Synthesis and catalytic activity of N-heterocyclic silylene (NHSi) iron (II) hydride for hydrosilylation of aldehydes and ketones

Xinyu Du[1] | **Xinghao Qi[1]** | **Kai Li[1]** | **Xiaoyan Li[1]** | **Hongjian Sun[1]** | **Olaf Fuhr[2]** | **Dieter Fenske[2]**

[1]School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Jinan, China

[2]Institut für Nanotechnologie (INT) und Karlsruher Nano Micro Facility (KNMF), Karlsruher Institut für Technologie (KIT), Eggenstein Leopoldshafen, Germany

Correspondence

Hongjian Sun, School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, Jinan 250100, China.
Email: hjsun@sdu.edu.cn

A novel silylene supported iron hydride [Si, C]FeH (PMe$_3$)$_3$ (**1**) was synthesized by C (sp^3)-H bond activation with zero-valent iron complex Fe (PMe$_3$)$_4$. Complex **1** was fully characterized by spectroscopic methods and single crystal X-ray diffraction analysis. To the best of our knowledge, **1** is the first example of silylene-based hydrido chelate iron complex produced through activation of the C (sp^3)−H bond. It was found that complex **1** exhibited excellent catalytic activity for hydrosilylation of aldehydes and ketones. The catalytic system showed good tolerance and catalytic activity for the substrates with different functional groups on the benzene ring. It is worth mentioning that, the experimental results showed that both ketones and aldehydes could be reduced in good to excellent yields under the same catalytic conditions. Based on the experiments and literature reports, a possible catalytic mechanism was proposed.

KEYWORDS

aldehyde, hydrosilylation, iron hydride, ketone, silylene

1 | INTRODUCTION

As carbene analogue, silylene has strong σ-donating/π-backdonation ability and unique stereoscopic characteristics. The transition metal complexes supported by silylene exhibit rich diversity in coordination mode, spatial structure, and electronic configuration.[1] Therefore, silylene metal complexes have important value in organosilicon chemistry and applied chemistry. In the past 20 years, the types of N-heterocyclic silylene (NHSi) have been greatly enriched, and the silylene chemistry has made significant progress in the construction of metal complexes, activation of small molecules, homogeneous catalysis, nitrogen reduction, and other fields. It has been found that NHSi supported transition metal complexes[2] as catalysts could be used in the Kumada reaction,[3] Sonogashira reaction,[4] reduction of amides,[5] hydrosilylation of aldehydes and ketones,[6] hydrosilylation of olefins,[7] and C-H borylation reaction.[8] Base metal iron complexes have gradually replaced precious metal complexes for a variety of catalytic reactions. Driess reported the first silylene iron complex and found that this complex could catalyze the hydrosilylation of ketones.[9] Huang successfully realized the hydrosilylation of ketones with iron silylene complex as catalyst.[10] Recently, Cui's research group published the first NHSi iron nitrogen complex, and proved that this complex has a good catalytic effect for nitrogen
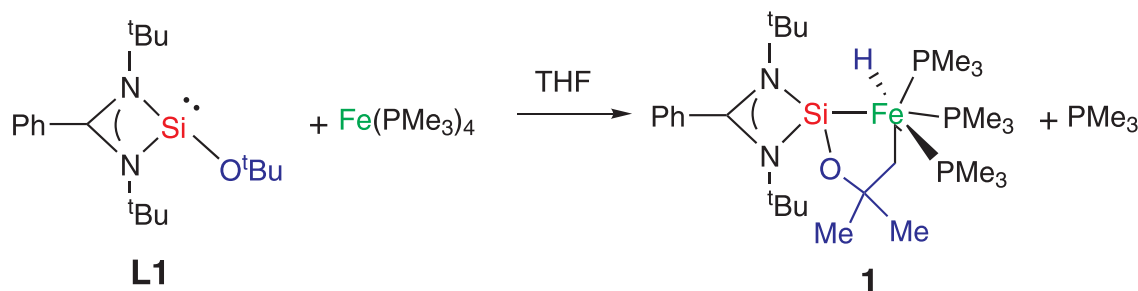
SCHEME 1 Synthesis of NHSi hydrido Fe (II) complex **1**

reduction.[11] However, there are still few examples on the synthesis and application of silylene Fe complexes.

Because metal hydride as catalyst or intermediate participates in many catalytic reactions, it has been widely concerned in organometallic chemistry.[12,13] In recent years, our group has also been devoted to metal hydride chemistry, and we synthesized various iron hydrides and
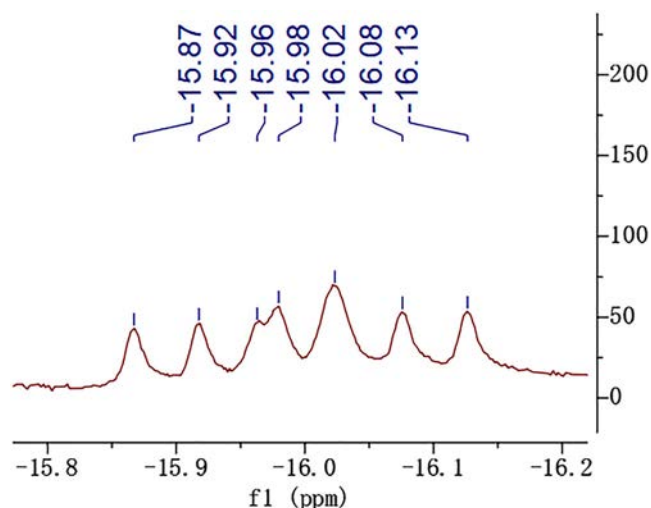

FIGURE 1 The hydrido resonance of **1**

studied the catalytic activity of these hydrides for different reactions.[14] Due to the diversity of the coordination chemistry of silylenes, we introduce silylenes into iron hydrides, and expect these hydrides to have special chemical properties and applications.

