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A Crystalline Doubly Oxidized Carbene

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SUMMARY: Carbon is the quintessential element of life. The chemistry of carbon is governed by the octet rule, which refers to its tendency to have eight electrons in its valence shell. However, a few exceptions do exist. More than a century ago, Gomberg discovered the trityl radical ($\text{Ph}_3\text{C}\cdot$)¹, which is a stable three-coordinate carbon species with seven valence electrons. Removing the non-bonding electron afforded the stable trityl carbocation (Ph_3C^+)² with only six valence electrons. In 1988, our group reported the isolation of a stable carbene ($\text{R}_2\text{C}:$)³ – a two-coordinate octet-defying species with formally six valence electrons. Carbenes are now among the most powerful tools in chemistry⁴, and have even found applications in material and medicinal sciences^{5,6}. Can we undress the carbene further by removing its non-bonding electrons? Herein, we describe the synthesis of a crystalline doubly oxidized carbene (R_2C^{2+}), through a two-electron oxidation/oxide-ion abstraction sequence from an electron-rich carbene⁷ bearing N-heterocyclic imine (NHI)⁸ substituents. Despite a cumulenec structure and strong delocalization of the positive charges, the dicoordinate carbon center maintains significant electrophilicity, and possesses the expected two accessible vacant orbitals. We show that the parent carbene can be regenerated by a two-electron reduction/deprotonation sequence, confirming that the carbene and its dication are related by two electrons. This work demonstrates that the use of bulky strong electron-donor substituents can simultaneously impart electronic stabilization and steric protection to both vacant orbitals on the central carbon atom, paving the way for the isolation of a variety of doubly oxidized carbenes.

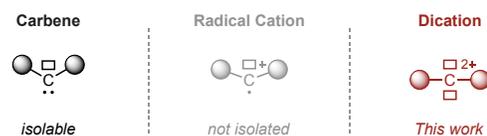
Carbenes constitute a class of neutral two-coordinate carbon species with six valence electrons (Fig. 1A)⁹. They violate the octet rule, a fundamental tenet governing main group elements. Since the discovery that strong π donor substituents permit their isolation under standard laboratory conditions^{3,10}, stable carbenes have become powerful tools in the chemical⁴ and material sciences^{5,6}.

Can we further deviate from the octet rule by removing one or two of the non-bonding electrons from the carbene center? This would lead to either a carbene radical cation or a carbene dication (Fig. 1A). Early studies showed that the diphenylcarbene radical cation ($\text{Ph}_2\text{C}^{\cdot+}$) can be transiently generated by single-electron oxidation of diazodiphenylmethane (Ph_2CN_2) followed by N_2 liberation, and could be spectroscopically characterized (Fig. 1B)^{11,12,13,14,15}. More recently, attention has shifted to the oxidation of stable singlet carbenes since they possess a more electron-rich carbon center¹⁶. Several groups have systematically explored the oxidation of N-heterocyclic carbenes (NHCs) and cyclic (alkyl)(amino)carbenes (CAACs) with various single-electron oxidants^{17,18,19,20}. In all cases the reaction afforded the conjugate acid of carbenes (Fig. 1B). It was proposed that this was the result of the generation of the desired carbene radical cations that abstract $\text{H}\cdot$ from the solvent²¹. NHC radical cations have also been invoked as key intermediates in the emerging field of NHC single-electron transfer catalysis, but never spectroscopically observed, clearly suggesting that they are only short-lived intermediates^{22,23,24,25}.

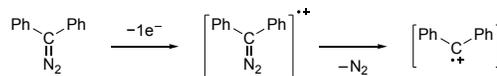
Carbene dications (R_2C^{2+}) – doubly oxidized carbenes – are hitherto hypothetical species that have never been discussed in the literature (Fig. 1A). This might be due to the transient nature of the carbene radical cations, which decompose/react before the second oxidation could occur. Carbene dications possess two vacant orbitals around the dicoordinate carbon atom, rendering them isoelectronic with borinium ions (R_2B^+)^{26,27,28}, an extremely electron-deficient class of boron cations^{29,30}. However, carbene dications bear an additional positive charge, thus they are expected to be significantly more electrophilic.

We recently demonstrated that an acyclic carbene bearing two strongly donating N-heterocyclic imine (NHI)^{8,31,32} substituents features exceptional nucleophilicity, enabling the dearomatization of a proximal inert arene ring⁷. We reasoned that the electron-rich nature of the bis(imino)carbene, coupled with its flexible acyclic framework is an ideal platform to access a doubly oxidized carbene. Herein, we report the synthesis and isolation of a crystalline carbene dication derived from a bis(imino)carbene through a two-electron oxidation/oxide-ion abstraction strategy that bypasses the carbene radical cation (Fig. 1C).

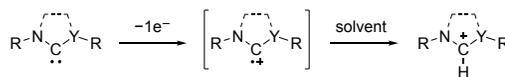
A. Carbenes in various oxidation states



B. Previous attempts at carbene oxidation



NHC or CAAC



C. This work

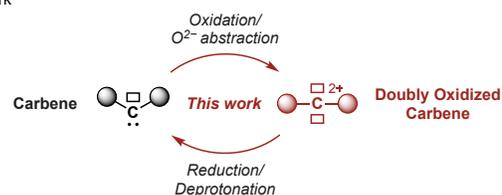


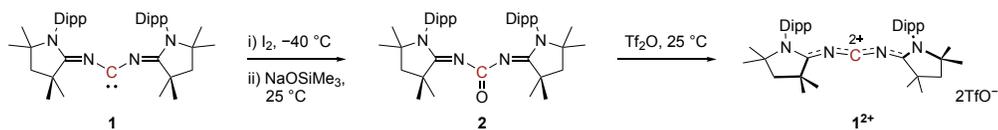
Fig. 1 | Carbenes and oxidized congeners. **A**, Carbenes in various oxidation states. **B**, Previous attempts at generating transient carbene radical cations. **C**, Present work on the isolation of a carbene dication through a two-electron oxidation/oxide-ion abstraction strategy and its two-electron reduction/deprotonation back to the carbene.

