Light-Promoted Transfer of an Iridium Hydride in Alkyl Ether Cleavage

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ABSTRACT: A catalytic, light-promoted hydrosilylative cleavage reaction of alkyl ethers is reported. Initial studies are consistent with a mechanism involving heterolytic silane activation followed by delivery of a photohydride-equivalent to a silyloxonium ion generated in situ. The catalyst resting state is a mixture of Cp*Ir(ppy)H (ppy = 2-phenylpyridine–κ*C*,*N*) and a related hydride-bridged dimer. Trends in selectivity in substrate reduction are consistent with non-radical mechanisms for C-O bond scission. Irradiation of Cp*Ir(ppy)H with blue light is found to increase the rate of hydride delivery to an oxonium ion in a stoichiometric test. A comparable rate enhancement is found in carbonyl hydrosilylation catalysis which operates through a related mechanism also involving Cp*Ir(ppy)H as the resting state.

INTRODUCTION

Transition metal photochemistry has been a driving force behind the development of many modern photocatalytic methods for the transformation of organic substrates.[1-7] Photocatalytic transformations can be categorized based on the reactivity of the photoexcited species. In photoredox methods, the excited photocatalyst undergoes single-electron transfer (SET) with a reaction partner, with the resulting singly oxidized or reduced photocatalyst being regenerated in a subsequent SET step.[8-12] Another major class of photocatalytic processes takes advantage of light-induced ligand dissociation or extrusion.[13-22] Photoexcited transition metal complexes can also engage in two-electron bimolecular reactivity with substrates, though this class of transformations has seen very limited application to catalytic processes.

One example of bimolecular, apparently non-radical photochemistry can be found in the a class of [Cp*IrH(bipyridine)]$^+$ complexes that have been shown to undergo photoexcitation to give monohydride intermediates with significantly increased hydricity. Miller and coworkers have demonstrated a stoichiometric photo-induced hydride delivery with a nicotinamide derivative serving as the hydride acceptor in which they hypothesized that the photoexcited complex [Cp*IrH(bipyridine)]$^{+*}$ (excited state half-life τ = 80 ns in MeCN)[23] serves as an intermediate (Figure 1).[24] This system has also been applied in catalytic light-promoted H_2 evolution[25-27] and in photo-induced hydrodechlorination, with a single example of catalytic hydrodechlorination when CD_2Cl_2 solvent serves as the substrate.[28] Studies on H_2 evolution and hydrodechlorination by [Cp*IrH(bipyridine)]$^+$ are consistent with bimolecular self-quenching mechanisms in those cases,[28-29] while a light-induced ligand dissociation is implicated in a related example of aqueous ketone reduction.[7] The variety of light-promoted mechanisms apparently available to this family of complexes necessarily complicates studies of reaction mechanism, but also highlights the role that light can play in modifying catalyst reactivity.

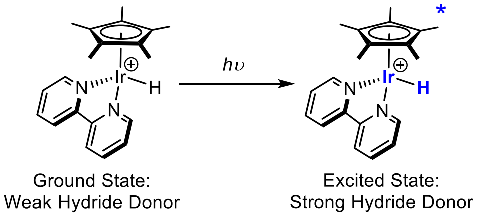
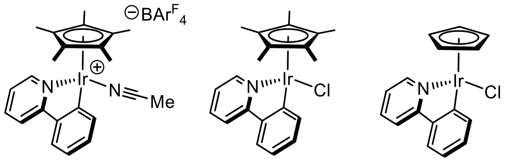


Figure 1. Role of light in modifying metal hydricity in [Cp*IrH(bipyridine)]$^+$ described by the Miller group.[24]

The use of light to increase the hydricity of a catalytic intermediate would be an unusual strategy to modify the reactivity of existing catalyst systems. A related Cp*Ir monohydride bearing a 2-phenylpyridine-κ*C*,*N* (ppy) ligand has been reported as a catalytic intermediate in alcohol dehydrosilylation catalysis.[30-31] The similarity of the [Cp*IrH(bipyridine)]$^+$ photohydride system[28] to the light-free dehydrosilylation system reported for the phenylpyridine-derived variant[30] inspired an examination of the effect of light on hydrosilylative alkyl ether cleavage catalysis using the family of iridium complexes **1**-**3** (Figure 2). We now report a catalytic method for alkyl ether cleavage which appears to proceed via light-induced hydride transfer from an iridium complex to a silyloxonium ion generated in situ.



