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### Azobenzene-Isomerization Induced Photomodulation of Electronic Properties of N-Heterocyclic Carbene

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Azobenzene-based N-heterocyclic carbenes (NHCs), N.N'-Abstract: protonated bis(azobenzene)imidazolium chlorides (IAz-X.HCl; X = OMe, Br, H) were successfully synthesized and switching abilities of the attached azobenzene units along with the concomitant photoinduced generation of geometric isomers were studied. Upon irradiation with 365 nm UV light, a p-methoxy-azobenzene derivative get transformed from all-trans isomer to nearly all-cis isomer at the photostationary state. The extent of photomodulation of electronic properties in the NHC's-ring of the p-methoxy-azobenzene derivative is determined via Tolman Electronic Parameter (TEP). Iridium complex, [(IAz-OMe)IrCl(CO)<sub>2</sub>] was synthesized and infrared spectra were recorded in dichloromethane solution via making film into NaCl crystals and by drop casting in an ATR crystal. Comparison in averaged carbonyl stretching frequency between all-trans isomer  $(\tilde{v}_{av}^{tt})$  and all-*cis* isomer  $(\tilde{v}_{av}^{cc})$  indicates a significant decrement of  $\Delta^{tt-cc}\tilde{v}_{av} = 2.7 \text{ cm}^{-1}$  (film) and 3.8 cm<sup>-1</sup> (ATR). Therefore, moderate to excellent enhancement of electron density ( $\Delta^{tt-cc}$  TEP = 2.3 cm<sup>-1</sup> <sup>1</sup> [film] and 3.2 cm<sup>-1</sup> [ATR]) at the C-2 position of the NHC is achieved via trans  $\rightarrow cis$ isomerization of the remotely placed azobenzene units. This fine phototuning of electron donating ability at the catalytic centre would pave the way to control NHC/NHC-metal catalyzed organic transformations via external stimuli.

Taking control over organic transformations via external non-invasive stimuli, such as light minimizes the need of synthesizing differentially substituted catalysts having varied electronic and /or steric properties. Alteration of the intrinsic properties of a catalyst to tune its reactivity is thus of huge interest among scientists, especially those who are working in the field of artificial switchable catalysis.<sup>1</sup> As early as in the seventies, light-controlled catalysis using photoswitchable enzymes drew attention to a range of research groups.<sup>2</sup> Inspired by photocontrolled enzymatic activity, Ueno and Osa developed azobenzene capped  $\beta$ -cyclodextrin to regulate the hydrolysis of *p*-nitrophenyl acetate.<sup>3</sup> Whereas, Hecht's group<sup>4</sup> have achieved a remote photocontrol over piperidine's basicity through brilliant incorporation of bulky azobenzene moiety into its structure. Cacciapaglia's group<sup>5</sup> described a phototunable bis-barium complex of azobis(benzo-18-crown-6), that controls the rate of ethanolysis of anilides. Of late, trans-form of an azobenzene-based thiourea was shown by Pericàs et al. as an efficient catalyst over the cis-form in Michael addition of acetylactone to mbromonitrostyrene.<sup>6</sup> On the other hand, photoswitchable catalysis using metal nanoparticlesmodified with photochromic organic ligands, such as azobenzenes have also been explored.<sup>7</sup> However, all the above discussed modification in catalytic activities was achieved mostly via steric, geometric or polarity changes and not via electronic changes between the isomeric states of the azobenzenes.