Results and Discussion

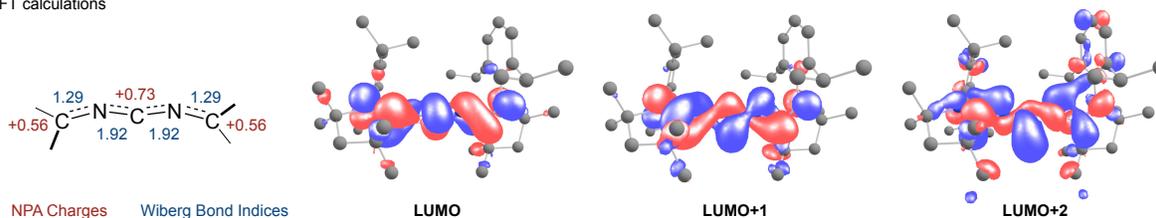
Synthesis and characterization of carbene dication 1^{2+} .

To bypass the generation of a carbene radical cation, we set out to explore an alternative strategy for the oxidation of bis(imino)carbene **1**. We envisaged a two-step approach, first by carbene coordination to a two-electron oxidant, then removing the oxidant along with two electrons. Accordingly, treating **1** with I_2 as the two-electron oxidant formed the (iodo)carbenium ion as evidenced by *in-situ* ^1H NMR (Fig. 2A, Fig. S27)³³. However, all attempts to abstract both iodides were unsuccessful, possibly due to the strong halophilicity of the target carbene dication (*vide infra*). This prompted us to exchange the iodides for O^{2-} , which could be easily achieved through a one-pot procedure from **1**. Thus, treating **1** with I_2 and then NaOSiMe_3 afforded the neutral bis(imino)carbonyl compound **2**³⁴. Gratifyingly, subjecting **2** to triflic anhydride as the O^{2-} abstracting agent led to a new species³⁵. The ^1H NMR spectrum displays only one set of signals associated with the two NHI units. The central carbon signal appears at 119.8 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR, in excellent agreement with DFT calculations for the target carbene dication 1^{2+} (PBE0/def2-TZVPP// r^2 SCAN-3c; 124.8 ppm). The ^{19}F NMR spectrum shows only one signal at -77.9 ppm which is in the typical range observed for an uncoordinated triflate anion.

A. Synthesis of carbene dication 1^{2+}



B. DFT calculations



C. Canonical forms of 1^{2+}

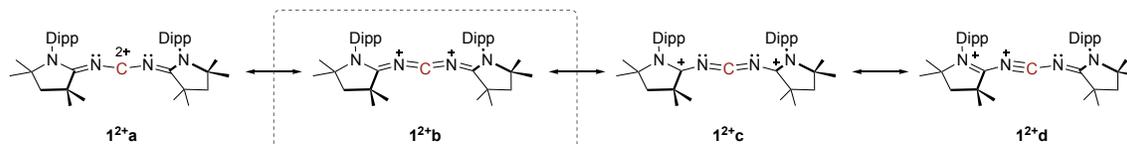


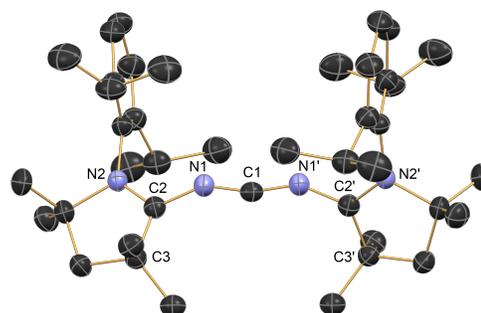
Fig. 2 | Synthesis and characterization of carbene dication 1^{2+} . A, Synthesis of $1^{2+}[\text{TfO}^-]_2$. B, Calculated NPA charges (red), WBI bond order (blue), LUMO, LUMO+1, and LUMO+2. C, Canonical forms 1^{2+a} to 1^{2+d} . (Dipp = 2,6-diisopropylphenyl).

Single crystal X-ray diffraction analysis unambiguously confirmed that $1^{2+}[\text{TfO}^-]_2$ features a central two-coordinate carbon atom (Fig. 3A). 1^{2+} adopts an overall zigzag geometry where the terminal CAACs are cis-bent. The central carbon C1 deviates slightly from linearity [$163.2(4)^\circ$] and the central C1–N1 and C1–N1' distances [mean: $1.197(2)$ Å] are within the range of $\text{C}_{\text{sp}}\text{--N}$ double bonds. The adjacent nitrogen atoms (N1 and N1') subtend a more acute angle [$147.8(3)^\circ$], revealing a hybridization halfway between sp and sp^2 . Additionally, the terminal C2–N1 and C2'–N1' distances [mean: $1.349(3)$ Å] are midway between $\text{C}_{\text{sp}^2}\text{--N}$ single and double bonds. These parameters indicate that the lone pairs on N1 and N1' are not only involved in π donation with central C1, but are also engaged in π back-bonding with the terminal CAAC carbon atoms (C2 and C2'). Strikingly, the terminal CAACs are almost orthogonal [$79.6(2)^\circ$] (Fig. 3C) – a distinct feature of even cumulenes³⁶. In fact, 1^{2+} is isoelectronic with [4]cumulenes ($\text{R}_2\text{C}=\text{C}=\text{C}=\text{CR}_2$)³⁷. Overall, based on the structural parameters of 1^{2+} , we rationalized that the origin of its stability is derived from cumulenic delocalization of the two positive charges across the CNCNC network. Hence, 1^{2+} can be considered a dicationic nitrogen analogue of [4]cumulene (1^{2+b} ; Fig. 2C).