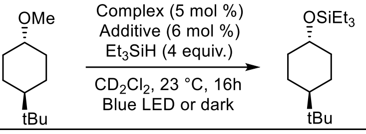
1 **2** **3**

Figure 2. Iridium phenylpyridine complexes examined.

RESULTS AND DISCUSSION

Complex **1** is a reported catalyst for the dehydrosilylation of alcohols using triethylsilane in the absence of light.[31] The proposed mechanism for this transformation involves the intermediacy of a cationic σ silane complex that undergoes heterolytic Si-H cleavage followed by bimolecular reaction of the resulting hydride and oxonium ions in a second step.[30-31] A closely-related mechanism is operative in hydrosilylative ether cleavage, a transformation with only a few reported catalysts comprised of either electron-deficient boranes[32-33] or cationic iridium complexes.[34-37] In the absence of light, **1** is a very poor catalyst for alkyl ether reduction, which we postulated might be due to the modest nucleophilicity of the hydride intermediate. Under blue-light irradiation however, **1** catalyzes the hydrosilylative demethylation of *trans*-4-(*t*-butyl)cyclohexyl methyl ether to the corresponding silyl ether in 43% yield (Table 1, entry 2).

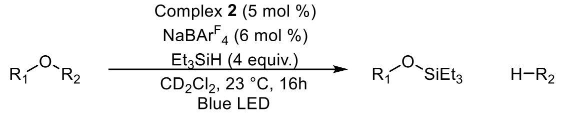
Table 1. Identification of conditions for photochemical alkyl ether cleavage

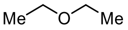
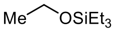
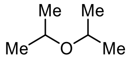
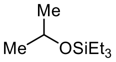
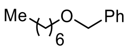
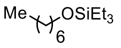
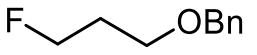
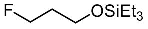
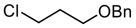
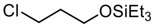
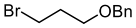
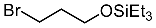
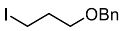
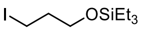
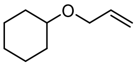
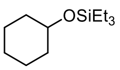
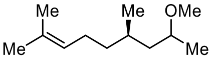
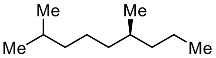


Entry	Complex	Additive	Light	Yield (%)
1	**1**	-	-	7
2	**1**	-	blue	43
3	**2**	-	blue	0
4	**2**	$NaBArF_4$	blue	93
5	**2**	$[Ph_3C]BArF_4$	blue	94
6	**2**	$NaBArF_4$	-	0
7	**3**	$NaBArF_4$	blue	0

Further optimization of the reaction conditions demonstrated that the parent chloride compound **2** gives a more effective catalytic system in the presence of $NaBAr^F_4$, which presumably effects chloride abstraction to give cationic intermediates.[38-40] These conditions allow for high yields with as little as 5 mol % **2**. Compound **2** is unreactive in the absence of $NaBAr^F_4$ (entries 3 & 4), which would be expected if the reaction proceeds via a cationic σ-silane intermediate similar to those previously reported for other ether cleavage catalysts.[26,29,30] $NaBAr^F_4$ can be substituted by $[Ph_3C][BAr^F_4]$ with similar catalytic performance (entry 5) , but this reagent offers no clear benefit over the stable, commercially available sodium salt. The improved catalytic performance of the **2**/$NaBAr^F_4$ system over that of **1** is likely attributable to modest catalyst inhibition by the disilylamine byproduct of acetonitrile hydrosilylation reportedly formed by the reaction of **1** with triethylsilane.[30] The Cp* ligand is also required for activity, as compound **3** bearing the smaller Cp ligand is inactive in hydrosilylative ether cleavage (entry 7).

