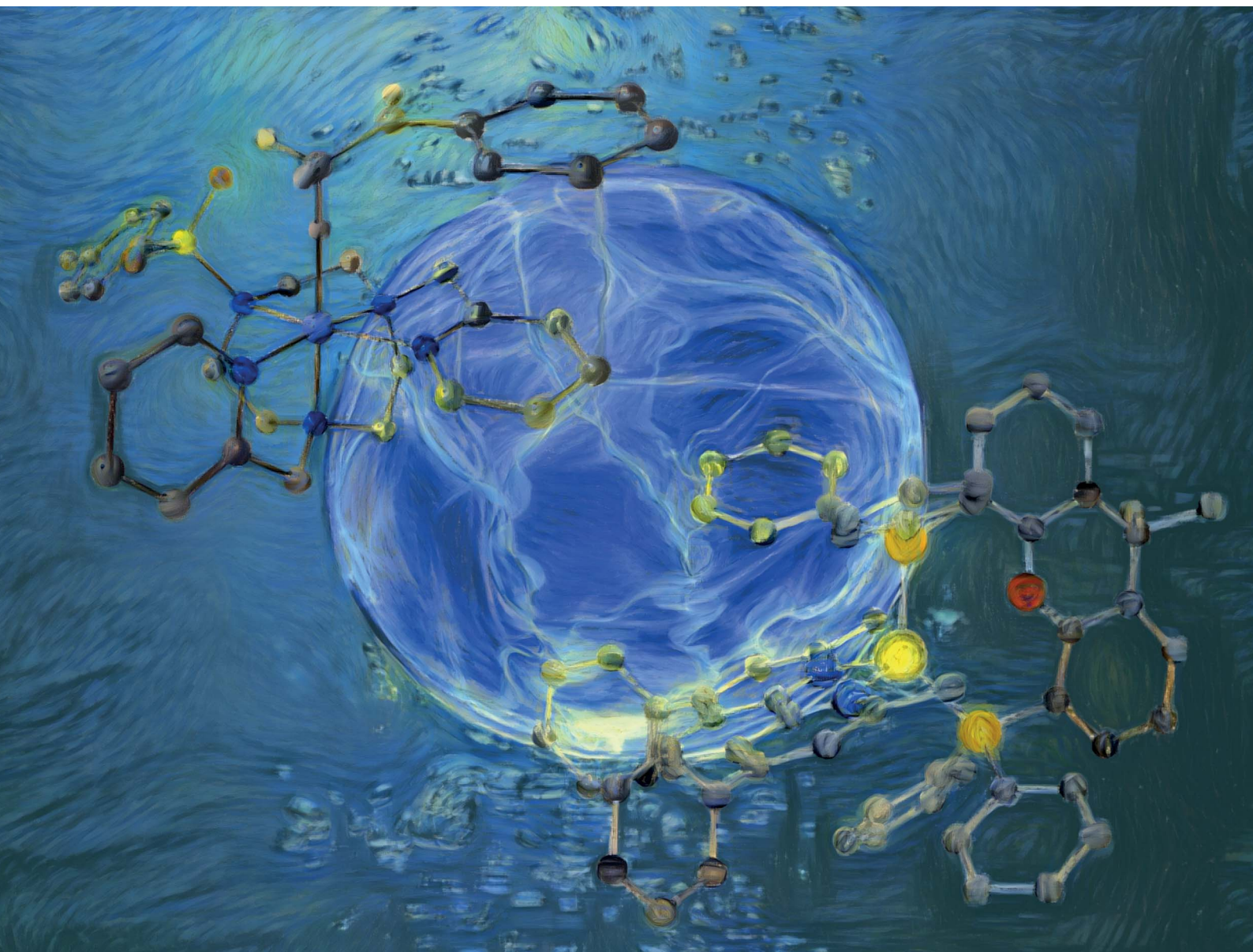


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Light-driven reduction of aromatic olefins in aqueous media catalysed by aminopyridine cobalt complexes†

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A catalytic system based on earth-abundant elements that efficiently hydrogenates aryl olefins using visible light as the driving-force and H₂O as the sole hydrogen atom source is reported. The catalytic system involves a robust and well-defined aminopyridine cobalt complex and a heteroleptic Cu photoredox catalyst. The system shows the reduction of styrene in aqueous media with a remarkable selectivity (>20 000) versus water reduction (WR). Reactivity and mechanistic studies support the formation of a [Co–H] intermediate, which reacts with the olefin via a hydrogen atom transfer (HAT). Synthetically useful deuterium-labelled compounds can be straightforwardly obtained by replacing H₂O with D₂O. Moreover, the dual photocatalytic system and the photocatalytic conditions can be rationally designed to tune the selectivity for aryl olefin vs. aryl ketone reduction; not only by changing the structural and electronic properties of the cobalt catalysts, but also by modifying the reduction properties of the photoredox catalyst.

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Introduction

The use of sunlight as driving force is a promising but challenging strategy towards sustainability in chemical production.^{1–4} Artificial photosynthesis (AP), as a technology to provide a clean source of reductive equivalents,^{4–8} has been mainly studied in the context of H₂O^{9–13} and CO₂ (ref. 14–18) reduction, with still limited progress towards organic transformations.^{1,2,4,8,19–32} A challenging transformation in the context of AP is the hydrogenation of double bonds.⁸ Among difficulties, most developed protocols employing the activation of H₂, silanes or alcohols are not suitable for operation under aqueous conditions.^{33–37} And only a few studies used light as a driving force and most of them have been carried out in the absence of water as a solvent. Moreover, selectivity of olefin reduction versus water reduction is needed for achieving a practical use in the context of AP. In the case of aromatic olefins, they are prompted to form radicals, tending to polymerize under such conditions.³⁸

In the context of AP, semiconductor materials such as TiO₂ and CdS were initially used as catalysts for the light-driven hydrogenation of electron-deficient olefins. These systems required UV light ($\lambda = 365$ nm) and noble metals to obtain moderate selectivity for alkane formation (Scheme 1a).^{39–41} Another remarkable example employed a B₁₂–TiO₂ hybrid for the UV light-driven reduction of alkenes to alkanes.⁴² Such highly energetic conditions led to the formation of dimeric products compromising the selectivity.⁴³

Holland, Corma and co-workers introduced the stereoselective hydrogenation of the conjugated C=C bond of ketoisophorone by combining the photocatalytic activity of Au nanoparticles supported on TiO₂ with the enzymatic activity of oxidoreductases by means of FAD⁺ as a mediator and cofactor (Scheme 1b).²² Likewise, Hartwig, Zhao and co-workers reported a cooperative chemoenzymatic reaction that combines the isomerization of C=C by an iridium photoredox catalyst with the hydrogenation activity of ene-reductases to selectively reduce electron-deficient aromatic olefins to their corresponding alkanes in high enantiomeric excess (88–99% ee).⁴⁴ All of these previous studies show that light-driven reduction of alkenes is feasible, albeit limited in substrate scope, selectivity and yield.