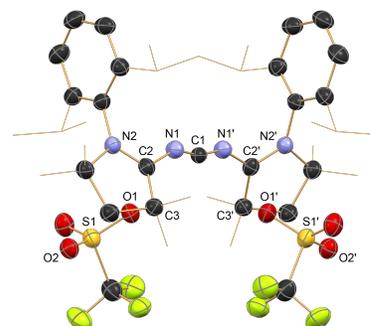
The two triflate anions in the outer sphere point directly at the central carbon C1 [mean S1–O1–C1 and S1'–O1'–C1 angle: $163.2(1)^\circ$], albeit from a considerable distance away [mean of C1–O1 and C1–O1': $3.020(3)$ Å] (Fig. 3B). This suggests that their approach to the central carbon is effectively impeded by the large steric profile of the flanking NHI substituents (for space-filling model see Table S1). Secondary interactions between the triflate anions and the CAAC carbon atoms also exist, but at an even further distance [mean of C2–O2 and C2'–O2': $3.995(3)$ Å]. These observations clearly indicate that the central C1 is the dominant

electrophilic site, while the CAAC carbon atoms (C2 and C2') play a secondary role.

A. Solid-state crystal structure of 1^{2+}



B. Side view showing outer sphere TfO^- anions



C. End-on view (C2 to C2')

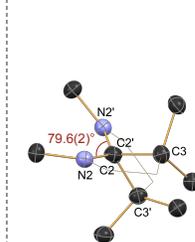


Fig. 3 | Solid-state crystal structure of carbene dication $1^{2+}[\text{TfO}^-]_2$. A, Cationic component 1^{2+} . B, Side view showing TfO^- anions. C, End-on view from C2 to C2' with N2–C2–C2'–N2' torsion angle labeled. (Thermal ellipsoids set at 50% probability and H atoms omitted for clarity.)

DFT calculations performed at the r^2 SCAN-3c level of theory accurately reproduced the structural parameters of $\mathbf{1}^{2+}$. Natural population analysis (NPA) reveals a large positive charge on the central C1 (+0.73), confirming that it is indeed the predominant electrophilic site of the molecule (Fig. 2B). On the other hand, the peripheral C2 and C2' (+0.56) share some of the positive charge through allylic-type delocalization. Wiberg bond indices (WBI) suggest double bond characters, albeit to a larger degree for the central C1–N1 and C1–N1' (mean: 1.92) than the terminal C2–N1 and C2'–N1' (mean: 1.29), consistent with an overall cumulene-type system with contiguous double bonds across the CNCNC unit (Fig. 2B). As for the molecular orbital picture, the LUMO and LUMO+1 could be viewed as the orthogonal vacant $p(\pi)$ -type orbitals on central C1, with contributions from C2 and C2' (Fig. 2B). Importantly, these orbitals possess Möbius-type helicity, as with the frontier orbitals of [4]cumulenes³⁷, confirming the cumulenic nature of $\mathbf{1}^{2+}$. Interestingly, the LUMO+2 bears a strong resemblance to the HOMO (lone pair orbital) of bis(imino)carbene $\mathbf{1}^7$, consistent with the notion that $\mathbf{1}^{2+}$ is the doubly oxidized analogue of carbene $\mathbf{1}$.

The electronic structure of $\mathbf{1}^{2+}$ could be illustrated by canonical forms $\mathbf{1}^{2+a}$ to $\mathbf{1}^{2+d}$ (Fig. 2C). $\mathbf{1}^{2+a}$ depicts a form in which both positive charges are purely localized on the central carbon, whereas $\mathbf{1}^{2+c}$ represents the opposite extreme where the positive charges reside solely on the terminal CAAC carbon atoms. The unsymmetrical form $\mathbf{1}^{2+d}$

illustrates the slightly higher degree of multiple bonding for central C1–N1 than terminal C2–N1. Based on the structural parameters and DFT calculations, it is apparent that the electronic structure of $\mathbf{1}^{2+}$ is highly delocalized² and resembles cumulenic $\mathbf{1}^{2+b}$ which lies between the extremes of $\mathbf{1}^{2+a}$ and $\mathbf{1}^{2+c}$.

We set out to assess the Lewis acidity of carbene dication $\mathbf{1}^{2+}$ by employing a combination of fluoride ion affinity (FIA) and hydride ion affinity (HIA) to gauge its hard and soft Lewis acidity, respectively³⁸. The calculated gas-phase affinities for $\mathbf{1}^{2+}$ (FIA: 890 kJ mol⁻¹; HIA: 1066 kJ mol⁻¹) reflect the softer nature of the central carbon. Remarkably, these values exceed those of trityl carbocation Ph₃C⁺ (FIA: 664 kJ mol⁻¹; HIA: 847 kJ mol⁻¹)³⁹ which is the archetypical carbon Lewis acid. When compared with other p-block element Lewis acids, we find that the affinities for $\mathbf{1}^{2+}$ fall between those of the isoelectronic bis(imino)borinium ion (t-Bu₃PN)₂B⁺ (FIA: 599 kJ mol⁻¹; HIA: 569 kJ mol⁻¹)²⁶ which also features an extended cumulenic structure, and the Lewis super acid (Cp*)P²⁺ (FIA: 1170 kJ mol⁻¹; HIA: 1238 kJ mol⁻¹)⁴⁰. In fact, they are comparable with those of tris(imino)phosphorus(V) dication (NHC=N)₃P²⁺ (FIA: 909 kJ mol⁻¹; HIA: 933 kJ mol⁻¹)⁴¹. Notably, we obtained the same trend when dichloromethane solvation was considered in the calculations (Table S7). Overall, this assessment suggests that $\mathbf{1}^{2+}$ maintains a significant Lewis acidity, despite cumulenic stabilization.

