N-Heterocyclic Carbenes

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Cyclic (Aryl)(Amido)Carbenes: NHCs with Triplet-like Reactivity

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Abstract: *The synthesis and study of a library of cyclic (aryl)(amido)carbenes (CArAmCs), which represent a class of electrophilic NHCs that feature low calculated singlet-triplet gaps ($\Delta E_{ST}=19.9$ kcal mol^{-1}; B3LYP/def2-TZVP) and exhibit reactivity profiles expected from triplet carbenes, are described. The electrophilic properties of the CArAmCs were quantified by analyzing their respective selenium adducts, which exhibited the largest downfield ^{77}Se NMR chemical shifts (up to 1645 ppm) measured for any NHC derivative known to date, as well as their Ir carbonyl complexes, from which large Tolman electronic parameter (TEP) values (up to 2064 cm^{-1}) were ascertained. The CArAmCs were found to engage in reactions that are typically observed with triplet carbenes, including C−H insertions, [2+1] cycloadditions with alkenes as well as alkynes, and spontaneous oxidation upon exposure to oxygen.*

Introduction

Although carbenes have served as reactive intermediates for the past two centuries,[1] remarkable growth in the field was triggered by the landmark reports of stable phosphinosilyl carbenes[2] (Bertrand, 1989) and a crystalline imidazol-2-ylidene[3] (Arduengo, 1991). Derivatives of the latter, which are typically described as *N*-heterocyclic carbenes (NHCs),[4] have been extensively developed over the past few decades and are frequently utilized as ligands in transition metal complexes,[4b,5] as reagents in chemical transformations,[6] and as catalysts.[4g,7] The broad utility stems in part from their high intrinsic nucleophilicities. Indeed, NHCs feature a bona fide resonance structure wherein a formal negative charge is assigned to the carbene nucleus. While many efforts have been directed toward enhancing and exploiting such nucleophilic properties, our group and others have been developing electrophilic analogues, in part by installing functional groups (e.g., carbonyls) that effectively siphon electron density away from the carbene nucleus.[8] For example, the *N*,*N*′-diamidocarbenes (DACs) (e.g., **1**; Figure 1),[8a–h] which feature amides N-bonded to the carbene nucleus, were found to function as electrophiles in a broad range of chemical reactions.[8b,9] The DACs were also found to retain some of the nucleophilic characteristics displayed NHCs, and thus may be best described as ambiphilic.[8a,b,f,9,10]

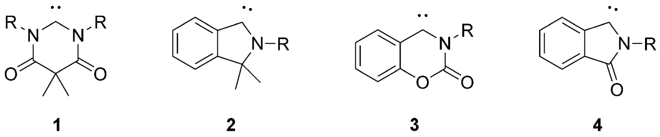
1 **2** **3** **4**

Figure 1. Generalized structures of selected electrophilic carbenes.

To realize a carbene that displayed an even higher degree of electrophilic properties than the DACs, we considered known triplet carbenes, particularly fluorenylidene in part because it has been reported to feature a singlet-triplet gap (ΔE_{ST}) of approximately 1 kcal mol^{-1}.[11] Although fluorenylidene is not isolable, it was hypothesized that the attachment of a functional group to the carbene nucleus would enhance stability while retaining a relatively high degree of electrophilicity. Bertrand's cyclic (amino)(aryl)carbenes (CAArCs)[12] (**2**) serve as examples of such systems. While a CAArC was calculated to exhibit a lower ΔE_{ST} value when compared to its analogous cyclic (amino)(alkyl)carbene (CAAC) (39.5 kcal mol^{-1} vs. 47.5 kcal mol^{-1}, respectively), a similar value was calculated for a DAC (42.3 kcal mol^{-1}).[8i] More recently, a coumaraz-2-on-4-ylidene (**3**),[8i] which features a carbene nucleus linked to a carbamoyl group, was reported by Song and Lee to exhibit a relatively low ΔE_{ST} value (26.7 kcal mol^{-1}).[8i] Using a similar level of theory (B3LYP/def2-TZVP), we calculated a ΔE_{ST} of 19.9 kcal mol^{-1} for a cyclic (aryl)(amido)carbenes (CArAmC) **4** (*R* = 2,6-diisopropylphenyl). Moreover, the LUMO for **4** was calculated (−3.02 eV) to be significantly lower in energy than the LUMOs calculated for DAC **1** (−2.20 eV), CAArC **2** (−1.47 eV), and coumaraz-2-on-4-ylidene **3** (−2.43 eV).[8i] Motivated by these results, we hypothesized that the CArAmCs should exhibit relatively strong electrophilic characteristics and may potentially react in a manner similar to that expected from a triplet carbene. Herein, we describe the synthesis of a library of CArAmCs that feature different N-substituents in order to facilitate isolation as well as derivatives with halogen groups to pronounce electrophilicity. The electronic properties as well as the chemistry of the CArAmCs are also presented.

