Visible Light Enhanced Cobalt-Catalyzed Hydrogenation: Switchable Catalysis Enabled by Divergence Between Thermal and Photochemical Pathways

Lauren N. Mendelsohn, Connor S. MacNeil, Lei Tian, Yoonsu Park, Gregory D. Scholes, and Paul J. Chirik*

Department of Chemistry, Frick Chemistry Laboratory, Princeton University, Princeton, New Jersey 08544, United States

ABSTRACT: The catalytic hydrogenation activity of the readily-prepared, coordinatively saturated cobalt(I) precatalyst, (*R*,*R*)-(^{iPr}DuPhos)Co(CO)$_2$H ((*R*,*R*)-^{iPr}DuPhos = (+)-1,2-bis[(2*R*,5*R*)-2,5-diisopropylphospholano]benzene) is described. While efficient turnover was observed with a range of alkenes upon heating to 100 °C, the catalytic performance of the cobalt catalyst was markedly enhanced upon irradiation with blue light at 35 °C. This improved reactivity enabled hydrogenation of terminal, di- and trisubstituted alkenes, alkynes, and carbonyl compounds. A combination of deuterium labeling studies, hydrogenation of alkenes containing radical clocks and experiments probing relative rates support a hydrogen atom transfer pathway under thermal conditions that is enabled by a relatively weak cobalt–hydrogen bond of 56 kcal/mol. In contrast, data for the photocatalytic reactions support light-induced dissociation of a carbonyl ligand followed by a coordination-insertion sequence where the product is released by combination of a cobalt alkyl intermediate with the starting hydride, (*R*,*R*)-(^{iPr}DuPhos)Co(CO)$_2$H. These results demonstrate the versatility with catalysis with Earth-abundant metals as pathways involving open- versus closed-shell intermediates can be switched by the energy source.

KEYWORDS: *cobalt, hydrogenation, switchable mechanism, radicals, visible light, alkene*

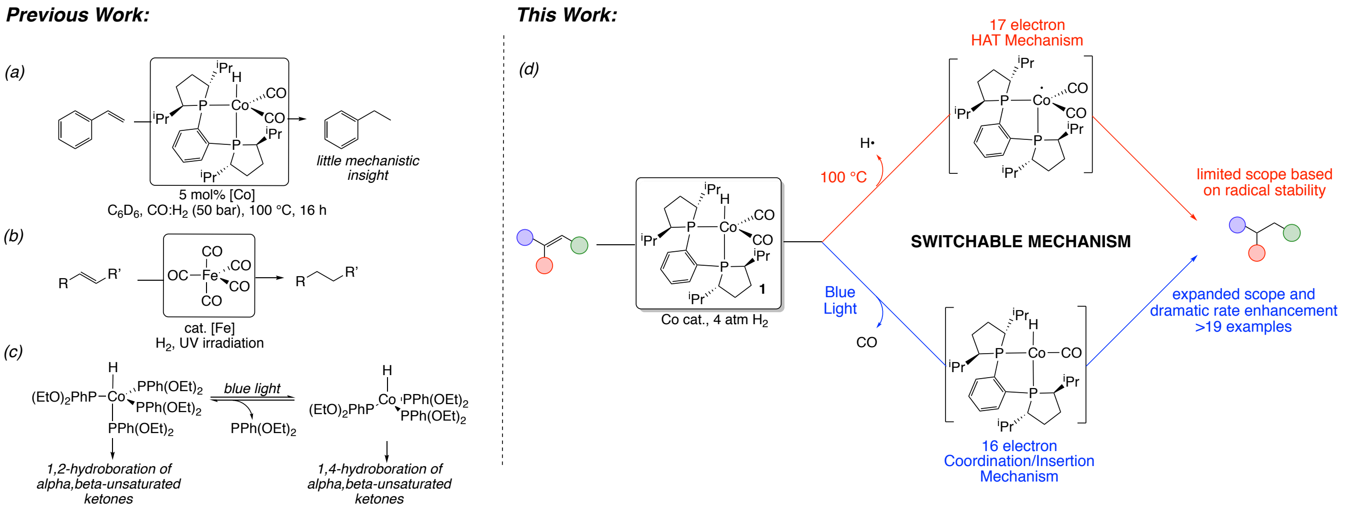
INTRODUCTION

The interaction of light with transition metal complexes opens new opportunities in catalysis as applied to organic synthesis.[1,2] Visible light is an attractive source of energy insofar as it is cost-effective, sustainable, and able to selectively excite photocatalysts over substrates in solution to enable distinct transformations.[3] Most methods have relied on iridium and ruthenium photocatalysts to transfer energy from their excited states to secondary catalysts and ultimately organic substrates.[4–6] Considerably less effort has been devoted to the excitation of transition metal complexes by visible light for direct use in catalysis.[7–15] One attractive feature of direct, visible light promoted catalysis is the potential to unlock mechanistic pathways under irradiation that are distinct from thermal reactivity.[16–19] In this way, by changing only the energy source, a single catalyst can follow divergent pathways for reaction with a substrate, leading to different products or enhancement in selectivity and scope.

Our laboratory recently reported the synthesis and initial reactivity studies of (*R*,*R*)-(^{iPr}DuPhos)Co(CO)$_2$H (**1**) in the context of alkene hydroformylation. In the presence of 50 bar of synthesis gas (1:1 H_2:CO), exclusive hydrogenation of styrene to ethyl benzene was observed (Scheme 1).[20] Density functional theory (DFT) calculations established a relatively weak Co–H bond dissociation free energy (BDFE) of 54 kcal/mol (wB97XD/{cc-pVDZ,def2-TZVP}), raising the possibility of a hydrogen atom transfer (HAT) pathway during catalysis.[21–26] The straightforward synthesis and bench stability of this complex motivated additional studies into catalytic applications with **1** using H_2 as the stoichiometric reductant.

While the relatively weak Co–H BDFE of **1** opens opportunities for catalytic HAT, it would be notable and potentially advantageous to use light to switch on distinct pathways involving closed-shell intermediates. For example, pioneering work by Wrighton, later supported by more detailed independent spectroscopic studies by Grant and Harris in addition to computational support from Weitz, demonstrated that irradiation of $Fe(CO)_5$ with UV light enabled catalytic hydrogenation of alkenes by a coordination-insertion pathway by photo-induced CO dissociation (Scheme 1b).[27–33] Subsequent work by Brown and coworkers further explored the unique photochemistry of a variety of metal carbonyl hydrides under UV irradiation.[34,35] UV irradiation of metal carbonyl complexes has also been reported to promote a variety of transformations including: hydrogenation, hydrosilylation, and hydroformylation.[36–46] More recently, Teskey and coworkers have used visible light to promote the divergent 1,2- and 1,4-selective hydroboration of α,β-unsaturated ketones by $[PPh(OEt)_2]_4CoH$ under thermal and photochemical conditions by proposed mechanisms involving electron transfer and single phosphine dissociation, respectively (Scheme 1c).[16,47] Use of visible light is an attractive alternative to avoid complications associated with traditional UV photochemistry for the excitation of metal carbonyls.

Scheme 1. Previous Work: (a) Reaction of 1 with styrene under thermal hydroformylation conditions yields exclusive hydrogenated product.[20] (b) UV irradiation promoted the hydrogenation of olefins by $Fe(CO)_5$.[28] (c) Blue light allows switchable hydroboration of *α,β*-unsaturated ketones by $[PPh(OEt)_2]_4CoH$.[48] This Work: (d) Switchable mechanism and scope of hydrogenation by 1 using heat or visible light.



Because of its absorption features, supporting CO ligands and preliminary hydrogenation activity, **1** was an attractive candidate for switchable catalysis between thermal HAT-type chemistry and photodriven organometallic chemistry. Alkene hydrogenation was selected as a representative transformation given its utility in synthesis, widespread use in industrial chemistry, the rich chemistry associated with bis(phosphine) cobalt complexes and demonstrated applications in metal-to-olefin HAT (MOHAT).[48–53] Here we describe the thermal and photochemical hydrogenation activity of **1**, and exploration of the mechanism of these transformations (Scheme 1d). In the thermal chemistry, an HAT mechanism is proposed while upon irradiation, the data support a pathway involving CO dissociation, followed by an alkene coordination-insertion sequence involving closed-shell intermediates.

