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Quantum chemical studies on substitution effects within silyl group in the silylative coupling of olefins

Adam Kubas · Marcin Hoffmann · Bogdan Marciniec

Abstract In this study quantum chemical calculations based on the density functional theory (DFT) have been carried out to examine the effects of methoxy substituent attached to a silicon atom on the reaction of silylative coupling of olefins. It has been shown, that substituted substrate undergoes the reaction according to the recently proposed insertion-rotation-elimination mechanism. During the rotation around C-C single bond additional stabilization by oxygen-ruthenium interaction was observed. Similarly to the (trimethylsilyl)ethene the rate determining step of the reaction is the insertion of the alkene into Ru-Si single bond. The substitution of $SiMe_3$ by $Si(OMe)_3$ decreases the energy span of the reaction by almost 3 kcal mol^{-1} that is from 21 kcal mol^{-1} to 18 kcal mol^{-1}. The decrease of the energy barrier of the reaction seems to be the result of the increase of point charge differences between the Ru and Si atoms which increases electrostatic attraction between these atoms. Moreover, for $Si(OMe)_3$ the rate-determining transition state is closer to the alkene interacting with the Ru centre side of the reaction.

A. Kubas · M. Hoffmann
BioInfoBank Institute,
Limanowskiego 24A,
Poznan, Poland

A. Kubas · M. Hoffmann (✉)
Quantum Chemistry Group, Department of Chemistry,
Adam Mickiewicz University,
Grunwaldzka 6,
60-780 Poznan, Poland
e-mail: hoffmann@man.poznan.pl

B. Marciniec (✉)
Department of Organometallic Chemistry,
Department of Chemistry, Adam Mickiewicz University,
Grunwaldzka 6,
60-780 Poznan, Poland
e-mail: marcinb@amu.edu.pl

Introduction

The silylative coupling of olefins is an effective method for obtaining substituted vinylsilanes which are important substrates in stereocontrolled organic syntheses [1–3]. So far various ruthenium catalysts and substrates have been successfully used in the reaction, yielding 1-silyl-1-alkenes as well as functionalized vinylsilanes [4–6], cyclosiloxanes [7] and 1,2-bis(silyl)ethenes [8] (see Fig. 1).

The mechanism of silylative coupling (see Fig. 2) differs from the cross-metathesis of olefins, even though both these reactions lead to similar products. Contrary to cross-metathesis, there is no carbene intermediate in the silylative coupling. Instead, the migratory insertion of a C=C double bond into the M-Si (or M-H, where M = Ru, Rh, Co) has been proposed based on the results of quantum chemical calculations [14, 15] and mass spectrometric studies of styrene and vinylsilanes [9–11].

The DFT approach has already proven its usefulness in the studies of the mechanism of olefin metathesis [12] or hydrosilylation of alkenes [13]. Recent quantum chemical studies of the mechanism of the silylative coupling of olefins [14, 15] showed that the energy barrier for the catalytic cycle of olefins is about 20 kcal mol^{-1}. Our earlier
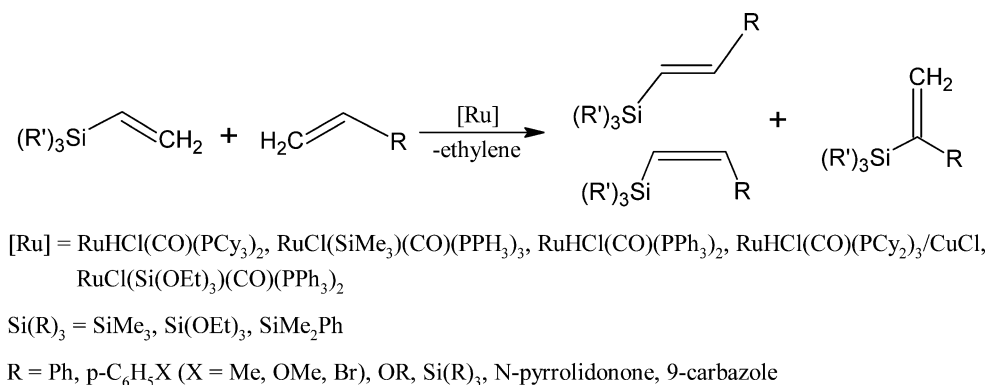
[Ru] = RuHCl(CO)(PCy$_3$)$_2$, RuCl(SiMe$_3$)(CO)(PPH$_3$)$_3$, RuHCl(CO)(PPh$_3$)$_2$, RuHCl(CO)(PCy$_2$)$_3$/CuCl, RuCl(Si(OEt)$_3$)(CO)(PPh$_3$)$_2$

