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Azo-MICs: Redox-Active Mesoionic Carbene Ligands Derived from Azoimidazolium Dyes

F. Mark Chadwick,[a] Basile F. E. Curchod,[b] Rosario Scopelliti,[a] Farzaneh Fadaei Tirani,[a] Euro Solari, and Kay Severin*[a]

Abstract: Azoimidazolium dyes were used as precursors for mesoionic carbene ligands (Azo-MICs). The properties of these ligands were examined by synthesizing Rh^I, Au^I, and Pd^{II} complexes. Experimental (NMR, IR) and theoretical investigations show that Azo-MICs are potent σ-donor ligands. Yet, they feature a small singlet-triplet gap and very low-lying LUMO levels. The unique electronic properties of Azo-MICs allow for reversible one-electron reductions of the metal complexes, as evidenced by cyclic voltammetry.

Mesoionic imidazolylidene and triazolylidene ligands are more electron donating than normal, C2-metallated N-heterocyclic carbene (NHC) ligands.[1] The good donor properties of mesoionic carbenes (MICs) are an attractive feature for applications in transition metal catalysis, and remarkable success has been made in this area.[1a] The superior σ-donor strength can be linked to high-lying HOMO levels. However, the energies of the LUMO levels are also increased, and MICs are less good π-acceptors than normal NHCs.[1a,2]

Similar to mesoionic carbene ligands, cyclic (alkyl)(amino)carbenes (CAACs)[3] feature only one stabilizing nitrogen atom next to the carbene atom. CAACs are also better σ-donor ligands than Arduengo-type NHCs. But in contrast to MICs, CAACs have a small singlet-triplet gap (E_{S-T}) and low-lying LUMO levels. Consequently, they are better π-acceptors.[3,4] The electronic properties of CAACs are crucial for the chemistry of these ligands. For example, CAACs are well suited to form complexes with low-valent metals or main group elements, and they can stabilize radicals.[3,5]

We wanted to explore if it is possible to modify the electronic properties of mesoionic imidazolylidene carbenes in a way that they would become more CAAC-like. In order to do so, one would have to selectively lower the LUMO level and to decrease the singlet-triplet gap without affecting the HOMO level, which is responsible for the good σ-donor properties of mesoionic

carbenes. Calculations have shown that such an electronic tuning is not straightforward. For example, annulated or carbonylated mesoionic carbenes were found to display better π-accepting properties, but these structural modifications went along with a reduced σ-donor strength.[6] Below, we show that the desired changes in electronic structure (small E_{S-T} and low-lying LUMO levels) can be achieved by introducing arylazo substituents in C2 position. The resulting Azo-MICs show a key characteristic of CAACs, namely the possibility to perform ligand-centered reductions.

Azoimidazolium salts are strongly colored compounds, which are produced on an industrial scale (Figure 1).[7] Their primary use is in the dying of fabrics and fibers, including hair. Several methods have been developed to synthesize these compounds, with our group contributing a versatile one-pot synthesis in 2015.[8]
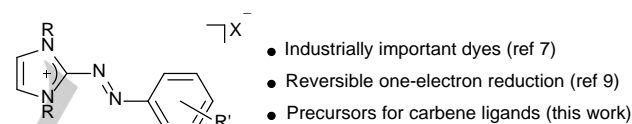
- Industrially important dyes (ref 7)
- Reversible one-electron reduction (ref 9)
- Precursors for carbene ligands (this work)

Figure 1. The general structure of azoimidazolium dyes

Azoimidazolium dyes can be reduced to give stable aminyl radicals.[9] Neutral radicals can also be obtained from imidazolium salts with aryl groups in C2 position, albeit at much more negative redox potentials.[10] Apparently, the presence of an azo-linker at C2 position allows for considerably more facile reduction.

For our studies, we used four different dyes, all of which contain bulky N-aryl substituents attached to the imidazole ring (Scheme 1). Previous investigations had shown that N-aryl groups are crucial for stabilizing the reduced radical form.[9] For comparison, we have also employed an imidazolium salt with a simple phenyl substituent in C2 position.

Deprotonation of the dyes with potassium bis(trimethylsilyl)amide (KHMDS) in THF and subsequent addition of [RhCl(COD)]$_2$ yielded the Rh^I complexes **1a–d** in yields between 40 and 77% (Scheme 1).