RESULTS AND DISCUSSION

Thermal and Photochemical Hydrogenation Activity of 1 with Unsaturated Substrates. Our studies commenced with the evaluation of **1** as a photocatalyst. Blue light irradiation was selected because of the yellow color and associated electronic transitions of **1**. A broad absorption band was observed with a maximum in the solvent region, extending to around 450 nm in the toluene solution UV-vis spectrum (Figure 1). Because blue Kessil LED lamps have a maximum emission at 465 nm, extending down to 390 nm (Figure 1), these were selected as the light source. Ground state DFT calculations (wB97XD/{cc-pVDZ,def2-TZVP}) shed light on the orbitals most likely involved in electronic transitions (Figure 2). Specifically, calculations showed cobalt-centered HOMO (highest occupied molecular orbital) and HOMO-1 states with electron density around the Co-CO bonding orbitals, LUMO and LUMO+1 states primarily centered on the benzene ring of the [(*R*,*R*)-^{iPr}DuPhos] ligand, and LUMO+2 and LUMO+3 states with a significant amount of electron density placed on the two equatorial CO ligands. Time dependent DFT (TD-DFT) calculations (wB97XD/{cc-pVDZ,def2-TZVP}) predicted a maximum absorbance at 267 nm, with a tail feature extending to 444 nm (Figure 1). Predicted lowest energy transitions include a singlet transition at 354 nm, corresponding to transitions from the HOMO and HOMO-1 orbitals to the LUMO+2 orbital. Three additional low-probability triplet transitions, calculated at 393, 422, and 444 nm, correspond primarily to transitions from the HOMO and HOMO-1 orbitals to the LUMO+2 and LUMO+3 orbitals (states). Excitation into either the predicted 354 nm singlet excited state or the low-probability triplet states, accessible by the emission of the blue LED, support the possibility of light-induced CO labilization.

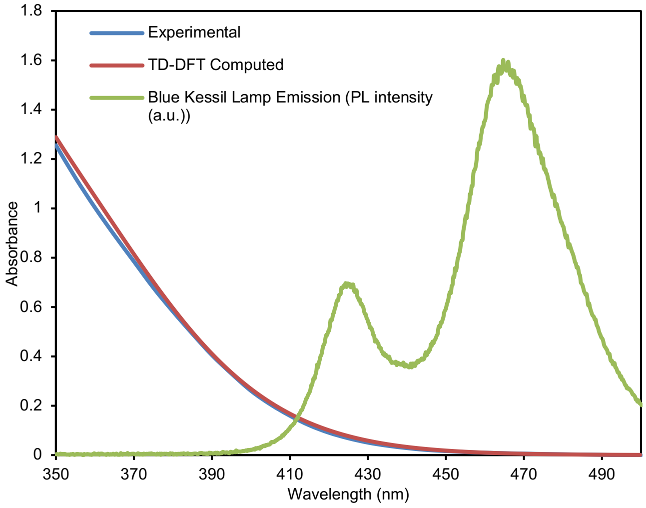


Figure 1. Experimental UV-vis spectrum of **1** (blue), TD-DFT computed UV/vis spectrum of **1** (red), normal emission spectrum of blue Kessil LED lamp (green).

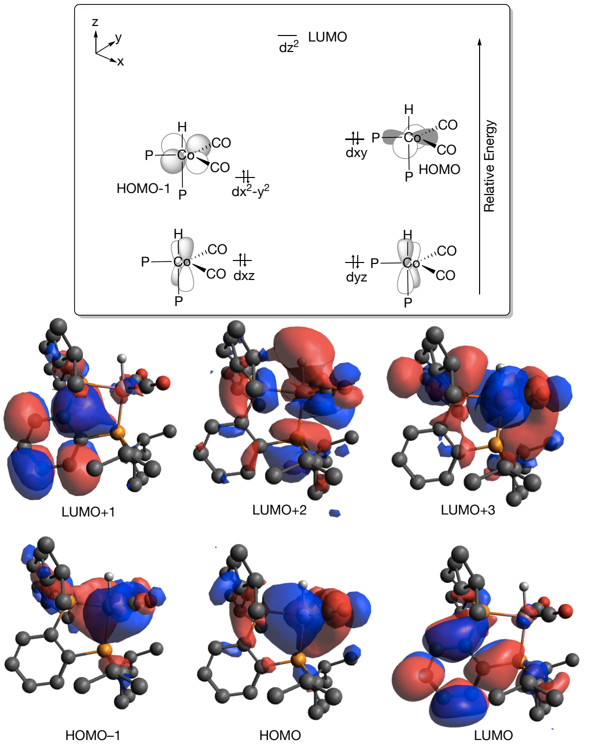
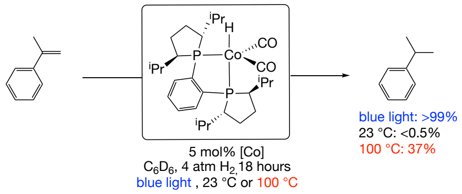


Figure 2. Selected, relevant DFT-computed molecular orbitals of **1** relevant to visible light absorption.

Subsequently, **1** was evaluated as a precatalyst for the visible light-driven hydrogenation of alkenes. Initial conditions employed a 0.1 M solution of substrate in benzene-*d*$_6$ with 5 mol% of **1** with 4 atm of H_2. In a typical experiment, the reaction vessel was irradiated with blue Kessil LED lamps for 18 hours, with an internal temperature of approximately 35 °C (see SI for details). Under these conditions, the hydrogenation of *α*-methyl styrene produced >99% yield by ^{1}H NMR spectroscopy of isopropyl benzene, while control reactions in the dark at room temperature reached <0.5% conversion (Scheme 2). Heating the hydrogenation to 100 °C for 18 hours produced alkane in 37% yield. Repeating the thermal and photochemical hydrogenations of *α*-methyl styrene in J-Young NMR tubes and monitoring the progress of the reaction demonstrated a dramatic rate enhancement for the photochemical reaction over the thermal one (Figure 3). After 45 minutes the thermal reaction proceeded to just over 5% yield while the photochemical reaction reached 66% yield, demonstrating a remarkable acceleration despite the significantly elevated temperature in the thermal case.

Scheme 2. Hydrogenation of *α*-methyl styrene by 1 under both thermal and photochemical conditions.