Very recently, X. C. Cambeiro and co-workers reported the use of an iridium photosensitizer in combination with a Hantzsch ester for the reduction of aromatic 1,2-disubstituted alkenes, albeit good yields were obtained only for activated olefins.⁴⁵ At the same time, M. Kojima, S. Matsunaga and co-workers found that glyoxime type complexes with a PCy₃ ligand

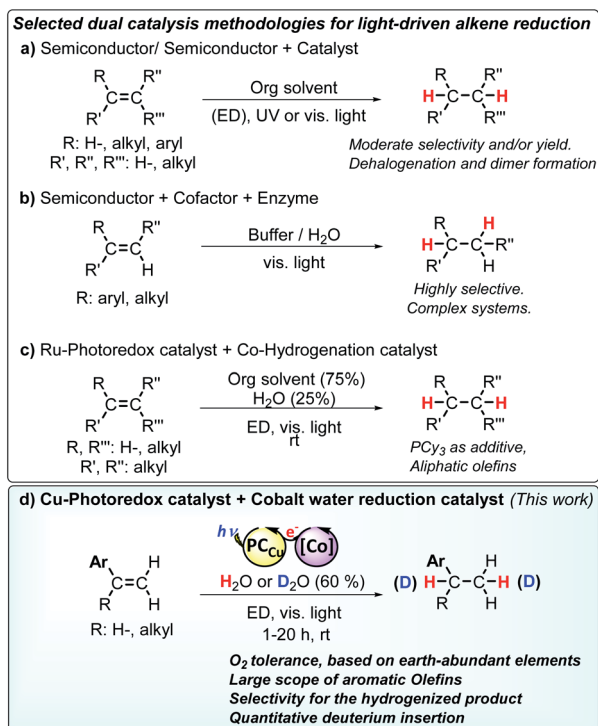
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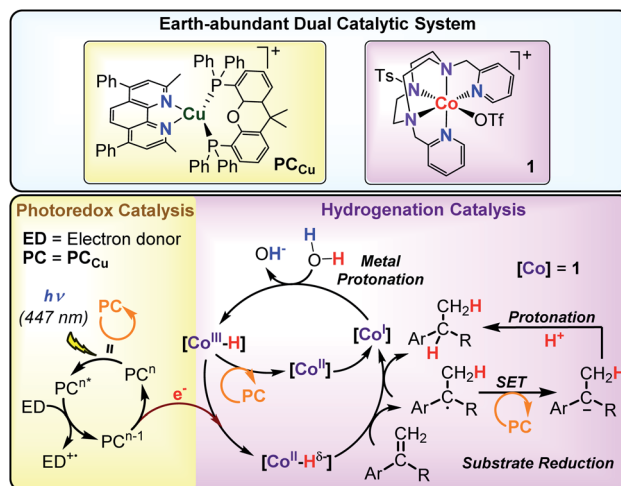




Scheme 1 Selected dual catalysis methodologies for the light driven reduction of olefins. Abbreviations: ED: electron donor. Selected references: (a) ref. 8 and 10, (b) ref. 11, (c) ref. 12 and (d) the developed methodology in this study.

and a ruthenium photoredox catalyst reduce aliphatic alkenes *via* a hydrogen atom transfer (HAT) mechanism.⁴⁶ However, aromatic alkenes have additional difficulties such as their tendency to engage in radical polymerization³⁸ or isomerization reactions^{47–49} under reductive conditions, which makes their reduction under photocatalytic conditions more challenging (Scheme 1). By a conceptually different approach, X. Guo, O. S. Wenger and co-workers recently reported the reduction of olefins by the photo-HAT reactivity of the organometallic iridium hydride complex [Cp*Ir^{III}(phen)-H] in acetonitrile.⁵⁰ Polyzos and co-workers showed the reduction of aromatic olefins *via* direct photoinduced electron transfer under highly reductive conditions and light intensity.⁵¹

Ideally, AP systems should employ water as a source of hydrogen atoms and efficiently use the photoredox catalyst in combination with molecular catalysts to facilitate the selective reduction of alkenes. Such an approach should identify catalysts' hits to develop more complex AP schemes. Towards this goal, we previously reported a dual catalytic system formed by [Co(OTf)(Py₂^{Ts}tacn)](OTf) (**1**) (Py₂^{Ts}tacn = 1,4-di(picoly)-7-(*p*-toluenesulfonyl)-1,4,7-triazacyclononane, OTf = trifluoromethanesulfonate anion) as a reduction catalyst and [Cu(bathocuproine)(xantphos)](PF₆)⁵² (PC_{Cu}) as a photoredox catalyst, which efficiently reduces water to hydrogen⁵³ and carbonyl groups to alcohols, using water as a hydrogen source.²⁹ Our mechanistic studies suggested that a cobalt(II) hydride ([Co(H)(Py₂^{Ts}tacn)]⁺, [Co^{II}-H]) was a common intermediate in both reduction reactions. Based on these precedents, we



Scheme 2 Earth-abundant dual catalytic system for the photoreduction of aromatic olefins.

hypothesized that [Co(H)(Py₂^{Ts}tacn)]⁺ should also be reactive enough to engage in the reduction of other organic functionalities without the need for strong reducing agents.⁵¹

Herein, we present a dual catalytic system consisting of cobalt complexes based on nitrogenated ligands (**1–15**), different Ir and Cu photoredox catalysts and an electron donor for the reduction of styrene derivatives using light as an energy source. The reduction operates without the use of typical reducing agents such as silanes, H₂, HCO₂H or alcohols. The best performing catalytic system is obtained by combining [Co(OTf)(Py₂^{Ts}tacn)](OTf) (**1**) and PC_{Cu} under light irradiation employing H₂O/Et₃N as a hydride source (Scheme 2).^{29–32} This synthetic methodology also allows for replacing H₂O by D₂O to produce the analogous deuterated alkanes. Reactivity and mechanistic studies based on kinetics, isotopic labelling and radical clock experiments suggest that the reduction of aromatic olefins occurs *via* a HAT mechanism, most likely through a [Co-H] intermediate. According to our mechanistic findings, the interplay between the catalyst/substrate redox potential, together with the light intensity, provides a way to control the selectivity for the reduction of aromatic olefins *versus* aromatic ketones and *vice versa*. This unique behaviour is rationalized by the different reduction mechanisms that each substrate undergoes.

Results and discussion

Based on previous studies,^{29,30} we hypothesized that the putative [Co(H)(Py₂^{Ts}tacn)]⁺ intermediate formed under photochemical conditions may engage in the reduction of more challenging substrates, such as styrene (**16**). The irradiation ($\lambda = 447 \pm 20$ nm ; $T = 35^\circ\text{C}$) of a solution containing styrene (**16**, 16.5 mM), complex **1** (1 mol%) as a reduction catalyst, PC_{Cu} (1.5 mol%) as a photoredox catalyst, and Et₃N (0.2 mL, 8.5 equiv.) as a sacrificial electron donor in a H₂O : CH₃CN (6 : 4 mL) solvent mixture, produced ethylbenzene (**16a**) in good yield (67%) (Table S.8, entry 1†). The reduction of styrene is accompanied by



small amounts of styrene dimerization (butane-2,3-diylidenebenzene, **16b**, 11% yield). The detection of this homocoupling product suggests the formation of benzylic radicals during the reaction, whose mechanistic implications will be discussed later (see the Mechanistic studies section).

(I) Screening of conditions and the catalytic system

The formation of homocoupling product **16b** was significantly minimized (4%) by increasing the catalyst and photoredox catalyst loadings (from 1.5 to 3 mol%) and reducing the styrene concentration (from 16.5 to 8.7 mM), yielding ethylbenzene (**16a**) in 86% yield. Further refinement of the reaction conditions was achieved by adjusting the reaction temperature. It is worth noticing that the reaction yield and selectivity are sensitive to the temperature. At 35 °C or higher, the yield of the reduced product drops in favour of the reduced homocoupling product. Therefore, the reaction temperature should be effectively controlled to prevent warming by light irradiation. Despite the common LED intensity (~2.1 W at 447 nm) used, the produced heat is enough to warm up the reactions to 45 °C if the temperature is not controlled.

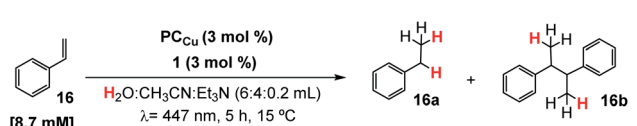
We have used an in-house developed parallel photoreactor to precisely control the temperature and light intensity (see the ESI for further details†).^{29,54} At 25 °C, the formation of the homocoupling product was only 3% (Table 1, entry 4) and negligible at 15 °C (Table 1, entry 5 and Table S8†). At lower temperatures, the homocoupling product was detected only in traces. We rationalized that the reduction of the selectivity at higher temperature is most likely due to accumulation of benzylic

radicals, which then favour dimerization. Under optimized conditions, the hydrogenation of styrene yields **16a** in 91% yield without detection of dimeric products (Table 1, entry 5).