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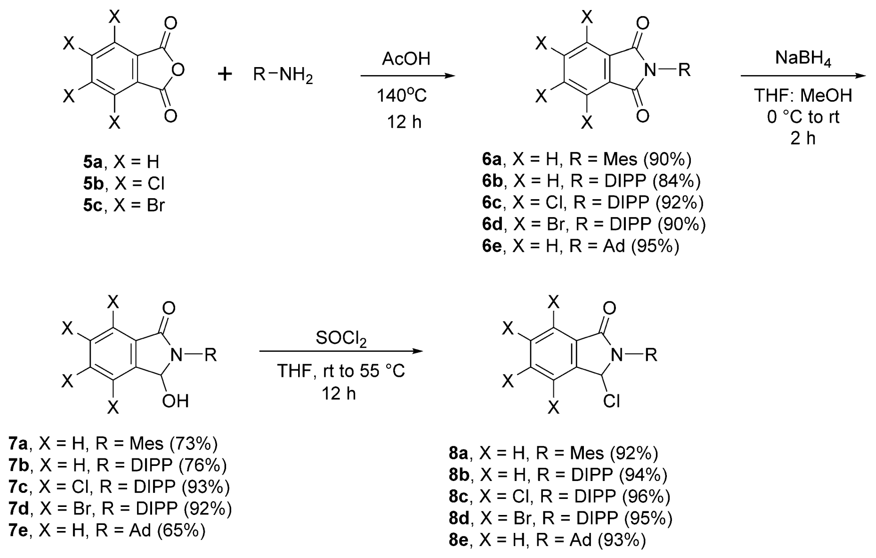
Results and Discussion

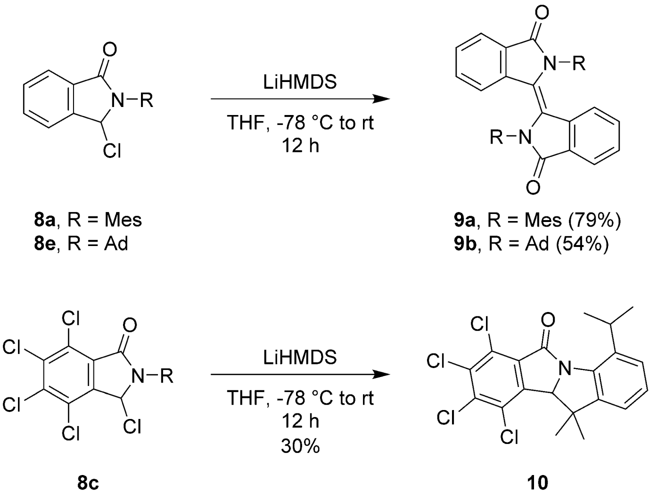
The syntheses of the precursors to various CArAmCs are summarized in Scheme 1. Commercially-available phthalic anhydrides (**5a**–**5c**) were first converted to their respective imides (**6a**–**6e**) by condensing the corresponding amines in acetic acid at 140 °C for 12 h. Pure imides were obtained in 84 to 95 % yield after sequentially washing the crude products with aqueous HCl (1N), an aqueous solution saturated with $NaHCO_3$, n-hexane, and Et_2O. Independently treating the imides with 1.2 equiv of $NaBH_4$ in a mixture of MeOH and THF (2:8, v/v) afforded the corresponding alcohols (**7a**–**7e**) in a 65 to 93 % yield after purification by washing with diethyl ether or silica gel column chromatography. Finally, chlorination of the alcohols with thionyl chloride ($SOCl_2$) afforded the HCl adducts of the targeted carbenes (**8a**–**8e**) in yields that exceeded 90 %.



