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Selective Dehydrogenative Silylation–Hydrogenation Reaction of Divinyldisiloxane with Hydrosilane Catalyzed by an Iron Complex

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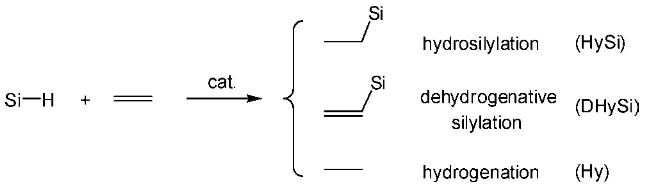
Supporting Information

ABSTRACT: A hydride and a silyl group of hydrosilane is introduced into 1,3-divinyldisiloxane in the presence of a catalytic amount of (η^5-C_5H_5)Fe(CO)$_2$Me. Instead of the product expected from the well-known hydrosilylation reaction, the product obtained is that characteristic of dehydrogenative silylation at one vinyl group and hydrogenation at the other vinyl group of 1,3-divinyldisiloxane. Based on deuterium labeling experiments, a catalytic cycle for this new reaction has been proposed.

Organosilicon compounds are present in many widely used products such as oil, grease, rubbers, cosmetics, medicinal chemicals, etc. Because the above-mentioned are not naturally occurring substances, the organosilicon compounds in them are also manufactured artificially. The addition of the Si–H bond in hydrosilane across a C═C double bond or a C≡C triple bond (hydrosilylation (HySi) reaction, Scheme 1) is a very commercially useful reaction in yielding a Si–C bond. A transition metal catalyst is required to drive this reaction.[1]

Scheme 1. Reaction of Alkene with Hydrosilane in the Presence of Catalyst



The use of many transition-metal-based catalysts has been reported for the hydrosilylation of alkenes. However, the hydrosilylation reaction is often accompanied by side reactions such as dehydrogenative silylation (DHySi) and hydrogenation (Hy) of alkenes (Scheme 1), in addition to isomerization, oligomerization, polymerization of alkenes, and redistribution of silicon hydride. Therefore, the discovery of new catalysts with higher selectivity as well as activity is important. In addition to hydrosilylation, the metal-catalyzed dehydrogenative silylation of alkenes has emerged as a powerful method to yield Si–C bonds.

Speier's catalyst and Karstedt's catalyst are known as very powerful and commercially used catalysts. Both of these are Pt-based complexes. Replacement of precious metal catalysts such as these by broadly applicable metal catalysts is becoming extremely important. Iron, for example, offers some advantages from a green and sustainable viewpoint, because it is abundant in nature and can be metabolized into nontoxic products. Several iron complexes have been reported in the catalytic hydrosilylation of C═O bonds in aldehydes and ketones.[2] In contrast, the number of reports on the use of iron complexes for catalyzing hydrosilane–alkene reactions is limited. In 1962, Nesmeyanov et al. reported that Fe(CO)$_5$ serves as a catalyst in the reaction of R$_3$SiH with alkenes to give a hydrosilylation (HySi) product and a dehydrogenative silylation (DHySi) product depending on the substrate and the reaction conditions.[3] Wrighton et al. examined the reaction of Cp*Fe(CO)$_2$R (Cp* = η^5-C_5Me_5, R = alkyl, silyl) with hydrosilane and alkene and highlighted the implications of inserting a C═C double bond into an Fe—Si bond on the mechanism of transition-metal-catalyzed hydrosilylation.[4] Murai et al. reported that $Fe_3(CO)_{12}$ catalyzes dehydrogenative silylation (DHySi) in the reaction of Et$_3$SiH with styrene and its derivatives, although it forms both a dehydrogenative silylation (DHySi) and a hydrogenation (Hy) product in the reaction of Et$_3$SiH with 1-hexene.[5] Adams et al. reported that a trinuclear complex containing Fe and Pt, FePt$_2$(CO)$_5$(PPh$_3$)$_2$(PhC$_2$Ph), shows activity in catalyzing the hydrosilylation (HySi) of alkynes, but the role of Fe might be unimportant in the catalytic system because its activity is much less than that of Pt(PPh$_3$)$_2$(PhC$_2$Ph).[6] Marciniec et al. showed that the reaction of CpFe(CO)$_2$(SiMe$_3$) (Cp = η^5-C_5H_5) with CH$_2$═CHR (R = SiMe$_3$, Ph, H) gives dehydrogenative silylation (DHySi) products but the iron complex does not show catalytic activity.[7] However, the Fe(CO)$_5$ + Et$_3$SiH system catalyzes the reaction of CH$_2$═CHSiMe$_2$OSiMe$_2$(CH═CH$_2$) with Et$_3$SiH to give dehydrogenative silylation (DHySi) and hydrogenation (Hy) products.[7] Recently, Chirik et al. reported that bis(imino)pyridine iron complexes perform as excellent catalysts for alkene hydrosilylation reactions.[8]

We have been engaged in chemistry of iron complexes having silyl ligand(s).[9] While studying the catalytic property of these iron complexes in the formation of a Si–C bond, we found that CpFe(CO)$_2$Me shows unprecedented catalytic activity in the reaction of 1,3-divinyldisiloxane with hydrosilane. We describe our findings in this paper.

