Si–Si Coupling

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Iron-Catalyzed Dehydrogenative Coupling of Tertiary Silanes**

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Silicon–silicon bond formation is an important step in the synthesis of disilanes, oligosilanes, and polysilanes with interesting electronic, optoelectronic, and photoreactive properties. One widely used method is the Wurtz-type condensation of halosilanes in the presence of alkali metals.[1] However, this conventional method has several drawbacks, including the harsh reaction conditions, the formation of by-products, such as di- or polysiloxanes (in which the oxygen atom stems from the sodium surface), and its inapplicability to functional silicon compounds. Transition-metal complexes have also been used as catalysts to form Si–Si bonds;[2–4] however, in most cases only complexes of Group 4, 9, and 10 transition metals can be used. They are effective for primary and secondary silanes but are much less active with tertiary silanes.[5] Despite the development of Zr,[6] Hf,[6] Ti/Zr,[7] Mn,[8] Rh,[9] Ir,[10] Pd,[11] Pt,[12] and Sm[13] catalysts, the need remains for new methods with cheap and environmentally friendly catalysts.

Recently, we found that catalytic C–CN bond cleavage and C–Si bond formation occurs in the reaction of organonitriles with $HSiR_3$ in the presence of $[CpFe(CO)_2Me]$ (Cp stands for η^5-cyclopentadienyl).[14] The main product was a silyl cyanide (R_3SiCN), but a trace amount of a disilane ($R_3Si{-}SiR_3$) was detected. If the reaction system could be modified to make the disilane become the main product, the reaction would be distinguished by its low cost, the ready availability of starting materials, and the environmentally benign character of the iron complex, in combination with applicability to tertiary silanes. Encouraged by the formation of the disilane product, although only a trace amount, we envisioned the application of iron catalysts in the dehydrogenative Si–Si coupling reaction [Eq. (1)].

$$2\,R_3Si{-}H \xrightarrow{\text{Fe (cat.)}} R_3Si{-}SiR_3 + H_2 \qquad (1)$$

According to reaction conditions described previously,[14c] $PhMe_2SiH$ was photolyzed in THF in the presence of a catalytic amount of $[CpFe(CO)_2Me]$ and in the absence of MeCN. Only a trace amount of $PhMe_2Si{-}SiMe_2Ph$ was formed (Table 1, entry 1). The same result was obtained when hexane and benzene were used as solvents (Table 1, entries 2 and 3). When dimethoxyethane (DME) was used, 24 % of the silane was converted into the corresponding disilane (Table 1, entry 4). Surprisingly, the disilane was formed in 83 % yield in MeCN (Table 1, entry 5); the corresponding silyl cyanide was not obtained. However, this system was not compatible with other tertiary silanes. In the reaction with Ph_2MeSiH, for example, only a trace amount of the disilane was formed, and most of the silane remained unreacted. Finally, dimethylformamide (DMF) was found to be an excellent solvent for the dehydrogenative coupling reaction. Quantitative disilane formation was observed upon photoirradiation for only 1 h (Table 1, entry 6). A decrease in the amount of the iron catalyst from 4 to 0.5 mol % also led to quantitative conversion upon photoirradiation for 48 h (Table 1, entry 7). The iron catalyst/DMF system was effective for the dehydrogenative coupling of other tertiary silanes: A C_6F_5-substituted silane, $(C_6F_5)Me_2SiH$, underwent the reaction to give the product in 83 % yield (Table 1,

Table 1: Iron-catalyzed dehydrogenative coupling of hydrosilanes.[a]

$$2R_3SiH \xrightarrow[h\nu]{\text{4 mol\% }[Cp(CO)_2FeMe]} R_3Si{-}SiR_3 + H_2$$

