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# Hydrosilylation of Aromatic Aldehydes and Ketones Catalyzed by Mono- and Tri-nuclear Platinum(0) Complexes

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#### Abstract

Hydrosilylation of aromatic aldehydes and acetophenone with H2SiPh2 were studied by using Pt complexes as the catalyst. Reaction of aromatic aldehydes, such as PhCHO, 4-FC6H4CHO, 4-MeC6H4CHO and 4-CF3C6H4CHO with H<sub>2</sub>SiPh<sub>2</sub> in the presence of [Pt(PPh<sub>3</sub>)<sub>3</sub>] catalyst proceeds smoothly at room temperature with similar reaction rates. The hydrosilvlation of PhCHO with H2Si(C6H4-4-Me)2 proceeds faster than that with H<sub>2</sub>SiPh<sub>2</sub>. Comparison of the reactions of PhCHO with H<sub>2</sub>SiPh<sub>2</sub> and with D<sub>2</sub>SiPh<sub>2</sub> demonstrated a large kinetic isotope effect (3.1). The hydrosilylation of the aldehydes catalyzed by [Pt(PMe3)(µ-SiPh2)]3, reported in our previous paper, shows large dependence of the reaction rate on the aryl group of the substrate, in the order, 4-MeC<sub>6</sub>H<sub>4</sub>CHO >> PhCHO = 4-FC<sub>6</sub>H<sub>4</sub>CHO > 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHO. Hydrosilylation of (3-vinyl)benzaldehyde and 10-undecenal in the presence of [Pt(PPh<sub>3</sub>)<sub>3</sub>] catalyst occurs at the carbonyl group selectively to form the corresponding alkoxysilanes. The hydrosilylation of acetophenone with H<sub>2</sub>SiPh<sub>2</sub> catalyzed by [Pt(PPh<sub>3</sub>)<sub>3</sub>] forms 1-phenylethyl(diphenylsilyl)ether, while the reaction using the Pt<sub>3</sub> catalyst is accompanied by dehydrosilylation to yield a mixture of the saturated and unsaturated silyl ethers.

# 1. Introduction

Hydrosilylation of carbonyl compounds such as aldehydes and ketones provide silyl ethers, which are regarded as synthetic equivalents of alcohols. Complexes of various late transition metals such as Rh,<sup>1)</sup> Cu,<sup>2)</sup> Fe,<sup>3)</sup> and Ni,<sup>4)</sup> catalyze the reaction. There have been only a limited number of reports on the hydrosilylation of carbonyl compounds using Pt catalyst, although molecular Pt complexes and Pt salts are known as the efficient catalyst for hydrosilylation of olefins.<sup>5)</sup> Pt complex catalyzes hydrosilylation of  $\alpha$ , $\beta$ -unsaturated aldehydes and ketones, and accompanying isomerization to produce the silyl enol ether.<sup>6)</sup> The hydrosilylation of aryl or aliphatic ketons catalyzed by Pt complexes were reported by Kumada,<sup>7a),7b)</sup> Trotter,<sup>7c)</sup> Vekki,<sup>7d)</sup> and Ruhland.<sup>7e)</sup>

Recently, we reported a triplatinum complex having bridging diarylsilylene ligands, form  $[Pt_3(PMe_3)_3(\mu-SiPh_2)_2(\mu-SiHPh_2)_2]$  reversibly. The equilibrated mixture catalyzes hydrosilylation of PhCHO with H<sub>2</sub>SiPh<sub>2</sub> to yield the corresponding benzyl silyl ether.<sup>8)</sup> The hydrosilylation of carbonyl compounds catalyzed by the platinum complexes is still rare, which prompted us to investigate the hydrosilylation of aldehydes catalyzed by common mononuclear Pt complexes. This paper presents the hydrosilylation of aromatic aldehydes catalyzed by [Pt(PPh<sub>3</sub>)<sub>3</sub>] complexes and comparison of the results with those using the Pt<sub>3</sub> complex as the catalyst.

2. Results and Discussion

Hydrosilylation of PhCHO with  $H_2SiPh_2$  was conducted in the presence of a catalytic amount of  $[Pt(PPh_3)_3]$  ([PhCHO] :  $[H_2SiPh_2]$  : [Pt] = 1.0 : 3.0 : 0.15) at 25 °C (Eq. 1).



Figure 1. Reaction profile of (a) hydrosilylation of 4-XC<sub>6</sub>H<sub>4</sub>CHO  $(X = -H, -CH_3, -F, -CF_3)$  with  $H_2SiPh_2$  catalyzed by  $[Pt(PPh_3)_3]$ (Inset, Arrhenius plot, X = H). Conditions: arylaldehyde (0.15 mmol), H2SiPh2 (0.44 mmol), [Pt(PPh3)3] (0.022 mmol), C6D6, 25 hydrosilylation of PhCHO °C: (b) with H<sub>2</sub>SiPh<sub>2</sub>.  $H_2Si(C_6H_4-4-Me)_2$ , and  $D_2SiPh_2$  catalyzed by  $[Pt(PPh_3)_3]$ . Conditions: PhCHO (0.050 mmol), diarylsilane (0.25 mmol), [Pt(PPh<sub>3</sub>)<sub>3</sub>] (0.0075 mmol), C<sub>6</sub>D<sub>6</sub>, 45 °C. The yields were obtained by <sup>1</sup>H NMR signal intensity using dibenzyl as an internal standard. The observed rate constants were described in experimental section.

