ORGANOMETALLICS

Photoswitchable Metal-Mediated Catalysis: Remotely Tuned Alkene and Alkyne Hydroborations

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Supporting Information

ABSTRACT: A photochromic dithienylethene-annulated N-heterocyclic Ph carbene (NHC)-Rh(I) complex was synthesized and found to undergo reversible electrocyclic ring closure upon alternate exposure to UV (λ_{irr} 313 nm) and visible (λ_{irr} >500 nm) radiation. Under ambient light, the Rh catalyst efficiently promoted the hydroboration of alkenes and alkynes with pinacolborane. However, upon UV irradiation to effect a photocyclization within the NHC ligand, the catalytic activity was reduced by up to an order of magnitude. The disparity in the rates was used to photoswitch the rates of a series of hydroboration reactions, thus demonstrating the first examples of photomodulating a transition-metal catalyst by tuning its electronic properties. The rate attenuation observed under UV irradiation was attributed



to inhibition of the rate-determining reductive elimination step arising from a decrease in electron-donating ability of the photocyclized NHC ligated to the Rh center.

INTRODUCTION

Developments in homogeneous organometallic catalysis have historically focused on improving catalytic activity and/or selectivity through ligand development. Once a ligand is chosen, however, the coordination environment of the catalyst active site typically dictates a fixed rate and selectivity for a given reaction. This restriction limits the versatility of state-ofthe-art catalysts as well as the degree of control maintained over the course of a given reaction. Recent efforts to address this issue have involved the development of "switchable catalysts,"1 in which reduction/oxidation processes,² acid-base chemistry,³ or light⁴ is utilized to actively modify catalytic activity or selectivity.

Photochemical stimuli are particularly attractive for switching the intrinsic properties exhibited by catalysts, as such methods are typically noninvasive and use an inexpensive, renewable resource. Despite these advantages, very few photoswitchable catalysts are known.⁵ Hecht et al., for example, used an elegantly designed photoswitchable azobenzene-annulated piperidine base to control the rate of the Henry reaction via changes in steric properties (Figure 1a).^{5a-c} Photoinduced steric changes have enabled control over metal-containing catalysts as well, as first demonstrated by Cacciapaglia and Mandolini, who used a Ba²⁺ crown ether complex to control the rates of ethanolysis reactions (Figure 1b).^{5e} In another seminal example of photoinduced steric switching, Branda et al. showed that the stereoselectivity of Cu(I)-catalyzed cyclopropanations may be modulated using a chiral bis(oxazoline) (Figure 1c).^{5k} More recently, Branda employed a photoresponsive pyridoxal-5'-phosphate mimic as an organocatalyst to alter the rates of amino acid racemizations through changes in electronic properties (Figure 1d).⁵¹ To the best of our knowledge,

however, the utilization of photoinduced changes in electronics to alter the outcomes of transition-metal-catalyzed transformations has not been realized.^{6,7} Adding a photoswitchable feature to metal-based catalysts is expected to endow them with enhanced control over their intrinsic activities and selectivities.

A promising method for photochemically tuning the electronic properties of metal complexes involves the use of ligands which feature photochromic⁸ diarylethene (DAE)⁹ moieties.^{10,11} We¹² and others¹³ have shown that the UVinduced cyclization of a DAE properly annulated to a Nheterocyclic carbene (NHC)¹⁴ scaffold significantly decreases the electron-donating ability of the NHC moiety¹⁵ in both organic and organometallic adducts. Indeed, photoswitchable DAE annulated NHCs were recently used to tune the rates of NHC-promoted transesterification and amidation reactions.¹⁶ Given this initial success and the large number of reactions facilitated by NHC-supported metal complexes,^{14,15} we sought to photomodulate catalytic activity via changes in ligand donicity and to establish a new concept in organometallic catalysis. Herein we report the first photochromic DAEannulated NHC-Rh(I) complex and demonstrate that its catalytic activity may be tuned using light.