A toluene solution containing 1,1,3,3-tetramethyl-1,3-divinyldisiloxane and pentamethyldisiloxane in a 1:3 molar ratio was heated at 80 °C for 24 h in the presence of 4 mol % of CpFe(CO)$_2$Me, causing the formation of

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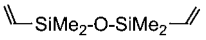
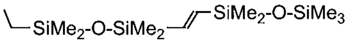
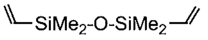
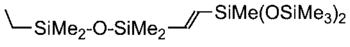
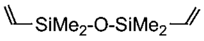
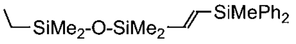
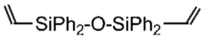
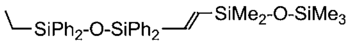
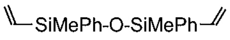
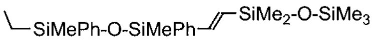
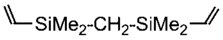
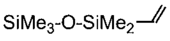
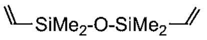
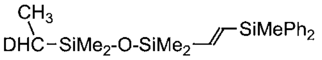
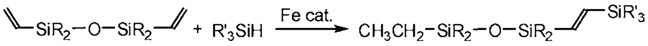
Table 1. Reaction of Olefin with Hydrosilane Catalyzed by CpFe(CO)$_2$Me in Toluene at 80 °C[a]

entry no.	olefin	R'$_3$SiH	time, h	product		isolation yield, %
1		Me$_3$Si-O-SiMe$_2$H	24		**1**	81
2		Me$_3$Si-O-SiMeH-O-SiMe$_3$	48		**2**	89
3		MePh$_2$SiH	48		**3**	72
4		Me$_3$Si-O-SiMe$_2$H	48		**4**	98
5		Me$_3$Si-O-SiMe$_2$H	48		**5**	44
6		Me$_3$Si-O-SiMe$_2$H	48	——		—
7		Me$_3$Si-O-SiMe$_2$H	24	——		—
8		MePh$_2$SiD	24		**6**	53

[a] Ratio of olefin/R'$_3$SiH is 1/3 (1/2 in entry 7). The amount of CpFe(CO)$_2$Me is 4 mol % based on olefin concentration (10 mol % in entry 4).

$C_2H_5SiMe_2OSiMe_2CH{=}CHSiMe_2OSiMe_3$ at an isolation yield of 81% (Table 1, entry 1). In this reaction, one of the vinyl groups of the divinyldisiloxane was dehydrogenatively silylated; during this process, the $SiMe_2OSiMe_3$ group is selectively introduced into the trans position relative to the original silyl group. The other vinyl group was hydrogenated. Consequently, this constitutes a sort of hydrosilylation (HySi) reaction, because both a hydrogen and a silyl group are introduced into the substrate. However, the reaction described here is not the well-known hydrosilylation, but a combination of DHySi and Hy reactions, wherein one vinyl hydrogen is replaced by a silyl group and this removed hydrogen and the hydrogen from hydrosilane are added to the other alkene portion to form an alkyl group. Therefore, this reaction should be referred to as a DHySi-Hy reaction. Because this type of reaction is unprecedented, we examined further instances of this reaction by utilizing different combinations of substances. The use of different hydrosilanes resulted in the formation of DHySi-Hy products in good yields (entries 2 and 3). Phenyl-substituted divinyldisiloxane also exhibited the same reaction (entry 4) although the yield was 14%; however, increasing the amount of catalyst from 4 to 10 mol % resulted in a yield of 98%. When 4 mol % of the iron catalyst was used, the yield was 14% presumably due to its low reactivity. Using divinyldisiloxane with methyl and phenyl substituents on the silicons also resulted in the DHySi-Hy reaction. In this case, because the Si is a chiral center, we used a diastereomeric mixture and no diastereoselectivity was observed in the DHySi-Hy reaction, suggesting that the catalytically active Fe species has no chiral center. The products of entries 1−5 were isolated and characterized by ^{1}H, ^{13}C, ^{29}Si, HRMS(EI) and elemental analyses. In contrast, $CH_2{=}CHSiMe_2CH_2SiMe_2CH{=}CH_2$ and $Me_3SiOSiMe_2CH{=}CH_2$ were not converted into the corresponding DHySi-Hy products (entries 6 and 7), and the starting vinyl compounds remained unchanged under the reaction conditions. These results indicate that the oxygen atom connecting the two vinyldimethylsilyl groups and the two vinyl groups are essential in DHySi-Hy reaction. The general scheme of the reaction we discovered is described in Scheme 2.

