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Photoactivated silicon–oxygen and silicon–nitrogen heterodehydrocoupling with a commercially available iron compound†

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Silicon–oxygen and silicon–nitrogen heterodehydrocoupling catalyzed by the commercially available cyclopentadienyl dicarbonyl iron dimer $[CpFe(CO)_2]_2$ (**1**) under photochemical conditions is reported. Reactions between alcohols and $PhSiH_3$ with catalytic **1** under visible-light irradiation produced silyl ethers quantitively. Reactions between either secondary or tertiary silanes and alcohols also produced silyl ethers, however, these reactions were marked by their longer reaction times and lower conversions. Reactions of either primary or secondary amines and silanes with catalytic **1** demonstrated mixed efficiency, featuring conversions of 20–100%. Mechanistic study indicates that an iron silyl compound is unimportant in the bond-formation step and argues for either a nucleophilic alkoxide or amide intermediate. Most important, mechanistic study reveals that the most immediate hurdle in the catalysis is the poor activation of **1**, demonstrating the necessity to fully activate the catalyst to realize the potential of iron in this reactivity.

Introduction

The dominance of noble metals in catalysis is, rightly, under assault. The importance of metals such as palladium, platinum, rhodium, and iridium is irrefutable, with some of the more representative transformations including palladium-catalyzed C–C or C–N cross-coupling,[1,2] platinum-catalyzed hydrosilylation of olefins,[3] rhodium-catalyzed hydrogenation and hydroformylation,[4,5] and iridium-catalyzed C–H activation.[6] Despite their high utility to both academia and industry, there has been a shift away from these noble metals due to their cost, toxicity, and most importantly, increasing scarcity.[7] In their stead, a plethora of transformations have emerged, including C–C cross-coupling,[8] hydrosilylation of olefins and aldehydes,[9,10] and C–H activation,[11,12] by base metals including iron, manganese, and cobalt. Iron is particularly attractive in catalysis due to its high abundance and access to a range of oxidation states.[13,14] However, a variety of factors limit base metal-catalyzed transformations, such as high catalyst loadings, significant heating, or other forcing conditions to achieve conversions comparable to those with noble metal catalysts.[15] Iron is no exception to these limitations, and it is also noteworthy to mention that examples of mild, photoactivated iron compounds are scarce in comparison to thermally activated catalysts.[15,16] This becomes an unfortunate realization, as the development and improvement of iron-based systems is paramount to inexpensive and green chemical transformations.

Concomitant with the improvement of base metal catalysis, chemists have been challenged with the development of greener, efficient synthetic pathways.[17] Heterodehydrocoupling has gained momentum in this aspect, due to the atom-economical formation of element–element bonds. The evolution of H_2 as the sole byproduct is also attractive, providing an excellent driving force and simplifying the purification of products. It is also important to recognize that dehydrocoupling is often symmetry forbidden, necessitating the use of either main group or transition-metal compounds.[18] Consequentially, the identification and development of heterodehydrocoupling catalysts is extremely attractive for green, catalytic transformations.

The commercially available iron dimer $[CpFe(CO)_2]_2$ (**1**) is a rare example of a mild, photoactivated iron compound. Heterodehydrocoupling *via* compound **1** has already been demonstrated on amine-borane substrates by Manners and co-workers as well as between dimethylformamide and $PhMe_2SiH$ by Waterman and co-workers.[19,20] Furthermore, compound **1** is known to photoactivate under either ultraviolet or visible-light irradiation to produce two equiv. of the 17-electron compound, **3**, *via* the all terminal carbonyl intermediate **2**

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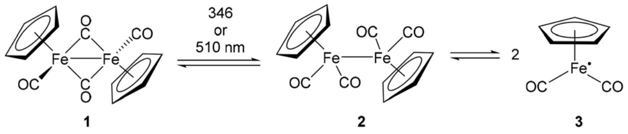


Scheme 1 Photoactivation pathway of compound **1** under either ultraviolet or visible-light irradiation.[17]

(Scheme 1).[21] Thus, the photoirradiation of compound **1** may provide a green and facile method to forming other element–element bonds in the main group.