Scheme 1. Synthesis of various carbene precursors. Mes = 2,4,6-trimethylphenyl. DIPP = 2,6-diisopropylphenyl. Ad = 1-adamantyl.

With **8** in hand, subsequent efforts were directed toward the generation of the corresponding carbenes (**4**). As summarized in Scheme 2, treating **8a** with lithium hexamethyldisilazide (LiHMDS) (1.1 equiv) at −78 °C in THF followed by warming the reaction mixture to room temperature afforded a yellow product, which was subsequently isolated by purification using silica gel column chromatography. NMR and IR spectroscopy along with a single-crystal X-ray diffraction analysis (see the Supporting Information) revealed the structure to be the carbene dimer **9a**. In contrast, deprotonation of **8c** afforded the C−H insertion product **10**, as determined in part by the observation of benzylic ($\delta = 5.18$ ppm, $CDCl_3$), methyl (1.85 ppm and 0.79 ppm), and other key ^{1}H NMR signals that were consistent with the cyclic product. The structure of **10** was unambiguously confirmed by a single crystal X-ray diffraction analysis (Figure 2). Similarly, deprotonation of the carbene precursor **8e** afforded carbene dimer **9b**.[13] Attempts to deprotonate the other precursors (e.g., **8b** and **8d**) afforded mixtures of unidentified products.

As isolation of the free carbenes proved to be challenging, in situ formation was probed using a trapping experiment.[14] As summarized in Scheme 3, the addition of LiHMDS (1.1 equiv) to a stirred solution of **8b** and elemental sulfur (2 equiv) in THF at −78 °C afforded the corresponding thione **11**. The structure of the compound was confirmed using NMR spectroscopy as well as mass spectrometry. The salient ^{13}C NMR signal assigned to the C=S bond ($\delta = 198$ ppm,



Scheme 2. Products obtained upon deprotonating carbene precursors **8a**, **8c**, and **8e**.

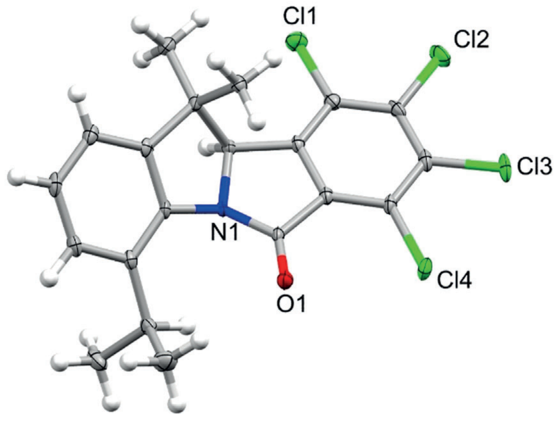
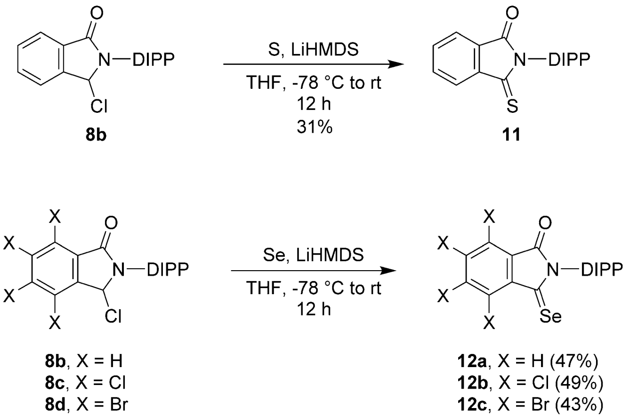


Figure 2. ORTEP diagram of **10** with thermal displacement ellipsoids drawn at the 50 % probability level.[29] Selected distances (Å): N1-C8, 1.472(2); N1-C1, 1.383(2); C1-O1, 1.2121(19); N1-C17, 1.4284(19); C3-Cl1, 1.7205(19). Selected angles (°): C8-N1-C1, 113.38(12); O1-C1-N1, 126.62(14); C1-N1-C17, 127.08(12).



Scheme 3. Generation and trapping of the carbenes by elemental S and Se.

