Photoswitches

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Photoswitchable N-Heterocyclic Carbenes: Using Light to Modulate Electron-Donating Properties**

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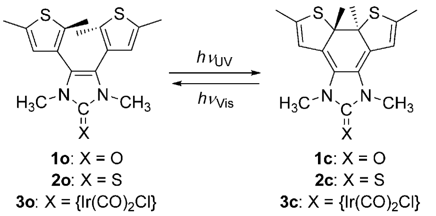
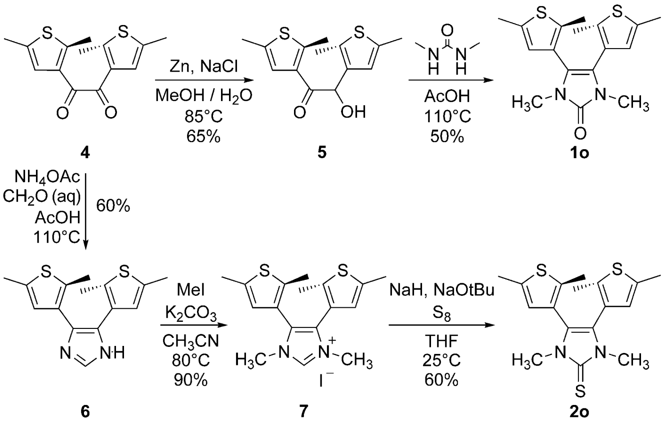
N-heterocyclic carbenes (NHCs) are a robust and well-studied class of ligands used to support a broad range of catalytically active transition metals.[1] The performance of these catalysts is strongly dependent on the electron-donating properties of the NHC ligands,[2] and an ability to modulate these properties using external stimuli should give access to switchable catalysts with controlled activities and selectivities.[3] We envisioned incorporating a photochromic[4] diarylethene (DAE)[5] into the backbone of a NHC scaffold[6] to facilitate the remote photomodulation and monitoring of the carbene's donating ability. For example, as illustrated in Scheme 1, the bonding pattern of an imidazol-2-ylidene scaffold properly outfitted with thiophene units at the 4- and 5-positions should change upon photoinduced electrocyclic ring closure. Considering that the product of this reaction extends the conjugation of the nitrogen atoms adjoining the carbenoid nucleus,[7] less electron density should be available for donation into the π* orbital of the C=X moiety and thus result in a stronger bond.[8] While photocyclization phenomena have been widely exploited in molecular switches[5] and modulating chemical reactivity,[9] they have rarely been used to control the electron-donating ability of ligands.[10] Herein we report the first example of photochemically tuning the electronic structure and donating properties of a photochromic NHC scaffold embedded within chalcogen (X = O, S) and metal (X = {Ir(CO)$_2$Cl}) adducts.



Scheme 1. Photochromism of various NHC adducts. The notation **o** and **c** refers to the ring-opened and -closed isomers, respectively.

The 4,5-diarylimidazolones[11] **1** and **2** were prepared as shown in Scheme 2. Acylation of commercially available 2,5-dimethylthiophene with aluminum trichloride and oxalyl chloride in the presence of pyridine afforded diketone **4**,[12] which was reduced to the α-hydroxy ketone **5** using zinc metal and sodium chloride in refluxing methanol/water (1:1 v/v).[13] Subsequent condensation of **5** with 1,3-dimethylurea in refluxing acetic acid afforded **1o**. Thiourea **2o** was also prepared from **4**, which underwent formylative cyclization under aqueous acidic conditions to give imidazole **6**.[8] Subsequent methylation with iodomethane in acetonitrile using potassium carbonate as a base gave known[6] imidazolium salt **7**, which was then deprotonated with sodium hydride and catalytic sodium *tert*-butoxide in the presence of elemental sulfur to yield **2o**.[14] Notably, the syntheses of **1** and **2** avoided the use of metal-catalyzed aryl–aryl cross-coupling reactions that are commonly used to prepare photochromic DAEs.[5,6,9]



Scheme 2. Synthesis of urea **1o** and thiourea **2o**.

