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Regioselectivity of Stoichiometric Metathesis of Vinylsilanes with Second-Generation Grubbs Catalyst: A Combined DFT and Experimental Study

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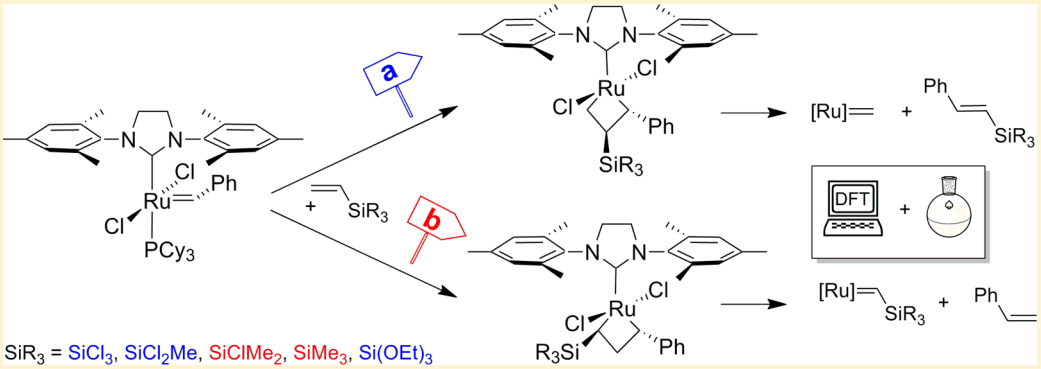
Supporting Information



ABSTRACT: The regioselectivity of metathesis reactions of trisubstituted vinylsilanes $H_2C{=}CHSiR_3$ (SiR_3 = $SiCl_3$, $SiCl_2Me$, $SiClMe_2$, $SiMe_3$, $Si(OEt)_3$) with the second-generation ruthenium alkylidene complex has been studied theoretically, by density functional theory (DFT), and experimentally. The DFT results indicate that cycloreversion is the rate-determining step and the formation of a thermodynamically stable ruthenium methylidene complex and $PhCH{=}CHSiR_3$ is generally preferred. However, the regioselectivity of the process can be also governed by the relative stabilities of the ruthenacyclobutane intermediates, which depend on the electronic and steric properties of the SiR_3 substituent. Higher stability of α,β-disubstituted ruthenacyclobutanes in comparison to α,α-disubstituted ruthenacyclobutanes is predicted, in contrast to the corresponding intermediates formed during metathesis of common α-olefins. The stabilizing $Ru{-}C_\beta$ interaction in the ring is strengthened by the electron-donor SiR_3 substituent at C_β. The experiments performed have shown selectivity toward styrene formation for SiR_3 = $SiClMe_2$, $SiMe_3$, whereas a preference for the formation of ruthenium methylidene and $PhCH{=}CHSiR_3$ has been observed for SiR_3 = $SiCl_3$, $SiCl_2Me$, $Si(OEt)_3$, in accordance with the theoretical predictions.

INTRODUCTION

Among functional olefins, vinylsilanes make up a group of compounds that differs from the most common α-olefins in their reactivity toward ruthenium olefin metathesis catalysts (Figure 1).[1] It has been shown that the equimolar reactions of vinylsilanes with first- and second-generation Grubbs catalysts occur with preferred formation of a methylidene complex and silylstyrene (path a, Scheme 1), which is the opposite of path b being preferred for α-olefins.[2,3]

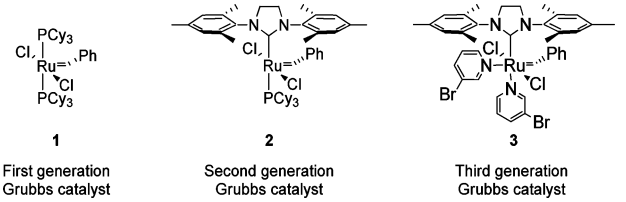
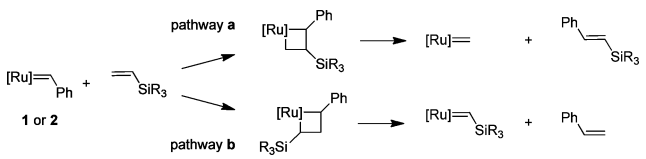


Figure 1. Well-defined ruthenium-based olefin metathesis catalysts.

The observed difference in regioselectivity must be a consequence of steric and electronic effects of the silyl groups on the properties of the double C=C bond. However, no

Scheme 1. Reactivity of Grubbs Catalysts toward Vinylsilanes



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explanation of the mechanism of steric and electronic effects on regioselectivity has been proposed.

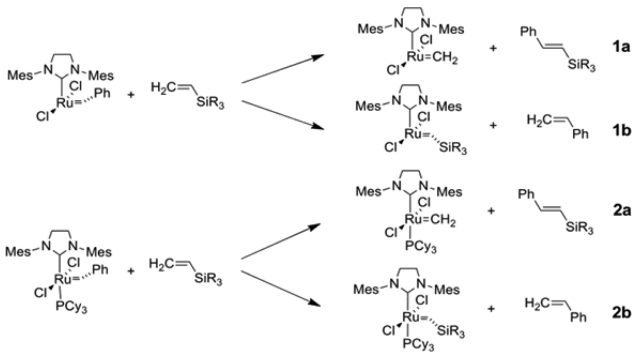
The progress in application of metathesis in the chemistry of vinylsilanes and vinylsiloxanes and in the design of new catalysts with improved catalytic performance toward organosilicon compounds requires a full understanding of the factors that determine the regioselectivity of vinylsilane addition to ruthenium alkylidene complexes.

