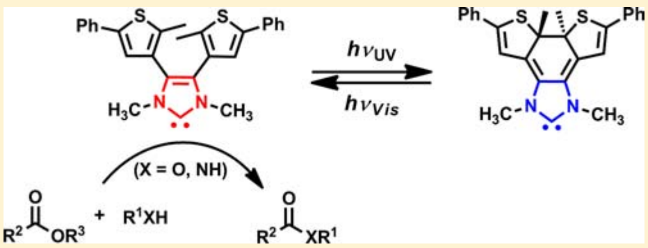
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

Photoswitchable Organocatalysis: Using Light To Modulate the Catalytic Activities of N-Heterocyclic Carbenes

Bethany M. Neilson and Christopher W. Bielawski*

Department of Chemistry and Biochemistry, The University of Texas, Austin, Texas 78712, United States

Ⓢ *Supporting Information*



ABSTRACT: A 4,5-dithienylimidazolium salt was found to undergo electrocyclic isomerization upon exposure to UV radiation (λ_{irr} = 313 nm) under neutral and basic conditions; subsequent exposure to visible light reversed the reaction. Under ambient light and in the presence of base, the imidazolium species catalyzed transesterifications as well as amidations in a manner similar to those of previously reported N-heterocyclic carbene precatalysts. However, upon UV irradiation to effect the aforementioned photocyclization, the rate of the transesterification reaction between vinyl acetate and allyl alcohol was significantly attenuated ($k_{vis/UV}$ = 12.5), as was the rate of the condensation of ethyl acetate with aminoethanol ($k_{vis/UV}$ = 100). The rates of these reactions were successfully toggled between fast and slow states by alternating exposure to visible and UV light, respectively, thus demonstrating a rare example of a photoswitchable catalyst that operates via photomodulation of its electronic structure.

■ INTRODUCTION

Photoswitchable catalysis is a burgeoning field of study that utilizes photochemical processes to alter the courses of chemically catalyzed transformations.[1] Although many known[2] photochromic moieties may be reversibly switched between states that feature different steric and/or electronic properties,[3] examples of using photochromism to modulate catalytic reactions are scarce.[4] Following Ueno's seminal report of an azobenzene-capped *β*-cyclodextrin which was used to modulate the hydrolysis of *p*-nitrophenyl acetate in 1981 (Figure 1a),[4e] Cacciapaglia and Mandolini described a photo-tunable "butterfly" crown ether that facilitated the ethanolysis of anilides (Figure 1b).[4f] Hecht subsequently reported an elegantly designed piperidine that enabled photoswitchable control over the Henry reaction (Figure 1c).[4a−c] In all of these and other examples, however, the catalytic activity was modulated through reversible steric shielding that resulted from a photochemically induced isomerization reaction.[4] Indeed, as recently noted by Hecht, "no example of successful reactivity switching by a photochrome-mediated electronic modulation of a catalyst's active site has been described to date."[1] Catalysts with photoswitchable electronic structures are expected to be broadly applicable while enabling precise control over intrinsic chemo- and/or regioselectivities.

To realize such a photoswitchable catalyst, we were drawn to the photochromic diarylethenes (DAEs),[5] which were recently shown by our group[6] and others[7] to alter the electron density at the C2 position of imidazolium salts and related N-heterocyclic carbene (NHC)[8] adducts. As NHCs and their complexes are known to catalyze a variety of useful synthetic transformations,[9] we envisioned that such photoinduced changes in electronic properties may be used to modulate the activities of NHC-based catalysts.[10] Herein, we report a DAE-annulated NHC organocatalyst and demonstrate that its activity may be switched through the remote photomodulation of electronic structure.

■ RESULTS AND DISCUSSION

Considering that the previously reported photochromic DAE-annulated NHC adducts and precursors required high energy radiation ($\lambda_{irr} \leq 297$ nm) to undergo cyclization,[6,7] we targeted a derivative that would isomerize under relatively mild conditions. As shown in Scheme 1, the NHC precursor **1·HPF$_6$** features phenyl substituents at the 5- and 5′-positions of the thiophene rings, which extend the conjugation length of the dithienyl backbone, and therefore was expected to undergo electrocyclic ring-closure upon exposure to relatively low energy radiation.

The synthesis of the open form of the aforementioned salt (**1o·HPF$_6$**) is summarized in Scheme 2. Acylation of commercially available 2-methyl-5-phenylthiophene with acetic anhydride and tin(IV) chloride afforded 3-acetyl-2-methyl-5-phenylthiophene **2**, which was then oxidized with selenium dioxide. The resulting glyoxal monohydrate **3** was coupled with 1 equiv of 2-methyl-5-phenylthiophene in the presence of tin(IV) chloride to give known[11] *α*-hydroxy ketone **4**. Oxidation of **4** with copper(II) acetate and ammonium nitrate in refluxing acetic acid afforded diketone **5**, which was formylatively cyclized to give imidazole **6**. Finally, methylation with iodomethane under basic conditions followed by anion metathesis[12] afforded imidazolium salt **1o·HPF$_6$**, as evidenced

