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Photochromic Diarylethene-Containing Ionic Liquids and N-Heterocyclic Carbenes

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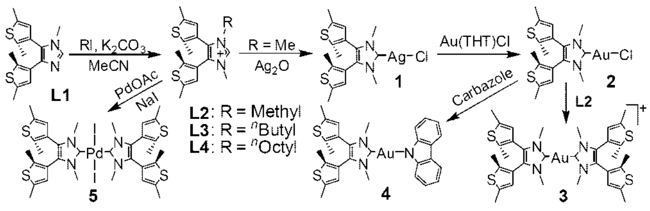
Metal N-heterocyclic carbene (NHC) complexes, in particular the Arduengo-type, have received enormous attention, particularly over the past decade, which mainly originates from the remarkable activity and spectacular achievements of a number of these NHC complexes in catalysis[1] and pharmaceutical applications.[2] This class of complexes can be readily obtained from the ligand precursors, *N*,*N′*-dialkylimidazolium salts, which are also very important in the areas of organic catalysis[3] and green chemistry; the latter of which is based on the ability of some of these salts to behave as room-temperature ionic liquids (RTILs).[4] With our successful demonstration in the design of diarylethene-functionalized ligands for the development of photoswitchable functional molecules,[5] we believe that incorporation of the diarylethene moiety into the core of the imidazolium salt would generate ionic liquids and novel NHC complexes with photoswitchable functional properties, such as switchable catalytic, regio-, or enantioselective activities, as well as physical and optical properties, which could be brought about by the reversible photochromic reactions that gave rise to electronic and conformational/steric changes. The tunability of the photochromic behavior through slight modification of the carbene complexes and N-substituents of the imidazole unit can also be expected. Herein, we report the syntheses, crystal structures, and physical and photochromic properties of a series of diarylethene-containing imidazolium salts and their NHC complexes.

With the utilization of our previously reported methodology using bis-Suzuki cross coupling reaction[5] between 4,5-dibromo-1-methylimidazole and 2,5-dimethyl-3-thienyl boronic acid, followed by subsequent alkylation of **L1** with alkyl iodide in the presence of K_2CO_3, a series of diarylethene-containing imidazolium salts, which is a versatile precursor for NHC complexes, such as those of Au(I), Ag(I) and Pd(II), is obtained (Scheme 1). By increasing the carbon number on the *N*-alkyl chain from **L2** to **L4**, the melting point of the imidazolium PF_6^- salt as determined by DSC was found to decrease (198 °C for **L2**; 175 °C for **L3**; 119 °C for **L4**). The melting point was also found to vary with the anion [**L3**, 175 °C (PF_6^-); 195 °C (BF_4^-); 201 °C (I^-); 197 °C (Br^-); < 20 °C (NTf_2^-)], with [**L3**]NTf_2 behaving as a RTIL. In-situ deprotonation of **L2** with basic Ag_2O afforded the Ag(I) NHC complex **1**. Subsequent transmetalation of **1** gave the NHC derivatives of Au(I) (**2**−**4**) (Scheme 1). Reaction of **L2** with $Pd(OAc)_2$ in the presence of KO^tBu and NaI gave **5**. All the compounds, including the RTIL [**L3**]NTf_2, displayed photochromic behavior.

The structures of **L1**, **L2**, **1**, **2** and **5** have been determined by X-ray crystallography. Except for **L1**, in which the crystal picked for structure determination showed a parallel conformation with the two thiophene rings related by C_s symmetry, the crystal structures of **L2**, **1**, **2** and **5** adopted an antiparallel conformation where the two thiophene rings are C_2-symmetry related.

Scheme 1



Both the imidazole and imidazolium ring adopted a pentagonal planar structure, with bond lengths and angles characteristic of the respective imidazole and imidazolium salts. The planes of the thiophene rings are twisted with respect to the imidazole and imidazolium rings, with interplanar angles of 45.6−56.3° in all the ligands and complexes. In **1** and **2**, the metal centers adopted an essentially linear coordination geometry with C−M−Cl bond angles of 170.96° (M = Ag) and 177.28° (M = Au) and M−C bond distances of 2.09 Å (M = Ag) and 1.99 Å (M = Au), which are comparable to those in the related systems,[6] while the Pd center in **5** adopted a distorted square-planar geometry with unremarkable bond lengths and angles.

L1−**L4** dissolved in MeCN to give colorless solutions with intense absorptions at ca. 230 nm, corresponding to mixture of $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions of imidazole or imidazolium and the thiophene rings. **1**−**3** showed similar absorption bands (Table S1) as their imidazolium salts, ascribed to the metal-perturbed ligand-centered (LC) $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions of the NHC ligands. In addition to this intense absorption, several lower-energy absorptions were also observed in the absorption spectra of **4** and **5**, which are assigned as the metal-perturbed LC transitions of the carbazole ligand and the iodide-to-metal ligand-to-metal charge transfer (LMCT) transitions typical of iodopalladium(II) complexes,[7] respectively.

