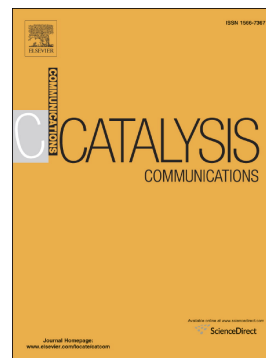# Accepted Manuscript

Catalytic hydrosilylation of carbonyl compounds by hydrido thiophenolato iron(II) complexes

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Catalytic Hydrosilylation of Carbonyl Compounds by Hydrido Thiophenolato Iron(II) Complexes

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Abstract: The hydrosilylation of aldehydes and ketones under mild conditions with hydrido thiophenolato iron(II) complexes [*cis*–Fe(H)(SAr)(PMe$_3$)$_4$] (**1 - 4**) as catalysts is reported using (EtO)$_3$SiH as an efficient reducing agent in the yields up to 95%. Among them complex **1** is the best catalyst. Complex **1** could also be used as catalyst to reduce the α,β-unsaturated carbonyl compounds selectively to the α,β-unsaturated alcohols in high yields.

Keywords: hydrosilylation / silane / iron hydride /α,β-unsaturated carbonyl compound / carbonyl compound

1. Introduction

Transition-metal-catalyzed hydrosilylation of carbonyl derivatives is an exceedingly attractive and convenient reduction method because it generates silyl protected alcohols in one step under mild conditions [1 - 4]. Hydrosilylation of unsaturated organic substrates containing C=C, C≡C, C≡N, and C=O bonds is an important industrial and laboratory reaction widely used for preparation of useful organosilicon monomers and polymers, crafting of surfaces, as well as production of special silicon chemicals [5 - 10]. Thus, transition-metal-catalyzed hydrosilylation is recognized as a powerful and indispensable tool in organic synthesis, because both the reduction and the protection steps are performed in a single, atom-efficient fashion.

Due to the high abundance, low cost and environmental friendliness of iron, iron compounds as catalysts have attracted more and more attention in the field of synthetic chemistry. Recently, Bauer and Knölker summarized iron-catalyzed organic reactions in organic synthesis [11] as a representative pioneering example, Brunner *et al*. reported the hydrosilylation of acetophenone with Fe(Cp)(CO) complex as catalyst under photo-irradiation [12, 13]. Chirik and co-workers studied complexes [Fe(*i*PrPDI)(CH$_2$TMS)$_2$] as catalysts for the hydrosilylation of ketones at room temperature achieving a good activity [14]. Beller described that simple complex Fe(OAc)$_2$ in the presence of phosphine ligands could be an active catalyst in the reductions of aldehydes and ketones with broad substrate scope and high tolerance against several functional groups [15]. Similarly, Nishiyama and co-workers also chose Fe(OAc)$_2$ but with nitrogen ligand as catalyst to be used in hydrosilylation of ketones to give the corresponding alcohols in high yields [16]. Simple amide catalyst [Fe(N(SiMe$_3$)$_2$)$_2$] could also catalyze hydrosilylation of carbonyl compounds at room temperature [17]. Although considerable progress has been made in iron-catalyzed hydrosilylations, up to date, there are only a few studies published on iron hydride complexes as pre-catalysts for hydrosilylation of carbonyl derivatives [18 - 21]. In 2008, Nikonov reported iron silyl dihydride displaying a good catalytic property in the hydrosilylation of carbonyls [18]. In 2011, Guan and co-workers described a family of well-defined iron POCOP-pincer hydrido complexes