Received: May 2, 2012
Published: July 19, 2012

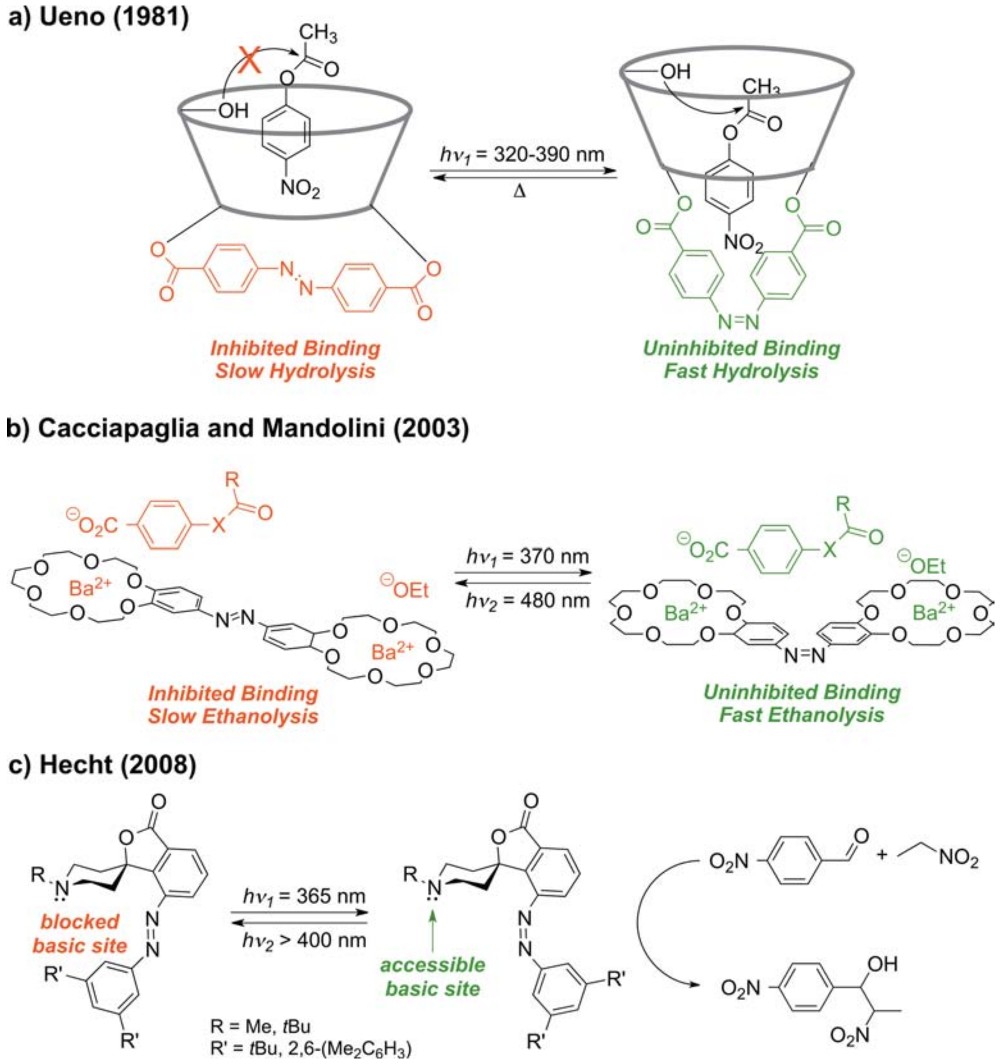
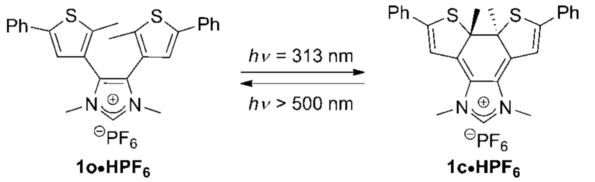


Figure 1. Representative examples of photoswitchable catalysts: (a) Ueno et al. reported a photoswitchable azobenzene-capped β-cyclodextrin in which the reversible $E \rightarrow Z$ isomerization resulted in a deeper cavity and enhanced substrate binding affinity, leading to faster hydrolysis.[4e] (b) The reversible $E \rightarrow Z$ isomerization of a phototunable crown ether facilitated the light-gated ethanolysis of anilide derivatives.[4f] (c) An azobenzene-annulated piperidine catalyzed the Henry reaction at a significantly faster rate in the Z form compared to the more stable E isomer due to steric shielding of the basic site.[4a].

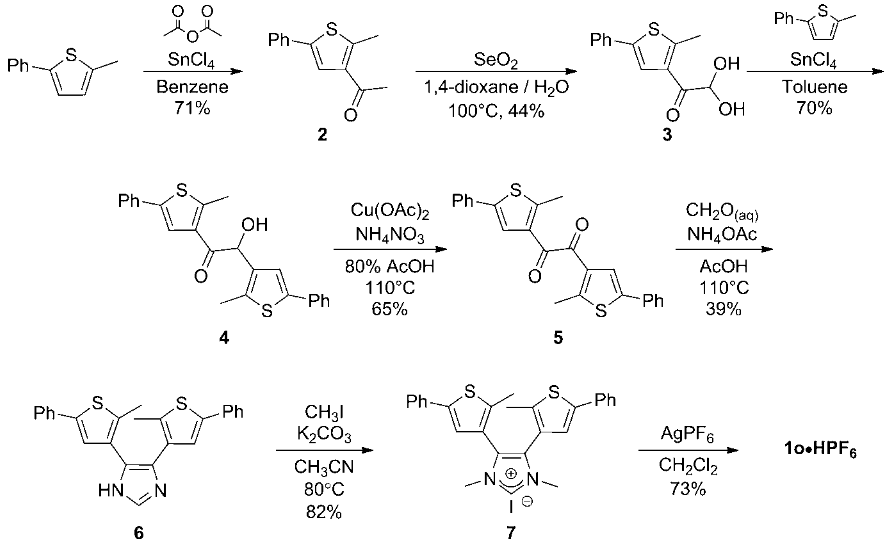
Scheme 1. Photochromism of NHC Precursor 1·HPF_6



in part by the appearance of diagnostic ^{1}H (δ = 8.6 ppm) and ^{13}C (δ = 142 ppm; $CDCl_3$) NMR signals, which corresponded to the proton and carbon nuclei at the C2 position, respectively (see the Supporting Information).

