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Communication

An Air-Stable "Masked" Bis(imino)carbene: A Carbon-Based Dual Ambiphile

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ABSTRACT: Carbenes, once considered laboratory curiosities, now serve as powerful tools in the chemical and material sciences. To date, all stable singlet carbenes are single-site ambiphiles. Here we describe the synthesis of a carbene which is a carbon-based *dual* ambiphile (both single-site *and* dual-site). The key is to employ imino substituents derived from a cyclic (alkyl)(amino)carbene (CAAC), which imparts a 1,3-dipolar character to the carbene. Its *dual* ambiphilic nature is consistent with the ability to activate simple organic molecules in both 1,1- and 1,3-fashion. Furthermore, its 1,3-ambiphilicity facilitates an unprecedented reversible intramolecular dearomative [3 + 2] cycloaddition with a proximal arene substituent, giving the carbene the ability to "mask" itself as an air-stable cycloadduct. We perceive that the concept of *dual* ambiphilicity opens a new dimension for future carbene chemistry, expanding the repertoire of applications beyond that known for classical single-site ambiphilic carbenes.

Carbenes are an intriguing class of neutral organic molecules featuring a divalent carbon atom.[1] With only six valence electrons, they defy the octet rule. While the parent carbene (H_2C:) has a triplet ground state and is only stable in interstellar medium, amino and phosphino carbenes have a singlet ground state which permits their isolation under standard laboratory conditions.[2,3] With regards to their reactivity and applications, stable singlet carbenes are classical single-site ambiphiles, with both donor and acceptor orbitals on the carbene center (Figure 1, top).[4] This feature was highlighted in 2007, when our group demonstrated that a cyclic (alkyl)(amino)carbene (CAAC) can split H_2 across a single carbon center,[5] drawing analogy to the oxidative addition chemistry of transition metals.[6]

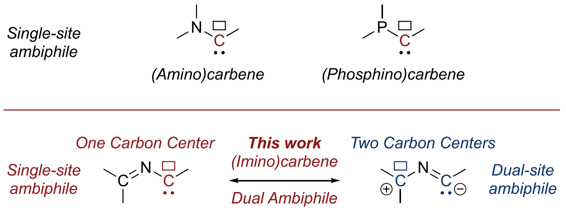

Figure 1. Amino and phosphino carbenes are archetypical single-site ambiphiles (top). Present work on an (imino)carbene which is a carbon-based *dual* ambiphile (bottom).

Another nitrogen-based substituent, which has never been employed in carbene chemistry, is the imino group. Its unsaturated nature allows for an allylic-type delocalization to a 1,3-dipolar resonance form (Figure 1, bottom). Strongly polarized zwitterions with separated donor and acceptor sites can act as dual-site ambiphiles.[7] Hence, we reasoned that (imino)carbenes could exhibit ambiphilicity based on both one carbon center *and* two carbon centers, a feature which is to date unknown in organic chemistry.[8]

N-Heterocyclic imines (NHIs)[9] derived from conventional N-heterocyclic carbenes (NHCs)[10,11] are powerful 2σ, 4π electron donor ligands with a large steric profile. NHIs have recently received significant attention due to their ability to stabilize a wide range of highly electron-deficient main group systems.[12−26] However, the moderate electrophilic properties of these NHIs limit them to being purely Lewis basic ligands. On the other hand, CAACs have higher nucleophilicity than NHCs, but are immensely more electrophilic,[27−29] leading us to believe that an NHI based on a CAAC might be a suitable donor to tame an (imino)carbene, but at the same time possess sufficient electrophilicity to act as a secondary Lewis acidic site.[30] Herein, we disclose a bis(imino)carbene (with CAAC-based NHIs) which possesses a *dual* ambiphilic nature—both single-site *and* dual-site reactivity (Figure 1, bottom). Its unique 1,3-ambiphilic character facilitates a reversible intramolecular dearomative [3 + 2] cycloaddition with a proximal arene substituent, giving the carbene the ability to "mask" itself as an air-stable cycloadduct.