RESULTS AND DISCUSSION

Considering that NHC–Rh(I) complexes are active catalysts for a wide variety of transformations, 17 we focused our attention on complex 1, which contains a photochromic DAE-annulated NHC ligand (Scheme 1). We envisioned that the conjugation of the nitrogen atoms adjoining the carbenoid

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Figure 1. Examples of photoswitchable catalysts: (a) reversible steric shielding of the basic site of an azobenzene-annulated piperidine catalyst altered the rate of the Henry reaction; $^{5a-c}$ (b) $E \rightarrow Z$ isomerization of a bis(Ba²⁺) crown ether complex modulated the rate of ethanolysis reactions; 5e (c) changes in sterics prevented Cu(I) chelation of a chiral bis(oxazoline) ligand upon UV irradiation and reduced the stereoselectivity of cyclopropanation reactions; 5k (d) photoinduced changes in electronic conjugation switched the rate of an alanine racemization reaction. 5l

Scheme 1. Reversible Photocyclization of 1



nucleus would be extended upon UV-induced photocyclization of the ring-opened isomer **1o** to the ring-closed form **1c**. As a result, less electron density should be available for donation into the carbene atom, and ultimately a ligated metal center, thus altering the catalytic activity displayed by the complex.

The synthesis of the photochromic NHC-Rh(I) complex 1 is summarized in Scheme 2. The known imidazolium iodide salt 2^{16} was treated with 0.5 equiv of silver(I) oxide in dichloromethane over 3 Å molecular sieves at 50 °C to afford the Ag complex 3 in 90% yield. Subsequent transmetalation of 3 with 0.5 equiv of $[Rh(cod)Cl]_2$ (cod = 1,5-*cis,cis*-cyclo-octadiene) in dichloromethane afforded the desired Rh complex 10 in 75% yield. The formation of 10 was evidenced

Scheme 2. Synthesis of Complex 1



by the characteristic ¹H NMR signals observed at 5.0 and 3.4 ppm, corresponding to the olefinic protons of the Rh-coordinated cod ligand, and by the doublet observed at 183 ppm in the ¹³C NMR spectrum, which was assigned as the Rh-coordinated carbenoid nucleus (CDCl₃).^{18,15a}

The UV-vis profile of **10** in cyclohexane or benzene featured an intense absorbance centered at 285 nm corresponding to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the N-heterocycle and phenylthiophene systems, respectively. Upon UV irradiation (λ_{irr} 313 nm), the pale yellow solution of **10** underwent a color change to bright blue, concomitant with a decrease in the intensity of the absorption band centered at 285 nm and the appearance of new bands at 391 and 630 nm (Figure 2a). The



Figure 2. (a) UV–vis spectral changes of **1o** in C_6H_6 ([**1o**]₀ = 3.3 × 10⁻⁵ M) upon UV irradiation (λ_{irr} 313 nm). (b) UV–vis spectrum of **1o** in C_6H_6 , the spectrum of the photostationary state (PSS) that was reached after UV irradiation of **1o** for 120 s, and the spectral changes of the PSS upon exposure to visible light (λ_{irr} >500 nm). The arrows indicate the evolution of the spectral changes over time. For spectra recorded in cyclohexane, see Figure S1 (Supporting Information).

development of the lower energy bands upon UV irradiation was consistent with an increase in π conjugation and the formation of the ring-closed isomer 1c. After 2 min of UV exposure, the spectroscopic changes reached a steady state, reflecting a 62% conversion of 1o to its ring-closed isomer 1c.¹⁹ When the UV-exposed solution was subsequently irradiated with visible light ($\lambda_{irr} > 500$ nm), the low-energy absorption bands were attenuated and, after 1 min of irradiation, the UV– vis spectrum of 1o was restored (98% conversion) (Figure 2b). The presence of an isosbestic point at 311 nm in the data for both the forward and reverse reactions indicated that the cyclization/cycloreversion process occurred without significant side reactions.