The UV/Vis spectra of **1o** and **2o** in acetonitrile exhibited intense absorptions between 210 and 300 nm, which were assigned to the n→π* and π→π* transitions of the N-heterocycle and thiophene systems, respectively.[6] UV irradiation ($\lambda_{irr} = 280$ nm) of a colorless solution of **1o** in acetonitrile resulted in the development of a bright orange color, concomitant with a decrease in the intensity of the absorption band centered at 214 nm and the appearance of a new band at 476 nm (Figure 1). Similarly, irradiation of **2o** under the same conditions resulted in the appearance of a new absorption band at 521 nm and the development of a red

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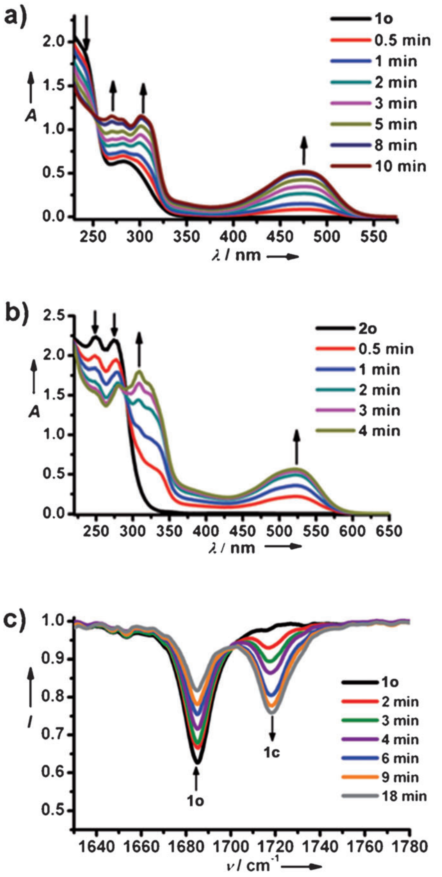


Figure 1. a) UV/Vis spectral changes of **1o** in acetonitrile ($[\mathbf{1o}]_0 = 10^{-4}$ M) upon UV irradiation ($\lambda_{irr} = 280$ nm). The spectra were recorded after irradiation for 0, 0.5, 1, 2, 3, 5, 8, and 10 min. b) UV/Vis spectral changes of **2o** in acetonitrile ($[\mathbf{2o}]_0 = 10^{-4}$ M) upon UV irradiation ($\lambda_{irr} = 280$ nm). The spectra were recorded after irradiation for 0, 0.5, 1, 2, 3, and 4 min. c) Normalized infrared spectral changes of the carbonyl stretching frequency upon photochemical conversion of **1o** (1688 cm^{-1}) to **1c** (1716 cm^{-1}) in acetonitrile ($[\mathbf{1o}]_0 = 10^{-2}$ M). The reaction was facilitated by 280 nm light in a CaF$_2$ IR solution cell, and the spectra were recorded after 0, 2, 3, 4, 5, 6, 7, 9, and 18 min of irradiation. The arrows indicate the evolution of the spectral changes over time.

color. Collectively, these spectral changes were consistent with the disruption of aromaticity in the thiophene rings in the aforementioned substrates and the formation of an extended π-conjugated system.[5,6] Moreover, the isosbestic points observed at 255 nm for **1o** and at 289 nm for **2o** suggested to us that the cyclization reactions proceeded without noticeable side reactions. Compounds **1o** and **2o** reached their photostationary states after 10 and 4 min of irradiation and were comprised of 75 % **1c** and 74 % **2c**, respectively.[15] Subsequent irradiation of these solutions with visible light ($\lambda_{irr} > 500$ nm) resulted in decoloration and attenuation of the broad, low energy absorption bands. The initial UV/Vis spectra were nearly completely restored (> 90 % conversion), indicating that the closed isomers returned to their ring-opened precursors with minimal decomposition.[16] Additionally, the cyclizations were confirmed by ^{1}H NMR spectroscopic analysis of the mixtures, which showed the expected upfield shifts of the signals assigned to the thiophenes (i.e., from $\delta = 6.4$ ppm in **1o** to 5.9 ppm in **1c**, and from $\delta = 6.6$ ppm in **2o** to 6.2 ppm in **2c**; CDCl$_3$).

