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Perspective

Singly and doubly oxidized carbenes and their applications in catalysis

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THE BIGGER PICTURE As organic compounds, singly and doubly oxidized carbenes possess the potential to address some of the drawbacks of current transition metal catalysis technology. Indeed, these compounds are less toxic and possibly less expensive than organometallic complexes (metal + ligand), at least at the academic and commercial research and development (R&D) levels, where the precious metals are not recovered. Moreover, the extraction and purification of precious metals is environmentally unfriendly, as it generates greenhouse gases. Another societal factor, which should not be neglected, is the human exploitation often associated with mining activity.

SUMMARY

Over the last three decades, the highly tunable properties of N-heterocyclic carbenes (NHCs) and other stable singlet carbenes have led to a variety of applications. This perspective shows a novel facet of carbenes—i.e., their reductive properties—that allows them to function as catalysts in single-electron transfer (SET) reactions. The isolation and even the spectroscopic characterization of a singly oxidized carbene have yet to be done, but these species readily abstract hydrogen atoms while giving back the carbene conjugate acid, which behaves as the resting state of catalytic cycles. In sharp contrast, a doubly oxidized carbene has been isolated, and there is a strong likelihood that many other carbene dications will be isolated. Their first Lewis acidity is very high, suggesting possible applications in Lewis acid catalysis.

INTRODUCTION

Although the octet rule was formulated by Lewis in 1916,[1] Gomberg had already reported the trityl radical **A** in 1900,[2] and von Bayer and Villiger had isolated the trityl carbocation **B** in 1902.[3] These compounds feature a three-coordinate carbon with only seven and six valence electrons, respectively (Figure 1). Almost a century later, another type of six-valence-electron two-coordinated carbon species, namely carbenes **C** and **D**, were isolated.[4–6] The hunt for stable electron-deficient species has not been limited to carbon. Considering only the second-row elements, nitrenium **E**[7] and singlet and triplet nitrenes **F**[8] and **G**[9] have also recently been isolated. Initially considered to be laboratory curiosities, these species currently rank among the most powerful tools in organic chemistry, with numerous applications in commercially important processes.[10] As an illustration, Herzberg and Olah received the Nobel Prize for the applications of radicals and carbocations, respectively. There are still many families of low-valent compounds that have yet to be isolated, either because they are perceived as fundamentally unstable or because they have eluded the synthetic skills of chemists. Can we undress carbon even more, as shown by **H** and **I**, which are formally singly and doubly oxidized carbenes? Can these species find applications in catalysis? This perspective summarizes what is known so far. Note that the myriad of papers dealing with oxidative N-heterocyclic carbene catalysis via single-electron transfer (SET) mechanisms involving Breslow intermediates are outside the scope of this article.[11–14]

A careful examination of the literature shows that there are only a few papers reporting attempted preparations of singly oxidized carbenes, and some of them have been debated. In 2004, Clyburn et al.[15,16] investigated the oxidation of two imidazol-2-ylidenes $\mathbf{NHC_{a,b}}$[17](Figure 2). Cyclic voltammetry showed irreversible oxidations at 1 and −30 mV, respectively, vs. SCE when oxidized using a glassy carbon electrode. The authors noted that the values of the potentials had to be taken with precaution due to possible side reactions of the carbenes with the solvent and electrolyte. Using tetracyanoethylene (TCNE) as a chemical oxidant, they observed the formation of salts $\mathbf{NHC_{a,b}\text{-}NHC_{a,b}}^{++}$, apparently formed by the dimerization of the desired carbene radical cations $\mathbf{NHC_{a,b}}^{+\bullet}$. Later on, Dutton et al.[18] postulated the formation of the same dicationic dimer when using

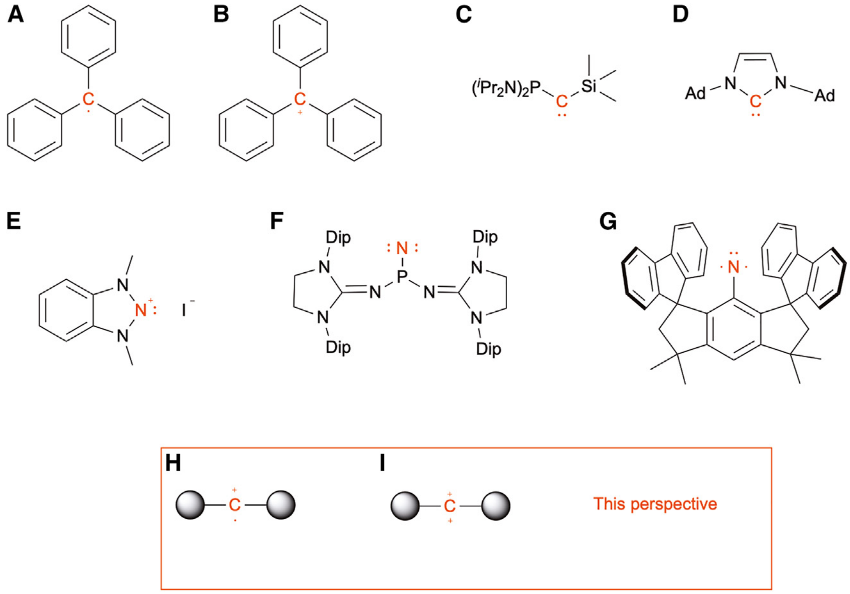

Figure 1. Some electron-deficient species

Selected examples of isolated low-valent carbon- and nitrogen-containing compounds (A–G) and singly and doubly oxidized carbenes (H and I).

