Visible Light Photocatalysis Using a Commercially Available Iron Compound

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Supporting Information

ABSTRACT: $[CpFe(CO)_2]_2$ (1) $(Cp = \eta^5 - C_5H_5)$ is an effective precatalyst for the hydrophosphination of alkenes with Ph₂PH under visible light irradiation, which appears to be a unique way to promote metal-catalyzed hydrophosphination. Additionally, 1 is a photocatalyst for the dehydrogenation of amine boranes and formation of siloxanes from tertiary silanes. These reactions have similar, if not improved, reactivity over the same transformations using 1 or related CpFeMe-(CO)₂ under UV irradiation, consistent with the notion that



hydrophosphination with 1 proceeds via formation of $CpFe(CO)_2^{\bullet}$. These results demonstrate that catalyst selection can avail the use of commercially available LED bulbs as photon sources, potentially replacing mercury arc lamps or other energy intensive processes in known or new catalytic reactions.

INTRODUCTION

Selective formation of P-C bonds is a continued synthetic challenge despite the ubiquity of tertiary phosphines in modern synthetic and catalytic protocols.¹⁻⁹ One attractive route for the catalytic synthesis of tertiary phosphines is metal-catalyzed hydrophosphination, which imparts selectivity to the P-C bond forming process and minimizes chemical waste.¹⁰⁻¹² A variety of catalysts have been shown to engage in this reactivity ranging from the s-block^{13,14} to lanthanides,^{15,16} transition metals,^{10,11} and even main-group compounds.^{17,18}

Commercial, inexpensive catalysts are likely to be widely adopted for any process.¹⁹ Despite the successes in catalytic hydrophosphination, relatively rare metals are still at the fore of research. Gaumont,²⁰ Webster,^{21–23} and Nakazawa^{24,25} have each made critical advances in the utilization of earth-abundant iron catalysts. At the same time, many hydrophosphination reactions require significant heating. $^{21-25}$ Photocatalyzed reactions using visible light have grown in importance because these reactions can be considered green due to the abundance of visible photons from solar irradiation.²⁶⁻³¹ However, highenergy light sources such as mercury arc lamps that emit photons in the UV (λ_{irr} < 300 nm) region remain commonplace for many photochemical/photocatalytic reactions. Ironbased catalysis via visible light activation is known, with a pioneering report by Nicholas in 2002 that used [Cp*Fe- $(CO)_2]_2$ (Cp* = η^5 -C₅Me₅) and near-IR irradiation to catalyze the allylic amination of olefins with nitroarenes.³² Reports by Sortais and Darcel that describe hydrosilylation of various C= O and C=N containing molecules have followed. However, these reactions often utilize more complex iron catalyst precursors.^{33–38} Herein, we report the hydrophosphination activity of $[CpFe(CO)_2]_2$ (Cp = η^5 -C₅H₅) (1) with visible light using commercial LED light, which, to the best of our knowledge, is the first example of visible light promoted

catalytic hydrophosphination. This activity is likely the result of a known photoactivation of 1, presumably generating CpFe- $(CO)_2^{\bullet, 39-42}$ This observation implied that visible light irradiation of 1 may promote additional reactions because $CpFe(CO)_2^{\bullet}$ is an intermediate in the UV activation of 1 as well.³⁹⁻⁴² To test this hypothesis, catalytic reactions reported with $CpFe(CO)_2$ derivatives promoted by UV irradiation were revisited using 1 under visible light irradiation. The visible light promoted processes display similar, and in some cases improved, reactivity over UV-activated processes involving 1 or derivatives. These observations support the idea that lowenergy activation pathways are available for commercial, abundant catalysts.

RESULTS AND DISCUSSION

Hydrophosphination. Hydrophosphination of a variety of alkenes with diphenylphosphine is possible with visible light activation of 1 (Table 1). Catalytic reactions of alkenes and diphenylphosphine with 5 mol % of 1 were run neat with irradiation using a commercial LED bulb (λ_{irr} > 500 nm). Reactions were shielded from ambient light and periodically monitored to ensure the reaction temperature held between 25 and 28 °C, or slightly above ambient temperature.⁴

Electron-deficient styrenes proved to be more readily hydrophosphinated than unsubstituted or electron-rich styrenes. Notably, styrene itself was almost completely unreactive in these systems despite the low, but reproducible, reactivity observed for electron-rich substituents. Indeed, several samples of freshly distilled styrene were used with the same result. ¹H NMR spectra of these reactions reveal some unproductive reaction of the styrene substrate, but the exact reaction (such as