The attempted formation of Au^I complexes via an analogous route was not successful. Instead, intractable mixtures of products were obtained, often combined with Au mirrors on the glassware. Therefore, an alternative route was sought. Mixing MeCN solutions of the dyes with Ag$_2$O in the presence of KCl and Cs$_2$CO$_3$ was expected to give intermediate Ag carbene complexes.[1a,11] After transmetalation with AuCl(SMe$_2$), we were

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able to obtain the desired Au complexes **2a–d** in acceptable yields (62–79%). The control complexes **1e** and **2e**, which contain a phenyl substituent instead of an arylazo group, were prepared in similar fashions.

Finally, we prepared two Pd^{II} complexes, **3a** and **3e**, using the same transmetalation strategy used for **2a–e**. As discussed in more detail below, these complexes are particularly useful for determining the electronic properties of the mesoionic carbene ligands.
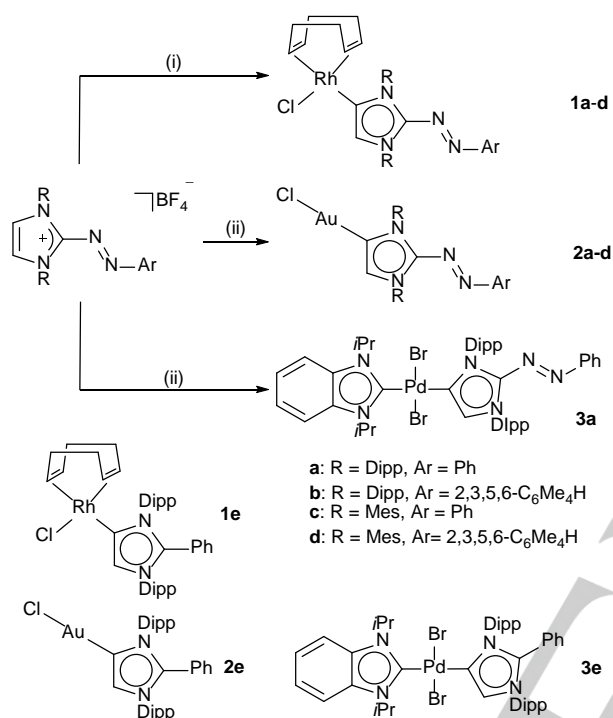
Scheme 1. Synthesis of the Rh^I complexes **1a–e**, the Au^I complexes **2a–e**, and the Pd^{II} complexes **3a** and **3e**. Reagents: (i) KHMDS (1.05 eq.) followed by [RhCl(COD)]$_2$ (0.5 eq.), THF, 25 °C, 16 h; (ii) Ag$_2$O (1.5 eq.), KCl (2 eq.), Cs$_2$CO$_3$ (3 eq.), MeCN, 25 °C, 16 h, followed by AuCl(SMe$_2$) (1 eq.) or [PdBr(μ-Br)(^{i}Pr$_2$-bimy)]$_2$ (0.5 eq.), CH$_2$Cl$_2$, 25 °C, 2 h.

All complexes are soluble in polar organic solvents such as dichloromethane, but they display very low solubility in alkane solvent. The solutions are stable when exposed to both air and water, and the compounds appear fully stable when stored as a solid under a N$_2$ atmosphere.

The new complexes were characterized by NMR spectroscopy, mass spectrometry, cyclic voltammetry, and – in most cases – by single crystal X-ray diffraction.[12] An overview of the structural data is given in the Supplementary Information (SI, Table S2). As representative examples, the solid state structures of the complexes **1a**, **2a**, and **3a** are shown in Figure 2.

There are few structural differences for the three families of compounds (SI, Table S2). As expected, the M-C$_{carbene}$ bond lengths have a small decrease when moving from Rh (Rh-C$_{carbene}$ ~ 2.04 Å) to Au (Au-C$_{carbene}$ ~ 2.00 Å), but altering the substituents on the mesoionic carbene ligand has little effect on these. It is worth noting that the NHC-N=N-aryl groups remain approximately