Table 2. Hydrosilylative alkyl ether cleavage by **2**/$NaBAr^F_4$

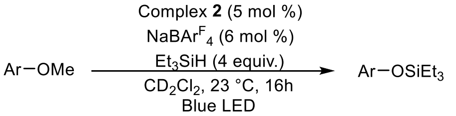


Entry	Substrate	Product	NMR Yield
1			21%
2			9%
3			75%
4			25%
5			68%
6			88%
7			-
8			87%
9			58%

The scope of photo-assisted hydrosilative alkyl ether cleavage by **2**/$NaBAr^F_4$ was explored for a variety of symmetrical and unsymmetrical ethers (Table 2). Diethyl ether and diisopropyl ether show low reactivity in line with previous non light-promoted iridium catalysts.[34] A selection of alkyl benzyl ethers undergo debenzylation, with a primary alkyl chloride and bromide being tolerated. The corresponding iodide undergoes hydrodehalogenation, while the fluoride halts at partial conversion. The compatibility of primary alkyl chlorides and bromides with this hydrosilylative catalytic system contrasts the reported photochemical hydrodechlorination chemistry of [Cp*IrH(bipyridine)H]$^+$, which likely occurs via a radical pathway.[28] The **2**/$NaBAr^F_4$ catalyst system also functions as a catalyst for hydrodechlorination of CD_2Cl_2 to CD_2HCl (9.3 TON), though this transformation need not involve the intermediacy of an alkyl radical under hydrosilylative conditions, as Brookhart that postulated that hydride transfer to a silyl halonium ion may be operative in a related case.[41] Cyclohexyl allyl ether undergoes selective deallylation, though the propene byproduct is not observed and is presumed to undergo hydrogenation under the reaction conditions (entry 8). As further evidence that olefins are not tolerated functionality, the reduction of a citronellol-derived secondary methyl ether gives the saturated product of demethoxylation and hydrogenation (entry 9),[42] a limitation also observed in previous iridium systems that do not require light.[34, 37]

In comparison to dialkyl ethers, anisole derivatives proved to be relatively challenging substrates for this system. The reactivity of the selection of anisoles shown in Table 3 appears to track with the electron-richness of the arene, with 4-F, 4-Br, and the parent anisole showing poor reactivity under our conditions. The more electron-rich methyl and dimethyl anisoles (Table 3, entries 4 and 5) do undergo demethylation to varying degrees, suggesting a role for the basicity of the ether in controlling their reactivity. A comparable trend has not been described for other anisole hydrosilylation catalysts, though both the borane catalyst $B(C_6F_5)_3$[33] and Brookhart's catalyst[37] are effective for hydrosilylative anisole demethylation at room temperature. In all cases in Table 3, the balance of the reaction is the unconverted starting material.

Table 3. Hydrosilylative anisole demethylation by **2**/NaBAr$^F_4$



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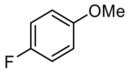
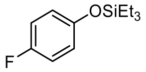
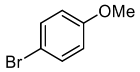
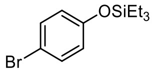
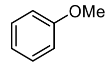
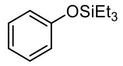
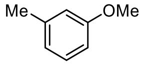
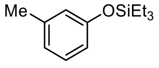
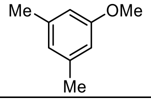
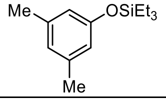
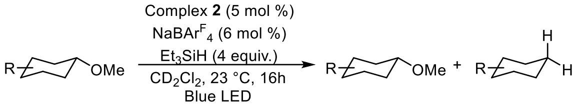
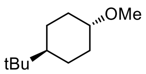
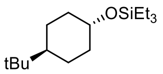
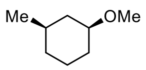
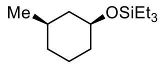
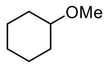
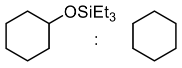
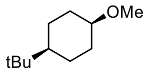
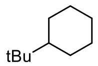
1			0%
2			8%
3			16%
4			50%
5			84%

Table 4. Cyclohexyl methyl ether cleavage by **2**/NaBAr$^F_4$



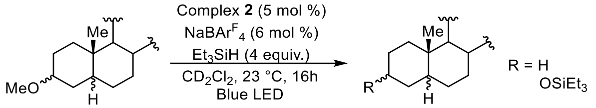
Entry	Substrate	Product(s)	E_{ax}-E_{eq}[a]	Yield[c]
1			11.3	93%
2			10.7	58%
3			4.9	74%:10%
4[b]			-0.6	74%

[a] Predicted difference in energy of equatorial and axial conformations of the corresponding triethylsilyloxonium ion. [b] 10 mol % catalyst was used. [c] NMR yield.