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 Table 1. Photocatalytic Hydrophosphination of Alkenes^c



^{*a*}Conversion measured by inverse-gated ³¹P{¹H} NMR spectroscopy.^{22,44,45} ^{*b*}Products found in a 5:2 ratio of anti-Markovnikov to Markovnikov. ^{*c*}Reaction conditions: 20.0 mg of 1 (0.056 mmol), 0.20 mL of Ph₂PH (1.13 mmol), alkene (1.13 mmol), ambient temperature, visible light irradiation.

polymerization vs H-abstraction or other events) is unclear. Michael acceptors such as methyl vinyl ester and acrylamide were excellent substrates for this reaction, which is consistent with previous studies of the hydrophosphination of these species.^{11,18,21,23,44} Neither reactions with secondary alkyl phosphines, Cy_2PH and ^tBu₂PH, nor unactivated alkenes (e.g., ethyl vinyl ether, Table 1) provide any significant formation of hydrophosphination products.

Control reactions provided some critical understanding of the catalysis. In the absence of iron, most of these reactions afford no new products. Similarly, without irradiation by visible light, there was no appreciable conversion, even in the presence of iron. For some Michael acceptors, there was competitive spontaneous hydrophosphination. For example, there is approximately 24% conversion of acrylamide to hydrophosphination products in the dark and 11% conversion in the absence of iron. This background reactivity is consistent with observation of additional Markovnikov products for acrylamide in the iron-catalyzed reaction.

Treatment of 1 with 1 equiv of Ph_2PH in benezene- d_6 solution, followed by irradiation in the visible for 30 min at ambient temperature, resulted in significant formation of P-H bond activation products as observed by multinuclear NMR spectroscopy (eq 1).46,47 Formation of CpFePPh₂(CO)₂ and $CpFeH(CO)_2$ is consistent with a direct activation of a single molecule of Ph₂PH by 1 equiv of photoactivated 1, or two Fpradicals. The observation of $CpFeH(PHPh_2)(CO)$ appears to be the reaction of Ph₂PH directly with CpFeH(CO)₂,⁴⁷ but that hydride is also known to decompose to 1.³⁹ Additionally, no P-H bond activation or any reaction was observed when 1 was treated with 1 equiv of Ph2PH in the dark at ambient temperature. These observations are consistent with the lack of hydrophosphination for most substrates in the dark and implicit of organometallic, rather than Lewis acidic, behavior from iron. These data further imply that the catalysis is a closed shell process rather than radical initiation by photogenerated CpFe(CO)₂• equivalents. Both phosphido compounds could be competent for a nucleophilic delivery of diphenylphosphide,⁴⁸ but we cannot discount insertion with our current data.



Photoactivation of 1. The photochemistry of 1 is a wellstudied process, with initial work dating back nearly 40 years.⁴⁹ Photoactivation of 1 and related CpFeX(CO)₂ (X = halide, pseudohalide, or methyl) derivatives occurs by several routes, though some common products arise. For CpFeX(CO)₂, dissociation of either the X⁻ or carbonyl ligand depends on the identity of X (Scheme 1A).^{50–54} For 1, irradiation in the UV commonly results in carbonyl ligand loss and ligand exchange. However, such irradiation also affords 2 equiv of CpFe(CO)₂^o either directly or via recombination with dissociated CO

Scheme 1. (A) Primary UV-Irradiation Products from Photoactivation of $CpFeX(CO)_2$ Derivatives Used in Catalysis.^{51-53,57} (B) Visible Light Photoactivation of 1 Utilized in This Work^{41,42}



(Scheme 1A).^{39–41} Likewise, some formation of $CpFe(CO)_2^{\bullet}$ can be observed for any $CpFeX(CO)_2$ derivative irradiated in the UV, even if primary products are CO or X⁻ dissociation (Scheme 1A). It is also known that irradiation in the visible affords 2 equiv of $CpFe(CO)_2^{\bullet}$ directly, and the individual steps have been probed in detail (Scheme 1B).⁴² This final activation route is attractive for providing primarily, if not exclusively, $CpFe(CO)_2^{\bullet}$ equivalents, which are doubtlessly important in photocatalytic reactions involving 1.^{40,42,55,56}