The photocyclization of 10 was further confirmed by NMR spectroscopy. After UV irradiation of 10 in cyclohexane²⁰ or benzene for 2 h ($[10]_0 = 1 \times 10^{-3}$ M), the solvent was removed under reduced pressure and the resulting blue solid was redissolved in CDCl₃. Subsequent ¹H NMR spectroscopic analysis revealed that the signals assigned to the thiophene protons shifted upfield from δ 6.9 to 6.5 ppm (CDCl₃), indicative of the loss of aromaticity upon photocyclization to 1c. Integration of these signals revealed that 73% of 10 converted to 1c in benzene. Moreover, a slight downfield shift of the signal assigned to the protons of the cyclooctadiene olefin in the position trans to the NHC ligand was observed from 5.5 to 5.6 ppm (CDCl₃; see Figures S15 and S16 in the Supporting Information), which was indicative of a decrease in the electron-donating ability of 1c in comparison with 10.^{15a} Exposure of the UV-treated solution to ambient light for 2 h reversed the aforementioned chemical shifts (>95% conversion), indicating that 1c underwent complete cycloreversion to regenerate 10. The ¹³C NMR spectrum provided additional evidence for the photocyclization, as a new signal was observed at 68 ppm (C_6D_6) and assigned to the sp³ carbon nuclei adjacent to the sulfur atoms in the newly formed dihydrothiophenes in 1c. Furthermore, a shift in the ¹³C NMR resonance corresponding to the carbenic carbon from 183 to 211 ppm (C_6D_6) was observed upon UV irradiation. The observed shift underscored the change in electron density at the carbenic carbon upon photocyclization and was consistent with disrupting the endocyclic double bond in the NHC backbone of 10 to form 1c (Figure S17 in the Supporting Information).²¹

Having demonstrated that 10 underwent the photocyclization in a reversible manner and with high fidelity, subsequent efforts were shifted toward utilizing the photochromic Rh complex in catalytic reactions. Attention was initially focused on the hydroboration of alkenes and alkynes,²² since these reactions are widely utilized in organic synthesis, are often catalyzed by Rh(I) species,²³ and are sensitive to minute changes in electron density at the metal center.^{15a} In an initial experiment, treatment of 1-octene (0.10 M) with pinacolborane (0.11 M) in C_6D_6 in the presence of 10 (1 mol %) at room temperature resulted in a 91% conversion of 1-octene to the corresponding linear hydroboration product after 16 h, as observed by ¹H NMR spectroscopy and gas chromatography (GC) (Figure 3). To determine if exposure to UV irradiation would affect the hydroboration reaction, a freshly prepared solution of 10 in C_6H_6 ([10]₀ = 1 × 10⁻³ M) was divided in half and placed in two separate quartz cuvettes, both of which were then individually sealed with Teflon-lined septum caps. The solution in one of the cuvettes was then subjected to UV irradiation (λ_{irr} 313 nm) for 2 h, while the other cuvette was kept in ambient light over the same period of time. Mesitylene (0.10 M) was subsequently added as an internal standard followed by 1-octene (0.10 M) and pinacolborane (0.11 M) to each reaction vessel separately. Aliquots were then periodically removed from each reaction mixture, diluted with wet THF to quench the reaction, and analyzed by GC. Each reaction was performed in triplicate.

Inspection of the data recorded from the aforementioned experiments revealed that the reaction in ambient light proceeded with a second-order rate constant, $k_{\rm vis}$, of $(1.9 \pm 0.5) \times 10^{-3} \, {\rm mol}^{-1} \, {\rm s}^{-1}.^{24}$ In contrast, the reaction that had been conducted under UV irradiation was significantly slower and proceeded with a rate constant, $k_{\rm UV}$, of $(7.8 \pm 2.1) \times 10^{-4}$



Figure 3. Plots of the percent conversion versus time for the hydroboration of 1-octene with pinacolborane catalyzed by 1 in C_6H_6 . The reactions were monitored over time by GC using mesitylene as an internal standard. Two reactions were run concurrently, with one vessel kept under ambient light (red squares) and one exposed to UV irradiation (λ_{irr} 313 nm) for 2 h prior to the addition of substrate (blue diamonds). The UV-treated reaction vessel was kept under UV irradiation for the first 4 h of the reaction and then was kept in the dark.

 $mol^{-1} \cdot s^{-1}$ (Figure 3 and Table 1). The observed 2.4-fold decrease in activity upon irradiation suggested to us that the photocyclized catalyst **1**c was less active for facilitating the hydroboration reaction than the ring-opened isomer **10**.