The <sup>1</sup>H NMR spectra of the reaction mixture showed decrease in the signals of SiH hydrogen of H<sub>2</sub>SiPh<sub>2</sub> and aldehyde (5.08 and 9.65 ppm) and growth of new signals at 5.71 and 4.73 ppm, which are assigned to PhCH<sub>2</sub>OSiHPh<sub>2</sub> *via* hydrosilylation of the aldehyde group. The reaction is almost completed within 46 h, and forms the product quantitatively. Arylaldehydes with para-substituents (X = -Me, -F, -CF<sub>3</sub>) also undergo the hydrosilylation with H<sub>2</sub>SiPh<sub>2</sub>.

Figure 1a shows profiles of the reaction using the four arylaldehydes as well as the curves obtained by assuming the first-order reaction rates. The kinetic parameters of the reaction of PhCHO were calculated from temperature dependence of the rate constants, to be  $E_a = 24.0 \text{ kcal mol}^{-1}$ ,  $\Delta H^{\ddagger} = 23.6 \text{ kcal mol}^{-1}$ ,  $\Delta S^{\ddagger} = -1.2 \text{ cal K}^{-1} \text{ mol}^{-1}$ , and  $\Delta G^{\ddagger} = 23.9 \text{ kcal mol}^{-1}$ , respectively, at 25 °C. These kinetic parameters suggest that the catalysis involves an intramolecular reaction, such as migratory insertion of the coordinated carbonyl compound into the M-H or M-Si bond, as the rate-determining step. The reaction rates of the arylaldehydes decrease in the order of the substituents, -H  $\ge$  -Me  $\ge$  -CF<sub>3</sub>  $\ge$  -F, although their difference is small.

The hydrosilylation of PhCHO with H<sub>2</sub>Si(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub> is faster than that with H<sub>2</sub>SiPh<sub>2</sub> in the presence of [Pt(PPh<sub>3</sub>)<sub>3</sub>] catalyst. It suggests that aryl groups on the Si atom affected the reaction rate of the hydrosilylation (Figure 1b). The reaction of PhCHO with D<sub>2</sub>SiPh<sub>2</sub> occurs more slowly ( $k_D = 0.58 \times 10^{-4} \text{ s}^{-1}$ ) than that with H<sub>2</sub>SiPh<sub>2</sub> ( $k_H = 1.79 \times 10^{-4} \text{ s}^{-1}$ ). The large kinetic isotope effect (KIE = 3.1) is in the range of primary isotope effect. It implies that the cleavage of Si-H/D bond is included in the rate-determining step of this catalytic reaction.

In contrast, the hydrosilylation catalyzed by the trinuclear complex,  $[Pt(PMe_3)(\mu-SiPh_2)]_3$ , differs in the reaction rate, depending on the substituents in the order of 4-MeC<sub>6</sub>H<sub>4</sub>CHO >> PhCHO = 4-FC<sub>6</sub>H<sub>4</sub>CHO > 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHO (Figure 2). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction of 4-MeC<sub>6</sub>H<sub>4</sub>CHO with H<sub>2</sub>SiPh<sub>2</sub> using the [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub> as the catalyst contains only the signals of [Pt<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>( $\mu$ -SiPh<sub>2</sub>)<sub>2</sub>( $\mu$ -SiHPh<sub>2</sub>)<sub>2</sub>] (-20.0 and -22.3 ppm) after 15 min. After completion of the





reaction (24 h), the signals of  $[Pt(PMe_3)(\mu-SiPh_2)]_3$  (-26.6 ppm) and minor uncharacterized complex (-18.4 and -68.4 ppm) were observed. Thus, the reaction was catalyzed by the trinuclear Pt complex rather than by its decomposition product.

The reaction rate clearly depends on the Pt complexes. [Pt{O(SiMe<sub>2</sub>CH=CH<sub>2</sub>)}<sub>2</sub>] (Karstedt's catalyst) completes the hydrosilylation of PhCHO with H<sub>2</sub>SiPh<sub>2</sub> within 15 min at 25 °C. The reaction catalyzed by [Pt(PPh<sub>3</sub>)<sub>3</sub>] and [Pt(PMe<sub>3</sub>)<sub>4</sub>] requires ca. 24 h for completion, and that catalyzed by [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub> is completed after 72 h.