Driess realized the catalytic hydrosilylation of carbonyl compounds with NHSi iron complex as catalyst for the first time.[9] We synthesized silylene iron hydride by activating the C (sp^2)-H bond on the pyridine ring to catalyze hydroboration of carbonyl compounds under mild conditions.[15] Recently, we reported a bis-silylene iron hydride obtained by activation of C (sp^3)-H bond.[16] It was proved that this iron hydride could effectively catalyze nitrogen reduction.

In this paper, chelated silylene iron hydride **1** was synthesized by activation of C (sp^3)-H bond. It was found that complex **1** has good catalytic activity for hydrosilylation of both aldehydes and ketones. In particular, it is worth mentioning that complex **1** has almost the same catalytic activity for ketones and aldehydes under the same conditions. Generally, for the same catalyst the conditions for ketone reduction are more severe than those for aldehyde reduction. In our system, ketones and aldehydes can be reduced under the same conditions. In comparison with the published work, our catalytic system has the advantages of lower
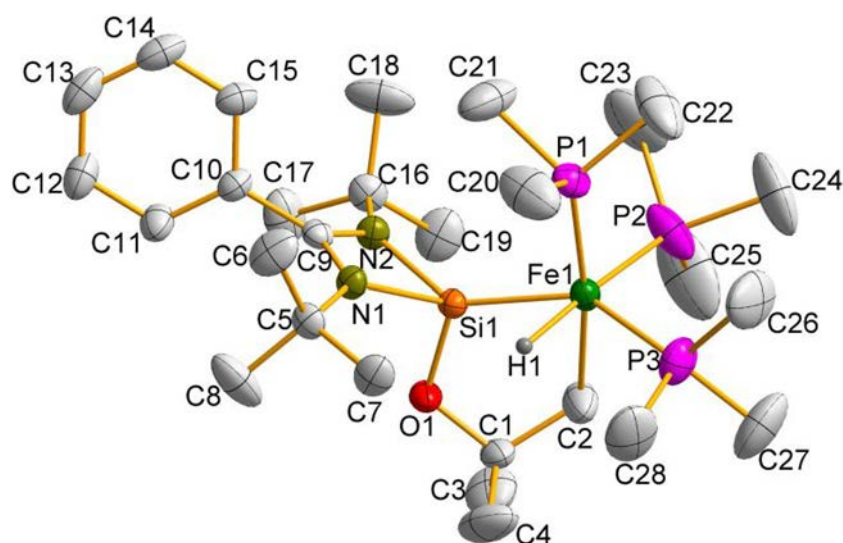

FIGURE 2 Molecular structure of **1**. The thermal ellipsoids are displayed at the 50% probability level, and most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles[deg]: Fe1 H1 1.50(4), Fe1 P1 2.1799(9), Fe1 P2 2.1792(10), Fe1 P3 2.1928(10), Fe1 Si1 2.1641(9), Fe1 C2 2.141(4), Si1 O1 1.666(2); P2 Fe1 H1 172.4(16), Si1 Fe1 P1 96.97(3), P1 Fe1 P3 96.85(4), C2 Fe1 P3 90.33 (14), C2 Fe1 Si1 74.85(12), C1 O1 Si1 112.75(19)
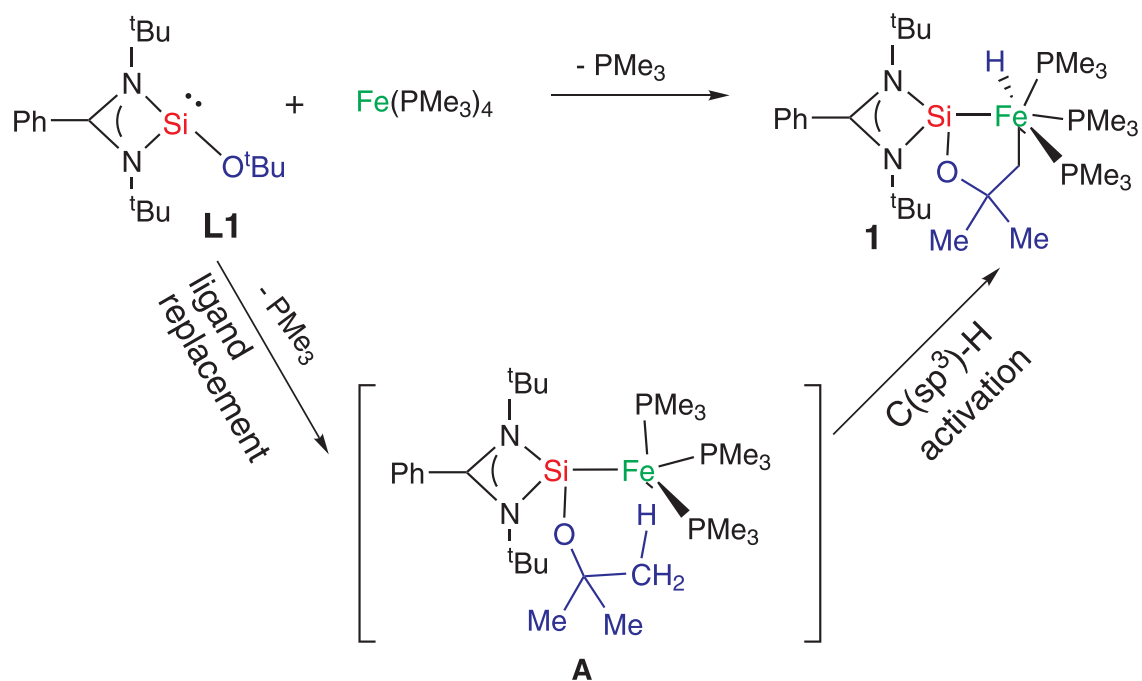
SCHEME 2 Pathway from L1 to complex **1**