Si(R)$_3$ = SiMe$_3$, Si(OEt)$_3$, SiMe$_2$Ph

R = Ph, p-C$_6$H$_5$X (X = Me, OMe, Br), OR, Si(R)$_3$, N-pyrrolidonone, 9-carbazole

studies [14] of the valence triple ζ basis set indicated that the insertion of alkene into the Ru-Si bond had the greatest activation energy while the studies of Lam et al. [15] performed in a smaller basis set of valence double ζ quality suggested that the activation energies required for alkene insertion into the Ru-Si and Ru-H bonds were of similar value. Moreover, it was suggested that substituents attached to the vinyl moiety or to the silicon atom may modify the ease of alkene insertion into the Ru-H or Ru-Si bonds through electronic and steric effects. This effect for alkoxy substituents attached to the silicon atom was observed experimentally in an increasing of yield of the disproportionation of various substituted alkenes [9] (see Table 1). These findings encouraged us to examine the replacement of all methyl groups attached to Si atom with methoxy groups in the silyl moiety, widely used in siloxane chemistry. We considered the same model system as a catalyst which was used in our earlier study of the reaction with ethylene [14].

Methods

A ruthenium catalyst RuHCl(CO)(PCy$_3$)$_2$ (Cy, cyclohexyl) in which two PCy$_3$ ligands were substituted, as usual, with smaller PH$_3$ groups [14, 15] served as a model catalyst (see Fig. 3). This selection enabled us to make a direct comparison with the previous results of quantum chemical studies of the mechanism of ethylene elimination in catalytic cycle of the silylative coupling of olefins. For all the molecules studied, geometries of potential energy minima and saddle points were optimized with density functional theory (DFT) with B3LYP (hybrid Becke's three parameter functional [16] and Lee-Young-Parr exchange-correlation potential [17]) and SDDAll basis set [18, 19]. Vibrational analyses were performed to confirm that geometry optimization led to a transition state or a minimum for all species considered. Moreover, intrinsic reaction coordinate (IRC) calculations were performed for each transition state to verify which potential energy
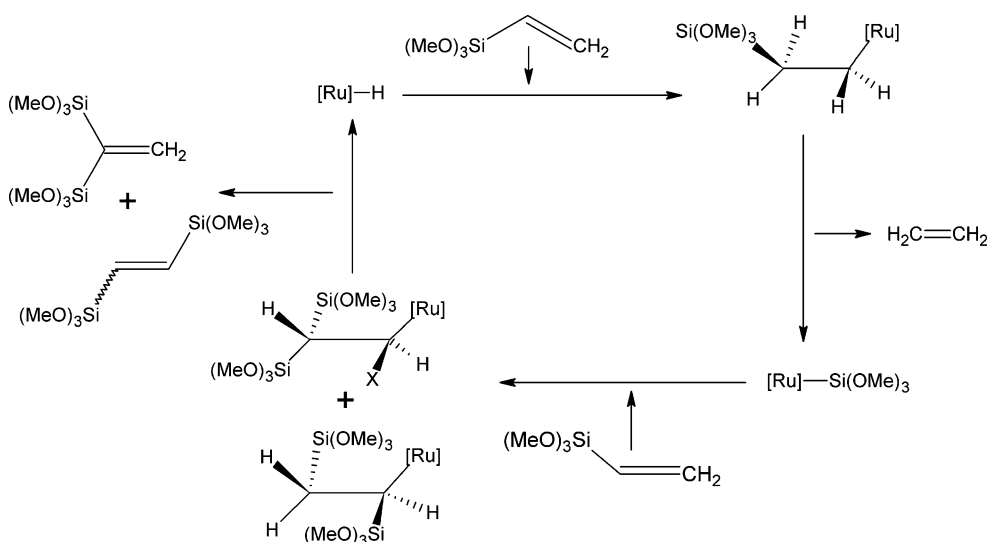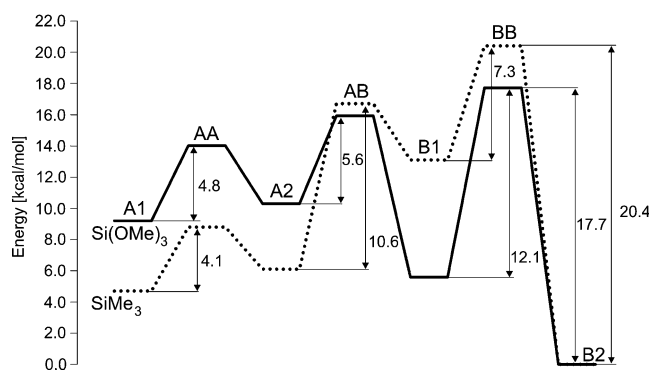

