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Photoactivated Silicon–Oxygen and Silicon–Nitrogen Heterodehydrocoupling with a Commercially Available Iron Compound

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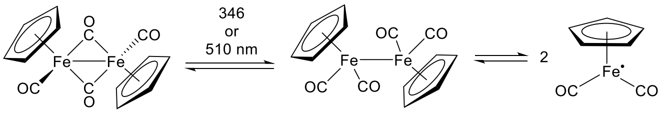
Silicon–oxygen and silicon–nitrogen heterodehydrocoupling catalyzed by the commercially available cyclopentadienyl dicarbonyl iron dimer $[CpFe(CO)_2]_2$ (**1**) under photochemical conditions is reported. Reactions between alcohols and $PhSiH_3$ with catalytic **1** under visible-light irradiation produced silyl ethers quantitively. Reactions between either secondary or tertiary silanes and alcohols also produced silyl ethers, however, these reactions were marked by their slower longer reaction times and lower conversions. Reactions of either production from either primary or secondary amines and silanes with catalytic **1** demonstrated mixed in efficiency, featuring conversions of 20 – 100%. Mechanistic study indicates that an iron silyl compound is unimportant in the bond–formation step and argues for a nucleophilic alkoxide 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 significant transformations including palladium–catalyzed C–C or C–N cross-coupling,[1] platinum–catalyzed hydrosilylation of olefins,[2] rhodium–catalyzed hydrogenation and hydroformylation,[3] and iridium–catalyzed C–H activation.[4] 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.[5] In their stead, a plethora of transformations have emerged, including C–C cross-coupling,[6] hydrosilylation of olefins and aldehydes,[7,8] and C–H activation,[9] 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.[10,11] 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. 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.[12,13] 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 development of base metal catalysis, chemists have been challenged with the development of greener synthetic pathways. Heterodehydrocoupling has gained momentum in green chemistry, due to the atom-economical formation of element–element bonds. The evolution of hydrogen as the sole by-product is also attractive, providing an excellent driving force and simplifying purification of products. Most dehydrocoupling reactions can only be accomplished catalytically with either a main group or transition–metal compound.[14] Consequentially, heterodehydrocoupling catalysts are attractive for green, catalytic transformations.

The commercially available iron dimer $[CpFe(CO)_2]_2$ (**1**) is a rare example that fulfils both previous points. Heterodehydrocoupling via compound **1** has been 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.[15,16] Furthermore, compound **1** is known to photoactivate under either ultraviolet or visible light irradiation to produce two equivalents of a $17e^-$ compound, **3,** via the all terminal carbonyl intermediate **2** (Scheme 1).[17] Thus, the photoirradiation of compound **1** may provide a green and facile method to forming other element–element bonds in the main group.



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

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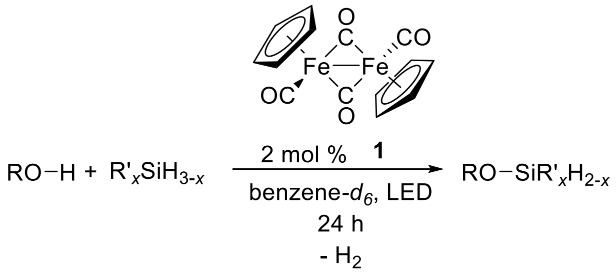
Silyl ethers, or small molecules containing Si–O bonds, are of importance in the protection of alcohols.[18] Poly(silyl ethers) are appealing due their hydrolytic instability in acidic and basic medium.[19] Molecules containing Si–N bonds such as silamines are well established as bases and silylating agents in organic syntheses,[20] while poly(silazanes) are sought after for their potential as ceramic precursors.[21] 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 1,15,16 initially investigating coupling of primary silanes and alcohols. An equimolar amount of nPrOH and PhSiH3 in the presence of 1 mol % of 1 in benzene-d6 solution was irradiated under visible-light from a commercial LED bulb. After 24 h, the mixture showed 32% conversion to PhSiH2(OnPr) and 43% conversion to PhSiH(OnPr)2 as measured by 1H NMR spectroscopy. The molar equivalences of alcohol and silane were varied in an effort to generate the third addition silyl ether product PhSi(OnPr)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(OnPr)3 in quantitative conversion after 24 h according to 1H NMR spectroscopy (Table 1, Entry 1).22 These reaction conditions were uniformly applied to other substrates (Eq. 1).

Catalytic Si-O Heterodehydrocoupling



(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).[23,24] Reactions between ^{i}PrOH 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 ^{i}PrOH and $PhSiH_3$ completely converted from $PhSiH_3$ by 24 h to $PhSi(O^{i}Pr)_3$ (Table 1, Entry 3).[24,25,26] Attempts at coupling $PhSiH_3$ with heavily encumbered alcohols such as ^{t}BuOH with **1** did not produce silyl ethers according to ^{1}H NMR spectroscopy.