The UV−vis spectra recorded for **1o·HPF_6** dissolved in benzene, tetrahydrofuran, or acetonitrile exhibited intense absorption bands between 275 and 325 nm, which were assigned to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the N-heterocycle and thiophene systems, respectively. Due to the phenyl groups in the 5- and 5′-positions of the thiophene moieties, the absorption spectrum of **1o·HPF_6** was bathochromically shifted when compared to those of previously reported 4,5-dithienyl N-heterocycles.[6,7a] As a result, exposing a solution of **1o·HPF_6** in benzene to relatively low energy radiation (λ_{irr} = 313 nm vs 280 nm[6]) resulted in a color change from pale yellow to bright blue. Concomitant with this color change, a decrease in the intensity of the absorption band centered at 292 nm and the appearance of a new band at 670 nm were observed (Figure 2a). The spectroscopic changes reached a steady state after 240 s of UV exposure and reflected an 88% conversion of **1o·HPF_6** to its ring-closed isomer **1c·HPF_6** upon measurement (see Scheme 1).[5,13a] Moreover, an isosbestic point was observed at 309 nm, which indicated that the cyclization proceeded without appreciable side reactions. Subsequent irradiation of the UV exposed solutions with visible light (λ_{irr} > 500 nm) resulted in the attenuation of the broad, low energy absorption bands. After 300 s of irradiation, the UV−vis spectrum of **1o·HPF_6** was nearly completely restored (>95% conversion),[13a] which suggested to us that the ring-closed product **1c·HPF_6** reverted back to the starting material (Figure 2b).

Scheme 2. Synthesis of 1o·HPF_6



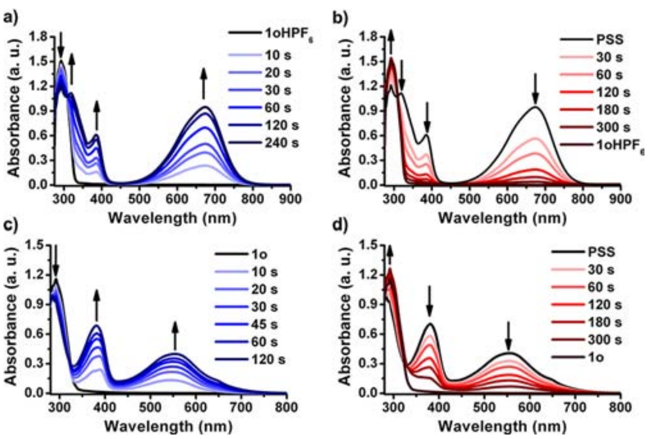


Figure 2. (a) UV−vis spectral changes of **1o·HPF_6** in C_6H_6 upon UV irradiation (λ_{irr} = 313 nm). (b) UV−vis spectrum in C_6H_6 of **1o·HPF_6**, the photostationary state (PSS) reached after UV irradiation of **1o·HPF_6** for 240 s, and spectral changes of the PSS upon visible irradiation (λ_{irr} > 500 nm). (c) UV−vis spectral changes of **1o** (generated in situ by treatment of **1o·HPF_6** with 1.0 equiv of NaHMDS) in C_6H_6 upon UV irradiation (λ_{irr} = 313 nm). (d) UV−vis spectrum in C_6H_6 of **1o**, the photostationary state (PSS) reached after UV irradiation of **1o** for 120 s, and spectral changes of the PSS upon visible irradiation (λ_{irr} > 500 nm). In all cases, the initial concentration of **1o** was 4×10^{-5} M and the spectra were recorded after irradiation for the indicated amount of time. The arrows indicate the evolution of the spectral changes over time.

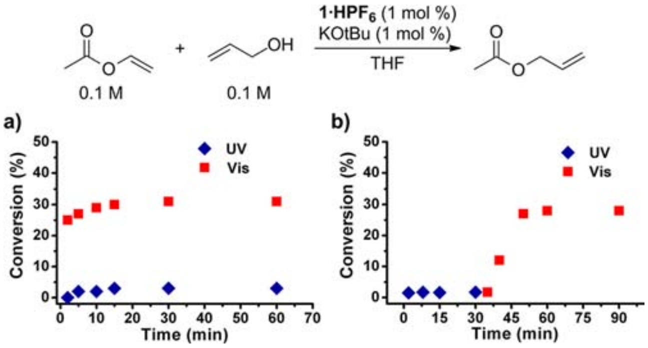


Figure 3. Plots of the percent of starting materials which have converted to products versus time for the condensation of vinyl acetate and allyl alcohol catalyzed by **1** (prepared in situ from **1·HPF_6** and KO*t*Bu) in THF. The reactions were monitored over time by GC using *n*-octane as an internal standard. (a) Two reactions were run concurrently with one vessel exposed to UV irradiation (λ_{irr} = 313 nm) for 1 h prior to substrate addition (blue diamonds) and one kept under ambient light (red squares). (b) A single reaction vessel was exposed to UV irradiation (λ_{irr} = 313 nm) for 1 h prior to substrate addition. The contents of the vessel were then stirred under UV light for 30 min (blue diamonds) prior to exposure to visible light (λ_{irr} > 500 nm) (red squares).

The photocyclizations were further confirmed by ^{1}H NMR spectroscopy. After irradiation of **1o·HPF_6** in CD_3CN at 313 nm for 45 min ([**1o·HPF_6**]$_0$ = 1×10^{-3} M), the signals assigned to the thiophene protons shifted upfield from δ 7.3 ppm to 6.9 ppm, and a significant upfield shift of the signal assigned to the proton at the C2 position in **1o·HPF_6** from 8.6 ppm to 8.1 ppm was observed (see Figure S20 of the Supporting Information). Integration of these signals revealed that 81% of **1o·HPF_6** converted to **1c·HPF_6**. Exposure of the UV treated solution to ambient light for 4 h reversed the aforementioned chemical shifts (>95% conversion).