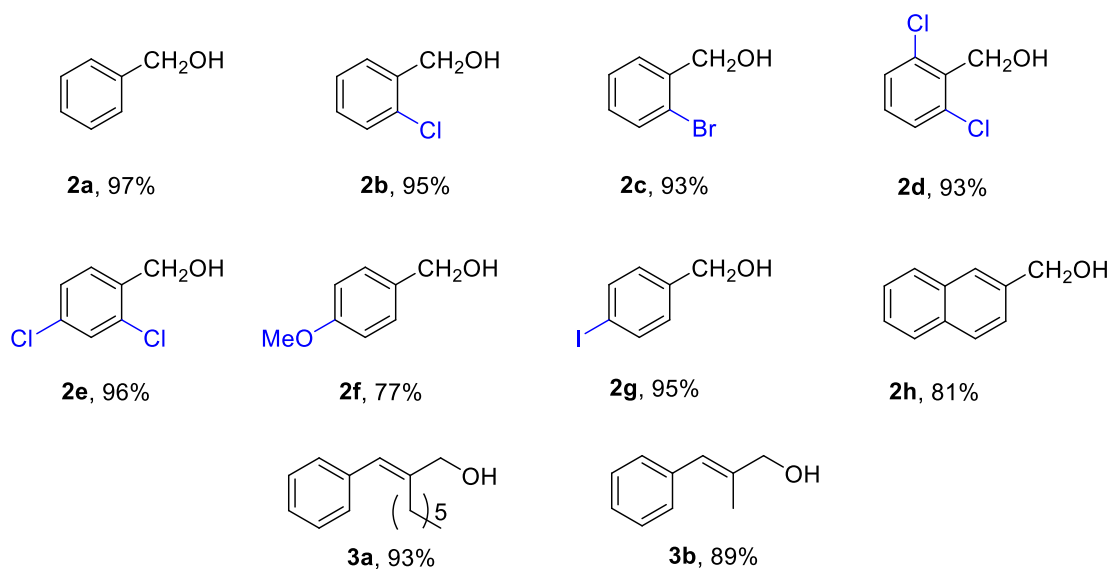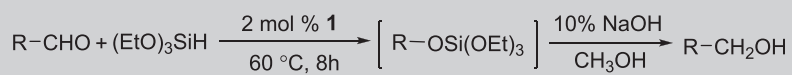**TABLE 1** Optimization of catalytic conditions for aldehydes[a]

entry	loading	silane	solvent	temp (°C)	time (hr)	Conv. (%)[b]
1	2%	$(EtO)_3SiH$	THF	60	6	86
2	2%	$(EtO)_3SiH$	THF	60	8	99
3	2%	$(EtO)_3SiH$	THF	50	8	88
4	1%	$(EtO)_3SiH$	THF	60	8	77
5	2%	$PhSiH_3$	THF	60	8	64
6	2%	Ph_2SiH_2	THF	60	8	23
7	2%	Ph_3SiH	THF	60	8	12
8	2%	Et_3SiH	THF	60	8	0
9	2%	$Me(EtO)_2SiH$	THF	60	8	80
10	2%	$(EtO)_3SiH$	Toluene	60	8	50
11	2%	$(EtO)_3SiH$	Dioxane	60	8	89
12	2%	$(EtO)_3SiH$	DMF	60	8	74
13	2%	$(EtO)_3SiH$	DME	60	8	90
14	2%	$(EtO)_3SiH$	Benzene	60	8	68
15	0%	$(EtO)_3SiH$	THF	60	8	0

[a]Catalytic reaction condition: Benzaldehyde (1.0 mmol), Hydrosilane (1.2 mmol) and Catalyst (2% mmol) in 2 ml THF, T °C, t hr.
[b]Determined by GC with dodecane as internal standard.

T A B L E 2 Products of hydrosilylation of aldehydes to alcohols[a,b]

$$R-CHO + (EtO)_3SiH \xrightarrow[60\,°C,\,8h]{2\ mol\%\ \mathbf{1}} \left[R-OSi(OEt)_3 \right] \xrightarrow[CH_3OH]{10\%\ NaOH} R-CH_2OH$$

2a, 97%   **2b**, 95%   **2c**, 93%   **2d**, 93%

2e, 96%   **2f**, 77%   **2g**, 95%   **2h**, 81%

3a, 93%   **3b**, 89%

[a]Catalytic reaction conditions: Aldehyde (1 mmol), (EtO)$_3$SiH (1.2 mmol), Catalyst (2 mol%) in 2 mL THF, 60°C, 8 hr.
[b]Isolated yield.