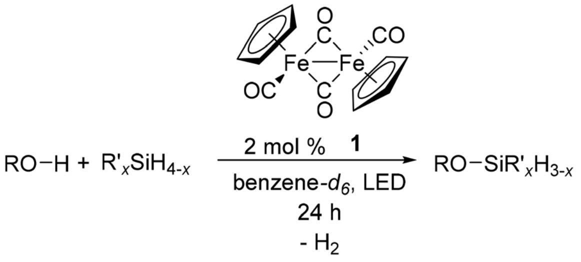
Molecules and materials containing Si–O and Si–N possess diverse applications due to their unique chemical characteristics. Silyl ethers, or small molecules containing Si–O bonds, are of importance in the protection of alcohols.[22] Poly(silyl ethers) are appealing compounds due their degradability in acidic and basic medium.[23] Molecules containing Si–N bonds such as silamines are well established as bases and silylating agents in organic syntheses,[24] while poly(silazanes) are sought after for their potential as ceramic precursors.[25] Although Si–O heterodehydrocoupling using **1** has not been reported, derivatives of **1** catalyzing similar transformations are known, most notably by Nakazawa and co-workers in Si–O and Si–S heterodehydrocoupling *via* $Cp(CO)_2FeMe$.[26,27] Herein, we report **1** as a heterodehydrocoupling catalyst in the formation of Si–O and Si–N bonds. Mechanistic study of the reaction indicates nucleophilic attack of a silane by an intermediate iron-alkoxide or -amide, but more germane to the further development of iron, complete activation of **1** was not achieved in these reactions, which suggests that full activation of iron catalyst precursors is an important pursuit in developing base metal catalysis.

Results and discussion

Condition optimization

This study sought to expand the scope of heterodehydrocoupling by **1**,[19,20] initially investigating coupling of primary silanes and alcohols. An equimolar amount of ^{n}PrOH and $PhSiH_3$ in the presence of 1 mol% of **1** in a benzene-d_6 solution was irradiated under visible-light from a commercial LED bulb. After 24 h, the mixture showed 32% conversion to $PhSiH_2(O^{n}Pr)$ and 43% conversion to $PhSiH(O^{n}Pr)_2$ as measured by ^{1}H NMR spectroscopy. Comparable conversions were not achieved under ultraviolet irradiation, which was attributed to a known, unproductive activation pathway of **1** involving the loss of CO.[21] The molar equivalences of alcohol and silane were varied in an effort to generate the third addition silyl ether product $PhSi(O^{n}Pr)_3$. Four-fold excess of silane to one equivalent of alcohol showed little effect on silyl ether generation. However, increasing the concentration of alcohol four-fold and the catalyst loading to 2 mol% of **1** generated $PhSi(O^{n}Pr)_3$ in quantitative conversion after 24 h according to ^{1}H NMR spectroscopy (Table 1, entry 1).[28] These reaction conditions were uniformly applied to other substrates (eqn (1)).

Catalytic Si–O heterodehydrocoupling



$$RO{-}H + R'_xSiH_{4-x} \xrightarrow[\text{benzene-}d_6\text{, LED; 24 h; - }H_2]{\text{2 mol \% } \mathbf{1}} RO{-}SiR'_xH_{3-x} \quad (1)$$

Coupling of alcohols such as BnOH ($Bn = CH_2Ph$) and ^{i}PrOH with $PhSiH_3$ was also accomplished with **1**. Reaction of BnOH and $PhSiH_3$ in a 4 : 1 ratio generated $PhSi(OBn)_3$ after 6 h, as determined by ^{1}H and $^{29}Si\{^{1}H\}$ NMR spectroscopy (Table 1, entry 2).[29,30] Analogously, Parkin and co-workers have reported Si–O heterodehydrocoupling between $PhSiH_3$ and BnOH *via*

Table 1 Catalytic conditions for the coupling of alcohols and silanes[a]