Control experiments determined that all components of the photocatalytic system (light, the cobalt catalyst, photoredox catalyst and electron donor) are necessary for the formation of **16a** or **16b**. In the absence of light, **1**, PC_{Cu} , or Et_3N (Table 1, entries 6–9), neither **16a** nor **16b** was observed. To discard the formation of benzylic radicals from a direct single electron transfer (SET) reduction from the reduced photoredox catalyst ($[\text{Cu}(\text{bathocuproine})(\text{xantphos})]_2$, $[\text{PC}_{\text{Cu}}]^0$) to styrene, we performed photocatalytic studies in the absence of complex **1**. Even when the reaction was performed at 55 °C using 32 mM **16** and 10 mol% PC_{Cu} , no dimeric products were observed, discarding direct SET from $[\text{PC}_{\text{Cu}}]^0$ to styrene (Table S.9†). Indeed, $[\text{PC}_{\text{Cu}}]^0$ is not reductive enough to transfer an electron to **16** ($E(\text{PC}_{\text{Cu}}^{1/0}) = -1.60$ and $E_{\text{red}} = -2.31$ V vs. SCE for **16**). Additionally, no reduced products were detected when **1** was replaced by cobalt salts such as the starting cobalt(II) triflate ($\text{Co}(\text{OTf})_2(\text{MeCN})_2$, Table 1 entry 10). We found practically that the reduction yield of **16** was equivalent when complex **1** was synthesized *in situ* by adding the $\text{Py}_2^{\text{Ts}}\text{tacn}$ ligand with an equimolar amount of $\text{Co}(\text{OTf})_2(\text{MeCN})_2$ (Table 1 entry 11) under catalytic conditions.

The effect of the photoredox catalyst. On the other hand, replacement of the photoredox catalyst PC_{Cu} by $[\text{Cu}(\text{bathocuproine-1})(\text{xantphos})](\text{PF}_6)$ ($^1\text{PC}_{\text{Cu}}$) or $[\text{Cu}(\text{bathocuproine-SO}_3^-)(\text{xantphos})](\text{Na})$ ($^{\text{SO}_3}\text{PC}_{\text{Cu}}$) produced **16a** in lower yield (21 and 78%, respectively). We also tested three different iridium photosensitizers with different substituents on the bipyridine

Table 1 Optimization of the catalytic conditions for the reduction of **16** using PC_{Cu} as a photoredox catalyst and **1** as a catalyst^a



Entry	Deviation from conditions	% 16a	% 16b
1	16.5 mM 16 , 35 °C, 1 (1 mol%), and PC_{Cu} (1.5 mol%)	67	11
2	16.5 mM 16 and 35 °C	81	6
3	35 °C	86	4
4	25 °C	90	3
5	None	91	n.d.
6	No light	n.d.	n.d.
7	No Et_3N	n.d.	n.d.
8	No PC_{Cu}	n.d.	n.d.
9	No 1	n.d.	n.d.
10	$\text{Co}(\text{OTf})_2(\text{MeCN})_2$ instead of 1	n.d.	n.d.
11	$[\text{Co}(\text{OTf})_2(\text{MeCN})_2 + \text{Py}_2^{\text{Ts}}\text{tacn}]$ instead of 1	91	n.d.
12	$^1\text{PC}_{\text{Cu}}$ instead of PC_{Cu}	21	n.d.
13	$^{\text{SO}_3}\text{PC}_{\text{Cu}}$ instead of PC_{Cu}	78	n.d.
14	$^{\text{H}}\text{PC}_{\text{Ir}}$ instead of PC_{Cu}	11	8
15	$^{\text{NMe}_2}\text{PC}_{\text{Ir}}$ instead of PC_{Cu}	67	n.d.
16	$^{\text{CO}_2\text{H}}\text{PC}_{\text{Ir}}$ instead of PC_{Cu}	47	8
17	$\mathbf{1}_{\text{Ni}}$ instead of 1	n.d.	n.d.

^a Conditions: **1** (mol%), PC (mol%), and **16** (mM) as indicated in the table in $\text{H}_2\text{O} : \text{CH}_3\text{CN} : \text{Et}_3\text{N}$ (6 : 4 : 0.2 mL), irradiation at $\lambda = 447$ nm for 5 h at 35, 25 or 15 °C under N_2 . Yields were determined by GC analysis after workup of the reaction and relative to a calibrated internal standard. Values are average of triplicates. $[\text{Ni}(\text{OTf})(\text{Py}_2^{\text{Ts}}\text{tacn})](\text{OTf})$ ($\mathbf{1}_{\text{Ni}}$). See the ESI for the synthesis and characterization of metal complexes.



Y-2-pyridyl)methyl]-4,7-dimethyl-1,4,7-triazacyclononane) have been reported among the fastest catalysts for H₂ production with TOF, TON, and quantum efficiencies as high as 52 000 h⁻¹, 9000, and 9.7% ± 1.0 for complex **13**.⁵⁵ In this regard, the photocatalytic reduction of **16** was accompanied by the formation of H₂ as a side-product, in analogy to ketone and aldehyde reduction reactivity.²⁹ The formation of H₂ during the styrene reduction was monitored using pressure sensors^{29,56} and quantified by analysis of the reaction headspace using Gas Chromatography-thermal conductivity detector (GC-TCD, see the ESI for further details†). As expected, the selectivity of the studied Co complexes for the substrate *vs.* water reduction (Sel_{16a/H₂} calculated as $n(\mathbf{16a})/n(\mathbf{H}_2)$) strongly depends on the ligand scaffold. Under optimized conditions, complex **1** is also the most active catalyst for H₂ evolution with a Sel_{16a/H₂} of 1.04 (Table 3 and Fig. S.30†). Nonetheless, considering the concentrations of water and **16** in catalysis (ratio H₂O/**16** ~ 19 100), the normalized selectivity for the olefin reduction is about 20 000. Reducing the water in the reaction decreased the formation of H₂ at the expense of diminishing the TON of olefin reduction.

The produced H₂ was lower for the non-tacn ligand-based catalysts (**2–8**), providing an excellent selectivity for **16** *versus* water reduction and also the yields (Sel_{16a/H₂} = 5.4–9.0, Fig. S.30†). For tetradentate tacn-based complexes **9–14**, increasing the electron donating character of the ligand disfavours the H₂ evolution, complex **10** being the most efficient for H₂ evolution in the presence of the alkene (Sel_{16a/H₂} = 0.8 for

10, Fig. S.31†).³⁰ The 15-fold selectivity difference between **9** and **10** (*p*-MeO- *versus* *p*-CF₃-) illustrates the ligand control in the selective olefin/water reduction.

(II) Scope of the reaction

With the optimal conditions in hand, we examined the scope of aromatic olefins.

Monosubstituted styrene derivatives. Monosubstituted styrene derivatives with either electron-withdrawing or donating groups at the arene (**16–27**) are reduced within 5 h with excellent yields (73–99%) (Table 3). The reduction of *p*-bromostyrene (**22**) to *p*-bromoethylbenzene (**22a**) is obtained in moderate yield (53%), attributed to the partial formation of the reduced dehalogenated product in 19% yield. This is consistent with the previously reported reduction of aryl halides giving aryl radicals by visible light-induced electron transfer processes.⁵⁷ In the case of styrenes containing chlorine and fluorine atoms at the aromatic ring (**23–25**), the hydrogenation occurred without dehalogenation (Table 2).⁵⁸ Interestingly, the CF₃ substituted aromatic styrene derivative (**26**) was compatible with the reaction conditions. Finally, substrate **27**, with potentially problematic pyridine coordination, yielded the reduced product with excellent yield (99%).