Fig. 2 Catalytic cycle of the silylative coupling of olefins. Half of the catalytic cycle has been chosen as a model. The first step is an insertion of a carbon-carbon double bond into the Ru-H bond; ethene is eliminated in the second step

Table 1 Disproportionation of alkenes catalyzed by RuHCl(CO)(PPh$_3$)$_2$ [9]

CH$_2$=CHSiMe$_2$R R	CH$_2$=CHR' R'	R'CH=CHSiMe$_2$R Yield (%)
Me	Ph	66
Me	CO$_2$Me	59
Me	OBu^n	75
OEt	Ph	72
OEt	CO$_2$Me	70
OEt	OBu^n	84

Fig. 5 Energetic diagram of the silylative coupling of olefins. Black dotted line represent model non-substituted vinylsilane [14]
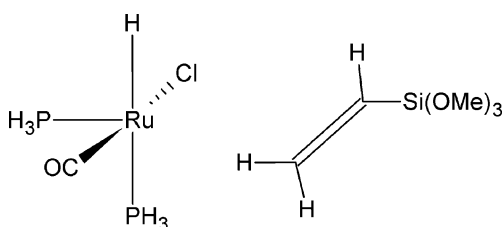
Fig. 3 System studied: ruthenium catalyst [Ru]-H interacting with alkene

Table 2 Relative energies (in kcal mol^{-1}) of the molecules involved in the first reaction step of the catalytic cycle studied. Baseline for methoxy substituent is -2068.7796678 a.u. and for the reference SiMe$_3$ structure –1842.891268 a.u. [14]

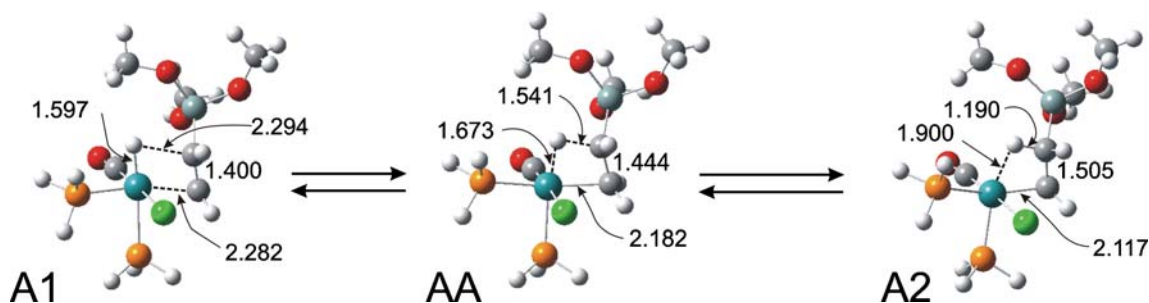|	A1	AA	A2
-SiMe$_3$	4.7	8.8	6.1
-Si(OMe)$_3$	9.2	14.0	10.3