Although a large number of theoretical studies on olefin metathesis catalyzed by Grubbs-type complexes have been reported so far,[4−20] computational works concerning metathesis reactions of vinylsilanes are lacking. Herein, we report a detailed study of the regioselectivity of cycloaddition of selected vinylsilanes to the second-generation ruthenium alkylidene complex, performed with density functional theory (DFT) calculations. We also have tried to understand how the properties of SiR_3 substituents influence the relative stability of the ruthenacyclobutane intermediates in the competitive reaction pathways, which may affect the regioselectivity of the process. Computational work has been supplemented by results of experimental studies on the reactivity of selected vinylsilanes in the presence of equimolar amounts of a second-generation ruthenium alkylidene complex.

RESULTS AND DISCUSSION

Thermodynamics of the Process. We have considered two competitive routes of the cycloaddition of vinylsilanes $H_2C{=}CHSiR_3$ (SiR_3 = $SiCl_3$, $SiCl_2Me$, $SiClMe_2$, $SiMe_3$, $Si(OEt)_3$) to the ruthenium alkylidene complex (pathways a and b, Scheme 2). Pathway a leads to the formation of a

Scheme 2. Reactions of Vinylsilanes $H_2C{=}CHSiR_3$ with 14-Electron Intermediate and Complex 2



ruthenium methylidene complex and silylstyrenes $PhCH{=}CHSiR_3$. The products of pathway b are ruthenium (silyl)-alkylidene complexes and styrene.

It is well established that 14-electron intermediates, initially formed after the dissociation of the phosphine ligand (first- and second-generation Grubbs catalysts) and pyridine or bromopyridine ligands (third-generation Grubbs catalysts) are the active ruthenium species playing the crucial role in the catalytic cycle of olefin metathesis.[4−22] Consequently, we assume the same dissociative mechanism for the metathesis of vinylsilanes. There are possible rotational isomers of the active $[Ru]{=}CHSiR_3$ species, where [Ru] = $Ru(Cl)_2(H_2IMes)$ (see Figure S1 in the Supporting Information). The perpendicular orientation of the alkylidene moiety to the mesityl group is more energetically favored, in comparison to the parallel orientation. An analogous geometrical preference is predicted for other 14-electron ruthenium alkylidene species,[7,8,10,11,20,23] which can be explained by analysis of molecular orbitals[7,8] and by a stabilizing interaction between the hydrogen from the benzylidene ligand of $[Ru]{=}CHPh$ species and the electron-deficient ruthenium center.[17] However, such interactions, involving H, Cl, or O atoms, are observed for both types of the conformers of the 14-electron $[Ru]{=}CHSiR_3$ intermediates (Figure S1).

Considering the reactions between the active ruthenium alkylidene species and vinylsilanes (**1a**,**b**, Scheme 2), pathway b is thermodynamically favored (Table 1). However, taking into

Table 1. Calculated Gibbs Energies[a] (ΔG_s, kJ mol^{-1}) for Reactions of Vinylsilanes $H_2C{=}CHSiR_3$ with Complex 2 (Scheme 2)

	reaction			
reactant	**1a**	**1b**	**2a**	**2b**
$H_2C{=}CHSiCl_3$	11	6	2	42
$H_2C{=}CHSiCl_2Me$	13	0	3	35
$H_2C{=}CHSiClMe_2$	14	3	4	35
$H_2C{=}CHSiMe_3$	14	−4	4	44
$H_2C{=}CHSi(OEt)_3$	12	−15	3	33

[a]M06/def2-TZVPP//PBE0/def2-SVP calculations for simulated dichloromethane solution.

account that the dissociation of the PCy_3 ligand in the second-generation Grubbs catalysts is an endergonic process,[4,5,10,11,14,16,20] which is also confirmed in the present work, the 16-electron ruthenium alkylidene complexes are expected to dominate in the reaction environment. Therefore, the thermodynamics of the overall reactions (**2a**,**b**, Scheme 2) should be considered instead. In this case, a clear thermodynamic preference for pathway a is predicted. This is explained by a much higher PCy_3 dissociation energy for the ruthenium methylidene complex formed according to pathway a, in comparison to that of the ruthenium complexes with the SiR_3 group in the alkylidene ligands, being the potential products of pathway b (Table 2). Hence, the ruthenium methylidene

Table 2. Calculated Gibbs Energies[a] (ΔG_s, kJ mol^{-1}) for PCy_3 Ligand Dissociation

complex	ΔG_s
$(H_2IMes)(Cl)_2Ru(=CHPh)(PCy_3)$ (**2**)	66
$(H_2IMes)(Cl)_2Ru(=CH_2)(PCy_3)$ (**4**)	76
$(H_2IMes)(Cl)_2Ru(=CHSiCl_3)(PCy_3)$	30
$(H_2IMes)(Cl)_2Ru(=CHSiCl_2Me)(PCy_3)$	32
$(H_2IMes)(Cl)_2Ru(=CHSiClMe_2)(PCy_3)$	34
$(H_2IMes)(Cl)_2Ru(=CHSiMe_3)(PCy_3)$	18
$(H_2IMes)(Cl)_2Ru(=CHSi(OEt)_3)(PCy_3)$	18