The conjugate acid (**1-HOTf**) of the desired carbene **1** was readily obtained by reaction of [$^{\mathrm{Me}}$**CAACBr**]**Br** with formamidine hydrochloride in the presence of excess triethylamine, followed by anion exchange (Scheme 1). Treating **1-HOTf** with K[N($SiMe_3$)$_2$] in THF at −78 °C immediately afforded a bright yellow solution, which decolorized upon warming to room temperature. Variable temperature NMR monitoring revealed the initial formation of the target bis(imino)carbene **1**, which is stable up to −20 °C. The ^{1}H

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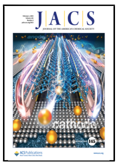

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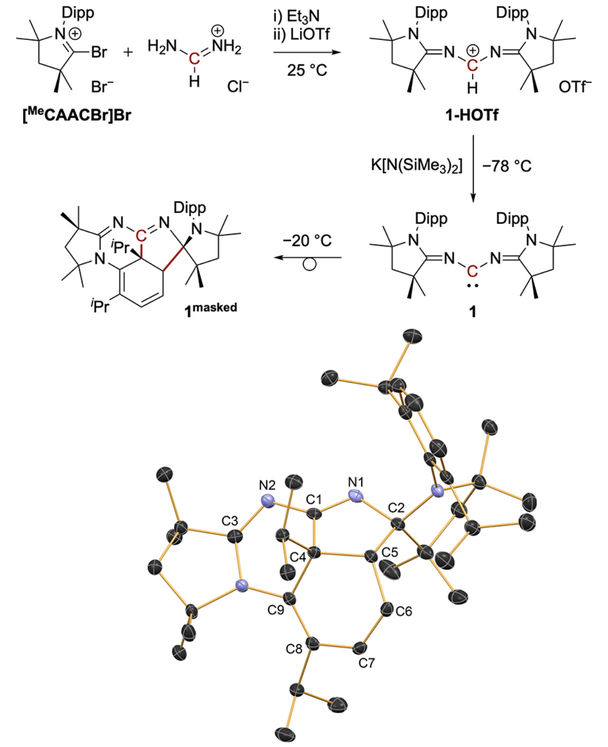
Scheme 1. Synthesis of Bis(imino)carbene 1, its Isomerization to 1^{masked}, and Solid-State Structure of 1^{masked}



NMR spectrum displays only one set of signals associated with the two NHI units. The characteristic carbene signal appears at 234.9 ppm in the $^{13}C\{^1H\}$ NMR, in excellent agreement with DFT calculations (233.8 ppm). This shift falls between those of CAACs (ca. 310 ppm)[31] and NHCs (ca. 210 ppm),[32] and is slightly upfield-shifted compared to acyclic $(^iPr_2N)_2C$: (255.5 ppm).[33] Above −20 °C, **1** rearranges quantitatively to an unsymmetrical species with two inequivalent NHI units. Single crystals of this isomer were obtained by slow evaporation of a benzene solution at room temperature. X-ray diffraction analysis revealed the polycyclic compound **1**^{masked}, resulting from a [3 + 2] cycloaddition involving the dearomatization of a Dipp (2,6-diisopropylphenyl) substituent (Scheme 1). Non-activated arenes generally do not participate in cycloaddition chemistry without photochemical activation or transition metal mediation,[34] with the exception of transient *triplet* carbenes[35,36] or extremely ambiphilic main group centers (B, Al, Si, P).[23−25,37−45] Hence, bis(imino)carbene **1** represents the first *singlet* carbene able to thermally activate an inert arene ring.