Entry	Silane	Alcohol	Equiv.[b]	Product	Conversion[c] (%)
1	$PhSiH_3$	^{n}PrOH	4.0	$PhSi(O^{n}Pr)_3$	100
2[d]	$PhSiH_3$	BnOH	4.0	$PhSi(OBn)_3$	100
3	$PhSiH_3$	^{i}PrOH	5.0	$PhSi(O^{i}Pr)_3$	100
4	$PhMeSiH_2$	^{n}PrOH	4.0	$PhMeSi(O^{n}Pr)_2$[e]	100
5	$PhMeSiH_2$	BnOH	4.0	$PhMeSi(OBn)_2$	100
6	$PhMeSiH_2$	^{i}PrOH	5.0	$PhMeSiH(O^{i}Pr)$[e]	9
				$PhMeSi(O^{i}Pr)_2$[e]	91
7	Ph_2SiH_2	^{n}PrOH	4.0	$Ph_2Si(O^{n}Pr)_2$[e]	100
8	Ph_2SiH_2	BnOH	4.0	$Ph_2Si(OBn)_2$	100
9	Ph_2SiH_2	^{i}PrOH	5.0	$Ph_2SiH(O^{i}Pr)$	100
10	$PhMe_2SiH$	^{n}PrOH	5.0	$PhMe_2Si(O^{n}Pr)$[e]	93
11	$PhMe_2SiH$	BnOH	5.0	$PhMe_2Si(OBn)$	100
12	$PhMe_2SiH$	^{i}PrOH	6.0	$PhMe_2Si(O^{i}Pr)$	93

[a] Conditions: 2.0 mol% of **1** under visible-light irradiation in benzene-d_6 solution at ambient temperature for 24 h unless otherwise specified. Catalyst loading was with respect to silane. Reactions were monitored by ^{1}H and $^{29}Si\{^{1}H\}$ NMR spectroscopy. [b] Refers to mol. of alcohol per mol. of silane. [c] Conversions were determined by ^{1}H NMR integration. [d] Reaction was complete in 6 h. [e] Literature spectral data of these silyl ethers have not been previously reported.

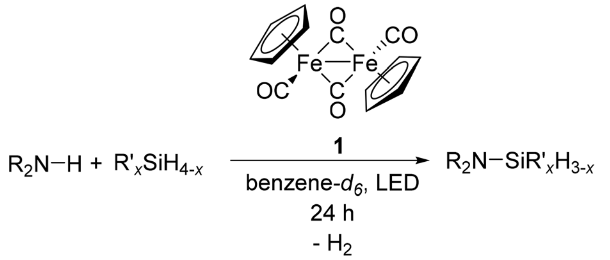
nickel-catalysts, however, to a mixture of $PhSiH(OBn)_2$ and $PhSi(OBn)_3$ after 24 h at 80 °C.[31] Reactions between ^iPrOH and $PhSiH_3$ at similar alcohol/silane ratio proceeded to incomplete conversion from $PhSiH_3$ after 24 h, which prompted an increase in the alcohol/silane ratio. Reaction of a 5 : 1 mixture of ^iPrOH and $PhSiH_3$ completely converted from $PhSiH_3$ by 24 h to $PhSi(O^iPr)_3$ (Table 1, entry 3).[30,32,33] The silyl ether $PhSi(O^iPr)_3$ has previously been synthesized utilizing a half-sandwich iron complex by Royo and co-workers; although this was accomplished at slightly lower catalyst loadings of 1 mol% after 8 h, only 66% conversion was afforded at 70 °C.[33] Attempts at coupling $PhSiH_3$ with heavily encumbered alcohols such as ^tBuOH with **1** did not produce silyl ethers according to ^1H NMR spectroscopy.