[a]M06/def2-TZVPP//PBE0/def2-SVP calculations for simulated dichloromethane solution.

complex, after phosphine binding, is predicted to be a stable thermodynamic product, in accordance with the present experimental results. In contrast, the calculated phosphine dissociation energies for the $[Ru]{=}CHSiR_3(PCy_3)$ complexes are much lower than that for the methylidene complex. Consequently, the ruthenium (silyl)alkylidene complexes are most unstable among all the ruthenium compounds present in the reaction environment, because of the easy formation of the 14-electron active species undergoing further metathesis

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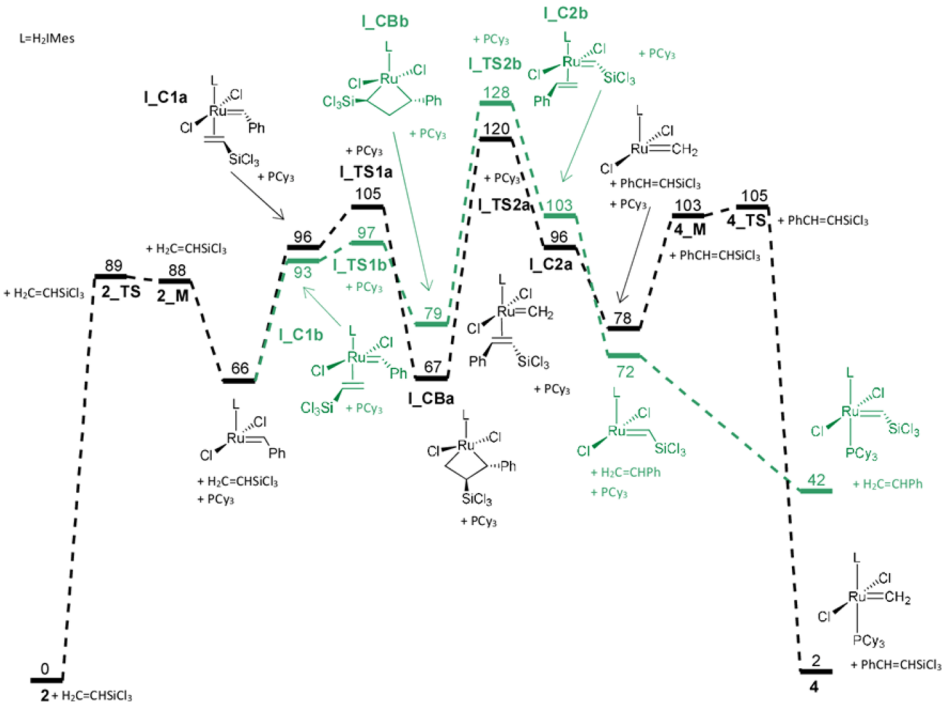

Figure 2. Gibbs energy profile (ΔG_s, kJ mol^{-1}) for the reaction of $H_2C{=}CHSiCl_3$ with the second-generation Grubbs catalyst **2** (pathways a and b) (M06/def2-TZVPP//PBE0/def2-SVP calculations for simulated dichloromethane solution).

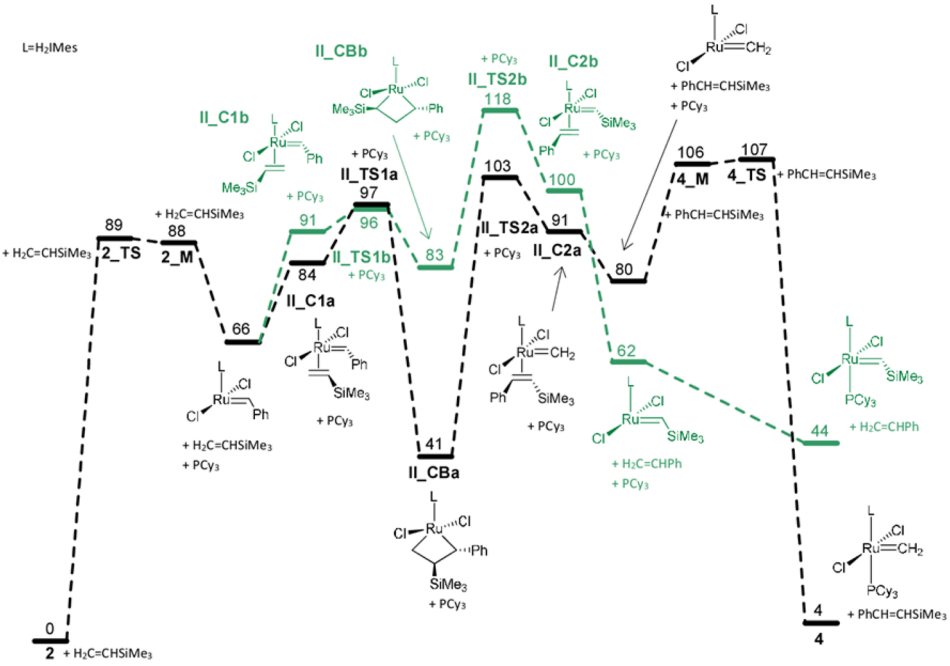

Figure 3. Gibbs energy profile (ΔG_s, kJ mol^{-1}) for the reaction of $H_2C{=}CHSiMe_3$ with the second-generation Grubbs catalyst **2** (pathways a and b) (M06/def2-TZVPP//PBE0/def2-SVP calculations for simulated dichloromethane solution).

transformations. This explains why such compounds are not observed experimentally, although the presence of other products indicates their formation as reaction intermediates.[2,3]

Regioselectivity of the Process. The calculated pathways of the reactions of the catalyst **2** with the exemplary vinylsilanes $H_2C{=}CHSiCl_3$ and $H_2C{=}CHSiMe_3$ in simulated dichloromethane solution are shown in Figures 2 and 3, respectively. The corresponding energy diagrams for other vinylsilanes are presented in Figures S3−S5 in the Supporting Information.