(3-Vinyl)benzaldehyde and 10-undecenal contain both vinyl and formyl groups and reacts with  $H_2SiPh_2$  in the presence of [Pt(PPh\_3)\_3] catalyst to yield  $H_2C=CHC_6H_4CH_2OSiHPh_2$  and  $H_2C=CH(CH_2)_9OSiHPh_2$ , respectively, as the hydrosilylation products in a NMR scale (Eq. 3, 4). The reaction mixture does not contain a product *via* hydrosilylation of the vinyl group nor the double hydrosilylation product. The former silyl ether was treated





**Figure 2.** Reaction profile of hydrosilylation of 4-XC<sub>6</sub>H<sub>4</sub>CHO (X = -H, -CH<sub>3</sub>, -F, -CF<sub>3</sub>) with H<sub>2</sub>SiPh<sub>2</sub> catalyzed by Pt<sub>3</sub> complex. Conditions: arylaldehyde (0.13 mmol), H<sub>2</sub>SiPh<sub>2</sub> (0.18 mmol), [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub> (0.0074 mmol), C<sub>6</sub>D<sub>6</sub>, 25 °C. The yields were obtained by <sup>1</sup>H NMR signal intensity using dibenzyl as an internal standard.

**Figure 3.** <sup>1</sup>H NMR spectra (400 MHz,  $C_6D_6$ , 298 K) of the reaction mixture of the hydrosilylation of PhCOCH<sub>3</sub> (0.25 mmol for Pt<sub>1</sub>, 0.16 mmol for Pt<sub>3</sub>) with H<sub>2</sub>SiPh<sub>2</sub> (0.25 mmol for Pt<sub>1</sub>, 0.17 mmol for Pt<sub>3</sub>) in catalyzed by (a) [Pt(PPh<sub>3</sub>)<sub>3</sub>] (0.022 mmol) at 60 °C for 24 h and (b) [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub> (0.0074 mmol) at 60 °C for 54 h. The yields were obtained by <sup>1</sup>H NMR signal intensity using dibenzyl as an internal standard.

with NBu<sub>4</sub>F to afford H<sub>2</sub>C=CHC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH. The isolated yield of the alcohol based on (3-vinyl)benzaldehyde) was 70%. Isolation of the product of hydrosilylation of 10-undecenal as well as its corresponding alcohol was not feasible. The reactions of (3-vinyl)benzaldehyde with H<sub>2</sub>SiPh<sub>2</sub> catalyzed by [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub> and by Karstedt's catalyst also caused selective hydrosilylation of the carbonyl group.<sup>9</sup> The hydrosilylation of styrene with H<sub>2</sub>SiPh<sub>2</sub> was catalyzed by Karstedt's catalyst, while [Pt(PPh<sub>3</sub>)<sub>3</sub>] and [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub> do not catalyze the reaction.

The reaction of PhCOCH3 with H2SiPh2 in the presence of [Pt(PPh<sub>3</sub>)<sub>3</sub>] and [Pt(PMe<sub>3</sub>)(µ-SiPh<sub>2</sub>)]<sub>3</sub> catalysts gave three products, Ph(CH3)CHOSiHPh2 (A) via hydrosilylation, Ph(CH<sub>2</sub>=)COSiHPh<sub>2</sub> (**B**) *via* dehydrosilylation, and Ph(CH<sub>3</sub>)CHOSiPh<sub>2</sub>CH<sub>2</sub>CH(Ph)OSiHPh<sub>2</sub> (C) via formal dimerization of the above products, as shown in Eq. 5. Relative yields of the products, determined by <sup>1</sup>H NMR spectra of the reaction mixture, differ largely depending on the catalysts (Figure 3). The catalytic reaction by [Pt(PPh<sub>3</sub>)<sub>3</sub>] formed compound A (4.95 and 5.67 ppm) as the major product (85%) and small amounts of compound **B** (4.65, 4.89, 5.89 ppm) (2%)and C (5.89 ppm) (7%). It is in contrast to the reaction catalyzed by [Pt(PMe<sub>3</sub>)(µ-SiPh<sub>2</sub>)]<sub>3</sub>, which produces **B** as the major product (45%).

Two major mechanisms were proposed for hydrosilylation of olefins catalyzed by Pt complexes. The hydride(silyl)platinum(II) complex, formed by oxidative addition of silanes to a Pt(0) precursor, undergoes insertion of olefin into the Pt-H bond (Chalk-Harrod mechanism).<sup>10</sup>) Ensuing coupling of the silyl and alkyl ligands forms the alkylsilane products. In the modified-Chalk-Harrod mechanism, insertion of olefin occurs into the Pt-Si bond preferentially, and induces reductive elimination of the product *via* coupling of the 2-silylethyl and hydride ligands.