Upon excitation into the LC transitions in the region of 200−300 nm, all the compounds displayed UV−vis spectral changes (Figure 2, Table S1) with the evolution of two new absorption bands at ca. 320−350 and 520−570 nm (Figure 1). These absorptions were ascribed to the absorptions of the closed form typically observed in diarylethenes upon photocyclization, which gives a more extended π-conjugation.[5,8] A slight red shift in the absorption of the closed forms of the imidazolium salt (~350, 570 nm) and the Ag(I) and Au(I) NHC complexes (~340, 560 nm) has been observed relative to that of imidazole (320, 520 nm). Similar to other compounds with two photochromic diarylethene moieties,[5c,9] the photocyclization of the

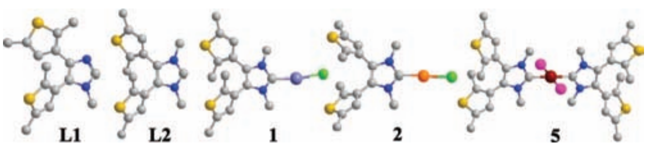


Figure 1. Perspective drawings of **L1**, the cation of **L2**, **1**, **2** and **5**.

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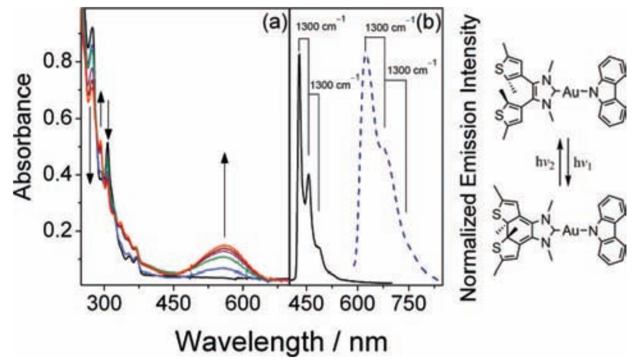

Figure 2. (a) UV−vis spectral changes of **4** in MeCN upon excitation at 285 nm. (b) Normalized emission spectra of the open (—) and closed form (---) of **4** in CH_2Cl_2−EtOH−MeOH (4:2:1 v/v/v) glass at 77 K.

second diarylethene moiety of **3** after ring closure of the first diarylethene moiety was not observed even upon prolonged irradiation, as revealed by well-defined isosbestic points and the close resemblance of the spectral changes with **2** and **4**, attributable to the quenching effect of the first ring-closed moiety. The closed form of **L1** is readily reverted to the open form at 25 °C, while the closed forms of the alkyl imidazolium salts and NHC complexes are much more stable with half-lives of 12−191 min at 25 °C (Table S2). The lower thermal stability of the closed forms of these compounds compared to that of the related perfluorocyclopentene may be attributed to the substantial loss of aromaticity in the imidazole or imidazolium ring upon photocyclization.

As the growth of the low-energy absorption at ca. 560 nm due to the photochromic reaction of **2**−**4** appeared to occur at energies similar to the surface plasmon resonance band of Au nanoparticles or colloids, the possibility of a demetalation or photoreduction process of Au(I) to Au(0) has been eliminated by the observation of reversible photochromic behavior upon alternate irradiation at the UV and visible region, which has also been confirmed by ^{1}H NMR studies. The quantum yields for both the photocyclization and photocycloreversion processes have been determined (Table S3). Except for **L3**, the quantum yields for the photocyclization ($\Phi_{285} = 0.13-0.47$) are much higher compared to that for the photocycloreversion ($\Phi_{510} = 0.006-0.14$). The quantum yields for the photocyclization reactions of the Au(I) NHC complexes were found to be improved when compared to that of **L2** ($\Phi_{285} = 0.21$ for **2**, 0.34 for **3**, and 0.47 for **4** vs 0.19 for **L2**). The higher quantum yields for photocyclization may be ascribed to the coordination of the NHC to the electron-rich d^{10} gold(I) center. An increase in the quantum yield has also been observed with increasing electron-donating ability (carbazolate in **4** > NHC in **3** > Cl in **2**) of the ancillary ligand trans to the NHC ligand. This is probably attributed to the enhanced electron density localized on the photochromic unit of the ligand, as revealed in the ^{1}H NMR signals of the N-Me group, which showed an upfield shift with more electron-rich NHC ligands [δ 3.94 (**2**), δ 3.66 (**3**), δ 3.62 (**4**)]. This trend is also consistent with previous studies on dithienyl-2-arylimidazole,[10] in which the presence of electron-withdrawing substituents on the imidazole unit would lead to a loss in photochromic reactivity.

With the exception of complex **4**, which showed a well-resolved vibronic structured LC emission at 397 nm with vibrational progressional spacings of around 1250−1300 cm^{-1}, typical of the ring breathing mode of the carbazolate ligand, the open form of all compounds in acetonitrile solution were found to be non-emissive at room temperature. On conversion of the open forms of **2**−**4** to their closed forms in the photostationary state, new emission bands were observed at ca. 635−660 nm in acetonitrile at 298 K upon excitation at 540 nm (Table S4). These emissions are tentatively assigned as metal-perturbed IL emissions of the condensed thiophene unit (closed form), probably with some mixing of an IL(carbene) character.

In summary, a series of diarylethene-containing NHC complexes of Au(I), Ag(I) and Pd(II) and their imidazolium salt precursors have been synthesized and their photophysical and photochromic properties studied. The electronic and conformational/steric changes associated with the photochromic reactions may open up new opportunities for the discovery of new classes of photochromic ligands and metal-containing materials and catalysts with photoswitchable functions, activities and regio-/enantioselectivities. Further developments of photochromic ionic liquids as well as imidazolium salts and NHC complexes with photoswitchable catalytic properties are in progress.

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Supporting Information Available: Synthetic procedures, characterization of **L1**−**L4** and complexes **1**−**4**, photophysical data of **1**−**5** and **L1**−**L4**, overlaid DSC heating curves of **L3** with different anions, perspective drawings and crystallographic data of **L1**, **L2**, **1**, **2**, **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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