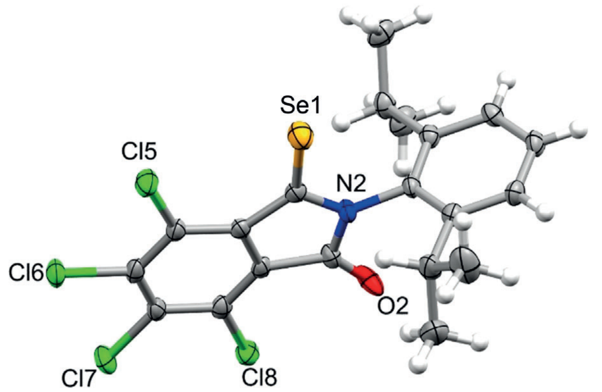


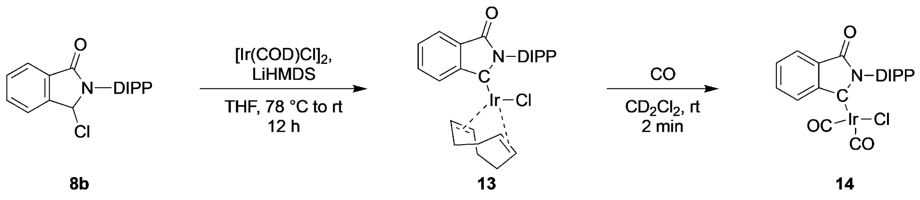
Figure 3. ORTEP structure of **12b** with thermal displacement ellipsoids drawn at the 50% probability level.[29] Note: although two crystallographically independent molecules were identified in the unit cell, only one is shown for clarity. Selected distances (Å): Se1-C8, 1.782(3); C1-O1, 1.245(5); N1-C5, 1.377(5); N1-C1, 1.402(5); C3-Cl1, 1.719(3). Selected angles (°): N1-C8-Se1, 123.50(3); O1-C1-N1, 124.90(3); C8-N1-C1, 112.10(3).

$CDCl_3$) was downfield when compared to the values reported for the sulfur adducts of DAC **1** ($\delta = 177$ ppm, $CDCl_3$)[15] as well as the sulfur adducts of **2** and **3** ($\delta = 191$–197 ppm, $CDCl_3$).[8i, 12]

Next, efforts were directed toward studying the electronic properties displayed by the carbenes. Ganter reported that the chemical shifts exhibited by the selenium nuclei of NHC-Se adducts reflect the π-accepting properties of the carbene nuclei and can be conveniently measured using ^{77}Se NMR spectroscopy.[16] The use of elemental Se instead of S in the aforementioned trapping experiment afforded carbene–selenium adduct **12a**. The ^{77}Se NMR signal recorded for **12a** ($\delta = 1204.4$ ppm, [D$_6$]acetone; 1267.9 ppm, $CDCl_3$) was found to be downfield when compared to the values reported for the Se adducts of a cyclic (alkyl)(amido)carbene (1179.71 ppm, [D$_6$]acetone), DAC **1** ($\delta = 847$ ppm, [D$_6$]acetone),[17] CAArC **2** ($\delta = 616$ ppm, [D$_6$]acetone),[12] and coumaraz-2-on-4-ylidene **3** ($\delta = 1103$ ppm, [D$_6$]acetone; $\delta = 1143.3$ ppm, $CDCl_3$).[8i] Likewise, the ^{13}C NMR signal assigned to carbene nucleus in **12a** was found to resonate at a relatively downfield value ($\delta = 202.8$ ppm, $CDCl_3$) when compared to the analogous signals recorded for the Se adducts of DAC **1** ($\delta = 182.7$ ppm, $CDCl_3$)[17] or coumaraz-2-on-4-ylidene **3** ($\delta = 197$ ppm, $CDCl_3$).[8i] The carbene-selenium adducts **12b** and **12c**, which were prepared in a similar manner as **12a**, exhibited the largest downfield ^{77}Se NMR signals reported to date (**12b**: $\delta = 1645.5$ ppm, [D$_6$]acetone; 1688.4 ppm, $CDCl_3$; **12c:** $\delta = 1690.7$ ppm, $CDCl_3$),[18] even though the C=Se bond distance measured (1.782(3) Å) in the solid state structure of **12b** (Figure 3) was within the range reported for other selenium adducts (1.765 Å).[8i]