Entry	Hydrosilane	Solvent	*t* [h]	Yield [%][b]
1	$PhMe_2SiH$	THF	24	trace
2	$PhMe_2SiH$	hexane	24	trace
3	$PhMe_2SiH$	benzene	24	trace
4	$PhMe_2SiH$	DME	24	24
5	$PhMe_2SiH$	MeCN	24	83
6	$PhMe_2SiH$	DMF	1	99
7[c]	$PhMe_2SiH$	DMF	48	99
8	$(C_6F_5)Me_2SiH$	DMF	6	83
9	Ph_2MeSiH	DMF	24	99
10[d]	Ph_3SiH	DMF	48	95
11	$(PhCH_2)Me_2SiH$	DMF	24	95
12	$(CH_2{=}CH)PhMeSiH$	DMF	24	91
13	$CpFe(C_5H_4Me_2SiH)$	DMF	24	92
14	Et_3SiH	DMF	12	51
15	$(i\text{PrO})PhMeSiH$	DMF	12	69
16	$(Me_3SiO)Me_2SiH$	DMF	12	65
17	$(Me_3SiO)_2MeSiH$	DMF	12	50
18[e]	$PhMe_2SiH$	DMF	6	72
19[e]	Ph_2MeSiH	DMF	48	50
20[e]	$(PhCH_2)Me_2SiH$	DMF	48	38
21[e]	$(CH_2{=}CH)PhMeSiH$	DMF	48	30

[a] Reaction conditions: hydrosilane (5.00 mmol), catalyst (0.20 mmol), DMF (4.6 mL), photoirradiation, room temperature. [b] Yield of the isolated product. [c] Catalyst: 0.5 mol %. [d] Catalyst: 10 mol %. [e] The reaction was carried out at 80 °C without photoirradiation.

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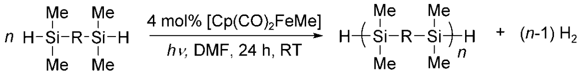
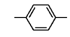
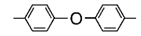
entry 8). Ph_2MeSiH, Ph_3SiH, $(PhCH_2)Me_2SiH$, $(CH_2{=}CH)PhMeSiH$, and $[CpFe(C_5H_4Me_2SiH)]$ were all converted into the corresponding disilanes in excellent yields (Table 1, entries 9–13). The result with the substrate $(CH_2{=}CH)PhMeSiH$ (Table 1, entry 12) was particularly pleasing, as the vinyl group remained intact under the hydrosilation conditions. Triethylsilane also underwent the coupling reaction in moderate yield (Table 1, entry 14), and the condensation of hydrosilanes containing one or two *i*PrO or Me_3SiO groups was successful (Table 1, entries 15–17). Further experiments demonstrated that photoirradiation was not necessary; the thermal reaction produced the corresponding disilanes, although the yields were lower (Table 1, entries 18–21).

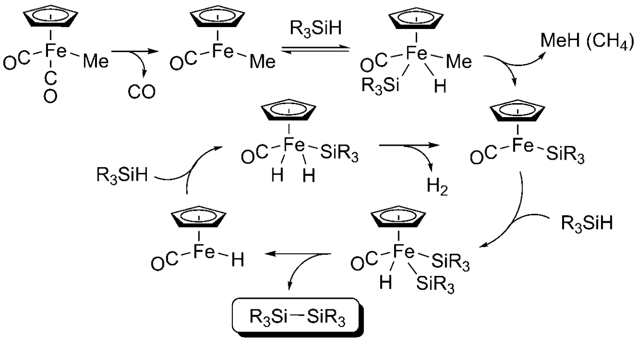
Our iron catalyst/DMF system is useful for the dehydrogenative coupling of $HR'_2Si{-}R{-}SiR'_2H$ to generate polymers with Si–Si bonds in the polymer backbone. The polycondensation of bis(dimethylsilyl)benzene, -amine, -ferrocene, and -diphenyl ether proceeded in excellent yields (Table 2). Although the polymer obtained from bis(dimethylsilyl)benzene (Table 2, entry 1) has been prepared by other synthetic routes,[11,13,15] our system gave the polymer with the highest average molecular weight. Various polyferrocenylsilanes with an (-Fe-Cp-Si-Cp-)$_n$ backbone were synthesized by Manners, who examined their properties extensively.[16] The polymer obtained from 1,1′-bis(dimethylsilyl)ferrocene (Table 2, entry 3) is the first example of polyferrocenyldisilane, with an (-Fe-Cp-Si-Si-Cp-)$_n$ backbone. The catalytic formation of a polymer with an (-R-Si-Si-)$_n$ backbone was only reported once previously.[12] A platinum catalyst was used, but the polycondensation mechanism was not described.

