Cyclic (Aryl)(Amido)carbenes: Pushing the π-Acidity of Amidocarbenes Through Benzannulation

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Cyclic (Aryl)(Amido)carbenes: Pushing the π-Acidity of Amidocarbenes Through Benzannulation†

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Cyclic(aryl)(amido)carbenes were synthesized, and studied via a combination of experimental and computational approaches. These carbenes undergo dimerization when isolation is attempted, however, are trapped with sulfur, selenium, and [Ir(cod)Cl]. The π-acidity, measured using ^{77}Se NMR, revealed that these are the most electrophilic singlet carbenes reported to date.

The continued interest in novel carbene architectures[1] has been motivated by the versatility of these remarkable compounds in the stabilization of exotic transition metal[2] and main group complexes,[3] paramagnetic species,[4] nanomaterials,[5] in catalysis,[6, 7] and more recently as emissive materials for OLED applications.[8] The isolation of the first N-heterocyclic carbene (NHC)[9] by Arduengo in 1990[10] was a landmark achievement; however, Bertrand's cyclic(alkyl)(amino)carbenes (CAACs, **A**, Figure 1) which feature higher and lower-lying HOMOs and LUMOs, respectively, marked a renaissance in the chemistry of stable carbenes.[11] The unique electronic structure of CAACs enables these carbenes to outperform NHCs for the stabilization of paramagnetic fragments and in the activation of enthalpically strong bonds.[12, 13]

In contrast, the introduction of π-withdrawing aryl and/or amido moieties adjacent to a carbene significantly lowers the LUMO energy levels when compared to NHCs and CAACs (**B**–**F**).[14, 15, 16, 17] For example, diamidocarbenes (DACs, **D**), pioneered by Bielawski are less nucleophilic yet more electrophilic. While DACs are adept at stabilizing low-valent main group and paramagnetic species,[18] their ability to activate enthalpically strong bonds pales in comparison to CAACs,[19, 20] presumably due to their low-lying HOMO and poor nucleophilic character.[15] Several modifications have been made to the structures of both CAACs and DACs to further tune their electronic properties. For example, Bertrand has shown that replacement of the alkyl groups in CAACs with an annulated aryl group affords cyclic (amino)(aryl) carbenes (CAArCs, **B**) which are both more electrophilic and nucleophilic when compared to CAACs.[14] Similarly, Bielawski demonstrated the nucleophilicity of DACs can be increased while retaining their electrophilic character by replacement of one amido group with an alkyl moiety to give cyclic(alkyl)(amido) carbenes (**C**).[16]

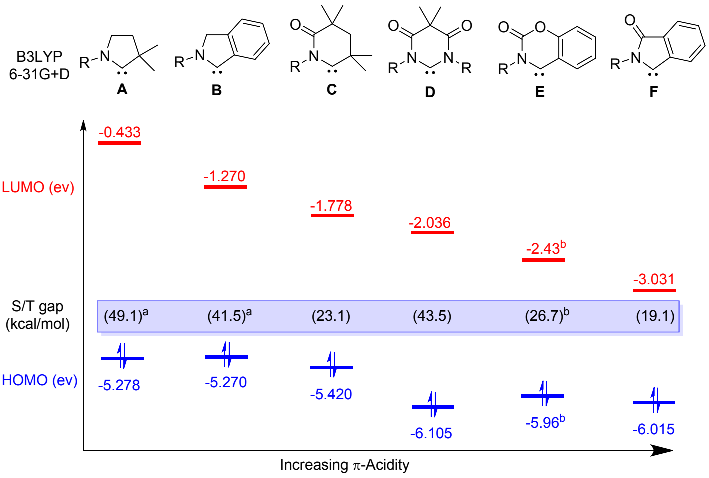

Figure 1. HOMO and LUMO energy levels (eV), and singlet–triplet gaps (ΔE S/T, kcal·mol^{-1} calculated at the B3LYP/6-31G+D level) of selected carbenes. ^{a}S/T gaps taken from reference 14, ^{b} energies taken from reference 22.

