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### Dehydrogenative Coupling of Alcohol with Hydrosilane Catalyzed by an Iron Complex

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**ABSTRACT**: Silane alcoholysis of triethylsilane (Et<sub>3</sub>SiH) with alcohol (ROH) with the help of  $CpFe(CO)_2Me$  (1) has been achieved to produce triethylsilyl ether (ROSiEt<sub>3</sub>) under the thermal condition. For some alchols, the iron complex served as a catalyst. A 16e silyl iron complex ( $CpFe(CO)(SiEt_3)$ ) was proposed to be one of active iron species.

### 1. INTRODUCTION

Silyl ethers have been widely used as agents in the synthesis of organic-inorganic hybrid materials, protection groups in organic synthesis, external electron donors in Ziegler-Natta catalytic polymerization processes, and precursors for the synthesis of silicon polymers, and thus are very useful silicon compounds [1-11]. In general, silvl ethers have been synthesized through the reactions of chlorosilanes [12] or disilazanes [13-16] with alcohols in the presence of a base such as pyridine. However, chlorosilanes are often not convenient for handling due to moisture sensitive and corrosive reagents. In addition, these reactions produce stoichiometric amount of salts as a byproduct. An alternative method for the synthesis of silyl ethers is catalytic dehydrogenative coupling of hydrosilanes with alcohols. The merit of the reaction is the formation of only H<sub>2</sub> as the co-product. To date, several metal catalysts derived from copper(II) [17, 18], alkali metal(I) [19, 20], rhodium(I) [21, 22], palladium(II) [23, 24], gold(III) [25-28], platinum(II) [29], ruthenium(II) [30, 31], zinc(II) [32], indium(III) [33], titanium(II) [34-36], manganese [37], rhenium [38], iron [39], iridium [40], nickel [41, 42] complexes and organocatalysts [43-45] have been reported.

Recently, we examined the dehydrogenative coupling reaction of hydrosilane with thiols in the presence of CpFe(CO)<sub>2</sub>Me (1) and found that (i) the dehydrogenative coupling could be achieved by the iron complex, (ii) the iron complex served as a catalyst irrespective of the existence of sulfur-containing compounds, and (iii) only silyl thioether was formed and homodehydrogenative coupling products such as disulfide and disilane were not produced [46]. These results prompted us to investigate reactions of alcohols instead of thiols with hydrosilane in the presence of 1. The following points were examined: (i) whether 1 serves as a catalyst in this reaction similar to the reaction between thiols and hydrosilane, (ii) whether substrates such as alcohols as starting materials and silvlethers as expected products work as catalyst poisons or not, and (iii) whether the selective formation of silyl ether is achieved or not. This paper reports the results of the reaction of alcohols with Et<sub>3</sub>SiH in the presence of 1.

Table 1. Thermal Coupling Catalyzed by an Iron Complex<sup>a</sup>

 $CpFe(CO)_2Me(1) + PhEH + Et_3SiH \xrightarrow{\Delta} PhE-SiEt_3$ 

entry	PhEH	[M]:[E]:[Si] <sup>d</sup>	TON <sup>e</sup>
1	PhOH	1:1:1	Trace
2	PhSH	1:1:1	0
3	PhOH	1:10:100	0.3
4 <sup>b</sup>	PhSH	1:10:100	5.8
5°	PhSH	1:100:1000	6.8

<sup>a</sup> Reactions were carried out for 24 h at 80 °C by using CpFe(CO)<sub>2</sub>Me (0.21 mmol) and substrates in toluene (The amount of toluene was adjusted to keep the concentration of the Fe complex at 0.025 M in entries 1-4). <sup>b</sup> See reference 46. <sup>c</sup> solvent free. <sup>d</sup> Molar ratio of an iron complex, (thio)alcohol and Et<sub>3</sub>SiH. <sup>e</sup> Calculated from the <sup>1</sup>H NMR spectrum. The values are based on the concentration of an iron complex.