in the same plane for all but one of the complexes (NHC-aryl canting ranges from 7.1° to 18.9°; for **2d**: 63.2°). The preference for a planar arrangement indicates electronic communication between the NHC and the arylazo group.
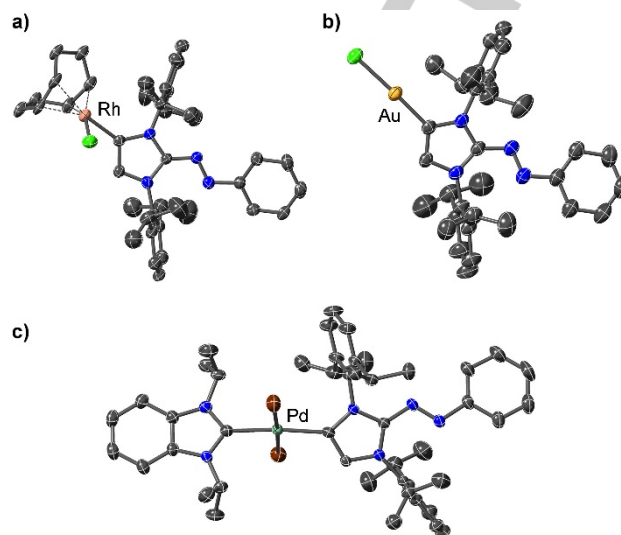

Figure 2. Molecular structures of the complexes **1a** (a), **2a** (b), and **3a** (c) in the crystal. The ellipsoids are at the 50% probability level. Color coding: grey = C, peach = Rh, green = Cl, blue = N, orange = Au, turquoise = Pd, red = Br.

The reduced symmetry of the carbene ligands compared to the imidazolium dyes results in separate NMR signals for the two N-aryl groups. Characteristic low-field shifts were observed in the ^{13}C{^{1}H} NMR for the M-C$_{carbene}$ atoms, which appeared at ~ 170 ppm for M = Rh and at ~ 156 ppm for M = Au. Again, there were only minor changes within a family of compounds (SI, Table S4).

In 2009, Huynh proposed that ^{13}C{^{1}H} spectroscopy may be used to investigate the σ-donor strength of a ligand L.[13] The method involves synthesis of a Pd complex, trans-[PdBr$_2$(^{i}Pr$_2$-bimy)L], and then measuring the trans-carbene ^{13}C{^{1}H} chemical shift (the Huynh Electronic Parameter, HEP). The more downfield the chemical shift, the more σ-donating the ligand L. HEPs for carbene ligands range from 175 to 184 ppm, with normal NHCs having values of around 178 ppm.[13,14] An HEP value of 181.1 ppm was observed for **3a**, and a value of 181.0 ppm for the control complex **3e**. These values are noteworthy for two reasons. First, they are both relatively high; second, the values are remarkably close to one another.

The HEP primarily measures the σ-donating ability of the carbene (and not the π-back-donation),[13,14] which originates from the ligand HOMO. The high HEP value observed for **3a** indicates that Azo-MICs are very strong σ-donor ligands. The presence of an azo group has apparently only a small influence on the σ-donor properties, as evidenced by the very similar HEP value of complex **3e**.

The electronic properties of carbene ligands can also be classified by comparing the IR carbonyl frequencies of RhCl(CO)$_2$(NHC) complexes.[14a] Therefore, we have converted the COD complex **1a** into the corresponding dicarbonyl complex

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by bubbling CO through a solution of **1a** in CHCl$_3$. IR analysis revealed an average ν(CO) band at 2031 cm^{-1} (CH$_2$Cl$_2$), corresponding to a Tolman Electronic Parameter of TEP = 2045 cm^{-1}. This value is lower than what is observed for normal NHC ligands (ν_{av} = 2035–2041 cm^{-1}, TEP = 2048–2053 cm^{-1}),[14a] but higher than what is found for complexes with mesoionic imidazolylidene ligands (TEP = 2037–2043 cm^{-1}).[15] For comparison, we have also converted the Rh complex **1e** into the corresponding carbonyl complex. The CO bands in CH$_2$Cl$_2$ appear at ν(CO)$_{av}$ = 2024 cm^{-1} (TEP = 2039 cm^{-1}). The TEP reflects the total electron donor properties of a ligand, and the IR data show that the normal mesoionic carbene ligand of **1e** is overall a better donor than the Azo-MIC of **1a**. Since the HEP values indicate very similar σ-donor properties of the two ligands, we assume that the difference of Δ(TEP) = 6 cm^{-1} is largely due to the better π-accepting properties of the Azo-MIC.

