

## A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

## **Accepted Article**

Title: Coumaraz-2-on-4-ylidene: Ambiphilic N-heterocyclic Carbenes with a Fine-Tunable Electronic Structure

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201804249 Angew. Chem. 10.1002/ange.201804249

Link to VoR: http://dx.doi.org/10.1002/anie.201804249 http://dx.doi.org/10.1002/ange.201804249

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## COMMUNICATION

# Coumaraz-2-on-4-ylidene: Ambiphilic *N*-heterocyclic Carbenes with a Fine-Tunable Electronic Structure

Hayoung Song,\*<sup>[a, b]</sup> Hyunho Kim,<sup>[a, b]</sup> and Eunsung Lee\*<sup>[a, b, c]</sup>

**Abstract:** Herein, a coumaraz-2-on-4-ylidene (1) as a new example of ambiphilic *N*-heterocyclic carbenes with fine tunable electronic properties is reported. The *N*-carbamic and aryl groups on carbene carbon provide exceptionally high electrophilicity and nucleophilicity simultaneously to the carbene center, as evidenced by the <sup>77</sup>Se NMR chemical shifts of their selenoketone derivatives and the CO stretching strengths of their rhodium carbonyl complexes. Since the precursors of 1 could be synthesized from various functionalized Schiff bases in a practical and scalable manner, the electronic properties of 1 can be fine-tuned in quantitative and predictable way using the Hammett  $\sigma$  constant of the functional groups on aryl ring. The facile electronic tuning capability of 1 may be further applicable to eliciting novel properties in main-group and transition metal chemistry.

*N*-heterocyclic carbenes (NHCs)<sup>[1]</sup> are enjoying the spotlight as versatile ligands that stabilize intricate chemical structures of transition metal complexes,<sup>[2]</sup> nanoparticles,<sup>[3]</sup> and main-group elements.<sup>[4]</sup> Such NHC-supported systems often exhibit unique properties and stand out as, for example, unprecedented catalysts<sup>[5], [6]</sup> and highly emissive materials.<sup>[7]</sup> These important applications of NHCs have motivated various structural modifications to attain desired electronic<sup>[8]</sup> and steric properties.<sup>[9]</sup> In particular, as interest in transition metal complexes of NHCs has increased for the development of more efficient catalysts or light emitting devices, the control of their electronic parameters has also become important. In an effort to systematically modify these electronic parameters, groups as diverse as amino,<sup>[10]</sup> amido,<sup>[11],[12],[13]</sup> alkyl,<sup>[14],[16]</sup> and even entirely inorganic groups<sup>[17]</sup> have been installed in the NHC backbone.

The control of the electronic parameters of NHCs is strongly associated with the electronegativity and  $\pi$ -basicity of neighboring functional groups of the carbene carbon. For example, replacing the nitrogen atom adjacent to carbene center with less electronegative carbon atom increases HOMO energy level of

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NHCs.<sup>[14],[15],[18]</sup> Similarly, introducing less  $\pi$ -basic aryl<sup>[16]</sup> or amide<sup>[11],[12],[13]</sup> groups on carbene carbon decreases the LUMO energy level of NHCs. Combining both approaches, there have been efforts to develop NHCs with high HOMO energy and low LUMO energy levels, which can be considered ambiphilic NHCs. Utilizing these approaches, the electronic parameters of several NHCs have been successfully modified (**Figure 1**). Although the electronic properties of the NHCs were adjusted qualitatively, quantitative fine-tuning the electronic parameters of the NHCs were not demonstrated to date, possibly due to the difficulty of structural modification or synthetic limitation of the NHCs.



Figure 1. HOMO and LUMO energy levels (eV), and singlet-triplet transition energy ( $\Delta E_{ST}$ , kcal/mol) of selected NHCs calculated at the B3LYP/def2-TZVP level of theory.

A new class of ambiphilic NHCs with fine-tunable electronic parameters could be available from coumaraz-2-on-4-ylidene (1) (Figure 1). Note that salicylaldehyde, a starting material of 1 has the great advantage that it offers the chance to introduction a broad range of substituents on aryl ring. This synthetic advantage allows the quantitative and predictable fine-tuning of the electronic parameter of 1 according to the Hammett  $\sigma$  constant of the substituent.