This unprecedented behavior led us to perform DFT analysis to gain further insights. Interestingly, while the HOMO of **1** is centered on the central carbene carbon, the LUMO is a π-type orbital with contributions from the carbene carbon and the peripheral CAAC carbon atoms, supporting the notion of having both carbene-centered and CAAC-centered acceptor sites (Figure 2a). The effect of having strong donor NHI substituents on bis(imino)carbene **1** is reflected by the very high HOMO energy level relative to those of other nucleophilic carbenes such as **CAAC** and acyclic di(amino)-carbenes **ADAC**. In fact, its donor strength even exceeds that of carbones, e.g., carbodiphosphorane **CDP**, which formally feature a zerovalent carbon atom bearing two electron lone pairs.[46] As such, we set out to determine experimentally the basicity of bis(imino)carbene **1**. Our group recently reported a systematic approach to scale carbene Brønsted basicity by proton exchange between the carbene conjugate acid and a neutral organic superbase.[47] While **1-HOTf** could be cleanly deprotonated by the Schwesinger phosphazene $((Me_2N)_3PN)_3PN^tBu$, an equilibrium was established with the cyclic bent allene $(PhN(XyO)C)_2C$, while the carbone $(Ph_3P)_2C$ was unable to deprotonate **1-HOTf**. These investigations suggest that **1** has a pK_a value between 34.4 and 37.7 in acetonitrile, ranking it among the most basic carbenes and organic superbases.

We next turned our attention to elucidating the mechanism of the [3 + 2] cycloaddition. Computations suggest a two-step

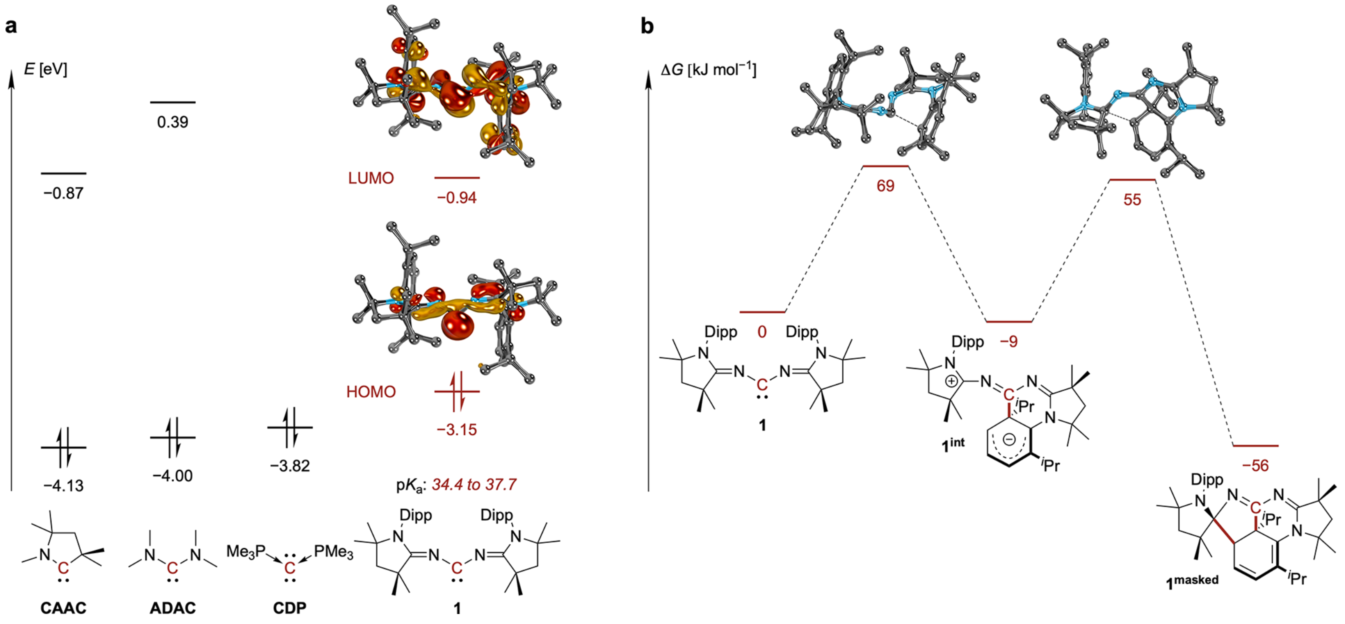
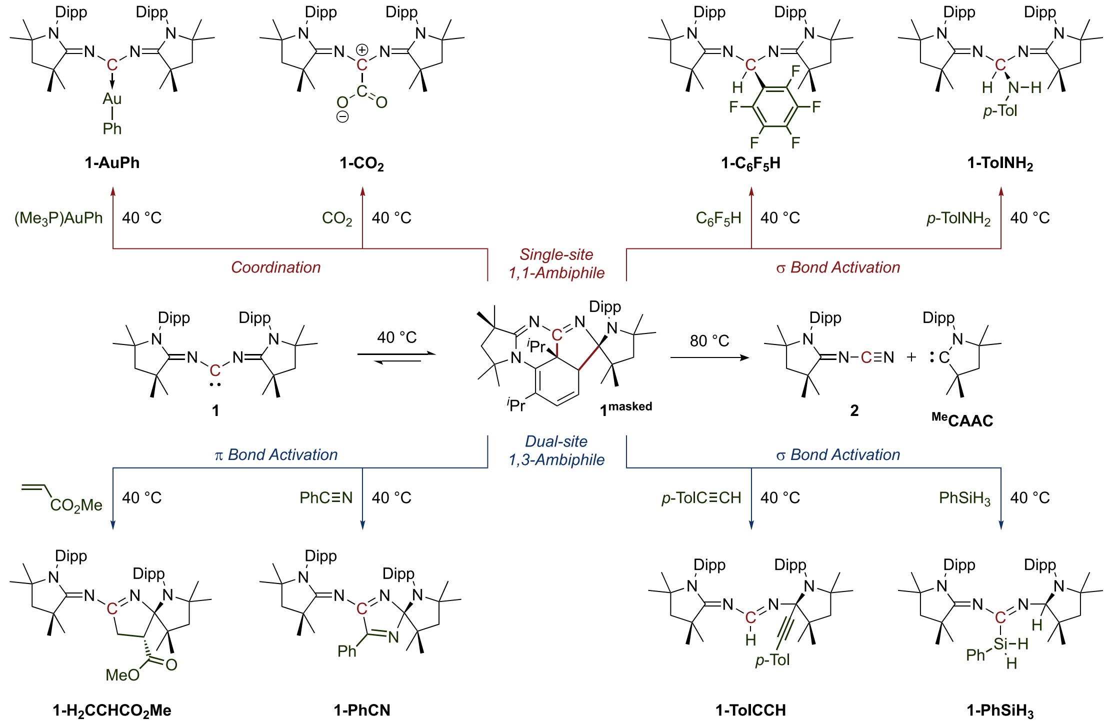