Because $CpFe(CO)_2^{\bullet}$ is a common product in the highenergy degradation of 1 (Scheme 1),⁵⁶ it was hypothesized that $CpFe(CO)_2^{\bullet}$, generated from visible light irradiated 1, could engage in the rich catalytic chemistry already demonstrated for 1 activated with UV irradiation. Evidence in support of this hypothesis would indicate if the visible light prompted hydrophosphination catalysis (vide supra) may be the basis for farther reaching photocatalysis. Therefore, a study of previously demonstrated catalytic dehydrocoupling of amine boranes using 1 with UV light was carried out with visible light.^{57–59} Such a study was undertaken to understand the broader applicability of 1 to promote additional, chemically important reactions under visible light irradiation.

Amine Borane Dehydrocoupling. Manners reported that the UV irradiation from a medium pressure Hg lamp of a THF solution of R_2 NHBH₃ (R = H, Me) with 5 mol % of 1 resulted in the dehydrocoupling of these compounds.^{57,59} When a THF solution of R₂NHBH₃ with 5 mol % of 1 at ambient temperature was irradiated with visible light (λ_{irr} > 500 nm, 6-15 W, 450-800 lm) open to a N₂ atmosphere for 4 h, a color change from dark red to green was observed with gas evolution. Analysis of the solutions by ${}^{11}B{}^{1}H$ NMR spectroscopy revealed conversions to products akin to what was observed by Manners and co-workers.^{57,59} The catalytic dehydrocoupling of Me₂NHBH₃ gave the cyclic dimer $(Me_2NBH_2)_2$ in 94% conversion as evidenced by ${}^{11}B{}^{1}H{}$ NMR spectroscopy ($\delta = 5.7$) as well as (Me₂N)₂BH ($\delta = 29$, Scheme 2).⁵⁷ Hydrogen evolution was measured using a gas buret, which showed 0.89 ± 0.02 equiv of hydrogen was produced over an average of three trials.

Scheme 2. Visible-Light-Catalyzed Dehydrocoupling of Me₂NHBH₃ (Top) and NH₃BH₃ (Bottom)^{a57,59,60}



"Percent conversions for the products are listed below, with literature values obtained by irradiation from a Hg lamp in parentheses.

Similar to Manners's system, irradiation throughout the reaction is not required despite the potentially different routes by which 1 may be of photoactivated.^{57,59} When a reaction mixture as described above was only irradiated for 1 h, and the reaction was then allowed to stir at ambient temperature for an additional 3 h, similar conversions to dehydrocoupled products were observed. Both 1 and photoirradiation are necessary for

dehydrocoupling to occur. A control reaction of Me_2NHBH_3 with 5 mol % of 1 at ambient temperature in the dark for 3 days failed to afford any dehydrocoupling products. Additionally, visible light irradiation of a THF solution of Me_2NHBH_3 or NH_3BH_3 at ambient temperature using only ambient lighting for 7 days failed to give any dehydrocoupling products, confirming the need for both 1 and irradiation to achieve dehydrocoupling in this system.

Similarly, reaction of a THF solution of NH₃BH₃ with 5 mol % of 1 under visible light irradiation gave a mixture of known products, though the ratio of products differed from those obtained under UV irradiation (Scheme 2).59 Indeed, the product distribution is consistent with greater hydrogen loss (i.e., activity) under these conditions. Nevertheless, the products observed are consistent with Manners's proposal of β -hydride elimination to afford H₂N=BH₂ for the UVactivated system.⁵⁷ In contrast to Me₂NHBH₃, when a mixture of 5 mol % of 1 and NH₃BH₃ in THF solution was irradiated with LED light for 1 h at ambient temperature and then the reaction was then was allowed to stir without irradiation for an additional 3 h at ambient temperature, there was no conversion to dehydrocoupling products as observed by ¹¹B NMR spectroscopy. This is also in contrast to a similar experiment using UV light,⁵⁷ which suggests that the different photoactivation pathways for 1 can cause substantial changes in reactivity in specific cases.^{41,42,49} Like the MeNH₂BH₃ reactions, both 1 and visible irradiation are required to release hvdrogen from ammonia borane.