#### 2. Results and discussion

A solution of an equimolar amount of CpFe(CO)<sub>2</sub>Me (1) (0.21 mmol) (Cp =  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), PhOH (0.21 mmol), and Et<sub>3</sub>SiH (0.21 mmol) in toluene (8.2 mL) was heated at 80 °C for 24 h (Table 1, entry 1). The solvent and Et<sub>3</sub>SiH were removed under reduces pressure, and then the residue was dissolved in  $C_6D_6$ . The <sup>1</sup>H NMR measurement of the solution at room temperature revealed the formation of a small amount PhOSiEt<sub>3</sub>. This result shows that 1 hardly helps the formation of PhOSiEt<sub>3</sub>. A stoichiometric reaction of 1, PhSH, and Et<sub>3</sub>SiH did not produce PhSSiEt<sub>3</sub> at all (entry 2). In contrast and surprisingly, the use of a catalytic amount of 1 showed much better results. When 10 mol% of 1 based on PhOH was used in the reaction of PhOH with Et<sub>3</sub>SiH, PhOSiEt<sub>3</sub> was formed in 30% yield (entry 3). This observation seems peculiar at a glance, but it can be understood if one thinks that large excess substances make their coordination to the active iron species easy, causing acceleration of dehydrogenative coupling and also retardation of decomposition of the iron active species. This tendency has been reported in the reaction of excess amounts of PhSH and Et<sub>3</sub>SiH to form PhSSiEt<sub>3</sub> (entries 3-5) [46]. And this effect is higher for PhSH than PhOH.

Table 2	. Dehv	drogenative	Coupling	of Alcohol	and Triet	hvlsilane <sup>a</sup>
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 $CpFe(CO)_2Me(1) + 10 eq. ROH + 100 eq. Et_3SiH \xrightarrow{\Delta} RO-SiEt_3$ 

entry	ROH	RO-SiEt <sub>3</sub>	TON <sup>b</sup>
1	EtOH	EtO-SiEt <sub>3</sub>	2.1
2	⊘−он	$\bigcirc$ -O-SiEt <sub>3</sub>	1.6
3	<sup>t</sup> BuOH	<sup>t</sup> BuO-SiEt <sub>3</sub>	1.4
4	PhOH	PhO-SiEt <sub>3</sub>	0.3
5	МеО∢⊃⊢ОН	MeO⟨_)−O−SiEt <sub>3</sub>	0.7
6	Ph <sup>^</sup> OH	Ph <sup>^</sup> O−SiEt₃	0.4
7	€∕он	O_O-SiEt <sub>3</sub>	0.7

<sup>a</sup> Reactions were carried out for 24 h at 80 °C by using CpFe(CO)<sub>2</sub>Me complex (0.112 mmol), ROH (1.12 mmol), Et<sub>3</sub>SiH (11.2 mmol) in toluene (0.46 mL, 4.3 mmol). <sup>b</sup> Calculated from the <sup>1</sup>H NMR spectrum. The values are based on the concentration of an iron complex.

To explore the scope and limitation of the catalytic activity of **1** the dehydrogenative coupling of several alcohols and  $Et_3SiH$  were examined (Table 2). The corresponding dehydrogenative coupling products were observed in all cases. Compared with entries 1-3, a bulky substituent on the alcohol seems to reduce the catalytic activity to some extent. An electron-donating substituent in alcohols exhibits better TONs (entry 1 vs 6 and 4 vs 5). The alcohol having a furan ring capable of coordination to the metal indicated the small TON (entry 7), although the corresponding thiol did not undergo the dehydrogenative coupling at all [46].

Scheme 1. Proposed Catalytic Cycles



For the dehydrogenative coupling of alcohol and  $Et_3SiH$  to give silyl ether, we proposed a reaction mechanism (Scheme 1) similar to that of dehydrogenative coupling of thiols and  $Et_3SiH$  [46]. Two plausible catalytic cycles were proposed. The 16e species 1' formed

from 1 induces the oxidative addition of  $Et_3SiH$  or PhOH, followed by the dissociation of MeCHO to give CpFe(CO)(SiEt<sub>3</sub>) (a) or CpFe(CO)(OPh) (a'), respectively. Complex a undergoes the oxidative addition of PhOH and the reductive elimination of PhOSiEt<sub>3</sub> to produce the hydride complex c. Complex c is also obtained from the reaction of a' with  $Et_3SiH$  via CpFe(CO)(H)(SiEt<sub>3</sub>) (b). The 16e complex c may exhibit two type additions with  $Et_3SiH$  and PhOH. The former addition regenerates complex a involving H<sub>2</sub> gas release (cycle A). In the latter reaction, a' is regenerated via the oxidative addition of PhOH and the reductive elimination of H<sub>2</sub> (cycle B)