Scheme 2. Iron-Catalyzed Dehydrogenative Silylation−Hydrogenation Reaction of Divinyldisiloxane with Hydrosilane



In order to understand the DHySi-Hy reaction mechanism, deuterium labeling studies were conducted using a reaction similar to that of entry 3, in which MePh$_2$SiD was used in place of MePh$_2$SiH (entry 8). The reaction was stopped after 24 h to avoid undesired deuterium scrambling, and the Si-containing compound (**6**) was isolated in 53% yield. In the ^{1}H and ^{13}C NMR spectra, the chemical shifts and the coupling patterns were identical to those of **3** (within experimental errors) except for the ethyl portion. In the ^{1}H NMR of **6**, the methylene group showed a multiplet with one proton intensity and the methyl group exhibited a doublet, indicating that the methylene carbon has only one proton. Moreover, the methylene carbon of **6** showed a coupling pattern caused by a C−D bond at 9.99 ppm in the ^{13}C{^{1}H} NMR. These spectroscopic data demonstrate the selective formation of $CH_3CHDSiMe_2OSiMe_2CH{=}CHSiPh_2Me$. Therefore, the hydrogenation process in the discovered DHySi-Hy reaction consists of two selective hydrogen introductions: the hydrogen introduced at the vinyl *α*-carbon comes from the hydrosilane added, and the hydrogen introduced at the vinyl *β*-carbon originates from the hydrogen on the *β*-carbon in the other vinyl group.

A reaction similar to that of entry 1 was performed in toluene-*d*$_8$ and monitored by ^{1}H NMR. A plot of product yield as a function of time (Figure 1) shows that there is an induction period, followed by an increase in the formation of the DHySi-Hy product over time. During the induction period, resonances due to the starting iron complex were observed; thereafter,

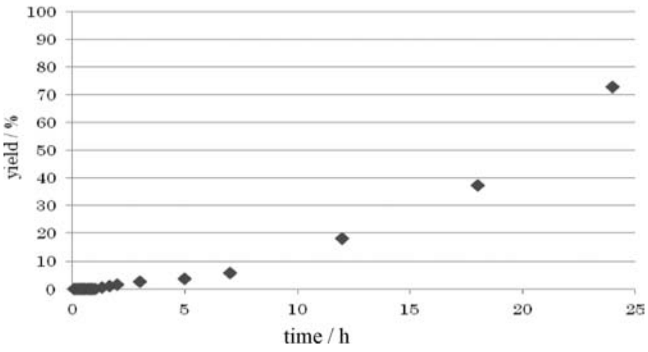


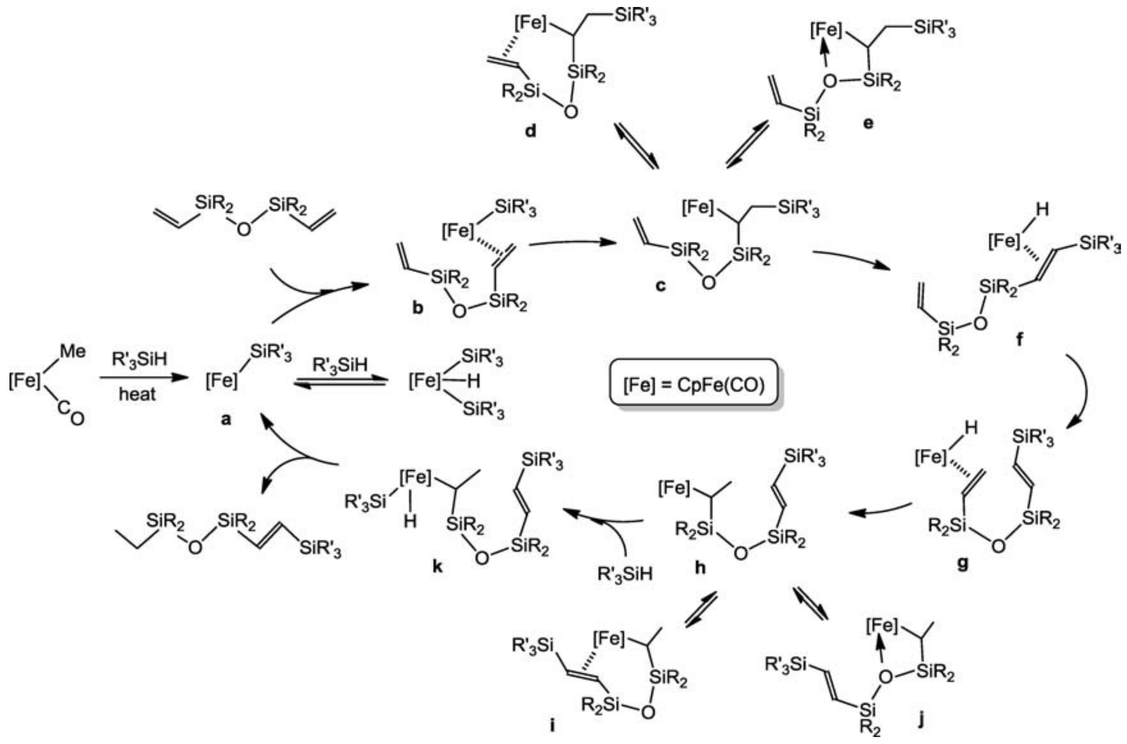
Figure 1. Plot of DHySi-Hy Product Yield As a Function of Time in $CpFe(CO)_2Me$-Catalyzed Reaction of $(CH_2CHSiMe_2)_2O$ with $Me_2SiOSiMe_2H$.