T A B L E 3 Optimization of catalytic reaction conditions for ketones[a]
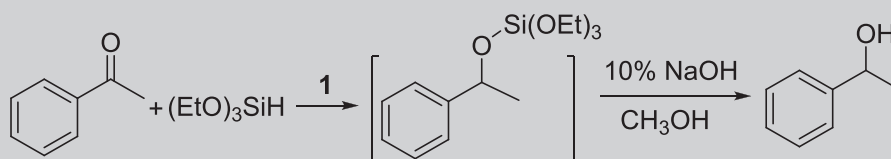
Entry	Loading	Silane	Solvent	Temp (°C)	Time (hr)	Conv. (%)[b]
1	2%	(EtO)$_3$SiH	THF	60	8	98
2	2%	(EtO)$_3$SiH	THF	60	6	80
3	2%	(EtO)$_3$SiH	THF	50	8	90
4	1%	(EtO)$_3$SiH	THF	60	8	46
5	2%	(EtO)$_3$SiH	C$_6$H$_6$	60	8	75
6	2%	(EtO)$_3$SiH	Toluene	60	8	88
7	2%	(EtO)$_3$SiH	DMF	60	8	95
8	2%	(EtO)$_3$SiH	Dioxane	60	8	91
9	2%	(EtO)$_3$SiH	None	60	8	89

[a]Catalytic reaction condition: Acetophenone (1.0 mmol), (EtO)$_3$SiH (1.2 mmol) and Catalyst (2% mmol) in 2 ml THF, 60°C, t hr.
[b]Determined by GC with n dodecane as an internal standard.

catalyst loading, lower reaction temperature, shorter reaction time and no additives for ketone substrates. We have made a preliminary study on the catalytic mechanism.

2 RESULTS AND DISCUSSION

### 2.1 Synthesis of silylene chelate iron hydride 1

When **L1** was mixed with zero valent iron complex Fe (PMe$_3$)$_4$ in THF, the color of reaction solution gradually changed from yellow to red (Scheme 1). After simple work-up, silylene chelate iron hydride **1** as red single crystals was separated from its n-pentane extract in 70% yield. On the one hand, silylene Si coordinates with Fe atom; on the other hand, a chelating five-membered ring is formed through the activation of the C (sp^3)-H bond of the *tert*-butoxyl group.

In the IR spectrum of **1** the typical signal of the Fe-H bond is located at 1860 cm^{-1}. In the ^{1}H NMR spectrum of **1** the hydrido resonance is situated at −15.96 ppm as a dddd signal caused by the H, P-coupling (Figure 1). Because of the existence of isomers in the solution, it is difficult to identify other hydrogen signals. The multiplets between 0.90–2.08 ppm belong to the three PMe$_3$ ligands, two *t*Bu, two Me groups, and methylene hydrogen. Five aromatic hydrogens are registered between 7.24 and 7.95 ppm as multiplets. The ^{31}P NMR of **1** indicates that two multiplets for PMe$_3$ ligands are positioned at 19.2–19.6 and 21.2–21.8 ppm in the integral of 1: 2. In the ^{29}Si NMR spectrum of **1**, the signal at 53.3 ppm is typical for the coordinated silylene ligands[15,16] while the free ligand **L1** has the Si resonance at −5.0 ppm.[17] The downfield shift is caused by the Si coordination.

Single crystals of **1** suitable for X-ray diffraction analysis were obtained from n-pentane at −20°C. **1** has a distorted octahedral geometry around the iron atom (Figure 2). The axial direction P2-Fe1-H1 (172.4[16]°) is almost perpendicular to the equatorial plane determined by [P1, Si1, Fe1, C2, P3]. The sum of the bond angles of the four coordination

TABLE 4 Products of hydrosilylation of aromatic ketones to alcohols[a,b]
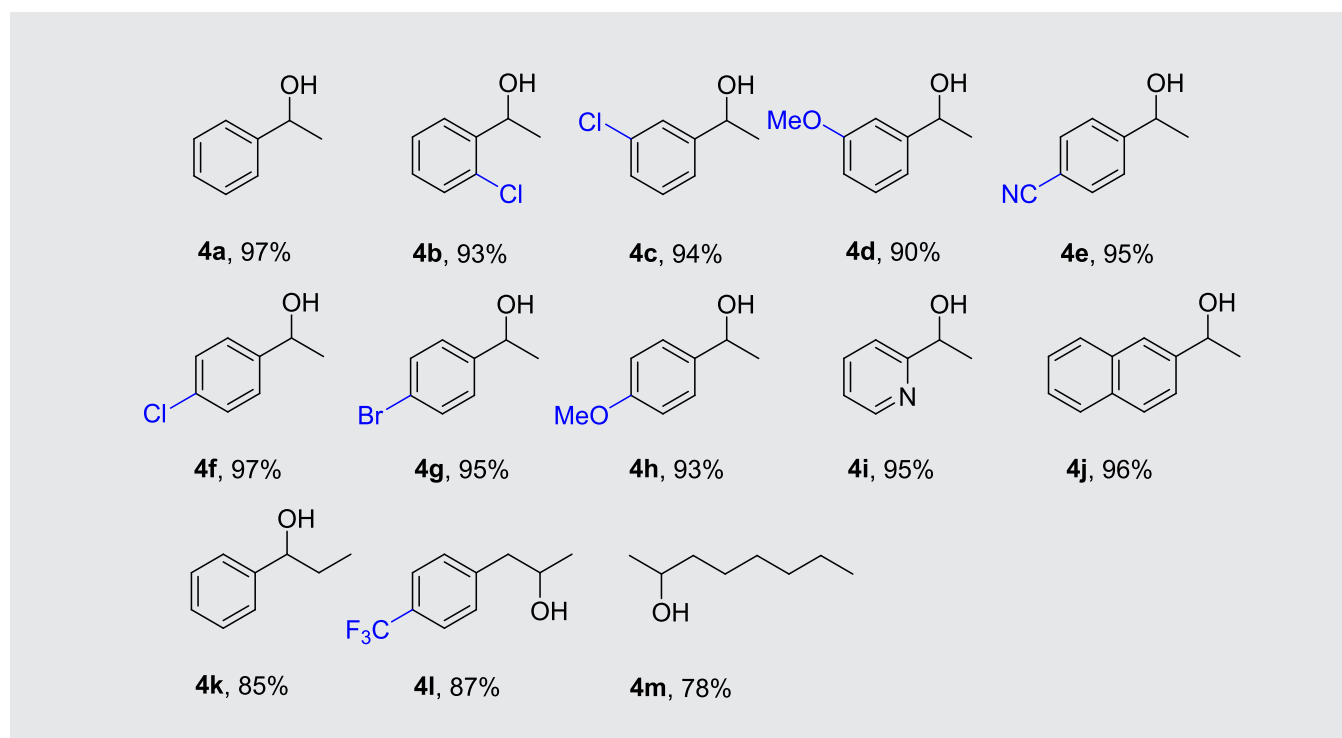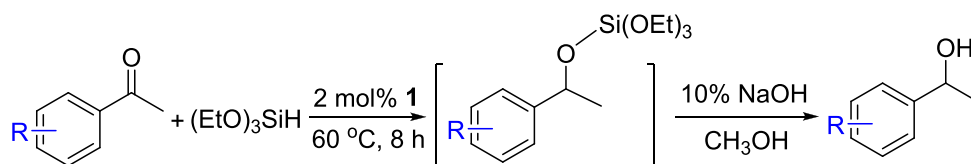
4a, 97% 4b, 93% 4c, 94% 4d, 90% 4e, 95%