Heterodehydrocoupling with secondary silanes using compound **1** was also investigated. Reaction of $PhMeSiH_2$ and ^nPrOH in a 1 : 4 ratio generated a single peak at δ −18.07 in $^{29}Si\{^1H\}$ NMR spectroscopy after 24 h under irradiation, consistent with $PhMeSi(O^nPr)_2$ (Table 1, entry 4). The final resonance generated at δ 3.89 in ^1H NMR spectroscopy indicated 100% conversion to $PhMeSi(O^nPr)_2$. A similar strategy was applied to reactions of ^iPrOH and $PhSiH_3$ in a 5 : 1 ratio, where $PhMeSi(O^iPr)_2$ was afforded in 91% conversion with 9% of $PhMeSiH(O^iPr)$ remaining after 24 h (Table 1, entry 6). Reaction of excess BnOH with $PhMeSiH_2$ produced $PhMeSi(OBn)_2$ in 100% conversion after 24 h (Table 1, entry 5).[34]

Reaction of ^nPrOH and Ph_2SiH_2 under visible-light irradiation in the presence of **1** proceeded slowly according to ^1H NMR spectroscopy, but all starting material was consumed to a single new product. Isolation of pure product from the highly soluble Fp-catalyst remains a challenge, but in comparison to similar resonances of known compounds, it is hypothesized that $Ph_2Si(O^nPr)_2$ was generated in 100% conversion (Table 1, entry 7). Reactions BnOH and Ph_2SiH_2 in a 4 : 1 ratio produced $Ph_2Si(OBn)_2$ in 100% conversion as measured by ^1H NMR spectroscopy (Table 1, entry 8).[30,35] Several examples of hard-acid catalysts such as $KN(SiMe_3)_2$ and a Mn(V)-salen complex have quantitatively afforded $Ph_2Si(OBn)_2$ in significantly shorter reactions times, however, elevated heating appears to be a necessary factor in these reactions.[31,36,37] Interestingly, reacting 5 equiv. of ^iPrOH with Ph_2SiH_2 exclusively yielded $Ph_2SiH(O^iPr)$[25] in quantitative conversion with no evidence of the fully substituted product $Ph_2Si(O^iPr)_2$ (Table 1, entry 9).[30]

Reaction of ^nPrOH and $PhMe_2SiH$ in a 5 : 1 ratio afforded a new product, tentatively assigned to $PhMe_2Si(O^nPr)$ based on analogy to $PhMe_2Si(OBn)$ and $PhMe_2Si(O^iPr)$, in 93% conversion as a resonance at δ 6.67 in the $^{29}Si\{^1H\}$ NMR spectrum (Table 1, entry 10). Reaction of excess BnOH and $PhMe_2SiH$, however, showed complete disappearance of $PhMe_2SiH$ in the ^1H NMR spectrum and generation of $PhMe_2Si(OBn)$ after 24 h (Table 1, entry 11).[34,38] Reaction of ^iPrOH and $PhMe_2SiH$ in a 6 : 1 ratio showed 93% conversion to $PhMe_2Si(O^iPr)$ after 24 h according to ^1H NMR spectroscopy (Table 1, entry 12).[39] Finally, attempts at coupling alcohols to the tertiary alkyl silane Et_3SiH produced no change in ^1H NMR spectroscopy after 24 h.

Catalytic Si–N heterodehydrocoupling



$$R_2N{-}H + R'_xSiH_{4-x} \xrightarrow[\substack{\text{benzene-}d_6\text{, LED} \\ 24\text{ h} \\ -\,H_2}]{\mathbf{1}} R_2N{-}SiR'_xH_{3-x} \quad (2)$$

Compound **1** also proved to be competent at Si–N heterodehydrocoupling but at higher catalyst loadings (eqn (2)). Silamines were produced less efficiently than were silyl ethers, as evident by the longer reaction times and mixture of silamine products.