More recently, our group found that DACs can be photolyzed from their singlet ground state to an excited triplet state which then undergoes reversible Büchner ring expansion reactions.[21] While we believe the low-lying LUMO of DACs is responsible for the observed photochemistry, there are no other carbenes which exhibit similar photochemistry. To explore other potentially photoactive carbene architectures, we have begun an *in silico*-guided research program to rationally design and identify novel carbenes with increasingly electrophilic and nucleophilic properties relative to DACs. In this

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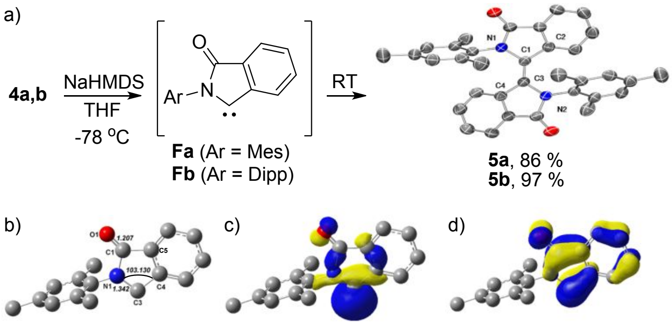
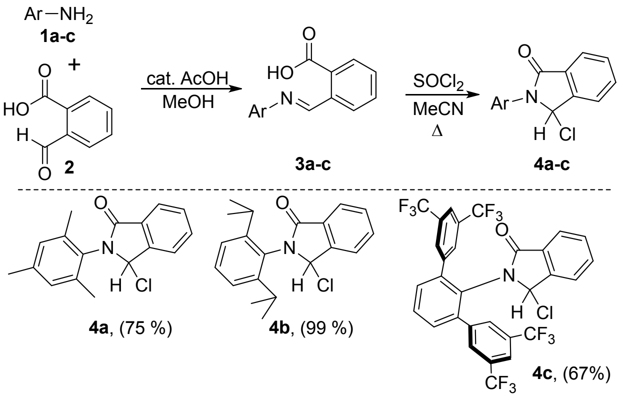
vein, computational data indicate that the replacement of one amido substituent within a DAC by an aryl group results in enhanced electrophilicity of the carbene center, concomitant with increased nucleophilicity. Thus, cyclic (aryl)(amido)carbenes **F** theoretically represent the most electrophilic carbenes with the smallest reported singlet-triplet (S/T) gap (19.1 kcal/mol) to date for any singlet carbene. During the course of our studies, Lee and co-workers published a beautiful paper describing the synthesis of a series of carbenes of type **E**, which are derived from coumarin.[22] Similar to our predicted results for carbenes of type **F**, these coumarin-derived analogs are very electrophilic species.

Encouraged by the *in-silico* data, we attempted the synthesis of carbenes of type **F** (Scheme 1). Carbene precursors could be readily prepared from commercially available aniline derivatives (**1**) and 2-carboxybenzaldehyde (**2**). Simple condensation reactions of **1** and **2** afford imines (**3**) good yields, which are then treated with thionyl chloride in refluxing acetonitrile to perform a two-step chlorination-cyclization reaction sequence in one reaction flask to give the 3-chloro-2-arylisoindolin-1-ones (**4**) in quantitative yields. The commercially-available aniline derivatives, 2,4,6-trimethylaniline (**1a**) and 2,6-diisopropylphenylaniline (**1b**) were explored; and, presumably any aniline derivative will work as evidenced by our successful condensation reaction of **2** with the bulky terphenyl-amino derivative, 2,6-bis[3,5-bis(trifluoromethyl)phenyl]aniline (**1c**). Note, the final step to provide carbene precursors **4** required no additional workup and compounds **4** were isolated in quantitative yield without further purification.

The deprotonation of compounds **4a-c** with several bases including: LDA, NaH/KOtBu, and NaHMDS was attempted in order to isolate the desired free carbenes, **Fa-c**. Ultimately, it was found that deprotonation of **4a** using NaHMDS in THF at -78 °C proceeded smoothly, however we were unable to isolate the free carbene **Fa**, and instead obtained the carbene dimer **5a** in 86% yield as a bright yellow powder (Scheme 2a, the dimer **5b** could also be isolated in a similar fashion in 97% yield, see ESI for full discussion). The identity of **5a** was confirmed by a combination of multinuclear NMR spectroscopy by: *i*) the disappearance of the proton at C3 in compound **4a** at 6.5 ppm, *ii*) the appearance of an olefinic carbon at 124.5 ppm, and *iii*) by single crystal X-ray diffraction. Interestingly, only a single isomer, the E-isomer, of carbene dimer **5a** is formed presumably due to large steric compression owing to the large N-mesityl substituents, and the metrical parameters are consistent with the formation of the olefin with a C1–C3 distance of 1.361(3) Å, consistent with a C=C double bond. In an attempt to prevent dimerization observed with carbenes **Fa** and **Fb**, we turned to the bulkier **4c**, which features the *m*-terphenyl N-substituent.[23] However, to date, we have not been successful in the deprotonation of **4c** regardless of conditions used (*i.e.* base, solvent, temperature).§