Once the expected photochemical processes were confirmed, the effect of the cyclization reaction on the C$_{\text{carbenoid}}$=X bonds in **1o** and **2o** was investigated with IR spectroscopy (Figure 1). Prior to the irradiation of **1o**, a signal was observed at 1688 cm^{-1} and was assigned to the urea C=O stretching frequency (ν_{CO}). Upon irradiation at 280 nm, a new band appeared at 1716 cm^{-1}, which was attributed to the ν_{CO} of **1c**. The 28 cm^{-1} shift to higher frequency reflected a significant difference in the electronic character of the two isomers.[17] While the thiophene rings in **1o** are electronically isolated, photocyclization enabled delocalization of the nitrogen lone pairs into the dihydrothiophene π-systems of **1c** and afforded a stronger C=O bond. Due to vibrational coupling effects,[18] only a small difference in the thiourea C=S stretching frequency (< 2 cm^{-1}) was observed when the IR spectra of **2o** and **2c** were compared.

In addition to demonstrating a photoinduced redistribution of electron density in the imidazolone ring of **1o** in situ, we also isolated and characterized the photocyclized product **1c**. After UV irradiation ($\lambda_{irr} = 280$ nm) in acetonitrile, the photocyclized urea **1c** was separated from its mixture with **1o** by column chromatography and isolated in 62 % yield. The UV/Vis, ^{1}H NMR, and IR spectra of this compound were in good agreement with the in situ experiments described above. Moreover, the ^{13}C NMR spectrum of **1c** featured a signal at $\delta = 67.8$ ppm (CDCl$_3$), which was assigned to the sp^3 carbon nuclei adjacent to the sulfur atoms in the dihydrothiophene moieties. Upon isolation and storage in the dark, **1c** was found to be stable in the solid state and in solutions of chloroform, toluene, and hexanes at room temperature for > 24 h, or for weeks at −20 °C (< 5 % decomposition was observed by ^{1}H NMR spectroscopy). In acetonitrile, **1c** cleanly reverted back to **1o** upon exposure to visible light ($\lambda_{irr} > 500$ nm) for 3 min, or upon standing in ambient light for 3 h.[19]

The structures of **1o** as well as **1c** were also confirmed by single crystal X-ray diffraction analysis.[20] The solid state structure of **1c** is to the best of our knowledge the first example of an isolated, photocyclized DAE containing a heterocyclic linker. As shown in Figure 2, the changes in bond lengths and angles from **1o** to **1c** were consistent with the aforementioned photocyclization reaction. For example, the C_2-symmetric thiophene rings in **1o** were twisted with respect to the imidazolone ring and featured an interplanar torsion angle of 57.3(3)°. In contrast, due to the formation of a bond between C6 and C7, the dihydrothiophene rings in **1c** were significantly more planar with respect to the imidazolone ring and featured an interplanar torsion angle of 16.40(12)°. The C6–C7 distance in **1c** (1.53(2) Å) was consistent with that of a C−C single bond, whereas the analogous distance in **1o** was significantly longer (3.23 Å). Additionally, the hybridization state of C7 changed from sp^2 in **1o** to sp^3 in **1c**, as evidenced by the sum of the bond angles around this atom (**1o**: 360°, **1c**: 324°[21]). As expected for a photochemical electrocyclic ring closure of a 1,3,5-hexatriene,[22] the C14 and C15 methyl groups in **1c** adopted a *trans* configuration.[23] Finally, the

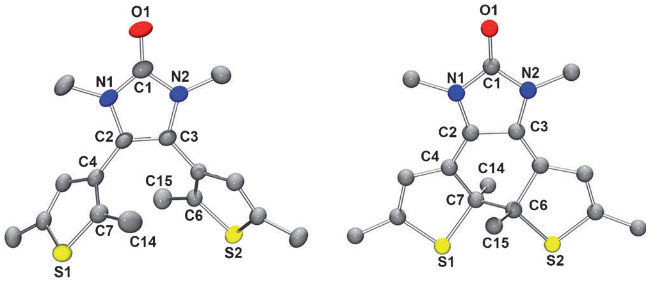
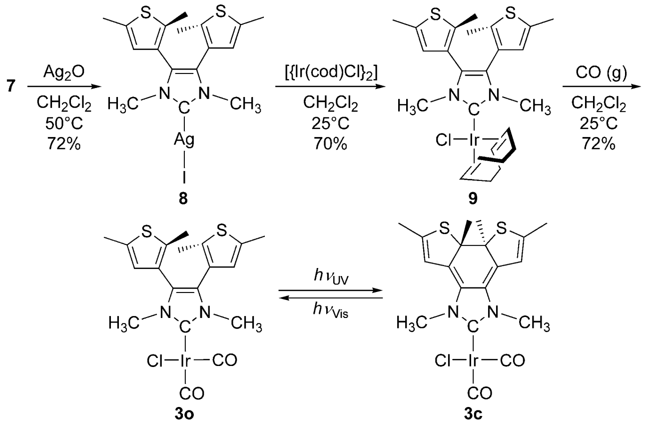