Treatment of $^nPrNH_2$ with $PhSiH_3$ in a 6 : 1 amine/silane ratio produced $PhSiH_2(HN^nPr)$ in only 13% conversion after 4 h by ^1H NMR spectroscopy. After 18 h, the reaction produced $PhSiH(HN^nPr)$ in 50% conversion and $PhSiH_2(HN^nPr)$ in 23% conversion (Table 2, entry 1).[40] Similar to trends in Si–O coupling, hard-acid catalysts appear to produce silamines in good conversions under heating.[41] The analogous reaction with $^tBuNH_2$ and $PhSiH_3$ produced $PhSiH_2(HN^tBu)$ in 100% after only 4 h according to ^1H NMR spectroscopy, and in 24 h, $PhSiH_2(HN^tBu)$ and $PhSiH(HN^tBu)$ were produced in 89% and 11% conversions (Table 2, entry 2).[42,43] The disparity between the two amines indicates that more basic (*i.e.*, nucleophilic) amines give greater silamine conversions. This observation was supported by reaction of 4 equiv. of $^iPrNH_2$ and $PhSiH_3$ to furnish $PhSiH_2(HN^iPr)$ in 100% conversion after 20 h according to ^1H NMR spectroscopy (Table 2, entry 4).[44] Moreover, reaction of 4.7 equiv. of Et_2NH with $PhSiH_3$ produced $PhSiH_2(NEt_2)$ and $PhSiH(NEt_2)_2$ in 29% and 71% conversions, respectively, after 24 h (Table 2, entry 5).[45] Finally, reaction of 4.6 equiv. of $PhNH_2$ with 9.3 mol% of 1, $PhSiH_2(HNPh)$ was afforded in only 20% conversion after 20 h (Table 2, entry 3).

Compound **1** was also demonstrated to be a competent heterodehydrocoupling with amines and $PhMeSiH_2$. Treatment of $^nPrNH_2$ with $PhMeSiH_2$ in a 5 : 1 amine/silane ratio affords the corresponding silamine $PhMeSiH(HN^nPr)$ in 60% conversion after 24 h by ^1H NMR spectroscopy (Table 2, entry 6).[44] Meanwhile, $PhMeSiH(HN^tBu)$ was generated in 100% conversion by ^1H NMR spectroscopy after 24 h (Table 2, entry 7).[44] Furthermore, reacting 4 equiv. of $^iPrNH_2$ with $PhMeSiH_2$ quantitatively produced $PhMeSiH(HN^iPr)$ after 24 h according to ^1H and ^1H–^{29}Si HSQC NMR spectroscopy (Table 2, entry 8).[44] The reaction between Et_2NH and $PhMeSiH_2$ in a 6 : 1 ratio quantitatively converted from $PhMeSiH_2$ after 24 h according to ^1H and ^1H–^{29}Si HSQC NMR spectroscopy (Table 2, entry 9).[45] Notably, in addition to $PhMeSiH(NEt_2)$, a second peak was also discernible ^1H–^{29}Si HSQC NMR spectroscopy. Although it was initially believed to be the second addition product

Table 2 Catalytic conditions for the coupling of amines and silanes[a]

Entry	Silane	Amine	Loading[b]	Equiv.[c]	Product	Conversion[d] (%)	Time (h)
1	$PhSiH_3$	$^nPrNH_2$	6.0	3.5	$PhSiH_2(HN^nPr)$ $PhSiH(HN^nPr)_2$	23 50	18
2	$PhSiH_3$	$^tBuNH_2$	7.8	6.0	$PhSiH_2(HN^tBu)$ $PhSiH(HN^tBu)_2$	89 11	24
3	$PhSiH_3$	$PhNH_2$	9.3	5.0	$PhSiH_2(HNPh)$	20	20
4	$PhSiH_3$	$^iPrNH_2$	8.5	4.0	$PhSiH_2(HN^iPr)$	100	20
5	$PhSiH_3$	Et_2NH	8.5	6.0	$PhSiH_2(NEt_2)$ $PhSiH(NEt_2)_2$	29 71	24
6	$PhMeSiH_2$	$^nPrNH_2$	9.3	5.0	$PhMeSiH(HN^nPr)$	60	24
7	$PhMeSiH_2$	$^tBuNH_2$	7.8	5.0	$PhMeSiH(HN^tBu)$	100	24
8	$PhMeSiH_2$	$^iPrNH_2$	9.3	4.0	$PhMeSiH(HN^iPr)$	100	24
9	$PhMeSiH_2$	Et_2NH	10.2	6.0	$PhMeSiH(NEt_2)$	100	24
10	Ph_2SiH_2	$^nPrNH_2$	6.8	3.0	$Ph_2Si(HN^nPr)$	74	24
11	Ph_2SiH_2	$^tBuNH_2$	8.1	6.0	$Ph_2Si(HN^tBu)$	40	24
12	Ph_2SiH_2	$^iPrNH_2$	7.8	6.0	$Ph_2Si(HN^iPr)$	100	24
13	Ph_2SiH_2	Et_2NH	8.5	7.0	$Ph_2SiH(NEt_2)$	22	24