N-heterocyclic carbenes (NHCs) are electron-rich, neutral  $\sigma$ -donor ligands, which along with their transition metal complexes have been studied by many research groups worldwide due to their enormous utilities. Pioneering work by Öfele,<sup>8</sup> Wanzlick<sup>9</sup> and Arduengo<sup>10</sup> (first stable and isolable NHC) have promoted the chemistry of NHCs to its high and the field no more remains a mere laboratory curiosity. A detail understanding and various aspects of varied kinds of NHCs have been documented in a number of reviews.<sup>11</sup> Catalytic activities of NHCs and their metal complexes are known to be governed by the electron donating abilities of the corresponding NHCs. Alterations in electronic properties of NHCs have been achieved mainly via chemical modifications such as varying the ring substituents and changing the heterocyclic backbone structure. Based on a fixed imidazole-2-ylidenes ring structure, Plenio and co-workers have investigated the alteration in electronic properties of NHCs with varied aryl groups.<sup>12</sup> In these cases, nitrogen (Fig. S1a) of the imidazolium ring were directly modified by attaching aromatic moieties having varied psubstituents. The electron withdrawing substituents, such as -SO<sub>2</sub>Ar were proved to reduce the electron donating capacity of the NHCs whereas, the electron donating groups (e.g. -NEt<sub>2</sub>) have been shown to significantly enhance the electron donating properties of the NHCs. However, photomodulation of electronic properties of NHCs were first reported by Bielawski and coworkers.<sup>13</sup> Here, the backbone of NHC precursors were modified with diarylethene (DAE) moiety in such a way that the double bond between  $C^4$ - $C^5$  carbon of NHCs become saturated (ring-closed form) upon photoinduced ( $\lambda = 315$  nm) electrocyclization reactions (Fig. S1b). In a report by Monkowius,<sup>14</sup> azobenzene functionality was unsymmetrically tagged to imidazolium ring to make azobenzene-containing (NHC)AuCl complexes, however, they have not described any study on electronic photomodulation. Hence, there is still an urgency to discover novel photoswitchable organocatalysts that would alter their electronic distribution over the catalytic site via external stimuli such as light. To the best of our knowledge, successful utilization of azobenzene molecular switches to alter electronic environment on the active site of a catalyst is rare.

Towards these objectives, a novel family of photoswitchable-NHC precursors, N,N'bis(azobenzene)imidazolium chlorides (IAz-X.HCl-**3a-c**, Scheme 1) were synthesized, where the substituted azobenzene-derivatives are symmetrically bonded to both the nitrogen of the protonated N-heterocyclic carbenes. A series of conventional synthetic procedures were modified and utilized to produce our desired products, IAz-OMe.HCl (**3a**), IAz-Br.HCl (**3b**) and IAz-H.HCl (**3c**) in moderate to good isolated yields (SI-3).



X = -OMe, 3a; -Br, 3b; -H, 3c

Scheme 1. Synthesis of N,N'-bis(azobenzene)imidazolium chlorides (IAz-X.HCl-3a-c).

The methoxy derivative, IAz-OMe.HCl-3a was first utilized to study the photoswitching ability of the attached azobenzene units with light irradiations (Fig. 1a-e). A solution of 3a in DMSO absorbs at  $\lambda_{max} \sim 360$  nm (Fig. 1b), which is the characteristic absorption band due to  $\pi \rightarrow \infty$  $\pi^*$  transition of *trans*-azobenzene units (<sup>trans</sup>Az-OMe) that are attached to the imidazolium moieties. UV-visible spectroscopic studies with varied concentration of 3a provides molar absorptivity of transAz-OMe at  $\lambda = 360$  nm is  $\varepsilon \sim 28400$  L mol<sup>-1</sup> cm<sup>-1</sup> (Fig. S2a-b, e). A series of UV-visible absorption spectra were then recorded after sequential irradiations of a  $2.5 \times 10^{-5}$  M solution of **3a** in DMSO with 365 nm UV light (I ~  $1.2 \text{ mW cm}^{-2}$ , Fig. 1b). It is evidenced from the spectral profile that 80 s of UV exposure is sufficient to reach to the photostationary state (PSS under UV), where absorption at ~360 nm nearly vanishes due to successful trans  $\rightarrow$  cis isomerization. And a new comparatively weaker  $\pi \to \pi^*$  absorption band of the corresponding *cis*-isomers centred at  $\lambda_{max}$ ~310 nm (<sup>*cis*</sup>Az-OMe;  $\varepsilon$  ~ 7600 L mol<sup>-1</sup> cm<sup>-1</sup>; Fig. S2c-e) arises along with another absorption band  $(n \rightarrow \pi^* \text{ transition of } c^{is}\text{Az-OMe units})$  in the visible region at  $\lambda_{max} \sim 440 \text{ nm}$  ( $\epsilon \sim 1700 \text{ L mol}^{-1} \text{ cm}^{-1}$ ; Fig. S2c-e). Upon sequential irradiation with blue light (Fig. 1c), the solution of 3a under PSS @ UV gradually transforms from cis- to the trans-isomers and finally a steady state is reached after 10 seconds of blue light exposure (PSS under blue light). However, a complete back isomerization to the *trans*-isomers requires further ~5 minutes of warming at around 110 °C. Noteworthy, the thermal stability of cis-isomers (cisAz-OMe in 3a) is found to be excellent at dark and the half-life is calculated to be ~18 h in DMSO at 26  $^{0}$ C (Fig. 1d and Fig. S3). The photoswitches were then tested for their recyclability as depicted in Fig. 1e. Greatly, the solution containing **3a** is highly photostable and fully reversible: even after 50 repeated cycles of exposures, where each cycle consists of 80 s UV followed by 20 s blue light irradiations, the system does not show any detectable fatigue. Effective photoswitchablity of **3a** were also observed in a variety of other solvents, including polar protic solvents like, water, methanol, ethanol, isopropanol (Fig. S4a-d), and aprotic solvents such as acetonitrile, tetrahydrofuran, chloroform and dichloromethane (Fig. S4e-h). Similarly, a detail UV-visible spectroscopic studies (SI-1, Fig. S5-10) of *trans*  $\leftrightarrow$  *cis* isomerization of azobenzene units in IAz-Br.HCl-**3b** and IAz-H.HCl-**3c** were also performed.