In a previous report on iridium-catalyzed hydrosilylative ether cleavage, we interrogated the selectivity obtained for an array of cyclohexyl methyl ethers using [(cod)Ir(PPh$_3$)$_2$]BAr$^F_4$ as a precatalyst.[35] In that case, we observed that the selectivity for demethylation versus 2° C-O cleavage depended on conformational factors, and showed that selectivity was correlated with the computationally predicted conformational preferences of the substrate triethylsilyloxonium ions. Substrates with strong preferences for the silyloxonium group in the equatorial conformation (E_{ax}-E_{eq} > 4 kcal·mol^{-1}) underwent preferential demethylation, while substrates predicted to have greater populations in the axial conformation underwent selective demethoxylation, with the switch in reactivity being ascribed to the relative rates of S$_N$2 demethylation versus S$_N$1 demethoxylation. A similar trend is observed here using the light-assisted **2**/NaBAr$^F_4$ system (Table 4). Substrates previously predicted[35] to have highly positive E_{ax}-E_{eq} values undergo selective demethylation (entries 1 and 2), while *cis*-4-(*t*-butyl)cyclohexyl methyl ether undergoes preferential cleavage at the secondary position. (entry 4)

Further similarities between this system and the previously reported bis(phosphine)iridium system can be found by examination of hydrosilylative ether cleavage in sterol-derived substrates. The A-ring methyl ethers in β- and α-methyl cholestanol are conformationally fixed in equatorial and axial dispositions respectively (Table 5, entries 1 and 2). The equatorial substrate (entry 1) undergoes catalytic demethylation with **2**/NaBAr$^F_4$, while the axial substrate undergoes demethoxylation. The cholic acid derivative in entries 3 and 4 undergo selective demethylation and demethoxylation of the A-ring methoxy groups respectively with **2**/NaBAr$^F_4$. This same selectivity was previously observed for the hydrosilylative ether cleavage catalyst [(cod)Ir(PPh$_3$)$_2$]BAr$^F_4$ and was ascribed to conformation effects resulting from substitution of the B ring.[35] In total, the conformational factors that influence selectivity in cyclohexyl ether cleavage using **2**/NaBAr$^F_4$ are essentially identical to those observed for [(cod)Ir(PPh$_3$)$_2$]BAr$^F_4$.[35] The principal factors distinguishing **2**/NaBAr$^F_4$ from [(cod)Ir(PPh$_3$)$_2$]BAr$^F_4$ are therefore the necessity of light and the requirement for somewhat higher catalyst loading of **2** versus [(cod)Ir(PPh$_3$)$_2$]BAr$^F_4$.[34-35]

Table 5. Sterol methyl ether cleavage by **2**/NaBAr$^{F}_{4}$



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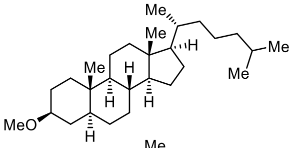
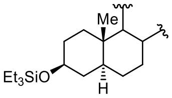
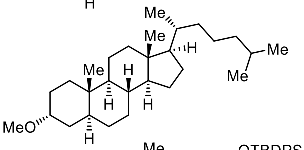
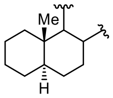
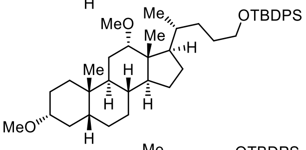
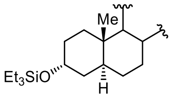
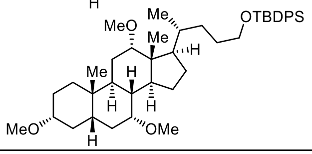
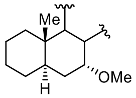
1			79%
2[a]			54%
3			39%
4			80%

[a] 10 mol % catalyst was used. [b] NMR yield.