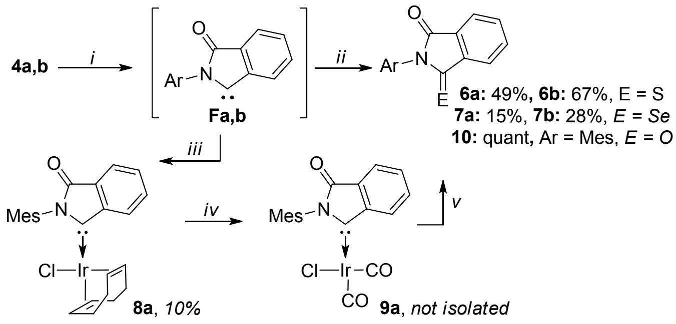
Scheme 2. a) synthesis of carbene dimers **5a,b** (crystal structure of **5a** (Ar= Mes) shown, 50% probability ellipsoids, H-atoms removed for clarity); b) optimized geometry of carbene **Fa**; c) calculated HOMO of **Fa**; d) calculated LUMO of **Fa**. (Mes = 2,4,6-$(CH_3)_3C_6H_2$, Dipp = 2,6-$(i\text{Pr})_2C_6H_3$).



Scheme 1. Synthesis of carbene precursors **4a-c** (yields reported are over both steps).

The optimized structure of **Fa** (Scheme 2b) revealed a planar isoindolinone core with an N1-C3-C4 angle of 103.13 which is smaller than both CAACs (ca. 106.5°) and CAArCs (105.0°)[14] and the C1–O1 distance of 1.207 Å is consistent with what has been reported for DACs (1.21 Å)[20, 24] indicating delocalization of the nitrogen atom lone pair into the carbonyl moiety for **Fa**. The HOMO is consistent with a lone pair localized in a n_σ orbital on the carbene carbon (Scheme 2c) whereas the LUMO (Scheme 2d) is a π-type orbital that is delocalized throughout the isoindolinone core similar to what Bertrand observed in CAArCs, and consistent with the π-accepting nature of the annulated aryl substituent.[14] In contrast to the CAArCs, the introduction of the carbonyl moiety in **Fa**, results in increased delocalization into the 5-membered ring which spans the N1-C1-C5 linkage.

To verify if the free carbenes **Fa** and **Fb** could be accessed at low temperature prior to dimerization, we performed the series of trapping experiments described in Scheme 3. First, addition of S_8 to solutions of **4a** or **4b** and NaHMDS in THF cooled to -78°C resulted in the formation of the of thiones **6a** or **6b** as bright pink solids in 49 and 67 % yield, respectively, indicating that the free carbenes could be prepared as a viable species at low temperature. Similarly, the selenones **7a** or **7b** were prepared as a sky blue solids in 15 and 28 % yield, respectively, by trapping **4a** or **4b** with selenium at low temperature. Compound **6a** and **6b** exhibited characteristic C=S carbon signals in the ^{13}C NMR spectra (C_6D_6) at 197 or 198 ppm (**6a** or **6b**, respectively), whereas the cooresponding C=Se carbon



Scheme 3. Trapping experiments conducted on carbenes **Fa** and **Fb**. Isolated yields are provided in the scheme. Conditions: *i*: NaHMDS, THF, -78°C, *ii*: S_8 or Se, *iii*: 0.5 eq. [(cod)IrCl]$_2$, *iv*: 1 atm CO in $CDCl_3$, $_v$) air in CH_2Cl_2.