4f, 97% 4g, 95% 4h, 93% 4i, 95% 4j, 96%

4k, 85% 4l, 87% 4m, 78%

[a]Catalytic reaction conditions: Aldehyde (1 mmol), (EtO)$_3$SiH (1.2 mmol), Catalyst (2 mol%) in 2 ml THF, 60°C, 8 hr.
[b]Isolated yield.

bonds in the equatorial plane is 359.0° with a little deviation of 360°. The bond length of Fe1-H1 bond (1.50[4] Å) is within the normal range of Fe-H bonds.[18] The bond length of Fe1-P3 (2.1928[10] Å) is longer than that of Fe1-P1 (2.1799[9] Å) and Fe1-P2 (2.1792[10] Å) due to the strong *trans*-influence of the Si atom. The bond length of Fe1-Si1 bond (2.1641[9] Å) is comparable to those of the reported silylene iron complexes.[15,16,19,20]

For the mechanism of the formation of complex **1** (Scheme 2), the substitution of PMe$_3$ ligand with ligand **L1** is the first step. In intermediate **A**, the coordination of Si decreases the distance between the central Fe and the C-H bond. The oxidative addition of the C-H bond at the electron-rich Fe center affords the final complex **1** with the formation of the chelate ring. To our knowledge, **1** is the first example of silylene-based chelate hydrido iron complex produced through activation of the C (sp^3)−H bond.

2.2 | Catalytic activity of complex 1 for hydrosilylation of carbonyl compounds

The conversion of aldehydes and ketones into alcohols by hydrosilylation is an important way to synthesize

alcohols.[12b] Due to the steric hindrance, it is more difficult to activate ketones than to activate aldehydes and the reaction conditions for activating ketones are more stringent. Therefore, how to improve the conversion of ketone is a subject worthy of exploration.