Figure 2. POV-ray representations of urea **1o** (left) and its cyclized derivative **1c** (right) showing ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Key distances [Å], angles [°], and torsions [°] with errors expressed in parentheses: **1o**: N1–C1 1.379(3), N2–C1 1.363(3), C1–O1 1.233(2), N1–C2 1.402(2), C2–C4 1.466(3), C4–C7 1.367(3), C2–C3 1.361(3); N1-C1-N2 106.29(16), N1-C2-C4 122.56(17), C3-C2-C4 130.37(17), C4-C7-S1 110.80(15), C14-C7-S1 120.60(16), C3-C2-C4-C7 57.3(3). **1c**: N1–C1 1.386(8), N2–C1 1.377(9), C1–O1 1.228(8), N1–C2 1.395(8), C2–C4 1.356(9), C4–C7 1.556(16), C2–C3 1.439(9), C7–C6 1.53(2); N1-C1-N2 107.4(6), N1-C2-C3 131.6(6), C3-C2-C4 122.4(6), C4-C7-S1 99.4(10), C14-C7-S1 109.7(10), C3-C2-C4-C7 −16.4(12).



Scheme 3. Synthesis and photochromism of complex **3**.

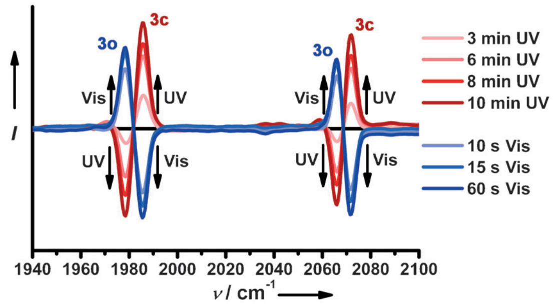


Figure 3. Red: Normalized infrared difference spectra showing the change in the ν_{CO}s upon the photochemical conversion of **3o** (2066 and 1978 cm^{-1}) to **3c** (2072 and 1986 cm^{-1}) in cyclohexane solution ([**3o**]$_0$ = 10^{-2} M). The reaction was promoted by 297 nm light in a quartz cuvette. Aliquots were transferred to a CaF_2 IR solution cell after 0, 3, 6, 8, and 10 min of irradiation, and then analyzed using an IR spectrometer. Blue: Normalized infrared difference spectra showing the change in the ν_{CO}s upon the photochemical reversion of **3c** (2072 and 1986 cm^{-1}) to **3o** (2066 and 1978 cm^{-1}). These spectra were recorded after irradiating a cyclohexane solution of **3o** ([**3o**]$_0$ = 10^{-2} M) at 297 nm for 10 min in a quartz cuvette followed by irradiating the same sample with visible light ($\lambda_{irr} > 500$ nm). Aliquots were removed periodically over time, transferred to a CaF_2 IR solution cell, and then analyzed using an IR spectrometer. The arrows indicate the evolution of the spectral changes over time.

aforementioned increase in ν_{CO} induced by the photocyclization reaction may be further rationalized by comparing the C2–C4 and C2–C3 distances measured in the solid-state structures of **1o** and **1c**. In the latter, each nitrogen atom is formally conjugated to a dihydrothiophene moiety, which effectively attenuates donation into the carbonyl's π*-orbital.[24]

Having demonstrated the ability of the DAE photocyclization to alter the bonding character of a NHC–chalcogen adduct, we sought to alter the ligand donating ability of a photochromic NHC contained within a metal complex. With NHC precursor **7** in hand, the {Ir(cod)Cl} (cod = 1,5-*cis*,*cis*-cyclooctadiene) complex **9** was synthesized through transmetallation from the silver complex **8**,[6] obtained by deprotonating **7** with silver oxide.[25] Bubbling 1 atm of carbon monoxide into a dichloromethane solution of **9** afforded the carbonyl complex **3o**, which was used to evaluate the change in electron-donating ability of NHCs by monitoring the $\Delta\nu_{CO}$ upon irradiation.[26]

