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Divergent Catalysis

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Visible-light controlled divergent catalysis using a bench-stable cobalt(I) hydride complex

*Enrico Bergamaschi[†], Frédéric Beltran[†] and Christopher J. Teskey**

***Abstract**: While the use of visible light in conjunction with transition metal catalysis offers powerful opportunities to switch between on / off states of catalytic activity, the next frontier would be the ability to switch the actual function of the catalyst and resulting products. Here we report such an example of multi-dimensional catalysis. Featuring an easily prepared, bench-stable cobalt(I) hydride complex in conjunction with pinacolborane, we can switch the reaction outcome between two widely employed transformations, olefin migration and hydroboration, with visible light as the trigger.*

Visible light excitation of metal complexes, which can act as a catalytic single electron reductant, single electron oxidant or an energy transfer agent, has transformed the field of organic synthesis in the last decades.[1,2] These modes of action mean that the vast majority of reactions reside in the area of radical transformations. However, interest in the direct visible light promotion of transition-metal catalysed processes is growing.[3–7] Clearly, visible light, as a widely-available, cheap, sustainable and non-invasive method of energy delivery, can exert precise spatial and temporal control over a chemical process. The use of light to switch a catalyst between active and inactive states has been termed light-gated catalysis.[8]

Considerably rarer than the switching of a catalytic process between active and inactive states, is switching selectivity between two different pathways.[9] Indeed, within the area of transition metal catalysis, only a handful of examples have been reported. Just recently, Zhu, Sarina and co-workers reported a specific example where gold-cobalt nanoparticles enabled the formation of imines from anilines and arylalkynes under visible light irradiation.[10] In contrast, without light, they observed only homocoupling of the alkyne. Greaney and co-workers have reported an example where, using a visible light absorbing copper catalyst, they could switch between methoxyazidation and double azidation of alkenes in the light and dark respectively.[11]

One method for activating transition metal complexes is to use light to dissociate a ligand (Scheme 1). This increases reactivity by opening up ligation sites at a coordinatively saturated metal centre in a non-invasive and reversible manner. Many such methods have been reported previously, particularly with metal carbonyl complexes, however commonly rely on high energy UV light.[12,13]

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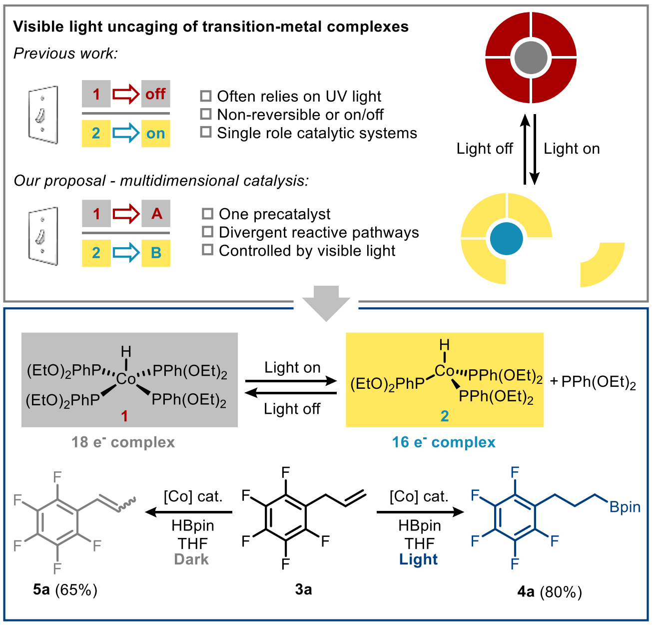
In this context, we were interested in the photochemistry of bench-stable cobalt complex **1**, $CoH[PPh(OEt)_2]_4$ which had been reported by Onishi and co-workers to undergo reversible photodissociation of a phosphonite ligand under irradiation from a high-pressure mercury lamp.[14,15] In all catalytic transformations reported to date, complex **1** has been assigned the 'off' state, only switching 'on' in the light when it becomes complex **2**. Despite this, there were some reports on stoichiometric redox reactions with **1** which encouraged us to investigate the catalytic activity both in the light and dark.[16,17]

Given the absorption spectra of **1**, we began our investigations with commercial blue LEDs using a simple-laboratory set-up. We elected to investigate the visible-light promoted hydroboration of alkenes: an atom-economical, value-adding transformation[18] which has provoked substantial research. Examples of both Markovnikov[19–22] and anti-Markovnikov[23–29] cobalt-catalysed hydroborations have been reported previously. Many of these examples, however, rely on complex ligand systems or use an air sensitive cobalt complex that must be manipulated in a glovebox.[30] Alternatively, additives are used to form the active catalyst *in situ*. Our approach would instead take an easily synthesised, non-precious and bench-stable pre-catalyst.