PhI(OTf)$_2$ as the oxidant. Interestingly, when ferrocenium [Cp$_2$Fe]$^+$ was the oxidant, the major compound appeared to be the protonated carbenes **NHC$_{a,b}$-H$^+$**, with no traces of dimers.

Clyburn et al.[15] postulated that the difference was due to the reaction being heterogeneous and slow. Under these conditions, the concentration of carbene radical cations remains low, slowing the rate of dimerization. Instead, the abstraction of a hydrogen atom from the solvent or other sources occurred.

In 2020, Severin et al.[19] reported that a slightly different imidazol-2-ylidene (**NHC$_c$**) reacted with NOSbF$_6$, also leading to the protonated carbene **NHC$_c$-H$^+$**. More interestingly, they also reacted **NHC$_c$** with the trityl cation. In toluene at −40°C, adduct **NHC$_c$-Trit**[20] was formed in nearly quantitative yield, whereas at room temperature, two additional products were observed, namely the protonated carbene **NHC$_c$-H$^+$** and triphenyl methane. These results were rationalized by a SET reaction, as the formation of

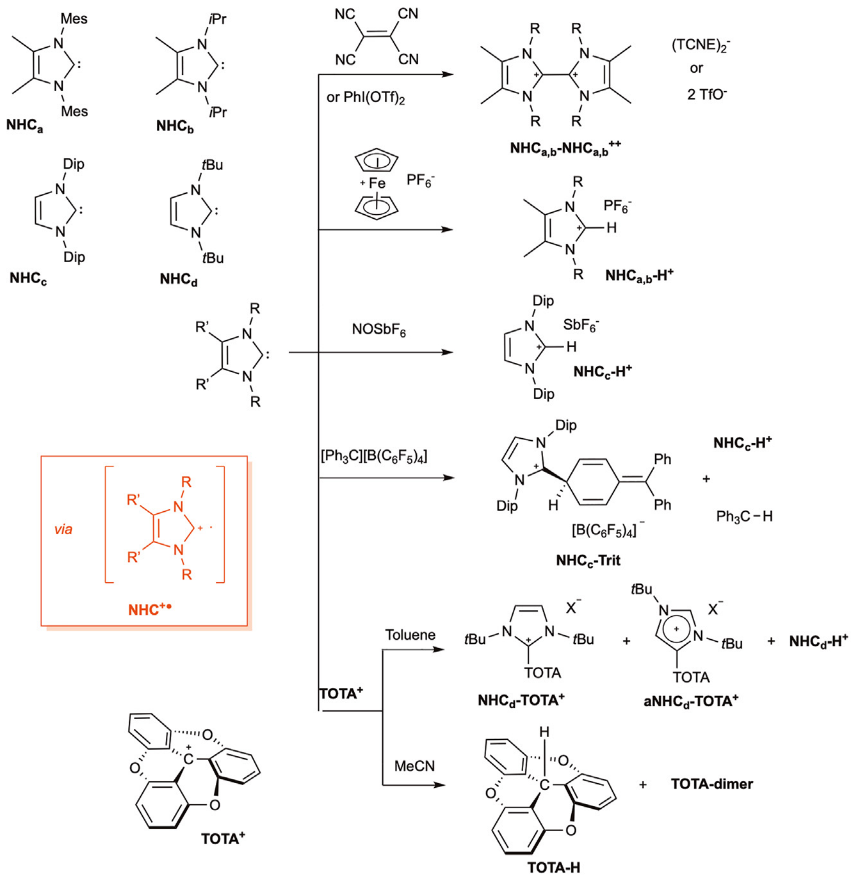

Figure 2. Attempted single-electron oxidation of imidazol-2-ylidenes

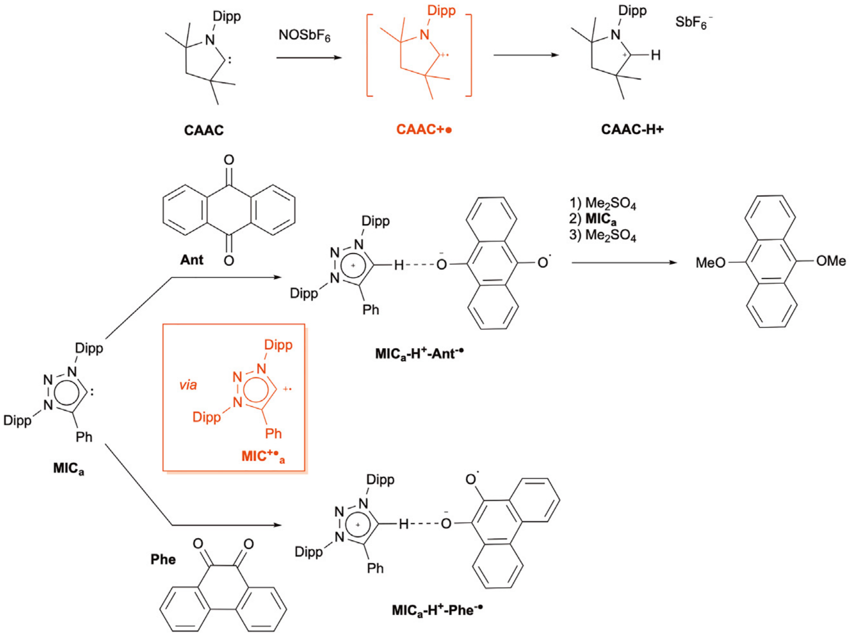

Figure 3. Attempted single-electron oxidation of CAAC and MIC

NHC$_c$-H$^+$ and triphenylmethane could come from the abstraction of an H atom from the solvent by **NHC$_c$$^{+\bullet}$** and Ph$_3C^\bullet$, while **NHC$_c$-Trit** could result from the cross-coupling of the carbene radical cation **NHC$_c$$^{+\bullet}$** with the trityl radical, in agreement with the behavior of the Gomberg radical. When the reaction was performed at room temperature and monitored by ultraviolet-visible spectroscopy (UV-vis), they observed a gradual decrease of a band at 438 nm, attributed to the trityl cation, and the appearance of two new bands at 343 and 591 nm. The former is indicative of the presence of the trityl radical. The latter vanished after 1 min and was tentatively attributed to the desired carbene radical cation **NHC$_c$$^{+\bullet}$**. EPR experiments confirmed the presence of the trityl radical, but **NHC$_c$$^{+\bullet}$** was not observed. Importantly, Severin et al. noted that when the reaction between **NHC$_c$** and the trityl salt was carried out in the presence of a better hydrogen donor, such as THF, the cross-coupling adduct **NHC$_c$-Trit** was not formed; instead, hydrogen atom abstraction occurred, leading to the carbene conjugate acid **NHC$_c$-H$^+$** along with a stoichiometric amount of Ph$_3$CH. In 2023, Song and Lee[21] revisited these results and showed that the UV band at 591 nm was not due to