Density functional theory (DFT) calculations were conducted to gain further insights into the electronic structure of the carbene ligands of **1a** and **1e**. The M06 functional[16] and a 631G* basis set was employed for the calculations (see SI for details and validation). The HOMOs of the hypothetical free carbenes mostly consist in the carbene lone pair (Figure 3a), with similar orbital energies of –5.27 eV (carbene of **1a**) and –4.97 eV (carbene of **1e**). The relatively small difference in energy is in line with the experimentally determined HEP values, which indicate that both ligands are nearly equally good σ-donors.
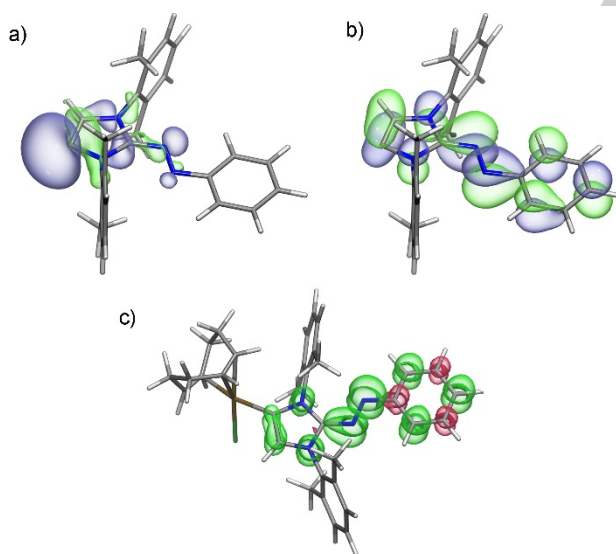

Figure 3. Kohn-Sham highest occupied (a) and lowest unoccupied (b) molecular orbital for the ligand of **1a**, obtained with DFT/M06/6-31G*, with energies of –5.27 eV and –2.43 eV, respectively. The spin density for the reduced complex [**1a**]$^-$ (c).

The LUMO of the ligand of **1a** (Figure 3b) is significantly lower in energy (–2.43 eV) than the one of **1e** (–0.94 eV). The pronounced difference of 1.49 eV is related to the more important electronic delocalization of the nearly planar NHC-N=N-Ph moiety, also observed experimentally, and contrasting with the twisted geometry of the phenyl group in **1e**. It is worth pointing out that

the LUMO of mesoionic carbene ligands can have a node at the carbene C-atom.[2] For the ligand of **1a**, this is *not* the case (Figure 3b), and π-back-donation from the metal to the ligand should therefore be possible.

We also computed the vertical electron affinity (vEA = E(L)– E(L$^-$), evaluated at the same molecular geometry) for both ligands and confirmed the trends observed earlier: the difference in vEA between the ligands in **1a** and **1e** is 1.49 eV, attesting from the much higher propensity of ligand **1a** to accommodate an additional electron.

The HOMO-LUMO difference of only 2.84 eV for ligand **1a** suggested a small singlet-triplet gap. Indeed, calculations at the DFT/M06/6-31G* level (see SI) show that the vertical E_{S-T} of ligand **1a** is only 154 kJ/mol, and much lower than what was calculated for ligand **1e** (284 kJ/mol). Allowing for structural relaxation (adiabatic E_{S-T}), the values further decrease to 105 kJ/mol for ligand **1a** and to 216 kJ/mol for ligand **1e.** It should be noted that the E_{S-T} for **1a** is even lower than what has been reported for CAACs and for cyclic (amino)(aryl)carbenes (CAArCs).[17]

The LUMO of the Rh complex **1a** displays a very similar shape as the one of the free ligand (see SI). Substituting **1a** for **1e** leads to an increase in LUMO energy by 1.40 eV and a drop in vertical electron affinity amounting to 1.43 eV. This result highlights that the Azo-MIC retains its strong electron affinity upon complexation. We have also computed the spin densities of the reduced complex [**1a**]$^-$, and the result suggest that a reduction of **1a** would be dominantly ligand-centered (Figure 3c).

Vertical transitions were calculated using linear-response time-dependent density functional theory for the compounds **1a** and **1e** (see SI for details). The first transition exhibiting a dominant HOMO→LUMO character is computed at 2.96 eV for **1a**. This value is, as expected, significantly lower than the corresponding transition energy for **1e** calculated at 4.50 eV.

The possibility to accommodate one electron on the carbene ligand is a key characteristic of CAACs. Our experimental and theoretical results suggested that ligand-centered reductions should also be possible with our new ligands. Therefore, we investigated the redox behavior of the Au and Rh complexes using cyclic voltammetry. For all complexes with Azo-MIC ligands, a reversible one-electron reduction was indeed observed, with half potentials between –1.09 V and –1.33 V (SI, Table S1).[18] The Rh complexes were found to display a slightly more negative reduction potential than the Au complexes.