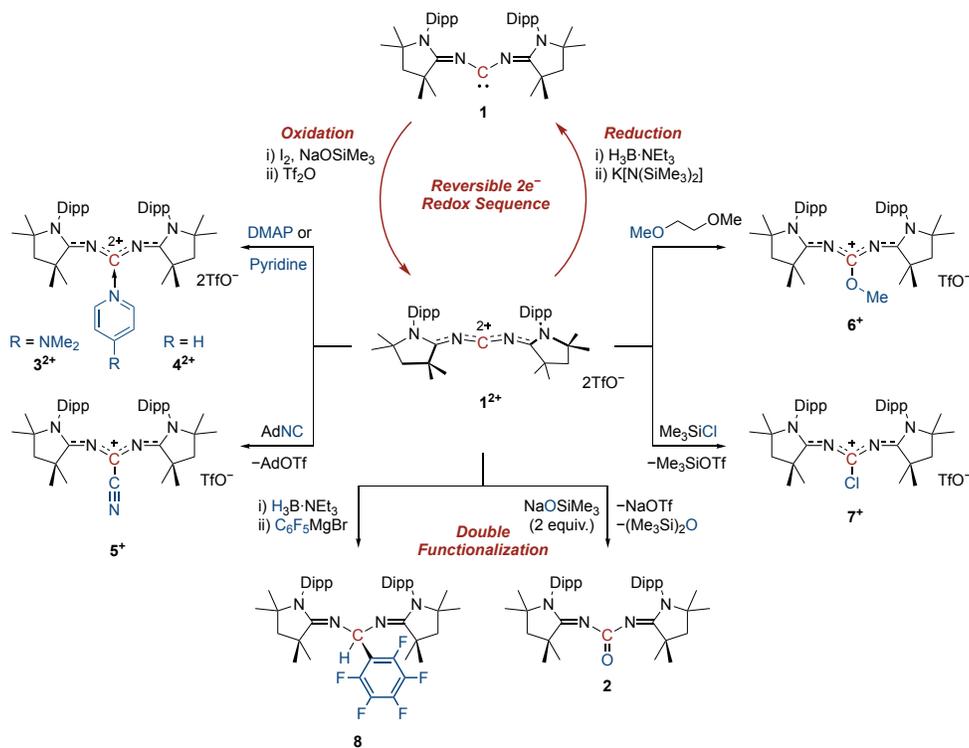


Fig. 4 | Reactivity of carbene dication $\mathbf{1}^{2+}$ and a reversible $\mathbf{1}/\mathbf{1}^{2+}$ redox system. $\mathbf{1}^{2+}$ can undergo addition of neutral bases (DMAP and pyridine), abstraction of CN⁻ from 1-adamantyl isocyanide, MeO⁻ from dimethoxyethane and Cl⁻ from Me₃SiCl, double functionalization with H⁻/C₆F₅⁻ and O²⁻; $\mathbf{1}^{2+}$ can participate in a reversible two-electron redox process with carbene $\mathbf{1}$. (Ad = 1-adamantyl).

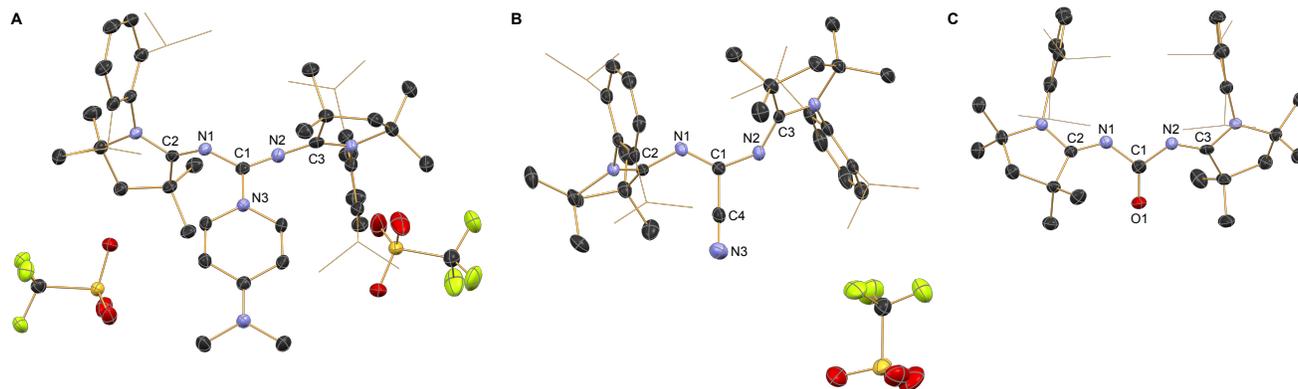


Fig. 5 | Solid-state crystal structures. A, Lewis-base stabilized carbene dication $3^{2+}[\text{TfO}]_2$. B, (Cyano)carbenium ion $5^+[\text{TfO}]$. C, Bis(imino)carbonyl **2**. (Thermal ellipsoids set at 50% probability. For clarity, H atoms are omitted and ^iPr groups are simplified as wireframes.)

Reactivity of carbene dication 1^{2+} . We turned our attention to explore the reactivity of 1^{2+} (Fig. 4). Subjecting 1^{2+} to neutral Lewis bases dimethylaminopyridine (DMAP) and even pyridine afforded base-stabilized carbene dications 3^{2+} (Fig. 5A) and 4^{2+} , respectively, confirming that the central dicoordinate carbon is indeed the dominant electrophilic site of the molecule. Surprisingly, employing 1-adamantyl isocyanide results in the formation of (cyano)carbenium ion 5^+ (Fig. 5B) and 1-adamantyl triflate. We surmised that the initial coordination of 1-adamantyl isocyanide to 1^{2+} forms a highly electron-deficient nitrilium dication, which fragments into 5^+ and 1-adamantyl carbocation⁴², since the corresponding $\text{S}_{\text{N}}2$ pathway is not permitted. Overall, this can be considered as a transfer of CN^- from an aliphatic carbocation⁴³ to 1^{2+} , reflecting the strong electrophilicity of the carbene dication.

Motivated by this finding, we then investigated the anion abstracting ability of 1^{2+} . The carbene dication can abstract MeO^- from dimethoxyethane and Cl^- from Me_3SiCl to form carbenium ions 6^+ and 7^+ (for SC-XRD Table S4) respectively, showcasing its strong oxophilic and halophilic nature. The latter observation stands in marked contrast to the borinium ion $(^i\text{Bu}_3\text{PN})_2\text{B}^+$,²⁶ which spontaneously ejects Cl^- , consistent with the stronger halophilicity of 1^{2+} as predicted by FIA measurements.