Table 2: Polycondensation of $HMe_2Si\text{-}R\text{-}SiMe_2H$.



$$n\ \mathrm{H{-}SiMe_2{-}R{-}SiMe_2{-}H} \xrightarrow[h\nu,\ \mathrm{DMF,\ 24\ h,\ RT}]{4\ \mathrm{mol\%}\ [\mathrm{Cp(CO)_2FeMe}]} \mathrm{H{-}(SiMe_2{-}R{-}SiMe_2)_{\mathit{n}}{-}H} + (n-1)\ \mathrm{H_2}$$

Entry	R	Yield [%]	M_n	M_w/M_n	n
1		99	4670	1.74	23
2	$-\overset{H}{N}-$	99	35410	1.64	270
3	$-(C_5H_4)Fe(C_5H_4)-$	96	6560	1.35	22
4		78	17790	2.17	63



Scheme 1. Proposed catalytic cycle.

A proposed catalytic cycle is presented in Scheme 1 for the reaction of R_3SiH with $[CpFe(CO)_2Me]$ as the catalyst precursor. One CO ligand in the precursor is released to yield [CpFe(CO)Me], which reacts with R_3SiH to give $[CpFe(CO)Me(H)(SiR_3)]$. The reductive elimination of CH_4 yields $[CpFe(CO)(SiR_3)]$, and the oxidative addition of an Si–H bond to the 16-electron iron complex then produces $[CpFe(CO)(H)(SiR_3)_2]$.[17] The two silyl groups in the complex are coupled to give a disilane[18,19] and [CpFe(CO)H], which then reacts with R_3SiH to give $[CpFe(CO)H_2(SiR_3)]$. The reductive elimination of H_2 reproduces $[CpFe(CO)(SiR_3)]$ to complete the catalytic cycle. A reaction mechanism involving σ-bond-metathesis reactions, which have been proposed for early-transition-metal complexes rather than the oxidative addition of the Si–H bond to a 16-electron iron species, can not be ruled out.[6] The evolution of CH_4 gas was confirmed.[14] To check the formation of H_2, the ^1H NMR spectrum of the reaction mixture was recorded in C_6D_6. A very weak signal at $\delta = 4.46$ ppm was assigned to H_2, and a strong and unexpected signal at $\delta = 2.05$ ppm was attributed to NMe_3. GC–MS of a reaction in $[D_7]$DMF revealed the formation of $(CDH_2)N(CD_3)_2$ (*m*/*z* 66). Therefore, the formation of NMe_3 is considered to be derived from the reaction of H_2 generated with DMF with the assistance of some iron catalyst that exists in this system.[20,21]

In the catalytic cycle, the hydrido(disilyl)iron complex $[CpFe(CO)(H)(SiR_3)_2]$ is the most important species for disilane formation. Therefore, we planned to isolate and check the catalytic activity of the complex. Tobita and co-workers reported that an iron pyridine complex was a good precursor for the oxidative addition of an Si–H bond to the iron center.[22] We also reported previously that an iron pyridine complex could be converted into a catalytically active species through the release of the pyridine ligand.[14c] We therefore examined the reactions of the corresponding pyridine complexes **1** and $[CpFe(CO)(py)(SiEt_3)]$ (py = pyridine) with $PhMe_2SiH$. We isolated the hydrido(disilyl)iron(IV) complexes $[CpFe(CO)(H)(SiMe_2Ph)_2]$ (**2**) and $[CpFe(CO)(H)(SiEt_3)(SiMe_2Ph)]$ (**3**), respectively (Scheme 2).