The initial step of both processes, phosphine ligand dissociation leading to the active catalyst species [Ru]=CHPh, is characterized by the transition state **2_TS** and associated minimum **2_M**. The predicted Gibbs energy (ΔG_s) barrier for this step (89 kJ mol^{-1}) is close to the experimental activation Gibbs energy determined for the PCy_3 ligand exchange in toluene solution (96 kJ mol^{-1}).[21,22] The corresponding theoretical values reported by other authors are similar (97−99 kJ mol^{-1}, toluene)[16,20] or clearly higher

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(123 kJ mol^{-1}, dichloromethane).[14] The 14-electron ruthenium intermediate can coordinate vinylsilanes to form the respective π complexes (**I_C1a**, **I_C1b**, **II_C1a**, **II_C1b**), localized on the potential energy surface (PES), but this is predicted to be unstable in terms of Gibbs energy. For both vinylsilane reactants, the cycloaddition step is slightly kinetically favored in the case of pathway b, whereas a clear thermodynamic preference, indicated by the relative stabilities of the ruthenacyclobutane intermediates (**I_CBa**, **I_CBb**, **II_CBa**, **II_CBb**), is seen for pathway a (Figures 2 and 3). However, cycloreversion, involving the highest-energy transition states (**I_TS2a**, **I_TS2b**, **II_TS2a**, **II_TS2b**), is the rate-determining step. The overall activation barriers, related to the reactants (**2** + $H_2C{=}CHSiR_3$), are lower for pathway a, suggesting that this route is kinetically preferred. This is a general tendency, predicted for all of the vinylsilanes considered (Table 3). Along

Table 3. Calculated Overall Activation Gibbs Energies[a] (kJ mol^{-1}) for the Reactions of Vinylsilanes $H_2C{=}CHSiR_3$ with Complex 2 and the Values Related to the Active 14-Electron Species $(H_2IMes)(Cl)_2Ru(=CHPh)$

	complex **2**		[Ru]=CHPh	
reactant	**2a**	**2b**	**1a**	**1b**
$H_2C{=}CHSiCl_3$	120	128	54	62
$H_2C{=}CHSiCl_2Me$	111	131	57	65
$H_2C{=}CHSiClMe_2$	107	119	57	53
$H_2C{=}CHSiMe_3$	103	118	62	52
$H_2C{=}CHSi(OEt)_3$	110	126	54	60

[a]M06/def2-TZVPP//PBE0/def2-SVP calculations for simulated dichloromethane solution.

the cycloreversion path, π-complex structures have been found on the PES (**I_C2a**, **I_C2b**, **II_C2a**, **II_C2b**), again being thermodynamically unstable species. As mentioned above (Table 1), the final products of pathway a ($PhCH{=}CHSiR_3$ and ruthenium methylidene complex **4**) are thermodynamically more stable than the products of pathway b (styrene and $[Ru](=CHSiR_3)(PCy_3)$ complex). Moreover, the calculated activation Gibbs energy of the PCy_3 dissociation for **4** (103 kJ mol^{-1}) is even higher than that for **2** (Figures 2 and 3), confirming that the former is the least reactive catalyst among the ruthenium alkylidene complexes considered.

Conclusions about the regioselectivity of the process may change if the catalyst dissociation stage is omitted in the consideration of the reaction pathway. Such an approach can be justified when phosphine is removed from the solution, for instance, by the reaction with CuCl; thus, the 14-electron ruthenium alkylidene intermediate dominates over the precursor in the reaction mixture. The dissociation stage is also less significant in the case of an excess of the vinylsilane reactant relative to the catalyst concentration. The calculated energy profiles can be then related to the energy level of the 14-electron intermediate + $H_2C{=}CHSiR_3$, and the overall activation barrier of the process can depend on the relative Gibbs energy of the ruthenacyclobutane intermediate. In the case of pathway a, the ruthenacyclobutane complex can be formed in an endergonic or exergonic reaction, depending on the vinylsilane reactant, whereas its formation according to pathway b is always endergonic (Figures 2 and 3 and Figures S3–S5 in the Supporting Information). Consequently, the formation of a stable ruthenacyclobutane structure in pathway a may result in the kinetic preference for pathway b. For the reaction of $H_2C{=}CHSiMe_3$ and $H_2C{=}CHSiClMe_2$ with [Ru]=CHPh, pathway b might be kinetically preferred, because the activation Gibbs energy for the cycloreversion step along pathway a is higher than the overall activation barrier calculated for pathway b (Figure 3 and Figure S4 in the Supporting Information; Table 3, entries 3 and 4). On the other hand, if a pre-equilibrium between the ruthenacyclobutane intermediates and the reactants is assumed, pathway a will always be favored. Our experimental results indicate the kinetic preference for pathway b when $H_2C{=}CHSiMe_3$ and $H_2C{=}CHSiClMe_2$ are the reactants, although this observation can be influenced by β-SiR_3 elimination being competitive with cycloreversion along pathway a (vide infra).