UV irradiation ($\lambda_{irr} = 297$ nm) of a cyclohexane[27] solution of **3o** resulted in a decrease in intensity of the high energy absorption centered at 227 nm and the appearance of a new band at 545 nm in the UV/Vis spectrum, consistent with the spectral changes expected for the photocyclization process shown in Scheme 3.[28] The cyclization was confirmed by ^{1}H NMR spectroscopy, wherein a signal was observed at δ = 5.38 ppm (C_6D_6) and attributed to the newly formed dihydrothiophene. Prior to irradiation, the IR spectrum of **3o** exhibited two signals at 2066 and 1978 cm^{-1}, which were assigned to the ν_{CO}s of the carbonyl ligands. Upon irradiation, two new bands appeared at 2072 and 1986 cm^{-1} and were assigned to the ν_{CO}s of **3c**; the formation of these signals was concomitant with a decrease in the intensity of the ν_{CO}s of **3o** (Figure 3). Subsequent irradiation with visible light ($\lambda_{irr} >$ 500 nm) resulted in reversion of **3c** to the starting material **3o**, as evidenced by the disappearance of the peaks at 2072 and 1986 cm^{-1} and an increase in the intensity of the signals previously observed at 2066 and 1978 cm^{-1}.[29] The Tolman electronic parameters (TEPs),[26] as calculated from these IR data,[26a] revealed that the ligand donating ability of the NHC in **3o** (TEP = 2049 cm^{-1}) falls within the range of known NHCs while that of **3c** (2055 cm^{-1}) approaches that of typical phosphines. In other words, the 6 cm^{-1} shift in TEP upon irradiation indicates that the photocyclization of **3o** to **3c** significantly decreases the ability of the NHC to donate electron density to the metal center. Since TEP values have been tied to activities of various catalysts,[2] the ability to photochemically alter a ligand's TEP may now be extended to the photomodulation of catalytic activity.

In conclusion, we report the first example of photochemically switching the electron-donating properties of a NHC by exploiting a photochromic DAE integrated with the backbone of an imidazol-2-ylidene. The chalcogen–NHC adducts

1o and **2o** were found to undergo photoinduced electrocyclic ring closure, as determined by NMR, IR, and UV/Vis spectroscopy, as well as X-ray crystallography for the former. Upon the photocyclization of **1o**, the donation of electron density from the nitrogen atoms to the carbonyl moiety was reduced, as evidenced by an increase in the measured ν_{CO}. Likewise, a significant change in the TEP of the NHC ligand contained within the $\{Ir(CO)_2Cl\}$ complex **3o** was measured upon irradiation. Collectively, these data establish a new approach to remotely changing the donating properties of NHCs and potentially the electronic characteristics of other heteroatomic systems.[30] In a broader perspective, the results described herein are expected to guide the discovery and development of NHC-based catalysts with photoswitchable activities, selectivities, and other functions.

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[1] For reviews on NHCs and their coordination chemistry, see: a) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; b) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; c) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91; d) W. A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256–2282; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187; e) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; f) T. Dröge, F. Glorius, *Angew. Chem.* **2010**, *122*, 7094–7107; *Angew. Chem. Int. Ed.* **2010**, *49*, 6940–6952.

