

A Theoretical Study on the Mechanism, Regiochemistry, and Stereochemistry of Hydrosilylation Catalyzed by Cationic Ruthenium Complexes

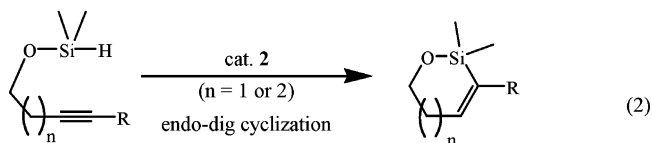
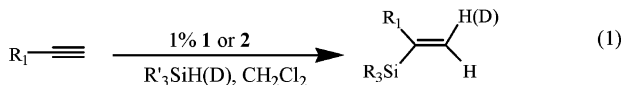
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Abstract: Density functional calculations have been carried out to understand the anti-addition stereochemistry and Markovnikov regiochemistry of the hydrosilylation of terminal alkynes and the endo-dig product of intramolecular hydrosilylation of homopropargyl alcohols catalyzed by cationic cyclopentadienyl-ruthenium complexes. It has been found that hydride or silyl insertion is concerted with the oxidative addition of the H–Si bond. Hydride insertion is much more favorable than silyl insertion. Such a hydride insertion nicely reproduces the observed regioselectivity, while silyl insertion would predict the opposite result. The hydride insertion leads to the formation of a η^2 -vinylruthenium intermediate for the reaction of acetylene or a metallacyclopropene intermediate for the reaction of propyne. In the formation of both intermediates, there is a C_α – C_β bond rotation so that the transferring hydride becomes anti to the silyl group. This is followed by a facile reductive α -silyl migration transition state, which results in the overall anti-addition stereochemistry. The proposed mechanism also rationalizes the observed regio- and stereochemistry of the intramolecular reaction.

Vinylsilanes are pivotal building blocks in organic synthesis. The hydrosilylation of alkynes catalyzed by transition-metal complexes is the most straightforward method for the preparation of vinylsilanes. Many transition-metal complexes catalyze this reaction, and usually linear anti-Markovnikov products are obtained.¹ Recently, two of us reported that the cationic ruthenium complexes, [CpRu(MeCN)₃]PF₆ (**1**) and [Cp*₂Ru(MeCN)₃]PF₆ (**2**), produce instead the branched, Markovnikov products (eq 1).² Furthermore, labeling experiments demon-



strate that the addition occurs exclusively in a trans manner.^{2a} Moreover, the intramolecular hydrosilylation catalyzed by **2**

affords endo-dig cyclization products of trans-addition (eq 2),^{2a} while hydrosilylation catalyzed by other complexes favors exo-dig cyclization products (n = 1) instead.³

Two mechanisms of hydrosilylation have been widely accepted, the Chalk–Harrod and the modified Chalk–Harrod mechanisms (see Scheme 1).^{1,4} Both mechanisms start with an oxidative Si–H addition to the metal. In the Chalk–Harrod mechanism, hydride insertion occurs first followed by rate-determining reductive elimination, while in the second mechanism, silyl insertion occurs first. Several theoretical calculations on the mechanism of hydrosilylation have been reported.⁵ The trans-hydrosilylation products are generally believed to be derived from initial syn silylmatalation, followed by olefin isomerization before reductive elimination.⁶ The peculiar regio- and stereochemistry observed with complexes **1** and **2** are inconsistent with such interpretations and call for more study. Here, we report on our preliminary investigations on the