Considering that catalytically active NHCs may be generated by exposing imidazolium salts to base, subsequent efforts focused on investigating the photochemical behavior of **1o·HPF_6** under basic conditions. Although the free NHC **1o** was not isolable, its formation was observed in situ by NMR spectroscopy upon treatment of **1o·HPF_6** with 1 equiv of KOtBu or NaHMDS, as evidenced by the loss of the imidazolium ^{1}H NMR signal at 8.82 ppm and the appearance of a ^{13}C NMR signal assigned to the carbenoid nucleus at 201.9 ppm (C_6D_6). Similar to that of its imidazolium precursor, the UV−vis spectrum of **1o** exhibited an intense absorption centered at 291 nm in benzene. Upon UV irradiation, a decrease in the intensity of this band was observed concomitant with the appearance of new bands at 378 and 554 nm, as well as an isosbestic point at 321 nm (Figure 2c). Measurement of these signals revealed that >99% of **1o** converted to its ring-closed isomer **1c** after 120 s of UV irradiation.[13b] As further confirmation of the forward cyclization reaction, the ^{1}H NMR signals assigned to the thiophene protons shifted upfield from δ

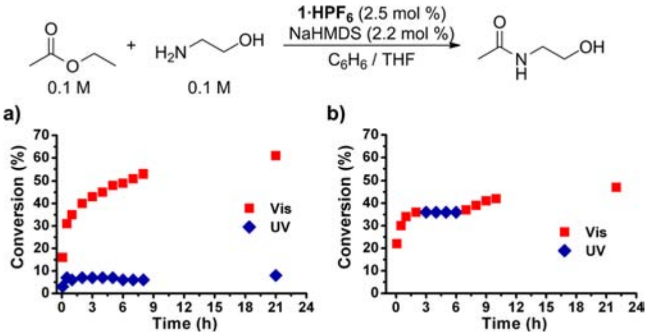


Figure 4. Plots of the percent of starting materials which have converted to products versus time for the condensation of ethyl acetate and 2-aminoethanol catalyzed by **1** (prepared in situ from **1·HPF$_6$** and NaHMDS) in 3:1 C$_6$H$_6$/THF (v/v). The reactions were monitored over time by GC, using *n*-octane as an internal standard. (a) Two reactions were run concurrently with one vessel exposed to UV irradiation (λ_{irr} = 313 nm) for 1 h prior to substrate addition (blue diamonds) and one kept under ambient light (red squares). (b) A single reaction was allowed to proceed in ambient light for 2 h (red squares) and then subjected to UV irradiation (blue diamonds) (λ_{irr} = 313 nm) for 1 h and kept in the dark for a further 3 h prior to exposure to visible light (λ_{irr} > 500 nm) (red squares). For experiments where the reaction was switched over different time scales, see the Supporting Information.

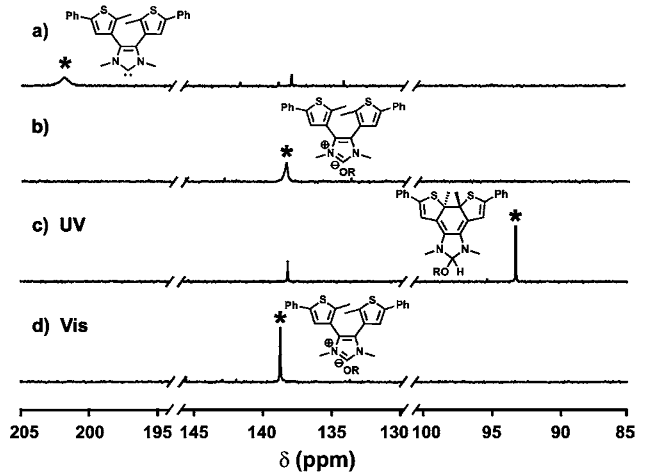


Figure 5. Quantitative ^{13}C NMR spectra collected sequentially in C$_6$D$_6$ over the course of the following experiment: A sample of (a) **1o** labeled at the C2 position with a ^{13}C atom (i.e., **1o***; [**1o***]$_0$ = 1.0 × 10^{-2} M) (b) was treated with equimolar quantities of 2-aminoethanol and ethyl acetate and (c) then exposed to UV irradiation for 1 h (λ_{irr} = 313 nm; [**1o***]$_0$ = 2.5 × 10^{-3} M) and finally (d) irradiated with visible light for an additional 2 h (λ_{irr} > 500 nm, [**1o***]$_0$ = 1.0 × 10^{-2} M). See text for additional details.

7.0 ppm to 6.7 ppm after irradiation of **1o** in C$_6$D$_6$ at 313 nm ([**1o**]$_0$ = 1 × 10^{-3} M), with the conversion of **1o** to **1c** reaching 71% after 1 h of irradiation. Additionally, a new ^{13}C NMR resonance was observed at δ 66.6 ppm, after irradiation of **1o** in C$_6$D$_6$, and assigned to the sp^3 carbon nuclei adjacent to the sulfur atoms in **1c**. Subsequent irradiation with visible light for 300 s reversed the observed UV–vis spectral changes, and the spectrum of **1o** was nearly restored (85% conversion),[13b] indicating that **1c** had undergone photocycloreversion (Figure 2d). Together, these results suggested to us that **1** underwent a reversible photochemical process analogous to its precursor **1·HPF$_6$**.