More numbers of mechanisms were proposed for hydrosilylation of carbonyl compounds catalyzed by late transition metal complexes. Ojima et al achieved asymmetric hydrosilylation of unsymmetrical ketones with secondary silanes using Rh complex having bidentate chiral phosphines as the catalyst. They compared the mechanism caused by insertion of carbonyl group into the Rh-H bond (Chalk-Harrod-type) and that involving insertion of C=O bond into the Rh-Si bond (modified-Chalk-Harrod-type, Scheme 1), and chose the latter because of better consistency with the results of asymmetric induction.<sup>11</sup> Prock and Giering also proposed the modified-Chalk-Harrod-type mechanism and intermediacy of the complex having a 1-phenyl(1-siloxy)ethyl ligand.<sup>11</sup>

Chalk-Harrod-type mechanism that should involve



B<sub>o</sub>SiH<sub>c</sub>

**Scheme 1.** Modified-Chalk-Harrod-type mechanism of hydrosilylation of ketone. <sup>11)</sup>



Scheme 2. Mechanism involving insertion of C=O group into M-H bond.  $^{\rm (12)\,(3)}$ 

formation of the hydride(silyl)metal intermediate and subsequent insertion of carbonyl group into the M-H bond, is less common in the hydrosilylation of carbonyl compounds.<sup>13, 14)</sup> Co(I) complex with a Cp\* ligand undergoes oxidative addition of diorgano(vinyl)silane to form Co(III) intermediate, having hydride and silyl ligands and  $\pi$ -coordinated ketone molecule. Insertion of C=O bond into the Co-H bond, forms the intermediate having the silyl and alkoxide ligands, and causes coupling of these ligands. The reaction is accompanied by intramolecular hydrogen transfer of the product.

Mechanism that involves insertion of the C=O bond into the metal hydride ligand was proposed for the hydrosilylation of carbonyl compounds catalyzed by Cu(I)-H complexes as well as Ni(II) and Fe(II) complexes having pincer-type ligands. The catalyst precursor contains a hydride ligand and no Si-ligands, and undergoes insertion of the carbonyl group into the M-H bond to generate the intermediate having an alkoxo ligand bonded to the metal. Further addition of organosilane results in formation of the alkoxysilane product and regenerates the hydride complex, as shown in Scheme 2.<sup>14</sup>)

Zheng and Chan reported hydrosilyl5tion reactions of enones using [RhH(PPh<sub>3</sub>)<sub>4</sub>] catalyst, and proposed a new kind of mechanism that involves coordination of carbonyl oxygen to Si atom of the hydride(silyl)rhodium intermediate, forming an intermediate having hypervalent Si center.<sup>16)</sup> (Scheme 3a) Tridentate and tetradentate ligands occupy multiple coordination sites, and the catalysis using the complexes of late transition metal often prefers the intermediate, formed via the reaction of uncoordinated carbonyl compounds with the Si-ligand.

Cationic Ir(III) complex with a pincer-type P-C-P ligand





(catalyst,  $[Rh(nbd){(tBuC_3H_3NO)(C_6H_2Me_3)(C_3H_2N)}])$ .<sup>18)</sup>

catalyzes the hydrosilylation of ketones and esters.<sup>17)</sup> It involves a reaction of uncoordinated carbonyl compounds with a  $\eta^1$ -silane ligand bonded to Ir as the Si-O bond-forming step. The resulted cationic silylated ketone (or ester) abstracts hydride from the complex to generate the silyl ether. The bond forming reactions in the catalysis resemble to the hydrosilylation of carbonyl compounds catalyzed by Lewis acids such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (Scheme 3b).

The hydrosilylation catalyzed by Rh complex having a chelating NHC ligand was proposed to involve the intermediate having a silylene ligand bonded to the metal center. The silyl-metal intermediate undergoes  $\alpha$ -hydrogen abstraction of the silyl ligand, generating a silylene ligand, which reacts with ketone to form a O-Si=M bond. A DFT study of the reaction pathway indicated two intermediates, the complex with  $\eta^2$ -silyl ligand bonded via a Si-H bond (**A**) and the complex having alkoxy-stabilized silylene ligand rather than those having a bare silylene ligand (**B**) (Scheme 4).<sup>18)</sup> The reaction mechanism based on the silylene intermediates was discussed in the catalysis using Rh complex with a bis-NHC ligand.<sup>19, 20)</sup>

Rh complexes with a N,Si,N-tridentated ligand, forming a facial structure, also catalyzes hydrosilylation of carbonyl compounds. It involves initial formation of hydrido(silyl)rhodium intermediate, and further reaction of the carbonyl group of free ketone with the hydride ligand, to form a mixture of the vinyl silyl ether and alkyl silyl ether.<sup>21)</sup>

The hydrosilylation reactions of aldehydes and ketone catalyzed by  $[Pt(PPh_3)_3]$  in this study, and by  $[Pt(PMe_3)(\mu-SiPh_2)]_3$  also proceed smoothly. The Pt<sub>3</sub> complex reacts with H<sub>2</sub>SiPh<sub>2</sub> to produce the Pt<sub>3</sub>Si<sub>4</sub> complex having two

 $\mu$ - $\eta^2$ -SiHPh<sub>2</sub> ligands, which is probably the active species of the catalysis. The complex contains two Si ligands that bridges two Pt centers via silylene coordination mode with a terminal hydride or  $\mu$ - $\eta^2$ -SiHPh<sub>2</sub> fashion. A possible pathway is shown in Scheme 5a, in which the carbonyl oxygen is associated with the Si atom and then undergoes Si-O bond formation. Coupling of a hydride ligand and the siloxymethyl ligand releases the product. The Pt centers are sterically congested, and external attack of the carbonyl group to the silylene (or  $\eta^2$ -silyl) ligand is favored to form the new Si-O bond. In the reaction of acetophenone,  $\beta$ -hydrogen abstraction yields the alkenyl silyl ether. The reaction rate is influenced largely by substituents of the aromatic aldehyde, and the rate-determining step of the catalysis exists in the latter part of the catalytic cycle, C-H bond formation.