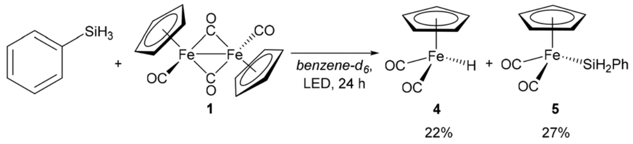
[a] Conditions: visible-light irradiation in benzene-d_6 solution at ambient temperature. Reactions were monitored by ^1H, $^{29}Si\{^1H\}$, and ^1H–^{29}Si HSQC NMR spectroscopy. [b] Mol% of **1** was with respect to silane. [c] Refers to mol. of amine per mol. of silane. [d] Conversions were determined by ^1H NMR integration.

$PhMeSi(NEt_2)_2$, literature chemical shifts do not agree,[45] and this minor byproduct remains unidentified.

Heterodehydrocoupling reactions with amines and Ph_2SiH_2 catalyzed by compound **1** were also tested. Reaction between $^nPrNH_2$ and Ph_2SiH_2 showed 74% conversion to $Ph_2SiH(HN^nPr)$ after 24 h according to ^1H NMR spectroscopy (Table 2, entry 10).[44] Conversely, reaction between Ph_2SiH_2 and $^tBuNH_2$ showed only 50% conversion to $Ph_2SiH(HN^tBu)$ after 24 h (Table 2, entry 11).[42] These observations indicated that steric factors can play a more significant role when both the amine and silane exhibit steric pressure. Of note, steric factors were more pronounced with the alcohol substrate in silyl ether reactions (*vide supra*). This supposition is buttressed by the reaction of Et_2NH and Ph_2SiH_2 in which 22% conversion to $Ph_2SiH(NEt_2)$ was observed after 24 h, despite 7 equiv. of amine to silane (Table 2, entry 13).[43] The balance can be tipped back with amine substitution where reaction of $^iPrNH_2$ and Ph_2SiH_2 gave nearly quantitative conversion to $Ph_2SiH(HN^iPr)$ with a minor byproduct discernible only in ^1H–^{29}Si HSQC NMR (Table 2, entry 12).[38] Finally, attempts at coupling these amines with tertiary silanes such as $PhMe_2SiH$ or Et_3SiH were unsuccessful.

Mechanistic study

Treatment of **1** with 1 equiv. of ^nPrOH resulted in no observable change as monitored by ^1H NMR spectroscopy after 24 h of visible-light irradiation in a benzene-d_6 solution. In contrast, reaction of equimolar **1** and $PhSiH_3$ over 24 h in benzene-d_6 under visible-light irradiation resulted in approximately 22% formation of hydride **4** as measured by ^1H NMR spectroscopy (eqn (3)).[46] A new iron compound, tentatively assigned as $Cp(CO)_2FeSiH_2Ph$ (**5**) based on resonances at δ 5.22 (Si*H*) and δ 3.98 (C_5H_5), was observed in approximately 27% conversion. The activation of an E–H bond under photolysis of **1** to form **4** has been observed with phosphines.[20]



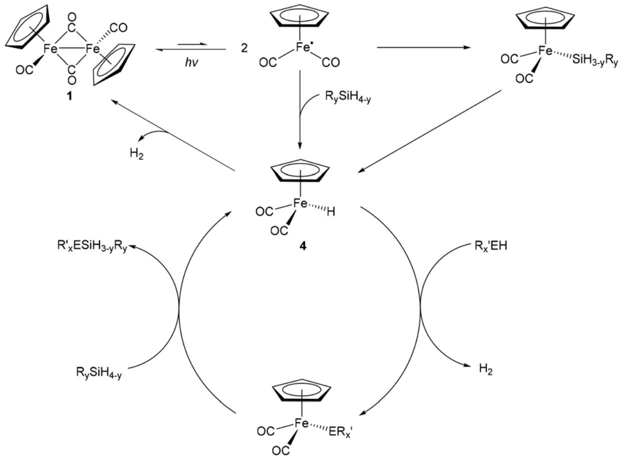
(3)