Fig. 4 First step of the silylative coupling of olefins: insertion of alkene into Ru-H bond. All distances are in angstroms

Table 3 Relative energies (in kcal/mol) of the crucial stationary points on the energy hypersurface corresponding to the rotation around C-C single bond

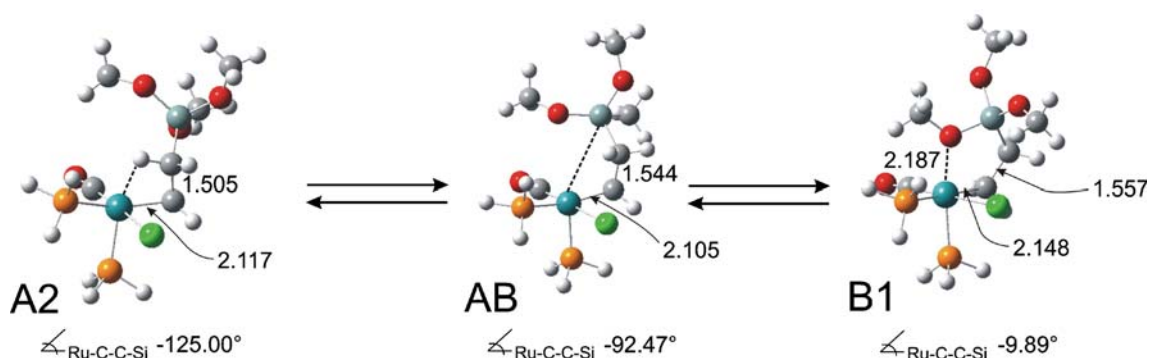|	A2	AB	B1
-SiMe₃	6.1	16.7	13.1
-Si(OMe)₃	10.3	15.9	5.6

Fig. 6 Rotation structures occurring in the reaction path of the silylative coupling of olefins. All distances are in angstroms
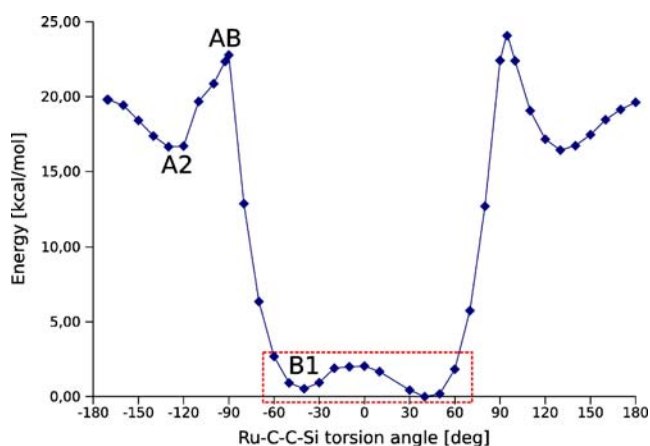