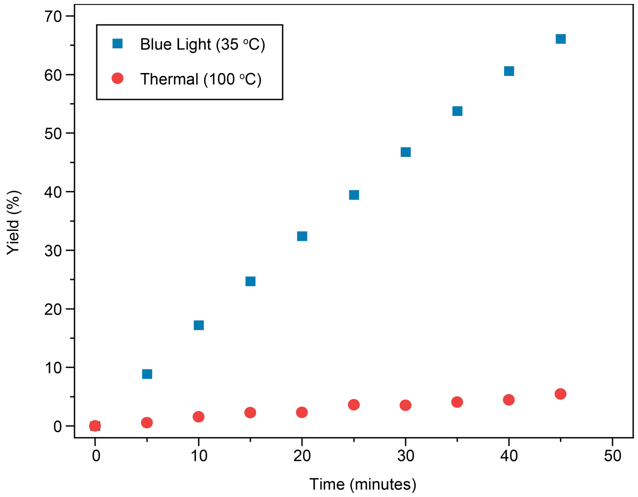


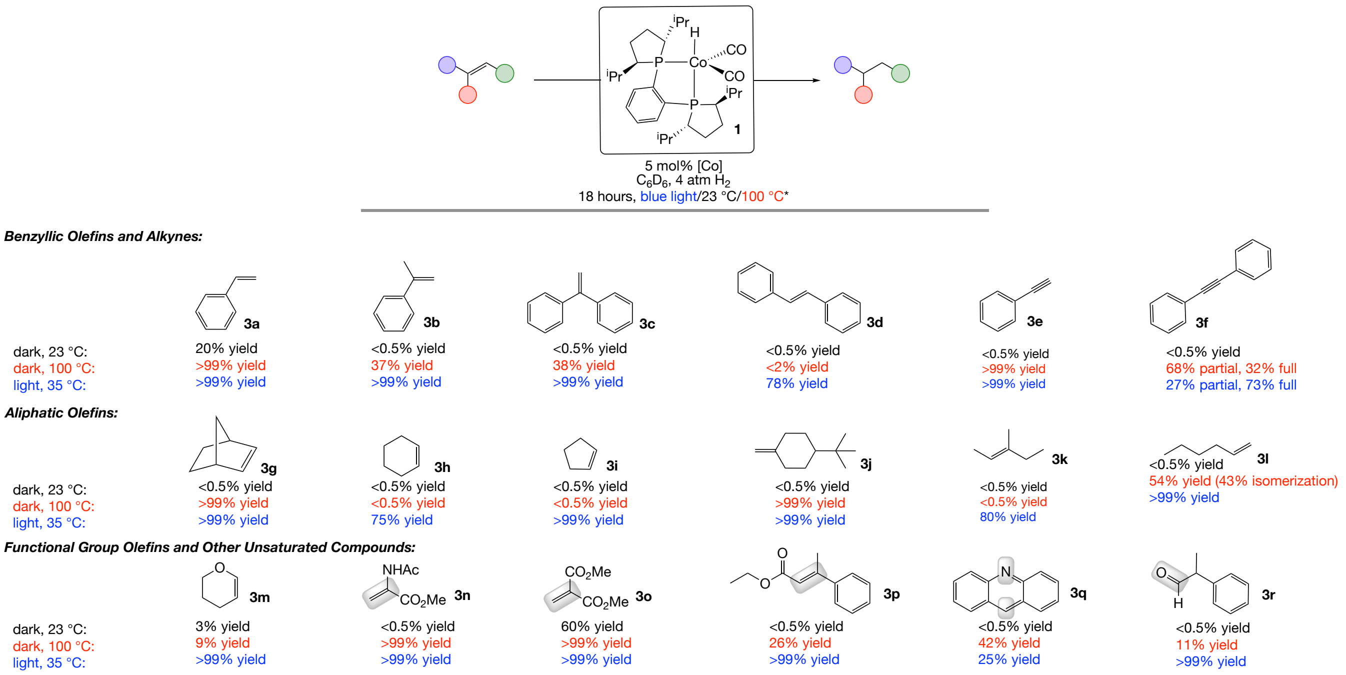
Figure 3. Reaction time courses for the hydrogenation of *α*-methyl styrene to isopropyl benzene under blue light (blue) and thermal (100 °C, red) conditions.

Inspired by these findings, the scope of the hydrogenation performance of **1** was explored. Both thermal (100 °C) and photochemical reactions (blue Kessil LED lamp) were carried out with a variety of alkenes, alkynes and carbonyl compounds (Table 1). Similar to the hydrogenation of *α*-methyl styrene, the yields for the catalytic hydrogenation of most alkene substrates varied among the three operating conditions. At room temperature and in the absence of ambient light, the olefin hydrogenation activity with **1** as the precatalyst was typically poor. For example, styrene (**3a**) was hydrogenated in 20% yield and 3,4-dihydropyran (**3m**) in 3% yield. Use of the activated alkene, dimethyl 2-methylenemalonate (**3o**) increased the yield to 60%. All other substrates evaluated under these conditions did not proceed to any appreciable yield. In this case, the low yields appear to be a result of slow reaction kinetics, rather than catalyst death, as **1** remained in intact as judged by ^{1}H and ^{31}P NMR spectroscopic analysis following each reaction. Heating the hydrogenation reactions to 100 °C under dark conditions improved the yields in some cases, but turnover remained poor for most sterically hindered, essentially unactivated alkenes.

Irradiation of the catalytic hydrogenation reactions promoted by **1** with blue light resulted in remarkably improved performance (Table 1). The photocatalytic method was effective with a range of mono-, di-, and trisubstituted alkenes and in most cases the corresponding alkane was obtained in >99% yield. Generally, thermal reactivity was more sensitive to the degree of substitution on the substrate than the photocatalytic method. As the substitution on the alkene was increased or more electron-rich substrates were used, the photocatalytic method outperformed the thermal one. For example, the thermal hydrogenation performance of **1** with arylated alkenes including: styrene (**3a**) (>99% yield), *α*-methyl styrene (**3b**) (37% yield), 1,1-diphenyl ethylene (**3c**) (38% yield), trans-stilbene (**3d**) (<2% yield), and trans-*α*-methyl stilbene (<0.5% yield), became progressively worse with increased substitution on the C=C bond. By contrast, the photocatalytic method was less sensitive to these changes as hydrogenations of styrene, *α*-methyl styrene and 1,1-diphenyl ethylene all proceeded to >99% yield, and trans-stilbene reached 78% yield. Similar to the dark (thermal) case, diminished yields in all reported thermal and photocatalytic reactions are a result of slow reaction kinetics rather than deactivation as **1** was observed as the exclusive cobalt product following the catalytic reactions. A similar trend was observed with arylated alkynes. While phenyl acetylene (**3e**) reached full conversion to ethyl benzene under both conditions, the hydrogenation of diphenylacetylene (**3f**) to 1,1-diphenylethane produced 73% yield upon irradiation but only 32% under thermal conditions. Attempts to hydrogenate trans-α-methyl stilbene with **1** under all three conditions did not produce any appreciable conversion, establishing a limit for the cobalt-catalyzed method.

Aliphatic alkenes followed an analogous trend in reactivity. While norbornene (**3g**), 4-tert-butylmethylenecyclohexene (**3j**), and 1-hexene (**3l**) reacted to complete conversion under both thermal and photocatalytic conditions, yields diverged with more substituted substrates. For example, hydrogenations of cyclohexene (**3h**) (75% yield), cyclopentene (**3i**)(>99% yield), and 3-methyl pent-2-ene (**3k**) (50% yield) reached significant conversion under photochemical conditions, but no appreciable yield of alkane was observed under thermal conditions.

Table 1. Scope of C=E hydrogenation with 1 as the precatalyst in the absence of light at room temperature, 100 °C (thermal), and with irradiation with blue light (35 °C).



*all yields based on ^{1}H NMR integration

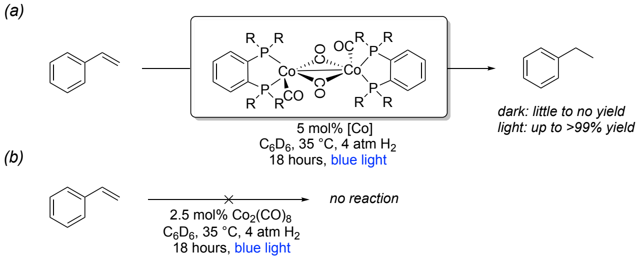
Both thermal and photocatalytic methods performed well with substrates bearing electron-withdrawing substituents. For example, methyl 2-acetamidoacrylate (MAA, **3n**) and dimethyl 2-methylene malonate (**3o**), both activated olefins, reached >99% yield under thermal and photocatalytic conditions. However, the thermal reaction remained more sensitive to steric effects as hydrogenations of 3,4-dihydropyran (**3m**) and ethyl (*E*)-3-phenylbut-2-enoate (**3p**) reached just 9% yield and 26% yield respectively under thermal conditions, while >99% yield was obtained upon irradiation with blue light.

Other substrates bearing carbon-element (C=E) unsaturated groups underwent hydrogenation using **1** as the pre-catalyst. Interestingly, acridine (**3q**) was hydrogenated in the 9,10-positions under both thermal and photochemical conditions. Under thermal conditions, a mixture of 9,10-dihydroacridine (20% yield) and the corresponding dimer, octahydro-9,9'-biacridine, (22% yield), were obtained. Under photocatalytic conditions, exclusive formation of the dimer was observed (25% yield). Acridine was the only substrate evaluated that was hydrogenated to a higher extent under thermal than photocatalytic conditions. Finally, 2-phenylpropanal (**3r**) was hydrogenated in >99% yield under photocatalytic conditions, but was hydrogenated to just 11% yield under thermal conditions.

To assess the use of blue LEDs with this cobalt complex, parallel hydrogenations of MAA (**3n**) (0.014 g, 0.012 mmol) with **1** (0.002 g, 0.004 mmol, 3.3 mol%) were performed with both blue light and UV irradiation. The solvent was changed from benzene to a mixture of pentane/THF (2:1) to accommodate UV irradiation. Identical solutions were irradiated for 7 minutes under 4 atm of H_2 by either 2 blue Kessil LED lamps (465 nm) or a UV irradiation box (Rayonet) cooled with water. Monitoring the outcomes of these reactions by ^{1}H NMR spectroscopy revealed that while >99% conversion to the hydrogenated product occurred with blue light, UV irradiation resulted in just 48% conversion to the alkane. The decrease in performance under UV conditions is likely a result of competing absorption by the organic starting material and product, illustrative of the problems associated with UV chemistry and further highlighting the advantage of visible light-promoted reactivity.