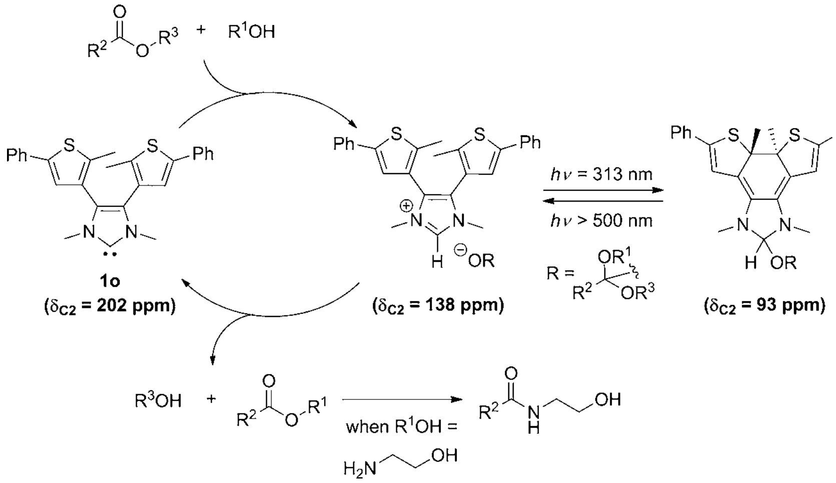
Having demonstrated that **1o·HPF$_6$** and **1o** underwent similar reversible photocyclizations, our attention shifted toward exploring the photoinduced isomerizations as a means to modulate catalytic activity. Our attention was directed toward transesterification and amidation reactions, as imidazolium salts in the presence of base have been shown to catalyze these useful transformations.[14] Moreover, Nolan and others have shown that the catalytic activities observed in various condensation reactions are sensitive to changes in the electronic structure of the NHC organocatalyst.[14c]

In a preliminary experiment, **1o** was found to promote the transesterification of allyl alcohol and vinyl acetate (Figure 3). A 35% conversion[15] to the expected ester product was observed after 1 h by ^{1}H NMR spectroscopy upon treatment of a THF solution containing equimolar quantities of the aforementioned alcohol and ester starting materials (initial concentration of each: 0.1 M) with **1o** (1 mol %; prepared in situ by treating **1o·HPF$_6$** with 1 equiv of KO*t*Bu) at room temperature. To determine if exposure to UV irradiation would influence the aforementioned condensation reaction, a freshly prepared solution of **1o** in THF ([**1o**]$_0$ = 1 × 10^{-3} M) was divided in half: one-half was placed in a quartz cuvette sealed with a Teflon-lined septum cap, and the other half was transferred to a flask and sealed with a rubber septum. The solution in the quartz cuvette was then subjected to UV irradiation (λ_{irr} = 313 nm) for 1 h while the other solution was kept in ambient light over the same period of time, after which equimolar amounts of vinyl acetate and allyl alcohol were added to each reaction vessel separately. Aliquots were then periodically removed from each mixture, diluted with methanol to quench the reaction, and analyzed by gas chromatography using *n*-octane as an internal standard. Inspection of these data revealed that the reaction exposed to ambient light proceeded with a second order rate constant, k_{vis}, of 5 ± 1 × 10^{-4} mol^{-1}·s^{-1} whereas the reaction that had been subjected to UV irradiation exhibited only negligible conversion to product (<3% by GC; k_{UV} = 4 ± 1 × 10^{-5} mol^{-1}·s^{-1}). The 10-fold decrease in reactivity suggested to us that photocyclization occurred upon UV irradiation and the corresponding changes in the electronic structure of **1** significantly attenuated its catalytic activity (Figure 3a).[16] Moreover, the differences in reactivity were consistent with Nolan's observation that imidazol-2-ylidene catalysts were more active than their relatively electron deficient imidazolin-2-ylidene analogues in similar transesterification reactions.[17]

Since **1o** and **1c** may be interconverted by exposure to light of different wavelengths, we sought to explore the potential of switching the catalytic activity over the course of a condensation reaction. When vinyl acetate and allyl alcohol were added to a THF solution of **1c**, no conversion was observed by GC for at least 30 min while the reaction vessel was irradiated with UV light. However, the rate of product formation significantly increased (Figure 3b) upon subsequent exposure to visible light (λ_{irr} > 500 nm), consistent with the formation of the catalytically active **1o** from **1c**. Unfortunately, multiple switching cycles were precluded by the relatively slow photocyclization and condensation kinetics.[15] Regardless, the result constituted the first example of using light to activate a latent NHC-based organocatalyst.[1,18]

Next, efforts were directed toward exploring photoswitchable amidation reactions, which were envisioned to be better suited for photoswitching as they generally proceed with consistently higher conversions and longer reaction times than analogous transesterification reactions.[14e] Initial studies showed that when

Scheme 3. Proposed Mechanism of Photoswitchable NHC Catalyzed Condensation Reactions



ethyl acetate and 2-aminoethanol were added to **1o** (2.5 mol %; prepared in situ from **1o·HPF$_6$** and 0.9 equiv of NaHMDS), a 61% conversion to the expected amide was observed by ^{1}H NMR spectroscopy after 21 h. Using similar comparative kinetics experiments as described above for the transesterification reactions, the aforementioned amidation reaction performed under ambient light proceeded with a second order rate constant of $k_{vis} = 5 \pm 4 \times 10^{-4}$ mol^{-1}·s^{-1} whereas an analogous reaction exposed to UV light was relatively slow ($k_{UV} = 5 \pm 4 \times 10^{-6}$ mol^{-1}·s^{-1}; $k_{vis/UV} = 100$); see Figure 4a.[19] The disparate rates enabled the photomodulation of the reaction kinetics over the course of a single amidation reaction. As shown in Figure 4b, after exposure to ambient light for 2 h ($k_{vis} = 6 \pm 5 \times 10^{-4}$ mol^{-1}·s^{-1}), the vessel containing an identical mixture to that described above was subjected to UV irradiation for 1 h, which effectively stopped the reaction. After a further 3 h in the dark, during which no conversion of starting material to product was observed, exposure to visible light ($\lambda_{irr} > 500$ nm) resulted in a significant restoration of the catalytic activity ($k = 1.3 \pm 0.5 \times 10^{-4}$ mol^{-1}·s^{-1}). The initial reaction rate was not fully restored, likely due to photochemical fatigue of the catalyst upon prolonged UV irradiation. However, since only a minor portion of the catalyst underwent decomposition,[20] it was possible to switch the catalytic activity over multiple time scales. A reaction duplicate to that described above was kept under ambient light for 30 min before being exposed to UV irradiation for 30 min, which effectively stopped the reaction. The reaction conversion remained stagnant while the reaction vessel was kept in the dark for a further 1 h; however, the catalytic activity was restored upon subsequent exposure to visible light (see Figure S1 of the Supporting Information). Collectively, these results suggested to us that the photocyclization process intrinsic to **1** was responsible for the changes in catalytic activity, which was consistent with our previous observation that the dithienylethene photocyclization decreases the electron density at the C2 position of the NHC.[6] Furthermore, since we have previously shown that the change in the steric properties of related photochromic NHCs upon photocyclization is minimal,[6] these results demonstrate that photoinduced changes in electronic structure may be used to reversibly tune the activity of a catalytic species.