**Figure 1.** (a) Isomerization of azobenzene units (Az-X) in 3. UV-visible spectra representing *trans*  $\leftrightarrow$  *cis* isomerization of Az-OMe in **3a** upon UV (b) and blue light irradiation (c). (d) Thermal stability (room temperature) of photoisomerized-**3a** (*cis*Az-OMe) at dark. (e) Recyclability between *trans*Az-OMe  $\leftrightarrow$  *cis*Az-OMe. [**3a**] = 2.5 × 10<sup>-5</sup> M in DMSO.

Photoinduced generation of geometric isomers and concomitant photomodulation over imidazolium moieties in N,N'-bis(azobenzene)imidazolium chloride-**3a-c** were then studied via <sup>1</sup>H-NMR spectroscopy. Nuclear magnetic resonance (NMR) spectra of **3a-c** (Fig. S270-t) show us the presence of single isomeric form in each salt under ambient conditions. And UV-visible spectroscopic studies also confirms the presence of *trans*-isomers in the solution. Thus the thermodynamically stable forms of imidazolium chlorides-**3** are denoted as, **3**<sup>trans-trans</sup> (Scheme 2). Photoisomerization of **3** would generate a total of three geometric isomers, **3**<sup>trans-trans</sup>, **3**<sup>trans-cis</sup> and **3**<sup>cis-cis</sup>. Figure 2a describes partial <sup>1</sup>H-NMR spectra of **3a**<sup>trans-trans</sup> in DMSO-d<sub>6</sub> (7.4 × 10<sup>-3</sup> M); showing important regions, where protons attached to the imidazolium ring (<sup>2</sup>C-H and <sup>4</sup>C/<sup>5</sup>C-H) and



Scheme 2. Photoisomerization of azobenzenes in IAz-X.HCl-3a-c (3<sup>trans-trans</sup>) to produce 3<sup>trans-cis</sup> and 3<sup>cis-cis</sup> isomers.