To determine if the [(*R,R*)-^{iPr}DuPhos] ligand was unique in promoting photodriven cobalt-catalyzed hydrogenation, a variety of other bis(phosphines) were also evaluated. Emphasis was placed on cobalt complexes with chelating ligands to avoid potential complications from phosphine dissociation with monodentate analogs. Treatment of $Co_2(CO)_8$ with a variety of bis(phosphines) generated $[(P\text{-}P)Co(CO)(\mu_2\text{-}CO)]_2$ complexes.[20,54] Derivatives with ^{Me}DuPhos, dppf, dcyp, and dppbenz (dppf = 1,1'-ferrocenediyl-bis(diphenylphosphine); dcyp = bis(dicyclohexylphosphino)ethane; dppbenz = 1,2-bis(diphenylphosphino)benzene) were synthesized and produced complete conversion to ethyl benzene in the photodriven hydrogenation of styrene (Scheme 3a). A variety of other substrates tested with the dcyp variant achieved similar yields to reactions with **1** (see SI for details). However, while general reactivity was not impacted, these complexes could not be generated as cleanly as the [(*R,R*)-^{iPr}DuPhos] variant. Additionally, complexes bearing the [(*R,R*)-^{iPr}DuPhos] ligand were selected for the added advantage of chirality as a mechanistic handle. A control reaction with $Co_2(CO)_8$ with blue light irradiation and 4 atm of H_2 produced no ethyl benzene (Scheme 3b). Although this cobalt precursor is red, this control experiment was conducted for completeness and to ensure that if blue light irradiation induced phosphine dissociation there was no background hydrogenation reaction.

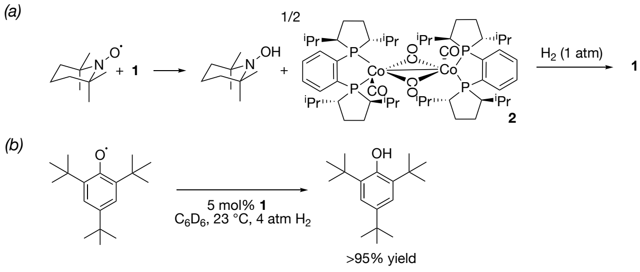
Scheme 3. (a) Hydrogenation of styrene using $[(P\text{-}P)Co(CO)(\mu_2\text{-}CO)]_2$ precatalysts bearing ^{Me}DuPhos, dppf, dcyp, and dppbenz ligands give >99% ethyl benzene under standard blue light conditions. (b) Dicobalt octacarbonyl gives only trace conversion of styrene under blue light conditions.



Mechanistic Investigations of Thermal Hydrogenation with 1. The hydrogenation activity of **1** under thermal (100 °C) and photocatalytic conditions, and remarkably improved performance upon irradiation prompted investigations into the mechanism of the reaction under both conditions. The relatively weak Co–H BDFE of 54 kcal/mol, previously reported for **1** raised the possibility of proton coupled electron transfer (PCET) or HAT as a possible mechanism for thermal hydrogenation.[21,23,25,55]

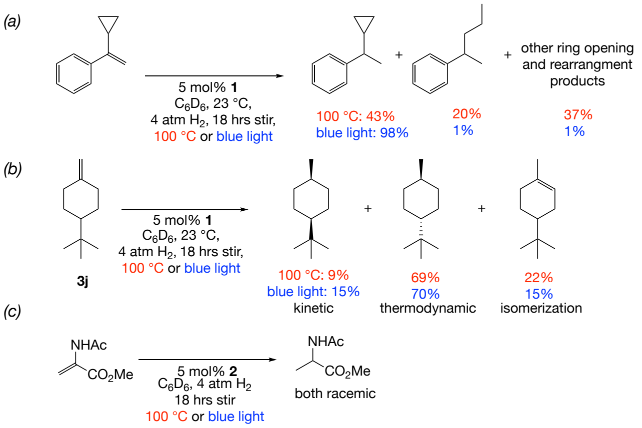
To explore potential radical reactivity, a 15 mM solution of **1** was treated with an excess (1.3 equivalents) of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy radical) (Scheme 4a). Monitoring the reaction by ^{1}H and ^{13}P NMR spectroscopy at ambient temperature revealed complete conversion to [(*R*,*R*)-^{iPr}DuPhosCo(CO)(μ$_2$-CO)]$_2$ (**2**) after 10 minutes. Subsequent exposure to 1 atm of H_2 gas resulted in complete regeneration of **1** after 10 hours at room temperature, demonstrating the ability of **1** to undergo HAT and subsequent reconstitution using hydrogen as the terminal reductant. Likewise, catalytic hydrogenation of 2,4,6-*tert*-butyl-phenoxy radical in the presence of 5 mol% of **1** and 4 atm of H_2 afforded 2,4,6-*tert*-butyl-phenol in >95% yield after three days, demonstrating the catalytic HAT performance of the cobalt hydride, **1** (Scheme 4b).

Scheme 4. Investigations into the role of radical intermediates in catalytic hydrogenations promoted by 1. (a) H-atom abstraction and regeneration of 1 with TEMPO and H₂. (b) Catalytic hydrogenation of 2,4,6-tri-*t*-butyl phenoxy radical under 4 atm of H₂.



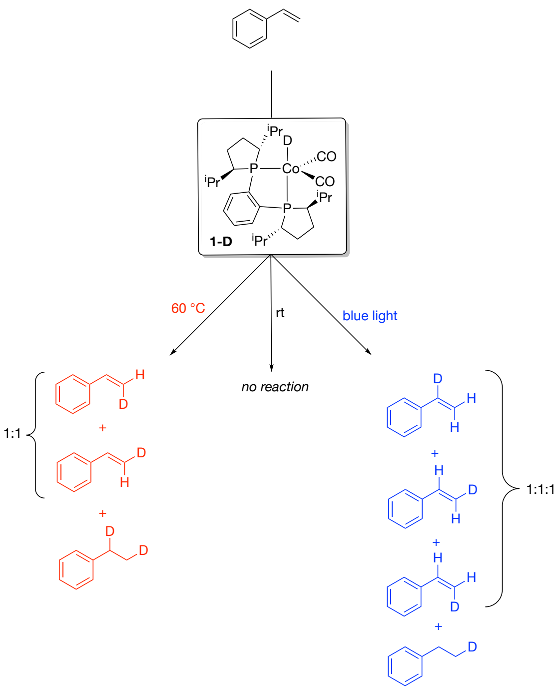
Three additional catalytic experiments were conducted to explore the possibility of HAT-type reactivity with alkenes. First, the catalytic hydrogenation of an established radical clock, α-cyclopropyl styrene (ring opening rate constant of 3.6 x 10^{5} at 20 °C)[56] was conducted. Under thermal conditions (100 °C) with 5 mol% of **1** full conversion to a mixture including α-cyclopropyl ethyl benzene, 2-phenyl pentane and 2-phenyl pent-2-ene was observed as judged by ^{1}H NMR spectroscopy and GC-MS (Scheme 5a). Observation of ring-opened products supports the formation of a benzylic radical during hydrogenation. Next, the catalytic hydrogenation of 4-*tert*-butylmethylenecyclohexene (**3j**) was performed. As reported by Shenvi and coworkers,[57] this alkene favors the formation of the *cis*-product under a classical hydrogenation pathway (kinetic control) and the *trans*-diastereomer from radical reactivity (thermodynamic control). With 5 mol% of **1** under thermal conditions, a 7.3:1 ratio favoring the *trans* diastereomer of the alkane along with a minor (22%) of the endocyclic olefin arising from isomerization (Scheme 5b) were observed, supporting radical chemistry. Finally, the hydrogenation of MAA at 100 °C in the presence of 5 mol % of **2** generated a racemic mixture of products (Scheme 5c). By comparison, [(*R*,*R*)-(^{iPr}DuPhos)Co(μ$_2$-CO)]$_2$, a precatalyst that differs by only one carbon monoxide ligand from **1**, hydrogenates MAA with >99% ee (enantiomeric excess), suggesting an outer-sphere pathway with **1**.[54]

Scheme 5. Radical probes for the catalytic reaction of 1 with alkenes. (a) Hydrogenation of α-cyclopropyl styrene. (b) Hydrogenation of 4-*tert*-butylmethylenecyclohexene and (c) of methyl acetimido acetate (MAA).