1,1-Disubstituted olefins. Under optimized reaction conditions, the reduction product of 1,1-disubstituted aryl-alkyl olefins (**28a–32a**, Table 3) was accompanied by the reductive coupling of two olefins (**28b–32b**, Table 3, conditions A). We

Table 3 Light-driven reduction of selected aromatic mono- and 1,1-disubstituted olefins

		Earth abundant metals Visible light, water/ED as a source of H Efficient, robust and O ₂ tolerant
R = -H 16–27 R = -alkyl 28–36 R' = substituent	R = -H 16–27a R = -alkyl 28–36a R' = substituent	R = -alkyl 28–36b R' = substituent
Styrene derivatives and heteroaromatic compounds^a		
CONDITIONS A		
16a , 91%	17a , 95% (92%)	18a , 94% (81%)
<i>p</i> -Me: 19a , 99% <i>m</i> -Me: 20a , 86% <i>o</i> -Me: 21a , 86%	22a , 55/ ^c 19%, (53%)	<i>p</i> -Cl: 23a , 90%, (66%) <i>o</i> -Cl: 24a , 86%, (61%)
25a , 99%	26a , 73%,	27a , 99%
1,1-disubstituted Ar-olefins^{a,b}		
CONDITIONS A		
28 , 0% 28a , 40% 28b , 45%	29 , 0% 29a , 71% 29b , 11%	30 , 41% 30a , 58% 30b , 1%
31 , 7% 31a , 83% 31b , 0%	32 , 100% 32a , 0% 32b , 0%	28a , 91% 28b , 9%
29a , 79%, (57%) 29b , n.d.	30a , 49% 30b , n.d.	32a , 0% 32b , 0%
33a , 84%, (74%) 33b , n.d.	34a , 80% 34b , n.d.	35a , 78%, (66%) 35b , n.d.
36a , 99%, (83%) 36b , n.d.		

^a Conditions A: **1** (3 mol%), PC_{Cu} (3 mol%), and the substrate (8.7 mM) in H₂O : CH₃CN : Et₃N (6 : 4 : 0.2 mL), irradiated for 5 h (447 nm) at 15 °C under N₂. ^b Conditions B: **1** (6 mol%), PC_{Cu} (6 mol%), and the substrate (4.4 mM) in H₂O : CH₃CN : ¹Pr₂EtN (6 : 4 : 0.2 mL), irradiated for 24 h (447 nm) at -3 °C under N₂. Yields after workup (average of triplicates) were determined by GC analysis relative to a calibrated internal standard. Isolated yields between parentheses (average of 16 parallel reactions). ^c Yield of the reduced dehalogenated product.



rationalized the formation of homocoupling products as an indication of the presence of highly reactive benzylic radicals. For 1,1-disubstituted aryl-alkyl alkenes, it can be argued that these benzylic radicals are more stable against a single electron reduction surviving long enough to dimerize (see the Mechanistic studies section).

Such benzylic radicals could be formed by a HAT reaction from the [Co-H] intermediate to the less hindered carbon of the olefin, in agreement with the previously observed selectivity for M-H species.⁵⁹⁻⁶¹ These results are also in agreement with recent reactivity reported on the reduction and homo- and heterocoupling of alkenes using silanes as reducing agents;^{62,63} and on the reactivity of putative [Co-H] species with olefins by J. Norton and co-workers,^{64,65} as well as the recent studies of M Kojima, S. Matsunaga and co-workers.⁴⁶ Nevertheless, it is well-known that cobalt hydride complexes can undergo HAT to alkenes, and it was recently shown that it can be photo-induced.^{35,66}

We noted that the yield of the reductive homocoupling product decreased with the alkyl substituent size at the olefin (from -Me to ⁱPr), suggesting that the steric effect of the substituent influences the product selectivity, as expected for radical couplings. Moreover, the conversion of the -Me and -Et substituted alkenes (**28** and **29**) was quantitative, but not for the one with the ⁱPr group (**30**). With the aim to give an explanation for the lack of reactivity, we calculated and compared first the redox potentials of the olefins. As expected, the one electron reduction potential of the studied olefins is very negative (see Fig. S.26 and S.48†). However, the reaction yields are excellent for *para*-substituted arenes with a methoxide **17** and a *tert*-butyl group **18**, despite having $E_{1/2}^{0/-1}$ redox potentials of -2.50 and -2.45 V vs. SCE, respectively. These redox potentials are more negative than that calculated for the 1,1'-disubstituted Ph, ⁱPr alkenes (**30**) (-2.40 V, V vs. SCE), suggesting that the lower reactivity for **30** could be related to steric effects. Indeed, for the bulkier ^tBu-substituted aryl-alkyl olefin (**32**), there was no conversion. This agrees with the HAT mechanism since it is very sensitive to steric effects.⁶⁷

On the other hand, the catalytic system is inefficient towards the reduction of 1,2-disubstituted styrene derivatives (**37-41**), yielding the *trans-cis* isomerization reaction as previously reported,⁴⁷⁻⁴⁹ and only a trace amount of the reduced product was observed (Table S.16†). This is an indication of a triplet energy transfer from PC_{Cu} to the disubstituted alkene. Moreover, the isomerization also occurs without the presence of the Co(II) complex **1**. However, we can reasonably propose that the energy transfer (ET) path is minor to olefins because the reductive quenching of PC_{Cu} considering the concentrations is 10-fold larger by Et₃N than by our model olefin **16**. Moreover, when increasing the amount of Et₃N added to the reaction, the reduction of **16** was also accelerated. If the ET mechanism was the productive path for the reduction of **16**, an increase in the Et₃N concentration should have decreased the production rate of the reduced product; however, the opposite effect was observed (Fig. S.36†).

It is worth noting that in the absence of the cobalt catalyst, neither olefin reduction nor homocoupling products were

detected for the 1,1-disubstituted alkenes studied (**28-31**, Table S.15†). These results agree with the low redox potentials of **28-31** (E_{red} -2.36, -2.37, -2.40 and -2.29 V vs. SCE, respectively, Fig. S.26 and S.48†), that are ≥ 690 mV more negative than the [PC_{Cu}]⁰ reduction redox potential ($E(PC_{Cu}^{1/0}) = -1.60$ V vs. SCE). This supports that for the studied olefins, the generation of benzylic radicals by single electron transfer (SET) from [PC_{Cu}]⁰ is not feasible.

At this point, we hypothesized that the selectivity towards olefin reduction could be improved by decreasing the temperature of the reaction. Such a decrease should have an impact on the rate of formation of [Co-H] species and then the following formation of benzylic radical species. Preventing the radical accumulation, thus, avoids the formation of homocoupling products since the reaction is second order with respect to the concentration of radicals (eqn (1) and (2), where v_{rad} and k_{rad} are the rate and the formation rate constant of the benzylic radical, respectively; [R] and [PC⁻] are the concentration of the substrate and reduced photoredox catalyst, and v_{dim} and k_{dim} are the rate and the formation rate constant of the dimeric product, respectively). Consequently, at higher temperatures (>35 °C), the yield of the reduced product drops in favour of the homocoupling product. In addition, small quantities of trimers or higher order coupling products can be also detected by GC-MS, indicating a higher formation of radicals. In contrast, at low temperatures (15 to -3 °C, as specified per case), the dimeric products are negligible (Fig. S.32†).

$$v_{rad} = k_{rad}[R] \times [PC^{n-1}] \quad (1)$$

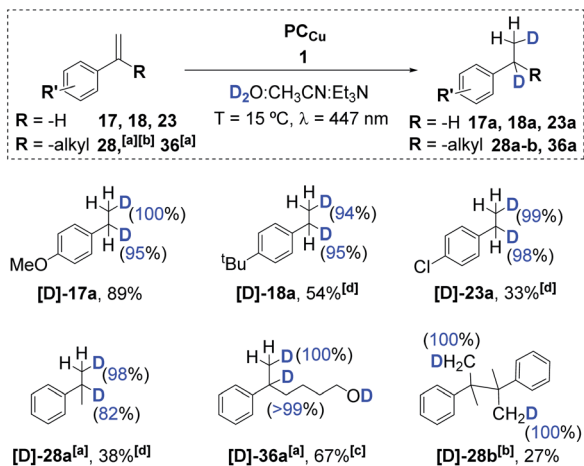
$$v_{dim} = k_{dim}[R]^2 \quad (2)$$

Further optimization showed that a bulkier electron donor such as diisopropylethylamine (DIPEA) favours the selectivity towards the reduced product (Tables S.8†), since it avoids formation of by-products between the electron donor and the substrate due to steric hindrance.⁶⁸ In addition, a finer tuning of the concentration of the substrate, catalyst **1** and photoredox catalyst PC_{Cu} (Tables S.11 to S.13†) allowed establishing optimal reaction conditions. Thus, by increasing the loading of **1** and PC_{Cu} (6 mol%), reducing the substrate concentration (4.4 mM), and using DIPEA at -3 °C, we achieved excellent selectivity for the reduction of 1,1-disubstituted aromatic alkenes (Table S.13† entry 5 and Table 1 conditions B).