We next sought to employ the photochromic Rh complex 1 to catalyze the hydroboration of other olefinic substrates. When styrene (0.10 M) and pinacolborane (0.11 M) were added to a solution of 10 ($[10]_0 = 1 \times 10^{-3}$ M) in C₆D₆, the complete loss of the starting material and conversion to the linear (L), branched (B), and E-olefin (E) products^{23d,g} in an L:B:E molar ratio of 0.5:1.0:0.9 was determined by ¹H NMR spectroscopy and GC after 8 h at room temperature (Figure 4). Using comparative kinetics experiments similar to those described above for 1-octene, the hydroboration of styrene with pinacolborane was measured to proceed in ambient light with a rate constant, $k_{\rm vis}$, of $(2.3 \pm 0.2) \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$, while the catalytic activity was significantly attenuated in UV light ($k_{\rm UV}$ = $(2.5 \pm 0.6) \times 10^{-4} \text{ mol}^{-1} \text{ s}^{-1}; k_{\text{vis}}/k_{\text{UV}} = 9.2)$ (Figure 4a and Table 1). The disparity in the rates enabled photoswitching of the catalytic activity over the course of a single reaction. After exposure to ambient light for 1 h ($k_{vis} = (1.8 \pm 0.9) \times 10^{-3}$ $mol^{-1} s^{-1}$), a freshly prepared solution identical to that described above was subjected to UV irradiation for an additional 4 h, during which the reaction rate was significantly reduced $(k_{\rm UV} = (2.3 \pm 0.5) \times 10^{-4} \text{ mol}^{-1} \text{ s}^{-1}; k_{\rm vis}/k_{\rm UV} = 7.8).$ Subsequent exposure to visible light to facilitate the cycloreversion of the catalyst restored the catalytic activity (k_{vis} = $(1.6 \pm 0.5) \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1})$ (Figure 4b). Collectively, these results suggested to us that the reversible photocyclization within the NHC ligand of 1 altered the propensity of the Rh center to facilitate the hydroboration reaction and enabled the remote tuning of its catalytic activity.

To verify that the rate attenuation observed under UV irradiation was a result of the photoinduced change in the structure of the catalyst, a series of control experiments was performed. When the hydroboration reaction between styrene and pinacolborane was conducted in the absence of catalyst 1, negligible conversion was observed under ambient light (k_{vis} =

substrate ^a	catalyst	$k_{\rm vis}~({\rm mol}^{-1}~{\rm s}^{-1})$	$k_{\rm UV} \; ({\rm mol}^{-1} \; {\rm s}^{-1})$	$k_{ m vis}/k_{ m UV}$	
1-octene	1	$(1.9 \pm 0.5) \times 10^{-3}$	$(7.8 \pm 2.1) \times 10^{-4}$	2.4	
styrene	1	$(2.3 \pm 0.2) \times 10^{-3}$	$(2.5 \pm 0.6) \times 10^{-4}$	9.2	
	none ^b	5.0×10^{-6}	5.0×10^{-6}	1	
	(IMe)Rh(cod)Cl ^c	6.0×10^{-2}	1.9×10^{-1}	0.3^d	
4-chlorostyrene	1	$(8.4 \pm 4.0) \times 10^{-4}$	$(1.3 \pm 0.8) \times 10^{-4}$	6.5 ^d	
4-methoxystyrene	1	$(5.7 \pm 3.0) \times 10^{-4}$	$(7.4 \pm 1.7) \times 10^{-5}$	7.7^{d}	
t-butylacetylene	1	$(3.3 \pm 0.6) \times 10^{-4}$	$(9.0 \pm 1.0) \times 10^{-5}$	3.7^{d}	

Table 1	. Summary	of the	Second-Or	der Rat	e Constants	Measured for	r Various	Hydroboration	Reactions	Catalyzed I	by I	l
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^{*a*}Reactions were performed with 0.1 M substrate and 0.11 M pinacolborane in benzene with 1 mol % catalyst. ^{*b*}Reaction was performed without a catalyst. ^{*c*}(IMe)Rh(cod)Cl = chloro(η^{4} -1,5-cyclooctadiene)(1,3-dimethylimidazol-2-ylidene)rhodium(I). ^{*d*}For the corresponding plots of percent conversion vs time, see Figures S2–S5 in the Supporting Information.