As has been reported previously,[20] the reaction of (*R*,*R*)-(^{iPr}DuPhos)Co(CO)$_2$D (**1-D**) with 5 equivalents of styrene in benzene at 60 °C for 3 hours resulted in deuterium incorporation into the two β-positions of the alkene as well as in the formation of a small amount of α,β-deuterated ethyl benzene (Scheme 6). Although exclusive β-deuteration is possible under a selective 2,1-insertion mechanism, this outcome is more consistent with an HAT pathway and when combined with the mechanistic probes detailed above, the observed β-deuteration likely arises from formation of a stabilized α-carbon radical. Reaction of **1-D** with 5 equivalents of styrene in benzene under 1 atm of CO for 3 hours at 75 °C established that the reaction proceeded in the presence of excess carbon monoxide, demonstrating that CO dissociation is not required for interaction of the alkene with the cobalt in the thermal pathway. Holistically, these results all point to HAT as the operative mechanism for thermal hydrogenation. Such a pathway also accounts for the lack of thermal hydroformylation activity observed with **1**.[20] Outer sphere HAT between **1** and the alkene suppresses subsequent and requisite insertion events required for carbonylation; instead capture of the alkyl and subsequent C–H bond formation releases alkane product.

Scheme 6. Reactions of 1-D with styrene.



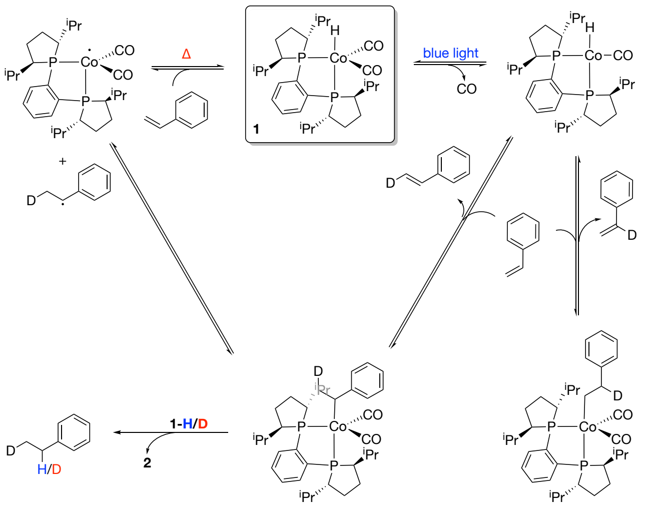
Investigations into the Mechanism of Light-Promoted Hydrogenation. The enhanced alkene hydrogenation performance upon irradiation with blue light prompted investigations into the mechanism of the photodriven reaction and what differences, if any, exist from the thermal process. Using the probes applied to the thermal reaction demonstrated similarities. For example, catalytic hydrogenation of **3** in the presence of 5 mol % of **1** and irradiation with blue light also favored the *trans* diastereomer of the alkane product (4.6:1 *trans:cis*), suggesting that the pathway is under thermodynamic control (Scheme 5b) Likewise, photocatalytic hydrogenation of MAA in the presence of 5 mol% of **1** and 4 atm of H_2 gave racemic product as judged by chiral GC analysis (Scheme 5c).

By contrast, photochemical hydrogenation of an alkene containing a radical clock, α-cyclopropyl styrene in the presence of 5 mol% of **1** resulted in 98% conversion to *α*-cyclopropyl ethyl benzene with less than 1% of each the ring opened and isomerized products (Scheme 5a). Photodriven hydrogenation of vinyl cyclopropane, a radical clock with a fast (1.2 x 10^8 s^{-1} at 37 °C)[56] ring-opening rate constant, produced only trace ring opening by ^{1}H NMR spectroscopy, suggesting that radical intermediates are not formed during hydrogenations of **1** with blue light (see SI for details). Together, these results suggest that while similarities in the overall thermal and photochemical reaction pathways may exist, the initial step is likely different and radical intermediates derived from the alkene are not formed with an appreciable concentration or lifetime.

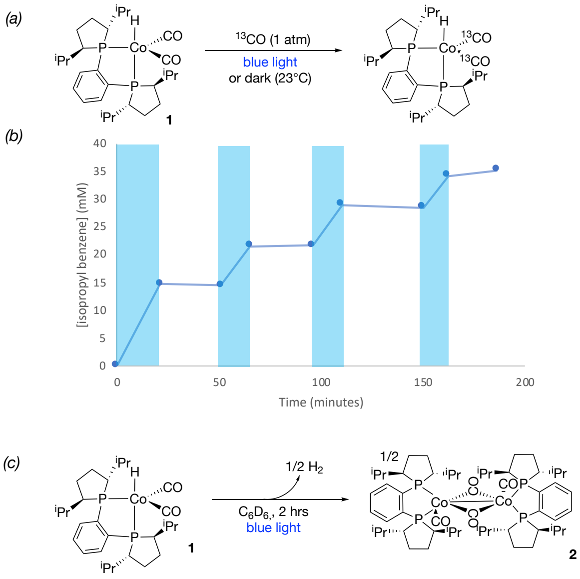
To further experimentally probe these mechanistic differences, five equivalents of styrene were added to a benzene solution of **1-D** and irradiated with blue light for 3 hours. Deuterium incorporation was observed in both the *α*- and *β*-positions of the alkene in a 1:1:1 ratio as judged by ^{2}H NMR spectroscopy while the ethyl benzene product was deuterated only in the *β*-position (Scheme 6). Repeating this experiment and monitoring the progress of the reaction by ^{2}H NMR spectroscopy over the course of 3 hours at ambient temperature established that the three styrene positions were deuterated at the same rate, and that the appearance of *β*-deuterated ethyl benzene was slower.

As shown in Scheme 7, it is likely that upon irradiation with blue light, CO dissociation occurs, opening a site for alkene coordination and insertion. The deuterium incorporation pattern in the recovered styrene demonstrates, for this substrate, that both 1,2- and 2,1-insertion pathways are operative and reversible. In the absence of H_2, the observed isotopomer of deuterated ethylbenzene demonstrates that only the 2,1-insertion intermediate is on the pathway for alkane formation. The formation of ethyl benzene may occur by a bimetallic event whereby the cobalt alkyl and **1** (or **1-D**) cooperatively release the alkane by either an inner or outer sphere pathway.[58] If the rate of insertion and elimination is much faster than the rate of reductive elimination or second HAT event in the absence of H_2, an abundance of Co–H generated from insertion/elimination would account for the observation of ethyl benzene deuterated only in the *β*-position. Such a pathway also resolves the seemingly conflicting outcomes from the radical probes outlined in the previous section. Specifically, while initial hydrogen transfer may occur by HAT in the thermal case and by a CO dissociation-alkene coordination-insertion sequence under photochemical conditions, formation of a common intermediate following these steps may enable identical pathways for reductive elimination.

Scheme 7. Proposed pathways to account for the deuteration of styrene and ethylbenzene in stoichiometric reactions with 1-D.



Scheme 8. Additional studies into the photochemical reactions of 1. (a) ^{13}CO exchange reactions; (b) Catalytic on-off reaction with α-methyl styrene; (c) Conversion of 1 to 2 upon irradiation with blue light.



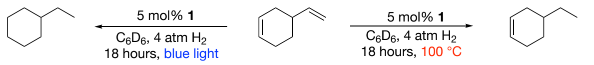
Guided by this hypothesis, additional experiments were conducted to understand the source of divergent reactivity in the initial reaction step(s). Light-induced labilization of monodentate ligands is well-established to promote hydrogenation and other alkene functionalization reactions by creating a vacant site for alkene coordination.[16,27,36] In contrast to Fe(CO)$_5$, which only undergoes exchange with ^{13}CO gas upon irradiation, the carbonyl ligands in **1** underwent rapid exchange with ^{13}CO gas under dark, room temperature conditions and at a variety of pressures.[59] Even at relatively low pressures (0.2 atm), isotopic exchange occurred too rapidly to studied quantitatively by ^{13}C NMR spectroscopy. While these results demonstrate that CO is labile under both dark and light conditions, they do not establish where the equilibrium lies between the 5-coordinate complex, **1**, and the putative 4-coordinate, mono(carbonyl) cobalt complex, (*R,R*)-(^{iPr}DuPhos)Co(CO)H nor its lifetime in solution. Because CO exchange is a thermoneutral process, when ^{13}CO is in excess, any amount of 4-coordinate (*R,R*)-(^{iPr}DuPhos)Co(CO)H formation results in exchange. On the other hand, CO for alkene exchange is an unfavorable reaction, and thus light-induced destabilization of **1** and formation of a greater population of (*R,R*)-(^{iPr}DuPhos)Co(CO)H is likely the origin of the observed rate enhancement in catalytic hydrogenation reactions.