Comparing the Au complexes **2a**–**d** (Figure 4), we note that the influence of the N-aryl substituents is small (Mes vs. Dipp, $\Delta E_{1/2}$ < 30 mV). Similar values are to be expected, since the N-aryl π-system is orthogonal to that of the carbene heterocycle. A greater difference is observed when the arylazo groups are changed. Moving from phenyl to the tetramethylphenyl results in an decrease of the reduction potential of 193 mV and 162 mV, respectively (SI, Table S1 and Figure 4). The change can be attributed to the electron donating effect of the four methyl groups.

The reduction process is strongly linked to the presence of an arylazo substituent, as evidenced by the cyclic voltammograms of the control complexes **1e** and **2e**. The potentials of these complexes are just within the solvent window at ~ 2.5 V. The difference between the potential of **1a** and **1e** is 1.39 V, in good agreement with computed difference in vEA of 1.43 eV. The

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results also show that the reduction is ligand-centered. For a reduction process involving the metal, the potentials of **1a**–**1d** and **2a**–**2d** on one hand, and of the control complexes **1e** and **2e** on the other hand, would expected to be more similar.
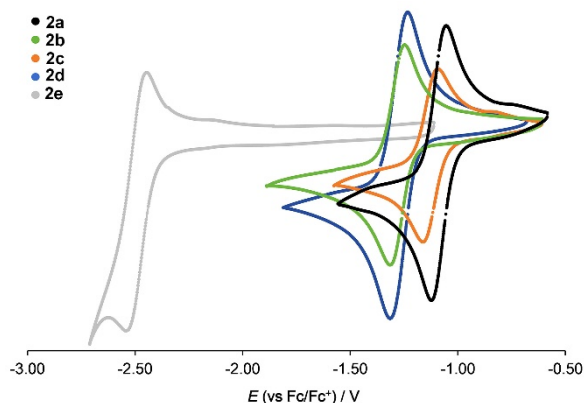

Figure 4. Cyclic voltammograms of the Au complexes **2a**–**2e**. Conditions: analyte (1 μM), MeCN, NBu_4PF_6 (0.1 M), $Ag/AgNO_3$ reference electrode (0.01 M), referenced to Fc/Fc^+ couple, set at 0 V.

In conclusion, we have shown that it is possible to alter the electronic structure of 4-imidazolylidene ligands considerably by introducing arylazo groups at C2 position. The resulting Azo-MICs are still potent σ-donors, but they show a small singlet-triplet gap and very low-lying LUMO levels. As a consequence, they are significantly better π-acceptors compared to 'standard' 4-imidazolylidene ligands with aryl groups in C2 position.

The unique electronic structure of Azo-MICs is expected to have a pronounced effect on the chemistry of metal complexes with these ligands. First experimental evidence is the reversible, ligand-centered reduction of Rh^I and Au^I complexes, as observed by cyclic voltammetry. Ligand-centered reductions are also detected for metal complexes with CAAC ligands, and it will be interesting to see if the functional analogy between Azo-MIC and CAAC ligands can be extended to other domains. For example, Azo-MICs appear to be well suited for stabilizing radicals. Investigations in this direction are pursued in our laboratory.

Acknowledgements

Keywords: N-Heterocyclic Carbenes, Mesoionic Carbenes, Rhodium, Gold, Azoimidazolium Dyes.

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[18] Complexes of the formula RhCl(COD)(NHC) are known to undergo a reversible Rh^I/Rh^{II} oxidation under cyclic voltammetry conditions (ref. 14a). For the Rh complex **1a**, however, an irreversible oxidation was observed. Therefore, the oxidation chemistry of the complexes was not investigated in more detail.

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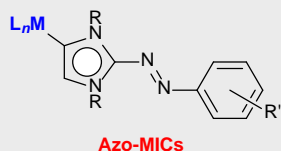
Good σ-donors
Small HOMO-LUMO gap
Small singlet-triplet gap
Reversible one-electron reduction

Azo-MICs

F. Mark Chadwick, Basile F. E. Curchod, Rosario Scopelliti, Farzaneh Fadaei Tirani, Euro Solari and Kay Severin*

Dyeing for a lower LUMO: Mesoionic carbenes derived from azoimidazolium dyes (Azo-MICs) are exceptionally good σ-donors. Furthermore, they have very low-lying LUMO levels, allowing for ligand-centered one-electron reductions.