[2] For studies of tuning the electron-donating ability of NHCs as a means to influence catalytic reactions, see: a) D. M. Khramov, E. L. Rosen, J. A. V. Er, P. D. Vu, V. M. Lynch, C. W. Bielawski, *Tetrahedron* **2008**, *64*, 6853–6862; b) M. D. Sanderson, J. W. Kamplain, C. W. Bielawski, *J. Am. Chem. Soc.* **2006**, *128*, 16514–16515; c) D. M. Khramov, V. M. Lynch, C. W. Bielawski, *Organometallics* **2007**, *26*, 6042; d) L. Benhamou, N. Vujkovic, V. César, H. Gornitzka, N. Lugan, G. Lavigne, *Organometallics* **2010**, *29*, 2616–2630; e) M. Süßner, H. Plenio, *Chem. Commun.* **2005**, 5417–5419; f) V. Sashuk, L. H. Peeck, H. Plenio, *Chem. Eur. J.* **2010**, *16*, 3983–3993; g) T. W. Hudnall, J. P. Moerdyk, C. W. Bielawski, *Chem. Commun.* **2010**, *46*, 4288–4290; h) J. P. Moerdyk, C. W. Bielawski, *Organometallics* **2011**, *30*, 2278–2284; i) A. Fürstner, M. Alcarazo, H. Krause, C. W. Lehmann, *J. Am. Chem. Soc.* **2007**, *129*, 12676–12677; j) T. W. Hudnall, A. G. Tennyson, C. W. Bielawksi, *Organometallics* **2010**, *29*, 4569–4578; k) C. J. O'Brien, E. A. B. Kantchev, G. A. Chass, H. Niloufar, A. C. Hopkinson, M. G. Organ, D. H. Setiadi, T. Tang, D. Fan, *Tetrahedron* **2005**, *61*, 9723–9735.

[3] For examples of switchable NHCs and related catalysts, see: a) A. G. Tennyson, V. M. Lynch, C. W. Bielawski, *J. Am. Chem. Soc.* **2010**, *132*, 9420–9429; b) M. Süßner, H. Plenio, *Angew. Chem.* **2005**, *117*, 7045–7048; *Angew. Chem. Int. Ed.* **2005**, *44*, 6885–6888; c) E. L. Rosen, C. D. Varnado, Jr., A. G. Tennyson, D. M. Khramov, J. W. Kamplain, D. H. Sung, P. T. Cresswell, V. M. Lynch, C. W. Bielawski, *Organometallics* **2009**, *28*, 6695–6706; d) L. H. Peeck, S. Leuthäusser, H. Plenio, *Organometallics* **2010**, *29*, 4339–4345; e) S. L. Balof, S. J. P'Pool, N. J. Berger, E. J. Valente, A. M. Shiller, H.-J. Schanz, *Dalton Trans.* **2008**, 5791–5799; f) S. L. Balof, B. Yu, A. B. Lowe, Y. Ling, Y. Zhang, H.-J. Schanz, *Eur. J. Inorg. Chem.* **2009**, 1717–1722; g) S. J. P'Pool, H.-J. Schanz, *J. Am. Chem. Soc.* **2007**, *129*, 14200–14212.

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

[5] a) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716; b) K. Matsuda, M. Irie, *J. Photochem. Photobiol. C* **2004**, 169–182; c) H. Tian, S. Yang, *Chem. Soc. Rev.* **2004**, *33*, 85–97; d) H. Tian, S. Wang, *Chem. Commun.* **2007**, 781–792; e) C. Yun, J. You, J. Kim, J. Huh, E. Kim, *J. Photochem. Photobiol. C* **2009**, *10*, 111–129; f) M. Akita, *Organometallics* **2011**, *30*, 43–51.

[6] For an investigation of the photophysical properties of metal complexes supported by 1,3-dimethyl-4,5-dithienylimidazolylidenes, see: a) V. W.-W. Yam, J. K. Lee, C. Ko, N. Zhu, *J. Am. Chem. Soc.* **2009**, *131*, 912–913; b) P. H.-M. Lee, C.-C. Ko, N. Zhu, V. W.-W. Yam, *J. Am. Chem. Soc.* **2007**, *129*, 6058–6059.

[7] a) A. R. Siamaki, D. A. Black, B. A. Arndtsen, *J. Org. Chem.* **2008**, *73*, 1135–1138.

[8] In support of this hypothesis, ring-opened 4,5-dithienylimidazolium salts were found to be more electrophilic than their ring-closed isomers; see: a) G. Duan, N. Zhu, V. W.-W. Yam, *Chem. Eur. J.* **2010**, *16*, 13199–13209; b) T. Nakashima, M. Goto, S. Kawai, T. Kawai, *J. Am. Chem. Soc.* **2008**, *130*, 14570–14575.