That P–H bond activation was also not quantitative, doubtlessly related to the kinetics of visible-light activation of **1**.[21] The known decomposition of **4** to **1** and the possibility of a process that directly converts **4** to **5** with free $PhSiH_3$ likely contribute to the ∼20% excess of **5** as compared to **4**.[47] Observation of catalytic reactions with $PhSiH_3$ by ^1H NMR spectroscopy confirm formation of **5** under catalytic conditions as well as apparently unreacted **1**. Apparent Si–H bond activation products at iron are consistently presented in catalytic reactions, regardless of substrate.

This observation suggests that iron could activate the organosilane substrate for nucleophilic attack by alcohol. To test this supposition, a known silyl derivative, $Cp(CO)_2FeSiMe_2Ph$ (**6**) was prepared.[48] Treatment of **6** with 1 equiv. of ^nPrOH failed to afford the anticipated silyl ether to any detectable extent by ^1H NMR spectroscopy, and variations on the reaction including 10 equiv. of alcohol, irradiation, or heating failed to afford silyl ether as well. However, treatment of 4 equiv. of BnOH with $PhSiH_3$ in the presence of 2 mol% of **6** resulted in formation of $PhSiH(OBn)_2$ and $PhSi(OBn)_3$ in 28% and 60% conversions, respectively, after 24 h of irradiation. While initially promising, comparative reaction with catalytic **1** fully converts $PhSiH_3$ and BnOH to $PhSi(OBn)_3$ after only 6 h (Table 1, entry 2). Moreover, the lack of reactivity between stoichiometric **6** and ^nPrOH cannot be ignored. These observations suggest that an iron-silyl species like **6** converts to **4** under catalytic conditions, but speciation is unclear during catalysis, though silyl derivatives are detectable in trace quantities by ^{1}H NMR spectroscopy in observations of catalytic reactions using **1**.

The prevalence of species such as **4**, **5**, and **6** in catalysis hints that active compounds are formally 18-electron derivatives, $Cp(CO)_2FeX$ (X = silyl, hydride, alkoxide, *etc.*). Testing for 17-election intermediates was inconclusive due to the necessary of $Cp(CO)_2Fe^{\bullet}$ as an intermediate under the photochemical conditions. However, 18-electron compounds are unavailable for organometallic steps such as oxidative addition or σ-bond metathesis due to formal electron count, and ligands such as silyl and hydride are less likely to engage in migratory insertion with carbonyl ligands to activate those derivatives compared to $Cp(CO)_2FeMe$, for example.[49,50] This deduction process leaves nucleophilic attack as the most viable mechanistic hypothesis with available data. Of course, many metals promote nucleophilicity of ligands.[51] While we cannot observe an iron-alkoxide or -amide compound in solution, we cannot discount it. Such an intermediate would be more nucleophilic than its parent alcohol. Indeed, the relative reactivity of $PhNH_2$ and $^iPrNH_2$ support nucleophilicity at the coupling partner. Moreover, attempts at synthesizing $Cp(CO)_2FeO^tBu$ or $Cp(CO)_2FeN(SiMe_3)_2$ *via* metathetical reaction of $Cp(CO)_2FeBr$ with the corresponding alkoxide or amide salt were unsuccessful. These results further substantiate the idea that these Fp-alkoxide or -amide intermediates are highly reactive, short-lived species. Indeed, Sadow and coworkers have proposed nucleophilic attack of a magnesium-amide intermediate and formation of a magnesium-hydride in Si–N heterodehydrocoupling.[44] Moreover, while literature on isolated piano-stool iron-alkoxides or -amides is scarce, Nakazawa and co-workers have implicated piano-stool iron-alkoxide and iron-thio intermediates in catalytic Si–O and Si–S heterodehydrocoupling, respectively.[26,27]