The products **1**–**3** were characterized by conventional spectroscopic and analytical methods, as well as X-ray crystallography.[23] The molecular structure of **1** is similar to that of previously reported silyl(pyridine)iron complexes.[14c,24] In the structures of **2** and **3** (Figure 1), the Fe^{IV} center has a four-legged-piano-stool geometry, with C_5H_5

$$\underset{\substack{L\,=\,3,5\text{-dimethylpyridine}\\ \mathbf{1}}}{[\mathrm{Cp(CO)Fe(L)(SiMe_2Ph)}]} \xrightarrow[\mathrm{C_6H_6,\ 50\ ^\circ C}]{\mathrm{PhMe_2SiH}} \underset{\mathbf{2}:\ 85\%}{[\mathrm{Cp(CO)FeH(SiMe_2Ph)_2}]} \xrightarrow[\mathrm{DMF,\ 3\ h}]{h\nu} \underset{100\%}{(\mathrm{PhMe_2Si})_2}$$

$$\underset{L\,=\,\text{pyridine}}{[\mathrm{Cp(CO)Fe(L)(SiEt_3)}]} \xrightarrow[\mathrm{C_6H_6,\ RT}]{\mathrm{PhMe_2SiH}} \underset{\mathbf{3}:\ 69\%}{[\mathrm{Cp(CO)FeH(SiEt_3)(SiMe_2Ph)}]} \xrightarrow[\mathrm{DMF,\ 12\ h}]{h\nu} \underset{\substack{33\%\\ (\mathrm{PhMe_2Si})_2\\ 33\%}}{\mathrm{Et_3Si{-}SiMe_2Ph}}$$

Scheme 2. Synthesis from pyridine complexes and reactivity of the hydrido(disilyl)iron(IV) complexes **2** and **3**.

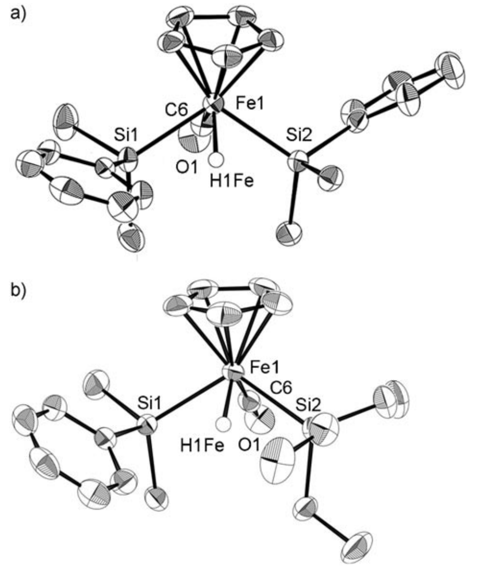


Figure 1. ORTEP drawings of a) **2** and b) **3** with thermal ellipsoids at the 50% probability level.

bound in an η^5 fashion, one terminal CO ligand, one hydrido ligand, and two silyl ligands. Only three crystal structures have been reported previously for hydrido(disilyl)iron(IV) complexes,[25] and **3** is the first example with two different silyl ligands. A photoreaction of **2** in DMF afforded $(PhMe_2Si)_2$ (100%), and the equivalent reaction of **3** gave a mixture of $Et_3Si{-}SiMe_2Ph$ (33%) and $(PhMe_2Si)_2$ (33%; Scheme 2). Thus, silyl-ligand exchange appears to occur at a similar rate to that of the silyl coupling. The photoreactions of **2** and **3** in benzene did not generate the corresponding disilane at all, which shows that DMF plays an important role in the reductive elimination of disilane. The catalytic activity of **2** was also examined. Photoirradiation of a solution of $PhMe_2SiH$ in DMF in the presence of **2** (4 mol%) yielded $(PhMe_2Si)_2$ quantitatively. This result demonstrates clearly that a hydrido(disilyl)iron(IV) complex is an intermediate in our catalytic system. The effective formation of an unsymmetrical disilane was observed in the photoreaction of $PhMe_2SiH$ and Et_3SiH in a 1:3 molar ratio in the presence of $[CpFe(CO)_2Me]$ (4 mol% with respect to $PhMe_2SiH$): The coupling product $PhMe_2Si{-}SiEt_3$ (78% yield with respect to $PhMe_2SiH$) was formed as the major product together with the homocoupling products $(PhMe_2Si)_2$ (10%) and $(Et_3Si)_2$ (18%) as by-products.