Benzaldehyde as a template substrate was selected to explore the hydrosilylation conditions (Table 1). The conversion could reach 99% at 60°C for 8 hr with 2 mol% **1** as catalyst and (EtO)$_3$SiH as hydrogen source (entry 2, Table 1). When the reaction time was shortened to 6 hr, the conversion of the reaction decreased to 86% (entry 1, Table 1). When the reaction temperature was reduced to 50°C or the catalyst loading decreased to 1 mol%, the conversion of the reaction decreased to 88% and 77% respectively (entries 3–4, Table 1). (EtO)$_3$SiH has the best catalytic effect compared with other silanes, such as PhSiH$_3$, Ph$_2$SiH$_2$, Ph$_3$SiH, Et$_3$SiH, and Me (EtO)$_2$SiH (entries 5–9, Table 1). When the reaction was carried out in different solvents (THF, toluene, dioxane, DMF, DME, and benzene), THF was the best reaction medium (entries 2 and 10–14, Table 1). Without catalyst **1**, no conversion was observed (entry 15, Table 1). Therefore, the optimal reaction conditions are as follows: 2 mol % catalyst, 60°C, THF, 8 hr (entry 2, Table 1).
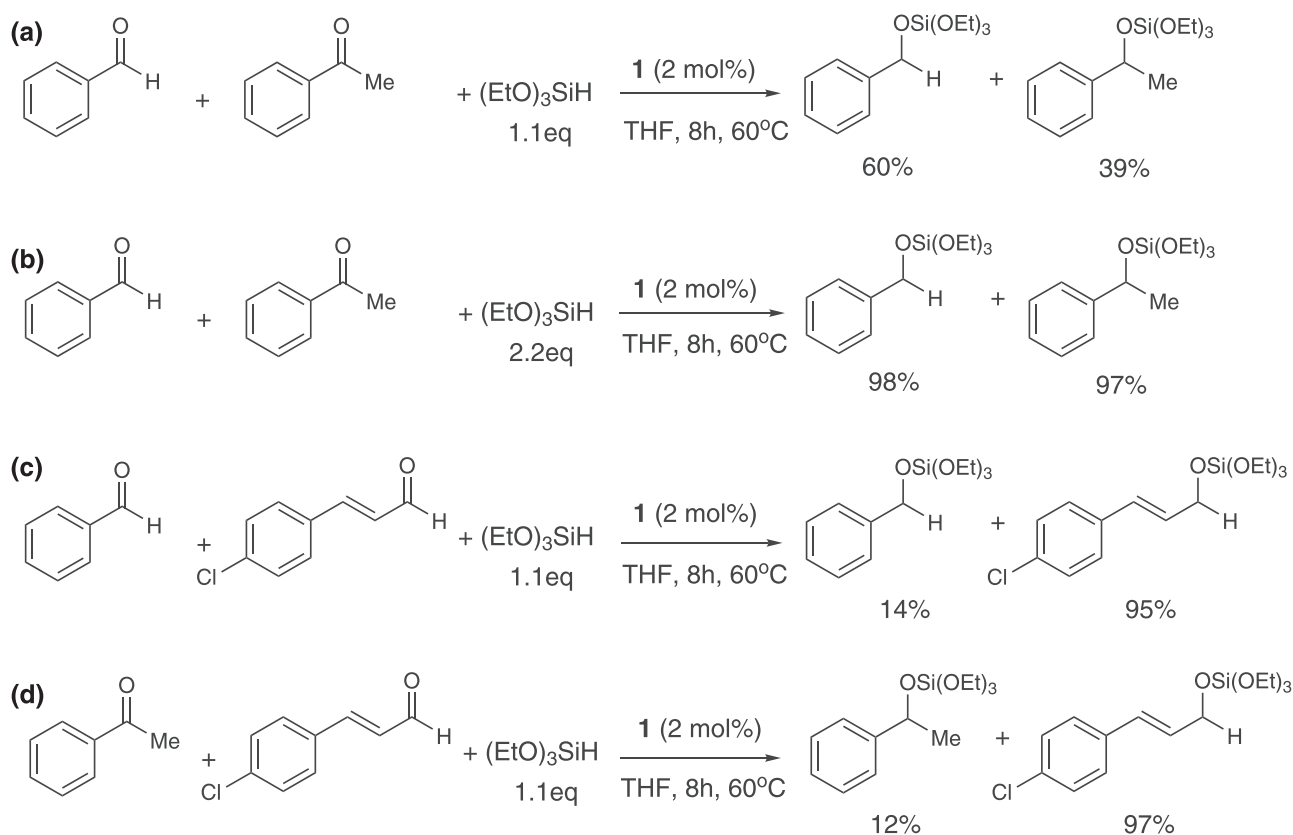
**SCHEME 3** Chemoselective Hydrosilylation Reactions^{a,b}. ^{a}Catalytic reaction condition: Catalyst (2 mol%) in 2 ml THF, 60°C, 8 hr. ^{b}Determined by GC with *n* dodecane as an internal standard

Under the optimized conditions, benzaldehyde substrates with different substituents were expanded (Table 2). The aromatic substrates (**2b**, **2c**, **2d**, **2e** and **2g**) with different functional groups in different positions on the phenyl ring have good yields (93%–95%). For substrate (**2f**) with electron donating group (such as methoxyl) good yield (77%) could also be achieved. The yield with 1-naphthaldehyde substrate (**2h**) is 81%. For cinnamaldehyde substrates (**3a** and **3b**), the C=O bond was selectively reduced while the C=C bond did not react. The yield with α-hexylcinnamaldehyde with long branched chain could reach 93% yield.

In general, it is more difficult to activate ketones than aldehydes. Surprisingly, under the optimal conditions of aldehydes, 99% conversion of acetophenone could also be achieved (entry1, Table 3). When the reaction time was

further shortened to 6 hr, the conversion was reduced to 80% (entry 2, Table 3). When the reaction temperature was reduced to 50°C, the conversion was 90% (entry 3, Table 3). When the catalyst loading was reduced to 1 mol%, the conversion was only 46% (entry 4, Table 3). At the same time, when the reaction solvent was changed to benzene, toluene, DMF, dioxane or without solvent, the conversion decreased to varying degrees (entries 5–9, Table 3). Therefore, it can be concluded that the optimized conditions for ketone and aldehyde substrates are the same (entry 1, Table 3).

