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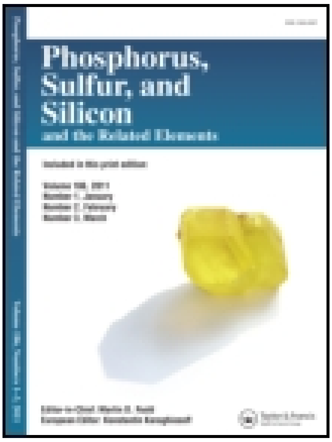

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Carboxylic Acids Promoted Speier'S Catalyst for the Hydrosilylation of Styrene with Triethoxysilane: Activity, Selectivity, and Mechanism

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CARBOXYLIC ACIDS PROMOTED SPEIER'S CATALYST FOR THE HYDROSILYLATION OF STYRENE WITH TRIETHOXYSILANE: ACTIVITY, SELECTIVITY, AND MECHANISM

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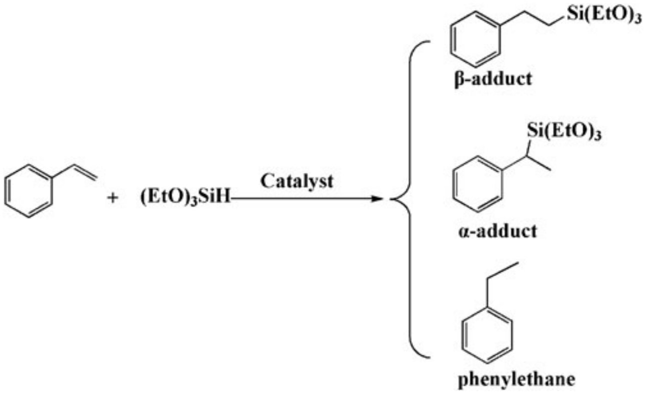
GRAPHICAL ABSTRACT



Abstract *Catalytic performances of Speier's catalyst with carboxylic acids were studied in the hydrosilylation reaction of styrene with triethoxysilane. The effect of carboxylic acids (RCOOH) with different pKa values and size was investigated, and the temperature and n(COOH)/n(Pt) ratios were also studied. The catalytic activity of the hydrosilylation reaction is related to the acid strength of the carboxylic acid, temperature, and n(COOH)/n(Pt) ratio, while the selectivity for the β-adduct is related to the size of carboxylic acid and the n(COOH)/n(Pt) ratio. Moreover, the influence of carboxylic acid on the hydrosilylation reaction was explained with the help of density functional theory calculations, and a reasonable mechanism was proposed.*

Keywords Hydrosilylation; carboxylic acids; DFT calculations

INTRODUCTION

Hydrosilylation, a reaction for Si–C bond formation, is very important for the synthesis of organofunctional silanes which have found many commercial applications, among

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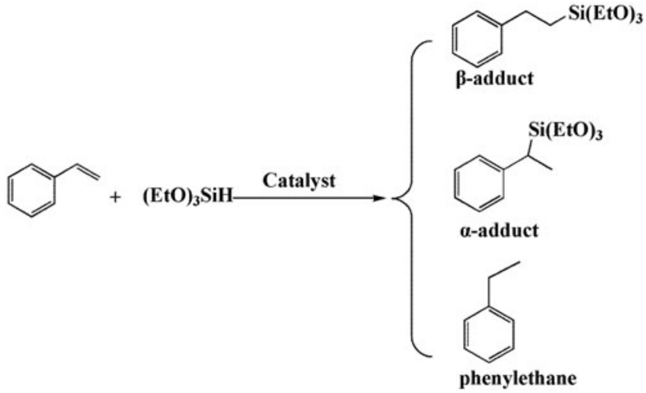


Scheme 1

others as adhesion promoters for inorganic-material–polymer systems and modifiers of mineral surfaces.[1,2] Generally, Group VIII metals and their complexes are known to be good catalysts for the title reaction, in particular the Pt-based catalysts.[3] As a Pt-based catalyst, Speier's catalyst[4] is efficient and commonly employed in industrial production. Nevertheless, it is still confronted with two main problems that are the relatively long induction time and low selectivity. Recently, a number of studies have revealed that the introduction of activators such as alkadienes, norbornenes, and cycloolefins into the Pt catalyst systems can improve the catalytic activity and selectivity for hydrosilylation of alkenes.[5–10] More recently, Lai, et al. demonstrated that carboxylic acids could significantly improve the catalytic activity and selectivity of Speier's catalyst for the hydrosilylation of alkenes.[11] However, the reason for the influence of carboxylic acid on the catalytic performance of Speier's catalyst is still not clear.