To gain additional insight into the photoswitchable NHC reactivity, the identities of the active and inactive adducts of the amidation catalyst were probed using ^{13}C NMR spectroscopy. Since low concentrations facilitated the photocyclization reactions, an analogue of **1o·HPF$_6$** that was isotopically labeled with a ^{13}C atom at the C2 position was used. The labeled precatalyst, **1o·HPF$_6$***, was synthesized via an analogous route to that employed for **1o·HPF$_6$**, with the exception that ^{13}CH$_2$O was used in the formylative cyclization step (see the Supporting Information). Upon treatment of **1o·HPF$_6$*** with 1 equiv of NaHMDS in C$_6$D$_6$, a ^{13}C NMR signal was observed at 201.9 ppm (Figure 5a), as expected[8,9] for the in situ formation of the free NHC **1o***. The addition of equimolar quantities of 2-aminoethanol and ethyl acetate to **1o*** (2.5 mol %) in C$_6$D$_6$ resulted in the formation of an imidazolium species,[21] as evidenced by the upfield shift of the C2 ^{13}C NMR signal from 201.9 ppm to 138.6 ppm (Figure 5b). UV irradiation of the mixture ($[\mathbf{1o^*}]_0 = 2.5 \times 10^{-3}$ M; $\lambda_{irr} = 313$ nm) for 1 h resulted in a further upfield shift of the signal assigned to the C2 atom (Figure 5c). The new resonance was observed at 93.3 ppm and identified as an NHC-alcohol adduct,[22,23] the formation of which may have been facilitated by the decreased electron density at the C2 position caused by the photocyclization reaction. Visible light irradiation reversed these spectroscopic changes and caused the signal at 93.3 ppm to shift downfield to 138.6 ppm, consistent with reversion to the imidazolium species (Figure 5d).[24] In combination with the results from the catalysis experiments described above, the ^{13}C NMR data suggested to us that the resting state of the active catalyst was an imidazolium species, which converted to a NHC-alcohol adduct upon UV irradiation and effectively suspended the catalytic cycle (Scheme 3). Moreover, the restoration in activity observed upon visible light irradiation demonstrated that the photocyclized adduct may be converted back to an imidazolium species that then re-engages the catalytic cycle.[25] Together, these results support the conclusion that the catalyst was reversibly switched with high fidelity between active and inactive adducts via photoinduced changes in electronic structure. Moreover, given that the transesterification reactions discussed above involve analogous alcohol and ester substrates, a similar photoswitching mechanism may be operative.

■ CONCLUSIONS

In summary, we report a rare[26] example of a photoswitchable catalyst that operates via the remote photomodulation of its electronic structure. By incorporating a dithienylethene moiety into the backbone of a NHC precursor, the activity of the corresponding organocatalyst was remotely tuned via exposure to UV or visible light. The rates of NHC-catalyzed transesterification and amidation reactions were attenuated by 1 to 2 orders of magnitude upon exposure to UV light, while subsequent exposure to visible light restored the catalytic activity. Given the vast array of reactions catalyzed by NHCs and NHC-supported metal complexes, the ability to remotely modulate catalyst electronic properties using light is expected to endow a broad range of catalysts with the ability to finely tune intrinsic chemo-, regio-, and stereoselectivities. Such catalysts are envisioned to find applications that range from the preparation of polymeric materials with sophisticated microstructures to facilitating the multistep syntheses of complex small molecules.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

bielawski@cm.utexas.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported in part by the U.S. Army Research Laboratory under Grant Number W911NF-09-1-0446. Additional support from the National Science Foundation (CHE-0645563) and the Robert A. Welch Foundation (F-1621) is also gratefully acknowledged. We thank Steve Sorey for his help with the quantitative ^{13}C NMR experiments.

■ REFERENCES

(1) Stoll, R. S.; Hecht, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 5054–5075.

(2) (a) Durr, H., Bouas-Laurent, H., Eds. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, The Netherlands, 2003. (b) Special Issue: "Photochromism: Memories and Switches"; Irie, M., Ed.; *Chem. Rev.* **2000**, *100*, 1683.

(3) (a) Russew, M.-M.; Hecht, S. *Adv. Mater.* **2010**, *22*, 3348–3360. (b) Guerchais, V.; Ordronneau, L.; Bozec, H. L. *Coord. Chem. Rev.* **2010**, *254*, 2533–2545. (c) Kuma, S.; Nishihara, H. *Dalton Trans.* **2008**, 3260–3271. (d) Ko, C.-C.; Yam, V.-W.-W. *J. Mater. Chem.* **2010**, *20*, 2063–2070. (e) Kobatake, S.; Irie, M. *Annu. Rep. Prog. Chem., Sect. C.* **2003**, *99*, 277–313. (f) Matsuda, K.; Irie, M. *J. Photochem. Photobiol. C: Photochem. Rev.* **2004**, *5*, 169–182. (g) Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85–97. (h) Tian, H.; Wang, S. *Chem. Commun.* **2007**, *8*, 781–792. (i) Yun, C.; You, J.; Kim, J.; Huh, J.; Kim, E. *J. Photochem. Photobiol. C: Photochem Rev.* **2009**, *10*, 111–129. (j) Akita, M. *Organometallics* **2011**, *30*, 43–51.