3

[2,6-$(R_2PO)_2C_6H_3$]Fe(H)(PMe$_3$)$_2$, [2,6-(i-Pr$_2$PO)$_2C_6H_3$]Fe(H)(PMe$_3$)(CO)$_n$ (n = 1, 2), which were active catalysts for the hydrosilylation of aldehydes and ketones with different functional groups [19]. Darcel reported the iron dihydrido complex [(dppe)$_2$Fe(H)$_2$] as the pre-catalyst for efficient hydrosilylation of carbonyl derivatives under visible light activation [20]. Most recently, some pincer-type iron complexes [22, 23], bidentate iron complexes [24, 25] and dinuclear iron complexes [26, 27] were reported as catalysts for the reduction of carbonyl compounds. Our group reported the synthesis of several pincer iron(II) hydrides and bidentate iron(II) hydrides which can be used as catalysts in the hydrosilylation of aldehydes and ketones (**Fig. 1**) [13, 28 - 32]. We have reported the synthesis of hydrido thiophenolato iron(II) complexes **1** - **4** by reaction of thiophenols with Fe(PMe$_3$)$_4$ (**Fig. 2**). Complexes **1 – 4** could be used as catalysts in the reduction of primary amides to nitriles under hydrosilation conditions [33, 34]. As continuation to our study in this direction, in this paper we reported the reduction of carbonyl derivatives under hydrosilylation condition in the presence of hydrido iron(II) complexes **1 – 4.** Complexes **1 – 4** showed excellent catalytic activity in the hydrosilylation of aldehydes and ketones using (EtO)$_3$SiH as a reducing agent under mild conditions in excellent yields with a broad functional group tolerance.
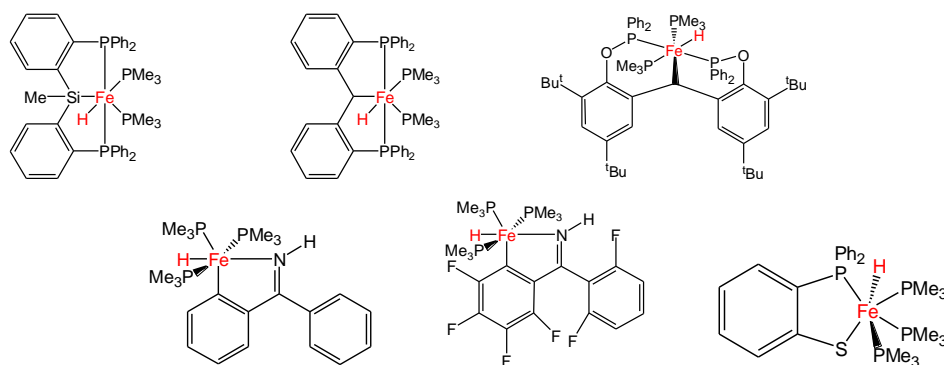

Fig. 1 Hydrido iron(II) precatalysts for hydrosilylation by our group

Furthermore, we have explored the selectivity of complex **1** as catalyst in the reduction of α,β-unsaturated carbonyl compounds to the corresponding alcohols in high yields.
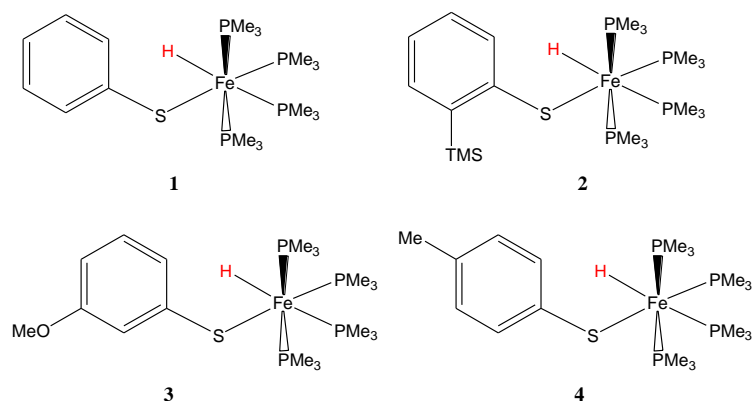
Fig. 2 Thiophenolato hydrido iron(II) complexes **1** - **4**

2. Experimental section

General procedures and materials. Standard vacuum techniques were used in the manipulations of volatile and air-sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. Infrared spectra ($4000 - 400$ cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT-IR instrument. NMR spectra were recorded using Bruker Avance 300 MHz spectrometers. GC-MS was recorded on a TRACE-DSQ instrument and GC was recorded on a Fuli 9790 instrument. 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. Fe(PMe$_3$)$_4$ [35] and complexes **1 − 4** [33, 34] were prepared according to literature procedures.

Caution! (EtO)$_3$SiH is flammable and highly toxic by inhalation and may cause skin irritation and blindness. Even if during our studies on the hydrosilylation of carbonyl compounds, we used it without incident, triethoxysilane should be used with precaution. Indeed, due to possible silane disproportionation, the formation of an extremely pyrophoric gas (possibly SiH4) has led to several fires and explosions reported in the literature. (See Buchwald safety letter, Chemical & Engineering News (29 Mar 1993) Vol. 71, No. 13, pp. 2.)