The relative stabilities of the ruthenacyclobutanes probably depend on the steric effects involving the substituents in the ring and on the electron-donor abilities of the SiR_3 group. In the case of the metathesis reactions between normal olefins, α,α-disubstituted metallacyclobutane intermediates are more stable than the corresponding α,β-disubstituted conformers.[19,24] This can be explained by weaker steric interactions between the substituents in α positions. It has been also shown that placing the substituents at C_α favors electron donation from the olefin fragment to the ruthenium alkylidene species.[19] Interestingly, our calculations for the metathesis of vinylsilanes indicate just the opposite trends (Figures 2 and 3 and Figures S3–S5 in the Supporting Information). The α,β-disubstituted ruthenacyclobutane complexes (pathway a) are always predicted to be more stable than their α,α-disubstituted analogues (pathway b). This might be partially explained by steric interactions between the substituent SiR_3 in an α position and the mesityl group of the NHC ligand (Figure 4). However, if analogous model compounds with the smallest SiH_3 substituent are considered, the calculated Gibbs energy for the α,α-disubstituted metallacycle is also higher, by 23 kJ mol^{-1}, in comparison to the α,β-disubstituted ruthenacyclobutane. This result shows that the unexpected energetic preference predicted for the reaction of vinylsilanes with the second-generation Grubbs catalyst is mainly of electronic nature.

This effect can be explained in terms of the electron-donor ability of the SiR_3 group. The electron-donor ability, estimated on the basis of the calculated NPA charges on the SiR_3 fragments of the vinylsilane molecules, increases in the order $SiCl_3$ < $SiCl_2Me$ < $SiClMe_2$ < $SiMe_3$ < $Si(OEt)_3$. The same order is obtained for the ruthenacyclobutane intermediates localized on pathway **a**. For the ruthenacyclobutanes on pathway **b**, the order is slightly changed (Table S1 in the Supporting Information). The predicted electron donation from the SiR_3 fragment is always stronger for the ruthenacyclobutane complexes on pathway a, in comparison to that of the corresponding intermediates on pathway b. The same tendency is observed for the charges calculated on the CH_2CHSiR_3 fragment (Table 4 and Table S1 in the Supporting Information). A stronger donation from the original vinylsilane moiety to the ruthenium alkylidene species is predicted for the α,β-disubstituted ruthenacyclobutanes (**CBa**, pathway a) than for the corresponding α,α-disubstituted intermediates (**CBb**, pathway b). This is in contrast to the theoretical results reported for the metathesis of common alkenes catalyzed by ruthenium systems[19] but is in agreement with the aforementioned opposite relative stabilities of the α,β- and α,α-disubstituted ruthenacyclobutane intermediates involved in vinylsilane metathesis (Table 4 and Table S1 in the Supporting Information) and metathesis of normal alkenes.[19]

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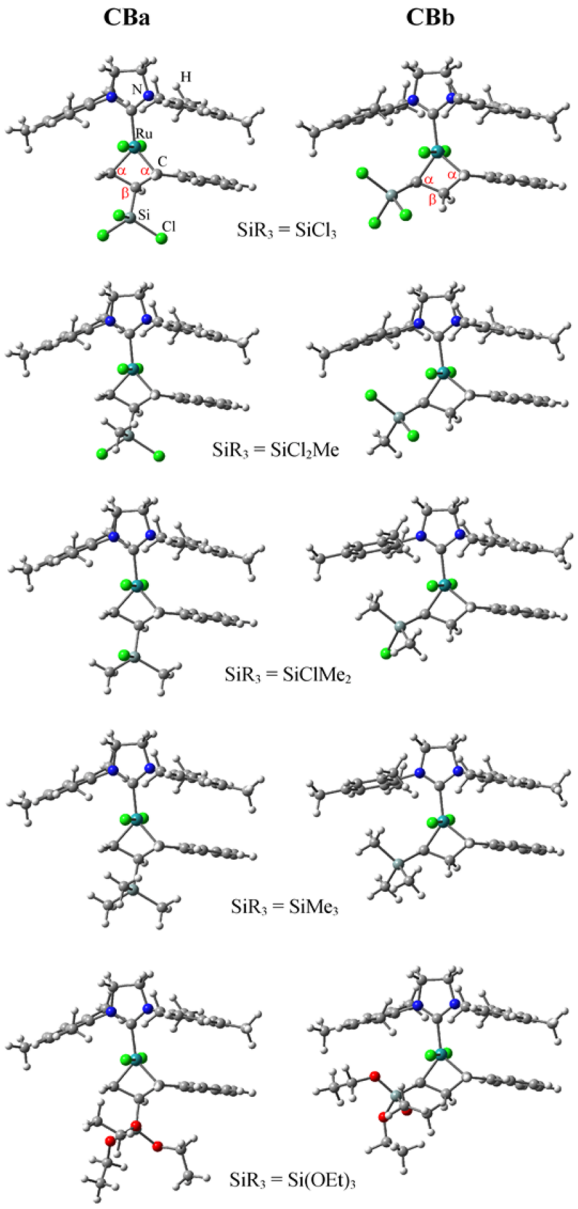

Figure 4. Structures of the ruthenacyclobutane intermediates formed during the reactions of $H_2C{=}CHSiR_3$ with **2**: pathway a (on the left) and pathway b (on the right).