[9] a) Y. Odo, K. Matsuda, M. Irie, *Chem. Eur. J.* **2006**, *12*, 4283–4288; b) V. Lemieux, M. D. Spantulescu, K. K. Baldridge, N. R. Branda, *Angew. Chem.* **2008**, *120*, 5112–5115; *Angew. Chem. Int. Ed.* **2008**, *47*, 5034–5037; c) H. D. Samachetty, N. R. Branda, *Chem. Commun.* **2005**, 2840; d) D. Sud, T. B. Norsten, N. R. Branda, *Angew. Chem.* **2005**, *117*, 2055–2057; *Angew. Chem. Int. Ed.* **2005**, *44*, 2019–2021; e) M. Herder, M. Pätzel, L. Grubert, Hecht, *Chem. Commun.* **2011**, *47*, 460–462; f) S. H. Kawai, S. L. Gilat, J. M. Lehn, *Eur. J. Org. Chem.* **1999**, 2359–2366; g) V. Lemieux, S. Gauthier, N. R. Branda, *Angew. Chem.* **2006**, *118*, 6974–6978; *Angew. Chem. Int. Ed.* **2006**, *45*, 6820–6824; h) D. Sud, T. J. Wigglesworth, N. R. Branda, *Angew. Chem.* **2007**, *119*, 8163–8165; *Angew. Chem. Int. Ed.* **2007**, *46*, 8017–8019; i) H. D. Samachetty, V. Lemieux, N. R. Branda, *Tetrahedron* **2008**, *64*, 8292–8300; j) R. S. Stoll, S. Hecht, *Angew. Chem.* **2010**, *122*, 5176–5200; *Angew. Chem. Int. Ed.* **2010**, *49*, 5054–5075; k) T. Hirose, K. Matsuda, M. Irie, *J. Org. Chem.* **2006**, *71*, 7499–7508; l) T. Hirose, M. Irie, K. Matsuda, *Adv. Mater.* **2008**, *20*, 2137–2141; m) M. Singer, A. Jäschke, *J. Am. Chem. Soc.* **2010**, *132*, 8372–8377.

[10] a) D. Sud, R. McDonald, N. R. Branda, *Inorg. Chem.* **2005**, *44*, 5960–5962; b) Y. Tanaka, A. Inagaki, M. Akita, *Chem. Commun.* **2007**, 1169–1171; c) K. Motoyama, T. Koike, M. Akita, *Chem. Commun.* **2008**, 5812–5814; d) Y. Tanaka, A. Inagaki, T. Koike, C. Lapinte, M. Akita, *Chem. Eur. J.* **2010**, *16*, 4762–4776; e) K. Uchida, A. Inagaki, M. Akita, *Organometallics* **2007**, *26*, 5030–5041.

[11] For other examples of photochromic 4,5-diarylimidazolones, see: M. M. Krayushkin, S. N. Ivanov, A. Y. Martynkin, B. V. Lichitsky, A. A. Dudinov, L. G. Vorontsova, Z. A. Starikova, B. M. Uzhinov, *Russ. Chem. Bull. Int. Ed.* **2002**, *51*, 1731–1736.

[12] L. I. Belen'kii, V. Z. Shirinyan, G. P. Gromova, A. V. Kolotaev, Y. A. Strelenko, S. N. Tandura, A. N. Shumskii, M. M. Krayushkin, *Chem. Heterocycl. Compd.* **2003**, *39*, 1570–1578.

[13] F. Toda, K. Tanaka, H. Tange, *J. Chem. Soc. Perkin Trans. 1* **1989**, 1555–1556.

[14] B. L. Benac, E. M. Burgess, A. J. Arduengo, *Org. Synth.* **1986**, *64*, 92.

[15] The conversion of the photocyclization reaction involving **1** was determined using the molar absorptivities of **1o** and **1c**. The conversion of the reaction involving **2** was determined using the

molar absorptivity of **2c**, as obtained from a combination of quantitative ^{1}H NMR and UV/Vis spectroscopy.

[16] Based on the extinction coefficient for the absorbance measured at 240 nm, $>90\%$ of the mixture returns to **1o**; see Supporting Information.

[17] Urea **1o** exhibited a ν_{CO} typical of amides while that of **1c** was more characteristic of aliphatic ketones; see: E. Pretsch, P. Buhlmann, M. Badertscher, *Structure Determination of Organic Compounds: Tables of Spectral Data*, 4th ed., Springer, Berlin, **2009**, pp. 310–324.