Going beyond [**CpFe**(**CO**)₂]₂. The success of replicating or even increasing the activity of 1 in the dehydrocoupling of amine boranes demonstrates that visible light activation of 1 has broader reaching potential in catalysis than hydrophosphination. The specific photochemistry of 1 and that of its derivatives are different (Scheme 1), but the possibility that $CpFe(CO)_2^{\bullet}$ may be common or play a key role in these reactions is tantalizing. To further probe the potential value of visible light photocatalysis with 1, a UV-catalyzed reaction with a derivative of 1, $CpFeMe(CO)_2$ (2), was tested using visible irradiation of 1.

Pannell reported that UV irradiation of a DMF solution of PhMe₂SiH in the presence of 5 mol % of 2 for 4 h at ambient temperature resulted in the quantitative formation of (PhMe₂Si)₂O.⁵⁴ Under LED irradiation at ambient temperature for 1 h, PhMe₂SiH was quantitatively converted to (PhMe₂Si)₂O by 4 mol % of 1 in DMF, as evidenced by mass spectrometry and ²⁹Si{¹H} NMR spectroscopy ($\delta = 0.6$) (eq 2).

$$PhMe_{2}SiH \xrightarrow{4 \text{ mol }\% \text{ I, LED}}_{DMF, 4 \text{ h}} (PhMe_{2}Si)_{2}O + H_{2}$$
(2)

Visible light irradiation was required to achieve the observed reactivity. Reactions performed in the dark utilizing otherwise identical conditions resulted in no conversion. This example illustrates that 1 can engage in the same catalytic reactivity under LED irradiation as that of 2 under UV irradiation. This is a noteworthy feature because 2 is a derivative of 1, which is a commercial product. In a broader sense, this example demonstrates that visible light activation of 1 may enable a yet broader scope of catalytic reactivity.

CONCLUSIONS

Compound 1 promotes the hydrophosphination of styrenes and terminal alkenes under mild conditions with visible light irradiation, which represents the first example of visible light promoted metal-catalyzed hydrophosphination. Additionally, 1 is a competent visible light activated precatalyst for other maingroup bond forming reactions. These reactions were previously catalyzed by 1 using UV light from a mercury arc lamp. By utilizing the low-energy activation pathway of 1 from commercially available LED bulbs, comparable reactivity is observed at lower energetic cost. These examples underscore that additional photocatalysis may be possible with 1 under visible irradiation.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an inert atmosphere of N2 using Schlenk line or glovebox techniques using oxygen-free, anhydrous solvents. NMR spectra were recorded using a Bruker AXR 500 MHz spectrometer, using external references of 10% BF3·Et2O in CDCl3 for ¹¹B NMR experiments, SiMe₄ in CDCl₃ for ²⁹Si experiments, and 85% H₃PO₄ in H₂O for ³¹P NMR experiments (all references correspond to $\delta = 0$). ¹H NMR spectra were recorded using a Bruker AXR 500 MHz spectrometer and were referenced to residual solvent impurities ($\delta = 7.16$ for benzene $d_{\rm A}$).⁶¹ GC spectra were collected using a Varian Saturn 2100T gas chromatograph, and mass spectra were collected on an Applied Biosystems 4000QTrap Pro. Ammonia borane was purchased from Sigma-Aldrich and opened August 2014, after which it was stored at -35 °C under an inert atmosphere of N2. Ph2PH62 and CpFeMe- $(CO)_2$ (2)⁶³ were prepared by modified literature procedures and were stored under an inert atmosphere of N2 prior to use. All other reagents were obtained from commercial suppliers and dried by conventional means as necessary. Three different commercially available LED light bulbs were used over the course of trials. Their UV/vis-NIR spectra were measured using a Princeton Instruments Acton 2300 spectrometer and are reported in the Supporting Information. The temperature in the experimental setup was measured to be slightly above room temperature (25-28 °C) and was checked routinely to ensure minimal fluctuations in temperature.

Hydrophosphination of Alkenes with Diphenylphosphine. A screw-top NMR tube was charged with 1 (20.0 mg, 0.057 mmol), an unsaturated organic (1.13 mmol), and diphenylphosphine (0.20 mL, 1.13 mmol) and was irradiated with visible light at ambient temperature for 6–72 h depending on substrate. Reactions were monitored by ${}^{31}P{}^{1}H{}$ NMR spectroscopy approximately every 1 h to ensure a complete reaction. Products were identified by their literature ${}^{31}P$ NMR chemical shifts.²¹

Dehydrocoupling of Me₂NHBH₃. A 50 mL Schlenk flask was charged with a stir bar, Me₂NHBH₃ (30.0 mg, 0.51 mmol), **1** (9.0 mg, 0.025 mmol), and THF (5 mL). The reaction was placed under a slight positive pressure of N₂ and was irradiated using an LED light source for 4 h at ambient temperature, after which an aliquot was taken and was analyzed by ¹¹B{¹H} NMR spectroscopy.