In order to obtain insight into catalytic cycle, the thermal reaction of CpFe(CO)(py)(SiEt<sub>3</sub>) (py = pyridine) (**2**), considered as a synthon of a 16e complex **a** [46-51], with excess EtOH was examined (Scheme 2). The <sup>1</sup>H NMR spectrum of the reaction mixture showed the formation of EtOSiEt<sub>3</sub> (21% yields based on **2**). This product is probably formed according to the reaction sequence of **2**→**a**→**b**→EtOSiEt<sub>3</sub>. This result shows that the reaction sequences of cycle A in Scheme 1 proceeds to some extend although a reaction pathway according to cycle B cannot be ruled out. As a 16e species CpFe(CO)(SiEt<sub>3</sub>) has been proposed to be involved in a catalytic cycle in the reaction of thiols with Et<sub>3</sub>SiH, we propose here that CpFe(CO)(SiEt<sub>3</sub>) is also one of active Fe species in the reaction of alcohol with Et<sub>3</sub>SiH.

Scheme 2. Thermal reaction of EtOH in the presence of a pyridine iron complex.



In summary, iron complex 1 was found to help dehydrogenative coupling in a stoichiometric reaction of PhOH with  $Et_3SiH$ , although not in the reaction of PhSH with  $Et_3SiH$ . Complex 1 also showed catalytic activity in dehydrogenative coupling reaction of several alcohols. The catalytic activities (TON) were in the range of 0.3 to 2.1. As the activity toward alcohol is lower than that toward

thioalcohol, the active iron species may suffer more catalytic activity loss from alcohol than thioalcohol. Selective formation of silyl ether was observed because no other compounds were detected in our system.

### 3. Experimental

#### 3.1 General Remarks

All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques. Toluene was distilled from sodium metal. This was stored under a nitrogen atmosphere. Complexes **1** and **2** were synthesized according to the literature methods [46, 49, 50]. The other chemicals were commercially available. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-AL400 and a Bruker Ultrashield 400 Plus spectrometers. All NMR data were referenced to Me<sub>4</sub>Si.

## 3.2 Thermal reaction of alcohol with triethylsilane and the methyl iron complex in toluene.

In stoichiometric reactions, a solution containing a methy iron complex **1** (40 mg, 0.21 mmol), alcohol (0.21 mmol) and triethylsilane (34  $\mu$ L, 0.21 mmol) in toluene (8.2 mL, 77 mmol) was heated at 80 °C for 24 h. The solvent and Et<sub>3</sub>SiH were removed under reduced pressure at 10 mmHg, and then the residue was dissolved in C<sub>6</sub>D<sub>6</sub> to subject NMR measurement. Yields of triethylsilylether were determined by <sup>1</sup>H NMR.

3.3 Dehydrogenative coupling of alcohol and triethylsilane catalyzed by the methyl iron complex.

In catalytic reactions, a solution containing **1** (21.5 mg, 0.112 mmol), ROH (1.12 mmol) and Et<sub>3</sub>SiH (1.79 mL, 11.2 mmol) in toluene (0.46 mL, 4.3 mmol) was heated at 80 °C for 24 h. The solvent and Et<sub>3</sub>SiH were removed under reduced pressure at 10 mmHg, and then the residue was dissolved in  $C_6D_6$  to subject NMR measurement. Yields of triethylsilylether of a solution were determined by <sup>1</sup>H NMR.

#### 4. Conclusion

Concerning a dehydrogenative coupling reaction of alcohol with hydrosilane catalyzed by an iron complex, Brookhart and coworkers reported the reaction of EtOH with  $Et_3SiH$  using a cationic iron complex in 1998 [39]. This paper describes that a neutral iron complex can serve as a catalyst of dehydrogenative coupling of alcohol with hydrosilane. In addition, our reaction system is available for several alcohols and reports that less bulky and electron-donating substituents in alcohols are favorable for this reaction. A plausible catalytic cycle involving 16e iron species, CpFe(CO)H and  $CpFe(CO)(SiEt_3)$ , is proposed.

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Accepter Me cat. C ROH + Et<sub>3</sub>SiH RO-SiEt<sub>3</sub>

Highlights

- Silane alcoholysis of Et<sub>3</sub>SiH with ROH was achieved to produce ROSiEt<sub>3</sub>.
- $(\eta^5-C_5H_5)Fe(CO)_2Me$  was served as the catalyst precursor. •
- Accepting

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