It was found that the catalytic system has good universality for the ketone substrates (Table 4). The aromatic ketones (**4b**, **4c**, **4f**, **4g**, **4e**, **4d**, and **4h**) containing different functional groups (such as halogen, nitrile, and methoxy) have good yields (90%–97%). For
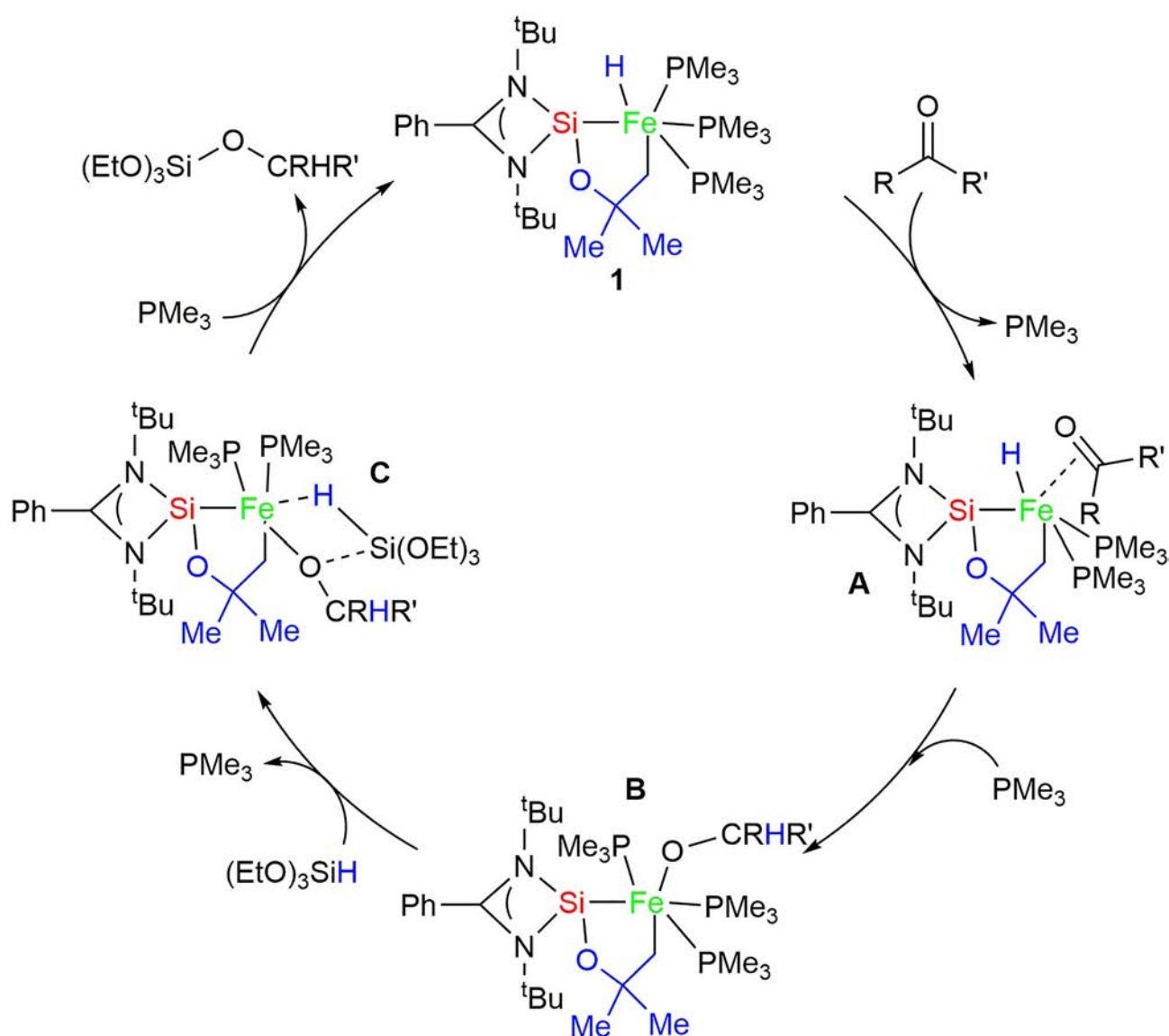
SCHEME 4 Proposed catalytic mechanism

2-acetonaphthalene (**4j**) the yield was 96%. For N-heterocyclic compound (2-acetylpyridine, **4i**) 95% yield could be reached. At the same time, the change of substituent position has little effect on the catalytic reaction. For ethyl phenyl ketone (**4k**), methyl (4-trifluoromethyl) benzyl ketone (**4l**) and methyl hexyl ketone (**4m**), the yields of the related alcohols are between 78% and 85%.

We also studied the effect of catalyst on the chemoselectivity of the system (Scheme 3). When 1 mmol of benzaldehyde and 1 mmol of acetophenone were used as substrates in the presence of 1.1 mmol silane, the conversion of aldehyde was much higher than that of ketone (Scheme 3a). When 2.2 mmol silane were added, almost equivalent conversion of aldehyde and ketone could be achieved (Scheme 3b). Interestingly, when α, β-unsaturated aldehyde (3-[4-chlorophenyl] acrylaldehyde) and benzaldehyde (Scheme 3c) or acetophenone (Scheme 3d) were used as substrates, the conversion of α, β-unsaturated substrate is much higher than that of aldehydes or ketones. Therefore, the order of substrate activity for this catalytic system is as follows: α, β-unsaturated aldehyde $\gg$ benzaldehyde > acetophenone.

2.3   Study on the catalytic reaction mechanism

In order to understand the reaction mechanism, the stoichiometric reaction of catalyst **1** with 2-acetonaphthone or (EtO)$_3$SiH was explored. The disappearance of Fe-H signal in the in situ IR indicated that both reactions took place, and the color of the reaction solution changed from red to green or yellow. Unfortunately, we cannot separate the products that can be characterized. These two experiments imply that the intermediates containing Fe-O or Fe-Si bond may be formed. Theoretical calculations show that the insertion of C=O bond into the M-H bond is preferred over that into the M-Si bond.[21] Based on the experiments and literature reports,[22] we propose a possible catalytic mechanism (Scheme 4). The first step from **1** to intermediate **A** is the ligand replacement. The insertion of C=O bond into the Fe-H bond affords intermediate **B**. After σ-bond metathesis via **C** the final product (EtO)$_3$Si-O-CRHR′ is formed with the recovery of catalyst **1**.