In this work, we endeavored to provide insight into the role of carboxylic acids in the Speier's catalyst catalyzed hydrosilylation of alkenes. The model reaction, hydrosilylation of styrene with triethoxysilane, was selected to check the catalytic performance (Scheme 1). The *pKa* values and size of carboxylic acids (RCOOH), temperature, and *n*(COOH)/n(Pt) ratio were all investigated to reveal the influence on the hydrosilylation reaction. The effect of carboxylic acids was further studied with the help of theoretical calculations performed with the density functional theory (DFT) approach. Furthermore, a reasonable mechanism for the reaction was proposed.

RESULTS AND DISCUSSION

Effect of *n*(COOH)/*n*(Pt) on the Hydrosilylation Reaction

Speier's catalyst solutions with differing acid contents were applied to the hydrosilylation reaction at 60°C, and the results are listed in Table 1 (using CH_3COOH as an example). Speier's catalyst without the addition of acid shows a 100% styrene conversion and 65% β-adduct selectivity after 360 min. When introducing the carboxylic acids to Speier's catalyst, the catalytic activity and selectivity of the β-adduct produced are obviously improved, which is consistent with previous reports.[11–13] Table 1 also reveals that the catalytic activity and selectivity of the β-adduct increase with the acid content. This is probably attributed to the increase of Pt–carboxylic acid species, which might be

Table 1 Effect of n(COOH)/n(Pt) ratios on the hydrosilylation reaction (using CH_3COOH as an example)

Entry	n(COOH)/n(Pt)	t_{100}^{a} (min)	β-adduct selectivity (%)	α-adduct selectivity (%)	Phenylethane selectivity (%)	$n(\beta)/n(\alpha)$
1	0	360	65.4	32.0	2.6	2.04
2	100: 10	20	72.4	24.7	2.9	2.93
3	100: 8	7	73.9	23.0	3.1	3.21
4	100: 6	5	75.6	20.9	3.5	3.62
5	100: 4	4.5	76.4	20.1	3.5	3.80
6	100: 2	4	80.8	15.6	3.6	5.18
7	100: 1	2	92.7	4.0	3.3	23.17
8	150: 1	2	92.3	4.4	3.6	19.60

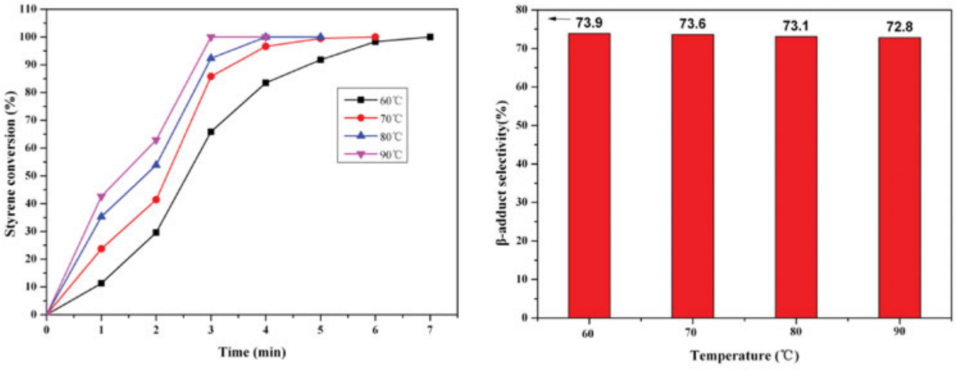
Reaction conditions: $n(\text{Pt})/n(\text{styrene}) = 1{:}4000$, $n((\text{EtO})_3\text{SiH})/n(\text{styrene}) = 1.1{:}1$, 60°C.

[a]The time needed for 100% styrene conversion.

more active than the Pt species in Speier's catalyst (see the theoretical calculation and proposed mechanism section). It is noteworthy that the hydrosilylation reaction rate and selectivity of β-adduct remain at steady levels when n(COOH)/n(Pt) is above 100:1, indicating that the Pt–carboxylic acid species is saturated at $n(\text{COOH})/n(\text{Pt}) = 100{:}1$. In addition, to better examine the influence of other factors on the catalytic activity and selectivity, the n(COOH)/n(Pt) ratio of 100: 8 was selected, due to its moderate reaction rate (Table 1).