these resonances disappeared and small resonances assignable to $CpFe(CO)(SiMe_2OSiMe_3)_2(H)$ were detected. Resonances from the DHySi product, $CH_2{=}CHSiMe_2OSiMe_2CH{=}CH(SiMe_2OSiMe_3)$, were not observed.

A proposed catalytic cycle of the unprecedented DHySi-Hy reaction is shown in Scheme 3. In the initial step, a thermal activation of the catalyst precursor, $CpFe(CO)_2Me$, generates a 16-electron species, **a**. This process requires some time. When **a** reacts with R'_3SiH, the oxidative addition product $CpFe(CO)(SiR'_3)_2(H)$ is formed. It has been reported that $CpFe(CO)(py)(EEt_3)$ reacts with $Et_3E'H$ to form $CpFe(CO)(EEt_3)(E'Et_3)(H)$ (E, E′ = Si, Ge, Sn), and the product $CpFe(CO)(EEt_3)(E'Et_3)(H)$ is in equilibrium with the reductive elimination products, $Et_3E'H$ and $CpFe(CO)(EEt_3)$.[9d,e] Another reaction of **a** is coordination of one vinyl group of 1,3-divinyldisiloxane to form **b** followed by the insertion of the vinyl group into the Fe−Si bond to give **c**, which may be in equilibrium either with **d** (produced when the other vinyl group associates with the Fe) or with **e** (produced when the siloxy oxygen associates with the Fe). Coordinatively unsaturated **c** undergoes β-hydride elimination to give **f**, which may be in equilibrium with **g** via olefin exchange. Olefin insertion into the Fe−H bond of **g** gives **h**, which may be in equilibrium with either **i** or **j**, in a manner similar to that described for **c**. Complex **h** is a 16e species that reacts with R'_3SiH to give an oxidative addition product **k**. Reductive elimination of the alkyl and hydride ligands in **k** generates the DHySi-Hy product, in addition to the regeneration of **a**. According to this reaction mechanism, the hydrogen in R'_3SiH is selectively introduced into the methylene carbon of the DHySi-Hy product. The complexes situated next to each other in the cycle, with the exception of **k** and **a**, might equilibrate. The reactions from **b** to **c** and **g** to **h** involve processes in which an 18e species forms a 16e species. The coordination of olefin or siloxy oxygen to the Fe center might help drive the reaction. Because $CH_2{=}CHSiMe_2CH_2SiMe_2CH{=}CH_2$ did not react with pentamethyldisiloxane (Table 1, entry 6), siloxy oxygen coordination, as shown in **e** and **j**, may play an important role in promoting the catalytic cycle. During the DHySi reaction, only the trans isomer around the olefin portion was produced. Examples of selective trans isomer formation by DHySi reaction using iron complexes have been reported by Murai[5] and Marciniec.[7] Another mechanism containing two independent catalytic cycles is conceivable, i.e., one cycle involving the DHySi reaction catalyzed by [Fe]−SiR'_3 and the other containing the Hy reaction catalyzed by [Fe]−H. However, because the DHySi product was not detected, the catalytic cycle proposed in Scheme 3 is more likely.

In conclusion, we found an unprecedented type of hydrosilylation in the reaction of divinyldisiloxane with hydrosilane catalyzed by an iron complex. In this reaction, H and SiR_3 are introduced into divinyldisiloxane, but a simple H

Scheme 3. Proposed Catalytic Cycle of Iron-Catalyzed Dehydrogenative Silylation−Hydrogenation Reaction



and SiR_3 addition at the olefin portion does not occur. Instead, dehydrogenative silylation at one vinyl group and hydrogenation at the other vinyl group of divinyldisiloxane take place. This discovery of a highly selective DHySi-Hy reaction is important from a synthetic viewpoint because the separation of hydrosilylation products, dehydrogenative silylation products, and hydrogenation products is generally difficult.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures and characterization of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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