The less  $\pi$ -basic carbamic and aryl group in **1** expectedly drives its LUMO down in energy to -2.43 eV, and so affords an exceptionally electrophilic carbene center in 1 - one even more so than that in the six-membered diamidocarbene (6-DAC, -2.20 eV) (Figure 1). At the same time, the HOMO of 1 (-5.96 eV) remains considerably higher than that of 6-DAC (-6.23 eV), and similar to that of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr, -5.96 eV), which is generally regarded as a potent nucleophile. These computed electronic characteristics of 1, together with the narrowest HOMO-LUMO gap and smallest  $\Delta E_{ST}$ among the NHCs synthesized so far, suggest that this new type of NHC might show unique ligand properties in transition metal complexes. Here we report the synthesis and characterization of precursors of 1 and their rhodium complexes in addition to their ambiphilic electronic properties demonstrated by <sup>77</sup>Se NMR chemical shifts and IR data.

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Scheme 1. Synthesis of substituted carbene precursor 1

The synthesis of 4-chloro-coumaraz-2-one (3), a precursor to 1, was carried out with a good isolated yield by a two-step procedure (**Scheme 1**), in which imine condensation of salicylaldehyde to salicylimine, also known as Schiff base (2), was followed by carbonylation with triphosgene and trimethylamine to give 3 after a simple purification. The procedure allows multigram scale synthesis, and accommodates well a number of substituents on the aryl and the carbamic *N*-group.

Owing to the electron-deficient nature of the coumaraz-2-one heterocycle, precursors 3 were isolated as neutral 4-chloro adducts - the form in which the Bielawski<sup>[12a, 12b]</sup> and Ganter<sup>[12c, 12d]</sup> groups reported their amidocarbene precursors. The structure of 4-chloro-coumaraz-2-one (3a) was elucidated by X-ray crystallographic analysis (see SI). The C-CI bond distance in 3a (1.854(1) Å) is closer to the average sp<sup>3</sup> C–Cl bond distance (ca. 1.76 Å)<sup>[19]</sup> than the C-Cl in 6-DAC•HCl (1.882(2) Å).<sup>[12b]</sup> Consistent with the LUMO energies computed for the free carbenes 1 and 6-DAC in Figure 1, the experimental C-CI distances suggest that the iminium precursor 1.H+ is likewise more electrophilic than 6-DAC•H<sup>+</sup>, and so binds the chloride at the 4-position of 1•H<sup>+</sup> more tightly. The presence of electron-donating groups in the para- aromatic positions of 3i' and 3j' expectedly reduces the electrophilicity of coumaraz-2-onium heterocycle, and permits dissociation of the chloride - at least in a dynamic, reversible process - as evidenced by the symmetric <sup>1</sup>H NMR spectra of 3i' and 3j' that feature only two methyl group resonances for the Dipp Pr groups in CDCI3. In contrast, the asymmetry of these Pr<sup>1</sup>H NMR resonances seen for 3a, 3e - 3h shows them to adopt neutral, 4-chloro-coumaraz-2-ones forms in  $CDCI_3$  and  $C_6D_6$  solutions.





Scheme 2. Attempted dehydrohalogenation of 3 and 4

To access a free carbene 1, we attempted the dehydrohalogenation of the precursors using sterically bulky strong bases (LiHMDS, KHMDS) (Scheme 2). However, for the N-aryl precursors (3a, 3b), only dimerized products 5 were observed, and were fully characterized (see SI). The dimerization of NHC is facile for free carbenes with a low  $\Delta E_{ST}^{[20]}$ , such as 5-DAC reported by Ganter.<sup>[12c, 12d]</sup> The *N*-alkyl precursors **3c**. **3d** gave only the Cl<sup>-</sup> metathesis products 6, analogous to those reported by Lassaletta<sup>[21]</sup> and Bertrand<sup>[22]</sup> groups for their NHCs. but considerably more stable to air and temperature. To prepare more acidic precursors, the Cl<sup>-</sup> in 2 was metathesized for OTf<sup>-</sup> to give ionic coumaraz-2-onium trflate 4a and 4c. Interestingly, the more acidic precursor 4a reacted by nucleophilic addition of the base at the 7-position of coumaraz-2-onium, to form the dearomatized product 7a which was isolated and characterized by X-ray crystallography (see SI). It is notable that a similar result was previously reported by the Bertrand group for their NHCs.[22]