Fig. 7 Rotation profiles around the C-C bond of the molecule studied. Broken line marks stabilization region, due to interactions between ruthenium and methoxy oxygen atom

minima are connected *via* a given transition state. Finally, single point energies were calculated in a larger composite basis set in which the ruthenium centre was treated at the SDD basis set while other atoms at 6-311+G(d,p) basis set [20–26]. Usual counterpoise correction calculations were carried out in this basis set to take into account basis set superposition error. To check the correctness of applied simplifications like replacement of PCy₃ ligands with PH₃ groups, the calculations for real system were carried out. Geometry optimization of all molecules involved in a discussed reaction with methoxy substituent on silicon atom as well as reference methyl group on this atom, was performed using the same hybrid B3LYP functional [16, 17]. For such a large system we used a composite basis set in which 6-31G(d) [20–24, 27–31] basis set was applied to Cl, P and Si atoms, minimal STO-3G [32, 33] basis set was employed to all atoms in Cy₃ groups while other atoms were treated with SDD [18, 19] basis set. All computations were carried out with Gaussian03 [34].
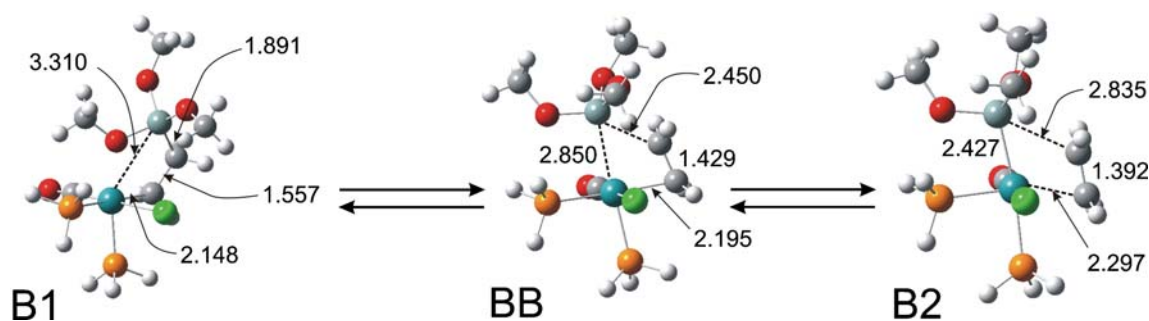

Fig. 8 Structures of molecules involved in the last step of the examined reaction. All distances are in angstroms

Table 4 Relative energies (in kcal/mol) of the key structures occurring in the silyl moiety migration

	B1	BB	B2
-SiMe$_3$	13.1	20.4	0.0
-Si(OMe)$_3$	5.6	17.7	0.0

Results and discussion

Results obtained for real system clearly show, that applied simplifications are suitable for the reaction of the silylative coupling of olefins. It was proved that the insertion of the olefin into Ru-Si bond is a crucial step in the mentioned reaction. Moreover the lowering of the energy barrier for the methoxy substituent towards methyl group approximately 17% is observed for real and model systems almost independently of the basis set in use. Therefore the discussion of substitution effects within silyl group in the silylative coupling of olefins would be limited to the model system. Table 1 in the supplementary material presents the calculated relative energies for real system. For clarity only the lowest energy isomers are presented in this report, as various conformations might obscure presentation of the results.

Olefine insertion

The catalytic cycle of silylative coupling of olefins starts with the insertion of a carbon-carbon double bond into the Ru-H single bond. Figure 4 presents model structures of the examined molecules occurring in the first step of the silylative coupling of olefins as well as crucial interatomic distances. In AA transition state the distances Ru...H and H...C are 1.673 Å and 1.541 Å, respectively. Therefore, during the hydrogen migration from ruthenium centre to the carbon atom bond lengths are nearly the same as for SiMe$_3$ substituent (1.663 Å and 1.584 Å respectively). Contrary to geometric parameters there are energetic differences between SiMe$_3$ and Si(OMe)$_3$ (Fig. 5). Energy barrier of this step of the reaction raises to 4.8 kcal mol^{-1} in the case of Si(OMe)$_3$ from 4.1 kcal mol^{-1} for SiMe$_3$. Moreover, for Si

(OMe)$_3$ substituent the relative energies of the A1, AA and A2 structures are ca. 4 kcal mol^{-1} greater than for SiMe$_3$ (Table 2 and Table 3). This might suggest that either OMe substituent attached to the silicon atom destabilizes the initial reaction complex A1 or it stabilizes the structure B2 (with Ru-Si bond).