Scheme 1. Visible light controlled catalysis and reaction discovery.

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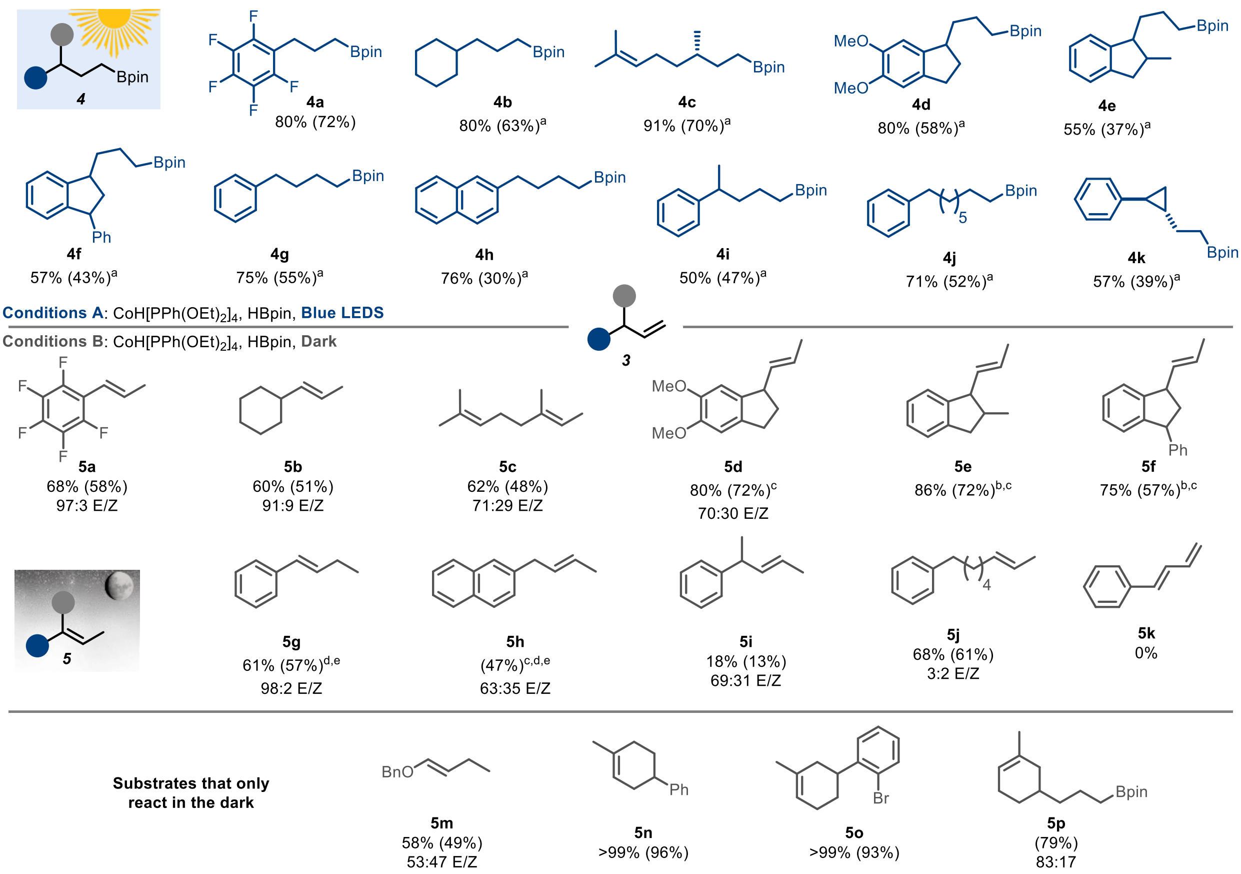