the carbene radical cation **NHC$_c$$^{+\bullet}$** but instead originated from a zwitterionic intermediate, resulting from the deprotonation of **NHC$_c$-Trit,** which appeared to be a strong single-electron donor. Moreover, using tetrahydrofuran-d^8 as a deuterium atom donor, no deuterated **NHC$_c$-H$^+$** was observed, implying that the latter was not formed via hydrogen atom abstraction by transient **NHC$_c$$^{+\bullet}$** from the solvent. They proposed that **NHC$_c$-H$^+$** comes from the deprotonation by the NHC of the initially formed **NHC$_c$-Trit** adduct by remaining free NHC. They concluded that the observations reported by Severin et al. do not involve the carbene radical cation **NHC$^{+\bullet}$$_c$**, nor a SET process, but rather an ionic pathway.

In 2021, Gianetti et al.[22] reported the reaction between **NHC$_d$** and trioxatriangulenium (TOTA+) as an oxidant. In toluene, they observed the formation of the NHC conjugate acid **NHC-H$^+$$_d$** and adducts **NHC$_d$-TOTA$^+$** and **aNHC$_d$-TOTA$^+$**, which, according to the authors, correspond to the homolytic cross-coupling product following a SET process. When the reaction was carried out in acetonitrile, they obtained again **NHC-H$^+$$_d$** but also **TOTA–H** and **TOTA-dimer**. Note that neither **TOTA-radical** nor the putative carbene radical cation **NHC$_d$$^{+\bullet}$** could be observed by EPR or UV-vis spectroscopy.

In 2022, Braunschweig et al.[23] reported that the oxidation of cyclic(alkyl)(amino) carbene (**CAAC**)[24,25] by NOSbF$_6$ at −78°C led to a pink solution, with the color persisting at this temperature. At room temperature, they isolated the CAAC conjugate acid **CAAC-H$^+$**, resulting from hydrogen abstraction (Figure 3). The high reactivity of **CAAC$^{+\bullet}$** in terms of hydrogen abstraction is supported by the high CH bond dissociation enthalpy (BDE) of **CAAC-H$^+$** of about 114 kcal mol^{-1}. The authors observed a transient weak three-line EPR spectrum with a g-factor of 2.0043 and a ^{14}N hyperfine splitting (hfs) of a(^{14}N) = 5.9 G, which they initially attributed to the desired **CAAC$^{+\bullet}$**. However, a few months later, they published a correspondence[26] stating that the EPR parameters, in particular the g-factor, could not be in agreement with the proposed radical cation (**CAAC$^{+\bullet}$**) and that they were not able to identify the paramagnetic species. Interestingly, they rightly concluded their correspondence by writing that "the formation of radical cation **CAAC$^{+\bullet}$** as a transient intermediate from the CAAC under one-electron oxidation is unambiguous."