Effect of Temperature on the Hydrosilylation Reaction

The effect of temperature on catalytic activity and selectivity of the hydrosilylation reaction is shown in Figure 1 (using Speier's catalyst with acetic acid as an example). With the increase of temperature, the time needed for 100% styrene conversion (t_{100}) is shortened, while the selectivity for the β-adduct is kept at around 73%. This indicates that the temperature promotes the catalytic activity but has only a slight influence on the β-adduct selectivity (Figure 1(b)).



(a) (b)

Figure 1 Effect of temperature on the hydrosilylation reaction: (a) catalytic activity and (b) selectivity to β-adduct.

Table 2 Effect of *pKa* values and size of carboxylic acids on the hydrosilylation reaction

Entry	Carboxylic acid	*pKa*	Size(Å^2)	t_{100} [a] (min)	β-adduct selectivity (%)	α-adduct selectivity (%)	Phenylethane selectivity (%)	$n(\beta)/n(\alpha)$
1	HCOOH	3.77	3.085 × 2.011	4	69.1	28.0	2.9	2.47
2	Benzoic acid	4.19	7.094 × 4.933	5	82.3	14.2	3.5	5.80
3	CH_3COOH	4.76	4.143 × 2.455	7	73.9	23.0	3.1	3.21
4	$CH_3(CH_2)_3COOH$	4.81	7.821 × 2.453	8	77.5	19.2	3.3	4.04
5	$CH_3(CH_2)_4COOH$	4.84	8.705 × 2.459	8	79.4	17.0	3.6	4.67
6	$CH_3(CH_2)_5COOH$	4.89	9.748 × 2.452	8	81.7	15.0	3.3	5.47
7				360	65.4	32.0	2.6	2.04
8	CH_3COONa			360	75.2	22.4	2.4	3.35

Reaction conditions: $n(\mathrm{Pt})/n(\mathrm{styrene}) = 1:4000$, $n((\mathrm{EtO})_3\mathrm{SiH})/n(\mathrm{styrene}) = 1.1:1$, 60°C, $n(\mathrm{COOH})/n(\mathrm{Pt}) = 100:8$.

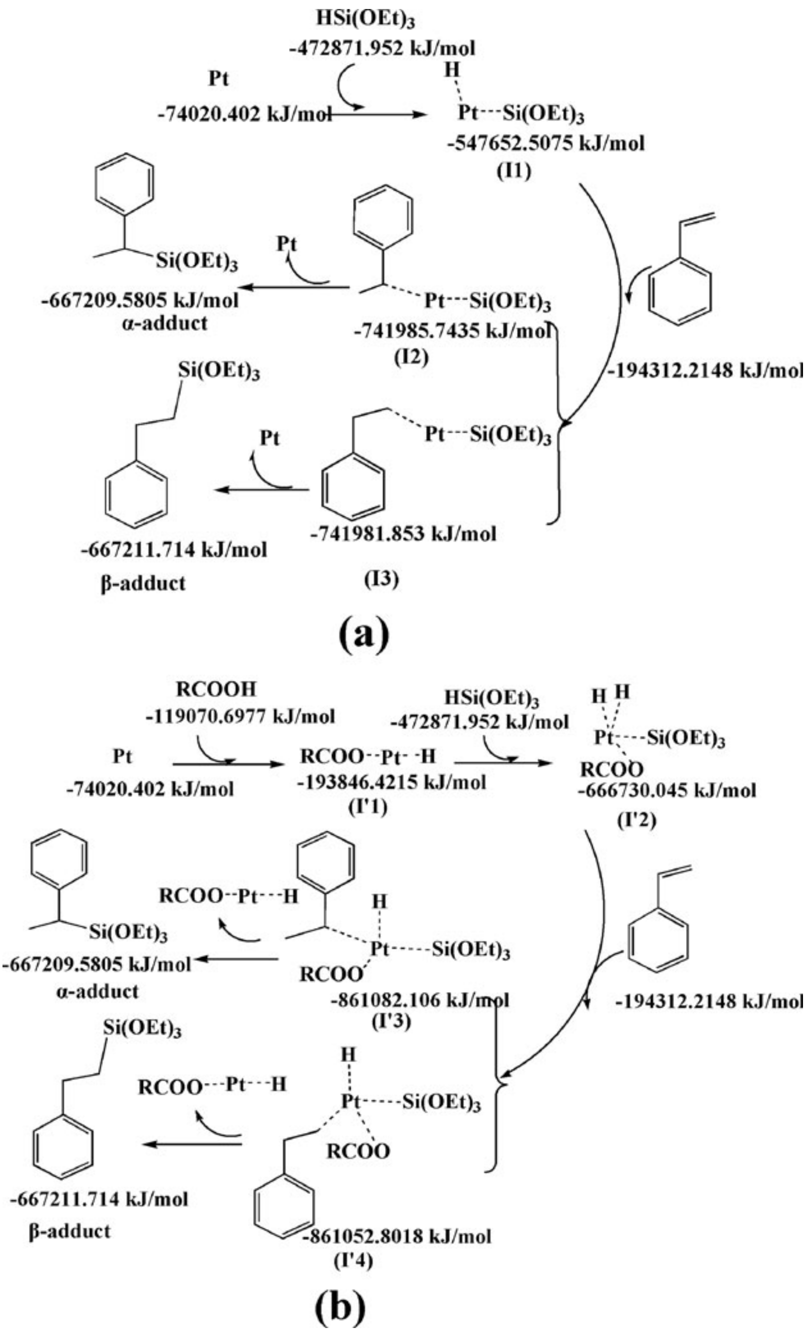
[a] The time needed for 100% styrene conversion.