Heterodehydrocoupling with secondary silanes using compound **1** was also investigated. Reaction of $PhMeSiH_2$ and ^{n}PrOH in a 1:4 ratio generated a single peak at δ -18.07 in $^{29}Si\{^{1}H\}$ NMR spectroscopy after 24 h under irradiation, consistent with $PhMeSi(O^{n}Pr)_2$ (Table 1, Entry 4). The final resonance generated at δ 3.89 in ^{1}H NMR spectroscopy indicated 100% conversion to $PhMeSi(O^{n}Pr)_2$. A similar strategy was applied to reactions of ^{i}PrOH and $PhSiH_3$ in a 5:1 ratio, where $PhMeSi(O^{i}Pr)_2$ was afforded in 91% conversion with 9% of $PhMeSiH(O^{i}Pr)$ 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).[27] Reaction of ^{n}PrOH and Ph_2SiH_2 under visible-light irradiation in the presence of **1** proceeded slowly according to ^{1}H 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 $Ph_2Si(O^{n}Pr)_2$ 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 ^{1}H NMR spectroscopy (Table 1, Entry 8).[24,28] Interestingly, reacting 5 equiv of ^{i}PrOH with Ph_2SiH_2 exclusively yielded $Ph_2SiH(O^{i}Pr)$[24] in quantitative conversion with no evidence of fully substituted product $Ph_2Si(O^{i}Pr)_2$ (Table 1, Entry 9).[24]

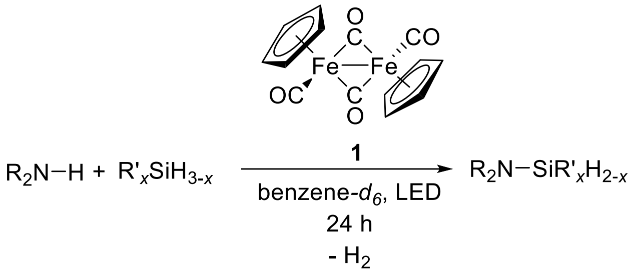
Reaction of ^{n}PrOH and $PhMe_2SiH$ in a 5:1 ratio afforded a new product, tentatively assigned to $PhMe_2Si(O^{n}Pr)$ based on analogy to $PhMe_2Si(OBn)$ and $PhMe_2Si(O^{i}Pr)$, in 93% conversion as a resonance at δ 6.67 in the $^{29}Si\{^{1}H\}$ NMR spectrum (Table 1, Entry 10). Reaction of excess BnOH and $PhMe_2SiH$, however, showed complete disappearance of $PhMe_2SiH$ in the ^{1}H NMR spectrum and generation of $PhMe_2Si(OBn)$ after 24 h (Table 1, Entry 11).[27,29] Reaction of ^{i}PrOH and $PhMe_2SiH$ in a 6:1 ratio showed 93% conversion to $PhMe_2Si(O^{i}Pr)$ after 24 h according to ^{1}H NMR spectroscopy (Table 1, Entry 12).[30]

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

entry	silane	alcohol	equiv[b]	product	conversion (%)[c]
1	$PhSiH_3$	^nPrOH	4.0	$PhSi(O^nPr)_3$	100
2	$PhSiH_3$	BnOH	4.0	$PhSi(OBn)_3$	100
3	$PhSiH_3$	^iPrOH	5.0	$PhSi(O^iPr)_3$	100
4	$PhMeSiH_2$	^nPrOH	4.0	$PhMeSi(O^nPr)_2$[d]	100
5	$PhMeSiH_2$	BnOH	4.0	$PhMeSi(OBn)_2$	100
				$PhMeSiH(O^iPr)$,[d]	9
6	$PhMeSiH_2$	^iPrOH	5.0	$PhMeSi(O^iPr)_2$[d]	91
7	Ph_2SiH_2	^nPrOH	4.0	$Ph_2Si(O^nPr)_2$[d]	100
8	Ph_2SiH_2	BnOH	4.0	$Ph_2Si(OBn)_2$	100
9	Ph_2SiH_2	^iPrOH	5.0	$Ph_2SiH(O^iPr)$	100
10	$PhMe_2SiH$	^nPrOH	5.0	$PhMe_2Si(O^nPr)$[d]	93
11	$PhMe_2SiH$	BnOH	5.0	$PhMe_2Si(OBn)$	100
12	$PhMe_2SiH$	^iPrOH	6.0	$PhMe_2Si(O^iPr)$	93

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

Catalytic Si-N Heterodehydrocoupling



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

Compound **1** also proved to be competent at Si–N heterodehydrocoupling but at higher catalyst loadings (Eq. 2). Silamines were produced less efficiently than silyl ethers, as evident by the overall 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).[31] However, 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).[32,33] 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).[34] 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).[35] 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).