Based on the stoichiometric reactions and observations of the catalysis (though NMR observations were made in the absence of active irradiation), an initial proposal for the catalytic cycle can be made (Scheme 2). From both stoichiometric and catalytic reactions, it is clear that the activation of **1** is not complete during the reaction, but irradiation would form two equiv. of **3**, which would activate silane substrate to hydride **4** and a silyl compound. While direct formation of **4** from **6** under H_2 was not observed, trace amounts of **4** are detected while using **6** catalytically. It is believed that some pathway allows for the conversion of iron-silyl to **4**, albeit in trace quantities due to the prevalence of these species during catalysis. Hydride **4** is known to decompose back to **1**, which may also contribute to the steady state concentration of **1** during catalysis as observed by ^{1}H NMR spectroscopy.[47] However, **4** likely reacts with alcohol or amine to give a highly unstable alkoxide or amide intermediate with evolution of H_2. This intermediate can then attack a silane substrate to form product and regenerate **4**.



Scheme 2 Proposed mechanism for Si–O and Si–N heterodehydrocoupling catalysed by **1**.

Although Si–O and Si–S heterodehydrocoupling by Nakazawa and co-workers *via* $Cp(CO)_2FeMe$ is a similar system, starting from **1** and the prevalence of 18-electron compounds such as **4**, **5**, and **6** as intermediates shows that a different activation step is likely here.[26,27] A 17-electron σ-silane intermediate could be a potential intermediate and highly reactive.[52] We have been unable to differentiate the influence of 17-electron compounds other than $Cp(CO)_2Fe^{\bullet}$, and the presence **4** and **5** challenge such a pathway in the absence of better data.

Perhaps the most important observation from this mechanistic proposal is not the Si–O or Si–N bond-forming step. There is far less active catalyst in the system than the loading of **1** would indicate, even if the silyl intermediate were completely inactive under catalytic conditions. This information is a clear indication that a meager fraction of potential activity is being realized, which limits catalyst activity. These issues are clearly important as the conversation over utilization of base metals and lower energy reactions continues.

Conclusions

Commercially available iron compound **1** is efficient at Si–O heterodehydrocoupling under visible-light irradiation. Reactions between alcohols and silanes catalyzed by **1** afforded silyl ethers often in quantitative conversions from starting silanes. Sterically encumbered silanes generally required longer reaction times but provided near quantitative conversion from starting silanes. Compound **1** is also a competent Si–N heterodehydrocoupling catalyst. However, longer reaction times and higher catalyst loadings were necessary to produce silamines in good conversions. Furthermore, electron-rich amines were shown to be the most effective substrates to convert to silamines. Mechanistic study is consistent with nucleophilic attack of an intermediate iron-alkoxide or -amide at the organosilane substrate. More important to future study, though, is the necessity for complete activation of catalyst to achieve optimal conversions. The ‘unactivated’ fraction of catalyst may be a significant factor in the disparity between base and noble metals in catalysis, suggesting an area for deeper investigation. More specifically, this work expands upon the heterodehydrocoupling capabilities of **1**,[19,20] and represents one of the few instances of mild, photoactivated iron-based catalysts.

Experimental

General information

All reactions were prepared under purified N_2 atmosphere in an M. Braun glovebox. Cyclopentadienyl dicarbonyl iron(II) dimer **1** was purified by sublimation. Alcohols and amines were distilled from CaH_2. Silanes were received from chemical vendors and used without further purification. Benzene-d_6 was vacuum transferred from NaK alloy. NMR spectra were acquired on either a Varian 500 MHz spectrometer or a Bruker AXR 500 MHz spectrometer. Spectra recorded on both instruments were reported to $SiMe_4$ (δ 0.00).

Catalytic experiment conditions

An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol%) was charged with silane, followed by excess alcohol, 0.5 mL benzene-d_6, and TMS. A similar method was performed with amine coupling, however, loading of **1** was determined by substrates. Mixtures were transferred to a J-Young type polytetrafluoroethylene-valved NMR tube and subsequently placed under visible-light irradiation. Reactions were subjected to a cycle of freeze–pump–thaw after 1 and 2 h of irradiation. All reactions were performed at ambient temperature under irradiation in the visible spectrum using a 40 W LED bulb.

Conflicts of interest

The authors have no conflicts of interest to declare.

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