Determination of Hydrogen Equivalents Produced from the Dehydrocoupling of Me₂NHBH₃. A 50 mL Schlenk flask was charged with a stir bar, Me₂NHBH₃ (30.0 mg, 0.51 mmol), 1 (9.0 mg, 0.025 mmol), and THF (5 mL). The reaction was attached to a gas buret and was irradiated using an LED light source for 4 h. After this time, the volume of H₂O displaced was measured and the equivalents of H₂ produced were determined by a previously described methodology.⁶⁴

Dehydrocoupling of Me₂NHBH₃, Timed Irradiation. A 50 mL Schlenk flask was charged with a stir bar, Me₂NHBH₃ (30.0 mg, 0.51 mmol), 1 (9.0 mg, 0.025 mmol), and THF (5 mL). The reaction was placed under a slight positive pressure of N₂ and was irradiated using an LED light source for 1 h at ambient temperature, then was covered in aluminum foil in the dark to exclude light for 3 h. An aliquot was then taken for ¹¹B{¹H} NMR spectroscopic analysis.

Dehydrocoupling of NH₃BH₃. A 50 mL Schlenk flask was charged with a stir bar, NH₃BH₃ (15.7 mg, 0.50 mmol), 1 (9.0 mg, 0.025 mmol), and THF (5 mL). The reaction was placed under a slight positive pressure of N₂ and was irradiated using an LED light source for 4 h at ambient temperature, after which an aliquot was taken and was analyzed by ¹¹B{¹H} NMR spectroscopy.

Dehydrocoupling of NH₃BH₃, Timed Irradiation. A 50 mL Schlenk flask was charged with a stir bar, NH₃BH₃ (15.7 mg, 0.50 mmol), 1 (9.0 mg, 0.025 mmol), and THF (5 mL). The reaction was placed under a slight positive pressure of N₂ and was irradiated using an LED light source for 1 h at ambient temperature, then was covered with aluminum foil in the dark for 3 h to exclude light. At this time, an aliquot was taken for ¹¹B NMR spectroscopic analysis.

Generation of (PhMe₂Si)₂O from PhMe₂SiH. A PTFE-sealed reaction vessel was charged with 1 (70.8 mg, 0.20 mmol), PhMe₂SiH (0.77 mL, 5.0 mmol), *N*,*N*-dimethylformamide (4.6 mL), and a stir bar. The reaction was irradiated using an LED light source for 1 h, after which an aliquot was taken for ²⁹Si{¹H} and MS analyses, which revealed a complete reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00499.

A photograph of the experimental setup, UV/vis–NIR spectra of LED bulbs used, and relevant spectra of reactions (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Gladysz, J. A.; Bedford, R. B.; Fujita, M.; Gabbaï, F. P.; Goldberg, K. I.; Holland, P. L.; Kiplinger, J. L.; Krische, M. J.; Louie, J.; Lu, C. C.; Norton, J. R.; Petrukhina, M. A.; Ren, T.; Stahl, S. S.; Tilley, T. D.; Webster, C. E.; White, M. C.; Whiteker, G. T. *Organometallics* **2014**, 33 (7), 1505–1527.

⁽²⁾ Fu, W.; Tang, W. ACS Catal. 2016, 6 (8), 4814-4858.

⁽³⁾ Demchuk, O. M.; Jasiński, R. Phosphorus, Sulfur Silicon Relat. Elem. 2016, 191 (2), 245–253.

⁽⁴⁾ Khusnutdinova, J. R.; Milstein, D. Angew. Chem., Int. Ed. 2015, 54 (42), 12236–12273.

⁽⁵⁾ Kendall, A. J.; Tyler, D. R. Dalton Trans. 2015, 44 (28), 12473-12483.

⁽⁶⁾ Fleming, J. T.; Higham, L. J. Coord. Chem. Rev. 2015, 297–298, 127–145.

(7) Misal Castro, L. C.; Li, H.; Sortais, J.-B.; Darcel, C. Green Chem. **2015**, *17* (4), 2283–2303.