For the reaction catalyzed by  $[Pt(PPh_3)_3]$ , it is not easy to assign the mechanism, unambiguously. A large KIE for the reactions using H<sub>2</sub>SiPh<sub>2</sub> and D<sub>2</sub>SiPh<sub>2</sub>, suggests that the rete-determining step of the reaction resides in oxidative addition of H<sub>2</sub>SiPh<sub>2</sub> (or D<sub>2</sub>SiPh<sub>2</sub>) to Pt(0) complex, giving the Pt(II) intermediate with hydride and silyl ligands or in insertion of C=O group into the Pt-H bond in Chalk-Harrod-type mechanism in Scheme 5b. Small influence of the aromatic group of the aldehyde to the rate constants may be consistent with the former.

## 3. Conclusion

Both [Pt(PPh3)3] and [Pt(PMe3)(µ-SiPh2)]3 catalyze hydrosilylation of aromatic aldehydes with H<sub>2</sub>SiPh<sub>2</sub>, although there have been only a few number of the reaction catalyzed by a Pt complex. Detailed studies of the reaction catalyzed by the Pt1 and Pt3 complexes revealed quite different reaction results depending on the catalysts. The rate of the reaction using the former catalyst is influenced by the aromatic group of the aldehyde less significantly than the latter. Hydrosilylation of acetophenone with H2SiPh2 provided different products depending on the catalysts; the reaction catalyzed by [Pt(PMe<sub>3</sub>)(µ-SiPh<sub>2</sub>)]<sub>3</sub> is accompanied by dehydrosilylation of the substrate. A number of reaction mechanisms were proposed for the hydrosilylation of carbonyl compounds catalyzed by transition metal complexes. [Pt(PMe<sub>3</sub>)(µ-SiPh<sub>2</sub>)]<sub>3</sub> catalysis probably involves O-Si bond formation at the initial stage of the reaction, followed by C-H bond formation, and the [Pt(PPh<sub>3</sub>)<sub>3</sub>] catalysis is considered to proceed via insertion of C=O bond into the Pt-H bond. Recently, Wei and Zhu found Suzuki-Miyaura reaction catalyzed by triangular Pd<sub>3</sub> complex, and revealed a new reaction mechanism based on the experimental and theoretical studies.<sup>22)</sup> The catalysis using



 $\label{eq:scheme 5. Proposed mechanisms of hydrosilylation catalyzed by (a) [Pt(PMe_3)(\mu-SiPh_2)]_3 \ and \ (b) [Pt(PPh_3)_3].$ 

multinuclear transition metal complexes will attract more attention than before because of their unique pathways and performance.

# 4. Experimental

All manipulations were carried out in a nitrogen-filled glovebox (Miwa MFG). The <sup>1</sup>H and <sup>31</sup>P $\{^{1}H\}$  NMR spectra were recorded on Bruker Biospin Avance III 400 MHz and Avance III H'D 500 MHz NMR spectrometers. The chemical shifts in <sup>1</sup>H NMR spectra were referenced to the residual peaks of the solvent used. The peak positions of the  $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$  NMR spectra were referenced to external 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta$  0) in deuterated solvents. Benzaldehyde was purchased from TCI and used after distillation. Karstedt's catalyst (Aldrich), H2SiPh2 (Aldrich), D2SiPh2 (Aldrich), (4-methyl)benzaldehyde (TCI), 10-undecenal (TCI), and methyl(phenyl)ketone (TCI) were purchased and used without further purification. [Pt(PMe<sub>3</sub>)(µ-SiPh<sub>2</sub>)]<sub>3</sub><sup>8b)</sup> and (3-vinyl)benzaldehyde <sup>23)</sup> were prepared according to the literature. [Pt(PPh<sub>3</sub>)<sub>3</sub>] was obtained from the reaction of K<sub>2</sub>PtCl<sub>4</sub> with PPh<sub>3</sub> in the presence of KOH. H<sub>2</sub>Si(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub> was obtained via LiAlH<sub>4</sub> reduction of Cl<sub>2</sub>Si(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub>.