(4) (a) Peters, M. V.; Stoll, R. S.; Kühn, A.; Hecht, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 5968–5972. (b) Stoll, R. S.; Peters, M. V.; Kühn, A.; Heiles, S.; Goddard, R.; Bühl, M.; Thiele, C. M.; Hecht, S. *J. Am. Chem. Soc.* **2009**, *131*, 357–367. (c) Stoll, R. S.; Hecht, S. *Org. Lett.* **2009**, *11*, 4790–4793. (d) Wei, Y.; Han, S.; Kim, J.; Soh, S.; Grzybowski, B. A. *J. Am. Chem. Soc.* **2010**, *132*, 11018–11020. (e) Ueno, A.; Takahashi, K.; Osa, T. *J. Chem. Soc., Chem. Commun.* **1981**, *3*, 94–96. (f) Cacciapaglia, R.; Di Stefano, S.; Mandolini, L. *J. Am. Chem. Soc.* **2003**, *125*, 2224–2227. (g) Sugimoto, H.; Kimura, T.; Inoue, S. *J. Am. Chem. Soc.* **1999**, *121*, 2325–2326. (h) Lee, W.-S.; Ueno, A. *Macromol. Rapid Commun.* **2001**, *22*, 448–450. (i) Keiper, S.; Vyle, J. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3306–3309.

(5) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.

(6) Neilson, B. M.; Lynch, V. M.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2011**, *50*, 10322–10326.

(7) (a) Yam, V. W.-W.; Lee, J. K.-W.; Ko, C.-C.; Zhu, N. *J. Am. Chem. Soc.* **2009**, *131*, 912–913. (b) Lee, P. H.-M.; Ko, C.-C.; Zhu, N.; Yam, V. W.-W. *J. Am. Chem. Soc.* **2007**, *129*, 6058–6059. (c) Duan, G.; Zhu, N.; Yam, V. W.-W. *Chem.—Eur. J.* **2010**, *16*, 13199–13209. (d) Nakashima, T.; Goto, M.; Kawai, S.; Kawai, T. *J. Am. Chem. Soc.* **2008**, *130*, 14570–14575.

(8) For reviews on NHCs and their coordination chemistry, see: (a) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122–3172. (b) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309. (c) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91. (d) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162–2187. (e) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676. (f) Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940–6952. (g) Tapu, D.; Dixon, D. A.; Roe, C. *Chem. Rev.* **2009**, *109*, 3385–3407.

(9) For reviews on NHC-based organocatalysts, see: (a) Zeitler, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7506–7510. (b) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606–5655. (c) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988–3000. (d) Nair, V.; Vellalath, S.; Babu, B. P. *Chem. Soc. Rev.* **2008**, *37*, 2691–2698. (e) Nair, V.; Menon, R. S.; Biju, A. T.; Sinu, C. R.; Paul, R. R.; Jose, A.; Vellalath, S. *Chem. Soc. Rev.* **2011**, *40*, 5336–5346. (f) Biju, A. T.; Kuhl, N.; Glorius, F. *Acc. Chem. Res.* **2011**, *44*, 1182–1195.

(10) For studies on tuning the electron donating properties of NHCs as a means to influence catalytic reactions, see: (a) Khramov, D. M.; Rosen, E. L.; Er, J. A. V.; Vu, P. D.; Lynch, V. M.; Bielawski, C. W. *Tetrahedron* **2008**, *64*, 6853–6862. (b) Benhamou, L.; Vujkovic, N. V.; César, V.; Gornitzka, H.; Lugan, N.; Lavigne, G. *Organometallics* **2010**, *29*, 2616–2630. (c) Süβner, M.; Plenio, H. *Chem. Commun.* **2005**, *43*, 5417–5419. (d) Sashuk, V.; Peeck, L. H.; Plenio, H. *Chem.—Eur. J.* **2010**, *16*, 3983–3993. (e) Moerdyk, J. P.; Bielawski, C. W. *Organometallics* **2011**, *30*, 2278–2284. (f) Fürstner, A.; Alcarazo, M.; Krause, H.; Lehmann, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 12676–12677. (g) O'Brien, C. J.; Kantchev, E. A. B.; Chass, G. A.; Niloufar, H.; Hopkinson, A. C.; Organ, M. G.; Setiadi, D. H.; Tang, T.; Fan, D. *Tetrahedron* **2005**, *61*, 9723–9735. (h) Balof, S. L.; P'Pool, S. J.; Berger, N. J.; Valente, E. J.; Shiller, A. M.; Schanz, H.-J. *Dalton Trans.* **2008**, *42*, 5791–5799. (i) Balof, S. L.; Yu, B.; Lowe, A. B.; Ling, Y.; Zhang, Y.; Schanz, H.-J. *Eur. J. Inorg. Chem.* **2009**, *13*, 1717–1722. (j) César, V.; Tourneux, J.-C.; Vujkovic, N.; Brousses, R.; Lugan, N.; Lavigne, G. *Chem. Commun.* **2012**, *48*, 2349–2351.

(11) Lemieux, V.; Spantulescu, M. D.; Baldridge, K. K.; Branda, N. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5034–5037.

(12) UV irradiation of the imidazolium iodide **7** resulted in decomposition; as such, the PF$_6$ anion was substituted for the iodide anion.

(13) (a) The conversions of the forward and reverse cyclizations were measured using the molar extinction coefficient for the absorbance of **1c·HPF$_6$** centered at 670 nm (ε = 24684 dm^3 mol^{-1}), as determined from a combination of ^{1}H NMR and UV-vis spectroscopy. (b) A similar procedure was used to determine the interconversion of **1o** and **1c** (**1c**: ε = 9767 dm^3 mol^{-1}).

