ORGANOMETALLICS
COMMUNICATION
pubs.acs.org/Organometallics

Dehydrogenative Coupling of Thiol with Hydrosilane Catalyzed by an Iron Complex

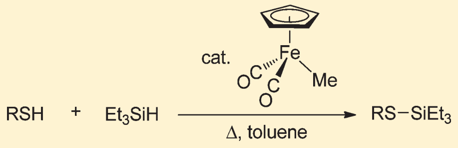
Kozo Fukumoto,[†] Michiho Kasa,[‡] Tsukuru, Oya,[‡] Masumi Itazaki,[‡] and Hiroshi Nakazawa*,[‡]

[†]Department of General, Kobe City College of Technology, Kobe 651-2194, Japan

[‡]Department of Chemistry, Graduate School of Science, Osaka City University, Osaka 558-8585, Japan

S *Supporting Information*

ABSTRACT: Thermal reaction of RSH with Et_3SiH in the presence of a catalytic amount of $CpFe(CO)_2Me$ exhibited dehydrogenative S−Si coupling to give $RSSiEt_3$. A plausible reaction mechanism is proposed involving an Fe(IV) complex with SR, $SiEt_3$, and H ligands, from which reductive elimination of SR and $SiEt_3$ takes place to give $RSSiEt_3$.



Displacement of labile hydrogen atom(s) in organic compounds by a silyl group is an important organic transformation. The silylation has frequently been used as a protection method[1,2] and also to obtain favorable solubility in nonpolar solvents. Another merit of silylation is the ease of removal of a silyl group, which is simply accomplished by acid- or base-induced hydrolysis with formation of only siloxane as a byproduct. Thiol is one of organic compounds bearing a labile hydrogen. Silylation of thiol (RSH) to give silylthioether ($RSSiR'_3$) has extensively been used not only for −SH group protection and increasing solubility but also for increasing volatility, which is important for gas chromatography and mass spectrometry. Although many reports concerning the properties and reactivities of silylthioethers have been published,[3] their preparative methods are quite limited. A widely used method is salt elimination from chlorosilane and metal thiolate such as lithium thiolate.[4] This method produces a salt such as LiCl as a byproduct, and thiol should be converted into metal thiolate prior to the salt elimination reaction. In contrast, dehydrogenative coupling of thiol and hydrosilane catalyzed by a transition metal complex seems to be more convenient. However, this method has attracted much less attention mainly because catalyst poisoning by sulfur is a major deterrent.[5−7] Only Wilkinson's catalyst, Pd nanoparticles, and $B(C_6F_5)_3$ have been reported as catalysts for the condensation.[8−10] We here report the first example of iron-catalyzed dehydrogenative coupling of thiols and hydrosilanes.

Toluene (0.46 mL), $CpFe(CO)_2Me$ (**1**) (0.112 mmol) (Cp = η^5-C_5H_5), PhSH (1.12 mmol), and Et_3SiH (11.2 mmol) were charged in a Schlenk tube, and the solution was heated at 80 °C for 24 h. The solvent and Et_3SiH were removed under vacuum, and then the residue was dissolved in C_6D_6. The ^1H NMR measurement of the solution at room temperature revealed the formation of $PhSSiEt_3$ (58% conversion based on PhSH). These results show that $CpFe(CO)_2Me$ catalyzes dehydrogenation of PhSH and Et_3SiH with a turnover number (TON) of 5.8. The same reaction of PhSH and Et_3SiH in the presence of a catalytic amount of **1** was performed in C_6D_6, and the ^1H NMR measurement of the resulting solution revealed the formation of H_2 and acetaldehyde. Modification of the Cp ligand in **1** affected the catalytic activity (Table 1). Increasing the methyl substitution on the Cp ring caused a decrease of the catalytic activity (entries 1−3). Introduction of I on the Cp ring shut down the catalytic activity (entry 4). The dehydrogenative coupling activities of the related methyl molybdenum complexes, (η^5-C_5R_5)$Mo(CO)_3Me$ (R_5 = H_5, H_4Me, Me_5), were sluggish (entries 5−7).