Scheme 2. Substrate scope for switchable hydroboration/isomerisation reaction. Conditions A: **3** (0.2 mmol), $CoH[PPh(OEt)_2]_4$ (2 mol%), HBpin (2 equiv.), THF (0.2 M), Blue LEDs. Conditions B: **3** (0.2 mmol), $CoH[PPh(OEt)_2]_4$ (2 mol%), HBpin (1.1 equiv.), CH_2Cl_2 (1 M), dark. Yields and E/Z ratios measured by ^1H NMR relative to CH_2Br_2 as an internal standard. Isolated yields are in brackets. [a]$KHBEt_3$ (5 mol%) was used as an additive. [b]The product was obtained as a mixture of diastereomers. [c]The two-bond isomerised product was obtained as a minor product. [d][5 mol%] of $CoH[PPh(OEt)_2]_4$ was used. [e]The reaction was run at 30°C.

Our studies began with investigating the hydroboration of allylpentafluorobenzene **3a** under visible light irradiation, with blue LEDs and at room temperature, using 2 mol% of complex **1**. We were delighted to observe hydroborated product **4a** in excellent yield (Scheme 1). Without pinacolborane in the light, starting material **3a** was recovered in almost quantitative yield. When carrying out the reactions in the dark, we observed one-carbon isomerised product, **5a** as the main product with excellent E/Z ratio (see supplemental information for full details). No conversion was observed in the dark without pinacolborane. Although alkene isomerisation has been reported with a wide array of metal catalysts including non-noble metal examples with nickel[31] or cobalt,[32–39] we believed that this method compares well, requiring no additional co-catalysts, ligands or bases.[40] It is noteworthy that few existing alkene isomerisation methods are reported to isomerise this particular electron-deficient substrate.[41]

We then proceeded to carry out the substrate scope of these two contrasting reactions, beginning with the visible-light mediated cobalt catalysed hydroboration (Scheme 2, top). In the majority of cases for hydroboration, addition of potassium triethylborohydride increased the yield of products **4** by around 10 – 20%. In all cases, only the anti-Markovnikov product was observed. Allylcyclohexane **3b** and (+)-β-citronellene **3c** gave hydroborated products in very good yields. Substrates **3d** – **3f**, derived from indanones, also yielded the hydroborated products in moderate to good yields. We then trialled 4-aryl-1-butene substrates which were hydroborated to give products **4g**, **4h** and **4i** with complete terminal selectivity.

This is in contrast to a similar system, reported by Chirik and co-workers, where the cobalt catalyst first isomerises the alkene into conjugation with the aromatic group before hydroboration occurs.[27] Longer chain alkene **3j** was also hydroborated at the terminal position in moderate yield. Cyclopropyl containing substrate was hydroborated in to give **4k** (with no traces of cyclopropyl ring-opened products observed).

Next we turned to the method in the dark for alkene isomerisation where better isolated yields were observed in chlorinated solvents chlorobenzene or dichloromethane. One bond isomerised product **5b** was selectively isolated in good yield and with good E/Z selectivity. (+)-β-citronellene gave trisubstituted alkene **5c** in moderate yield. Indanone derivatives also gave one bond isomerised products **5d** – **5f** in good yields, however as a mixture of E/Z products and diastereomers.[§] Product **5g** was obtained with 5 mol% of $CoH[PPh(OEt)_2]_4$ at 30 °C as a result of two bond isomerisation. Analogous naphthyl compound **3h**, however, gave mainly one bond isomerised products **5h** under the same conditions along with the two-bond isomerised compound as a minor product. Starting material **3i** did not undergo efficient isomerisation under the reaction conditions with largely starting material recovered. The longer chain substrate **3j** gave only one bond-isomerised product **5j** in reasonable conversion but with some starting material remaining. Finally, starting material **3k** did not undergo any isomerisation giving the first mechanistic hint for this reaction.