Even more recently, our group[27] attempted the preparation of a carbene radical cation based on a 1*H*-1,2,3-triazol-5-ylidene (**MIC$_a$**),[28,29] using phenanthrenequinone and anthraquinone as oxidants. Both reaction mixtures quickly turned deep purple, and after workup, **MIC$_a$-H$^+$-Phe**$^{-\bullet}$ and **MIC$_a$-H$^+$-Ant**$^{-\bullet}$ salts were isolated in nearly quantitative yields (Figure 3). Their paramagnetic nature was evidenced by EPR spectroscopy, and their structure was confirmed by single-crystal X-ray crystallography. These results confirm that **MIC**$_a$ was oxidized into the corresponding **MIC**$_a$$^{+\bullet}$. However, we were unable to characterize this radical cation. **MIC**$_a$$^{+\bullet}$ was likely instantaneously converted into **MIC$_a$-H$^+$** via an H-atom transfer likely from tetrahydrofuran (BDE = 92 kcal mol^{-1}),[30] as in prior reports on carbene radical cations. Note that even at higher temperatures, the second reduction of the quinones by free **MIC$_a$** did not occur. Similar observations have been made by Thorley et al. for the reduction of quinones by lithium diisopropylamide (LDA).[31] This is not surprising since calculations predicted that the first reduction of the quinone is exothermic by 23.76 kcal mol^{-1}, while the second is