General Procedure for Catalytic Hydrosilylation of Aldehydes. To a 25 mL Schlenk tube containing a solution of **1** in 2 mL of THF was added an aldehyde (1.0 mmol) and $(EtO)_3SiH$ (0.20 g, 1.2 mmol). The reaction mixture was stirred at 50 - 55°C until there was no aldehyde left (monitored by TLC and GC-MS). The reaction was then quenched by MeOH (2 mL) and a 10% aqueous solution of NaOH (5 mL) with vigorous stirring at 60°C for about 24h. The organic product was extracted with diethyl ether (10 mL × 3), dried over anhydrous $MgSO_4$, and concentrated under vacuum. The alcohol product was further purified using flash column chromatography (elute with 5 - 10% ethyl acetate in petroleum ether). The ^{1}H NMR and ^{13}C NMR spectra of the alcohol products are provided in the Supporting Information.

General Procedure for the Catalytic Hydrosilylation of Ketones. Ketones were reduced following a similar procedure to the one used for aldehydes except that the reaction time of heat was extended to 24h and the temperature rised to 60°C. The ^{1}H NMR and ^{13}C NMR spectra of the alcohol products are provided in the Supporting Information.

General Procedure for the Catalytic Hydrosilylation of α,β-unsaturated carbonyl compounds. α,β-unsaturated carbonyl compounds were reduced following a similar procedure to the one used for aldehydes. The ^{1}H NMR and ^{13}C NMR spectra of the corresponding alcohol products are provided in the Supporting Information.

3. Results and discussion

3.1. Catalytic application of iron hydrido complexes 1 - 4 in hydrosilylation of aldehydes and ketones

As mentioned previously, transition-metal catalysts can effectively reduce a wide variety of unsaturated organic substrates. Our group have recently reported the hydrosilylation of carbonyls catalyzed by different iron(II) hydrides[13, 25-29]. In comparison with the above-mentioned hydrides, as monodentate hydrido complexes,

1 - **4** as catalysts have more advantages. For example, the synthesis of complexes **1** - **4** is easier and they are more inexpensive. Therefore, to extend the scope of the iron-based catalyst, the catalytic property of complexes **1** - **4** was further studied.
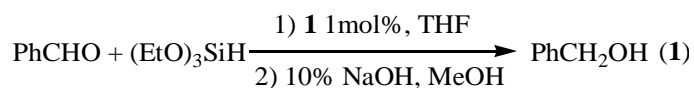
$$PhCHO + (EtO)_3SiH \xrightarrow[\text{2) 10\% NaOH, MeOH}]{\text{1) 1 1mol\%, THF}} PhCH_2OH \text{ (1)}$$

Table 1 Exploration of Reduction of Benzaldehyde Catalyzed by **1 - 4**[a]

Entry	Complex	Loading (mol%)	Hydrogen source	Solvent	Temp. (℃)	Time (h)	[b]Conv. (%)
1	**1**	0	$(EtO)_3SiH$	THF	50	2	0
2	**1**	0.5	$(EtO)_3SiH$	THF	50	2	67
3	**1**	1	$(EtO)_3SiH$	THF	50	2	99
4	**1**	1	$(EtO)_3SiH$	THF	50	0.5	29
5	**1**	1	$(EtO)_3SiH$	THF	50	1.0	57
6	**1**	1	$(EtO)_3SiH$	THF	50	1.5	83
7	**1**	1	Et_3SiH	THF	50	2	0
8	**1**	1	Ph_3SiH	THF	50	2	0
9	**1**	1	Me_2PhSiH	THF	50	2	31
10	**1**	1	Ph_2SiH_2	THF	50	2	59
11	**1**	1	PhSiH3	THF	50	2	87
12	**1**	1	TMDS	THF	50	2	43
13	**1**	1	PMHS	THF	50	2	0
14	**1**	1	$(EtO)_3SiH$	THF	15	2	49
15	**1**	1	$(EtO)_3SiH$	THF	30	2	83
16	**1**	1	$(EtO)_3SiH$	THF	60	2	88
17	**1**	1	$(EtO)_3SiH$	Toluene	50	2	57
18	**1**	1	$(EtO)_3SiH$	Ether	50	2	51
19	**1**	1	$(EtO)_3SiH$	Pentane	50	2	26
20	**1**	1	$(EtO)_3SiH$	Isopropanol	50	2	43