Figure 2. (a) Calculated HOMO and LUMO energy levels of **1** with comparisons to representative carbene and carbone systems (r^{2}SCAN-3c). (b) Calculated mechanism of the dearomative [3 + 2] cycloaddition of **1** to **1**^{masked} (DLPNO-CCSD(T)(CPCM=THF)/def2-TZVPP//r^{2}SCAN-3c).

Scheme 2. Reactivity of "Masked" Carbene 1^{masked} as a Carbon-Based *Dual* Ambiphile



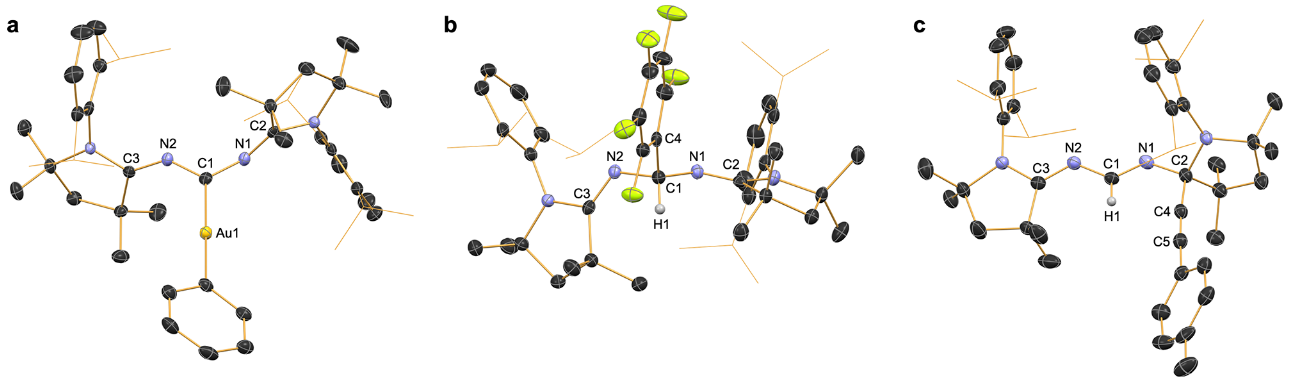


Figure 3. Solid-state structures of **1-AuPh** (a), **1-C_6F_5H** (b), and **1-TolCCH** (c). Thermal ellipsoids set at 50% probability. For clarity, H atoms are omitted and ^{i}Pr groups are simplified as wireframes.

closed-shell process (Figure 2b). First, **1** undergoes a dearomative nucleophilic attack on the *ortho* position of the Dipp to form the zwitterionic Meisenheimer-type intermediate $\mathbf{1}^{int}$.[48] Subsequent charge recombination between the *meta* position of the Dipp and the CAAC carbon closes the ring to afford $\mathbf{1}^{masked}$. The small activation barrier (69 kJ mol^{-1}) associated with the initial dearomatization event is a manifestation of the pronounced nucleophilic character of **1**.

Reversible bond activation plays a central role in transition metal catalysis. Recently, a few reports have emerged showing that highly ambiphilic main group systems can not only activate inert arenes but also do so in a reversible fashion.[23−25,42−45] DFT analysis suggested that the energy difference between **1** and $\mathbf{1}^{masked}$ was only 56 kJ mol^{-1}, and that the barrier for rearomatization of $\mathbf{1}^{masked}$ to **1** was 125 kJ mol^{-1}, hinting at the possibility of regenerating **1** by cycloreversion (Figure 2b). Hence, we set out to confirm the equilibrium between $\mathbf{1}^{masked}$ and **1**. Treating $\mathbf{1}^{masked}$ at 40 °C with $(Me_3P)AuPh$, a transition metal complex well-known to react with nucleophilic carbenes,[10] led to the quantitative conversion of $\mathbf{1}^{masked}$ to a new species with equivalent NHI units (Scheme 2). In the $^{13}C\{^1H\}$ NMR spectrum, a diagnostic signal at 220.3 ppm was observed, which is slightly upfield-shifted with respect to "free" carbene **1** (234.9 ppm). X-ray diffraction analysis confirmed the formation of bis(imino)-carbene-gold complex **1-AuPh** (Figure 3a). Hence, $\mathbf{1}^{masked}$ acts as a surrogate of "free" carbene **1** and consequently can be regarded as a "masked" carbene.

The utility of $\mathbf{1}^{masked}$ as a "masked" bis(imino)carbene is not limited to the formation of transition metal complexes, but can also be harnessed for the σ bond activation of simple organic molecules. Gentle heating of $\mathbf{1}^{masked}$ at 40 °C in the presence of C_6F_5H and p-$TolNH_2$ led to single-site C−H and N−H bond insertions, affording 1,1-addition products **1-C_6F_5H** (Figure 3b) and **1-$TolNH_2$** respectively, highlighting the carbene character of **1** (Scheme 2). Interestingly, with *p*-TolCCH and $PhSiH_3$, nonclassical C−H and Si−H dual-site 1,3-addition products **1-TolCCH** (Figure 3c) and **1-$PhSiH_3$** were obtained respectively (Scheme 2). This reactivity suggests that the secondary acceptor site on the CAAC carbon is more sterically hindered, allowing exclusively small anionic fragments such as *p*-TolCC$^-$ and H$^-$ to slip in. Overall, we show that **1**$^{\text{masked}}$ is amenable toward C−H bond activation in both single- *and* dual-site fashion, with selectivity governed by the substrate size (C_6F_5H versus *p*-TolCCH). Moreover, for the dual-site activation of *p*-TolCCH and $PhSiH_3$, the position of the H atom (carbene- versus CAAC-center) is determined by its protic or hydridic nature, in line with frustrated Lewis pair systems.[49]