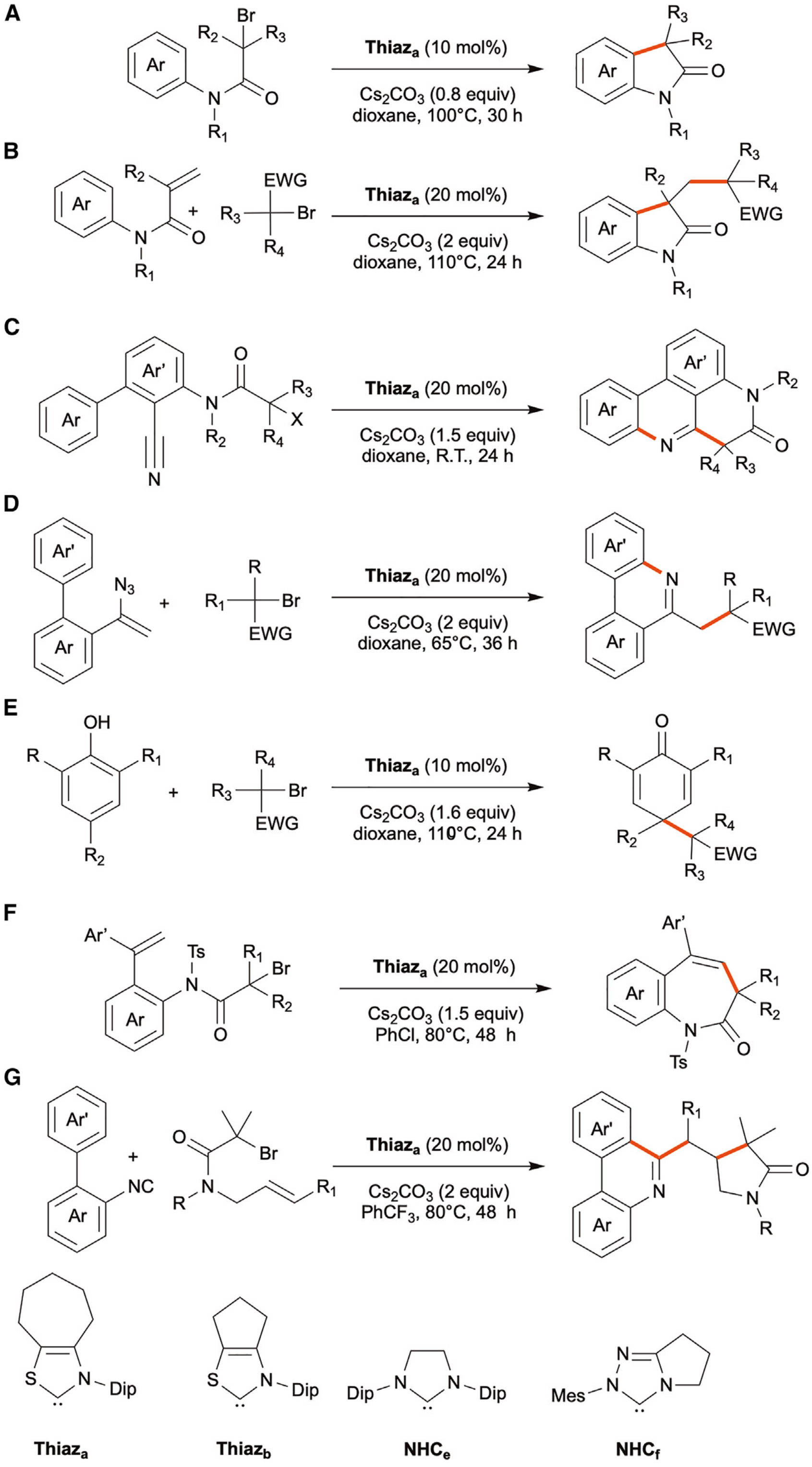

Figure 4. NHC-catalyzed SET reactions

endothermic by 14.32 kcal mol^{-1}. However, it has been shown that the corresponding neutral radical obtained by the addition of an electrophile to the anionic semiquinone radical can be readily reduced by LDA to the doubly reduced hydroquinone. Similarly, we reacted **MIC$_a$-H$^+$-Ant$^{-\cdot}$** with Me$_2$SO$_4$ and then added a second equivalent of **MIC**$_a$, followed by a second equivalent of Me$_2$SO$_4$, and we observed the formation of 9,10-dimethoxyanthracene, which was isolated in 30% yield.

The results summarized above clearly indicate that the isolation and even the spectroscopic characterization of a carbene radical cation have yet to be achieved. Nevertheless, there is no doubt that these five-valence-electron carbon species can be transiently generated. In most cases, they abstract an H atom to give the protonated carbene. Further studies are necessary to determine the source of hydrogen, as the use of deuterated solvents such as d^8-THF has not been conclusive. Nevertheless, these results inspired us and others to use carbenes as catalytic organic reducing agents without the need of a photocatalyst.[32],[33] Note that several organic neutral superelectron donors acting as stoichiometric reducing agents are known.[34–36] However, it was only in 2019 that Murphy et al.[37] published a seminal paper entitled "Neutral Organic Super Electron Donors Made Catalytic."

The first report on the NHC-catalyzed SET reaction was published by Wang and Liu in 2021.[38] They showed that in the presence of 10 mol % thiazolylidene **Thiaz$_a$** and 0.8 equiv of cesium carbonate, α-bromoamides were converted into a variety of oxindoles after 30 h at 100°C in good to excellent yields (Figure 4A). Following this initial report, Wang et al. expanded this chemistry. First, they reported an intermolecular version that allowed for the preparation of oxindoles featuring a quaternary carbon center (Figure 4B).[39] Interestingly, during the optimization process, they observed that the transformation was highly dependent on the nature of the carbene. Good yields were obtained with thiazolylidenes **Thiaz$_{a,b}$**, but no reaction was observed with the imidazolin-2-ylidene **NHC$_e$**. Using a similar approach, the same group reported the elegant preparation of highly functionalized N-polyheterocycles (Figure 4C),[40] as well as rapid access to phenanthridines from vinyl azides,[41] employing again thiazolylidene **Thiaz$_a$** as catalyst (Figure 4D). In the latter paper, the key