21	**2**	1	(EtO)$_3$SiH	THF	50	2	47
22	**2**	1	(EtO)$_3$SiH	THF	50	6	99
23	**3**	1	(EtO)$_3$SiH	THF	50	2	79
24	**3**	1	(EtO)$_3$SiH	THF	50	3	99
25	**4**	1	(EtO)$_3$SiH	THF	50	2	65
26	**4**	1	(EtO)$_3$SiH	THF	50	4	99

[a] Catalytic reaction conditions: PhCHO (1.0 mmol), (EtO)$_3$SiH (1.2 mmol), *n*-dodecane (internal standard) (1.0 mmol), **1** - **4** (0.01 mmol) in 2 ml THF, T℃, t h.
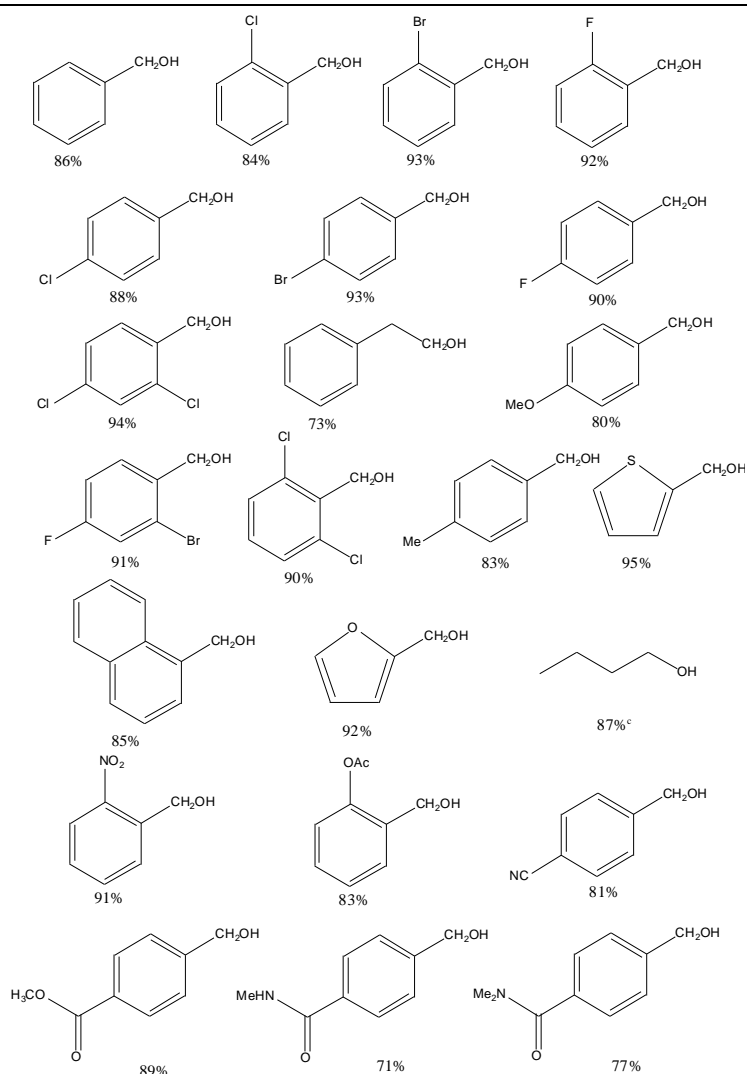
[b] Determined by GC analysis.