O₂ tolerance. It is worth noticing that the photocatalytic system maintains its activity even when having O₂ in the headspace. The reduction of **16** and **28** is accomplished in 91 and 81% yields, respectively, when the reaction is carried out in air and using non-degassed solvents (Table S.17†). We rationalize these results using the capacity of the catalytic system to reduce O₂ to H₂O before reducing the olefins as we observed previously for the reduction of ketones.^{29,53,69} This contrasts with the high sensitivity of organometallic complexes to O₂ when performing hydrogenation reactions.^{33,70-72}

Deuteration of olefins. Since H₂O is the source of hydrogen atoms in the developed method, we also explored the possibility to obtain deuterated products by using D₂O as a solvent. Thus,





Scheme 3 Deuterium labelling studies of aromatic olefins (17, 18, 23, 28 and 36). Conditions: **1** (3 mol%), PCu (3 mol%), the substrate (8.7 mM) in $\text{H}_2\text{O} : \text{CH}_3\text{CN} : \text{Et}_3\text{N}$ (6 : 4 : 0.2 mL) irradiated for 5 h (447 nm) at 15 °C under N_2 .^[a] Conditions: **1** (6 mol%), PCu (6 mol%), and the substrate (4.4 mM) in $\text{D}_2\text{O} : \text{CH}_3\text{CN} : ^i\text{Pr}_2\text{EtN}$ (6 : 4 : 0.2 mL), irradiated (447 nm) for 24 h at -3 °C under N_2 .^[b] Conditions [a] modifying [Subs.] to 16 mM and 5 h at 30 °C. ^[c] NMR yield. ^[d] Low isolated yields were obtained due to the high volatility of the products. Isolated yields (average of 16 reactions). D-insertion analysed by NMR.

olefins 17, 18, 23, 28 and 36 were reduced with the dual $\text{PCu}/\mathbf{1}$ catalytic system in a $\text{D}_2\text{O} : \text{CH}_3\text{CN}$ mixture. We observed nearly quantitative olefin deuteration (see Fig. S.50–S.65[†]). Analytics showed the incorporation of one deuterium atom at each carbon atom of the double bond (α and β) (Scheme 3). Moreover, D-labelling studies of α -methylstyrene (28) under catalytic conditions that favour the reduced homocoupling product (high temperature and concentration of the substrate) showed the incorporation of only two deuterium atoms – each one at a different methyl group of the coupling product (Fig. S.56 and S.57[†]).

This agrees with the formation of M-deuteride species ($[\text{Co-D}]$) that are involved in a deuterium atom transfer (DAT) mechanism with the olefin, forming the corresponding benzylic radical, which dimerizes or ends up reduced and deuterated, affording the deuterated product. Moreover, we did not observe double deuteration at the same carbon nor H/D scrambling. Therefore, if organometallic cobalt species are formed after the insertion of Co–D/H in the olefin, the reversibility of the reaction *via* beta-hydride elimination should be negligible. Thus, it is more likely that benzylic radicals are directly formed *via* DAT/HAT from Co–D/H, supported by the observation of benzylic radical species. Nevertheless, an irreversible metal hydride insertion cannot be fully discarded.

(III) Mechanistic studies

To gain insight into the nature of the active species and the mechanism, we performed kinetic and reactivity studies, including D-labelling and radical clock experiments (Fig. 1).

First, kinetic studies in the presence of mercury showed that the photocatalytic activity is not inhibited, even in the presence

of a large amount of mercury (>2000 eq. vs. **1**, Fig. 1a). This suggests that the catalysis is not related to metal (0) nanoparticles, and thus, agrees with the homogeneous nature of the active species. We also studied the influence on the reduction rate for **16** in both H_2 and N_2 atmospheres (Fig. 1b). The kinetic traces were identical regardless of the atmosphere used, indicating that the source of hydrogen in the reduced products does not come from the H_2 generated under photocatalytic conditions. Indeed, both H_2 evolution and olefin reduction are competing pathways that share a common intermediate, since with catalyst **1**, the H_2 produced decreased at higher concentrations of styrene (Fig. S.33[†]).

By initial reaction rate analyses, we found that both **1** and PCu have a first-order reaction (Fig. 1d, S.34 and S.35[†]), in agreement with the bimolecular reduction mechanism of the cobalt catalyst by PCu . On the other hand, the reaction order found in olefin is close to zero (Fig. S.33[†]). Quenching studies with the copper photoredox catalyst (PCu) in the presence of TEA and styrene as a model substrate show similar quenching constants ($K_{\text{SV}} = 94.9 \text{ M}^{-1}$ and 109.8 M^{-1} , respectively). However, since the concentration of TEA under catalytic conditions is 10 times higher than that of styrene, we can consider the energy transfer pathway to the organic substrate to be negligible (Fig. 1e).

As introduced in the previous section, the exchange of H_2O by D_2O led to the formation of deuterated olefins with exclusive deuteration on the carbons of the olefin, and only two deuterium atoms were introduced one on each of the olefinic carbon atoms (Scheme 3 and ESI section 13[†] for NMR analyses). The absence of scrambling and double deuterium insertions indicates that regardless of the mechanistic path, the reaction is not reversible. On the other hand, when we employed 1,2-disubstituted olefin **41**, we did not observe deuterium insertion (Fig. S.62 and S.63[†]), indicating that although isomerization takes place, it is most likely to proceed through a photochemically generated excited state without the intervention of $[\text{Co-H}]$ insertion–elimination steps.⁵⁰ As introduced above, we discard the energy transfer as a significant path responsible for the reduction of olefins since the increase of the Et_3N concentration increased the reaction rate, despite both showing a similar quenching rate of the photoredox catalyst.

Experiments with radical clocks were performed to evaluate the formation of benzylic radicals *via* a HAT mechanism as already suggested by the formation of dimeric products. Olefins containing a 2-aryl-cyclopropyl moiety at the α -position are commonly used as probes for the formation of radicals in organic transformations.^{50,73} These radical clocks are very convenient because if a radical is generated in the benzylic position, it will trigger the cyclopropane ring opening with a high rate constant. For the (1-(2-phenylcyclopropyl)vinyl)benzene (**42**), cyclopropane ring opening is about 10^8 s^{-1} .^{74,75} Moreover, the presence of an aromatic group at the olefin is necessary to stabilize the benzylic radical after the cyclopropane ring-opening. Without the stabilizing group, the resulting product from the cyclopropane ring-opening is endergonic and could yield wrong conclusions (Fig. S.49[†]).^{74,75} Under catalytic