Iridium olefin complexes are commonly used to quantify the electron-donating or accepting abilities of NHCs and other ligands.[19] NMR analyses of the former provide a means to measure the π-accepting abilities of the corresponding carbene nuclei. NHCs that are relatively strong π-acceptors often give NMR signals that are comparatively downfield. As shown in Scheme 4, treating a mixture of **8b** and [Ir(COD)Cl]$_2$ (COD = 1,5-cyclooctadiene) (0.5 equiv) with LiHMDS (1.1 equiv) in THF at −78 °C afforded the Ir complex **13**. ^{1}H NMR analysis of **13** revealed that the signals assigned to the olefins in the COD ligand ($\delta = 5.52$ and 5.22 ppm, $CDCl_3$) were the most downfield for any NHC-Ir complex known to date. Moreover, the ^{13}C NMR resonance of the carbene nucleus in **13** was recorded at $\delta = 249.3$ ppm ($CDCl_3$), which is significantly downfield when compared to the values reported for DAC **1** (231.3 ppm; C_6D_6)[8b] and other NHC complexes (179.6–208.2 ppm; $CDCl_3$)[20] reported in the literature but upfield when compared to a cyclic (alkyl)(amido)carbene (287.6 ppm; $CDCl_3$).[8f] Collectively, the downfield NMR signals indicated that **4b** is a strong π-acceptor. Further support for this conclusion was achieved through a single-crystal X-ray diffraction analysis (Figure 4). Reflective of their relative π-back-bonding interactions, the distance between the Ir and C$_{\text{carbene}}$ nuclei in the solid-state structure of **13** (1.937(3) Å) was measured to be shorter than the corresponding value reported for an analogous complex supported by **1** (1.998 Å).[21] Likewise, the distances of the C=C bonds within the coordinated COD ligand were measured to be shorter (1.379(6) and 1.408(7) Å) as well (c.f., 1.387 and 1.412 Å, respectively). Collectively, these structural features reflect the relatively strong π-acceptor characteristics of **4b**.

Ir carbonyl complexes also enable the comparison of the donating properties of NHCs, primarily through the calcu-



Scheme 4. Structures of the Ir complexes that were used to evaluate electronic properties of the cyclic (aryl)(amido)carbene **4b**.

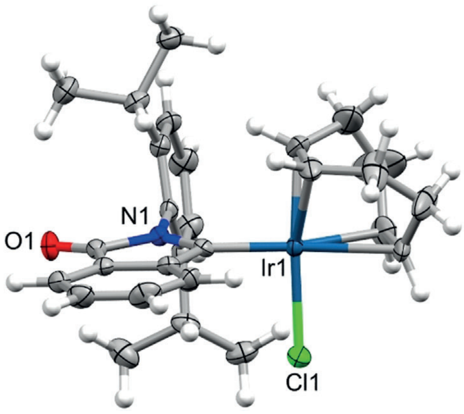
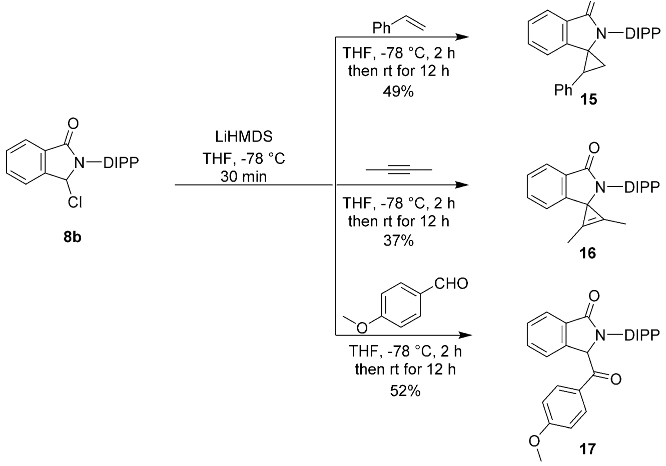


Figure 4. ORTEP diagram of **13** with thermal displacement ellipsoids drawn at the 50% probability level.[29] Selected distances (Å): Ir1-Cl1, 2.3598(10); Ir1-C8, 1.937(3); C21-C22, 1.408(7); C26-C27, 1.379(6). Selected angles (°): C8-Ir1-Cl1, 92.40(9); N1-C8-Ir1, 128.00(2); O1-C1-N1, 124.00(3).