the azobenzene moieties resonate in a 500 MHz instrument. Aromatic protons of thermodynamically stable *trans*-azobenzenes (*trans*Az-OMe) are shown at the right panel (Fig. 2a, right panel), whereas, the corresponding imidazolium ring protons, denoted as  ${}^{2}C-H^{tt}$  and  ${}^{4}C/{}^{5}C-H^{tt}$ are shown in the left and the middle panel of Fig. 2a respectively. Upon sequential UV-irradiations (Fig. 2b-d), evolution of peaks due to *cis*-azobenzenes (<sup>*cis*</sup>Az-OMe) appear gradually and proton peaks due to the *trans*Az-OMe started reducing accordingly. And after 2 h exposure with UV light the photostationary state is reached where peaks due to the *trans*-azobenzenes nearly disappear. Integration of azobenzenes protons at PSS under UV provide ~96% cis-isomers (Fig. 2d, Fig S12). As seen from the spectra that upon *trans*  $\rightarrow$  *cis* isomerization, the intensity of proton resonance peak at 9.85 ppm ( $^{2}C-H^{tt}$ ) gets reduced and a couple of new peaks arises at 9.76 and 9.67 ppm. And overall integration of the three mentioned peaks count a single proton. We assign these peaks at 9.76 ppm as <sup>2</sup>C-H<sup>tc</sup> (3a<sup>trans-cis</sup>) and at 9.67 ppm as <sup>2</sup>C-H<sup>cc</sup> (3a<sup>cis-cis</sup>). Concomitantly, other imidazolium ring protons (<sup>4</sup>C/<sup>5</sup>C-H) also get shifted from 8.44 ppm (<sup>4</sup>C/<sup>5</sup>C-H<sup>tt</sup>) to 8.38, 8.35 ppm for  ${}^{4}C/{}^{5}C-H^{tc}$  and 8.29 ppm for  ${}^{4}C/{}^{5}C-H^{cc}$ . Noteworthy, the **3a**<sup>trans-trans</sup> isomer is fully absent (no indication of  ${}^{2}C-H^{tt}$  peak) at the photostationary state and the ratio of  $3a^{trans-cis}$  and  $3a^{cis-cis}$  is about 8:92 (Fig. S12). Therefore, 2 h of UV-irradiations transforms **3a**<sup>trans-trans</sup> isomers to nearly **3a**<sup>cis-cis</sup> isomers even at the concentration as high as  $\sim 10^{-2}$  M in DMSO. NMR study on the back isomerization reactions reveals a complete back reaction after irradiation of the  $3a^{cis-cis}$  with 30 minutes of blue light followed by 1 h of warming at ~110 °C (Fig. 2e and 2f, respectively). However, blue light irradiations generates another photostationary state with overall 72% transisomers and the relative ratio of the three geometrical isomers of 3a is  $3a^{trans-trans}: 3a^{trans-cis}: 3a^{cis-cis} =$ 52:40:8 (Fig. S13). In contrast, a detail <sup>1</sup>H-NMR spectroscopic studies (SI-2, Fig. S14-20) of IAz-Br.HCl-**3b** and IAz-H.HCl-**3c** revealed that *trans*  $\rightarrow$  *cis* isomerization in both the imidazolium salts remains incomplete (61% cisAz-Br and 49% cisAz-H at the PSS under UV).



**Figure 2.** Partial <sup>1</sup>H-NMR (500 MHz, DMSO- $d_6$ ) spectra of IAz-OMe.HCl-**3a:** (a) at ambient conditions, (b-d) after UV irradiations, (e) followed by blue light irradiation and (f) followed by heating. [For the full spectra see Fig. S11].

The extent of *trans*  $\rightarrow$  *cis* isomerization being nearly complete in case of **3a**, we have made use of this imidazolium salt to determine the extent of photoinduced electronic modification on its carbene carbon centre. A recent review by H. V. Huynh<sup>15</sup> on determination of electronic properties of various carbenes revealed that one of the best ways in determining electron densities on the carbene carbon of NHCs is via determining Tolman Electronic Parameter<sup>16</sup> (TEP). Nickel complexes of the type [(NHCs)Ni(CO)<sub>3</sub>] were initially been used for the calculation of TEP via measuring stretching frequencies of the carbonyl (CO) functionality. However, nowadays less toxic complexes cis-[(NHCs)RhCl(CO)<sub>2</sub>] and cis-[(NHCs)IrCl(CO)<sub>2</sub>] are mostly preferred. The averaged CO stretching frequencies ( $\tilde{v}_{av}$ ) of a fixed metal (Rh/Ir) complex could simply be used to determine the changes in electron-donating ability of the NHCs: a smaller averaged wavenumber indicates a stronger net donor. To correlate the TEP values obtained from different complexes a number of mathematical formulae have also been derived.<sup>17</sup> To this end, we have synthesized iridium complexes of imidazolium salt-3a following the modified Herrmann's<sup>18</sup> procedures. Towards this, solid powder of **3a** was added to a suspension of  $[IrCl(cod)]_2$  (cod = cyclooctadiene) and potassium tert-butoxide in dry tetrahydrofuran under inert atmosphere and stirred for about 5 h to yield [(IAz-OMe)IrCl(cod)] (4, Fig. 3a). A solution of 4 in dry dichloromethane was then reacted with excess carbon monoxide gas to produce our desired product, [(IAz-OMe)IrCl(CO)<sub>2</sub>] (5<sup>trans-trans</sup>) - as characterized by <sup>1</sup>H-, <sup>13</sup>C-NMR and high-resolution mass spectra (Fig. S27w, S27x and S28, respectively).