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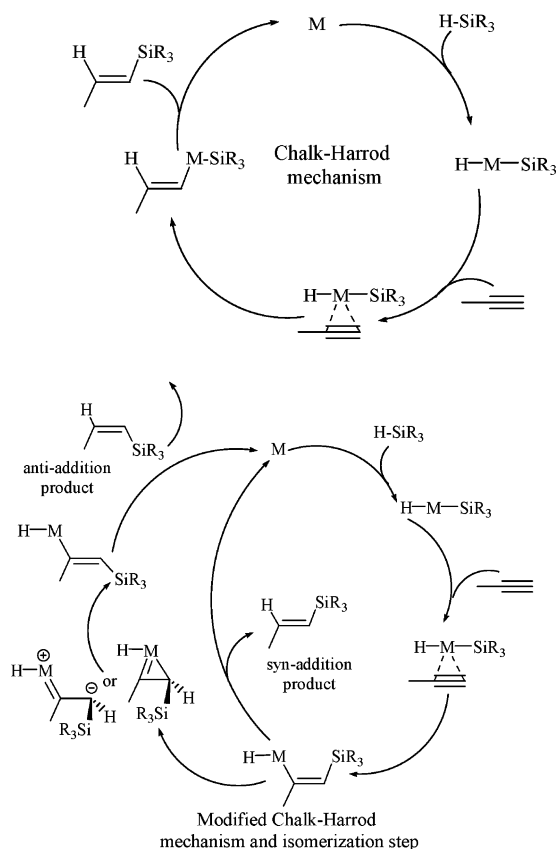
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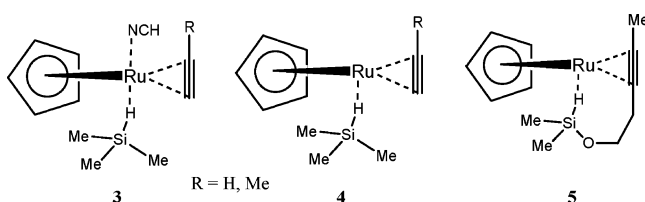
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Scheme 1



Scheme 2



hydrosilylation of systems **3**–**5** (Scheme 2) using density functional theory calculations.

Method of Calculation

All calculations were carried out with the Gaussian 98 program.⁷ All geometries of the reactants, transition structures, and intermediates were fully optimized by the B3LYP method.⁸ The 6-31G* basis set was used for H, C, N, and O atoms, while the LanL2dz basis set and ECP⁹ were used for Si and Ru atoms. The Si and Ru were augmented with d-polarization functions¹⁰ and f-polarization functions,¹¹ respectively. The harmonic vibration frequency calculation was performed

Table 1. The Calculated Relative Free Energies (kcal/mol) for Markovnikov and Anti-Markovnikov Transition Structures for Hydrosilylation of **3** and **4** (R = Me) (Data Are Given for Hydride Insertion (H-TS) and Silyl Insertion (Si-TS))

reaction system	Markovnikov TS		anti-Markovnikov TS	
	H-TS	Si-TS	H-TS	Si-TS
3	0.0	21.4	0.5 (1.5) ^a	10.6
4	5.0	12.3	7.1	4.7

^a Data for calculation with Et₃SiH, an experimentally relevant silane.

Table 2. Calculated Geometrical Parameters and Relative Energies (kcal/mol) of Structures on the Potential Energy Surface of C_α–C_β Bond Rotation of the Metallacyclopene Intermediate (**11**) (Distances Are in Angstroms and Angles Are in Degrees)

H ⁺ CCRu	–91° (14)	–60°	–30°	–7° (13)	30°	60°	85° (11)
RuC _α	1.909	1.947	1.992	2.078	1.986	1.940	1.926
RuC _β	2.228	2.385	2.564	2.451	2.519	2.345	2.228
C _α C _β	1.392	1.370	1.351	1.313	1.356	1.376	1.392
CpRuN ^a	125	127	128	129	126	122	121
CpRuSi	111	107	106	109	111	113	114
CpRuC _α	122	124	124	119	126	135	139
CpRuC _β	148	148	149	135	119	119	118
C _β C _α RuSi	13	7	3	–27	–59	–65	–68
CpRuC _α C _β	145	146	151	129	88	79	74
r _{H/H} ^b	2.33	2.29	2.26	2.38	2.88	2.57	2.44
	(2.36)	(2.33)	(2.31)				
E _{rel} ^c	1.0	3.7	6.2	9.8	3.8	1.2	0.0

^a Cp is the centroid of the Cp ring. ^b The shortest H/H distance between the trimethylsilyl and C₆H₅ groups. ^c The relative energy is in terms of electronic energy.

for each structure, from which the zero-point energy, thermal energy, entropy, and free energy were derived. All energies are given in terms of free energy except for those in Table 2, which are given in terms of electronic energy. An intrinsic reaction coordinate calculation was performed to ascertain the stereospecific rotation of the C_α–C_β bond in the hydride-insertion process (**10** → **11**).¹²

Results and Discussion

A. Intermolecular Reaction. 1. Hydride Insertion versus Silyl Insertion. Our calculations indicate a mechanism wherein ruthenium orchestrates a direct addition of the silane to the alkyne. For the reaction of acetylene, precursor complexes **3** and **4** are regarded as three- and two-legged piano stools, respectively. Complex **3** is calculated to be about 2.6 kcal/mol more stable than complex **4**. The silane coordinates to ruthenium in an η¹ manner in both complexes. Attempts to locate the corresponding oxidative-addition adducts have not been successful, probably due to the high instability of Ru(IV) silyl hydride.

