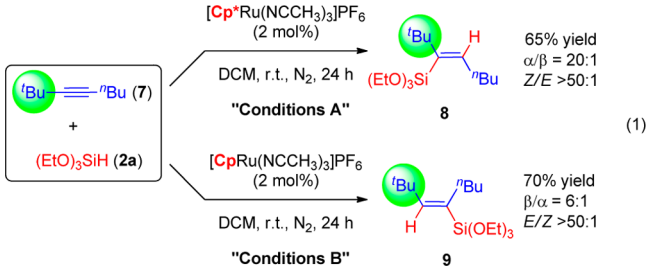
Scheme 3. Proposed Catalytic Cycles



alkyne substrates are critically important. It is the interplay between the bulky silyl group and the ligand that ultimately determines the observed complete regio- and stereodivergence. Thus, we further hypothesized that other bulky substituents, such as *t*-butyl group, may also result in similar selectivity divergence. We carried out additional calculations with ^{t}BuC≡CMe as the substrate, and the results show that similar ligand-controlled regio- and stereodivergence can also be observed (Figure S7).[23]

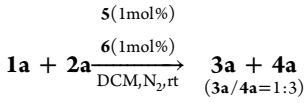
Some experiments were carried out to confirm the theoretical results. First, alkyne **7** was subjected to the standard reaction conditions. As shown in eq 1, the reactions proceed selectively



(1)

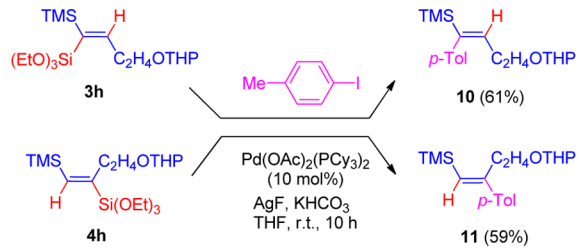
to afford the *α anti* addition product **8** with catalyst **5** and the *β syn* addition product **9** with catalyst **6**. Both reactions exhibit good regio- and stereoselectivity. More importantly, the ligand-controlled selectivity divergence is exactly the same as that observed with silyl alkynes, which is consistent with the theoretical prediction. However, replacement of ^{t}Bu with ^{i}Pr in the alkyne results in almost complete loss of regioselectivity.

The calculations also indicate that the activation barrier for the *α anti* addition with catalyst **5** (Cp*) is higher ($\Delta G^{\ddagger}$ = 26.4 kcal/mol) than that for the *β syn* addition with catalyst **6** (Cp, $\Delta G^{\ddagger}$ = 21.7 kcal/mol). Thus, we evaluated the reaction of **1a** and **2a** in the presence of an equal amount of catalysts **5** and **6** (eq 2). A mixture of **3a** (*α anti* product) and **4a** (*β syn* product) was obtained in good yield, with the latter being the major (**3a**/**4a** = 1:3). The results are in qualitative agreement with the theoretical studies.



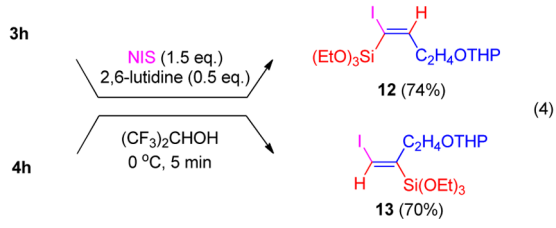
(2)

Product Derivatizations. In order to demonstrate the utility of our efficient regio- and stereoselective hydrosilylation processes, we have done derivatization reactions of the vinyldisilane products **3h** and **4h**, representing the *α anti* and *β syn* addition products. For example, they can undergo Hiyama cross-coupling reactions with *p*-tolyl iodide to form products **10** and **11**, respectively (eq 3). The triethoxysilyl unit, rather than



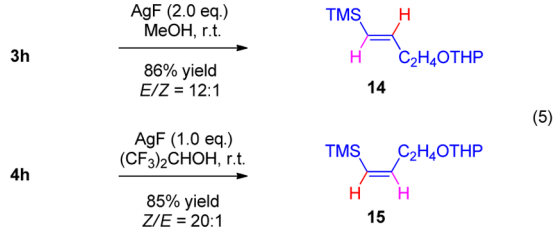
(3)

the TMS group, was selectively reacted, and the reactions are stereospecific in terms of alkene configuration. Alternatively, under electrophilic iodination conditions, the TMS group can be selectively converted, with the triethoxysilyl unit untouched (eq 4).The vinyl iodide products **12** and **13** are useful for



(4)

subsequent cross-coupling reactions toward various stereo-defined multisubstituted alkenes. Finally, protodesilylation was also achieved selectively on the triethoxysilyl group, providing *E*- and *Z*-alkenes **14** and **15**, respectively (eq 5).[26] It is worth



(5)

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mentioning that, although the AgF-mediated protodesilylation of **3h** in MeOH as solvent is highly stereoselective, the same reaction protocol cannot be extended to **4h**, which gives a mixture of *Z*/*E* isomers (*Z*/*E* = 3:2). Nevertheless, brief condition optimization identified hexafluoroisopropanol as the solvent of choice for excellent stereoselectivity (*Z*/*E* = 20:1).

CONCLUSION

In summary, we have developed the first highly efficient ligand-controlled regio- and stereodivergent intermolecular hydrosilylation processes of internal alkynes. In the presence of cationic ruthenium complex **5** or **6**, the hydrosilylation reactions of a variety of silyl alkynes and silanes proceed efficiently to form a range of vinyldisilanes with excellent but opposite regio- and stereoselectivity. The mild conditions also tolerate a diverse set of functional groups. The remarkable and complete switching of product regio- and stereochemistry (*α anti* vs *β syn* addition) caused by subtle variation of the catalyst ligand (Cp* vs Cp) is unprecedented. The importance of the silyl group in the alkyne substrates is 2-fold: it not only provides a steric differentiation of the two sides of alkyne triple bond to ensure excellent regio- and stereoselectivity in the hydrosilylation process but also serves as an excellent masking group that is easily convertible to other useful functional groups in a stereodefined fashion. Thus, the present reactions provide an attractive solution to the current limitations in regio- and stereoselective intermolecular hydrosilylations of internal alkynes. DFT calculations combined with experimental evidence provide important insight into the reaction mechanism, in which steric effect plays a critical role and the interplay between the bulky silyl group and the ligand controls the remarkable regio- and stereodivergence. Our proposed mechanism involving metallacyclopropene-like intermediates and reductive silyl migration (instead of reductive elimination of *σ*-vinyl intermediates) leading to both *syn* and *anti* addition products is unique. Similar mechanisms may also operate in reactions catalyzed by other (middle) transition metal complexes as well as other alkyne *trans*-addition reactions catalyzed by ruthenium-based catalysts.[27]

ASSOCIATED CONTENT

Supporting Information

Experimental and computational details, computational and characterization data, and complete ref 19. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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