In summary, we have described an unprecedented iron-catalyzed dehydrogenative coupling of hydrosilanes. This catalytic system is applicable not only to tertiary silanes, which are known to be difficult to convert into disilanes, but also to functionalized tertiary silanes with halophenyl, vinyl, alkoxy, or siloxy substituents. A variety of silanes $R_2R'SiH$ can be prepared from chlorosilanes $R_2Si(H)Cl$, which are available as by-products of industrial syntheses. However, the dehydrogenative coupling reactions required to link these "monomers" have proved elusive. Our findings open a convenient synthetic route to a variety of disilanes, including unsymmetrical disilanes and polymers with Si–Si bonds in the backbone. Consideration of the catalytic reaction pathway revealed the intermediacy of a hydrido(disilyl)iron(IV) complex. Furthermore, DMF was found to play an essential double role in promoting catalysis: It forces the elimination of the disilane from an otherwise inert iron disilyl complex to occur with high efficiency and specificity, and it scavenges the H_2 produced in the reaction and thus prevents the formation of the messy product mixtures observed with other solvents.

Experimental Section

Typical procedure for disilane synthesis: A solution of $PhMe_2SiH$ (5.00 mmol, 766 μL) and $[CpFe(CO)_2Me]$ (4 mol%, 0.20 mmol, 38 mg) in DMF (4.6 mL) was irradiated with a 400 W medium-pressure mercury arc lamp at 25 °C for 1 h under a nitrogen atmosphere. Volatile materials were then removed under reduced pressure, and the resulting mixture was purified directly by flash chromatography (CH_2Cl_2/hexane 1:3) to afford $PhMe_2Si{-}SiMe_2Ph$ (676 mg, >99%).

2: A solution of $[CpFe(CO)(SiMe_2Ph)(dmp)]$ (**1**; 0.55 mmol, 215 mg; dmp = 3,5-dimethylpyridine) and $PhMe_2SiH$ (1.64 mmol, 252 μL) in benzene (10 mL) was stirred at 50 °C for 2 h. Volatile materials were then removed under reduced pressure, and a solution of $PhMe_2SiH$ (1.10 mmol, 168 μL) in benzene (10 mL) was added. Volatile materials were again removed under reduced pressure, and the resulting dark red oil was dissolved in hexane (1 mL). The solution was cooled at −65 °C for 4 weeks, and the resulting colorless crystals were filtered off and dried in vacuo to give **2** (195 mg, 85%). ^{1}H NMR (400 MHz, C_6D_6): $\delta = -13.22$ (s, 1 H, FeH), 0.63 (s, 6 H, $Si(CH_3)_2Ph$), 0.77 (s, 6 H, $Si(CH_3)_2Ph$), 3.86 (s, 5 H, C_5H_5), 7.26–7.35 (m, 6 H, C_6H_5), 7.65–7.72 ppm (m, 4 H, C_6H_5); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6): $\delta = 7.3$ ($Si(CH_3)_2Ph$), 8.0 ($Si(CH_3)_2Ph$), 84.8 (C_5H_5), 133.1 (C_6H_5), 147.6 (*ipso*-C_6H_5), 214.0 ppm (CO); $^{29}Si\{^1H\}$ NMR (79.3 MHz, C_6D_6): $\delta = 30.0$ ppm; elemental analysis: calcd (%) for $C_{22}H_{28}OSi_2Fe$: C 62.84, H 6.71; found: C 62.70, H 6.76%.