Effect of *pKa* values and Size of Carboxylic Acids on the Hydrosilylation Reaction

Table 2 summarizes the catalytic results of Speier's catalyst with carboxylic acids with different *pKa* values and size. It can be seen that t_{100} decreases from 8.0 to 4.0 min when the *pKa* ranged from 4.89 to 3.77, indicating that increasing the acid strength of the carboxylic acids can improve the catalytic activity of the hydrosilylation reaction. From Table 2, we can also find that the high selectivity for the β-adduct is obtained. The large-sized carboxylic acid indicates that the size of carboxylic acid has a significant influence on the selectivity to β-adduct. It should be pointed out that the different size acids $CH_3(CH_2)_3COOH$, $CH_3(CH_2)_4COOH$, and $CH_3(CH_2)_5COOH$ that possess similar *pKa* values show the same t_{100} (8.0 min) but display different selectivities for the β-adduct (77.5%, 79.4%, 81.7%). This suggests that the acid strength of the carboxylic acid has a negligible influence on the selectivity for the β-adduct, and the size of carboxylic acid has a slight influence on the catalytic activity. Consequently, it can be concluded that the improvement of the catalytic activity and selectivity are attributed to the acid strength and size of carboxylic acids, respectively. This result might be helpful in the design of an efficient promoter for the Speier's catalyst. Noticeably, upon the addition of CH_3COONa to Speier's catalyst, the catalytic activity is not promoted (Table 2). The above result reveals that the activated hydrogen of the promoter is important for hydrosilylation activity. To obtain further insight into the influence of carboxylic acid, theoretical calculations were performed.

Theoretical Calculation and Proposed Mechanism

The Chalk–Harrod mechanism is commonly proposed to explain the Pt-catalyzed hydrosilylation of alkenes,[14–16] which involves elementary steps such as oxidative addition of Si–H to the metal center, insertion of the alkene into the M–H bond and reductive elimination of the Si–C product. Based on this mechanism, we investigated the role of carboxylic acid (HCOOH was taken as an example) by a theoretical calculation method.



Scheme 2 Proposed mechanism for hydrosilylation of styrene with triethoxysilane catalyzed by (a) Speier's catalyst and (b) Speier's catalyst with carboxylic acid.