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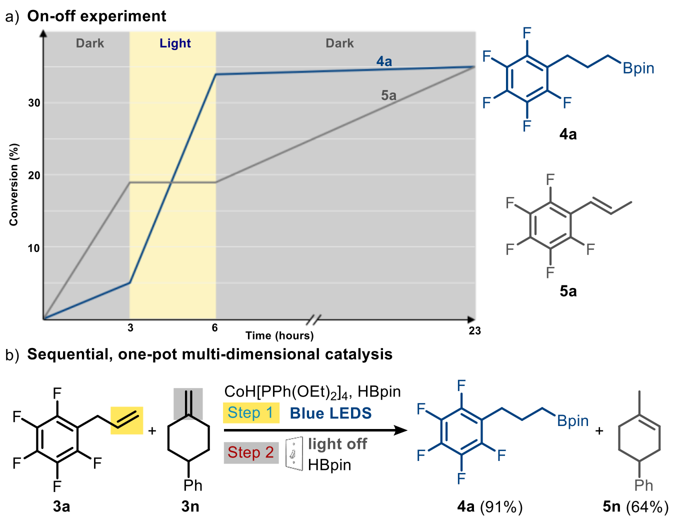
During the course of our investigations, we discovered that certain substrates, that were unreactive in the light, still isomerised in the dark. Firstly, benzyl protected alcohol **3m** underwent two bond alkene isomerisation to give the allyl ether **5m** but with no E/Z selectivity. Although the hydroboration method was only amenable to terminal alkenes, exo-endo isomerisation was possible, giving product **5n** in almost quantitative yield. Varying the substitution pattern on the ring did not affect this efficient exo-endo isomerisation. Product **5o**, containing a useful aryl bromide functionality for further derivatisation was obtained in excellent yield. Finally, taking a substrate containing an alkyl boronic ester (which had been produced first *via* selective hydroboration of a terminal alkene under the light conditions) saw efficient isomerisation of the exocyclic double bond in the dark (albeit as a mixture of regioisomers) to give **5p**.

Next, we looked to showcase the switchability of this reaction system, beginning with a simple on-off experiment with substrate **3a**. Monitoring the conversion into either **4a** or **5a** demonstrates clearly that control over hydroboration or isomerisation could be exerted solely by switching the light on or off (Scheme 3a). This clearly distinguishes this work from other reported catalytic methods for these transformations and opens up a unique opportunity to perform both reactions in the same vessel with the reaction outcome dictated by a simple switch of the light. We then exploited this by taking substrates **3a** and **3n** in the same pot with CoH[PPh(OEt)$_2$]$_4$ and pinacolborane in THF. First, we performed the hydroboration in the light, selectively targeting the terminal alkene before turning off the light and adding a further equivalent of HBpin to allow isomerisation of the exocyclic alkene to occur (Scheme 3b). This one-pot, dual-function approach allows the same catalyst, added from the start, to carry out two separate transformations.

Having demonstrated the unique synthetic utility of CoH[PPh(OEt)$_2$]$_4$ for two valuable, atom-economical processes, our attention turned to the mechanism of this unusual light switchable process. Previous work by Onishi[14,15] and similar catalytic systems[27] give good evidence that the light mediated processes occur *via* a mechanism which involves coordination of the alkene to the 16 electron, photogenerated, cobalt complex **2** (Scheme 4h, right). It was not clear to us, however, what the role of the cobalt complex was for the isomerisation that occurs in the dark.



Scheme 3. Switchable catalysis.

To this end, we began by monitoring the isomerisation of allyl pentafluorobenzene **3a** with pinacolborane by NMR spectroscopy. Here we observed formation of hydrogen gas at the start of the reaction as well as a new signal by ^{11}B NMR. Cognizant of work by Norton[34] and Shenvi[33] on cobalt-hydride mediated H· addition to alkenes, we trialled two substrates which we believed should undergo cycloisomerisation or radical ring opening if this was the mechanistic pathway (Scheme 4a and b). Only starting material was observed in both cases, however. Additionally, we carried out the isomerisation of **3a** in the presence of different radical traps (Scheme 4c). Excellent yields of product were observed in all cases suggesting that a radical mechanism is unlikely to be operative.