Scheme 5. Carbene generation from **8b** followed by addition with styrene, 2-butyne or *p*-anisaldehyde.

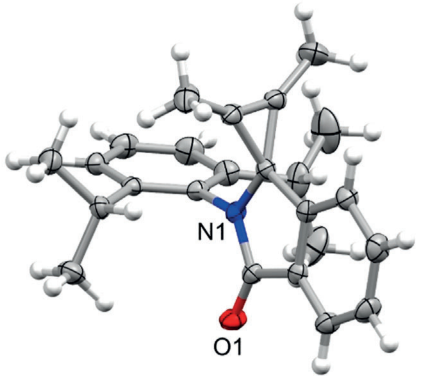


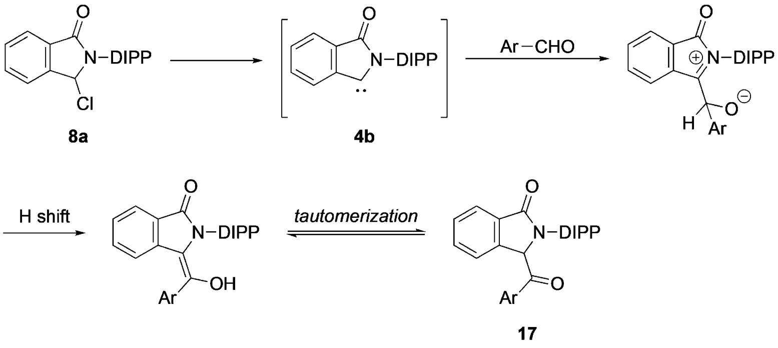
Figure 5. ORTEP diagram of compound **16** with thermal displacement ellipsoids drawn at the 50% probability level.[29] Selected distances (Å): N1-C1, 1.3636(14); N1-C8, 1.4760(13); O1-C1, 1.2296(13); N1-C13, 1.4330(13). Selected angles (°): C1-N1-C8, 112.66(8); C13-N1-C8, 122.66(8); N1-C8-C9, 122.66(8).

lation of a Tolman electronic parameter (TEP), a comparative value that is derived from the observed carbonyl stretching frequencies (ν_{CO}) displayed by the corresponding complex.[19,22] Carbonyl complexes supported by NHCs with relatively strong π-acceptor characteristics generally exhibit relatively high TEP values. Conversion of **13** to dicarbonyl complex **14** was achieved by bubbling a CD_2Cl_2 solution of **13** with carbon monoxide. The IR spectrum recorded for **14** exhibited two prominent ν_{CO} absorption bands at 2078.8 and 1998.9 cm^{-1} (CD_2Cl_2). Converting the IR data using Nolan's method[16b,20a,23] afforded a TEP value (2064 cm^{-1}) that was significantly higher than that reported for DAC **1** (2057 cm^{-1})[21] as well as carbenes **2** and **3** (2050 cm^{-1}).[8i,12] Moreover, a ^{13}C NMR signal assigned to the carbene nucleus in **14** was recorded at $\delta = 247.9$ ppm, which is significantly downfield when compared to DAC **1** ($\delta = 224.1$ ppm, C_6D_6) and other NHC-Ir complexes (179.9–209.5, $CDCl_3$).[8b]