**Figure 3.** (a) Synthesis of iridium complex-**5**,  $[(IAz-OMe)IrCl(CO)_2]$  from **3a**. (b) Isomerization of azobenzene units attached to the iridium complex-**5** in chloroform ([**5**] =  $2.5 \times 10^{-5}$  M). (c) Schematic representation of isomerization of **5** and the corresponding IR spectrum (film) of carbonyl functionalities. (d) Equation for calculating TEP.

Isomerization of the azobenzene units attached to the NHC-iridium-complex (5) was then studied (Fig. 3b-c). According to our expectations, an excellent trans  $\rightarrow$  cis isomerization is accomplished via UV-visible spectroscopy in solvents like chloroform (Fig. 3b) and dichloromethane (Fig. S21). The extent of isomerization is obtained by <sup>1</sup>H-NMR spectroscopy (Fig. S22). It is evidenced from the spectra that the resonance peak due to *ortho*-methyl groups of the azobenzene units remains well resolved among all the three possible geometric isomers. The relative ratio of the three geometric isomers at the PSS under UV is thus calculated to be, 5<sup>trans-trans</sup>:  $5^{trans-cis}$ :  $5^{cis-cis} = 0:12:88$  (trans:cis = 6:94). Infrared spectra were then recorded in dichloromethane to monitor the carbonyl stretching frequencies in those iridium-NHC complexes. To be noted here, the percentage isomerization (*trans*  $\rightarrow$  *cis*) of the azobenzene units in 5 is in fact same in chloroform and dichloromethane (Fig. S21e). To this end, a stock solution of 5 in dichloromethane  $(5 \times 10^{-3} \text{ M})$  was divided into two parts; one part was kept under UV illumination for about 2 h (5<sup>cis-</sup> *cis*) while the other part was kept at dark (5<sup>trans-trans</sup>). Infrared spectra were then recorded individually under a fixed instrumental conditions via making film - by placing dichloromethane solution between two NaCl crystal plates. Carbonyl stretching frequencies of 5<sup>trans-trans</sup> are observed at 2068.5 and 1981.5 cm<sup>-1</sup> (Fig. 3c, left and Fig. S23) with an average,  $\tilde{v}_{av}^{tt}$  (CO) = 2025 cm<sup>-1</sup>. Interestingly, the UV-irradiated sample,  $5^{cis-cis}$  (mixed with ~12%  $5^{trans-cis}$ ) provides carbonyl stretching frequencies at 2064.7 and 1979.8 cm<sup>-1</sup> (Fig. 3c, right and Fig. S24) with an average value of  $\tilde{v}_{av}^{cc}$  (CO) = 2022.3 cm<sup>-1</sup>. Therefore, the reduction in averaged frequency is  $\Delta^{tt-cc}\tilde{v}_{av}$  (CO) = 2.7  $cm^{-1}$ , which indicates moderate to high enhancement of net-electron donating ability of NHC in 5<sup>cis-</sup> cis as compared to  $\mathbf{5}^{trans-trans}$ . UV-induced alteration in electron donating properties of the carbene

carbon of the corresponding imidazolium salt-**3a** is then obtained via calculating TEP values using the equation (Fig. 3d) by Nolan,<sup>19</sup> one of the pioneers in this field. TEP values of **5**<sup>trans-trans</sup> is calculated to be 2052.4 cm<sup>-1</sup> whereas the same for the **5**<sup>cis-cis</sup> is 2050.1 cm<sup>-1</sup>; which account as high as 2.3 cm<sup>-1</sup> reduction in TEP values ( $\Delta^{tt-cc}$ TEP = 2.3 cm<sup>-1</sup>) simply via *trans*  $\rightarrow$  *cis* isomerization of the attached azobenzene (Az-OMe) units to the NHC ring.