Having established that the central carbon of carbene dication 1^{2+} is the dominant electrophilic site for the initial nucleophilic attack, we were curious to ascertain the position for which a second nucleophile would react. With this in mind, we first treated 1^{2+} with H^- (via $\text{H}_3\text{B}\cdot\text{NET}_3$), and subsequently with C_6F_5^- (via $\text{C}_6\text{F}_5\text{MgBr}$) and observed the formation of the neutral compound **8** (Fig. 4). **8** features both nucleophilic components on its central carbon, confirming the presence of two accessible coordination sites on the dicoordinate carbon center of 1^{2+} . In fact, **8** can also be attained via the reaction of parent bis(imino)carbene **1** with $\text{C}_6\text{F}_5\text{H}^7$, fully consistent with the description of 1^{2+} as bis(imino)carbene dication. Next, we wondered whether the central carbon of 1^{2+} can also engage in a double bond. Employing NaOSiMe_3 as O^{2-} transfer reagent afforded the neutral bis(imino)carbonyl compound **2** (Fig. 5C), further corroborating the existence of both vacant orbitals on the central carbon.

Reversible $1/1^{2+}$ redox system. Reversible two-electron redox processes are the hallmark of transition metal catalysis. In stark contrast, main group p-block compounds rarely exhibit such processes^{44,45,46}. Having established that bis(imino)carbene **1** can undergo a two-electron oxidation sequence to carbene dication 1^{2+} (Fig. 4), we set out to explore the reverse two-electron reduction by employing a similar two-step strategy. We reasoned that this could be achieved by first employing H^- as the two-electron reductant, then removing H^+ and leaving behind two electrons. Accordingly, subjecting 1^{2+} to $\text{H}_3\text{B}\cdot\text{NET}_3$ afforded the protonated bis(imino)carbene, which could be deprotonated by $\text{K}[\text{N}(\text{SiMe}_3)_2]$, leading to the successful regeneration of **1**. Hence, $1/1^{2+}$ constitutes an unprecedented reversible two-electron redox system between a carbene and its dication⁴⁷. More importantly, this is a further demonstration that 1^{2+} behaves as a doubly oxidized carbene.

Conclusion

More than thirty years after the discovery of a stable carbene, this work shows that a doubly oxidized carbene can be isolated as well. In his Nobel lecture, Olah stated, “it should be clear that in carbocationic systems, varying degrees of delocalization always exist⁴⁸.” Despite the cumulenoid delocalization of the positive charges, carbene dication 1^{2+} displays significant electrophilicity at the dicoordinate carbon center. It is amenable to two successive nucleophilic attacks, in line with the existence of two accessible coordination sites at the central carbon. We also show that it can participate in an unprecedented reversible two-electron redox system with parent bis(imino)carbene, fully consistent with its description as a doubly oxidized bis(imino)carbene. This work demonstrates that bulky strong electron-donor substituents can be used to mask both vacant orbitals at the central carbon atom and prevent the two anions from coordination, paving the way for the isolation of a variety of doubly oxidized carbenes.

Methods

General Consideration. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon. Solvents were dried over sodium benzophenone ketyl or calcium hydride (*n*-hexane, chloroform), degasses and stored over activated molecular sieves or K mirror. Nuclear magnetic

resonance (NMR) spectra were recorded on a Jeol 400 spectrometer, at ambient temperature unless otherwise noted. Mass spectra were performed at the UC San Diego Mass Spectrometry Laboratory on an Agilent 6230 Accurate-Mass TOFMS spectrometer. Single crystal X-ray diffraction data were collected on Bruker Apex diffractometers using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) or Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$) at the UC San Diego Crystallography Facility.

Starting materials

$[\text{MeCAACN}]_2\text{CH}^+[\text{TfO}]^-$ is prepared according to literature procedure⁷. All other reagents were purchased from commercial sources and used without further purification unless otherwise noted.

Synthetic procedures

Preparation of 2. A mixture of $[\text{MeCAACN}]_2\text{CH}^+[\text{TfO}]^-$ (90 mg, 0.12 mmol) and $\text{K}[\text{N}(\text{SiMe}_3)_2]$ (24 mg, 0.12 mmol) in a vial was cooled to $-40 \text{ }^\circ\text{C}$ in the glovebox. THF (3 mL) at $-40 \text{ }^\circ\text{C}$ was added to the mixture to form an orange-red solution which was stirred for 5 minutes. I_2 (30 mg, 0.12 mmol) was added, and the resulting mixture was allowed to stir for an additional 5 minutes before warming up to room temperature. NaOSiMe_3 (27 mg, 0.24 mmol) was added, and the mixture stirred overnight at room temperature. The mixture was filtered, and the filtrate dried under vacuum. The filtrate was redissolved in benzene (2 mL) and filtered. The filtrate was then dried under vacuum to yield **2** (19 mg, 26% yield) as a light yellow powder. Single crystals suitable for X-ray crystallography were obtained by evaporation from a benzene solution at room temperature. Alternative synthesis of **2** from $\text{I}_2^{2+}[\text{TfO}]_2$: To a mixture of $\text{I}_2^{2+}[\text{TfO}]_2$ (460 mg, 0.50 mmol) and NaOSiMe_3 (114 mg, 1.0 mmol) was added benzene (5 mL) and sonicated overnight. The suspension was then filtered and the filtrate dried under vacuum to yield **2** (199 mg, 63% yield) as a light yellow powder. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 297 K): $\delta = 1.15$ (s, 12H, $\text{C}(\text{CH}_3)_2$), 1.16 (d, $^3J_{\text{HH}} = 6.5 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.23 (d, $^3J_{\text{HH}} = 6.9 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.29 (s, 12H, $\text{C}(\text{CH}_3)_2$), 1.94 (s, 4H, CH_2), 3.02 (sept, $^3J_{\text{HH}} = 6.7 \text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 7.15 (d, $^3J_{\text{HH}} = 7.7 \text{ Hz}$, 4H, Dipp-*m*-CH), 7.25 (t, $^3J_{\text{HH}} = 7.6 \text{ Hz}$, 2H, Dipp-*p*-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 297 K): $\delta = 23.2$ ($\text{CH}(\text{CH}_3)_2$), 26.7 ($\text{CH}(\text{CH}_3)_2$), 28.7 ($\text{C}(\text{CH}_3)_2$), 29.0 ($\text{CH}(\text{CH}_3)_2$), 29.4 ($\text{C}(\text{CH}_3)_2$), 43.1 ($\text{C}(\text{CH}_3)_2$), 54.5 (CH_2), 61.7 ($\text{C}(\text{CH}_3)_2$), 123.7 (Dipp-*m*-CH), 127.9 (Dipp-*p*-CH), 132.7 (Dipp-*i*-C), 149.0 (Dipp-*o*-C), 164.5 (C_{CAAC}), 167.7 (CO). HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{41}\text{H}_{63}\text{N}_4\text{O}$, 627.4996; found, 627.5002.