We then turned our attention to *π* bond activation. While carbenes are known to undergo [2 + 1] cycloaddition with alkenes, **1**$^{\text{masked}}$ undergoes a nonclassical [3 + 2] cycloaddition with methyl acrylate at 40 °C to afford **1-H$_2$CCHCO$_2$Me** as a single diastereomer, which was confirmed by X-ray diffraction analysis (Scheme 2). Arguably, this stems from the preference of **1** to form a five-membered ring instead of a strained three-membered ring. Notably, such a reactivity pattern resembles nitrile ylides, which are highly reactive species that participate in 1,3-dipolar cycloaddition reactions.[50] The 1,3-*π* bond activation can also be extended to the triple bond of benzonitrile to afford **1-PhCN**, which was characterized by X-ray diffraction spectroscopy (Scheme 2). While nitriles are generally considered to be electron-rich species which undergo electrophilic activations, the facile nature of the cycloaddition with benzonitrile reflects the exceptionally strong nucleophilic character of bis(imino)carbene **1**.

To date, only one type of air-stable carbene has been reported, which is based on the NHC scaffold.[51] Its stability has been attributed to the strong electronic perturbation by the two halogen atoms at the 4, 5-position of the imidazole ring, with the overall effect of sharply reducing the carbene's basicity *and* electrophilicity, hence attenuating its reactivity. To evaluate the air stability of **1**$^{\text{masked}}$, we exposed a powder sample to air and moisture at room temperature. Impressively, no sign of decomposition was observed by ^{1}H NMR even after a month, reflecting its air-stable nature, despite **1** being superbasic. **1**$^{\text{masked}}$ also appears to be remarkably air-persistent in C_6D_6, with a half-life of 13 h. Importantly, subjecting **1**$^{\text{masked}}$ to CO_2 (1 bar) at 40 °C in the presence of air and moisture quantitatively afforded **1-CO$_2$** as confirmed by X-ray crystallography, thereby establishing its status as an air-stable carbene surrogate (Scheme 2).[52] Next, we set out to probe its thermal stability. Heating **1**$^{\text{masked}}$ at 80 °C for 1 h led to its conversion to NHI-substituted nitrile **2** and $^{\text{Me}}$**CAAC** (Scheme 2). This presumably involves the cycloreversion of **1**$^{\text{masked}}$ to **1**, followed by cheleotropic fragmentation to **2** and $^{\text{Me}}$**CAAC**. Notably, this process is reminiscent of the release of N_2 from diazoalkanes in the generation of transient carbenes.

In conclusion, we disclose the synthesis of the acyclic bis(imino)carbene **1**, which is a carbon-based *dual* ambiphile. Its unique 1,3-ambiphilic nature facilitates an unprecedented intramolecular dearomative [3 + 2] cycloaddition with the proximal Dipp group to furnish **1**$^{\text{masked}}$, which is air-stable in the solid state despite its superbasic nature. Importantly, this process is fully reversible, and cycloreversion to regenerate "free" carbene **1** proceeds under mild conditions. This allows **1**$^{\text{masked}}$ to be directly employed as an air-stable "masked" carbene, providing access to coordination compounds, and elicit both single- *and* dual-site activation of simple organic substrates, showcasing its *dual* ambiphilic nature. We perceive that our present strategy opens an avenue to discover new carbene reactivity and applications beyond that known for classical single-site ambiphilic carbenes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c12847.

General methods and materials, experimental procedures and characterization data, X-ray structure determination, computational details, NMR spectra, and crystallographic data (PDF)

Accession Codes

CCDC 2215574−2215580 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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