The hydrosilylation of aldehydes using (EtO)$_3$SiH as the reducing silylating agent was studied with thiophenolato hydrido iron(II) complexes **1 – 4** as catalysts (**Eq. (1)**, Table 1). To explore the activity of complexes **1** - **4** in hydrosilylation, benzaldehyde was chosen as the model substrate by using (EtO)$_3$SiH as a hydrogen source in THF at 50℃. The reaction didn't proceed without any catalyst (entry 1, Table 1). To our delight, in the presence of 1 mol% of **1**, the reaction was completely finished within 2h (entry 2, Table 1). However, at the given conditions, complexes **2 - 4** seemed to be less active than **1** (entries 21 - 26, Table 1). The conversion was lower when reaction time was shorter than 2h (entries 4 - 6, Table 1).). When (EtO)$_3$SiH was replaced by other silanes, such as Et$_3$SiH, Ph$_3$SiH, Me$_2$PhSiH, Ph$_2$SiH$_2$, PhSiH$_3$, TMDS or PMHS, the results were unsatisfactory (entries 7 - 13, Table 1). Temperature and solvent were two factors in this hydrosilylation reaction. The conversion was not good at the temperature below or above 50℃ (entries 14 - 16, Table 1). The conversion in polar solvent (THF) (entry 3, Table 1) was better than those in the other four solvents (entries 17 - 20, Table 1). The optimized catalytic reaction conditions can be summarized as follows: PhCHO (1.0 mmol), (EtO)$_3$SiH (1.2mmol), and **1** (0.01 mmol) in 2.0 ml of THF, 50℃, 2h.

8

$$\text{RCHO} + \text{(EtO)}_3\text{SiH} \xrightarrow[\text{2) 10\% NaOH, MeOH}]{\text{1) 1 1mol\%, THF}} \text{RCH}_2\text{OH} \, (2)$$
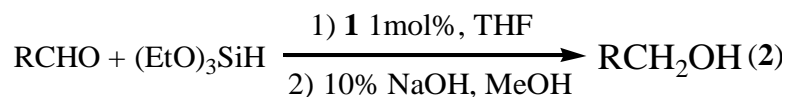
After optimization of the catalytic reaction conditions, more substrates of aldehydes bearing different functional groups were selected to explore the scope of this catalytic system (**Eq.** (**2**), Table 2). After workup, the corresponding alcohols were settled in high yields (Table 2). It could be concluded that the substrates substituted by halogen (either mono-substituted or bis-substituted) converted to corresponding alcohols in good yields under the mild conditions. The substrates with electron-donating group (Me, MeO) gave moderate yields (83% and 80% respectively). In addition, heterocyclic compounds furaldehyde and thiophenecarboxaldehyde also reacted well and the yields were very high (92%, 95%). Aliphatic aldehyde like phenylacetaldehyde and *n*-butanal performed in good yields (73% and 87%). The aldehydes bearing different functional groups such as nitro, ester, nitrile, tertiary amides, secondary amides and ester could also be reduced to the corresponding alcohols in high yields (91%, 83%, 81%, 77%, 71% and 89% respectively).
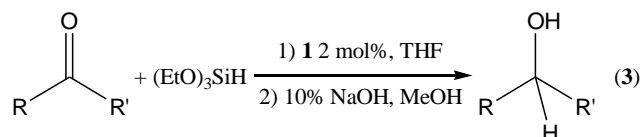
Table 2 Catalytic Hydrosilylation of Aldehydes with **1** as Catalyst.[a,b]

For ketones, these hydrosilylation reactions were obviously sluggish during the required reaction time and their yields were lower within 2 h. Therefore, increasing the catalyst loading to 2%, extending reaction time to 24h and raising the temperature seemed to be useful for the reaction (**Eq**. (**3**), Table 3). This result might be attributed

to the steric hindrance in the reaction. So in the catalytic exploration of ketones, the reaction process seems difficult.

Table 3 Catalytic Hydrosilylation of Ketones with **1** as Catalyst.[a,b]