Figure 4. Plots of the percent conversion versus time for the hydroboration of styrene with pinacolborane catalyzed by 1 in C_6H_6 . The reactions were monitored over time by GC using mesitylene as an internal standard. (a) Two reactions were run concurrently with one vessel kept under ambient light (red squares) and one exposed to UV irradiation (λ_{irr} 313 nm) for 2 h prior to the addition of substrate (blue diamonds). The reaction vessel exposed to UV was irradiated for the first 4 h of the reaction and then was kept in the dark. (b) A single reaction was allowed to proceed in ambient light for 1 h (red squares), subjected to UV irradiation (blue diamonds) (λ_{irr} 313 nm) for 2 h, and then kept in the dark for a further 2 h prior to exposure to visible light ($\lambda_{irr} >500$ nm) (red squares).

 $5.0 \times 10^{-6} \text{ mol}^{-1} \text{ s}^{-1}$) or UV irradiation ($k_{\rm UV} = 5.0 \times 10^{-6} \text{ mol}^{-1} \text{ s}^{-1}$), indicating that the latter alone was not responsible for the decrease in activity (Figure S2 (Supporting Information) and Table 1). Moreover, a significant reduction in activity was not observed under UV irradiation compared with ambient light ($k_{\rm vis} = 6.0 \times 10^{-2} \text{ mol}^{-1} \text{ s}^{-1}$; $k_{\rm UV} = 1.9 \times 10^{-1} \text{ mol}^{-1} \text{ s}^{-1}$; $k_{\rm vis}/k_{\rm UV} = 0.3$) (Figure S3 (Supporting Information) and Table 1) when the reaction was performed using chloro(η^4 -1,5-cyclooctadiene)(1-methyl-3-methylimida-zole-2-ylidene)rhodium(I), a structurally related NHC-Rh(I) complex which lacks a photochromic dithienylethene moiety, as the catalyst. Collectively, the results of these control experiments suggested to us that the decrease in rate upon UV

exposure was unique to complex 1 and was due to the photocyclization of 1o to 1c.

In an effort to expand the substrate scope of the photocontrolled hydroboration reaction and to determine if the electronic properties of the substrate would affect the rate disparity, our attention next turned toward substituted styrene derivatives. The hydroboration of 4-chlorostyrene with pinacolborane was significantly faster in ambient light (k_{vis} = $(8.4 \pm 4.0) \times 10^{-4} \text{ mol}^{-1} \text{ s}^{-1})$ than under UV irradiation ($k_{\text{UV}} = (1.3 \pm 0.8) \times 10^{-4} \text{ mol}^{-1} \text{ s}^{-1}$; $k_{\text{vis}}/k_{\text{UV}} = 6.5$), as was the reaction between 4-methoxystyrene and pinacolborane ($k_{vis} = (5.7 \pm 3.0) \times 10^{-4} \text{ mol}^{-1} \text{ s}^{-1}$; $k_{UV} = (7.4 \pm 1.7) \times 10^{-5} \text{ mol}^{-1}$ s⁻¹; $k_{vis}/k_{UV} = 7.7$) (see Figures S4 and S5 (Supporting Information) and Table 1). The observed decreases in catalytic activity upon UV exposure were in good agreement with the aforementioned results observed with styrene and suggested to us that the method is not limited by the electronic properties of the olefin starting material. Moreover, the aforementioned results indicated that the rate-determining step of the hydroboration mechanism was not significantly affected by the electronic character of the substrate (see below).