3   CONCLUSION

In this paper, a novel silylene chelate iron hydride **1** was synthesized by Csp^3-H bond activation using zero-valent iron complex Fe (PMe$_3$)$_4$. It has been found that complex

1 is an effective catalyst for hydrosilylation of aldehydes and ketones. Interestingly, the experimental results showed that both ketones and aldehydes could be reduced in good to excellent yields under the same catalytic conditions. Chemoselective hydrosilylation reactions indicate that the order of substrate activity for this catalytic system is as follows: α, β - unsaturated aldehyde $\gg$ benzaldehyde > acetophenone under the same conditions. Based on the experiments and literature reports, a possible catalytic mechanism was proposed.

4   EXPERIMENTAL SECTION

4.1   General procedures and materials

All experiments and manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques, unless otherwise noted. All solvents were dried by general methods and freshly distilled before use. Chlorosilylene,[23] PhC (N^{t}Bu)$_2$SiO^{t}Bu,[17] Fe (PMe$_3$)$_4$[24] was prepared according to the reported procedures. All the aldehydes, ketones and α, β-unsaturated carbonyl compounds were purchased and used without further purification. The purity of the triethoxysialne used is 95%, the other 5% is tetraethoxysialne. The silanes were purchased from J&K scientific. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bruker ALPHA FT-IR instrument by using Nujol mulls between KBr disks. ^{1}H, ^{13}C {^{1}H}, ^{31}P {^{1}H} and ^{29}Si {^{1}H} NMR spectra were recorded on Bruker Avance 300- and 400-MHz spectrometers. Gas chromatography was performed by using a Fuli 9790 instrument with *n*-dodecane as an internal standard. Melting point was measured in capillarie sealed under N$_2$ and was uncorrected. Elemental analyses were carried out on an Elementar Vario ELIII instrument.

4.2   Synthesis of 1

A solution of ligand **L1** (1.20 g, 3.61 mmol) in 30 ml of THF was slowly added to a solution of Fe (PMe$_3$)$_4$ (1.30 g, 3.61 mmol) in 30 ml of THF at −78°C, forming a red reaction mixture. The reaction mixture was stirred overnight. All volatiles were removed in vacuo. The residue was extracted with 70-ml *n*-pentane. The combined organic solutions were concentrated to 40 mL and red crystals were formed at −20°C. Yield: 1.55 g, 70%. Dec: >157 °C Anal. calcd for C$_{28}$H$_{59}$FeN$_2$OP$_3$Si (616.65 g/mol): C, 54.54; H, 9.64; N, 4.54. Found: C, 54.79; H, 9.50; N, 4.67. IR (Nujol mull, KBr, cm^{-1}): 1860 ν (Fe-H), 930 ρ (PCH$_3$). ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K, ppm): −15.96 (dddd, $^2J_{P,H}$ = 15 Hz, $^2J_{P,H}$ = 30 Hz,

$^2J_{P,H}$ = 36 Hz, 1H, Fe-H), 0.90–2.08 (m, 53H, C [CH_3]$_3$), PCH_3, CH_3, CH_2) 7.24–7.95 (m, 5 H, Ar-H). ^{31}P NMR (121 MHz, C$_6$D$_6$, 298 K, ppm): 19.2–19.6 (m, 1P), 21.2–21.8 (m, 2P). ^{13}C NMR (75 MHz, C$_6$D$_6$, 298 K, ppm): 24.7 (m), 29.0 (m), 29.9, 32.0 (d, $^2J_{P,C}$ = 8 Hz), 33.2, 35.8, 53.4, 54.5, 77.7 (Fe-CH_2), 129.0 (C_{arom}), 129.7 (C_{arom}), 134.0 (C_{arom}), 171.3 (NCN). ^{29}Si NMR (59.59 MHz, C$_6$D$_6$, 298 K, ppm): 53.3 (m).

4.3 Representative experimental procedure for the hydrosilylation reactions

Under a nitrogen atmosphere, 1-mmol aldehyde or ketone substrate was weighed into a 20 mL Schlenk tube containing a magnetic stirring. Later, 1.2-mmol (EtO)$_3$SiH and 2 mmol% iron hydride **1** were added to the tube. The system was then heated at 60°C for 8 hr. The conversion was determined by GC with n-dodecane as an internal standard. After cooling to room temperature, the mixture was quenched with MeOH (2 ml) and a 10% aqueous solution of NaOH (2 ml) under vigorous stirring at 60°C for about 24 hr. The product alcohol was extracted with 60-ml diethyl ether three times and dried over Na$_2$SO$_4$. After filtration, the volatile materials were evaporated in vacuo. The crude product was purified by column chromatography over silica gel with a mixture of petroleum ether and ethyl acetate (10:1) as the eluent to yield the product. The pure product was characterized by NMR analysis.

4.4 X-ray structure determinations

Intensity data were collected on a Stoe Stadi Vari diffractometer equipped with graphite-monochromatized Ga Kα radiation (λ = 1.34143 Å). Crystallographic data for complex **1** are summarized in the Supporting Information. The structure was solved by direct methods with the OLEX 2 program[25] and refined with full-matrix least squares on all F^2 (SHELXL).[26] All non-hydrogen atoms were refined anisotropically. CCDC 1865448 (**1**) contains supplementary crystallographic data for this paper.

DATA AVAILABILITY STATEMENT
The data that supports the findings of this study are available in the supporting information of this article.

CONFLICT OF INTEREST
There are no conflicts to declare.

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