The quantum yield for the catalytic hydrogenation of styrene with 1 was measured by using an iron(oxalate) photochemical standard.[60] With 0.8 mmol styrene and 0.2 mol% of **1** in 1 mL of benzene-*d*$_6$, an 11% yield of ethyl benzene was obtained in 4 minutes following irradiation by a blue Kessil LED lamp (440 nm) fitted with a 420 nm long pass filter, corresponding to a quantum yield of 0.17. Performing an "on-off" experiment for the photodriven hydrogenation of α-methyl styrene demonstrated that light was required for catalytic turnover (Scheme 8b). Monitoring the hydrogenation by NMR spectroscopy demonstrated that **1** was the only cobalt complex observed during the course of the reaction, both in the light and in the dark. Transient absorption spectroscopic measurements conducted at 420 nm established an excited state lifetime of 37 ps and no appreciable excited state quenching was observed in the presence of styrene, cyclopentene, or CO (see SI for details). These results demonstrate that **1** does not react directly with substrate, but is rapidly converted to another intermediate upon irradiation. After 54 ps, a slightly positive TA signal was observed in the absence of quencher or in the presence of CO, while a slightly negative signal was obtained in the presence of cyclopentene or styrene. While these results suggest partial photodegradation of **1** by alternate pathways, the newly formed species cannot be assigned from TA data alone. Additional experiments were performed to understand the fate of **1** following photolysis.

While heating a benzene solution of **1** at 120 °C for 7 days in the absence of alkene showed no conversion of the metal complex, irradiation with blue light at 35 °C rapidly produced a color change from yellow to orange. Monitoring the photochemical reaction by ^{31}P NMR spectroscopy established 16 % conversion of **1** to **2** after two hours with concomitant formation of H$_2$ gas (Scheme 8c). Repeating the photolysis under H$_2$ or CO gas fully suppressed this reactivity.

These results are analogous to those reported by Brown and coworkers in the study of HCo(CO)$_4$ and other related metal carbonyl hydrides.[34,35] The data support a radical pathway initiated by photo-induced cleavage of Co$_2$(CO)$_8$ to form Co(CO)$_4$• that in turn initiates a chain reaction resulting in conversion of HCo(CO)$_4$ to Co$_2$(CO)$_8$ and H$_2$. Invoking this precedent, the photoconversion of **1** to **2** and H$_2$ is likely initiated by the photolysis of **2**, a red compound, to generate (*R,R*)-(^{iPr}DuPhos)Co(CO)$_2$•. However, no reaction was observed upon exposure of a benzene-*d*$_6$ solution of **1** to green LEDs (525 nm), which emit light within the absorption range of **2** but not **1**, suggesting that the photoinitiation step is not homolytic cleavage of **2**. While additional exposure to a blue LED fitted with a 475 nm long pass filter for one hour produced trace (<2%) conversion of **1** to **2**, exposure to a blue LED fitted with a 420 nm long pass filter resulted in a 9% conversion from **1** to **2**. These results support the conclusion that visible light transitions of **1** are responsible for photodegradation activation mode. Because of the sterically demanding phosphines, it is more likely that blue light assists in the photodissociation of a carbonyl ligand from **1** to generate (*R,R*)-(^{iPr}DuPhos)Co(CO)H. This intermediate then likely reacts with **1** to form a bimetallic intermediate that releases H$_2$ and generates **2**. This conclusion is consistent with previously reported experiments from our group, whereby treatment of (*R,R*)-(^{iPr}DuPhos)Co(CO)Cl with NaHBEt$_3$ rapidly produced [(*R,R*)-(^{iPr}DuPhos)Co(μ_2-CO)]$_2$, demonstrating the instability of the proposed (*R,R*)-(^{iPr}DuPhos)Co(CO)H intermediate.[20]

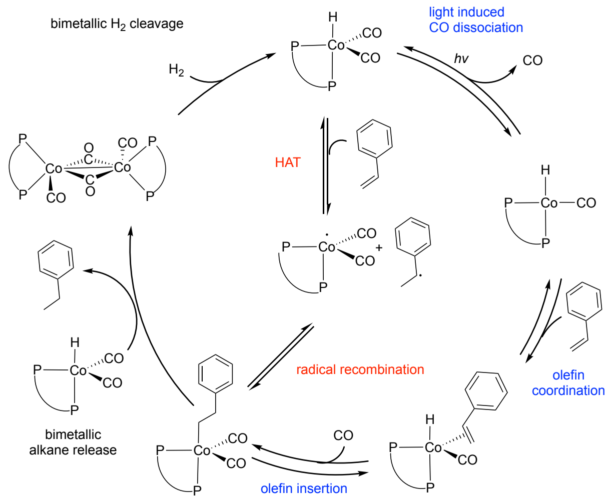
Scheme 9. Divergent outcomes from the hydrogenation of 4-vinylcyclohex-1-ene from thermal versus photochemical conditions.



To demonstrate the impact of switchable catalysis, **1** was used to hydrogenate 4-vinylcyclohex-1-ene, a substrate containing both an endocyclic and a terminal alkene, under both thermal and photocatalytic conditions (Scheme 9). The thermal procedure resulted in the exclusive hydrogenation of the terminal alkene, forming 4-ethylcyclohex-1-ene in 45% yield and leaving the endocyclic double bond untouched. By contrast, the photochemical reaction resulted in the hydrogenation of both the endocyclic and terminal alkenes to give ethylcyclohexane in 85% yield. These divergent outcomes, obtained from simply changing from heat to light stimulus, demonstrates the ability to alter the chemoselectivity of the reaction using an Earth-abundant metal catalyst.

The combined experimental data support the pathway presented in Scheme 10. While experimental results strongly suggest that the thermal reaction occurs by initial hydrogen atom transfer, the enhanced reactivity of **1** under light is likely the distinct result of photo-induced CO dissociation, followed by substrate coordination and migratory insertion into the cobalt-hydride bond. By opening this pathway, light enables the hydrogenation of a variety of substrates that are unreactive towards HAT, which relies on the stability of the incipiently formed radical. While caged-radical pairs for the thermal reaction and H_2 oxidative addition in the photochemical reaction have not been ruled out, similarities in experimental results regarding the final hydrogenation step suggest that following either radical recombination or migratory insertion, both the thermal and photochemical pathways may reach the same cobalt-alkyl intermediate. This intermediate is then intercepted with another equivalent of **1** to cooperatively release the saturated substrate and **2**, which can homolytically cleave H_2 to restart the catalytic cycle.

Scheme 10. Proposed catalytic cycle for thermal and photo-driven hydrogenation with 1.



CONCLUSIONS

The coordinatively-saturated, air-stable cobalt hydride, (*R,R*)-(^{iPr}DuPhos)Co(CO)$_2$H is active for the catalytic hydrogenation of a host of alkenes under both thermal and photochemical conditions. Competition, deuterium labeling and radical clock experiments established two distinct pathways from each of the catalytic conditions. In the thermal reactions, the data are most consistent with a hydrogen atom transfer pathway, consistent with the relatively weak cobalt–hydrogen bond of 56 kcal/mol. Notably, the cobalt catalyst can be regenerated using H_2 following HAT to the substrate.

Performing the catalytic hydrogenations with blue light significantly enhanced reactivity and expanded the scope of the cobalt-catalyzed method to include sterically hindered, unactivated alkenes and carbonyl compounds. Mechanistic experiments support a pathway that involves initial photodissociation of a carbonyl ligand followed by coordination-insertion of the substrate into the metal–hydrogen bond. This work opens new opportunities for catalysis with Earth abundant elements as weak metal-hydrogen bonds under thermal conditions can be applied to outer sphere reactivity while exposure to visible light can be used to open coordination sites and enhance performance.