The H–Ru (1.597–1.686 Å) and Si–Ru (2.618–2.892 Å) bonds in the transition structures (Figure 1) are considerably formed, suggesting that oxidative addition is concerted with hydride or silyl insertion.^{13,14} The hydride insertion in both **H-TS3** and **H-TS4** occurs nearly in the RuCC plane. However,

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- (14) This is supported by the observation that no ruthenium hydride is observed in the ¹H NMR spectrum when the silane is mixed with a stoichiometric amount of the cationic ruthenium complexes.

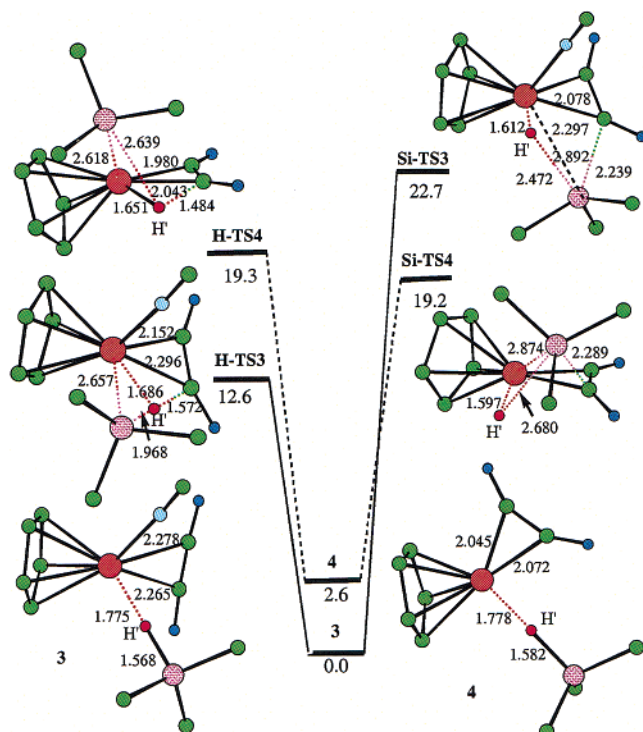


Figure 1. Calculated precursor complexes (**3**, **4**, R = H) and transition structures resulting from hydride and silyl insertion with relative free energies (kcal/mol) and selected bond distances (Å). Methyl, nitrile, and Cp hydrogen atoms are omitted for clarity.

the silyl group is out-of-plane by 18° in **H-TS3** and by 40° in **H-TS4**. Hydride insertion is favored when an HCN ligand is present (i.e., **3**), probably due to weaker acetylene coordination in **3**. Thus, the activation energy with **H-TS3** is lower than with **H-TS4** by about 4.1 kcal/mol (6.7 kcal/mol if the 2.6 kcal/mol destabilization of **4** is included). Accordingly, **H-TS3** is an earlier transition state than **H-TS4**, as indicated by shorter Si-H and longer H-C distances in **H-TS3**. On the other hand, silyl insertion is favored in the absence of the HCN ligand (i.e., **4**). In **Si-TS4**, the silyl group attacks acetylene in a perpendicular fashion, while the silyl attacks acetylene in a syn manner in **Si-TS3**. Overall, hydride insertion (**H-TS3**) is much favored over silyl insertion.

2. Regiochemistry. As shown in Table 1, the calculated results for the hydrosilylation of propyne are similar to those of the reaction of acetylene. Hydride insertion is favored with a nitrile ligand (i.e., **3**), while silyl insertion is favored in the absence of a nitrile (i.e., **4**). Overall, hydride insertion is favored over silyl insertion. In terms of regiochemistry, silyl insertion strongly favors the anti-Markovnikov transition structure by about 7.6 kcal/mol. This is understandable because there are severe steric interactions between the silyl group and the propyne methyl group in the Markovnikov transition structure (see Supporting Information for details). On the other hand, hydride insertion favors the Markovnikov transition structure over the anti-Markovnikov one. This preference is about 0.5 kcal/mol with the CpRu(HCN)⁺ catalyst. Using the CpRu(HCN)⁺ catalyst, we calculated an increased regioselectivity when using the experimentally relevant H-SiEt₃. As shown in Figure 2, transition structure **6**, which leads to the formation of the Markovnikov product, is calculated to be more stable than transition structure **7**, which gives the anti-Markovnikov product,