(14) (a) Nyce, G. W.; Lamboy, J. A.; Connor, E. F.; Waymouth, R. M.; Hedrick, J. L. *Org. Lett.* **2002**, *4*, 3587–3590. (b) Grasa, G. A.; Kissling, R. M.; Nolan., S. P. *Org. Lett.* **2002**, *4*, 3583–3586. (c) Grasa, G. A.; Güveli, T.; Singh, R.; Nolan, S. P. *J. Org. Chem.* **2003**, *68*, 2812–2819. (d) Singh, R.; Kissling, R. M.; Letellier, M.-A.; Nolan., S. P. *J. Org. Chem.* **2004**, *69*, 209–212. (e) Movassaghi, M.; Schmidt, M. A. *Org. Lett.* **2005**, *7*, 2453–2456.

(15) Similar conversions (11–31%) have been observed in analogous NHC-catalyzed transesterifications of vinyl esters, see: Pignataro, L.; Papalia, T.; Slawin, A. M. Z.; Goldup, S. M. *Org. Lett.* **2009**, *11*, 1643–1646.

(16) When a control reaction was performed in the absence of **1o** under ambient light, a background reaction was observed with the KO*t*Bu acting as the catalyst (31% conversion after 1 h). However, when an analogous reaction was exposed to UV light, no significant reduction of catalytic activity was observed (26% conversion after 1 h), indicating that UV irradiation alone did not impede the reaction. Similarly, UV irradiation did not reduce the catalytic activity when 1,3-dimesitylimidazolinylidene (SIMes), an NHC-based organocatalyst which lacks a photochromic moiety, was used in lieu of **1o** (conversion after 1 h: 39% under ambient light; 58% under UV light).

(17) Nolan reported that unsaturated NHCs were more active transesterification catalysts than their saturated analogues; see ref 14c. While no formal change in unsaturation occurs upon conversion of **1o** to **1c**, the disruption of the endocyclic double bond in **1o** upon photocyclization has a similar effect on the nucleophilicity of the NHC, which was reflected by the reduction in reaction rate observed under UV irradiation and in accord with the previous demonstration that the electron donating ability of the NHC was reduced upon photocyclization; see ref 6.

(18) For other examples of light-activated latent catalysts, see: (a) Sun, X.; Gao, J. P.; Wang, Z. Y. *J. Am. Chem. Soc.* **2008**, *130*, 8130−8131. (b) Ben-Asuly, A.; Aharoni, A.; Diesendruck, C. E.; Vidavsky, Y.; Goldberg, I.; Straub, B. F.; Lemcoff, N. G. *Organometallics* **2009**, *28*, 4652−4655. (c) Hafner, A.; Muhlengach, A.; van der Schaaf, P. A. *Angew. Chem., Int. Ed.* **1997**, *36*, 2121−2124. (d) Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 2038−2039. (e) Wang, D.; Wurst, K.; Knolle, W.; Decker, U.; Prager, L.; Naumov, S.; Buchmeiser, M. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 3267−3270.

(19) When a control reaction was performed in the absence of **1o**, a background reaction was observed with NaHMDS acting as the catalyst (44% conversion after 4 h) under ambient light. However, no attenuation of catalytic activity was observed under UV light (53% conversion after 4 h). When imidazolium salts without photochromic moieties, such as 1,3-dimesitylimidazolium chloride or 1,3-dimesitylimidazolinium chloride, were used the precatalyst, no significant conversion to product was observed under ambient light or UV irradiation after 4 h.

(20) Decomposition (29%) of **1c** was observed by UV−vis spectroscopy upon prolonged UV irradiation (>0.5 h, $[\mathbf{1o}]_0 = 4 \times 10^{-5}$ M); see Figure S7.

(21) The observed results were consistent with the formation of an imidazolium alkoxide intermediate, as proposed in a previous report of NHC-catalyzed amidation reactions; see ref 14e.

(22) (a) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546−2558. (b) Csihony, S.; Culkin, D. A.; Sentman, A. C.; Dove, A. P.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 9079−9084.

(23) When a stoichiometric quantity of 2-aminoethanol was added to **1o*** (generated in situ), a signal assigned to the C2 nucleus of the NHC was observed at 165 ppm and in agreement with a proton transfer reaction. Upon UV irradiation, the signal shifted upfield to 102 ppm, which was consistent with the formation of a NHC-alcohol adduct. Visible light irradiation reversed the spectral changes, which suggested to us that the decreased electron density at the C2 position upon photocyclization resulted in the reversible formation of a NHC-alcohol adduct; see the Supporting Information.

(24) UV irradiation of **1o*** was performed in 4 mL of C_6D_6 in a quartz cuvette ($[\mathbf{1o^*}]_0 = 2.5 \times 10^{-3}$ M). Prior to NMR analysis, the solution was concentrated under reduced pressure to a volume of approximately 1 mL ($[\mathbf{1o^*}] = 1.0 \times 10^{-2}$ M). The visible light irradiation was carried out directly on the concentrated sample in the NMR tube.

(25) Using quantitative ^{13}C NMR analysis of **1o*** versus *p*-xylene as an internal standard, a small amount (13%) of the catalyst was observed to decompose to insoluble byproduct(s) after UV irradiation ($[\mathbf{1o^*}]_0 = 2.5 \times 10^{-3}$ M; $\lambda_{irr} = 313$ nm for 1 h) followed by visible irradiation ($\lambda_{irr} > 500$ nm for 2 h) ($[\mathbf{1c^*}] = 1.0 \times 10^{-2}$ M). The decomposition may account for the inability to fully restore the initial reaction rate after irradiation.

(26) During the preparation of this manuscript, an elegant example of photomodulating deuterium exchange reactions using a pyridinium catalyst electronically linked to a DAE scaffold was reported; see: Wilson, D.; Branda, N. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 5431−5434.

■ NOTE ADDED AFTER ASAP PUBLICATION

Part b of Figure 4 was incorrect in the version published ASAP July 19, 2012. The correct Figure 4 reposted July 24, 2012.