Scheme 3. Trapping of [1] *in situ* (R = Dipp)

Although our attempts to produce free **1** in at least an observable form have yet to succeed, trapping experiments suggested that **1** might be forming *in situ* as a free NHC from the dehydrohalogenation of **3**. When treatment of **3** with LiHMDS at – 78 °C was followed by addition of addition of either isocyanate, elemental sulfur, or styrene, products **8**, **9**, or **10** were isolated in good yields (**Scheme 3**), and were also characterized by X-ray crystallography (see SI). However, the less sterically bulky *N*-alkyl

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precursors **3c** could not be trapped by the same method, giving instead the base adduct **6c**. This result stresses the importance of steric protection of 4-position in **3** to *in situ* generate free carbene **1**.



Figure 2. HOMO (in orange) and LUMO (in blue) energy levels of 1 vs the Hammett constant  $\sigma$  of the aromatic substituents R in 1 (calculated at B3LYP/def2-TZVP).

The extent of the substituent effect in the correlation of the HOMO and LUMO energy levels of **1** with their Hammett  $\sigma$  constants is presented in **Figure 2**. A linear relationship between frontier orbital energy levels of **1** and the  $\sigma$  constants of each substituent was successfully established.



Scheme 4. Synthesis of selenoketone 11, and their  $^{77}$ Se NMR chemical shifts and  $^{1}J_{C-Se}$  coupling constants

Furthermore, use of elemental Se to trap 1 in situ gave the respective selenoketone 11 (Scheme 4), whose <sup>77</sup>Se-NMR data offer useful experimental probes of the electronic characteristics of their parent free NHCs.<sup>[23]</sup> In particular, <sup>77</sup>Se-NMR chemical shifts were found to correlate with the LUMO,<sup>[23a]</sup> and  ${}^{1}J_{C-Se}$ coupling constants with the HOMO energies computed for the parent free NHCs.<sup>[23b]</sup> All of the selenoketone **11** showed highly deshielded <sup>77</sup>Se NMR resonances, to an extent exceeding that in selenoketones of 5- and 6-DAC (850 ppm, vs 1103 ppm for 11a, in  $d_6$ -acetone),<sup>[23b]</sup> and rivaling that of the selenoketone of a cyclic (alkyl)(amido)carbene (1179 ppm), which was known to be the most  $\pi$ -acidic NHC to date.<sup>[13c]</sup> As the shielding of Se in NHC=Se trends directly with the LUMO energy level computed for the parent free NHC (Figure 3 and Table S1), the <sup>77</sup>Se NMR data for 11 suggest their parent 1 to exhibit exceptionally high  $\pi$ -acidity – as gauged by its computed LUMO energy level, and to rival the highest  $\pi$ -acidity metrics found yet for NHCs.<sup>[13c]</sup> Better still, the  $\pi$ -acidity of NHCs based on **1** should be possible to vary in practice, both predictably and considerably, thanks to the ready selection of the aromatic ring substituents R in the synthesis of precursors **3** (Scheme 4 and Figure 3). However, contrary to the previous assertion of a link between the  ${}^{1}J_{C-Se}$  coupling constants in NHC=Se and the HOMO energy levels of the free NHCs, <sup>[23b]</sup> we observed that the  ${}^{1}J_{C-Se}$  values of **11** were all effectively constant (Scheme 4 and Figure S1).



**Figure 3.**  $\delta$ (<sup>77</sup>Se) (ppm, in *d*<sub>6</sub>-acetone) of NHC=Se (data for **11** are in orange, all typical NHC=Se including **11** are in blue) vs LUMO of the free NHCs (calculated at B3LYP/def2-TZVP).