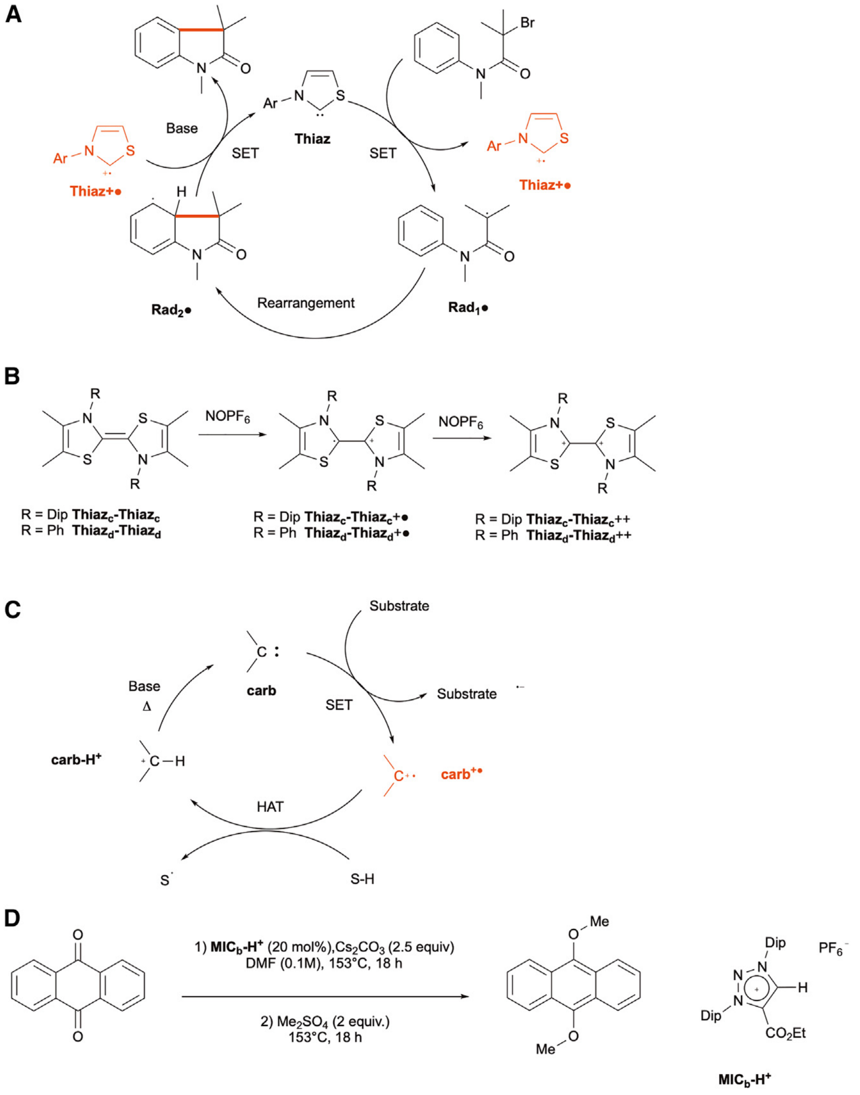

Figure 5. Mechanistic studies

(A) Mechanism of the NHC-catalyzed α-bromoamide single-electron reduction by Wang.

(B) Singly and doubly oxidized thiazol-2-ylidene dimers reported by Martin et al.[48]

(C) Our postulated mechanism for carbene-catalyzed single-electron reduction.

(D) MIC-catalyzed bis-reduction/methylation of quinones.

step is the alkyl radical addition to the vinyl azide inducing N_2 elimination and formation of an iminyl radical. These radicals have often been used for the synthesis of phenanthridines.[42] It is interesting to note that, once again, imidazol-2-ylidenes (**NHC$_e$**) do not catalyze this reaction. Lastly, Wang et al. found that the **Thiaz$_a$**-catalyzed SET reaction allowed for the dearomatization of phenol, with concomitant formation of a quaternary carbon center using simple α-bromo esters and also other α-bromo substrates with other functional groups, such as ketone, cyano, and nitro moieties (Figure 4E).[43] Zhou et al. extended the scope of these SET reactions further to the preparation of benzazepine derivatives (Figure 4F)[44] and, later, to 2-pyrrolidinone-functionalized phenanthridines via the tandem cyclization/addition/cyclization reaction of 2-isocyanobiaryls and α-bromo-N-cinnamylamides (Figure 4G).[45] For both processes, they found that **Thiaz$_{a,b}$** were much more efficient than imidazol-2-ylidene (**NHC$_e$**) and 1,2,4-triazolylidene (**NHC$_f$**).

All the aforementioned NHC-catalyzed SET reactions benefit from straightforward procedures and good functional group tolerance and, in most cases, can be performed at the gram scale. However, the postulated mechanisms of these reactions are highly debatable. Wang et al.[38–41,43] and Zhou et al.[44,45] proposed that in all cases, the mechanism involved two SET processes. As exemplified with α-bromoamides, **Thiaz** engages in an initial SET that affords the aryl amide radical **Rad$_1$$^{\bullet}$**, along with the carbene radical cation (**Thiaz$^{+\bullet}$**). Then, the carbon-centered radical **Rad$_1$$^{\bullet}$** adds to the aromatic ring, affording **Rad$_2$$^{\bullet}$**. At this stage, a base-promoted homolytic aromatic substitution (HAS) reaction[46] (i.e., a second SET process), combined with a deprotonation by a base (which would explain the necessity of a base), gives rise to the oxindole and regenerates the carbene (**Thiaz**) (Figure 5A). Several control experiments have been performed to determine unambiguously the involvement of radical intermediates. For example, when TEMPO and O_2 were added to the reaction mixtures, the oxindoles were obtained in less than 5% yield. However, because of the short lifetime and high reactivity of carbene radical cations, it is hard to believe that **Thiaz$^{+\bullet}$** could engage in a second SET process. Additionally, thiazol-2-ylidenes, even with a bulky N-Dip substituent, are prone to dimerization at room temperature[47] and thus cannot be the resting state of catalytic cycles. Very recently, Martin et al.[48] prepared the respective carbene dimers (**Thiaz-Thiaz**) and found that their cyclic voltammograms feature two reversible oxidations that correspond to the formation of **Thiaz-Thiaz$^{+\bullet}$** and **Thiaz-Thiaz^{++}**, respectively (Figure 5B). Notably, they were able to isolate the radical cations **Thiaz$_{c,d}$-Thiaz$_{c,d}$$^{+\bullet}$** prepared by treating the dimers **Thiaz$_{c,d}$-Thiaz$_{c,d}$** with $NOPF_6$, finding that **Thiaz$_c$-Thiaz$_c$$^{+\bullet}$** was even air persistent at room temperature. They also isolated the dication **Thiaz$_c$-Thiaz$_c$$^{++}$** synthesized by treating the dimer **Thiaz$_c$-Thiaz$_c$** with two equivalents of $NOPF_6$. Note that this dication is reminiscent of the **NHC$_{a,b}$-NHC$_{a,b}$$^{++}$** obtained by Clyburn[15] and Duton[18] by oxidating **NHC$_{a,b}$**. Importantly, **Thiaz$_c$-Thiaz$_c$** with the bulky N-Dip substituent has the lowest oxidation potential (−0.80 V vs. SCE), as predicted by Munz et al.[49] Clearly, **Thiaz$_c$-Thiaz$_c$** is a strong reducing olefin, and Martin et al.[48] suggested that in the