Reaction Mechanism

The similar conformational influences on selectivity observed for light-promoted hydrosilylative alkyl ether cleavage with **2**/NaBAr$^{F}_{4}$ and the thermal bis(phosphine)iridium systems strongly imply mechanistic similarities between the two systems. A proposed mechanism for the light-promoted hydrosilylative cleavage of alkyl ethers by **2**/NaBAr$^{F}_{4}$, is given in Figure 3.

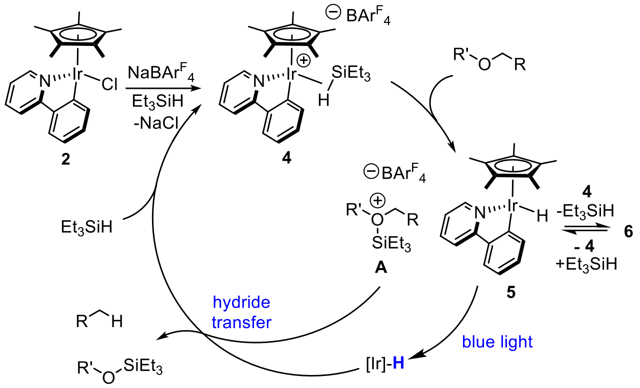
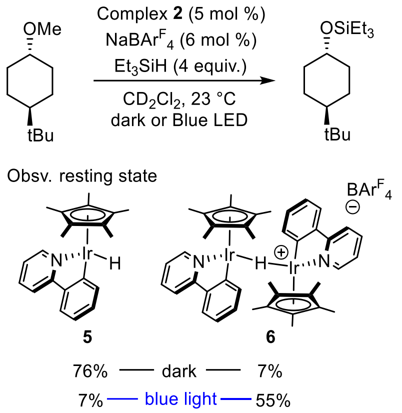


Figure 3. Proposed mechanism for catalytic ether cleavage via photochemical hydride transfer to silyloxonium ions.

This proposal is inspired by work on related systems which operate without light,[33-37, 43-44] as well as the reported photochemical behavior of the bipyridine-supported iridium hydride reported by Miller.[24] Complex **2** likely reacts with NaBAr$^{F}_{24}$ and triethylsilane to form an electrophilic σ-silane complex **4** that has been previously characterized by Djukic and coworkers under relevant alcohol dehydrosilylation conditions.[30] **4** transfers 1 equivalent of triethylsilylium ion to substrate ether to give the neutral monohydride complex Cp*Ir(ppy)H (**5**) and 1 equivalent of silyloxonium ion (**A**). Since visible light absorption is necessary for efficient catalytic turnover, we hypothesize photoexcitation of complex **5** give a more nucleophilic hydride complex[45] which reacts with silyloxonium ion **A** by delivery of the hydride.



(1)

Aspects of the proposal in Figure 3 can be tested experimentally. First, we examined the metal complexes which are formed under catalytic conditions in the absence of illumination (eqn. 1). Under these conditions no catalytic turnover is observed and **5** is detected as the major Ir-containing product by ^{1}H NMR. The same species is observed after illumination for 20 minutes (*ca.* 1.4 TON), though a second complex **6** represents the major metal-containing species at this point. The identity of **5** was confirmed by comparison of the upfield region of the ^{1}H NMR spectrum of the dark reaction to the hydride resonance of independently synthesized **5**. The second, major species is the known monocationic dimer **6** formed by capture of **5** by an equivalent of [Cp*Ir(ppy)]BAr$^{F}_{4}$. Complexes **5** and **6** have been reported to exist in equilibrium during catalytic dehydrosilylation of alcohols,[30-31] and so their observation here is consistent with the operation of a related mechanism. The visible absorbance spectrum of **5** overlaps well with the 34W H150 Blue LED Lamp used under catalytic conditions. (Figure 4).