AUTHOR INFORMATION

Corresponding Author

*pchirik@princeton.edu

ORCID

Lauren Mendelsohn: 0000-0002-0596-6938
Connor MacNeil: 0000-0001-6434-8394
Lei Tian: 0000-0002-4225-0038
Yoonsu Park: 0000-0003-1511-0635
Gregory D. Scholes: 0000-0003-3336-7960
Paul J. Chirik:0000-0001-8473-2898

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, compound characterization data and preparation, characterization data for hydrogenation products, spectroscopic and transient absorption data (PDF)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Catalysis Science program, under Award DE-SC0006498.

REFERENCES

(1) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113* (7), 5322–5363.

(2) Meggers, E. Asymmetric Catalysis Activated by Visible Light. *Chem. Commun.* **2015**, *51* (16), 3290–3301.

(3) Shin, N. Y.; Ryss, J. M.; Zhang, X.; Miller, S. J.; Knowles, R. R. Light-Driven Deracemization Enabled by Excited-State Electron Transfer. *Science* **2019**, *366*, 364–369.

(4) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. Photoredox Catalysis in Organic Chemistry. *J. Org. Chem.* **2016**, *81* (16), 6898–6926.

(5) Xuan, J.; Xiao, W. J. Visible-Light Photoredox Catalysis. *Angew. Chem., Int. Ed.* **2012**, *51* (28), 6828–6838.

(6) Inagaki, A.; Akita, M. Visible-Light Promoted Bimetallic Catalysis. *Coord. Chem. Rev.* **2010**, *254* (11–12), 1220–1239.

(7) Li, M. M.; Wei, Y.; Liu, J.; Chen, H. W.; Lu, L. Q.; Xiao, W. J.

Sequential Visible-Light Photoactivation and Palladium Catalysis Enabling Enantioselective [4+2] Cycloadditions. *J. Am. Chem. Soc.* **2017**, *139* (41), 14707–14713.

(8) Meng, Q.; Schirmer, T. E.; Katou, K.; König, B. Controllable Isomerization of Alkenes by Dual Visible-Light-Cobalt Catalysis. *Angew. Chem., Int. Ed.* **2019**, *131* (17), 5779–5784.

(9) Zhong, J. J.; Liu, Q.; Wu, C. J.; Meng, Q. Y.; Gao, X. W.; Li, Z. J.; Chen, B.; Tung, C. H.; Wu, L. Z. Combining Visible Light Catalysis and Transfer Hydrogenation for in Situ Efficient and Selective Semihydrogenation of Alkynes under Ambient Conditions. *Chem. Commun.* **2016**, *52* (9), 1800–1803.

(10) Theunissen, C.; Ashley, M. A.; Rovis, T. Visible-Light-Controlled Ruthenium-Catalyzed Olefin Metathesis. *J. Am. Chem. Soc.* **2019**, *141* (17), 6791–6796.

(11) Sattler, W.; Ener, M. E.; Blakemore, J. D.; Rachford, A. A.; Labeaume, P. J.; Thackeray, J. W.; Cameron, J. F.; Winkler, J. R.; Gray, H. B. Generation of Powerful Tungsten Reductants by Visible Light Excitation. *J. Am. Chem. Soc.* **2013**, *135* (29), 10614–10617.

(12) Huang, X.; Quinn, T. R.; Harms, K.; Webster, R. D.; Zhang, L.; Wiest, O.; Meggers, E. Direct Visible-Light-Excited Asymmetric Lewis Acid Catalysis of Intermolecular [2+2] Photocycloadditions. *J. Am. Chem. Soc.* **2017**, *139* (27), 9120–9123.

(13) Huang, X.; Quinn, T. R.; Harms, K.; Webster, R. D.; Zhang, L.; Wiest, O.; Meggers, E. Direct Visible-Light-Excited Asymmetric Lewis Acid Catalysis of Intermolecular [2+2] Photocycloadditions. *J. Am. Chem. Soc.* **2017**, *139* (27), 9120–9123.

(14) Torres, G. M.; Liu, Y.; Arndtsen, B. A. A Dual Light-Driven Palladium Catalyst: Breaking the Barriers in Carbonylation Reactions. *Science* **2020**, *368*, 318–323.

(15) Call, A.; Casadevall, C.; Acuña-Parés, F.; Casitas, A.; Lloret-Fillol, J. Dual Cobalt-Copper Light-Driven Catalytic Reduction of Aldehydes and Aromatic Ketones in Aqueous Media. *Chem. Sci.* **2017**, *8* (7), 4739–4749.

(16) Bergamaschi, E.; Beltran, F.; Teskey, C. Visible-light Controlled Divergent Catalysis Using a Bench-stable Cobalt(I) Hydride Complex. *Chem. Eur. J.* **2020**, *26*, 5180–5184.

(17) Teator, A. J.; Shao, H.; Lu, G.; Liu, P.; Bielawski, C. W. A Photoswitchable Olefin Metathesis Catalyst. *Organometallics* **2017**, *36* (2), 490–497.

(18) Peiris, E.; Sarina, S.; Waclawik, E. R.; Ayoko, G. A.; Han, P.; Jia, J.; Zhu, H. Y. Plasmonic Switching of the Reaction Pathway: Visible-Light Irradiation Varies the Reactant Concentration at the Solid–Solution Interface of a Gold–Cobalt Catalyst. *Angew. Chem., Int. Ed.* **2019**, *58* (35), 12032–12036.

(19) Fumagalli, G.; Rabet, P. T. G.; Boyd, S.; Greaney, M. F. Three-Component Azidation of Styrene-Type Double Bonds: Light-Switchable Behavior of a Copper Photoredox Catalyst. *Angew. Chem., Int. Ed.* **2015**, *127* (39), 11643–11646.

(20) MacNeil, C.; Mendelsohn, L.; Zhong, H.; Pabst, T.; Chirik, P. J. Synthesis and Reactivity of Organometallic Intermediates Relevant to Cobalt-Catalyzed Hydroformylation. *Angew. Chem., Int. Ed.* **2020**, *59*, 8912–8916.

(21) Shenvi, R. A.; Matos, J. L. M.; Green, S. A. Hydrofunctionalization of Alkenes by Hydrogen-Atom Transfer. In *Organic Reaction.* John Wiley & Sons, Inc., 2020; Vol. 100, Chapter 7, pp 383–468.

(22) Hu, Y.; Shaw, A. P.; Estes, D. P.; Norton, J. R. Transition-Metal Hydride Radical Cations. *Chem. Rev.* **2016**, *116* (15), 8427–8462.

(23) Estes, D. P.; Grills, D. C.; Norton, J. R. The Reaction of Cobaloximes with Hydrogen: Products and Thermodynamics. *J. Am. Chem. Soc.* **2014**, *136* (50), 17362–17365.

(24) Hartung, J.; Pulling, M. E.; Smith, D. M.; Yang, D. X.; Norton, J. R. Initiating Radical Cyclizations by H• Transfer from Transition Metals. *Tetrahedron Lett.* **2008**, *64* (52), 11822–11830.

(25) Estes, D. P. Transition Metal Hydrides That Mediate Catalytic Hydrogen Atom Transfers. PhD Thesis, Columbia University: New York, NY, 2014.

(26) Pappas, I.; Chirik, P. J. Catalytic Proton Coupled Electron Transfer from Metal Hydrides to Titanocene Amides, Hydrazides and Imides: Determination of Thermodynamic Parameters Relevant to Nitrogen Fixation. *J. Am. Chem. Soc.* **2016**, *138* (40), 13379–13389.

(27) Schroeder, M. A.; Wrighton, M. S. Pentacarbonyliron(0) Photocatalyzed Hydrogenation and Isomerization of Olefins. *J. Am. Chem. Soc.* **1976**, *98* (2), 551–558.

(28) Mitchener, J. C.; Wrighton, M. S. Photogeneration of Very Active Homogeneous Catalysts Using Laser Light Excitation of Iron Carbonyl Precursors. *J. Am. Chem. Soc.* **1981**, *103* (4), 975–977.

(29) Cedeño, D. L.; Weitz, E. Density Functional Theory Study of $Fe(CO)_3(\eta^2\text{-}C_3H_6)$, $HFe(CO)_3(\eta^3\text{-}C_3H_5)$, and the Iron-Allyl Bond Energy. *Organometallics* **2003**, *22* (13), 2652–2659.

(30) Kismartoni, L. C.; Weitz, E.; Cedeño, D. L. Density Functional Study of Fe(CO) 3 and Fe(CO) 3(L) with H 2 and C 2H 4, Where L = H 2 or C 2H 4: Reactions Relevant to Olefin Hydrogenation. *Organometallics* **2005**, *24* (20), 4714–4720.