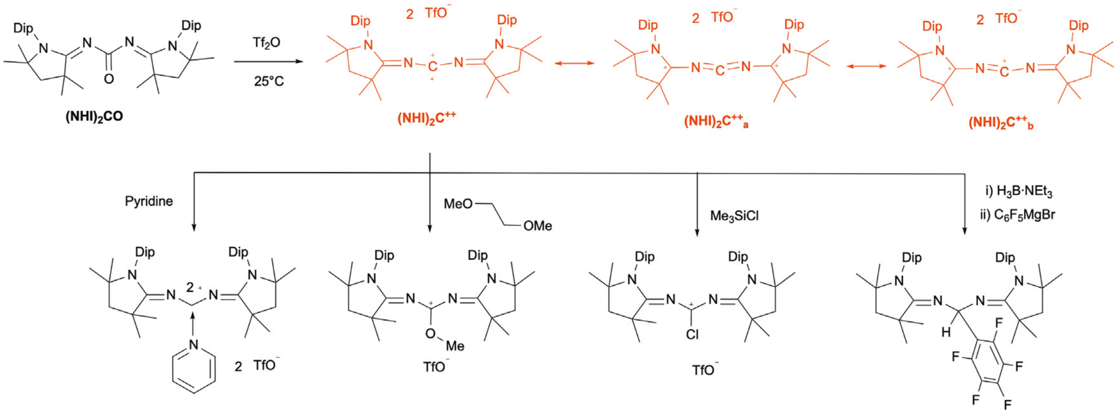

Figure 6. Synthesis and reactivity of the doubly oxidized carbene $(NHI)_2C^{++}$

so-called NHC-catalyzed SET reactions developed by Wang et al.[38–41,43] and Zhou et al.,[44,45] thiazol-2-ylidene dimers (**Thiaz-Thiaz**) could be either resting state reservoirs for **Thiaz** or catalysts on their own.

In all the published attempts to generate a carbene radical cation, the corresponding protonated carbene was obtained (*vide supra*). As illustrated in Figure 5C, we hypothesized that a protonated carbene (**carb-H$^+$**) could be the resting state of the catalytic cycle. Indeed, a simple deprotonation would give the free carbene **(carb)**. Upon releasing one electron, the carbene would be transformed into the transient carbene radical cation **carb$^{+\bullet}$**, which, after H-atom abstraction, would regenerate the starting protonated carbene **carb-H$^+$**. To test our hypothesis (Figure 5D), we chose 1*H*-1,2,3-triazol-5-ylidene **MIC$_a$**[28,29] because MICs do not dimerize even with small substituents, and they are stronger reducing agents than thiazolylidenes (**Thiaz**).[50–52] Due to difficulties in quantifying the amount of radical anion formed, we chose to optimize the catalytic bis(reduction)/bis(alkylation) process leading to bis(methylated)hydroquinone, as Thorley et al.[31] did using LDA as stoichiometric reducing agent (*vide supra*). After heating under reflux for 18 h a DMF solution containing anthraquinone, 2.5 equiv of Cs_2CO_3 as a base, and 20% of **MIC$_b$-H$^+$**, the first reduction was accomplished. Then, after cooling to room temperature, two equiv of Me_2SO_4 were added, and the solution was heated again under reflux for another 18 h without further addition of a carbene source. Under these conditions, 9,10-dimethoxyanthracene was obtained in 81% yield, and no side products were observed. Interestingly, we found that 1,2,4-triazolylidenes and thiazolylidenes, which are routinely used in carbene-based organocatalysis, induce some conversion but display significantly lower activity than **MIC$_b$**.