Table 1. Thermal Reactions of PhSH with Et_3SiH in the Presence of a Transition Metal Complex[a]

$$\text{Complex} + 10\ \text{equiv PhSH} + 100\ \text{equiv}\ Et_3SiH \xrightarrow[24\ \text{h},\ \text{toluene}]{\Delta} PhS-SiEt_3$$

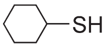
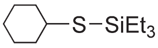
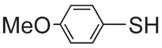
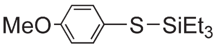
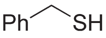
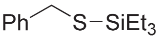
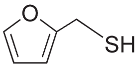
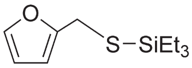
entry	complex	TON[b]
1[c]	$(C_5H_5)Fe(CO)_2Me$ (**1**)	5.8
2[c]	$(C_5H_4Me)Fe(CO)_2Me$	4.9
3[c]	$(C_5Me_5)Fe(CO)_2Me$	trace
4[c]	$(C_5H_4I)Fe(CO)_2Me$	no reaction
5[d]	$(C_5H_5)Mo(CO)_3Me$	0.4
6[d]	$(C_5H_4Me)Mo(CO)_3Me$	0.3
7[d]	$(C_5Me_5)Mo(CO)_3Me$	trace
8[c]	$[(C_5H_5)Fe(CO)SPh]_2$ (**3**)	0.4

[a] Reactions were carried out for 24 h by using Me complex (0.112 mmol), PhSH (1.12 mmol), Et_3SiH (11.2 mmol) in toluene (0.46 mL, 4.3 mmol). [b] Calculated from the ^1H NMR spectrum. The values are based on the concentration of a transition metal complex. [c] At 80 °C. [d] At 100 °C.

Received: May 7, 2011
Published: June 20, 2011

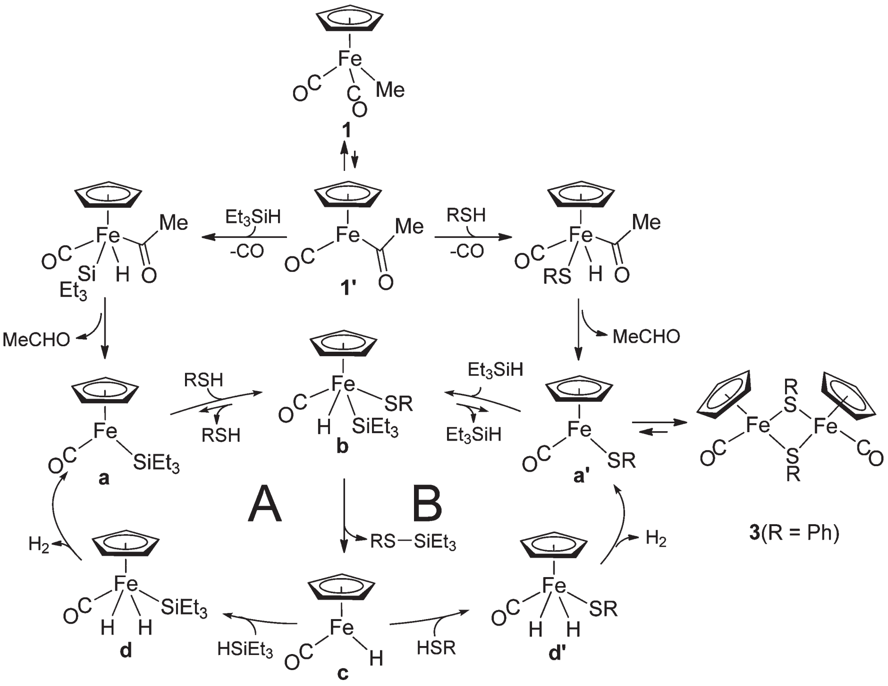
Table 2. Dehydrogenative Coupling of Thiol and Hydrosilane[a]

$$CpFe(CO)_2Me(\mathbf{1}) + 10 \text{ equiv } RSH + 100 \text{ equiv } R'_3SiH \xrightarrow[24 \text{ h, toluene}]{\Delta} RS - SiR'_3$$

entry	RSH	R'$_3$SiH	RS-SiR'$_3$	TON[b]
1	EtSH	Et$_3$SiH	EtS−SiEt$_3$	8.4
2		Et$_3$SiH		10
3	^{t}BuSH	Et$_3$SiH	^{t}BuS−SiEt$_3$	6.4
4	PhSH	Et$_3$SiH	PhS−SiEt$_3$	5.8
5		Et$_3$SiH		7.2
6		Et$_3$SiH		0.6
7		Et$_3$SiH		no reaction
8	PhSH	Me$_2$PhSiH	PhS−SiMe$_2$Ph	7.6
9	PhSH	MePh$_2$SiH	PhS−SiMePh$_2$	3.6

[a] Reactions were carried out for 24 h at 80 °C by using $CpFe(CO)_2Me$ complex (0.112 mmol), RSH (1.12 mmol), R'_3SiH (11.2 mmol) in toluene (0.46 mL, 4.3 mmol). [b] Calculated from the ^1H NMR data. The values are based on the concentration of a transition metal complex.