Hydrosilylation of 4-XC<sub>6</sub>H<sub>4</sub>CHO (H, -Me, -F, -CF<sub>3</sub>) with H2SiPh2 catalyzed by [Pt(PPh3)3] and [Pt(PMe3)(µ-SiPh2)]3. (a) Catalyst =  $[Pt(PPh_3)_3]$ : To a C<sub>6</sub>D<sub>6</sub> solution (0.6 mL) of 4-XC<sub>6</sub>H<sub>4</sub>CHO (0.15 mmol) in a J. Young NMR tube were added H2SiPh2 (82 mg, 0.44 mmol), [Pt(PPh3)3] (22 mg, 22 µmol), and dibenzyl (7 mg, 38 mmol). (b) Catalyst = [Pt(PMe<sub>3</sub>)(µ-SiPh<sub>2</sub>)]<sub>3</sub>: In a NMR tube with a septum cap to a  $C_6D_6$  solution (0.6 mL) of [Pt(PMe\_3)(\mu-SiPh\_2)]\_3 (10 mg, 7.1) µmol) were added H2SiPh2 (36 mg, 0.16 mmol) and 4-XC<sub>6</sub>H<sub>4</sub>CHO (0.13 mmol). These reactions were performed at 25 °C for 46 h, which was monitored by <sup>1</sup>H NMR, to afford  $(4-X-C_6H_4)CH_2OSiHPh_2$  as the product. X = -H: 100% (k =  $3.70 \times 10^{-5} \text{ s}^{-1}$ ) for [Pt(PPh\_3)\_3], 93% for [Pt(PMe\_3)(\mu-SiPh\_2)]\_3, by NMR. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.67-7.65 (d, 4H, C<sub>6</sub>H<sub>5</sub>, J = 7.6 Hz), 7.26 (d, 2H, C<sub>6</sub>H<sub>5</sub>, J = 7.4 Hz), 7.17-7.13 (m, 7H, C<sub>6</sub>H<sub>5</sub>), 6.98 (d, 2H, C<sub>6</sub>H<sub>5</sub>, J = 7.4 Hz), 5.71 (s, 1H, SiH), 4.73 (s, 2H, CH<sub>2</sub>). **X** = -**F**: 93% ( $k = 1.72 \times 10^{-5} \text{ s}^{-1}$ ) for  $[Pt(PPh_3)_3]$ , 89% for  $[Pt(PMe_3)(\mu-SiPh_2)]_3$ , by NMR. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.63-7.61 (d, 4H, C<sub>6</sub>H<sub>5</sub>), 7.20-7.12 (m, 8H, C<sub>6</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>4</sub>), 6.75 (t, 2H, C<sub>6</sub>H<sub>4</sub>, J = 8.7 Hz), 5.65 (s, 1H, SiH), 4.57 (s, 2H, CH<sub>2</sub>). **X** = -CH<sub>3</sub>: 100% ( $k = 3.75 \times 10^{-5}$  $s^{-1}$ ) for [Pt(PPh\_3)\_3], 100% for [Pt(PMe\_3)(\mu-SiPh\_2)]\_3, by NMR. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.67 (d, 4H, C<sub>6</sub>H<sub>5</sub>, J = 7.6 Hz), 7.21 (d, 2H, C<sub>6</sub>H<sub>4</sub>, J = 7.6 Hz), 7.15-7.06 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 6.98 (d, 2H,  $C_6H_4$ , J = 7.6 Hz), 5.71 (s, 1H, SiH), 4.75 (s, 2H, CH<sub>2</sub>), 2.08 (s, 3H, CH<sub>3</sub>). **X** = -CF<sub>3</sub>: 98% ( $k = 2.38 \times 10^{-5} \text{ s}^{-1}$ ) for [Pt(PPh<sub>3</sub>)<sub>3</sub>], 43% for [Pt(PMe<sub>3</sub>)(µ-SiPh<sub>2</sub>)]<sub>3</sub>, by NMR. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.60 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.29 (d, 2H, C<sub>6</sub>H<sub>4</sub>, J = 8.0 Hz), 7.2-6.9 (m, 8H, C<sub>6</sub>H<sub>4</sub>), 5.64 (s, 1H, SiH), 4.55 (s, 2H, CH<sub>2</sub>).

Variable-temperature hydrosilylation of PhCHO with H<sub>2</sub>SiPh<sub>2</sub> catalyzed by [Pt(PPh<sub>3</sub>)<sub>3</sub>]. To a C<sub>6</sub>D<sub>6</sub> solution (0.5 mL) of PhCHO (5.3 mg, 0.050 mmol) in a J. Young NMR tube were added H<sub>2</sub>SiPh<sub>2</sub> (46 mg, 0.25 mmol), [Pt(PPh<sub>3</sub>)<sub>3</sub>] (7.4 mg, 7.5 µmol), and dibenzyl (2.3 mg, 0.13 mmol). The reaction was performed at 30 °C, 35 °C, 40 °C, and 45 °C, which were monitored by <sup>1</sup>H NMR. The rate constant (*k*) was determined by pseudo-first-order plot based on NMR yield. 30 °C:  $k = 2.51 \times 10^{-4} \text{ s}^{-1}$ , 35 °C:  $k = 4.20 \times 10^{-4} \text{ s}^{-1}$ , 40 °C:  $k = 1.22 \times 10^{-3} \text{ s}^{-1}$ , 45 °C:  $k = 1.49 \times 10^{-3} \text{ s}^{-1}$ . The kinetic parameters were calculated from these rate constant;  $E_a = 24.0 \text{ kcal mol}^{-1}$  by the Arrhenius plot,  $\Delta H^{\ddagger} = 23.6 \text{ kcal mol}^{-1}, \Delta S^{\ddagger} = -1.2 \text{ cal K}^{-1} \text{ mol}^{-1}$ ,  $\Delta G^{\ddagger} = 23.9 \text{ kcal mol}^{-1}$ , by the Eyring.