With the knowledge that it is possible to remove one non-bonding electron from a carbene to give a transient but synthetically useful radical cation, the next question was whether it would be feasible to remove an additional non-bonding electron to generate a dication, i.e., a doubly oxidized carbene. Such species had never been discussed in the literature, but they are isoelectronic to borinium ions (R_2B^+), which have been isolated.[53–55] Of course, compared to the latter, R_2C^{++} were expected to be significantly more electrophilic since they bear an additional positive charge. Therefore, we chose to use the strongly electron-donating N-heterocyclic imine (NHI) substituents,[56] based on cyclic (alkyl)(amino)carbenes[57] (Figure 6). Since singly oxidized carbene precursors were not available, we prepared the bis(imino)carbonyl compound **$(NHI)_2CO$** in the hopes of removing the oxygen along with two electrons. After several attempts, we found that triflic anhydride acted as the desired O^{2-} abstracting agent,[58] cleanly affording the doubly oxidized carbene **$(NHI)_2C^{++}$**.[59] The central carbon signal appeared at 119.8 ppm in the $^{13}C\{^1H\}$-NMR (nuclear magnetic resonance) spectrum, and single-crystal X-ray diffraction analysis showed that the compounds adopt an overall zigzag geometry with the NCN fragment, deviating slightly from linearity (163.2(4)°). Importantly, the two triflate anions pointed directly at the central carbon but from a considerable distance (C-O = 3.020(3) Å), suggesting that the sterically hindering NHI substituents prevent their approach. Additionally, these substituents allow for the delocalization of the positive charges as illustrated by the resonance form **$(NHI)_2C^{++}{}_a$** and **$(NHI)_2C^{++}{}_b$**. Natural population analysis reveals that despite sharing the positive charge with the peripheral carbons (+0.56), the central carbon has a large positive charge (+0.73), confirming that it is indeed the predominant electrophilic site of the molecule.

This conclusion was confirmed by the reactivity of **$(NHI)_2C^{++}$**. The dication reacted with pyridine to afford the corresponding base-stabilized dication. It can abstract MeO^- from dimethoxyethane and Cl^- from Me_3SiCl to form carbenium ions, showcasing its strong oxophilic and halophilic nature. To prove the presence of two accessible coordination sites on the dicoordinate carbon center, we first treated **$(NHI)_2C^{++}$** with $H_3B{\bullet}NEt_3$ and then with C_6F_5MgBr. We observed the formation of the neutral compound, which featured both nucleophilic components (H^- and $C_6F_5{}^-$) on its central carbon. In fact, the same compound can also be attained via the reaction of parent bis(imino)carbene with C_6F_5H,[60] fully consistent with the description of **$(NHI)_2C^{++}$** as a doubly oxidized bis(imino)carbene.

For future applications, it is interesting to note that the calculated gas-phase fluoride ion affinity (FIA = 890 kJ mol^{-1}) and hydride ion affinity (HIA = 1066 kJ mol^{-1}) exceed those of trityl carbocation Ph_3C^+ (FIA: 664 kJ mol^{-1}; HIA: 847 kJ mol^{-1}),[61] which is the archetypical carbon-based Lewis acid. The values for **$(NHI)_2C^{++}$** fall between those of the isoelectronic bis(imino)borinium ion $(^tBu_3PN)_2B^+$ (FIA: 599 kJ mol^{-1}; HIA: 569 kJ mol^{-1})[62] and those of the Lewis super acid $(Cp^*)P^{2+}$ (FIA: 1170 kJ mol^{-1}; HIA: 1238 kJ mol^{-1}).[63] They are comparable with those of tris(imino)phosphorus(V) dication $(NHC{=}N)_3P^{2+}$ (FIA: 909 kJ mol^{-1}; HIA: 933 kJ mol^{-1}).[64]

CONCLUSION AND PERSPECTIVES

During the last three decades, the highly tunable properties of NHCs and other stable singlet carbenes have been leveraged to enable a variety of applications.[10] This perspective shows an additional facet of carbenes that has only recently been disclosed: their strong reductive properties. This feature allows carbenes to engage in SET reactions, some of which can be rendered catalytic. The isolation and even the spectroscopic characterization of a singly oxidized carbene have yet to be done. This is a difficult task, as these species readily abstract hydrogen atoms to give back the carbene conjugate acid, which becomes the resting state of catalytic cycles. In contrast, a doubly oxidized carbene has been isolated.[59] There is a strong likelihood that by using bulky electron donor substituents in conjunction with sterically hindered anions, many others carbene dications will be isolated. Their first Lewis acidity is very high, and thus possible applications in Lewis acid catalysis can be envisaged. Although singly and doubly oxidized carbenes are still laboratory curiosities, it is necessary to keep in mind that three decades ago, stable carbenes were also considered exotic species. Note that **$carb^{+\cdot}$** and **$carb^{++}$** are less toxic and possibly less expensive than organometallic complexes (metal + ligand), at least at the academic and commercial research and development (R&D) levels, where the precious metals are not recovered. Moreover, the extraction and purification of precious metals is environmentally unfriendly, as it generates greenhouse gases. Another societal factor, which should not be neglected, is the human exploitation often associated with mining activity. For these reasons, we believe that **$carb^{+\cdot}$** and **$carb^{++}$** have a prolific future.

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AUTHOR CONTRIBUTIONS

All authors contributed to writing the paper.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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