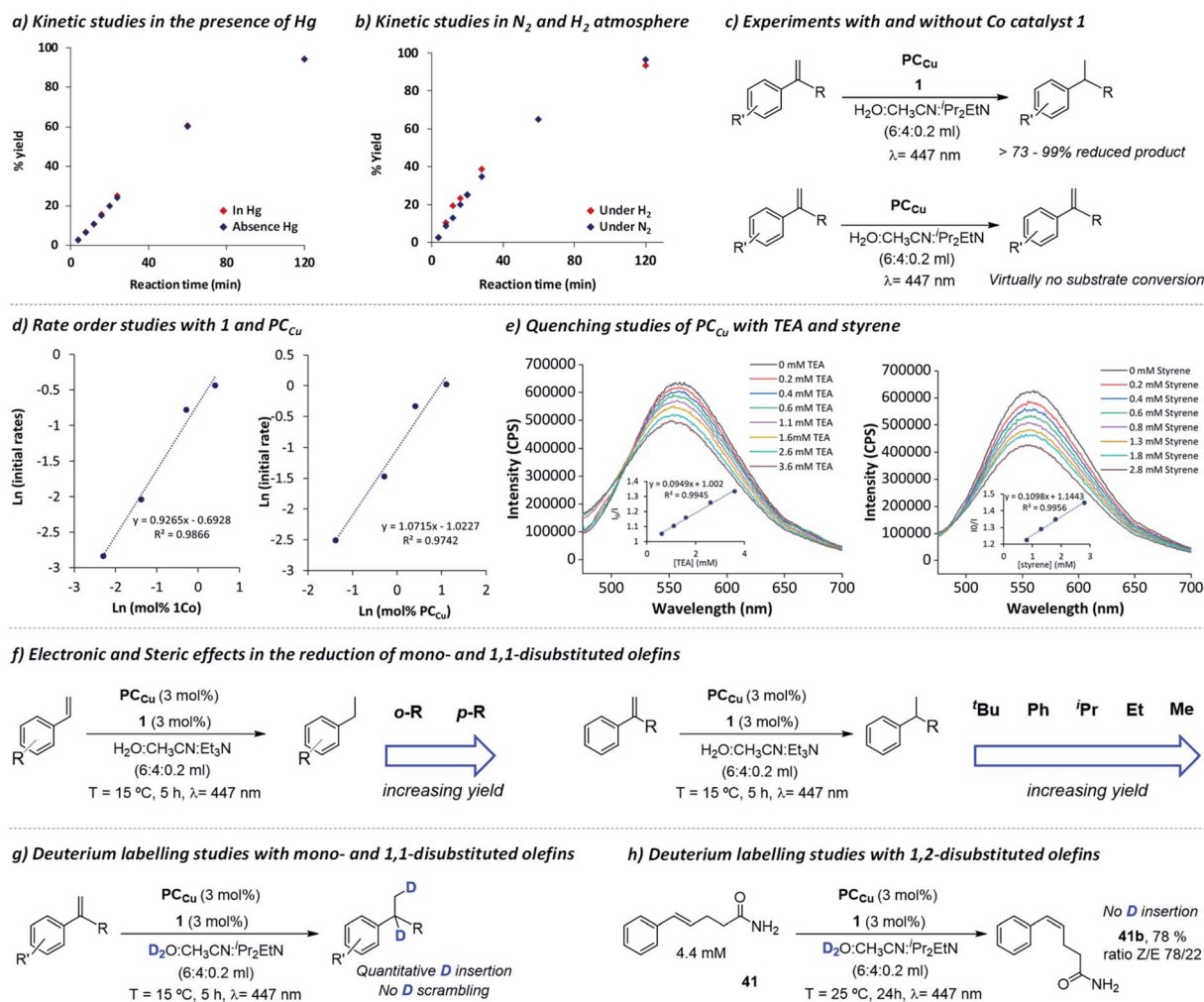


Fig. 1 Mechanistic studies. Formation of **16a** in (a) the absence (red diamonds) and presence of Hg(0) (>2000 eq.) (blue diamonds); and in (b) H₂ (red diamonds) or N₂ (blue diamonds) atmosphere. (c) Experiments with and without complex **1**. (d) Reaction rate kinetics regarding complex **1** and PC_{Cu}. (e) Reductive quenching studies of PC_{Cu} with TEA and styrene. (f) Steric effects in alkene reduction. Deuterium labelling studies of mono- and 1,1-disubstituted olefins (g) and 1,2-disubstituted olefin **41** (h, Z/E ratio analysed by NMR). See Experimental section 3 for the procedure details.†

conditions, the reduction of **42** only affords the ring-opening product (**42b**) without detection of **42a** (Scheme 4).

When the reaction was performed in D₂O, quantitative D-insertion at the β and benzylic positions was observed ([D]-**42b**, see Fig. S.64–S.70†). With the lack of the cobalt catalyst **1**, no ring-opening products were detected, fully recovering the substrate after irradiation. Both **42b** and [D]-**42b** can be formed *via* initial HAT (or DAT) from [Co–H] (or [Co–D]) followed by ring-opening and rearrangement to the most stable radical (Scheme 4).

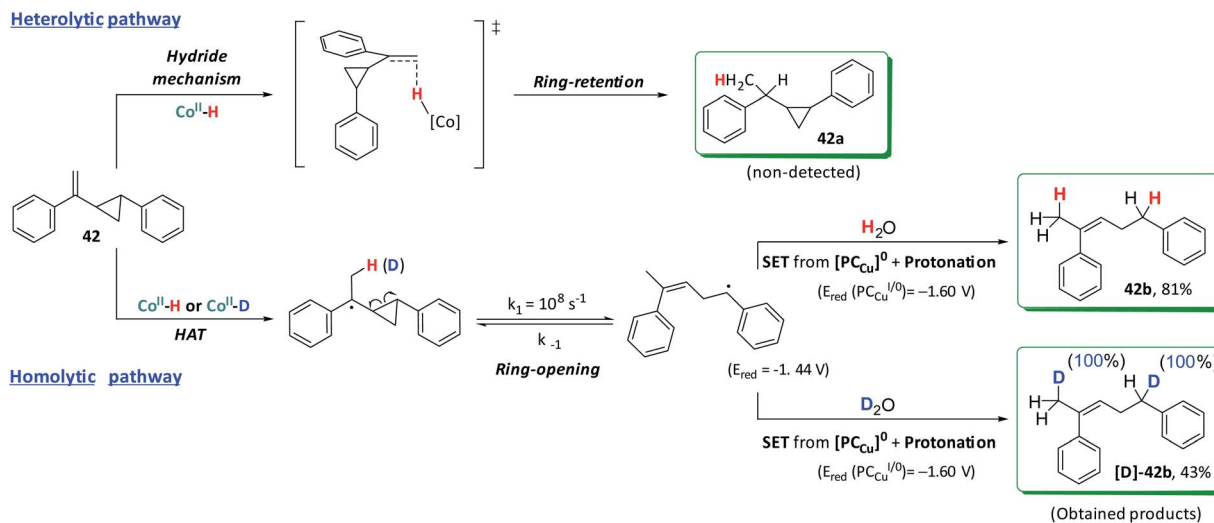
(IV) Mechanistic discussion

Mechanisms in Scheme 5 were proposed considering the collection of experimental results. It is well-established that light irradiation (447 nm) of [Cu(bathocuproine)(xantphos)]⁺ ([PC_{Cu}]⁺) leads to the formation of the * [PC_{Cu}]⁺ excited state, which is reductively quenched in the presence of an excess of aliphatic amine (Et₃N or ⁱPr₂EtN was used as quenchers in our

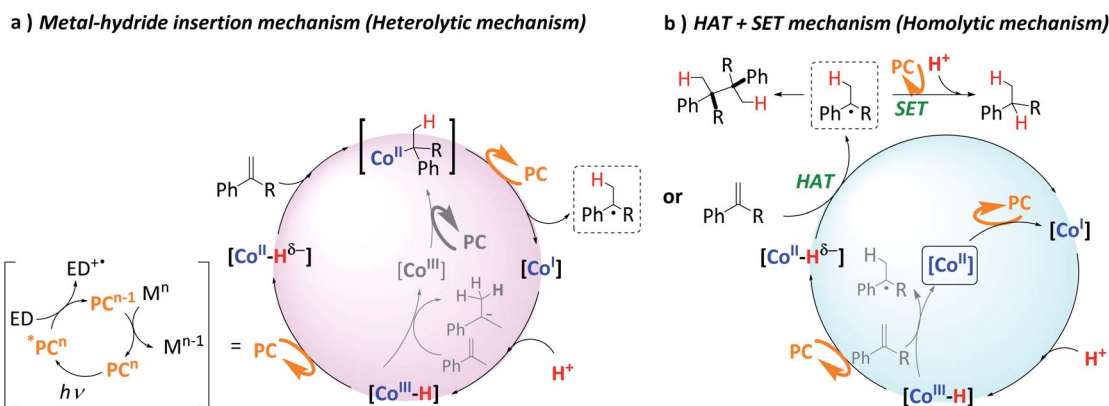
study).⁵² The reaction then affords the one-electron reduced [PC_{Cu}]⁰ species ($E(\text{PC}_{\text{Cu}}^{1/0}) = -1.60 \text{ V vs. SCE}$).^{76,77} The reduction potentials of the studied olefins are in the range of –2.1 to –2.6 V vs. SCE⁵⁰ (Fig. S.48† for the theoretical values). Therefore, based on the thermodynamics of the process, the direct reduction of the studied olefins by the singly reduced species [PC_{Cu}]⁰ could be discarded (ΔG of the reaction is endergonic by 12 to 23 kcal mol^{–1} depending on the olefin).²⁹