Rotation around C-C single bond

After the formation of the substituted β-silylethyl complex with ruthenium catalyst the rotation around the formerly double and currently single C-C bond takes place to orient the silyl group in the vicinity of the ruthenium centre (Fig. 6). We have investigated rotation profiles for the molecule studied and present the results in Fig. 7 depicting relative energy as a function of the Ru-C-C-Si torsion angle. Four energy minima and four transition states have been found as expected based on the results for SiMe$_3$ [14]. Interestly in the range of torsion angle from -60° to 60° all structures with Si(OMe)$_3$ have lower relative energies (broken line in Fig. 7). The inspection of the geometric parameters (Fig. 6) indicates that for the methoxy substituent the structure with the torsional angle gains additional stabilization as the methoxy oxygen atom is close enough to the ruthenium centre to act as a ligand (2.187 Å).

Silyl moiety migration

Migration of the silyl moiety occurs after the rotation around the C-C bond places the Si atom in the vicinity of the Ru atom. Figure 8 present structures involved in this step of the reaction. Relative energies of these species are presented in Fig. 5 and in Table 4. The substitution of Me by OMe in the silyl group decreases the energy barrier of this rate-limiting step of the catalytic cycle, *i.e.* insertion of ethene in the Ru-Si bond. For (trimethylsilyl)ethene the energy difference between BB and B2 states is 20.4 kcal mol^{-1} while for (trimethoxysilyl)ethene it is 17.7 kcal/mol. Thus the energy barrier is lower by 2.7 kcal mol^{-1} for Si(OMe)$_3$ than SiMe$_3$. In the transition state BB the increase of the negative point charge was observed at the Ru atom from -0.215e (SiMe$_3$) to -0.404e

Table 5 Point charges of selected atoms obtained from Mulliken population analyses for the transition state BB. Atom numbers are presented graphically ([Ru] = {RuCl(CO)(PH3)2})

R	Si	C^1	C^2	Ru
-SiMe$_3$	0.815	-0.614	-0.276	-0.215
-Si(OMe)$_3$	1.352	-0.452	-0.281	-0.404

(Si(OMe)$_3$) (Table 5). Moreover, the Mulliken derived point charge at Si atom is 1.352e for Si(OMe)$_3$, which is larger than 0.815e calculated for SiMe$_3$. The larger differences of the point charges at Si and Ru atoms seem to lead to greater electrostatic attraction between Ru and Si which shortens Ru...Si distance in the BB transition state from 3.233Å for SiMe$_3$ to 2.850Å for Si(OMe)$_3$. Therefore, the rate-determining transition state for Si(OMe)$_3$ is closer to the alkene interacting with the Ru centre side of the reaction as also the forming C=C double bond was shorter (*i.e.* 1.429Å) than for SiMe$_3$ (*i.e.* 1.526Å).

Conclusions

The results obtained, further support the finding that the rate-determining step in the catalytic cycle of the silylative coupling of olefins is the insertion of an alkene into the Ru-Si bond coupled with silyl moiety migration from Ru to C atoms (Fig. 5). Moreover, our results show that electron-withdrawing methoxy substituents attached to the Si atom decrease the energy span of the catalytic cycle of the silylative coupling of olefins by 2.7 kcal mol^{-1} from 20.4 kcal mol^{-1} to 17.7 kcal mol^{-1} upon substitution of -SiMe$_3$ by -Si(OMe)$_3$. Thus the substitution of methyl groups by methoxy groups strongly affects the ease of the reaction. Our findings suggest that alkoxy groups attached to silicon atom in vinylsilanes are likely to facilitate silylative coupling of olefins, as compared to alkyl groups.

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