73%   82%   70%

79%   77%   89%

69%   70%   87%[c]
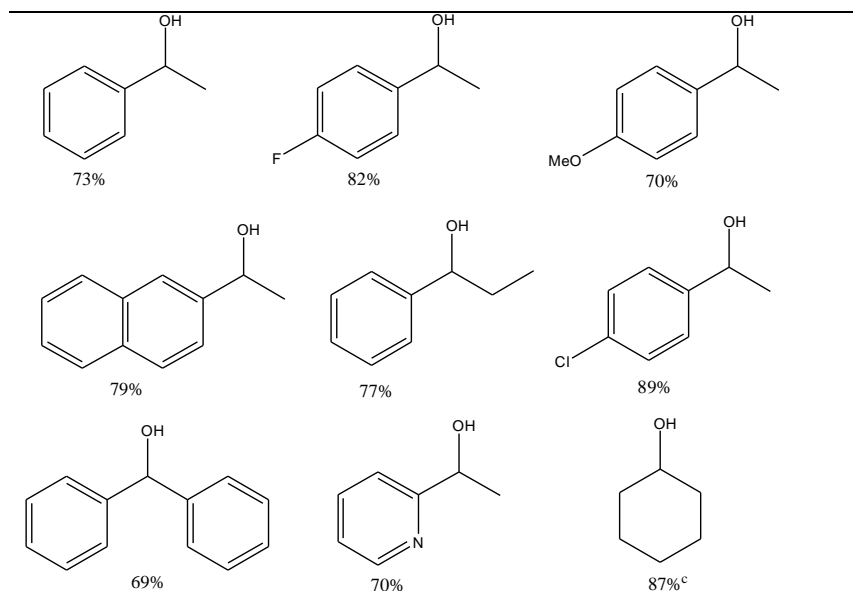
[a] Catalytic reaction conditions: (1) RCOR' (1.0 mmol), (EtO)$_3$SiH (1.2 mmol) and **1** (0.02 mmol) in 2 ml THF, 60℃, 24h. (2) MeOH (2 mL) and 10% aqueous solution of NaOH (5 mL) with vigorous stirring at 60°C for about 24h.

[b] Isolated Yield.

[c] GC Yield.

3.2. Selective reduction of α,β-unsaturated carbonyls catalyzed by complex 1.

Using complexes **1** as catalysts, we have further explored the reduction of cinnamaldehydes. It was found that the cinnamaldehydes were selectively reduced to the corresponding cinnamyl alcohols in good yields under mild conditions. This selectivity is similar with our early reported system [28, 29]. Several substrates were studied in order to explore the scope of this catalytic system (**Eq.** (**4**), Table 4). Cinnamyl alcohols could be obtained from corresponding cinnamaldehydes whatever the substituent group was. It's worth noting that the α-Me substitutional cinnamyl alcohol was obtained in the highest yield. We think that the methyl, as an electron-donating group, increased the electron density at the oxygen atom. This

11

makes the O atom easier to coordinate to central iron atom, thus, the yield was enhanced. In the case of α-bromocinnamaldehyde, 3-phenyl-2-propyn-1-ol was isolated in the yield of 75 %, this is produced by the elimination of HBr from the corresponding cinnamyl alcohol [28]. α,β-Unsaturated ketones are also applicable to this catalytic system by increasing the catalyst loading to 2%, extending reaction time to 24h and raising the temperature to 60°C (**Table 4)**.
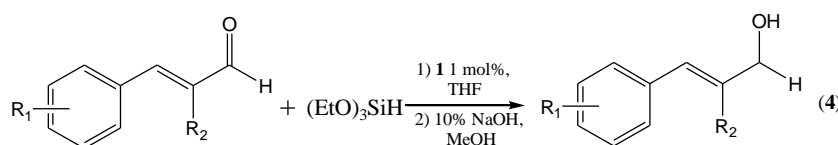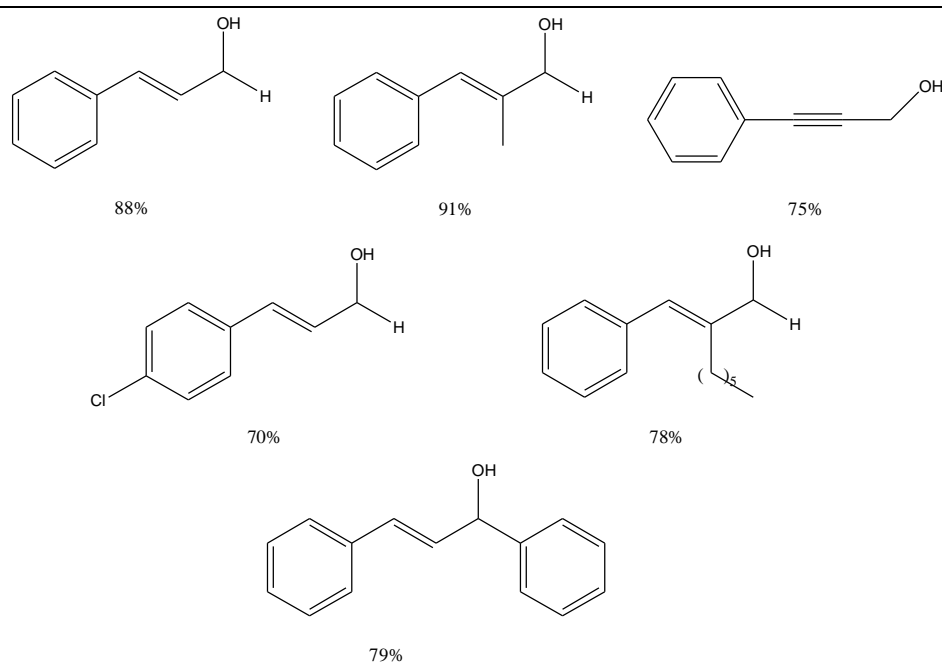