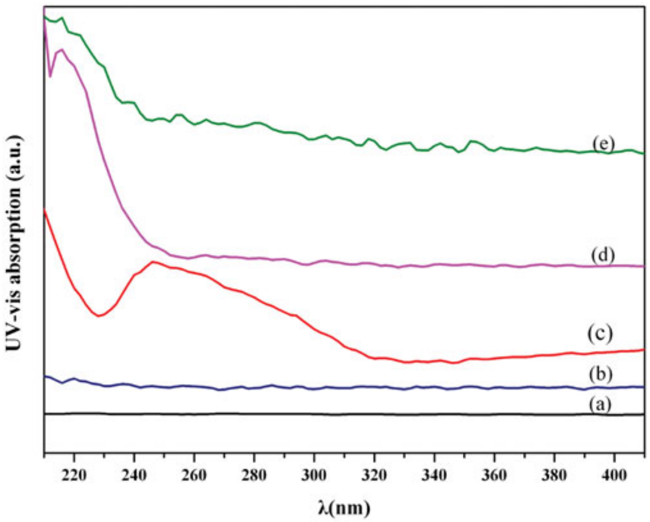


Figure 2 UV–VIS absorption of samples: (a) $^{i}PrOH$, (b) HCOOH, (c) Speier's catalyst, (d) Speier's catalyst with HCOOH, and (e) addition of $HSi(OEt)_3$ in the Speier's catalyst with HCOOH.

In this calculation, the Pt(0)[17–18] was adopted as the model catalysts since the low-valence Pt species are generally considered as the active sites of Speier's catalyst.[15,19–21] According to the theoretical calculations, a reasonable mechanism is proposed and shown in Scheme 2. Scheme 2 depicts four elementary steps: (a) the Pt interacted with carboxylic acid to form the Pt–carboxylic acid intermediated **I'1** with the reaction energy $\delta G = -755.3218$ kJ/mol, which was supported by the shift of UV–VIS absorption (Figure 2) of the Pt species (from 245 to 215 nm);[17,18,22] (b) the addition of triethoxysilane to the Pt center of **I'1** (**I'2**) with $\delta G = -11.6715$ kJ/mol, which is consistent with the slight shift of UV–VIS absorption as compared with **I'1**; (c) insertion of the styrene into the Pt–H bond of **I'2** produces **I'3** and **I'4** with $\delta G = -39.8462$ J, -10.5420 kJ/mol, respectively; (d) reductive elimination of α- and β-adducts. In step (d), the Pt species may eliminate in the forms of Pt(0) or **I'1**. As revealed by the theoretical calculation results, the elimination of Pt(0) exhibits a higher reaction energy than the elimination of **I'1** (Scheme 2). This suggests that the Pt species in step (d) is probably eliminated in the **I'1** form. Moreover, the Si–C reductive elimination of Scheme 2b displays a lower reaction energy than that of Scheme 2a, where carboxylic acids are not introduced. It may explain why the carboxylic acids can significantly improve the catalytic activity of Speier's catalyst. To get the relationship between the size of carboxylic acid and the selectivity of β-adduct, step (c) was examined. The steric hindrance of **I'2** increases with the size of carboxylic acid, which facilitates the formation of **I'4** when inserting styrene. This explains why using the larger sized carboxylic acid can result in higher selectivity β-adduct.

CONCLUSION

In this work, the effect of carboxylic acids with different *pKa* values and size on the Speier's catalyst-catalyzed hydrosilylation of alkenes was carried out on the hydrosilylation of styrene with triethoxysilane at different temperatures and *n*(COOH)/*n*(Pt) ratios. The results show that the acid strength of the carboxylic acid is related to the catalytic activity of the hydrosilylation reaction, the size of carboxylic acid has a significant influence on the selectivity for the β-adduct, n(COOH)/n(Pt) affects both of the catalytic activity and selectivity, and the temperature promotes the catalytic activity but has only a slight impact on selectivity to β-adduct. Additionally, DFT calculations were performed to better understand the influence of carboxylic acid on the hydrosilylation reaction, and a reasonable mechanism was proposed. As revealed by the proposed mechanism, step (d) displays a lower reaction energy than the Si–C reductive elimination step of Speier's catalyst without carboxylic acids. It may be the reason that the carboxylic acids can significantly improve the catalytic activity. In step (c), the large size of carboxylic acid facilitates the formation of **I'4**. This explains why using the larger sized carboxylic acid can result in higher β-adduct selectivity. These results might be helpful in the design of novel Pt catalysts with high catalytic activity and selectivity for the hydrosilylation of alkenes.

EXPERIMENTAL

Materials

All reactants were obtained commercially and used without further purification. Styrene (AR), $H_2PtCl_6 \cdot 6H_2O$ (AR), and phenylethane (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. $HSi(OEt)_3$ (99%) was purchased from Qufu Chenguang Chemical Co., Ltd. All carboxylic acids (AR) were purchased from Aladdin Reagent Co., Ltd. Speier's catalyst was prepared by dissolving chloroplatinic acid (1 g) in isopropanol (50 mL) at room temperature for 7 days.