Preparation of $\text{I}_2^{2+}[\text{TfO}]_2$. To **2** (600 mg, 0.96 mmol) in benzene (6 mL) was added trifluoromethanesulfonic anhydride (0.48 mL, 2.9 mmol) dropwise while stirring at room temperature. The orange solution turned dark brown with concomitant formation of a white precipitate. After stirring for an additional 5 minutes, the suspension was filtered off and the residue dried under vacuum to yield $\text{I}_2^{2+}[\text{TfO}]_2$ (832 mg, 89% yield) as an off-white powder. Single crystals suitable for X-ray crystallography were obtained by slow evaporation from a concentrated chloroform solution at room temperature. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 297 K): $\delta = 1.03$ (d, $^3J_{\text{HH}} = 6.6 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.32 (d, $^3J_{\text{HH}} = 6.6 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.52 (s, 12H, $\text{C}(\text{CH}_3)_2$), 1.80 (s, 12H, $\text{C}(\text{CH}_3)_2$), 2.62 (s, 4H, CH_2), 2.74 (sept, $^3J_{\text{HH}} = 6.6 \text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 7.32 (d, $^3J_{\text{HH}} = 7.9 \text{ Hz}$, 4H, Dipp-*m*-CH), 7.52 (t, $^3J_{\text{HH}} = 7.8 \text{ Hz}$, 2H, Dipp-*p*-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 297 K): $\delta = 22.7$ ($\text{CH}(\text{CH}_3)_2$), 26.8 ($\text{CH}(\text{CH}_3)_2$), 27.4 ($\text{C}(\text{CH}_3)_2$), 28.2 ($\text{C}(\text{CH}_3)_2$), 29.6 ($\text{CH}(\text{CH}_3)_2$), 47.8 (CH_2), 49.7 ($\text{C}(\text{CH}_3)_2$), 79.1 ($\text{C}(\text{CH}_3)_2$), 119.8 ($\text{C}_{\text{central}}$), 120.9 (q, $^1J_{\text{CF}} = 286.6 \text{ Hz}$, CF_3), 126.1 (Dipp-*m*-CH), 126.5 (Dipp-*i*-C), 132.6 (Dipp-*p*-CH), 145.4 (Dipp-*o*-C), 175.5 (C_{CAAC}). $^{19}\text{F NMR}$ (376 MHz, CDCl_3 , 297 K): $\delta = -77.9$.

Preparation of $\text{I}_2^{2+}[\text{TfO}]_2$. To a solution of $\text{I}_2^{2+}[\text{TfO}]_2$ (27.6 mg, 0.030 mmol) in CDCl_3 (0.5 mL) was added 4-dimethylaminopyridine (3.7 mg, 0.030 mmol) at room temperature and the resulting solution stirred for 5 minutes. Single crystals of $\text{I}_2^{2+}[\text{TfO}]_2$ (8 mg, 26% yield) suitable for X-ray crystallography were obtained by slow evaporation of concentrated fluorobenzene solution at room temperature. $^1\text{H NMR}$ (400 MHz, C_6D_6 , 297 K): $\delta = 1.05$ (d, $^3J_{\text{HH}} = 5.7 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.24 (s, 12H, $\text{C}(\text{CH}_3)_2$), 1.34 (d, $^3J_{\text{HH}} = 6.5 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.38 (s, 12H, $\text{C}(\text{CH}_3)_2$), 2.37 (brs, 4H, CH_2), 2.95 (brs, 4H, $\text{CH}(\text{CH}_3)_2$), 3.46 (s, 6H, $\text{N}(\text{CH}_3)_2$), 7.28 (d, $^3J_{\text{HH}} = 7.8 \text{ Hz}$, 4H, Dipp-*m*-CH), 7.43 (t, $^3J_{\text{HH}} = 7.7 \text{ Hz}$, 2H, Dipp-*p*-CH), 7.65 (d, $^3J_{\text{HH}} = 8.0 \text{ Hz}$, 2H, DMAP-CH), 8.08 (d, $^3J_{\text{HH}} = 8.0 \text{ Hz}$, 2H, DMAP-NCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 297 K): $\delta = 23.7$ ($\text{CH}(\text{CH}_3)_2$), 27.9 ($\text{CH}(\text{CH}_3)_2$), 29.0 ($\text{C}(\text{CH}_3)_2$), 29.1 ($\text{C}(\text{CH}_3)_2$), 41.9 ($\text{N}(\text{CH}_3)_2$), 47.6 ($\text{C}(\text{CH}_3)_2$), 50.3 (CH_2), 70.2 ($\text{C}(\text{CH}_3)_2$), 110.4 (DMAP-CH), 120.9 (q, $^1J_{\text{CF}} = 220.3 \text{ Hz}$, CF_3), 125.6 (Dipp-*m*-CH), 128.9 (Dipp-*i*-C), 130.6 (Dipp-*p*-CH), 137.8 (DMAP-NCH), 146.0 (CN_3), 147.1 (Dipp-*o*-C), 158.2 (Me_2NC), 172.4 (C_{CAAC}). $^{19}\text{F NMR}$ (376 MHz, CDCl_3 , 297 K): $\delta = -78.1$. HRMS (m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{50}\text{H}_{72}\text{F}_6\text{N}_6\text{O}_6\text{S}_2\text{Na}$, 1053.4751; found, 1053.4761.