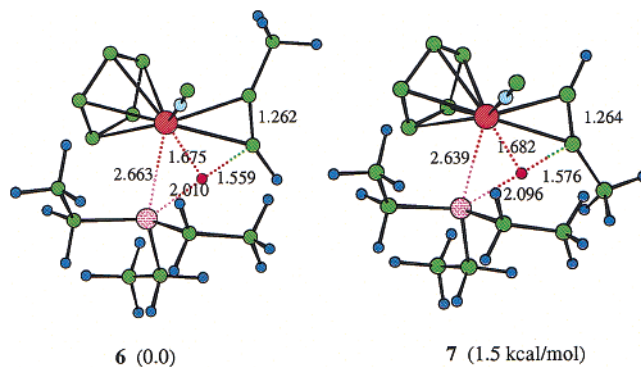


Figure 2. The calculated hydride-insertion transition structures for the reaction of triethylsilane with propyne. The hydrogen atoms of the Cp group and nitrile are omitted for clarity.

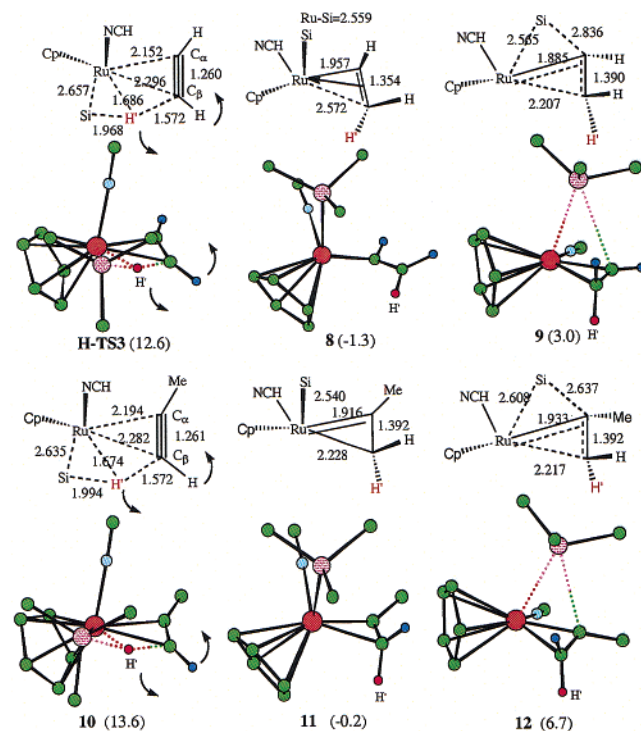


Figure 3. Calculated hydride-insertion transition structures (**H-TS3** and **10**), η^2 -vinylruthenium (**8**) and metallacyclopentene (**11**) intermediates, and α -silyl migration transition structures (**9** and **12**) for the reaction of Cp-Ru(HCN) trimethylsilane with acetylene and propyne (**3**, R = H and Me). The values in parentheses are calculated relative free energies with respect to their precursor complexes. The hydrogen atoms of the Cp and methyl groups and nitrile are omitted for clarity.

by about 1.5 kcal/mol. Structure **7** is apparently destabilized by the steric interaction between the bulky silyl group and the propyne methyl group. These results are in qualitative agreement with observed regioselectivities.^{2b}

3. Stereochemistry. The above results indicate that the hydride-insertion (**H-TS3** and **10**) is more favorable than the silyl-insertion, and the former also reproduces the observed regiochemistry. Next, we tried to locate the resulting hydro-metalated intermediates by full geometric optimization from both **H-TS3** and **10**. Unexpectedly, the calculations did not render an assumed planar 16-electron η^1 -vinylruthenium(IV) intermediate. Instead, they resulted in the formation of 18-electron η^2 -vinylruthenium (**8**) and metallacyclopentene (**11**) intermediates¹⁵