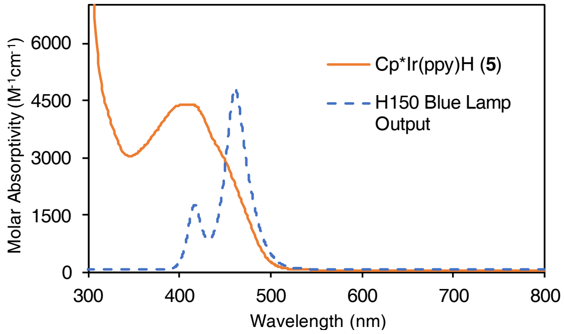
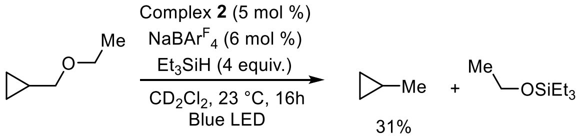
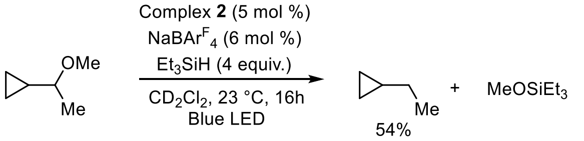


Figure 4. Comparison of absorbance spectrum of **5** with the output of the commercial 34W H150 Blue LED Lamp used in this study.

Evidence that C-O bond scission occurs via a non-radical mechanism can be obtained through the analysis of the fate of substrates containing fast radical clocks. The cyclopropyl alkyl ether substrates cyclopropylmethyl ethyl ether and (1-methoxyethyl)cyclopropane were selected to examine the mechanism for primary and secondary alkyl ether cleavage respectively.



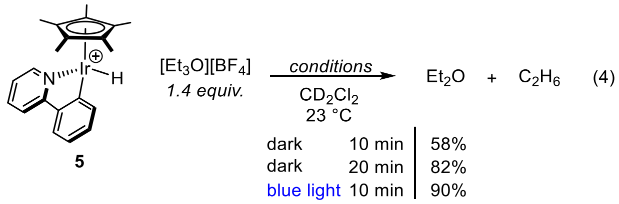
(2)



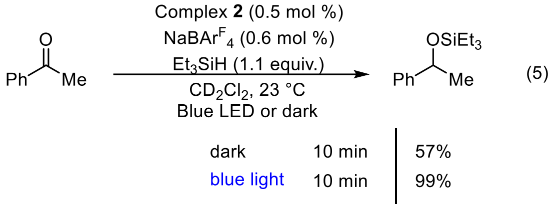
(3)

Light-promoted hydrosilylative ether cleavage of cyclopropylmethyl ethyl ether produces methylcyclopropane in 31% yield with the cyclopropyl ring intact (eqn. 2). The balance of the substrate is converted to (cyclopropylmethoxy)triethylsilane via cleavage of the unsymmetrical ether at the ethyl group. As the cyclopropylmethyl radical has a reported rate of ring opening of $1 * 10^8$ s^{-1}, the lack of observed products of ring opening is inconsistent with a long-lived alkyl radical intermediate.[46] Reduction of (1-methoxyethyl)cyclopropane gives cyclopropyl ethane as the only observed product of secondary C-O cleavage in 54% yield (eqn. 3). The reported rate for ring opening of the 1-cyclopropylethyl radical is $4 * 10^7$ s^{-1}.[46] Together, these observations argue for a non-radical mechanism for light-promoted hydrosilylative ether cleavage in this case, an outcome consistent with the 2-electron proposal in Figure 3. That said, the fast radical clocks selected for this analysis only allow us to rule out the intermediacy of cyclopropylmethyl radicals with lifetimes on the order of their intramolecular ring-opening rates, and not, for instance, the intermediacy of odd-electron metal-containing species. This limitation is potentially significant since Miller has found that light-promoted hydrodehalogenation of chloroalkanes by $[Cp^*Ir(bipyridine)H]^+$ likely proceeds via bimolecular quenching of the photoexcited catalyst and the involvement of short-lived alkyl radical intermediates.[28] In the case of catalysis by **2**/$NaBAr^F_4$, SET reduction of silyloxonium ion intermediates is very unlikely to give the selectivity observed for substrates in Tables 4 and 5, which has been previously rationalized in the context of competitive S_N1 and S_N2 processes.[35]