Since we previously demonstrated that the rates of Rh(I)promoted alkyne hydroborations were sensitive to the electrondonating character of the NHC ligated to the metal center,^{15a} subsequent efforts focused on alkynes. The hydroboration of phenylacetylene with pinacolborane in the presence of 10 in C₆H₆ primarily resulted in the formation of poly- $(phenylacetylene)^{25}$ (>80%) rather than the desired olefin hydroboration products. Alternatively, when tert-butylacetylene (0.10 M) was treated with pinacolborane (0.11 M) in the presence of 10 ([10]₀ = 1×10^{-3} M), a 67% conversion to the (E)-olefin product was observed after 13 h, as evidenced by ${}^{1}H$ NMR spectroscopic analysis of the crude reaction mixture (Figure 5). To explore the effect of UV irradiation on the reaction outcome, a comparative kinetics experiment analogous to those described above for the olefinic substrates was performed. Under ambient light, the hydroboration of tertbutylacetylene with pinacolborane proceeded with a rate constant, $k_{\rm vis}$, of (3.3 \pm 0.6) \times 10⁻⁴ mol⁻¹ s⁻¹, while the reaction exposed to UV proceeded more slowly ($k_{\rm UV}$ = (9.0 ± 1.0) × 10⁻⁵ mol⁻¹ s⁻¹; k_{vis}/k_{UV} = 3.7; Figure 5 and Table 1). These results were consistent with the disparate rates observed with the alkenes and suggested to us that the alkyne hydroboration proceeded via a similar mechanism (see below). Furthermore, the aforementioned results demonstrated that the photocyclization of 10 to 1c is an effective method for modulating hydroboration rates for a wide variety of substrates.

A proposed catalytic cycle for the hydroboration reactions catalyzed by 1 is given in Scheme 3. Since the overall



Figure 5. Plots of the percent conversion versus time for the hydroboration of *tert*-butylacetylene with pinacolborane catalyzed by 1 in C_6H_6 . The reactions were monitored over time by GC using mesitylene as an internal standard. Two reactions were run concurrently with one vessel exposed to UV irradiation (λ_{irr} 313 nm) for 2 h prior to the addition of substrate and throughout the reaction (blue diamonds) and one was kept under ambient light (red squares).

hydroboration rate was reduced upon UV irradiation to form **1c** (which features a less electron donating NHC ligand), the rate-determining step must be inhibited by the presence of a more electron deficient Rh center. Of the four general steps of the hydroboration cycle, the reductive elimination step should be slower in the presence of a less donating ligand. Furthermore, the rate of the reductive elimination would not be significantly affected by the electronic properties of the olefin substituents, which is supported by the observation that the light induced changes in the rate constants measured for various styrene derivatives were similar to those measured for styrene. Collectively, and consistent with previous reports,²⁶ the results described above suggested to us that the rate-determining step of the catalytic cycle is the reductive

elimination. The decrease in the hydroboration rate observed upon UV irradiation indicates that the photocyclization of **1o** to **1c** decreased the donating ability of the NHC ligand in **1** and thus the propensity of the complex to undergo reductive elimination. Given that *tert*-butylacetylene exhibited a similar decrease in rate upon UV irradiation, an analogous mechanism may be operative for the hydroboration of alkyne substrates.

CONCLUSIONS

In summary, we have developed a photochromic Rh(I)complex and demonstrated that a UV-induced electrocyclic ring-closing reaction decreased the electron-donating ability of the NHC ligand. Ring closure was reversed upon exposure to visible light, resulting in the first Rh(I) complex to be switched with high fidelity between two electronic states via remote lightbased stimuli. While the open form of the catalyst (10) efficiently facilitated the hydroboration of alkenes and alkynes, the catalytic activity was significantly attenuated upon UV irradiation to form the ring-closed isomer (1c). Remarkably, the rate of the hydroboration of styrene was reduced by nearly an order of magnitude upon UV irradiation, which was sufficient to enable remote photomodulation of the catalytic activity over the course of the reaction. The attenuated activity of 1c in comparison with 1o was attributed to the decrease in donicity of the NHC ligand upon photocyclization, which inhibited the rate-determining reductive elimination step of the hydroboration mechanism.