It has been proposed that ruthenacyclobutane complexes are stabilized by four-center–two-electron α,β-(C–C–C) agostic bonding in the ring, resulting in σ donation from the C–C–C fragment to the ruthenium center.[25,26] As a covalent two-center Ru–C_β interaction is shown to be dominant,[27] an electron-donor substituent at C_β (Figure 4) should additionally stabilize the ring. The calculated Ru–C_β distances are indeed a bit shorter in the ruthenacyclobutane intermediates formed along pathway a (2.20–2.21 Å), in comparison to those for the intermediates formed along pathway b (2.22–2.23 Å), suggesting stronger Ru–C_β bonding in the former species. These observations are additionally confirmed by the analysis of the Ru–C_β bond indices. To focus on the electron-donor effect and avoid an overly significant influence of the steric effects, the ruthenacyclobutane with the most bulky SiR_3 group, $Si(OEt)_3$, is omitted in Table 4 (complete results are presented in Table S1 in the Supporting Information). For the remaining α,β-disubstituted ruthenacyclobutane intermediates (**CBa**, pathway a), a correlation between the electron-donor ability of the SiR_3 group and the Ru–C_β bond indices is clearly seen. It is also predicted that the electron donation from the SiR_3 group and the Ru–C_β bond index correlate positively, in general, with the energetic stability of the α,β-disubstituted ruthenacyclobutane complex, although this relationship is not as smooth. In contrast, such correlations between the calculated charges on the SiR_3 fragments and the Ru–C_β bond indices or the relative energies are not observed at all for the α,α-disubstituted ruthenacyclobutanes (**CBb**, pathway b).

To conclude, the regioselectivity of the reactions between trisubstituted vinylsilanes $H_2C{=}CHSiR_3$ and the Grubbs-type ruthenium alkylidene catalyst can be governed by the relative stability of the ruthenacyclobutane intermediates (Figure 4), which is affected by the electronic and steric properties of the SiR_3 moieties. A higher stability of α,β-disubstituted ruthenacyclobutanes (bearing a silyl group at C_β) than α,α-disubstituted ruthenacyclobutanes is always predicted, in contrast to the corresponding metallacycles formed during metathesis of common α-olefins.[19] The stabilizing Ru–C_β interaction is strengthened by the electron-donor SiR_3 substituent at C_β (pathway a), whereas a destabilizing steric interaction takes place between the bulk SiR_3 substituent at C_β and the phenyl substituent at C_α (pathway a) or between the bulk SiR_3 substituent at C_α and the mesityl group of the NHC ligand (pathway b).

Investigation of Equimolar Reactions. In order to verify the results of calculations concerning the kinetic preference for pathways a or b, a series of tests were performed in which catalyst **2** was treated with 3 equiv of vinylsilanes examined ($H_2C{=}CHSiCl_3$, $H_2C{=}CHSiCl_2Me$, $H_2C{=}CHSiClMe_2$, $H_2C{=}CHSiMe_3$, $H_2C{=}CHSi(OEt)_3$). A 3-fold excess of vinylsilane was necessary to speed up the reactions, which hardly proceeded when an equimolar ratio of reagents was applied. The reactions were performed in NMR tubes and monitored by ^1H NMR spectroscopy. In general, the

Table 4. NPA Charges[a] on the SiR_3 Groups in the Ruthenacyclobutane Intermediates (CBa, CBb), NPA Charges[a] on the Vinylsilane Fragments CH_2CHSiR_3 of the Ruthenacyclobutane Intermediates, Wiberg Bond Indices[a] for the Ru–C_β Bonds in the Ruthenacyclobutane Intermediates and the Relative Energies[a,b] (ΔE, kJ mol^{-1}) of the Ruthenacyclobutane Intermediates

	$q(SiR_3)$		$q(CH_2CHSiR_3)$		$P(Ru–C_\beta)$		ΔE	
SiR_3	CBa	CBb	CBa	CBb	CBa	CBb	CBa	CBb
$SiCl_3$	0.526	0.410	0.166	0.097	0.177	0.165	−92	−82
$SiCl_2Me$	0.537	0.450	0.194	0.127	0.186	0.165	−102	−73
$SiClMe_2$	0.569	0.447	0.225	0.160	0.198	0.166	−99	−88
$SiMe_3$	0.573	0.470	0.256	0.191	0.208	0.166	−110	−79

[a]PBE0/def2-SVP calculations. [b]Energies related to $(H_2IMes)(Cl)_2Ru(=CHPh)$ + $H_2C{=}CHSiR_3$.