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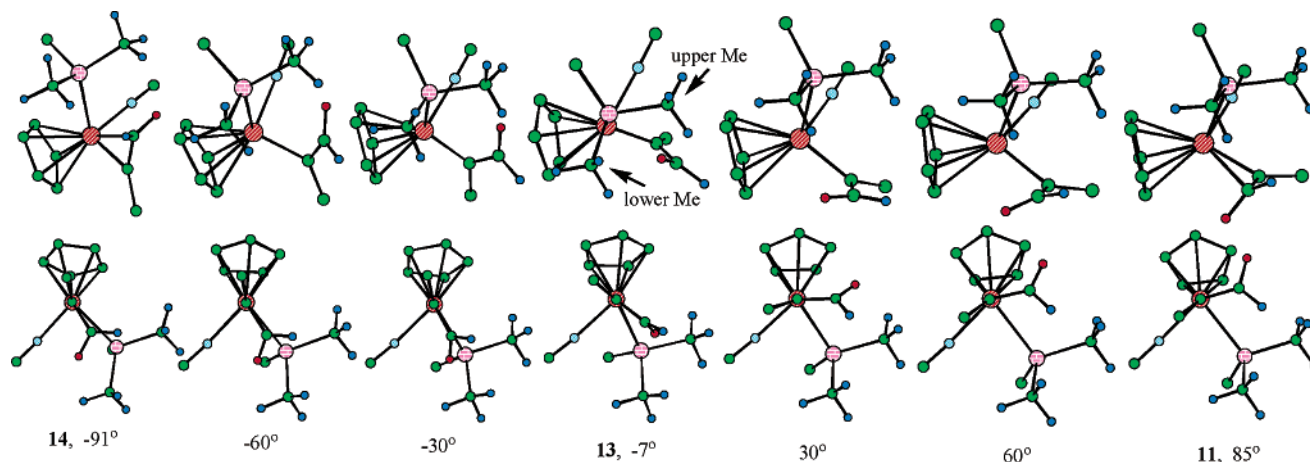


Figure 4. Calculated structures on the potential energy surface for the isomerization of metallacyclopropene intermediate **11** by C_{α} - C_{β} bond rotation. The top structures are side views, and the bottom structures are Newman projections about the Ru- C_{α} bond.

for the reactions of acetylene and propyne, respectively. Interestingly, the formation of both **8** and **11** was accompanied by a counterclockwise rotation of the C_{α} - C_{β} bond (see arrows in **H-TS3** and **10** in Figure 3), so that the transferring hydride became anti to the silyl group. The dihedral angle of Ru- C_{α} - C_{β} -H' is about 45° in **8** and 85° in **11**. The intrinsic reaction coordinate calculation on **10** indicates that the reaction coordinate features the initial transferring of the H' to C_{β} so that a "planar η^1 -vinylruthenium structure" is formed. Once the C_{β} -H' bond is largely formed, the C_{α} - C_{β} bond starts to rotate to form the metallacyclopropene intermediate (**11**). The intrinsic reaction coordinate calculation also confirms the stereospecific counterclockwise rotation of the C_{α} - C_{β} bond. At this stage, the stereochemical course of the reaction is determined. Casey et al. observed hydride-insertion onto alkynes to give metallacyclopropene intermediates in CpRe systems, which were characterized by NMR, X-ray crystallography, and computational studies.¹⁶ The transferring hydride was found to be syn to the Cp ring in a crystal structure.¹⁶

Attempts to locate a transition structure for a subsequent normal silyl reductive elimination from **8** to give a syn addition product were unsuccessful. Only α -silyl migration transition states **9** and **12** were located in which a metallacyclopropene form was adopted. Computation suggests that the silyl migration to C_{α} is very facile with an activation free energy of about 4.3 and 6.9 kcal/mol for **9** and **12**, respectively. This results in an overall trans R_3SiH addition to alkyne, in accordance with the experimental results.² The energetics of the overall catalytic cycle are distinct from those of the hydrosilylation catalyzed by platinum^{5c} and rhodium^{5b} catalysts based on the Chalk-Harrod mechanism.