This is supported by the lack of reduced, dimerized or ring-opening products formed when radical clock **42** ($E(\text{42}^{0/-}) = -2.36 \text{ V vs. SCE}$) was tested in the absence of complex **1**. However, [PC_{Cu}]⁰ is reductive enough to reduce complex **1** ($E(\text{Co}^{\text{II/I}}) = -1.15 \text{ V vs. SCE}$) affording Co^I species.⁵³ We previously studied the formation of similar Co^I species under photo- and electrochemical conditions.^{55,78} These low-valent intermediates can be protonated by water to form a putative [Co^{III}–H]. We previously reported that the reduction of [Co^{III}–H] to [Co^{II}–H] by [PC_{Cu}]⁰ is largely exergonic (–17.6 kcal mol^{–1}),^{29,53} and





Scheme 4 Two possible reduction pathways for (1-(2-phenylcyclopropyl)vinyl)benzene (42).



Scheme 5 Possible mechanistic scenarios for the reduction of aromatic olefins by the light-driven dual-copper–cobalt catalytic system in aqueous media. The highlighted $[\text{Co}^{\text{I}}]$ intermediate indicates the beginning of the catalytic cycle. Acronyms stand for PC = photoredox catalyst; ED = electron donor; SET = single electron transfer and HAT = hydrogen atom transfer.

therefore, we can reasonably consider a fast ET to yield $[\text{Co}^{\text{II}}-\text{H}]$. Therefore, under such reducing photochemical conditions, $[\text{Co}^{\text{III}}-\text{H}]$ should be easily converted into $[\text{Co}^{\text{II}}-\text{H}]$ species.^{29,55}

On the other hand, it is interesting that the reaction order found in the olefin is close to zero (Fig. S.33†). The fact that the reaction rate does not depend on the alkene concentration is consistent with our previous studies on hydrogen evolution and the reduction of ketones and aldehydes.^{29,55} Thus, we interpreted this result as the formation of the $[\text{Co}^{\text{III}}-\text{H}]$ complex as a rate-determining step, since the following reduction to $[\text{Co}^{\text{II}}-\text{H}]$ species and their subsequent HAT to the olefin are fast. Moreover, as discussed above, this $[\text{Co}^{\text{III}}-\text{H}]$ is a common intermediate for both H_2 evolution and olefin reduction.

The formation of homocoupling products and the isotopic D-labelling pattern observed, together with the radical clock experiments support that the reaction proceeds *via* the formation of benzylic radical species. As explained above, the most likely pathway to form the benzylic radicals is a HAT from $[\text{Co}^{\text{II}}-\text{H}]$ to the β carbon of the olefin, whereas a potential metal hydride insertion is less likely, but cannot be discarded.

Although it cannot be completely ruled out, since no doubly-deuterated terminal-carbons in the reduced products were detected, this indicates that neither β -hydride elimination nor reversible HAT occurs (Scheme 5a). Then, the fastest and most likely scenario is that benzylic radicals undergo a reduction ($E_{\text{red}}^{\text{theor}} = -1.44$ to -1.69 V vs. SCE) by $[\text{PCu}^{\text{I}}]^0$ ($E = -1.60$ V vs. SCE), which after subsequent protonation gives the alkane (Scheme 5b). We discard the HAT from the oxidized amine because the deuteration of the benzylic position is virtually quantitative.

(V) Mechanistically designed ketone/olefin reduction selectivity

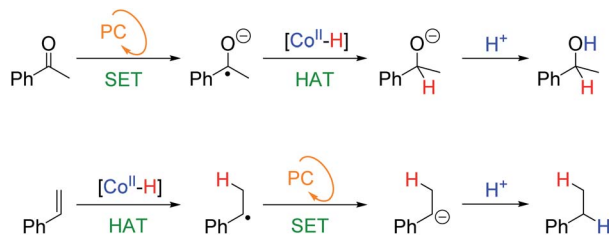
(V) Mechanistically designed ketone/olefin reduction selectivity

The postulated HAT mechanism for olefin reduction (Scheme 5b) implies that the selectivity could be modulated against functional groups that are reduced *via* a different mechanism



such as SET. This is the case for our previously reported reduction of aromatic ketones using the dual catalytic system.²⁹

To test our hypothesis, we used styrene (**16**) and acetophenone (**43**) as competing substrates. We previously determined, that under equivalent photocatalytic conditions, **43** is reduced to 1-phenylethanol *via* a SET mechanism from [PC_{Cu}]⁰ yielding



Scheme 6 Different substrate-dependent mechanisms for the observed selectivity. KRA stands for the ketyl radical anion and PC for the photoredox cycle.

the ketyl radical anion (KRA) as an intermediate ($E_{\text{red}} = -1.65$ V *vs.* SCE).^{29,30} Then the generated KRA is trapped by [Co-H] to form the reduced product *via* HAT (Scheme 6). Therefore, it should be possible to differentiate the KRA formation *via* SET from the HAT mechanism of the olefin, designing rationally the photocatalytic conditions.

This rationalization suggests that the counterintuitive idea of increasing the redox potential of the photoredox catalyst should make the catalytic system more selective. For instance, under more reducing conditions, a SET mechanism should be favoured, and therefore, the reduction of the ketone would be preferred, while the opposite would favour otherwise.

First, when similar catalytic conditions to those reported for the selective reduction of aromatic ketones *vs.* aliphatic aldehydes²⁹ were used (**1** (1 mol%), PC_{Cu} (1.5 mol%), total substrates (**16** + **43**, 16.5 mM, 1 : 1) in H₂O : CH₃CN : Et₃N (6 : 4 : 0.2 mL) irradiated for 4 h at 25 °C under N₂), acetophenone (**43**) was preferentially reduced in the presence of **16** (Sel_{43a/(16a+43a)} = 65%, Fig. 2a, Table S.18 and Fig. S.37†). Then, we modified the