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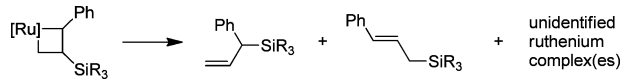
postreaction mixture contains a variety of components that are products of pathways a and b, products of vinylsilane homometathesis (when applied) as well as products of potential β-silylsubstituted ruthenacyclobutane decomposition via β-SiR_3 elimination (Scheme 3).[2,3,28]

Scheme 3. Decomposition of β-Silyl-Substituted Ruthenacyclobutanes via β-SiR_3 Elimination



The composition of the reaction mixture and relative concentrations of individual components depend on the SiR_3 group and the catalyst used. In this study it was assumed that a measure of the kinetic preference for pathway a or b is the concentration ratio of silylstyrene to that of styrene monitored in the first stage of the reactions (Scheme 1). It was confirmed that silylstyrene formed does not undergo any chemical change. Homometathesis of the styrene transformation that could affect its concentration and in consequence distort the observed silylstyrene to styrene ratio proceeds negligibly slowly and can be ignored in the first stage of the reactions. A reaction of styrene with the silylcarbene complex leading to silylstyrene could not be experimentally excluded. However, it was found that most of the silylcarbene complex formed in the systems studied is consumed in the reaction with vinylsilane that leads to the formation of bis(silyl)ethenes and/or 1,1- and 1,3-bis(silyl)propenes-1.[29]

For SiR_3 = $SiMe_3$, β-silyl-substituted ruthenacyclobutane formed in pathway a (Scheme 1) undergoes cycloreversion, leading to silylstyrene, but there is also a tendency for decomposition via β-SiR_3 elimination (Scheme 3).[2,3,28] Being competitive to cycloreversion, β-elimination affects the silylstyrene to styrene ratio. Thisis why for SiR_3 = $SiMe_3$ it was assumed that a measure of the kinetic preference for pathway a or b is the ratio of the sum of concentrations of silylstyrene and (phenyl,silyl)-substituted propenes, formed via β-elimination (Scheme 3), to the concentration of styrene, monitored in the first stage of the reactions. The concentration ratios of silylstyrene to styrene were determined on the basis of ^{1}H NMR spectrum analysis and are presented in Table 5. The observed regioselectivity for the reaction of vinylsilanes with catalyst **2** is in agreement with the DFT calculation results. For H_2C=CHSiCl$_3$, H_2C=CHSiCl$_2$Me, and H_2C=CHSi(OEt)$_3$, the observed kinetic preference for pathway a has always been predicted (Table 3). For H_2C=CHSiMe$_3$ and H_2C=CHSiClMe$_2$, the preferable formation of silylstyrene (via pathway a) is no longer observed, which can be explained by significant stabilization of the ruthenacyclobutane intermediate on pathway a, resulting in a higher activation barrier for the cycloreversion step, in comparison to the overall barrier for pathway b (Figure 3 and Figure S4 in the Supporting Information; Table 3, entries 3 and 4). As the initial form of catalyst **2** and the 16-electron methylidene complex **4** are the most stable compounds in both pathways, the removal of PCy_3 from the reaction environment (via reaction with CuCl), favoring the formation of the 14-electron ruthenium alkylidene species, should also additionally favor pathway b (Table 3, Figures 2 and 3). However, in the presence of CuCl, the reaction was so fast that the initial stage could not be observed. In this case, the data from Table 5 (entry 5) describe the composition of the postreaction mixture.

Table 5. Silylstyrene/Styrene Molar Ratio for Reactions of Catalysts 2 with H_2C=CHSiR$_3$ Measured in a First Stage of the Reaction[a]

entry	H_2C=CHSiR$_3$	time (h)	[silylstyrene]/[styrene]
1	H_2C=CHSiCl$_3$	0.17	5.6/1 (3.2/1)[b]
2	H_2C=CHSiCl$_2$Me	0.17	1.9/1 (2.6/1)[b]
3	H_2C=CHSiClMe$_2$	0.17	0.3/1 (0.17/1)[b]
4	H_2C=CHSiMe$_3$	0.17	0.1/1 (0.4/1)[c]
5	H_2C=CHSiMe$_3$ (+3 equiv CuCl)	0.08	0.01/1[d] (0.9/1)[c,d]
6	H_2C=CHSi(OEt)$_3$	0.17	2.2/1 (2.6/1)[b]

[a]Conditions: [Ru]: [C=C] = 1:3; 303 K, CD_2Cl_2. [b]Measured on the basis of GC (FID) analysis. [c]([silylstyrene] + [(phenyl,silyl)-propenes])/[styrene]. [d]295 K.

The experimental studies confirmed also the stability of complex **4** predicted by the calculations. In the reaction conditions applied, complex **4** did not react with any of vinylsilanes used.

CONCLUSION

On the basis of the results of DFT calculations, cycloreversion is predicted to be the rate-determining step for the reactions between trisubstituted vinylsilanes H_2C=CHSiR$_3$ and the second-generation Grubbs catalyst. The energy of the rate-determining transition state for the pathway leading to the ruthenium methylidene complex and silylstyrene is always lower than that for the alternative pathway giving ruthenium (silyl)methylidene complex and styrene. However, the regioselectivity of the process may be governed by the relative stabilities of the ruthenacyclobutane intermediates on the competitive pathways, which depend on the electron-donor ability and steric properties of the SiR_3 substituent. An opposite trend in the relative stabilities of the silyl-substituted ruthenacyclobutanes, in comparison to the corresponding intermediates involved in the metathesis of common α-olefins,[19] is predicted. This trend is manifested by the higher stability of α,β-disubstituted ruthenacyclobutanes (bearing a silyl group at C_β) than α,α-disubstituted ruthenacyclobutanes and is explained mainly by the electronic effects.