Given that the outcomes of a wide variety of transformations catalyzed by NHC-supported metal complexes are dependent on the electron-donating properties of the NHC ligand,¹⁵ the methodology described herein is expected to be extended and generalized to hydrosilylations,²⁷ hydrogenations, cross-couplings, metathesis, and other reactions. Furthermore, in addition to expanding the scope of photoswitchable catalysis, this system offers new opportunities in tandem homogeneous catalysis.²⁸ While the photocyclized catalyst **1c** is less electron rich and is relatively ineffective for hydroboration reactions, the

Scheme 3. Proposed Catalytic Cycle for the Photoswitchable Hydroboration Catalyzed by 1^{*a,b*}



^{*a*}The photocyclized complex may be generated during any step of the catalytic cycle; however, for clarity it is only shown at the reductive elimination step. ^{*b*}An alkyne substrate is expected to coordinate to the Rh center and undergo the subsequent steps in a manner analogous to the alkenes, but this is not shown for clarity.

complex is structurally robust and remains soluble, characteristics which may enable it to facilitate reactions that are orthogonal to the hydroboration chemistry promoted by its counterpart **10**. Such an ability to alter catalytic activity by remotely photomodulating the electronic state of the catalyst is expected to facilitate multistep synthesis of complex small molecules and macromolecules.

EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise specified, reagents were purchased from commercial sources and used without further purification. Styrene, 4-chlorostyrene, 4-methoxystyrene, 1-octene, phenylacetylene, and tert-butylacetylene were dried over 4 Å molecular sieves and bubbled with dry N2 before use. All syntheses were performed under ambient conditions unless specified otherwise. Solvents were dried and degassed using a solvent purification system. ¹H and ¹³C NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts δ (in ppm) are referenced to tetramethylsilane using the residual solvent as an internal standard: for ¹H NMR, CDCl₃ 7.24 ppm, C₆D₆ 7.15 ppm; for ¹³C NMR, CDCl₃ 77.0 ppm, C₆D₆ 128.0 ppm. Coupling constants (J) are expressed in hertz (Hz). Melting points were obtained with an automated melting point apparatus and are uncorrected. Mass spectra (MS, ESI or CI) are reported as m/z (relative intensity). UV-vis spectra were acquired in quartz cuvettes with 1.0 cm path lengths and 3.0 mL sample solution volumes. Beer's law measurements were performed using 10, 20, 30, and 40 μ M sample concentrations. The photochemical reactions were performed in the same quartz cuvettes using 4.0 mL sample solution volumes. The irradiation source for photochemical reactions was a 350 W Hg lamp in a housing equipped with a liquid filter containing HPLC grade H₂O, an electronic safety shutter, and a filter holder. The cuvette holder was placed at a distance of 8 cm from the end of the source. The irradiation wavelength for the photocyclization reactions was obtained using a 313 nm bandpass filter. A long-pass edge filter (>500 nm) was used to introduce visible light. The reactions conducted under ambient light utilized standard indoor fluorescent lights. Elemental analyses were performed using standard combustion analysis on an organic elemental analyzer. Gas chromatography (GC) was performed on a gas chromatograph (nonpolar column, L = 30 m, i.d. = 0.32 mm) equipped with a flame ionization detector. The GC oven temperature was held at 40 °C for 3 min and then increased to 100 °C at 10 °C min⁻¹ and finally increased to 250 °C at 20 °C min⁻¹. The conversion of starting materials to their corresponding products and the respective reaction rates were calculated by monitoring the loss of starting material with respect to the internal standard, mesitylene (see the Supporting Information). The product mixtures were determined by ¹H NMR spectroscopy at the end of each reaction. The ¹H NMR data were consistent with those obtained via GC.

Synthesis of [Ag{4,5-bis(2'-methyl-5'-phenylthien-3'-yl)-1,3dimethylimidazolylidene [1] (3). Under an atmosphere of nitrogen in a glovebox, a 30 mL vial equipped with a stir bar was charged with 200 mg (0.35 mmol) of 1,2-bis(2'-methyl-5'-phenylthien-3'-yl)-1,3-dimethylimidazolium iodide (2),¹⁶ 40 mg (0.17 mmol) of Ag_2O , 3 Å molecular sieves, and 25 mL of CH2Cl2. The vial was sealed with a Teflon-lined cap, covered with aluminum foil, removed from the glovebox, and heated to 50 °C for 16 h. The reaction mixture was filtered through a frit of coarse porosity while hot, and the filter cake was washed thoroughly with 250 mL of CH2Cl2. The filtrate was concentrated under reduced pressure, the residue was triturated in diethyl ether, and 214 mg (90% yield) of the desired product was collected by filtration as a beige powder. Mp: 124 °C dec. UV-vis (CH_2Cl_2) : λ_{abs} 291 nm ($\varepsilon = 20936$ dm³ mol⁻¹). ¹H NMR (400 MHz, CDCl₃): δ 2.06 (s, 6H), 3.80 (s, 6H), 7.08 (s, 2H), 7.35 (m, br, 6H), 7.49 (m, br, 4H). Characterization of this compound via ¹³C NMR spectroscopy was not possible due to its poor solubility. HRMS (m/z): calcd for $C_{27}H_{24}N_2S_1I^{107}Ag [M - I]^+$ 547.0432; found 547.0436; calcd for $C_{27}H_{24}N_2S_2I^{109}Ag [M - I]^+$ 549.0428, found 549.0452.