Preparation of $\text{I}_2^{2+}[\text{TfO}]_2$. To a solution of $\text{I}_2^{2+}[\text{TfO}]_2$ (30 mg, 0.033 mmol) in CDCl_3 (0.5 mL) was added pyridine (0.01 mL, 0.12 mmol) at room temperature and the resulting solution stirred for 5 minutes. Volatiles were removed *in vacuo* to yield $\text{I}_2^{2+}[\text{TfO}]_2$ (32 mg, 98% yield) as an off-white powder. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 297 K): $\delta = 0.93$ (brs, 12H, $\text{CH}(\text{CH}_3)_2$), 1.23 (brs, 12H, $\text{C}(\text{CH}_3)_2$), 1.30 (d, $^3J_{\text{HH}} = 6.6 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.38 (s, 12H, $\text{C}(\text{CH}_3)_2$), 2.37 (s, 4H, CH_2), 2.75 (sept, $^3J_{\text{HH}} = 6.5 \text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 7.29 (d, $^3J_{\text{HH}} = 7.8 \text{ Hz}$, 4H, Dipp-*m*-CH), 7.48 (t, $^3J_{\text{HH}} = 7.8 \text{ Hz}$, 2H, Dipp-*p*-CH), 8.64–8.70 (m, 3H, Py-*m*-CH and Py-*p*-CH), 8.77 (d, $^3J_{\text{HH}} = 5.2 \text{ Hz}$, 4H, Py-*o*-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 297 K): $\delta = 23.5$ ($\text{CH}(\text{CH}_3)_2$), 27.1 ($\text{CH}(\text{CH}_3)_2$), 28.6 ($\text{C}(\text{CH}_3)_2$), 29.3 ($\text{C}(\text{CH}_3)_2$), 28.6 ($\text{CH}(\text{CH}_3)_2$), 47.9 ($\text{C}(\text{CH}_3)_2$), 51.7 (CH_2), 71.9 ($\text{C}(\text{CH}_3)_2$), 120.9 (q, $^1J_{\text{CF}} = 320.5 \text{ Hz}$, CF_3), 125.9 (Dipp-*m*-CH), 129.0 (Dipp-*i*-C), 131.2 (Py-*m*-CH), 131.4 (Dipp-*p*-CH), 142.4 ($\text{C}_{\text{central}}$), 142.0 (Py-*o*-CH), 145.8 (Dipp-*o*-C), 150.8 (Py-*p*-CH), 176.4 (C_{CAAC}). $^{19}\text{F NMR}$ (376 MHz, CDCl_3 , 297 K): $\delta = -78.1$.

Preparation of $\text{I}_2^{2+}[\text{TfO}]_2$. To a solution of $\text{I}_2^{2+}[\text{TfO}]_2$ (30 mg, 0.033 mmol) in CDCl_3 (0.5 mL) was added 1-adamantyl isocyanide (9.8 mg, 0.066 mmol) at room temperature and the resulting solution stirred for 5 minutes. Volatiles were removed *in vacuo*. The residue was dissolved in Et_2O (2 mL) and sonicated for 5 minutes, resulting in the formation of white precipitates. The suspension was filtered, and the solids washed with Et_2O ($2 \times 0.5 \text{ mL}$). The solids were then dried under vacuum to yield $\text{I}_2^{2+}[\text{TfO}]_2$ (15 mg, 58% yield) as an off-white powder. Single crystals suitable for X-ray crystallography were obtained by slow evaporation from a concentrated chloroform solution at room temperature. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 297 K): $\delta = 0.90$ (d, $^3J_{\text{HH}} = 6.7 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.27 (d, $^3J_{\text{HH}} = 6.7 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.36 (s, 12H, $\text{C}(\text{CH}_3)_2$), 1.53 (s, 12H, $\text{C}(\text{CH}_3)_2$), 2.41 (brs, 4H, CH_2), 2.67 (sept, $^3J_{\text{HH}} = 6.4 \text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 7.21 (d, $^3J_{\text{HH}} = 7.8 \text{ Hz}$, 4H, Dipp-*m*-CH), 7.40 (t, $^3J_{\text{HH}} = 7.8 \text{ Hz}$, 2H, Dipp-*p*-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 297 K): $\delta = 23.4$ ($\text{CH}(\text{CH}_3)_2$), 26.7 ($\text{CH}(\text{CH}_3)_2$), 28.9 ($\text{C}(\text{CH}_3)_2$), 29.0 ($\text{C}(\text{CH}_3)_2$), 29.5 ($\text{CH}(\text{CH}_3)_2$), 47.8 ($\text{C}(\text{CH}_3)_2$), 51.0 (CH_2), 71.3 ($\text{C}(\text{CH}_3)_2$), 112.4 ($\text{C}_{\text{C=N}}$), 121.2 (q, $^1J_{\text{CF}} = 320.9 \text{ Hz}$), 125.3 (Dipp-*m*-CH), 128.4 (Dipp-*i*-C), 130.6 ($\text{C}_{\text{central}}$), 130.8 (Dipp-*p*-CH), 146.2 (Dipp-*o*-C), 176.6 (C_{CAAC}). $^{19}\text{F NMR}$ (376 MHz, CDCl_3 , 297 K): $\delta = -77.9$. HRMS (m/z): $[\text{M}-\text{OTf}]^+$ calcd. for $\text{C}_{42}\text{H}_{62}\text{N}_5$, 636.5000; found, 636.5008.