The theoretically predicted possible kinetic preference for the formation of (silyl)methylidene complex in the reactions of second-generation Grubbs catalyst with H_2C=CHSiMe$_3$ or H_2C=CHSiClMe$_2$ has been confirmed experimentally. The selectivity of the reaction toward the formation of styrene and the silylcarbene complex (undetectable by ^{1}H NMR spectroscopy) has been observed. Thus, we have demonstrated the possibility of controlling the regioselectivity of the reaction (so that it would occur via pathway b) by selecting a relatively small and strong electron-donor SiR_3 substituent. This possibility should facilitate the design of effective catalysts of metathetic transformations of vinylsilanes and analogous vinylmetalloids.

EXPERIMENTAL SECTION

General Methods and Chemicals. Unless mentioned otherwise, all operations were performed by using standard Schlenk techniques. Chemicals were obtained from Aldrich. Alkyl-, aryl-, and alkoxy-substituted vinylsilanes were dried in a Schlenk tube over CaH_2 for 24 h, and after that they were distilled under argon. Chloro-substituted vinylsilanes were distilled prior to use under argon. All vinylsilanes were additionally degassed by repeated freeze−pump−thaw cycles. All

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solvents were dried prior to use over CaH_2 and stored under argon over 4 Å molecular sieves. CD_2Cl_2 was additionally passed through a column of alumina. ^1H NMR measurements were performed on Bruker Avance DRX 600 spectrometer, operating at a frequency of 600.13 MHz. All spectra were recorded at 298 K.

Procedure for Equimolar Reactions Study. The equimolar reactions of vinylsilanes with complex **2** were performed under argon in Wilmad LPV NMR tubes and monitored by ^1H NMR spectroscopy. In a typical procedure complex **2** (0.01 g, 1.18×10^{-5} mol) and anthracene (internal standard; 0.002 g) were dissolved in 0.65 mL of CD_2Cl_2. Then the ^1H NMR spectrum of the starting mixture was recorded and 3 equiv of the corresponding vinylsilane was added under argon using a microliter syringe. The reaction mixture was monitored by ^1H NMR spectroscopy at 23 °C and by GC (FID) analysis. The styrene/silylstyrene product ratio was determined on the basis of olefinic proton integration (NMR) or integration of the corresponding peaks (GC).

Computational Details. All structures were fully optimized using the hybrid PBE0 functional[30] and the split-valence def2-SVP basis set.[31] The 28 innermost electrons of Ru were replaced by the Stuttgart effective core potential.[32] This methodology was previously shown to be accurate in predicting the geometry of the Grubbs catalyst on the basis of test calculations using many popular DFT functionals.[11] Harmonic vibrational frequencies were calculated for each structure to confirm the potential energy minimum or the transition state and to obtain Gibbs energy corrections (T = 298.15 K, p = 1 atm). The transition states were additionally verified by IRC calculations.[33,34] Single-point energy calculations were performed for the optimized geometries by applying the hybrid M06 functional[35] combined with the triple-ζ valence def2-TZVPP basis set.[31,32] The M06 method was developed as a general-purpose hybrid meta-GGA functional recommended for main-group-element and transition-metal thermochemistry, kinetics, and studies of noncovalent interactions.[35] A good performance of the M06 method in reproducing energies of metathesis reactions involving ruthenium alkylidene complexes[9,11,18] and the dissociation energy for the second-generation Grubbs catalyst[10,11] was proved. On the other hand, within the methodology applied, the PBE0 functional predicts more accurate bond distances than M06 for the ruthenium alkylidene complex **2**.[11] For this reason, the former has been chosen for the geometry optimization in this work. Performed tests indicate that the formation energies for ruthenacyclobutanes **I_CBa** and **I_CBb** slightly change, by 3 and 13 kJ mol^{-1}, respectively, if M06-optimized geometries are taken for the single-point calculations instead of the PBE0-optimized geometries.

The polarizable continuum model (PCM)[36] was used to estimate solvent effects (dichloromethane). The PBE0/def2-SVP Gibbs energy corrections were added to the PCM single-point energies to obtain a better estimate of Gibbs energies (ΔG_s) of the compounds in the solvent. The reaction pathways in this paper are discussed in terms of Gibbs energies calculated at the M06/def2-TZVPP//PBE0/def2-SVP level for simulated dichloromethane solution.

Electronic properties of the vinylsilanes studied and the ruthenacyclobutane intermediates were analyzed by using the natural population analysis (NPA)[37,38] and Wiberg bond indices[39] at the PBE0/def2-SVP level. All calculations were carried out with the Gaussian 09[40] set of programs. For the graphic presentation of the systems studied, GaussView 5.0 software[41] was used.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00878.

Results of the natural population analysis for the vinylsilanes and ruthenacyclobutane intermediates and the ruthenacyclobutane relative energies, structures, selected atomic distances, and relative energies of conformers for the ruthenium alkylidene products of the metathesis reactions studied, Gibbs energy profiles for the reactions of vinylsilanes ($H_2C{=}CHSiCl_2Me$, $H_2C{=}CHSiClMe_2$, $H_2C{=}CHSi(OEt)_3$) with **2**, chemical shifts of signals used for determination of selectivity and relevant ^1H NMR spectra, and experimental details on the determination of regioselectivity via GC (calibration curves and GC chromatograms) (PDF)

Cartesian coordinates of all computed molecules (XYZ)

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Notes

The authors declare no competing financial interest.

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