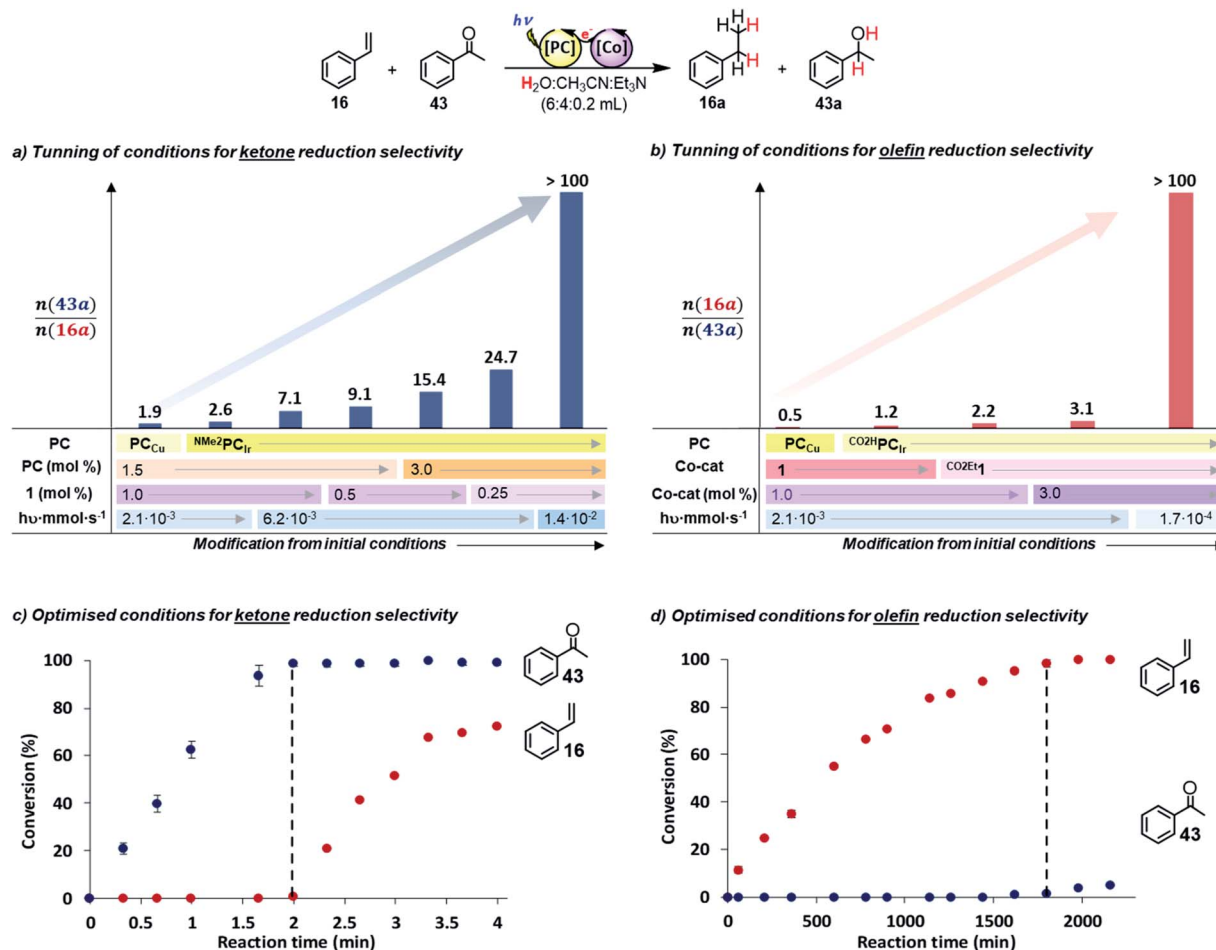


Fig. 2 Competition studies between styrene (**16**) and acetophenone (**43**). (a and b) Optimization of the photocatalytic conditions for selective reduction of **43** and **16**, respectively. Conditions: (c) **1** (0.25 mol%), NMe₂PC_{Ir} (3 mol%), total substrate concentration (**16** + **43**, 16.5 mM, 1 : 1) in a H₂O : CH₃CN : Et₃N (3 : 2 : 0.1 mL) mixture, irradiated at 447 nm (7 LED at 700 mA, 1.44 × 10⁻² mmol hv s⁻¹ of photons⁵⁹) for 4 min at 25 °C under N₂. (d) CO₂Et₁ (3 mol%), CO₂HPC_{Ir} (1.5 mol%), total substrate concentration (16.5 mM) in a H₂O : CH₃CN : Et₃N (3 : 2 : 0.1 mL) mixture, irradiated at 447 nm (1 LED at 50 mA 1.67 × 10⁻⁴ mmol hv s⁻¹ of photons⁵⁵) for 36 h (2160 min) at 25 °C under N₂. The black dotted line indicates where substrates **16** (c) and **43** (d) start reacting.



reaction conditions to test the hypothesis of favouring either the SET to **43** or the HAT to **16**. Under stronger reducing conditions, which favour the SET initial step, we sequentially increased the reduction potential, concentration of PC and the light irradiation intensity. Moreover, we also decreased the concentration of complex **1** to disfavour the HAT process. To our delight, an improvement in the selectivity was observed by using $\text{NMe}_2\text{PC}_{\text{Ir}}$ instead of PC_{Cu} (from 65 to 72% selectivity).

Further improvement was obtained by increasing the light intensity up to $6.2 \times 10^{-3} \text{ mmol hv s}^{-1}$ vs. the normal $2.1 \times 10^{-3} \text{ mmol hv s}^{-1}$,⁵⁵ which presumably increased the concentration of the reduced photoredox catalyst ($[\text{NMe}_2\text{PC}_{\text{Ir}}]^0$), and thus, accelerating the SET reaction (from 72 to 88% Table S.18 and Fig. S.38 and S.39†). In contrast, the effect of complex **1** concentration was minor (from 88 to 90%). As a result, 100% selectivity for ketone **43** reduction (in 2 min) was obtained in the presence of styrene **16** using $\text{NMe}_2\text{PC}_{\text{Ir}}$ (3 mol%, $E_{1/2}(\text{Ir}^{\text{III/II}}) = -1.80 \text{ V vs. SCE}$), complex **1** (0.25 mol%, $E(\text{Co}^{\text{II/I}}) = -1.15 \text{ V vs. SCE}$) and irradiation at higher light intensity ($1.4 \times 10^{-2} \text{ mmol hv s}^{-1}$) (Fig. 2a and c).

To favour the HAT, we modified the reaction conditions to make them less reducing. First, we used the less reductive photoredox catalyst $\text{CO}_2\text{HPC}_{\text{Ir}}$ ($E_{1/2}(\text{Ir}^{\text{III/II}}) = -1.01 \text{ V vs. SCE}$), and the selectivity for styrene reduction was increased by 20% (Fig. 2b, Table S.19 and Fig. S.44†). Likewise, using a less reductive Co catalyst $[(\text{Co}^{\text{II}}(\text{OTf}))(\text{H}, \text{CO}_2\text{EtPy}_2^{\text{TS}}\text{tacn})]$ ($\text{CO}_2\text{Et}1$, $E(\text{Co}^{\text{II/I}}) = -0.96 \text{ V vs. SCE}$), the selectivity also improved by 14%. Then, we increased the $\text{CO}_2\text{Et}1$ concentration with the idea to increase [Co-H] and thus the HAT product ($\text{Sel}_{16\text{a}/(43\text{a}+16\text{a})} = 76\%$, Fig. S.45 and S.46†).

Finally, lowering the light intensity ($1.7 \times 10^{-4} \text{ mmol hv} \cdot \text{s}^{-1}$), **16** was selectively reduced over **43** with 100% selectivity (Fig. 2d and Table S.19†). GC monitoring of the reactions showed that **16** was consumed and converted to **16a**, whereas **43** remained virtually intact and *vice versa* (Fig. 2c and d).

As a summary of this section, the observed selectivity agrees with the existence of two competitive mechanistic scenarios involving: (i) SET + HAT for substrates than can be directly reduced such as acetophenone, and (ii) HAT for substrates with low reduction potentials that cannot be directly reduced by one electron from the PC such as aromatic olefins.

Conclusions

We developed a dual cobalt–copper catalytic system capable of reducing aromatic olefins under simple operational conditions, solely using H_2O and an amine (Et_3N or $i\text{Pr}_2\text{EtN}$) as the source of hydrides and visible light as the driving force. Our mechanistic studies based on reactivity and selectivity studies, catalyst design, deuterium-labelling and radical-clock experiments support a well-defined cobalt hydride as the intermediate responsible for the reductions, most likely through a HAT mechanism, discarding free radical diffusion as the main pathway. These results show that the selectivity of the metal hydrides in basic media can be controlled and directed to the reduction of organic functionalities. For this reason, we envision that other readily available H_2O reduction catalysts could

also be active in the reduction of other functional groups and more complex organic structures. These results pave the way for the development of selective organic reductions and solar-chemical generation using artificial catalytic systems that operate entirely with earth-abundant elements, using visible light as the driving force and H_2O as a source of hydrides.

Data availability

All the data is provided in the ESI.†

Author contributions

AC identified the potential of olefin reduction at an early stage; CC performed most of the experiments as well as the DFT calculations, worked with AC and ICR on the synthesis of the photoredox catalysts, with AC on the optimisation studies, with DP and JA on the selectivity studies, wrote the manuscript together with JL and brought the project to completion. JL oversaw the project, discussed the results, and edited the manuscript. Moreover, all authors contributed with fruitful discussions to the manuscript.

Conflicts of interest

There are no conflicts to declare.

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