- (8) Wauters, I.; Debrouwer, W.; Stevens, C. V. Beilstein J. Org. Chem. 2014, 10, 1064–1096.
- (9) Nell, B. P.; Tyler, D. R. Coord. Chem. Rev. 2014, 279, 23-42.
- (10) Waterman, R. Dalton Trans. 2009, No. 1, 18–26.
- (11) Bange, C. A.; Waterman, R. Chem. Eur. J. 2016, 22 (36), 12598-12605.
- (12) Trifonov, A. A.; Basalov, I. V.; Kissel, A. A. Dalton Trans. 2016, 45 (48), 19172–19193.
- (13) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. Organometallics **2008**, 27 (4), 497–499.
- (14) Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B.; Lomas, S. L.; Mahon, M. F.; Procopiou, P. A. *Dalton Trans.* **2010**, *39* (31), 7393–7400.
- (15) Douglass, M. R.; Marks, T. J. J. Am. Chem. Soc. 2000, 122 (8), 1824–1825.
- (16) Douglass, M. R.; Stern, C. L.; Marks, T. J. J. Am. Chem. Soc. **2001**, 123 (42), 10221-10238.
- (17) Erickson, K. A.; Dixon, L. S. H.; Wright, D. S.; Waterman, R. Inorg. Chim. Acta 2014, 422, 141–145.
- (18) Stelmach, J. P. W.; Bange, C. A.; Waterman, R. Dalton Trans. 2016, 45 (14), 6204–6209.
- (19) Grubbs, R. H. Angew. Chem., Int. Ed. 2006, 45 (23), 3760-3765.
- (20) Routaboul, L.; Toulgoat, F.; Gatignol, J.; Lohier, J.-F.; Norah, B.; Delacroix, O.; Alayrac, C.; Taillefer, M.; Gaumont, A.-C. *Chem. - Eur. J.*
- **2013**, *19* (27), 8760–8764.
- (21) Gallagher, K. J.; Webster, R. L. Chem. Commun. 2014, 50 (81), 12109-12111.
- (22) Espinal-Viguri, M.; King, A. K.; Lowe, J. P.; Mahon, M. F.; Webster, R. L. ACS Catal. 2016, 6 (11), 7892–7897.
- (23) Gallagher, K. J.; Espinal-Viguri, M.; Mahon, M. F.; Webster, R. L. Adv. Synth. Catal. 2016, 358 (15), 2460–2468.
- (24) Kamitani, M.; Itazaki, M.; Tamiya, C.; Nakazawa, H. J. Am. Chem. Soc. 2012, 134 (29), 11932–11935.
- (25) Itazaki, M.; Katsube, S.; Kamitani, M.; Nakazawa, H. Chem. Commun. 2016, 52 (15), 3163-3166.
- (26) Yoon, T. P.; Ischay, M. A.; Du, J. Nat. Chem. 2010, 2 (7), 527-532.
- (27) Yoon, T. P. ACS Catal. 2013, 3 (5), 895-902.
- (28) Schultz, D. M.; Yoon, T. P. Science 2014, 343, 1239176.
- (29) Chen, J.; Cen, J.; Xu, X.; Li, X. Catal. Sci. Technol. 2016, 6 (2), 349–362.
- (30) Ciriminna, R.; Delisi, R.; Xu, Y.-J.; Pagliaro, M. Org. Process Res. Dev. 2016, 20 (2), 403-408.
- (31) Douglas, J. J.; Sevrin, M. J.; Stephenson, C. R. J. Org. Process Res. Dev. 2016, 20, 1134–1147.
- (32) Srivastava, R. S.; Kolel-Veetil, M.; Nicholas, K. M. *Tetrahedron Lett.* **2002**, 43 (6), 931–934.
- (33) Wu, X.-F.; Bezier, D.; Darcel, C. Adv. Synth. Catal. 2009, 351 (3), 367–370.
- (34) Wu, X.-F.; Darcel, C. Eur. J. Org. Chem. 2009, 2009 (8), 1144–1147.
- (35) Wu, X.-F.; Darcel, C. Eur. J. Org. Chem. 2009, 2009 (28), 4753–4756.
- (36) Bézier, D.; Jiang, F.; Roisnel, T.; Sortais, J.-B.; Darcel, C. Eur. J. Inorg. Chem. **2012**, 2012 (9), 1333–1337.
- (37) Bézier, D.; Venkanna, G. T.; Castro, L. C. M.; Zheng, J.; Roisnel, T.; Sortais, J.-B.; Darcel, C. Adv. Synth. Catal. **2012**, 354 (10), 1879–1884.
- (38) Castro, L. C. M.; Sortais, J.-B.; Darcel, C. Chem. Commun. 2012, 48 (1), 151–153.
- (39) Davison, A.; McCleverty, J. A.; Wilkinson, G. J. Chem. Soc. 1963, 0 (0), 1133–1138.
- (40) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. J. Am. Chem. Soc. 1983, 105 (19), 6018–6021.
- (41) Dixon, A. J.; George, M. W.; Hughes, C.; Poliakoff, M.; Turner, J. J. J. Am. Chem. Soc. **1992**, 114 (5), 1719–1729.