(31) Sawyer, K. R.; Glascoe, E. A.; Cahoon, J. F.; Schlegel, J. P.; Harris, C. B. Mechanism for Iron-Catalyzed Alkene Isomerization in Solution. *Organometallics* **2008**, *27* (17), 4370–4379.

(32) Miller, M. E.; Grant, E. R. Gas-Phase Organometallic Catalysis: Kinetics and Mechanism of the Hydrogenation of Ethylene by Fe(CO)3(C2H4)2. *J. Am. Chem. Soc.* **1987**, *109* (26), 7951–7960.

(33) Weiller, B. H.; Grant, E. R. Gas-Phase Organometallic Kinetics. 2. Dissociative Substitution Kinetics of $Fe(CO)_2(C_2H_4)_3$ by Transient IR Absorption Spectrometry. *J. Am. Chem. Soc.* **1987**, *109* (4), 1051–1055.

(34) Wegman, R. W.; Brown, T. L. Photochemical and Thermal Decomposition of $HCo(CO)_4$ 1. Evidence for a Radical Pathway Involving $Co_2(CO)_8$. *J. Am. Chem. Soc.* **1980**, *102* (7), 2494–2495.

(35) Wegman, R. W.; Brown, T. L. Thermal and Photochemical Reactions of Dinuclear Metal Carbonyl Compounds with Metal Hydrides. *Organometallics* **1982**, *1* (1), 47–52.

(36) Wrighton, M. S.; Ginley, D. S.; Schroeder, M. A.; Morse, D. L. Generation of Catalysts by Photolysis of Transition Metal Complexes. *Pure Appl. Chem.* **1975**, *41*(4), 671–697.

(37) Wrighton, M. S. The Photochemistry of Metal Carbonyls. *Chem. Rev.* **1974**, *74*(4), 401–430.

(38) Wrighton, M. S.; Hammond, G. S.; Gray, H. B. Group VI Metal Carbonyl Photoassisted Isomerization of Olefins. *J. Organomet. Chem.* **1974**, *70*(2), 283–301.

(39) Wrighton, M. S.; Schroeder, M. A. Structure and Reactivity Relationships in Chromium Carbonyl Photoassisted Hydrogenation of 1,3-Dienes. *J. Am. Chem. Soc.* **1973**, *95*(17), 5764–5765.

(40) Nasielski, J.; Kirsch, P.; Wilputte-Steinert, L. Photo-Induced Hydrogenation of Conjugated Dienes Catalyzed by Chromium

Hexacarbonyl. *J. Organomet. Chem.* **1971**, *27*, C13–14.

(41) Bogdan, P. L.; Sullivan, P. J.; Donovan, T. A.; Atwood, J. D. Photocatalysis of Hydrogenation and Isomerization of Alkenes by cis-HMn$(CO)_4PPh_3$. *J. Organomet. Chem.* **1984**, *269*, C51–C54.

(42) Sweany, R. L. Photolyis of Matrix-Isolated Hydridotetracarbonylcobalt(I). Comparison of the Probabilities of Carbonyl Loss with Hydrogen Atom Loss. *Inorg. Chem.* **1982**, *21*, 752–756.

(43) Graff, J. L.; Wrighton, M. S. Photochemistry and Photocatalytic Activity of $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ for Isomerization and Hydrogenation of Alkenes. *Inorg. Chim. Acta* **1982**, *63*, 63–70.

(44) Bogdan, M.; Kownacki, I.; Chadyniak, D. Photochemically Induced Insertion of an Olefin into the Co–Si Bond; The Key Step for Silylative Coupling with Vinylsubstituted Organosilicon Compounds. *Inorg. Chem. Commun.* **1999**, *2*(12), 581–583.

(45) Gordon, E. M.; Eisenberg, R. Photochemical Hydroformylation Catalysis Using Ruthenium Complexes. *J. Organomet. Chem.* **1986**, *306*(2), C53–C57.

(46) Mirbach, M. J.; Topalsavoglu, N.; Phu, T. N.; Mirbach, M. F.; Saus, A. Photochemical Hydroformylation. **1981**, *Angew. Chem., Int. Ed.* **1981**, *20*(4), 381–382.

(47) Beltran, F.; Bergamaschi, E.; Funes-Ardoiz, I.; Teskey, C. J. Photocontrolled Cobalt Catalysis for Selective Hydroboration of Alpha,Beta-Unsaturated Ketones. *Angew. Chem., Int. Ed.* **2020**, *59*, 21176–21182.

(48) Chirik, P. J. Iron- and Cobalt-Catalyzed Alkene Hydrogenation: Catalysis with Both Redox-Active and Strong Field Ligands. *Acc. Chem. Res.* **2015**, *48* (6), 1687–1695.

(49) Seo, C. S. G.; Morris, R. H. Catalytic Homogeneous Asymmetric Hydrogenation: Successes and Opportunities. *Organometallics* **2019**, *38* (1), 47–65.

(50) Agbossou, F.; Carpentier, J. F.; Mortreux, A. Asymmetric Hydroformylation. *Chem. Rev.* **1995**, *95* (7), 2485–2506.

(51) Hebrard, F.; Kalck, P. Cobalt-Catalyzed Hydroformylation of Alkenes: Generation and Recycling of the Carbonyl Species, and Catalytic Cycle. *Chem. Rev.* **2009**, *109* (9), 4272–4282.

(52) Crossley, S. W. M.; Obradors, C.; Martinez, R. M.; Shenvi, R. A. Mn-, Fe-, and Co-Catalyzed Radical Hydrofunctionalizations of Olefins. *Chem. Rev.* **2016**, *116* (15), 8912–9000.

(53) Cui, X.; Burgess, K. Catalytic Homogeneous Asymmetric Hydrogenations of Largely Unfunctionalized Alkenes. *Chem. Rev.* **2005**, *105* (9), 3272–3296.

(54) Zhong, H.; Friedfeld, M. R.; Camacho-Bunquin, J.; Sohn, H.; Yang, C.; Delferro, M.; Chirik, P. J. Exploring the Alcohol Stability of Bis(Phosphine) Cobalt Dialkyl Precatalysts in Asymmetric Alkene Hydrogenation. *Organometallics* **2019**, *38* (1), 149–156.

(55) Sweany, R. L., Halpern, J. Hydrogenation of A-Methylstyrene by Hydridopentacarbonylmanganese(I). Evidence for a Free-Radical Mechanism. *J. Am. Chem. Soc.* **1977**, *99* (25), 8335–8337.

(56) Nonhebel, D. C. The Chemistry of Cyclopropylmethyl and Related Radicals. *Chem. Soc. Rev.* **1993**, *22* (5), 347–359.

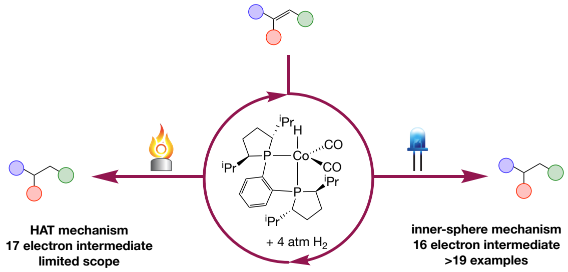
(57) Iwasaki, K.; Wan, K. K.; Oppedisano, A.; Crossley, S. W. M.; Shenvi, R. A. Simple, Chemoselective Hydrogenation with Thermodynamic Stereocontrol. *J. Am. Chem. Soc.* **2014**, *136* (4), 1300–1303.

(58) Klähn, M.; Garland, M. V. On the Mechanism of the Catalytic Binuclear Elimination Reaction in Hydroformylation Systems. *ACS Catal.* **2015**, *5* (4), 2301–2316.

(59) Noack, K.; Ruch, M. Carbon Monoxide Exchange in Pentacarbonyliron and Tetracarbonyl(Triphenylphosphine)Iron. *J. Organomet. Chem.* **1969**, *17* (2), 309–322.

(60) Wang, D.; Loose, F.; Chirik, P. J.; Knowles, R. R. N-H Bond Formation in a Manganese(V) Nitride Yields Ammonia by Light-Driven Proton-Coupled Electron Transfer. *J. Am. Chem. Soc.* **2019**, *141* (12), 4795–4799.

For Table of Contents Use



Blue Light Enhances Rate and Scope Through Switchable Mechanism