Table 4 Selective reduction of α,β-unsaturated carbonyls catalyzed by **1**.[a,b]

[a] Catalytic reaction conditions: (1) cinnamaldehyde (1.0 mmol), (EtO)₃SiH (1.2 mmol) and **1** (0.01 mmol) in 2 ml THF, 50℃, 4h. (2) MeOH (2 mL) and 10% aqueous solution of NaOH (5 mL) with vigorous stirring at 60°C for about 24h.

[b] Isolated Yield.

In comparison with our early reported systems, we can find that, as monodentate hydrido complexes, **1** - **4** as catalysts have almost the similar activity as the pincer

iron(II) hydrides [13, 26, 27] and bidentate iron(II) hydrides [25, 28, 29] in the hydrosilylation of aldehydes and ketones. In most cases, the catalytic activity of complexes **1-4** are more higher than that of the related bidentate iron(II) hydrides with [P, S]-cheating ligand, especially in the hydrosilylation of ketones [29].

4. Conclusions

In conclusion, hydrido thiophenolato iron(II) complexes [*cis*–Fe(H)(SAr)(PMe$_3$)$_4$] (**1 - 4**) could be used as catalysts for the hydrosilylation of carbonyl compounds. Among them complex **1** is the best catalyst. Furthermore, α,β-unsaturated alcohols could be obtained from the selective reduction reactions of the corresponding α,β-unsaturated carbonyls catalyzed by hydrido iron(II) complex **1**. We have compared the efficiency of our catalyst (1 mol%, 50 °C, 2 h for aldehydes and 2 mol%, 60 °C 24 h for ketones) with Chirik's [14], Nikonov's [18] and Tilley's [17] results. In general, catalyst efficiency of Chirik's catalytic system (0.1% - 1 mol% catalyst loadings and at 23°C) is better than that of our catalytic system. Although the catalyst loadings (5 mol% and 2.7 mol%) of Nikonov's and Tilley's system are larger than that of our system (1 mol% and 2 mol%), even if the reaction temperatures (22 and 23 °C) and times (3 and 0.3 h) are more advantageous.

Supplementary material: Electronic Supplementary Information (ESI) available: ^{1}H NMR and ^{13}C NMR spectra for the alcohol products.

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Graphical abstract

38 examples, yields: 69 - 95%
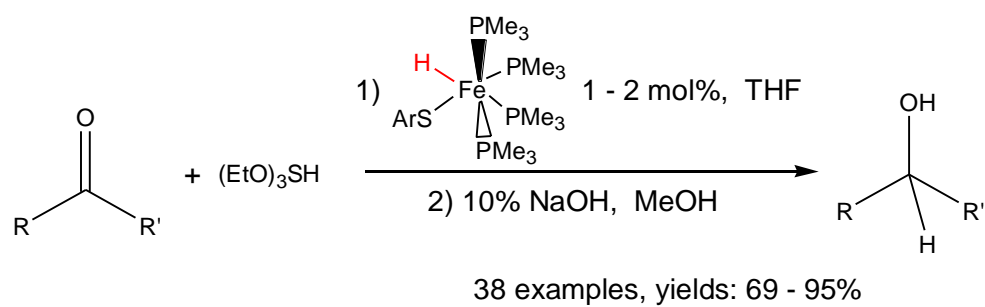
Highlights

- Hydrosilylation of aldehyde and ketone was catalyzed by iron(II) hydride.

- Reduction of aldehyde and ketone was studied with $(EtO)_3SiH$ as reducing agent.

- α,β-Unsaturated carbonyl compound was reduced to α,β-unsaturated alcohols.