In order to reconfirm the alteration of TEP values, IR spectra using ATR technology were also recorded. Sample preparation was kept constant in dichloromethane as mentioned above. A droplet of solution (~10 µL) of complex-5 was placed at the ATR crystal and scanned till solvent gets evaporated (~20 scans). Sharp peaks of CO functionality were recorded in both the geometric isomers of the complex. Whereas,  $5^{trans-trans}$  shows peaks at 2066.5 and 1975.7 cm<sup>-1</sup> (Fig. S25,  $\tilde{v}_{av}^{tr}$ (CO) = 2021.1 cm<sup>-1</sup> and TEP<sup>tt</sup> = 2049.1), peaks in  $5^{cis-cis}$  (mixed with ~12%  $5^{trans-cis}$ ) appears at 2059.3 and 1975.2 cm<sup>-1</sup> (Fig. S26,  $\tilde{v}_{av}^{cc}$  (CO) = 2017.3 cm<sup>-1</sup> and TEP<sup>cc</sup> = 2045.9). Therefore, the extent of alteration in the averaged carbonyl frequency upon trans  $\rightarrow cis$  isomerization in ATR technology is as high as,  $\Delta^{tt-cc} \tilde{v}_{av}$  (CO) = 3.8 cm<sup>-1</sup> and the corresponding decrement in TEP is  $\Delta^{tt-cc}$  $^{cc}$ TEP = 3.2 cm<sup>-1</sup>. We have then compared this extent of photomodulation with the extent of chemically modified derivatives of similar heterocyclic ring system. Metal complexes of NHCs having a fixed imidazolin-2-ylidene ring that differs in N-alkyl substituents, such as tert-butyl, isopropyl, cyclohexyl and cyclododecane, apparently have no difference in their averaged CO stretching frequencies.<sup>15</sup> However, NHCs, that differs in N-aryl substituents, such as [N,N'bis(aryl)imidazole]-2-ylidene (varied para-substituted aryl group, Fig. S1a) have dissimilar electron donating capacity. The most electron-rich NHC in the mentioned N-aryl series ( $R = -NEt_2$ , Fig. S1a) was reported to have  $\tilde{v}_{av}$  (CO) of the corresponding iridium complex that is diminished by 2 cm<sup>-1</sup> as compared to one of the most common and conventional mesityl derivative (R= Me, Fig. S1a).<sup>12</sup> Therefore, the most popular and verified TEP based methodology to quantify electronic properties of NHCs unambiguously proves that our azobenzene-based NHC and its metal complex have the potentiality to alter reaction kinetics via remote photomodulation. Secondly, this proof-ofconcept could be exploited to procure even better alteration in electronic properties by varying the attached azobenzene derivatives in our novel class of photoswitchable-NHC. Nonetheless, the switching of photoinduced steric influences to the metal center (percent volume buried;  $%V_{bur}$ ) could be an interesting additional investigation to better understand the overall alteration of the stereoelectronic effect on these NHCs.

In summary, fine tuning of intrinsic electron-donating properties of a novel class of azobenzene-based photoswitchable-NHC is achieved via external stimuli. Towards this, three derivatives of N,N'-bis(azobenzene)imidazolium chlorides were synthesized, where azobenzene-derivatives differ at the 4'-substitutions. *Trans*  $\rightarrow$  *cis* isomerization of the N-attached azobenzenes were studied via UV-visible spectroscopy as well as <sup>1</sup>H-NMR spectroscopy. Successful synthesis of the iridium complex ([(IAz-OMe)IrCl(CO)<sub>2</sub>]) provided us the percentage isomerization of the attached azobenzenes in the complex at the photostationary state under UV (94% *cis*) is virtually same as that of the NHC salt. Electron-donating ability of the photoswitchable-NHC before and after UV irradiation is measured via averaged carbonyl stretching frequency ( $\tilde{v}_{av}$  (CO)) and is expressed in terms of TEP values. Upon isomerization,  $\tilde{v}_{av}$  (CO) get diminished by at least 2.7 cm<sup>-1</sup> (3.8 cm<sup>-1</sup> in ATR technology) in dichloromethane, which accounts for the reduction in TEP values

of  $\Delta^{tt-cc}\text{TEP} = 2.3 \text{ cm}^{-1}$  or more (3.2 cm<sup>-1</sup> in ATR technology). Therefore, *trans*  $\rightarrow$  *cis* isomerization of the azobenzene units significantly enhances the electron donating ability of our novel azobenzene-based NHC. Utilization of such phototuning of electron density at the active site of a catalyst to alter reaction kinetics of organic transformations is currently under progress.

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#### Table of Contents:



**Photoswitches:** The photoinduced *trans*  $\rightarrow$  *cis* isomerization can alter the electron-donating abilities of azobenzene-based N-heterocyclic carbene. Appropriate iridium-complex (see figure) was synthesized and utilized to calculate Tolman Electronic Parameter (TEP) to provide the extent of alteration.