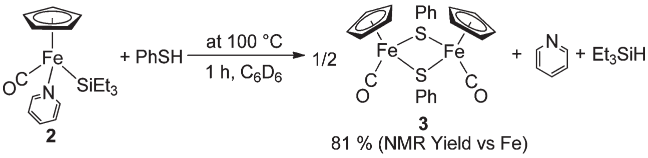
Scheme 1. Proposed Catalytic Cycles



To explore the scope and limitation of the catalytic activity of **1** for the dehydrogenative coupling, several thiols and tertiary silanes were examined. Table 2 shows the results. It suggests that (i) thiols having an electron-donating substituent exhibit better TONs (entries 1, 2, 4, 5), (ii) a bulky substituent on thiol seems to reduce the catalytic activity to some extent (entry 3), (iii) a thiol substituent capable of coordinating to the metal seems unfavorable for this coupling (entries 6, 7), and (iv) substituents on tertiary silane also affect TONs (entries 4, 8, 9); a bulky substituent seems to reduce the catalytic activity.

On the basis of the NMR experiments described above two plausible catalytic cycles are conceivable (Scheme 1). $CpFe(CO)_2Me$

Scheme 2. Synthesis of SPh-Bridged Dinuclear Fe Complex



(**1**) is in equilibrium with CpFe(CO){C(O)Me} (**1′**). This 16*e* species reacts with either Et_3SiH or RSH existing in solution. In the reaction with Et_3SiH, the Si−H oxidative addition and subsequent reductive elimination of MeC(O)H yield CpFe(CO)($SiEt_3$) (**a**), which then reacts with RSH to give **b**. Complex **b** is alternatively produced in the reaction of **1′** with RSH, followed by MeC(O)H dissociation and Si−H oxidative addition of Et_3SiH. As **b** has three different one-electron-donor ligands, **b** may exhibit three kinds of couplings: coupling with H and SR to give **a**, H and $SiEt_3$ coupling to give **a′**, and coupling with SR and $SiEt_3$ to give **c**. The first two are reversible, but the last one is presumably irreversible. Complex **c** thus formed reacts with Et_3SiH to give **d**, followed by H_2 reductive elimination to reproduce **a** (cycle A). Alternatively, **c** reacts with RSH to give **d′**, followed by H_2 reductive elimination to regenerate **a′** (cycle B).

In order to obtain insight into the catalytic cycle, a stoichiometric reaction of CpFe(CO)(py)($SiEt_3$) (py = pyridine) (**2**) with PhSH was examined. Complex **2** is considered to be a synthon of **a**, because the py in **2** is known to dissociate readily to give **a**.[11] The products in this reaction were SPh-bridged dinuclear Fe complex (**3**), free py, and Et_3SiH (Scheme 2). Complex **3** is presumably formed according to the reaction sequence of **2** → **a** → **b** → **a′** → **3**. Next, a reaction of PhSH with Et_3SiH in the presence of **3** as a catalyst was examined under the same reaction conditions shown in Table 1, and a TON of 0.4 was obtained (Table 1, entry 8). The value is less than one-tenth of that when **1** is used as a catalyst. The results suggest that the dehydrogenative coupling of thiol and hydrosilane catalyzed by **1** does not proceed *via* **a′**; that is, cycle A rather than cycle B is more plausible. Other results supporting cycle A were obtained in a stoichiometric reaction of **1**, Et_3SiH, and PhSH in a 1:1:1 ratio. In this reaction 12% of **3** based on **1** was formed. The low yield suggests that **1′** favorably reacts with Et_3SiH to give **a**. If **1′** mainly reacts with PhSH, **a′** would be formed and then converted into **3**, causing a higher yield of **3**.