The observation that **2**/$NaBAr^F_4$ catalyzes the hydrosilylation of carbonyl derivatives[39-40] and dehydrosilylation of alcohols[30] in the dark, but does not catalyze hydrosilylative ether cleavage in the absence of light can be interpreted in the context of the relative reactivity of the plausible reaction intermediates. These three transformations share similar mechanisms, with heterolytic Si-H cleavage giving silyloxycarbenium,[38-39] and mono-[30] and dialkyl silyloxonium[34-35, 47] ions respectively. Our observation that the catalyst resting state after illumination is a mixture of the neutral monohydride complex **5** and the dimeric monohydride **6** is consistent with a catalytic cycle resting at the silyloxonium/**5** reactant pair (with **5** in equilibrium with **6**). Absorption of a blue photon is presumably required to enable C-O bond cleavage via nucleophilic attack on the silyloxonium ion, and thus catalyst turnover. This hypothesis can be tested in stoichiometric fashion by examining the reaction of Cp*Ir(ppy)H (**5**) with the closely-related triethyloxonium electrophile. In the dark, Cp*Ir(ppy)H reacts at a moderate rate with $[Et_3O][BF_4]$ to produce ethane and diethyl ether, achieving 58% conversion with respect to Et_2O formation after 10 minutes, and reaching 82% after 20 minutes. In contrast, the same transformation proceeds more-rapidly under irradiation with blue light, leading to near-quantitative (90%) ethane formation in just 10 minutes.



A final piece of evidence can be obtained by examining the role of light in related catalytic transformations where **5** serves as an intermediate. When acetophenone is subjected to hydrosilylation by **2**/$NaBAr^F_4$ in the dark, complex **5** is observed as the catalyst resting state by ^1H NMR spectroscopy. Although the reaction is relatively fast in the absence of light, a significant rate enhancement is observed under illumination. Catalytic acetophenone hydrosilylation subjected to blue light is complete within 10 minutes, while at the same point the corresponding dark reaction has only reached 57% yield (eqn. 5).[48] Although both 1-[49] and 2-electron light-induced reactivity is known for Cp*Ir monohydride complexes, the balance of our catalytic and stoichiometric observations argue for the role of light in modulating the nucleophilicity of iridium hydride complex **5** or a closely-related species formed on illumination.



CONCLUSION

In summary, the hydrosilylative cleavage of alkyl ethers by **2**/$NaBAr^F_4$ has been demonstrated to occur via a light-promoted path. Experiments support a mechanism where the iridium complex [Cp*Ir(ppy)H] (**5**) or a related complex serves as a hydride source for the C-O cleavage of an alkyl ether-derived silyloxonium ion after light absorption. Selectivity trends in the cleavage of unsymmetrical alkyl ethers align with a previous non-photochemical system shown to result from competitive S_N1 and S_N2 reduction of silyloxonium ion intermediates. The identity of the two species observed as the catalyst resting state have been confirmed by NMR experiments. Lack of ring-opening observed for a pair of cyclopropyl substrates argue against a 1 e^- pathway for C-O bond scission involving alkyl radical intermediates, providing further evidence for a polar, 2 e^- mechanism involving heterolytic Si-H cleavage followed by hydride delivery in a subsequent step. The apparently increased hydride nucleophilicity under illumination also manifested in stoichiometric oxonium ion reduction and in acetophenone hydrosilylation, a related catalytic transformation that shares the same catalyst resting state. This system is a rare example of photohydride transfer chemistry in a catalytic application to organic synthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at the ACS publications website at "http://pubs.acs.org."

Experimental procedures, summaries of experimental results, and compound characterization data. (PDF)

X-ray crystallographic data. (CIF)

CCDC 2093170–2093171 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interests

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Graphical Abstract