- (42) George, M. W.; Dougherty, T. P.; Heilweil, E. J. J. Phys. Chem. 1996, 100 (1), 201–206.
- (43) See the Supporting Information for a figure of the experimental setup as well as UV/visible-near infrared spectra of three commercially available LED bulbs used in this study.
- (44) Ghebreab, M. B.; Bange, C. A.; Waterman, R. J. Am. Chem. Soc. 2014, 136 (26), 9240–9243.
- (45) Di Giuseppe, A.; De Luca, R.; Castarlenas, R.; Perez-Torrente, J. J.; Crucianelli, M.; Oro, L. A. *Chem. Commun.* **2016**, 52 (32), 5554–5557.
- (46) Nakazawa, H.; Ueda, Y.; Nakamura, K.; Miyoshi, K. Organometallics 1997, 16 (8), 1562–1566.
- (47) Nakazawa, H.; Kubo, K.; Kai, C.; Miyoshi, K. J. Organomet. Chem. 1992, 439 (2), C42-C45.
- (48) Glueck, D. S. Dalton Trans. 2008, No. 39, 5276-5286.
- (49) Bitterwolf, T. E. Coord. Chem. Rev. 2000, 206–207, 419–450.
 (50) Hashimoto, H.; Tobita, H.; Ogino, H. J. Organomet. Chem.
- 1995, 499 (1-2), 205-211.
- (51) Nakazawa, H.; Kamata, K.; Itazaki, M. *Chem. Commun.* **2005**, *31*, 4004–4006.
- (52) Nakazawa, H.; Itazaki, M.; Kamata, K.; Ueda, K. *Chem. Asian J.* 2007, 2 (7), 882–888.
- (53) Itazaki, M.; Ueda, K.; Nakazawa, H. Angew. Chem., Int. Ed. 2009, 48 (18), 3313–3316.
- (54) Sharma, H. K.; Pannell, K. H. Angew. Chem., Int. Ed. 2009, 48 (38), 7052–7054.
- (55) Abrahamson, H. B.; Palazzotto, M. C.; Reichel, C. L.; Wrighton, M. S. J. Am. Chem. Soc. **1979**, 101 (15), 4123–4127.
- (56) Caspar, J. V.; Meyer, T. J. J. Am. Chem. Soc. 1980, 102 (26), 7794-7795.
- (57) Vance, J. R.; Schäfer, A.; Robertson, A. P. M.; Lee, K.; Turner, J.; Whittell, G. R.; Manners, I. J. Am. Chem. Soc. **2014**, 136 (8), 3048– 3064.
- (58) Fukumoto, K.; Kasa, M.; Nakazawa, H. Inorg. Chim. Acta 2015, 431, 219-221.
- (59) Vance, J. R.; Robertson, A. P. M.; Lee, K.; Manners, I. Chem. -Eur. J. 2011, 17 (15), 4099–4103.
- (60) Kalviri, H. A.; Gartner, F.; Ye, G.; Korobkov, I.; Baker, R. T. Chem. Sci. 2015, 6 (1), 618-624.
- (61) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. Organometallics **2010**, *29* (9), 2176–2179.
- (62) Roering, A. J.; Leshinski, S. E.; Chan, S. M.; Shalumova, T.; MacMillan, S. N.; Tanski, J. M.; Waterman, R. Organometallics **2010**, 29 (11), 2557–2565.
- (63) Piper, T. S.; Wilkinson, G. J. Inorg. Nucl. Chem. 1956, 3 (2), 104–124.
- (64) Pagano, J. K.; Stelmach, J. P. W.; Waterman, R. Dalton Trans. 2015, 44 (27), 12074–12077.