Catalyst Characterization

Absorption spectra were recorded on UV–VIS spectrophotometer ("Hitachi" U4100, Japan) using a 1.0 cm quartz cell in the range of 500–200 nm (n-hexane as solvent and reference).

Products Characterization

GC–MS confirmation was carried out using an Agilent Technologies 7890A network GC system equipped with a mass-selective detector (MSD) model 5975C network, and a 30 m × 0.25 mm HP-5 MS fused-silica capillary column (0.25 μm film thickness). The test conditions: split, 50: 1; flow, 1 mL min^{-1}; injector temperature, 260°C; column temperature program: 50°C, held for 1 min; increased at a rate of 15°C min^{-1} up to 260°C, held for 10 min.

^{1}H-NMR spectra were recorded on a Bruker AV400 MHz spectrometer using TMS as an internal standard in $CDCl_3$:[23,24]

β-adduct, ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.01 (t, $J = 9.0$ Hz, 2H, Si-CH_2), 1.25 (t, $J = 7.0$ Hz, 9H, CH_3), 2.75 (t, $J = 8.6$ Hz, 2H, Ph-CH_2); 3.86 (q, $J = 7.0$ Hz, 6H, O-CH_2), 7.18–7.29 (m, 5H, Ph).

α-adduct, ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.18 (t, $J = 7.0$ Hz, 9H, CH_3), 1.42 (d, $J = 8.0$ Hz, 3H, CH_3) 2.34 (q, $J = 8.0$ Hz, 1H, Ph-CH); 3.73 (q, $J = 7.0$ Hz, 6H, O-CH_2), 7.12–7.19 (m, 5H, Ph).

Phenylethane, ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.16 (t, $J = 8.0$ Hz, 3H, CH_3), 2.66 (q, $J = 8.0$ Hz, 2H, Ph-CH_2), 7.13–7.27(m, 5H, Ph).

Catalytic Test

Typical hydrosilylation reaction procedures were as follows: styrene (20 mmol) and Pt-catalysts (0.005 mmol; Speier's catalyst with or without carboxylic acids) were combined and stirred at reaction temperature for 10 min in a 20-mL round flask equipped with a mechanical stirrer. Then, triethoxysilane (22 mmol) was added to the reaction mixture. The products were detected by a GC with FID detector.

Conversion of styrene and selectivity of all products were calculated with the following equations:

$$\text{Styrene conversion}(\%) = \left(\frac{\text{moles of styrene consumed}}{\text{moles of styrene initial}}\right) \times 100;$$

$$\text{Phenylethane selectivity}(\%) = \left(\frac{\text{moles of phenylethane produced}}{\text{moles of styrene consumed}}\right) \times 100;$$

$$\begin{aligned}\text{ß} - \text{adduct selectivity}(\%) &= \left(\frac{\text{moles of}\,\beta - \text{adduct produced}}{\text{moles of styrene consumed}}\right) \times 100 \\ &= [100 - Phenylethane\,selectivity(\%)] \times ; \left(\frac{\mathrm{A}_\beta}{\mathrm{A}_\alpha + \mathrm{A}_\beta}\right);\end{aligned}$$

$$\alpha\text{−adduct selectivity}(\%) = 100 - \text{Phenylethane selectivity}(\%)\text{ß} - \text{adduct selectivity}(\%).$$

A_α: the GC area of α-adduct, A_β: the GC area of β-adduct, the response factors of the two isomers (α- and β-adduct) were the same in the GC, which was verified by proton NMR integration. The styrene and phenylethane have their own standard curves by the standard samples.

All results were reproducible within experimental error.

Theoretical Calculation

Geometries of reactants, transition states, and products were optimized *via* DFT calculations using the Becke3LYP (B3LYP) functional within the Gaussian 09 suite of ab initio programs.[25–28] For Pt atom, the effective core potential basis set Lanl2dz (Los Alamos ECP plus double-ζ) was used.[29–31] For Si, O, C, and H atoms atoms, the all-electron split valence basis set 6-31G (d, p) was used. Frequency calculations at the same level of theory have also been performed to identify all of the stationary points as minima. The energy difference between products and reactants (δG) is calculated with the following equation: δG = energy of product – energy of reactants.

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