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

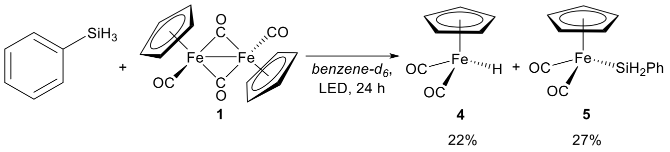
[a] Conditions: visible–light irradiation in benzene-d_6 solution at ambient temperature. Reactions were monitored by ^1H, $^{29}Si\{^1H\}$, and ^1H-^{29}Si HSQC NMR Spectroscopy. [b] Mol % of **1** was with respect to silane. [c] Equiv of amine per 1 equiv of silane. [d] Conversions were determined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

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).[34] Meanwhile, $PhMeSiH(HN^tBu)$ was generated in 100% conversion by ^1H NMR spectroscopy after 24 h (Table 2, Entry 7).[34] 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).[34] 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).[35] 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 $PhMeSi(NEt_2)_2$, literature chemical shifts do not agree,[35] and this minor byproduct remains unidentified.

Finally, 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).[34] 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).[32] The 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 just 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 seven equivalent of amine to silane (Table 2, Entry 13).[33] 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).[35]

Mechanistic Study

Treatment of **1** with 1 equiv of ^nPrOH resulted in no change as observed 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 22% formation of hydride **4** as measured by ^1H NMR spectroscopy (Eq. 3).[36] A new iron compound, tentatively assigned as Cp(CO)$_2$FeSiH$_2$Ph (**5**) based on resonances at δ 5.22 (SiH) and δ 3.98 (C$_5$$H_5$), was observed in 27% conversion. Such reactivity, the activation of an E–H bond under photolysis of **1** has been observed with phosphines.[16]

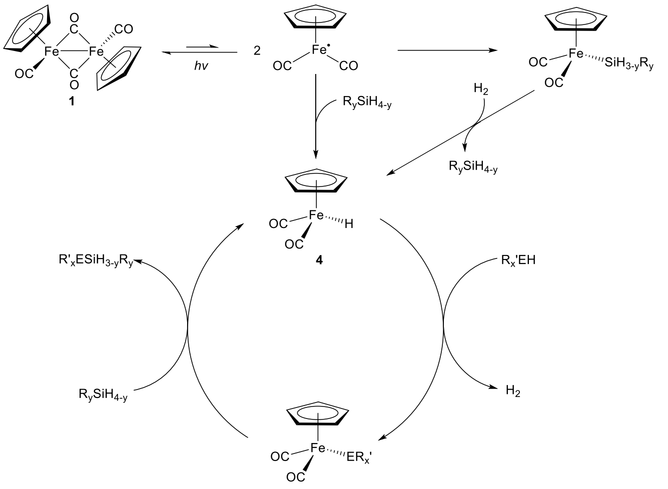


(3)

That P–H bond activation was also not quantitative, doubtlessly related to the kinetics of visible–light activation of **1**.[17] 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**. Observation of catalytic reactions with PhSiH$_3$ by ^{1}H 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)$_2$FeSiMe$_2$Ph (**6**) was prepared.[37] Treatment of **6** with 1 equiv of ^{n}PrOH failed to afford the anticipated silyl ether to any detectable extent by ^{1}H NMR spectroscopy, and variations on the reaction including 10 equiv of alcohol, irradiation, or heating failed to afford silyl ether as well. These observations demonstrate that the silyl derivative is an off-cycle spectator, affirming the long-standing observation that visible "intermediates" are not necessarily catalytically relevant and that unseen compounds are often the critical and active intermediates.[38]

Despite these negative results, the persistence of **1** and silyl derivatives like **5** at the end of catalysis indicate that the iron compound is largely preserved. Therefore, active compounds are formally 18-electron derivatives, Cp(CO)$_2$FeX (X = silyl, hydride, alkoxide, etc.). Such compounds are unavailable for organometallic (i.e., oxidative addition or σ-bond metathesis) steps due to formal electron counts and the inaccessibility of these X ligands for migratory insertion with carbonyl ligands.[39,40] Such deduction leaves nucleophilic attack as the most viable mechanistic hypothesis. Many metals promote nucleophilicity of ligands.[41] While we cannot observe an iron alkoxide compound in solution, we cannot discount it. Such an intermediate would be more nucleophilic than its parent alcohol. Indeed, the relative reactivity of aniline and iPrNH$_2$ support nucleophilicity at the coupling partner. While literature on isolated piano-stool iron alkoxides or amidos is scarce, Nakazawa and coworkers have implicated piano-stool iron-alkoxide and iron-thio intermediates in catalytic silicon-oxygen and silicon-sulfur heterodehydrocoupling, respectively.[42,43]



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

Based on the stoichiometric reactions and observations of the catalysis, 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, but irradiation would form two equiv of **3**, which would active silane substrate to hydride **4** and a silyl compound. The silyl compound is an inactive spectator that may be converted to **4** as hydrogen is evolved. Hydride **4** can decompose back to **1**, which may also contribute to the steady state concentration of **1** during catalysis as observed by ^{1}H NMR spectroscopy. However, **4** likely reacts with alcohol to give a highly unstable alkoxide intermediate with evolution of hydrogen. This alkoxide intermediate can then attack a silane substrate to form product and regenerate **4**.

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.

Conclusions

A 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 ether 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 organosilanes 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**,[15,16] and represents one of the few instances of mild, light-activated iron-based catalysts.

Experimental

General Information

All reactions were prepared under purified a 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 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 TMS (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.

Acknowledgements

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