The counterclockwise rotation of the C_{α} - C_{β} bond is most intriguing and critical to the trans-stereochemistry. To gain more information about this, we explored the potential energy surface for the isomerization of the metallacyclopropene intermediate **11** to its isomer (**14**) by C_{α} - C_{β} bond rotation. Structure **13** in Figure 4 is the calculated transition structure for the isomerization. This structure is similar to but not exactly the same as the "planar η^1 -vinylruthenium intermediate", which is a point in the hydride insertion process (**10** \rightarrow **11**). The Ru- C_{α} - C_{β} -

H' dihedral angle in **11** is about -7° . Structures with the constraint of the Ru- C_{α} - C_{β} -H' dihedral angle at -60° , -30° , 30° , and 60° were also calculated. The selected geometrical parameters of these structures along with those of the fully optimized isomeric metallacyclopropene intermediates (**11** and **14**) are collected in Table 2. Two stereoviews of all of these structures are given in Figure 4, the top structures are side views, while the bottom structures are Newman projections about the C_{α} -Ru bond.

Several geometrical features are observed: (1) The Ru- C_{β} distance is the largest in the -30° and 30° structures (Table 2). (2) During the C_{α} - C_{β} bond rotation, the geometry of the CpRu-(NCH)(SiMe₃) moiety undergoes only a minor change as indicated by the small variation of the CpRuN and CpRuSi angles. (3) As the C_{α} - C_{β} bond rotates in a clockwise manner (-30° , -60° , -91°), there is also an overall clockwise rotation of the vinyl moiety with respect to the CpRu(NCH)(SiMe₃) moiety as indicated by the SiRu $C_{\alpha}C_{\beta}$ and CpRu $C_{\alpha}C_{\beta}$ dihedral angles. This makes the C_{α} - C_{β} nearly eclipsed with the Ru-Si bond. On the other hand, the counterclockwise rotation of the C_{α} - C_{β} bond (30° , 60° , 85°) is accompanied by a counterclockwise rotation of the vinyl moiety. Similarly, the C_{α} - C_{β} bond tends to be anti to the Ru-N bond (N-Ru- C_{α} - C_{β} = -151°).^{15,17} (4) In the planar structure **13**, the transferring hydride is close to the upper methyl (shortest H'/H = 2.376 Å) of the silyl group, but it has no interaction with the lower methyl (shortest H'/H = 3.049 Å), indicating that the lower position is less crowded for the counterclockwise rotation. The steric hindrance is increased in the -30° and -60° structures because the $C_{\beta}H_2$ becomes closer to the silyl group as indicated by the reduced H/H distances (Table 2), but there is no short H/H distance in the 30° and 60° structures.

The counterclockwise rotation from structure **13** is apparently more energetically favorable than the clockwise rotation. The energy difference between the 30° and -30° structures is about 2.4 kcal/mol. The -30° structure is destabilized by steric interactions as indicated by the short H/H distances (Table 2). We also calculated the two structures by replacing the trimethylsilyl group with an experimentally relevant triethylsilyl group

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(17) Example of C-C eclipsed with metal-ligand: Carfagna, C.; Carr, N.; Deeth, R. J.; Dossett, S. J.; Green, M.; Mahon, M. F.; Vaughan, C. *J. Chem. Soc., Dalton Trans.* **1996**, 415.

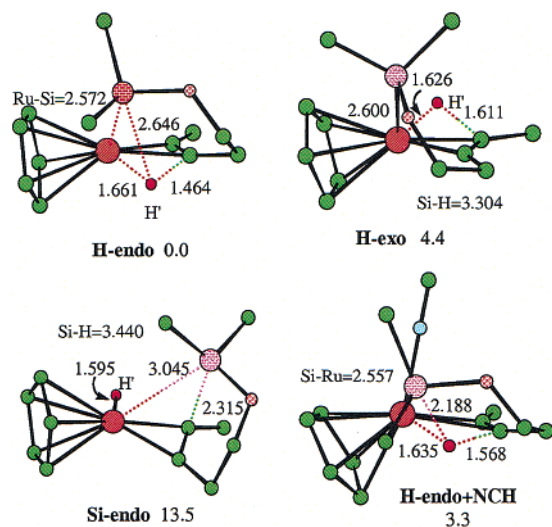


Figure 5. Calculated transition structures and relative free energies (kcal/mol) for intramolecular hydrosilylation of **5**. The hydrogen atoms of the Cp and methyl groups and nitrile are omitted for clarity.