To confirm the potential for the ligand application of transition metal complexes, the rhodium–1 complexes (12) were successfully synthesized by the reaction of *in situ* generated free carbene 1 with [Rh(cod)Cl]<sub>2</sub> (Scheme 5). The complexes were stable enough to be isolated by column chromatography. Complexes 12a and 12j exhibit <sup>13</sup>C-NMR peaks at 273.88 and 258.40 ppm in CDCl<sub>3</sub>, which are assigned as the electron deficient carbene carbons. The single crystal structures of 12a and 12j were also elucidated by X-ray crystallographic analysis (see SI).



Scheme 5. Synthesis of their (1,5-cyclooctadiene)rhodium chloride (12) and dicarbonyl complexes(13)

To investigate the electron donating effect of **1** using the average IR frequency  $(v^{av}_{CO})$  of rhodium carbonyl complexes, the complexes **13** were also prepared *via* carbon monoxide bubbling of **12**. The IR spectrum of **13a** exhibited two IR absorptions at 1992.9 and 2081.6 cm<sup>-1</sup> (ATR). The  $v^{av}_{CO}$  of **13a** is 2037.3 cm<sup>-1</sup>, which is larger than the value of cAAC (2035.5 cm<sup>-1</sup>), and smaller than that of regular NHCs (2040.5 cm<sup>-1</sup>).<sup>[24]</sup> Interestingly, the  $v^{av}_{CO}$  of **13j** is significantly reduced at 2035.2 cm<sup>-1</sup> (1993.6 and 2076.8 cm<sup>-1</sup> (ATR)) compared to the  $v^{av}_{CO}$  of **13a**, and even closer to the  $v^{av}_{CO}$  of cAAC. The result shows that the introduction of functional groups on the aryl ring can significantly change the ligand properties of carbenes. Interestingly, the  $v^{av}_{CO}$  of **13** is much lower

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than the  $v^{av}_{CO}$  of 5-DAC<sup>[12d]</sup> and 6-DAC<sup>[25]</sup> complexes (2060 cm<sup>-1</sup> and 2045 cm<sup>-1</sup>) even though their electrophilicity is similar. The result shows that the high nucleophilicity of **1** engenders an even more electron-rich transition metal center than DAC.

In summary, we have successfully designed and synthesized coumaraz-2-on-4-ylidene (1) precursors and their metal complexes. Furthermore, their electronic properties could be fully characterized by <sup>77</sup>Se-NMR and  $v^{av}_{CO}$  measurement. Although their narrow HOMO-LUMO energy gap and low singlet triplet transition energy prevents the isolation of 1 in solid form, the solution of 1 could be generated *in situ*, leading to the synthesis of small molecule adducts and even metal complexes. We expect to be able to isolate the 1 using other strategies such as reductive generation of free carbene<sup>[12f]</sup>, which do not include any proton.<sup>[20]</sup> Currently, such attempts are under investigation. We believe that these new ambiphilic NHCs offer exciting new applications for both small molecules' activation and transition metal catalysis.

#### Acknowledgements

This work was supported by Institute for Basic Science (IBS) [IBSR007-D1] and a National Research Foundation of Korea (NRF) grant funded by the Korean government [Ministry of Science, ICT and Future Planning (MSIP)] (No. NRF-2016H1A2A1907122 – Global Ph.D. Fellowship Program). The X-ray crystallography analysis with synchrotron radiation was performed at the Pohang Accelerator Laboratory (PLS-II BL2D SMC beamline). We thank Dr. Gregory B. Boursalian and Dr. Dmitry V. Yandulov for helpful discussions.

**Keywords:** Carbene ligand • Ligand design • Main group elements • N-heterocyclic carbene • Transition metal complex

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Coumaraz-2-on-4-ylidene

- $\checkmark$  Practical synthetic method
- ✓ Strong σ-basicity and  $\pi$ -acidity
- ✓ Tunable electronic structure

Coumaraz-2-on-4-ylidene, as a new ambiphilic *N*-heterocyclic carbene platform, is reported. The precursors were synthesized from various functionalized Schiff bases in a practical and scalable manner. Due to the synthetic advantage, electronic properties of coumaraz-2-on-4-ylidene can be also easily fine-tuned in quantitative and predictable way, as proved by the Hammett  $\sigma$  constants of the functional groups on aryl ring.

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