Hydrosilylation of PhCHO with H2SiPh2,

H<sub>2</sub>Si(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub>, and D<sub>2</sub>SiPh<sub>2</sub> catalyzed by [Pt(PPh<sub>3</sub>)<sub>3</sub>]. To a C<sub>6</sub>D<sub>6</sub> solution (0.5 mL) of PhCHO (0.05 mmol) in a J. Young NMR tube were added diarylsilane (0.25 mmol), [Pt(PPh<sub>3</sub>)<sub>3</sub>] (7.4 mg, 7.5 µmol), and dibenzyl (2.3 mg, 0.013 mmol). The reaction was performed at 45 °C, which monitored by <sup>1</sup>H NMR, hydrosilylated product, PhCH<sub>2</sub>OSiHPh<sub>2</sub>, to afford PhCH<sub>2</sub>OSiH(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub>, PhCHDOSiDPh<sub>2</sub>, respectively. **H<sub>2</sub>SiPh<sub>2</sub>:** 90% NMR yield ( $k = 1.79 \times 10^{-4} \text{ s}^{-1}$ ), H<sub>2</sub>Si(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub>: 99% NMR yield ( $k = 5.15 \times 10^{-4} \text{ s}^{-1}$ ). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.67 (d, 4H, C<sub>6</sub>H<sub>4</sub>, J = 7.6 Hz), 7.32 (d, 2H, C<sub>6</sub>H<sub>5</sub>, J = 7.3 Hz), 7.07-6.89 (m, 7H, C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>, signals are overlapped with unreacted silane and catalyst), 5.79 (s, 1H, SiH), 4.81 (s, 2H, CH<sub>2</sub>), 2.19 (s, 3H, CH<sub>3</sub>). **D<sub>2</sub>SiPh<sub>2</sub>:** 49% NMR yield ( $k = 0.58 \times 10^{-4} \text{ s}^{-1}$ ). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.68-7.67 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.28 (d, 2H, C<sub>6</sub>H<sub>5</sub>, J = 7.4 Hz), 7.21-7.15 (m, 7H, C<sub>6</sub>H<sub>5</sub>), 7.08 (d, 2H,  $C_{6}H_{4}$ , J = 7.5 Hz), 4.73 (s, 1H, CH).

Hydrosilylation of (3-vinyl)benzaldehyde with H<sub>2</sub>SiPh<sub>2</sub> catalyzed by [Pt(PPh<sub>3</sub>)<sub>3</sub>], [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub>, and Karstedt's catalyst. To a C<sub>6</sub>D<sub>6</sub> solution (0.5 mL) of (3-vinyl)benzaldehyde (33 mg, 0.25 mmol) in a J. Young NMR tube were added H<sub>2</sub>SiPh<sub>2</sub> (46 mg, 0.025 mmol), Pt catalyst (39 µmol for [Pt(PPh<sub>3</sub>)<sub>3</sub>] and Karstedt's catalyst, 13 µmol for [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub>). The reaction was performed at 25 °C for 18 h to afford H<sub>2</sub>C=CHC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OSiHPh<sub>2</sub> in all catalysts. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, r.t.):  $\delta$  7.67-7.66 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.33 (s, 1H, C<sub>6</sub>H<sub>4</sub>), 7.20-7.14 (m, 8H, C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>), 7.10 (q, 1H, C<sub>6</sub>H<sub>4</sub>, *J* = 7.6, 15.1 Hz), 6.57 (q, 1H, C<sub>2</sub>H<sub>3</sub>, *J* = 10.9, 17.6 Hz), 5.72 (s, 1H, SiH), 5.60 (d, 1H, C<sub>2</sub>H<sub>3</sub>, *J* = 17.6 Hz), 5.69 (q, 1H, C<sub>2</sub>H<sub>3</sub>, *J* = 10.9 Hz), 4.73 (s, 2H, CH<sub>2</sub>).