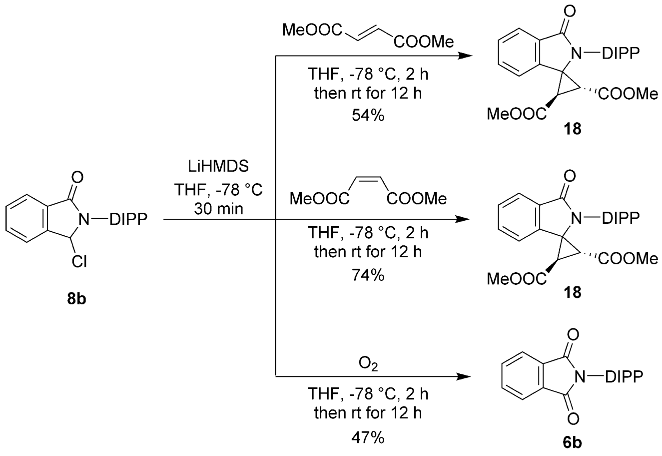
Based on the aforementioned results, we concluded that **4** was relatively electron deficient and hypothesized that it should react as an electrophile. Since nucleophilic NHCs generally do not undergo cycloaddition reactions with alkenes, whereas electrophilic derivatives engage in such chemistry,[9] a series of cycloaddition reactions were explored (Scheme 5). Deprotonation of **8b** using LiHMDS (1.1 equiv) in THF at −78 °C followed by the addition of excess (5 equiv) styrene or 2-butyne afforded the corresponding cycloadducts **15** or **16**, respectively, as determined by NMR spectroscopy and mass spectrometry. For example, ^1H NMR analysis of **15** revealed diagnostic signals at $\delta = 2.69$, 1.75 and 1.67 ppm ($CDCl_3$), which were consistent with the formation of a cyclopropyl system. Likewise, a singlet was observed at $\delta = 2.01$ ppm in the ^1H NMR spectrum recorded for **16** and attributed to six equivalent methyl protons. The structures of **15** (see Supporting Information) and **16** (Figure 5) were independently elucidated by single-crystal X-ray diffraction analyses.

Electrophilic carbenes, such as the DACs, have also been shown to undergo [2+1] cycloadditions with aldehydes.[9] When cyclic (aryl)(amido)carbene **4b** was treated with *p*-anisaldehyde, ketone **17** was obtained as the major product, as determined in part by NMR spectroscopy. For example, the ^1H NMR spectrum recorded for **17** revealed a singlet at $\delta = 6.29$ ppm ($CDCl_3$) which was assigned to the salient methine. The carbonyl groups assigned to the ketone and amide groups resonated at $\delta = 191.9$ and 169.6 ppm, respectively, upon ^{13}C NMR analysis of the compound. A mechanism similar to that deduced by Berkessel[24] for the formation of Breslow's intermediate is proposed in Scheme 6.[25] The carbene **4b**, generated in situ by treatment of **8b** with LiHMDS, may condense with *p*-anisaldehyde to form a zwitterionic adduct that subsequently undergoes a hydrogen shift to afford the enol tautomer of ketone **17**. Such transformations can be expected to be facilitated by electrophilic NHCs.[25,26]

Because of the unique reactivity profile observed by the cyclic (aryl)(amido)carbene **4** as well as the low singlet-triplet gap calculated for the compound, subsequent efforts were directed toward determining if the carbene could react in a manner similar to that of a triplet carbene. Cycloheptatrienylidene, a triplet carbene that must be generated in situ via photolysis or thermolysis of the sodium salt of tropone



Scheme 6. Proposed mechanism for the formation of ketone **17**.



Scheme 7. In situ generation of cyclic (aryl)(amido)carbene **4b** followed by cycloaddition with dimethyl maleate or fumarate or reaction with oxygen.

tosylhydrazone, has been reported to form *trans*-cyclopropyl products when reacted with dimethyl maleate or fumarate.[27] Deprotonating **8b** with LiHMDS (1.1 equiv) in THF at −78 °C followed by the addition of excess of dimethyl fumarate (2 equiv) afforded corresponding *trans*-cyclopropane derivative **18** (54 % yield). Treating **8b** with dimethyl maleate under similar conditions also afforded **18** (74 % yield). The structure of **18** was confirmed by ^{1}H and ^{13}C NMR ($CDCl_3$) spectroscopy, IR spectroscopy, mass spectrometry, as well as X-ray crystallography (Figure 6). Formation of the *cis* isomer was not observed when the crude reaction mixtures were monitored by NMR spectroscopy. Although the mechanism to obtain **18** from dimethyl fumarate is consistent with a concerted process, isomerization and thus a stepwise process is required to obtain the same product from dimethyl maleate. Collectively, these results suggested to us that **4** reacts as a triplet carbene when treated with disubstituted olefins.[27]