3: In a procedure analogous to that outlined above, $[CpFe(CO)(SiEt_3)(py)]$[14c] (1.42 mmol, 489 mg) and $PhMe_2SiH$ (8.53 mmol, 1.31 mL) gave **3** (395 mg, 0.986 mmol, 69%) as colorless crystals. ^{1}H NMR (400 MHz, C_6D_6): $\delta = -13.71$ (s, 1H, FeH), 0.68 (s, 3 H, $Si(CH_3)_2Ph$), 0.76 (s, 3 H, $Si(CH_3)_2Ph$), 0.87 (q, $J_{H,H} = 7.6$ Hz, 6 H, $Si(CH_2CH_3)_3$), 1.10 (t, $J_{H,H} = 7.6$ Hz, 9 H, $Si(CH_2CH_3)_3$), 3.98 (s, 5 H, C_5H_5), 7.26 (t, $J_{H,H} = 7.6$ Hz, 3 H, C_6H_5), 7.72 ppm (d, $J_{H,H} = 7.6$ Hz, 2 H, C_6H_5); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6): $\delta = 7.3$ (CH_3), 7.9 (CH_3), 9.6 ($Si(CH_2CH_3)_3$), 12.9 ($Si(CH_2CH_3)_3$), 84.1 (C_5H_5), 127.9 (C_6H_5), 128.1 (C_6H_5), 133.1 (C_6H_5), 148.0 (*ipso*-C_6H_5), 214.2 ppm (CO); $^{29}Si\{^1H\}$ NMR (79.3 MHz, C_6D_6): $\delta = 29.8$, 45.8 ppm; elemental analysis: calcd (%) for $C_{20}H_{32}OSi_2Fe$: C 59.98, H 8.05; found: C 60.07, H 7.98.

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[23] X-ray crystallographic data for **1**: $C_{21}H_{25}NOSiFe$, MW = 391.36, orthorhombic, $P2_12_12_1$, $a = 8.070(3)$, $b = 13.160(5)$, $c = 18.770(7)$ Å, $V = 1993.4(12)$ Å^3, $T = 203(2)$ K, $Z = 4$, $\rho_{cald} = 1.304\ g\,cm^{-3}$, 19600 reflections collected, 4532 unique reflections ($R_{int} = 0.0892$), $R[I > 2\sigma(I)] = 0.0886$, $wR_2 = 0.1573$, GOF = 1.000; **2**: $C_{22}H_{28}OSi_2Fe$, $MW = 420.47$, orthorhombic, *Pbca*, $a = 13.2567(14)$, $b = 17.2015(17)$, $c = 18.947(2)$ Å, $V = 4320.6(8)$ Å^3, $T = 200(2)$ K, $Z = 8$, $\rho_{cald} = 1.293\ g\,cm^{-3}$, 40211 reflections collected, 4920 unique reflections ($R_{int} = 0.0352$), $R[I > 2\sigma(I)] = 0.0545$, $wR_2 = 0.0941$, GOF = 1.000; **3**: $C_{20}H_{32}OSi_2Fe$, $MW = 400.49$, monoclinic, $P2_1/c$, $a = 14.6337(11)$, $b = 18.6605(12)$, $c = 8.1950(6)$ Å, $\beta = 106.560(3)°$, $V = 2145.0(3)$ Å^3, $T = 203(2)$ K, $Z = 4$, $\rho_{cald} = 1.240\ g\,cm^{-3}$, 16209 reflections collected, 4840 unique reflections ($R_{int} = 0.0318$), $R[I > 2\sigma(I)] = 0.0432$, $wR_2 = 0.1073$, GOF = 1.000. CCDC 677314 (**1**), CCDC 677315 (**2**), and CCDC 677316 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

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