Preparation of $\text{I}_2^{2+}[\text{TfO}]_2$. Dimethoxyethane (0.5 mL) was added to $\text{I}_2^{2+}[\text{TfO}]_2$ (14 mg, 0.015 mmol) in a J-Young NMR tube. The suspension was sonicated for 5 minutes. Volatiles were removed *in*

vacuo, and the yield of $6^+[\text{TfO}^-]$ (89% yield) was determined by ^1H NMR using C_6Me_6 as internal standard. ^1H NMR (400 MHz, CDCl_3 , 297 K): $\delta = 1.02$ (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.29 (s, 12H, $\text{C}(\text{CH}_3)_2$), 1.32 (s, 12H, $\text{C}(\text{CH}_3)_2$), 2.22 (s, 4H, CH_2), 2.73 (sept, $^3J_{\text{HH}} = 6.5$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 3.60 (s, 3H, OCH_3), 7.22 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, Dipp-*m-CH*), 7.38 (t, $^3J_{\text{HH}} = 7.7$ Hz, 2H, Dipp-*p-CH*). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 297 K): $\delta = 23.4$ ($\text{CH}(\text{CH}_3)_2$), 26.6 ($\text{CH}(\text{CH}_3)_2$), 28.9 ($\text{C}(\text{CH}_3)_2$), 29.0 ($\text{CH}(\text{CH}_3)_2$), 29.1 ($\text{C}(\text{CH}_3)_2$), 45.8 ($\text{C}(\text{CH}_3)_2$), 52.7 (CH_2), 56.7 (OCH_3), 68.2 ($\text{C}(\text{CH}_3)_2$), 121.1 (q, $^1J_{\text{CF}} = 339.9$ Hz, CF_3), 125.2 (Dipp-*m-CH*), 129.4 (Dipp-*i-C*), 130.1 (Dipp-*p-CH*), 146.7 (Dipp-*o-C*), 158.7 (COMe), 176.5 (C_{CAAC}). ^{19}F NMR (376 MHz, CDCl_3 , 297 K): $\delta = -77.8$. HRMS (m/z): $[\text{M}-\text{OTf}]^+$ calcd. for $\text{C}_{42}\text{H}_{65}\text{N}_4\text{O}$, 641.5153; found, 641.5155.

Preparation of $7^+[\text{TfO}^-]$. To a solution of $1^{2+}[\text{TfO}^-]_2$ (92 mg, 0.10 mmol) in CDCl_3 (0.5 mL) was added trimethylchlorosilane (0.03 mL, 0.24 mmol) at room temperature and the resulting solution stirred for 5 minutes. Volatiles were removed *in vacuo* to yield $7^+[\text{TfO}^-]$ (69 mg, 86% yield) as a light yellow powder. Single crystals suitable for X-ray crystallography were obtained by slow evaporation from a concentrated fluorobenzene solution at room temperature. ^1H NMR (400 MHz, CDCl_3 , 297 K): $\delta = 1.07$ (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.33 (s, 12H, $\text{C}(\text{CH}_3)_2$), 1.35 (s, 12H, $\text{C}(\text{CH}_3)_2$), 2.29 (s, 4H, CH_2), 2.69 (sept, $^3J_{\text{HH}} = 6.5$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 7.23 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, Dipp-*m-CH*), 7.41 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, Dipp-*p-CH*). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 297 K): $\delta = 23.6$ ($\text{CH}(\text{CH}_3)_2$), 26.7 ($\text{CH}(\text{CH}_3)_2$), 28.7 ($\text{C}(\text{CH}_3)_2$), 28.9 ($\text{C}(\text{CH}_3)_2$), 29.4 ($\text{CH}(\text{CH}_3)_2$), 47.2 ($\text{C}(\text{CH}_3)_2$), 51.5 (CH_2), 69.9 ($\text{C}(\text{CH}_3)_2$), 120.7 (q, $^1J_{\text{CF}} = 271.1$ Hz, CF_3), 125.3 (Dipp-*m-CH*), 128.8 (Dipp-*i-C*), 130.5 (Dipp-*p-CH*), 136.6 (CCl), 146.6 (Dipp-*o-C*), 172.0 (C_{CAAC}). ^{19}F NMR (376 MHz, CDCl_3 , 297 K): $\delta = -77.8$.

Preparation of $[(^{\text{Me}}\text{CAACN})_2\text{CH}^+][\text{TfO}^-]$. To a solution of $1^{2+}[\text{TfO}^-]_2$ (3.6 g, 3.65 mmol) in CHCl_3 (4 mL) was added $\text{H}_3\text{B}\cdot\text{NEt}_3$ dropwise (0.81 mL, 5.47 mmol) while stirring at room temperature. After stirring for 5 minutes, volatiles were removed *in vacuo*, and the residue washed with *n*-hexane (36 mL) and Et_2O (2 \times 36 mL) by cannula filtration. The resulting residue was dried under vacuum to yield $[(^{\text{Me}}\text{CAACN})_2\text{CH}^+][\text{TfO}^-]$ (2.428 g, 88% yield) as an off-white powder. All spectroscopic data match literature values⁷.

Preparation of **8.** To a solution of $\text{C}_6\text{F}_5\text{Br}$ (0.01 mL, 0.079 mmol) in THF (0.5 mL) was added Mg dust (6 mg, 0.25 mmol) and sonicated for an hour. The resulting suspension was filtered into another flask containing $[(^{\text{Me}}\text{CAACN})_2\text{CH}^+][\text{TfO}^-]$ (30 mg, 0.039 mmol) and stirred for 5 minutes. Volatiles were removed *in vacuo*. To the solids were added C_6D_6 (0.5 mL) and filtered. The yield (40%

yield) of **8** was determined by ^1H NMR using C_6Me_6 as internal standard. All spectroscopic data match literature values⁷.

Preparation of $[(^{\text{Me}}\text{CAACN})_2\text{Cl}^+][\text{I}^-]$. A mixture of $[(^{\text{Me}}\text{CAACN})_2\text{CH}^+][\text{TfO}^-]$ (90 mg, 0.12 mmol) and $\text{K}[\text{N}(\text{SiMe}_3)_2]$ (24 mg, 0.12 mmol) in a vial was cooled to -40 °C in the glovebox. THF (3 mL) at -40 °C was added to the mixture to form an orange-red solution which was stirred for 5 minutes. I_2 (30 mg, 0.12 mmol) was added, and the resulting mixture was allowed to stir for an additional 5 minutes before warming up to room temperature. Volatiles were removed *in vacuo* and solids were dissolved in CDCl_3 for ^1H NMR. $[(^{\text{Me}}\text{CAACN})_2\text{Cl}^+][\text{I}^-]$ was not isolated.

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Additional information
Supplementary information is available for this paper.
Experimental details (PDF).
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