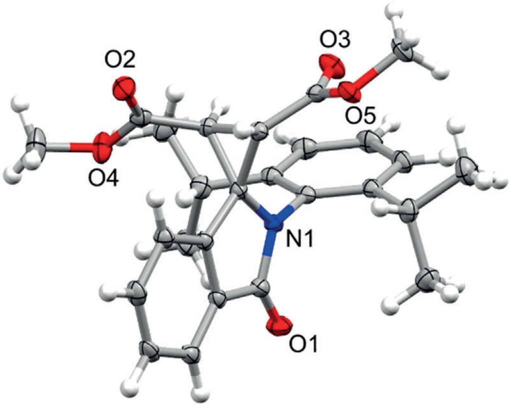


Figure 6. ORTEP diagram of **18** with thermal displacement ellipsoids drawn at the 50 % probability level.[29] Selected distances (Å): O1-C1, 1.2195(13); N1-C8, 1.4457(13); N1-C1, 1.3866(13); C8-C9, 1.5059(15). Selected angles (°): N1-C8-C9, 122.60(8); N1-C8-C12, 127.89(8); C1-N1-C8, 111.41(8).

To gain additional support for the notion that **4** can react as a triplet carbene, other reactions were explored. For example, triplet carbenes are known to react with molecular oxygen to form corresponding carbonyl products.[11,28] When the carbene precursor **8b** was treated with LiHMDS (1.1 equiv) in THF at −78 °C under an atmosphere of oxygen, imide **6b** was isolated as the major product. For comparison, hydrolysis of the carbene precursor **8b** formed the corresponding alcohol **7b** in quantitative yield; spontaneous oxidation to form **6b** was not observed.

Conclusion

In conclusion, we disclose the synthesis and study of a series of cyclic (aryl)(amido)carbenes. The carbenes were generated in situ from their corresponding HCl adducts, which were prepared in three steps from readily available starting materials and in good overall yield. The electronic properties of the carbenes were examined from their adducts with selenium and iridium, which collectively indicated that the carbenes are among the most highly π-accepting carbenes to date. Such characteristic manifested in a range of reactions that can be expected from electrophilic carbenes, including C−H insertions, cycloadditions with alkenes and alkynes, and formation of Breslow intermediates upon treatment with aldehydes. In some cases, triplet-like reactivity was observed. For example, [2+1] cycloaddition with dimethyl maleate or fumarate afforded the *trans*-cyclopropane product and the carbenes underwent spontaneous oxidation upon exposure to oxygen. In a broader context, these results provide a new direction toward achieving neoteric classes of electrophilic carbenes and enrich methodology for probing the chemistry displayed by such compounds.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: N-heterocyclic carbenes · organic reaction mechanisms · singlet carbenes · synthetic methods · triplet carbenes

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[29] CCDC 1946786 (**9**), 1946787 (**10**), 1946788 (**12b**), 1946789 (**13**), 1946790 (**15**), 1946791 (**16**), and 1946792 (**18**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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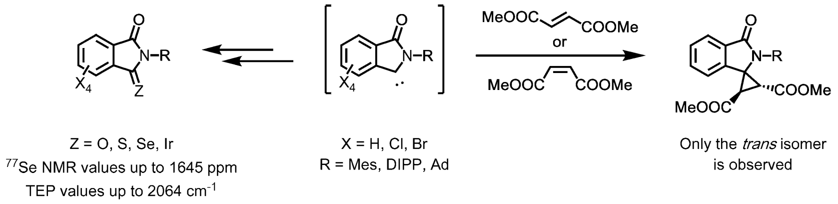
Research Articles

N-Heterocyclic Carbenes

P. R. Sultane, G. Ahumada, D. Janssen-Müller, C. W. Bielawski* ——— ▮▮▮▮–▮▮▮▮

Cyclic (Aryl)(Amido)Carbenes: NHCs with Triplet-like Reactivity



Triplet curious carbenes: The cyclic (aryl)(amido)carbenes (CArAmCs) constitute a class of NHCs that react in a manner akin to triplet carbenes. Examining the electronic properties of the carbenes revealed that they are among the most highly π-accepting and electrophilic carbenes to date. Such features enabled the CArAmCs to undergo C–H insertions, engage in [2+1] cycloadditions, and oxidize spontaneously upon exposure to oxygen.