Synthesis of (3-vinyl)benzyl alcohol via hydrosilylation of (3-vinyl)benzaldehyde with H<sub>2</sub>SiPh<sub>2</sub> catalyzed by [Pt(PPh<sub>3</sub>)<sub>3</sub>]. To a toluene solution (5 mL) of (3-vinyl)benzaldehyde (26 mg, 0.20 mmol) were added H<sub>2</sub>SiPh<sub>2</sub> (37 mg, 0.20 mmol) and [Pt(PPh<sub>3</sub>)<sub>3</sub>] (30 mg, 30 µmol). The reaction mixture was stirred at 25 °C for 24 h. Tetra-n-butylammonium fluoride (1.0 M THF solution, 0.4 mL, 0.4 mmol) was added to the mixture and stirred additional 1 h at 25 °C. The solvent was removed under vacuum and the crude product was purified by silica gel column chromatography (Hexane/AcOEt = 7:3) to afford (3-vinyl)benzyl alcohol (19) mg, 0.14 mmol, 70%) as a pale yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, r.t.):  $\delta$  7.35-7.32 (m, 4H, C<sub>6</sub>H<sub>3</sub>), 6.73 (q, 1H, C<sub>2</sub>H<sub>3</sub>, J = 10.9, 17.6 Hz), 5.77 (d, 1H, C<sub>2</sub>H<sub>3</sub>, J = 17.6 Hz), 5.27 (d, 1H, C<sub>2</sub>H<sub>3</sub>, *J* = 10.9 Hz), 4.70 (d, 1H, CH<sub>2</sub>, *J* = 4.6 Hz), 1.63 (t, 1H, OH, J = 5.2 Hz). <sup>1</sup>H NMR data was matched with the reported literature.24)

Hydrosilylation of 10-undecenal with H<sub>2</sub>SiPh<sub>2</sub> catalyzed by [Pt(PPh<sub>3</sub>)<sub>3</sub>]. To a C<sub>6</sub>D<sub>6</sub> solution (0.5 mL) of 10-undecenal (16 mg, 0.15 mmol) in a J. Young NMR tube were added H<sub>2</sub>SiPh<sub>2</sub> (82 mg, 0.44 mmol), [Pt(PPh<sub>3</sub>)<sub>3</sub>] (4.8 mg, 13 µmol). The reaction was performed at 25 °C for 24 h to afford H<sub>2</sub>C=CH(CH<sub>2</sub>)<sub>9</sub>OSiHPh<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, r.t.): δ 5.86-5.76 (m, 1H, C<sub>2</sub>H<sub>3</sub>), 5.73 (s, 1H, SiH), 5.04-4.99 (m, 2H, C<sub>2</sub>H<sub>3</sub>), 3.77 (t, 2H, CH<sub>2</sub>, J = 8.1 Hz), 2.03-1.98 (m, 2H, CH<sub>2</sub>), 1.63-1.56 (m, 2H, CH<sub>2</sub>), 1.38-1.15 (br, 12H, CH<sub>2</sub>).

Hydrosilylation of PhCOCH<sub>3</sub> with H<sub>2</sub>SiPh<sub>2</sub> catalyzed by [Pt(PPh<sub>3</sub>)<sub>3</sub>] and [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub>. (a) Catalyst = [Pt(PPh<sub>3</sub>)<sub>3</sub>]: To a C<sub>6</sub>D<sub>6</sub> solution (0.5 mL) of [Pt(PPh<sub>3</sub>)<sub>3</sub>] (37 mg, 37 µmol) in a J. Young NMR tube were added H<sub>2</sub>SiPh<sub>2</sub> (46 mg, 0.25 mmol), PhCOCH<sub>3</sub> (30 mg, 0.25 mmol) and dibenzyl (2.3 mg, 13 mmol). The reaction was performed at 60 °C for 30 h. (b) Catalyst = [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub>: In a NMR tube with a septum cap to a C<sub>6</sub>D<sub>6</sub> solution (0.6 mL) of [Pt(PMe<sub>3</sub>)( $\mu$ -SiPh<sub>2</sub>)]<sub>3</sub> (10 mg, 7.4 µmol) were added H<sub>2</sub>SiPh<sub>2</sub> (31 mg, 0.17 mmol), PhCOCH<sub>3</sub> (19 mg, 0.16 mmol) and dibenzyl (7 mg, 38 mmol). The reaction was performed at 60 °C for 54 h. These reaction mixtures contained hydrosilylated product **A**, dehydrosilylated product **B**, and dimer **C**. The NMR yields of these products were summarized in Eq. 4. <sup>1</sup>H NMR for **A** (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  5.67 (s, 1H, SiH), 4.95 (q, 1H, CH, *J* = 6.4 Hz), 1.42 (d, 3H, CH<sub>3</sub>, *J* = 6.4 Hz). <sup>1</sup>H NMR for **B** (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  5.89 (s, 1H, SiH), 4.89 (d, 1H, = CH<sub>2</sub>, *J* = 2.4 Hz), 4.65 (d, 1H, = CH<sub>2</sub>, *J* = 2.4 Hz). <sup>1</sup>H NMR for **C** (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  5.89 (s, 1H, SiH). These data were consistent with the literature.

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(9) The hydrosilylation products in this study tend to decompose slowly under air and moisture, which rendered their isolation difficult. We treated the hydrosilylation product with NBu4F, and isolated the resulting (3-vinyl)benzyl alcohol after purification by silica gel chromatography (Hexane/AcOEt = 7:3) in 70%. The hydrosilylation of 10-undecenal with H<sub>2</sub>SiPh<sub>2</sub> in an NMR-scale formed H<sub>2</sub>C=CH(CH<sub>2</sub>)<sub>9</sub>OSiHPh<sub>2</sub> with high selectivity, but isolation of the product nor its desilylated alcohol was not feasible.

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