We had observed during the course of our studies that the use of complex **1** with visible light but without pinacolborane gave isomerised products in select cases, consistent with previous work.[14] However, we ruled out pinacolborane induced ligand dissociation in the dark to give complex **2** given that only starting material was recovered with compound **3a** under light irradiation with complex **1** without pinacolborane. Previous literature has reported that CoH[PPh(OEt)$_2$]$_4$ can undergo single electron oxidation to the corresponding cobalt(II) complex, [CoH[PPh(OEt)$_2$]$_4$]$^+$ and also to dihydride cobalt(III) complex [CoH$_2$[PPh(OEt)$_2$]$_4$]$^+$.[16,17]

Indeed, there is an isolated report by Onishi which reports a moderate yield of alkene isomerisation using Co(II) species,[42] and a peak in the ^{1}H NMR at -12.4 ppm suggests that Co(III) dihydride is produced in small quantities during the course of the reaction.[43] We therefore elected to prepare both of these complexes *in situ* but in neither case were more than traces of the product observed (Scheme 4d). Additionally, carrying out the isomerisation of **3n** with 10 mol% of deuterated catalyst CoD[PPh(OEt)$_2$]$_4$ gave the product without any deuterium incorporation (Scheme 4e). This suggests that the catalytically active species is unlikely to be a cobalt hydride.

We then carried out a competition experiment between non-deuterated compound **3n** and deuterated compound **3q**. Analysis by ^{1}H and ^{2}H NMR revealed approximately 30% deuterium incorporation into the product **5n** with only 60% deuterium at the allylic position in **5q**. However, when substrate **3q** is isomerised by itself, there is also approximately 30% loss of deuterium in the product suggesting that there may be some exchange with the pinacolborane. Given that we had ruled out a radical mechanism and insertion of a cobalt-hydride species also seems unlikely, we therefore suggest that a π-allyl-type mechanism could be operative.[44] ^{1}H NMR monitoring of the reaction indicates that the reaction begins only once the signal corresponding to the cobalt hydride of the starting complex **1** has decreased to a constant level, implying initial reaction between pinacol borane and **1** to generate the active catalytic species.

Taken together with the evolution of H_2 gas that was observed, we suggest that we may form the 18 electron complex **7**.[‡] This could then, *via* ligand exchange and reversible HBpin formation, form a cobalt π-allyl species from which isomerisation occurs. This is a clear demonstration that modification of the active catalytic site affects the reactivity of the system prompting a different mechanistic and reaction outcome.[45] Alternatively, we cannot rule out that a cationic cobalt(I) complex to which an alkene can coordinate is formed before undergoing anion assisted cobalt π-allyl formation. Further investigations to confirm this are currently underway in our laboratory.