atoms resonated at 201 or 203 ppm (**7a** or **7b**, respectively). To further corroborate their identity, compounds **6a** and **7a** were characterized by single crystal X-ray diffraction (Figure 2). The ^{77}Se NMR spectra for compounds **7a** and **7b** exhibited singlets at 1240.9 and 1263.9 ppm ($CDCl_3$), respectively. For comparison to other carbene-derived selenones,[25] the ^{77}Se chemical shifts for **7a** and **7b** in d_6-acetone were observed at 1204.5 and 1231.1 ppm, respectively. These values were considerably downfield compared to Lee's selenones derived from carbenes of type **E** (values ranging from 1003–1135 ppm in d_6-acetone)[22] and even downfield when compared to what Bielawski observed (1179.1 ppm)[16] with carbene **C**. To date, the observed low field ^{77}Se signals for compounds **7a** and **7b** are the most downfield recorded for a selenone derived from a carbene, and are consistent with the low-lying LUMO of carbenes of type **F** and attendant electrophilic nature. To further interrogate the electronic properties, we attempted to measure the Tolman electronic parameter (TEP)[26] of **Fa** by measuring the carbonyl stretching frequency (ν_{CO}) of the complex **Fa**-(Ir(CO)$_2$Cl).[27, 28] First, carbene **Fa** was successfully coordinated to the [Ir(cod)Cl] (cod = 1,5 cyclooctadiene) fragment to give complex **8a** which was isolated as an orange solid in 10 % yield. Complex **8a** was found to be very fragile, and all attempts to recrystallize this compound, improve the yield of the reaction, or obtain passing elemental analysis resulted in further decomposition. For this reason, only ^{1}H and ^{13}C NMR spectroscopy as well as high resolution mass spectrometry (HRMS) were obtained to confirm the identity of **8a**. The most diagnostic data was the chemical shift of the carbene nucleus in **8a** (250.10 ppm, $CDCl_3$) which was similar to what Lee and Bielawski observed for Rh(cod)Cl (273.95 ppm, $CDCl_3$)[22] and Ir(cod)Cl (286.9 ppm, $CDCl_3$)[16] complexes of carbenes **E** and **C**, respectively, and in the range of known carbene-[Ir(cod)Cl] complexes.[28, 29]

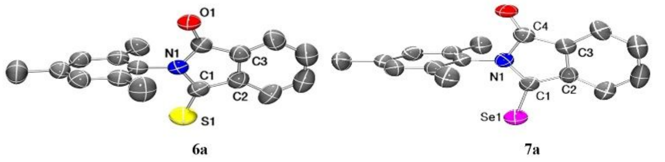


Figure 2. Single crystal x-ray structures of **6a** (left) and **7a** (right). Rendered using POV-Ray with 50% probability ellipsoids, and hydrogen atoms removed for clarity.

Next, **8a** was treated with carbon monoxide in $CDCl_3$, to cleanly release the cyclooctadiene ligand and give the desired complex, **Fa**-[(CO)$_2$IrCl] (**9a**), in quantitative yield by NMR spectroscopy. **9a** could not be isolated, and was found to decompose even under inert atmosphere. If isolation is attempted in air, it is oxidized to give *N*-mesitylphthalimide (**10**). The liberated [Ir(CO)$_2$Cl] fragment undergoes disproportionation to give Ir^0 and [Ir(CO)$_6$][Cl$_3$] as evidenced by ^{13}C NMR and FTIR spectroscopy.[†] To our knowledge, this is the first example where a carbene-Ir(I) complex becomes oxidized at the carbene center, and is surprising given singlet carbenes do not react with molecular oxygen. This unique reactivity may stem from the small calculated S/T gap of **Fa**. Despite this instability, we were able to measure the ν_{CO} of **9a** in $CDCl_3$, and determined the TEP which was 2065 cm^{-1} and notably larger than what has been measured for DACs (2057 cm^{-1}), carbene **C** (2053 cm^{-1}),[25] and carbenes **E** (2048 cm^{-1}),[22] making it the weakest σ-donating carbene reported to date.

In this study we demonstrated that the electrophilicity and singlet-triplet gap of amido carbenes can be increased and decreased, respectively through the benzannulation to the carbene center. The resultant cyclic(aryl)amido carbenes (**Fa** and **Fb**) represent the most electrophilic singlet carbenes reported to date. Moreover, these carbenes have the smallest calculated singlet-triplet gaps (19.1 kcal/mol) for cyclic, singlet ground state carbenes. Collectively the low-lying LUMO and small S/T gap rendered these carbenes very reactive leading to dimerization. While the use of a bulky m-terphenyl substitutent at nitrogen was explored to prevent dimerization, the deprotonation of the carbene precursor, **4c**, was unsuccessful.

To measure the electronic properties of carbens **Fa** and **Fb** experimentally, a series of trapping experiments were performed. The π-acidic nature of these carbenes was interrogated by measuring the ^{77}Se NMR chemical shift of the corresponding carbene-derived selenones **7a** and **7b**, which were the most deshielded selenium nuclei reported for these types of compounds. Finally, the measured TEP of **Fa** revealed that this is the weakest σ donating carbene reported to date. Current efforts to synthesize isolable analogues of carbenes of type **F** to further interrogate their electronic properties, and to explore potential novel photochemistries are underway.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

§ Deprotonation of **4c** using: nBuLi, LDA, potassium benzyl, KHMDS, NaHMDS. Chloride abstraction from **4c** using Me_3Si-SO_3CF_3 according to reference 21 also resulted in no reaction.

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