[18] a) C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York, **1963**, pp. 298–303; b) M. Davies, J. Jones, *J. Chem. Soc.* **1958**, 955–958.

[19] See Supporting Information for UV/Vis spectral data for the photocycloreversion of isolated **1c** to **1o**.

[20] See Supporting Information for additional details of the X-ray diffraction analyses. CCDC 821251 (**1o**) and CCDC 821252 (**1c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] The sum of the following angles was calculated to be 324°: C4-C7-C14, C14-C7-S1, C4-C7-S1.

[22] R. B. Woodward, R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, **1970**.

[23] The solid-state structure of **1c** was slightly disordered due to the existence of two enantiomers in the sample, with one having the *S*,*S* configuration at C6 and C7 and the other having the *R*,*R* configuration at the same atoms. See Supporting Information for additional discussion. Similar disorder has been observed in previously reported structures of ring-closed perfluorocyclopentene-based dithienylethenes; see: a) S. Kobatake, M. Yamada, T. Yamada, M. Irie, *J. Am. Chem. Soc.* **1999**, *121*, 8450–8456; b) M. Morimoto, M. Irie, *J. Am. Chem. Soc.* **2010**, *132*, 14172–14178; c) H. Choi, H. Lee, Y. Kang, E. Kim, S.-O. Kang, J. Ko, *J. Org. Chem.* **2005**, *70*, 8291–8297; d) M. Irie, T. Lifka, S. Kobatake, N. Kato, *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876; e) S. Kobatake, K. Shibata, K. Uchida, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 12135–12141; f) M. Irie, S. Kobatake, M. Horichi, *Science* **2001**, *291*, 1769–1772; g) M. Morimoto, S. Kobatake, M. Irie, *Chem. Eur. J.* **2003**, *9*, 621–627; h) M. Morimoto, S. Kobatake, M. Irie, *Photochem. Photobiol. Sci.* **2003**, *2*, 1088–1094; i) T. Kodani, K. Matsuda, T. Yamada, S. Kobatake, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 9631–9637.

[24] Nearly identical percent buried volumes (%V_{bur}) were calculated for **1o** (30.1%) and **1c** (30.2%). The calculations were performed using the web application Sam*V*ca with Bondi radii scaled by 1.17, $R=3.5$ Å for the sphere radius, $d=2.10$ Å for the distance between C1 and O1, and $s=0.05$ Å for the mesh spacing; see: A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* **2009**, 1759–1766.

[25] a) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663–1667; b) H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972–975.

[26] a) R. A. Kelly III, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* **2008**, *27*, 202–210; b) C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.

[27] Decarbonylation was observed by IR spectroscopy when **3o** was irradiated in acetonitrile or dichloromethane; see Supporting Information.

[28] See Supporting Information for the UV/Vis spectral data accompanying the cyclization of **3o** to **3c**.

[29] The conversion of **3o** to **3c** was calculated to be 18% by IR spectroscopy after 10 min of irradiation at 297 nm. After 45 min of irradiation, the conversion was calculated to be 29% by IR spectroscopy (see Supporting Information). These conversions are in accord with other reported photochromic DAE-containing metal complexes; see: a) S. Kume, H. Nishihara, *Dalton Trans.* **2008**, 3260–3271; b) W. Tan, J. Zhou, F. Li, T. Yi, H. Tian, *Chem. Asian J.* **2011**, *6*, 1263–1268; c) Ref. [6a].

[30] The results reported herein demonstrate that the bonding characteristics of carbamides may be modulated using only electronics as opposed to stereoelectronic approaches; see: a) C. Chan, R. Heid, S. Zheng, J. Guo, B. Zhou, T. Furuuchi, S. J. Danishefsky, *J. Am. Chem. Soc.* **2005**, *127*, 4596–4598; b) J. Clayden, W. Moran, *Angew. Chem.* **2006**, *118*, 7276–7278; *Angew. Chem. Int. Ed.* **2006**, *45*, 7118–7120; c) K. Tani, B. M. Stoltz, *Nature* **2006**, *441*, 731–734; d) M. Szostak, L. Yao, V. W. Day, D. R. Powell, J. Aubé, *J. Am. Chem. Soc.* **2010**, *132*, 8836–8837; e) T. W. Hudnall, C. W. Bielawski, *J. Am. Chem. Soc.* **2009**, *131*, 16039–16041.