Synthesis of Chloro(η^4 -1,5-cyclooctadiene)(4,5-bis(2'-methyl-5'-phenylthien-3'-yl)-1,3-dimethylimidazolylidene)rhodium(I) (10). Under an atmosphere of nitrogen in a glovebox, a 30 mL vial with a stir bar was charged with 309 mg (0.46 mmol) of Ag complex 2, 112 mg (0.23 mmol) of [Rh(cod)Cl]₂, and 20 mL of CH₂Cl₂. The vial was sealed with a foil-lined cap and stirred at room temperature for 1 h, during which time a white precipitate formed. The vial was removed from the glovebox, after which the reaction mixture was passed through a 0.2 μ m PTFE filter and the filtrate was concentrated under reduced pressure at room temperature. The resulting yellow residue was purified by column chromatography on silica gel with a 3/1 v/v mixture of hexanes and acetone as eluent to afford 237 mg (75% yield) of the desired product. Mp: 151 °C dec. UV-vis (C_6H_6) : λ_{abs} 284 nm (ε = 33314 dm³ mol⁻¹), λ_{abs} 394 nm (ε = 1580 dm³ mol⁻¹). ¹H NMR (400 MHz, CDCl₃): δ 1.98 (d, J = 8.8, 8H), 2.43 (m, J = 12 4H), 3.41 (s, 2H), 4.01 (s, 6H), 5.05 (s, 2H), 7.03 (s, 2H), 7.25 (t, J = 8, 2H), 7.34 (t, J = 8, 4H), 7.49 (d, J = 8, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 14.1, 28.9, 30.8, 32.9, 36.2, 67.8, 68.0, 98.6, 98.7, 123.8, 125.4, 125.8, 127.4, 127.6, 128.9, 133.6, 141.4, 182.9, 183.4. HRMS (m/z): calcd for C₃₅H₃₆N₂S₂Rh [M - Cl]⁺ 651.16395, found 651.13706. Anal. Calcd for C35H36ClN2S2Rh: C, 61.18; H, 5.28; N, 4.08. Found: C, 60.78; H, 5.38; N, 3.75.

General Procedure Used for the Hydroboration Reactions. Under an atmosphere of N₂ in a glovebox, a vial was charged with 5.5 mg (0.008 mmol) of 10 and 4 mL of C₆H₆. A 2 mL portion of the catalyst solution was added to each of two quartz cuvettes equipped with magnetic stir bars, and 2 mL of C_6H_6 was added to each cuvette. The cuvettes were then sealed with Teflon-lined septum caps and removed from the glovebox. The solution in one cuvette was irradiated with UV light (λ_{irr} 313 nm) with stirring for 2 h, while the solution in the second cuvette was stirred under ambient light with stirring. After 2 h, 56 μ L (0.4 mmol) of mesitylene (internal standard) was added to each cuvette via a N2-purged syringe, followed by the substrate (0.4 mmol) and 64 μ L (0.44 mmol) of pinacolborane. The UV-treated reaction vessel was kept under UV irradiation for the first 4 h of the reaction and then was kept in the dark. The second reaction vessel was kept under ambient light throughout the course of the reaction. Aliquots were removed after given amounts of time, diluted with wet THF to quench the reaction, and analyzed by GC. For the photoswitching experiments, a single reaction was set up as described above in a quartz cuvette and irradiated with UV or visible light after the indicated amounts of time.

ASSOCIATED CONTENT

S Supporting Information

Text and figures giving additional experimental procedures, spectral data, and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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