and found that the energy preference for the 30° structure over the -30° structure is increased to about 3.7 kcal/mol. This indicates that steric factors are important for the favored counterclockwise rotation of the $C_\alpha-C_\beta$ bond in the hydride-insertion reaction (**10** \rightarrow **11**). At this point, we cannot rule out an electronic contribution to the preference for the counterclockwise rotation of the $C_\alpha-C_\beta$ bond.¹⁸

B. Intramolecular Reaction. The intramolecular hydrosilylation with ruthenium catalyst **2** is especially troubling for the previously proposed mechanisms of hydrosilylation. Initial cis-endo-silylmatalation affords an untenable trans-cyclohexene. Alternatively, as we have previously noted,^{2a} the observed stereochemistry could arise through initial exo-silylmatalation, a proposal requiring subsequent silyl migration and olefin isomerization steps with no obvious or general driving force.¹⁹

Thus, we are pleased to find that our calculations indicate that the general mechanism we have detailed here nicely predicts results for 6-endo intramolecular hydrosilylation reactions as well. Shown in Figure 5 are the transition structures for intramolecular hydrosilylation (**5**). We were unable to locate a **Si-exo** transition structure, apparently due to the high instability of the five-membered-ring intermediate. The geometries of these transition structures are similar to those of the intermolecular reactions (Figure 1). Once again, hydride insertion is more favorable than silyl insertion. We found that **H-endo** is more stable than **H-exo** by about 4.4 kcal/mol, due to ring strain and a loss of the stabilizing interaction²⁰ between the hydride and the silyl group in **H-exo**. The **H-endo** transition structure leads to the formation of a η^2 -vinylruthenium intermediate similar to

structure **8** (not shown), which, upon C_α -silyl elimination, results in the observed endo-dig product (trans addition).

Curiously, although in the intermolecular reaction HCN association was favorable in the transition state, adding an HCN ligand to the **H-exo** structure resulted in HCN dissociation, while the **H-endo** structure with a HCN was less stable than that without HCN by about 3.3 kcal/mol, apparently due to a reduced dihedral angle of Si-Ru- C_α - C_β increasing the ring strain and a closer distance between the oxygen and the hydride.

Conclusion

We have found that oxidative addition is concerted with hydride-insertion for hydrosilylation of alkynes catalyzed by cationic ruthenium complexes. Hydride insertion is favored over silyl-insertion in both inter- and intramolecular reactions. The trans addition stereochemistry results from the formation of a η^2 -vinylruthenium or metallacyclopropene intermediate upon hydride-insertion followed by a stereospecific counterclockwise rotation of the $C_\alpha-C_\beta$ bond. The intermediate undergoes a facile α -silyl migration through a metallacyclopropene-like transition structure to give a trans addition product.

These conclusions stand in stark contrast to the accepted mechanisms²¹ in other transition-metal catalyzed hydrosilylations. Any plausible mechanism for alkyne hydrosilylation with complex **2** should account for the unique Markovnikov regiochemistry and complete selectivity for trans-addition in intermolecular cases, as well as for endo-cyclization in intramolecular reactions. Simple modifications of the Chalk-Harrod model require isomerization or silyl migration steps for which the driving force is difficult to envision. We therefore believe that the concerted oxidative addition-hydride insertion and ruthenacyclopropene intermediate presented here provides a single pathway to all current product types and is the model most consistent with all current data.

Acknowledgment. We thank Prof. Z. Y. Lin of HKUST for helpful discussions, and the Research Grants Council of Hong Kong for financial support of the research. B.M.T. and Z.T.B. thank the National Science Foundation for their generous support.

Supporting Information Available: Calculated transition structures for the hydrosilylation reaction of propyne and Cartesian coordinates of all reactants, transition states, and intermediates (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) When we replaced the SiMe_3 group in **13** by a SiH_3 group so that the steric interaction was diminished, full geometric optimization still led to the formation of the metallacyclopropene intermediate with a counterclockwise rotation of the $C_\alpha-C_\beta$ bond.
 (19) A recent commentary favors such a mechanism: Crabtree, R. H. *New J. Chem.* **2003**, *27*, 771–772.

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 (21) There was a proposal for *trans*-addition hydrosilylation based on the Chalk-Harrod mechanism.^{6a,22} This mechanism involved hydride insertion to give a *cis* η^1 -vinyl-M intermediate followed by isomerization of the olefin to afford a *trans* η^1 -vinyl-M intermediate, which undergoes normal reductive elimination to give a *trans* addition product.
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