In conclusion, we have established an unprecedented dehydrogenative coupling of thiol and hydrosilane catalyzed by an iron complex to give silylthioether. It should be noted that (i) the dehydrogenative coupling can be attained by a complex of a readily available and environmentally friendly iron, (ii) the iron complex serves as a catalyst, although sulfur-containing compounds such as thiol and silylthioether exist in the reaction system, and (iii) the iron catalyst produces only a hetero-dehydrogenative coupling product (silylthioether) and no homo-dehydrogenative coupling products such as disulfide or disilane. A plausible catalytic cycle is proposed that involves a 16*e* species CpFe(CO)(SiR'_3) reacting with RSH to give an Fe(IV) species CpFe(CO)(SR'_3)(SR)(H), followed by reductive elimination to give $RSSiR'_3$.

■ ASSOCIATED CONTENT

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

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nakazawa@sci.osaka-cu.ac.jp.

■ ACKNOWLEDGMENT

This work was supported by a Challenging Exploratory Research (No. 21655022) grant from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

■ REFERENCES

(1) (a) Green, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; John Wiley & Sons: New York, 1999; p 116. (b) Sartori, G.; Ballini, R.; Bigi, F.; Bosica, G.; Maggi, R.; Righi, P. *Chem. Rev.* **2004**, *104*, 199–250.

(2) Cooper, B. E. *Chem. Ind.* **1978**, 794–797.

(3) (a) Abel, W. W. *J. Chem. Soc.* **1960**, 4406–4409. *J. Chem. Soc.* **1961**, 4933–4935. (b) Ruehlmann, K.; Kaufmann, O.; Knopf, D. *J. Prakt. Chem.* **1962**, *18*, 131–140. (c) Gilman, H.; Lichtenwalter, G. D. *J. Org. Chem.* **1960**, *25*, 1064–1065. (d) Birkofer, L.; Ritter, A.; Goller, H. *Chem. Ber.* **1963**, *96*, 3289–3292. (e) Wang, J. T.; van Dyke, C. H. *Chem. Commun.* **1967**, *24*, 928–929. (f) Thomson, J. B.; Djerassi, C. *J. Org. Chem.* **1967**, *32*, 3904–3919.

(4) Armitage, D. A. F. *Chemistry of Compounds with Silicon-Sulphur, Silicon-Selenium and Silicon-Tellurium Bonds*; Patai, S.; Rappoport, Z. Eds.; John Wiley & Sons: Toronto, 1991; p 213 and references therein.

(5) Baruah, J. B.; Osakada, K.; Yamamoto, T. *Organometallics* **1996**, *15*, 456—459, and references therein.

(6) Corriu, R. J. P.; Fernadez, J. M.; Guerin, C.; Kpton, A. *Bull. Soc. Chem. Belg.* **1980**, *39*, 783–790.

(7) Sommer, L. H.; Citron, J. P. *J. Org. Chem.* **1967**, *32*, 2470–2472.

(8) (a) Ojima, I.; Nihonyanagi, M. *J. Organomet. Chem.* **1973**, *50*, C26–C28. (b) Ojima, I. *J. Organomet. Chem.* **1973**, *57*, C42–C44. (c) Brauah, J. B.; Osakada, K.; Yamamoto, T. *J. Mol. Catal. A: Chem.* **1995**, *101*, 17–24. (d) Chauhan, B. P. S.; Boudjouk, P. *Tetrahedron Lett.* **2000**, *41*, 1127–1130.

(9) Chung, M.-K.; Schlaf, M. *J. Am. Chem. Soc.* **2004**, *126*, 7386–7392.

(10) Harrison, D. J.; Edwards, D. R.; McDonald, R.; Rosenberg, L. *Dalton Trans.* **2008**, 3401–3411.

(11) (a) Iwata, M.; Okazaki, M.; Tobita, H. *Chem. Commun.* **2003**, 2744–2745. (b) Hashimoto, H.; Matsuda, A.; Tobita, H. *Chem. Lett.* **2005**, *34*, 1374–1375. (c) Nakazawa, H.; Itazaki, M.; Kamata, K.; Ueda, K. *Chem. Asian J.* **2007**, *2*, 882–888. (d) Fukumoto, K.; Oya, T.; Itazaki, M.; Nakazawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 38–39. (e) Itazaki, M.; Kamitani, M.; Ueda., K.; Nakazawa, H. *Organometallics* **2009**, *28*, 3601–3603.