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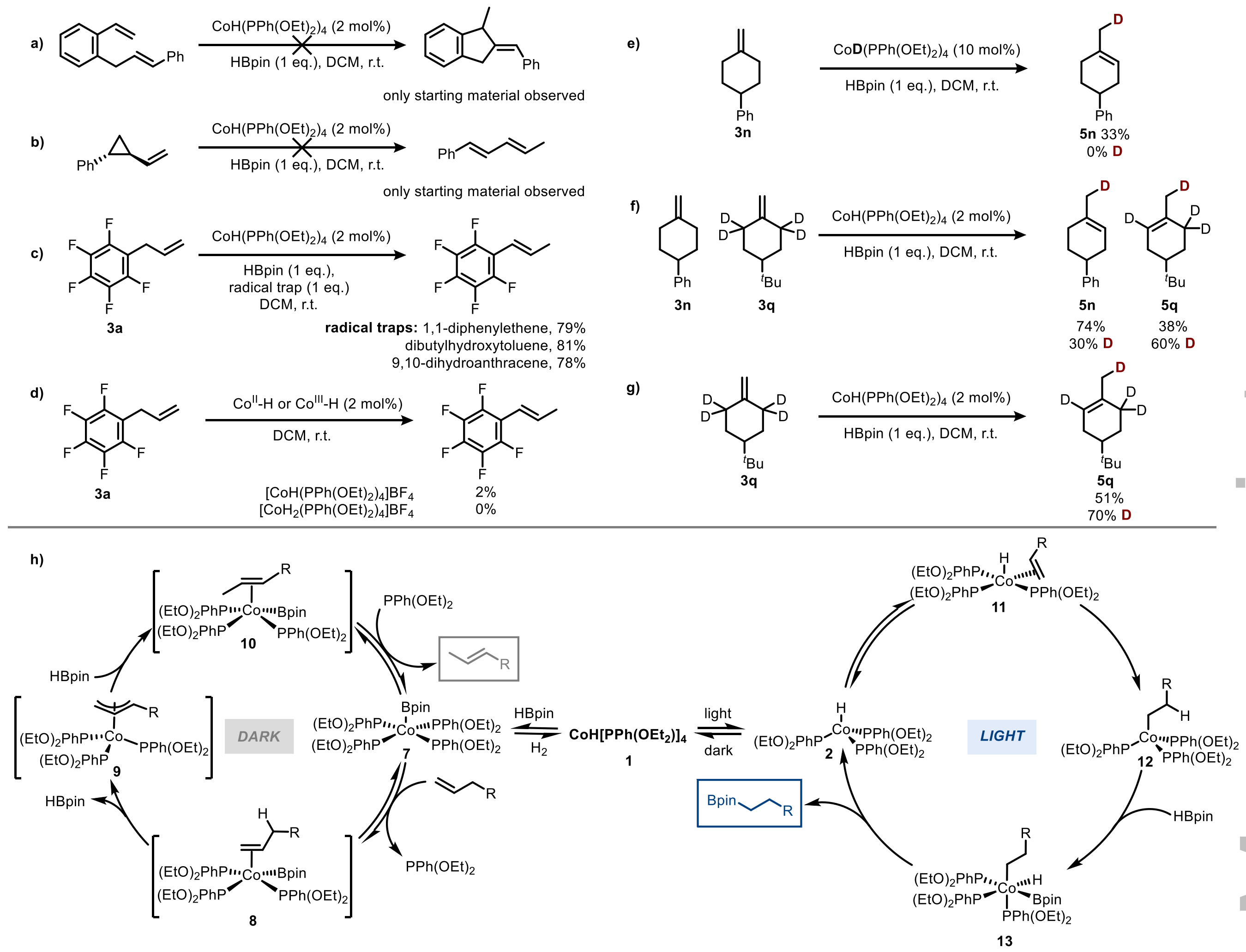

Scheme 4. Mechanistic experiments and tentative mechanism.

In conclusion, we have demonstrated switchable reactivity of bench-stable cobalt hydride complex **1** for alkene isomerisation and hydroboration. By controlling the coordination sphere and thus the active site around the cobalt centre with visible light, different mechanistic pathways result. Photodissociation of a phosphonite ligand (carried out for the first time with visible light) gives 16 electron complex **2** with a free ligation site allowing insertion of the alkene into the Co–H bond. Without light, we propose the 18 electron complex **1** instead reacts first with pinacol borane to form a new cobalt species which isomerises alkenes *via* a π-allyl mechanism. This conceptually new strategy opens up a new frontier of switchable transition metal-catalysed processes in which the reaction outcome can be controlled solely *via* visible light. We anticipate this leading to development of more dual-function catalytic systems.

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Conflict of interest

The authors declare no conflict of interests.

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§ As a result of this it was not possible to determine the E/Z ratio for **5e** and **5f**.

‡ **5a** was obtained in 72% yield from substrate **3a** (as determined by ^{1}H NMR) using only 20 mol% of HBpin, however, with other substrates, isolated yields were lower when using less than 1 equiv. of HBpin.

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Divergent catalysis

Enrico Bergamaschi, Frédéric Beltran and Christopher J. Teskey*

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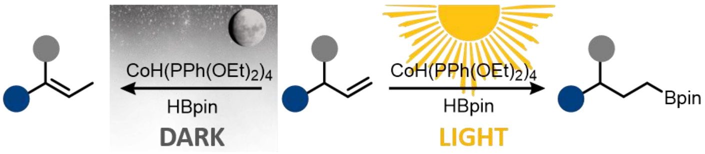
Visible-light controlled divergent catalysis using a bench-stable cobalt(I) hydride complex



Night and Day: A rare example of switching product outcome depending on light/dark is reported. Using a cobalt(I) hydride complex, hydroborated products are obtained under visible-light irradiation whereas, in contrast, alkene isomerisation occurs in the dark. This dual-function catalysis results from alteration of the coordination sphere surrounding the metal centre.

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