Radical Cations

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NHC-CAAC Heterodimers with Three Stable Oxidation States

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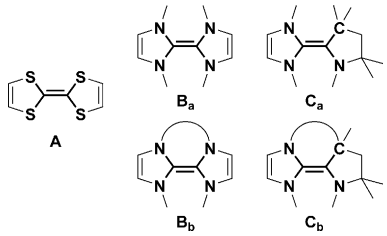
In memory of Jean-François Normant

Abstract: *The synthesis of N-heterocyclic carbene (NHC)–cyclic (alkyl)(amino) carbene (CAAC) heterodimers is presented. As the free carbenes do not react together in solution, the synthetic approach involves the addition of a free NHC to a cyclic iminium salt, which results in the formation of the protonated heterodimer. Subsequent deprotonation leads to the isolation of the corresponding mixed Wanzlick dimers. One- and two-electron oxidations of these triazaolefins result in the formation of stable cationic radicals and bis(cations), respectively, which have been isolated and fully characterized. Cyclic voltammetry, UV/Vis spectroscopy, spin density, and DFT calculations suggest that these heterodimers feature complementary electronic properties to tetrathiafulvalenes (TTFs).*

Electron-rich olefins exhibit exciting redox properties and reactivity due to their small HOMO–LUMO gap.[1] Among them, tetrathiafulvalenes **A** (TTF, Scheme 1), which are the dimer of the kinetically unstable 1,3-dithiol-2-ylidenes, are



Scheme 1. Tetrathiafulvalenes (**A**), tetraazafulvalenes (**B**), and the herein reported NHC-CAAC heterodimers (**C**).

arguably the most studied.[2,3] TTF derivatives have found applications in supramolecular chemistry,[4] (photo)electronic and photovoltaic devices,[5] electrically conducting materials for organic field-effect transistors,[6] redox-active ligands in organometallic chemistry,[7] chemical sensors, shuttles, and switches.[8] The success of TTF resides in its three stable oxidation states. Of particular interest are the radical cations, which are generated at low potentials and are isolable. The nitrogen analogues of TTF, namely tetraazafulvalenes **B** (dimers of imidazol-2-ylidenes[9]), feature more negative redox potentials[10] and have found recent applications as super-electron donors[11] and organocatalysts.[12] However, they do not yet rival TTFs, partly because of the low dissociation barrier into the two corresponding carbenes (Wanzlick's equilibrium),[13] and more importantly because cationic radicals derived from **B** are typically not isolable.[14] The first issue can be addressed by using small substituents at nitrogen[15] or by linking the carbene units by a tether ($\mathbf{B_b}$).[16] The second issue is more difficult to solve as the close proximity of the two redox potentials [$E_{1/2}(\mathbf{B}/\mathbf{B}^+)$ and $E_{1/2}(\mathbf{B}^+/\mathbf{B}^{2+})$] results in a facile two-electron oxidation process.[17] Linking the carbene units increases the electronic coupling but it remains small ($\Delta E_{1/2} < 0.3$ V).[11]

About a decade ago, we prepared cyclic (alkyl)(amino) carbenes (CAACs),[18,19] which are simultaneously more nucleophilic and more electrophilic than NHCs,[20] due to the replacement of one of the π-donor and σ-attractor nitrogen atoms by a carbon atom.[21] Of particular interest, CAACs are redox-active, which has allowed for the isolation of a variety of paramagnetic organic, main-group, and transition-metal compounds.[19] We therefore reasoned that olefins of type **C** derived from an NHC and a CAAC would combine the advantageous redox properties of both **A** and **B**. In other words, we hypothesized that such mixed carbene dimers would feature strong reducing properties approaching those of **B**, while displaying three stable redox states similar to **A**. Furthermore, owing to the small HOMO–LUMO gap of CAAC, we anticipated a much higher stability[22] of the derived olefins than observed for tetraazafulvalenes **B**. Herein we show that indeed both tethered and non-tethered neutral, monocationic, and dicationic NHC-CAAC heterodimers can be isolated. Their solid-state structures and electronic properties are discussed based on cyclic voltammetry, EPR and UV/Vis spectroscopy, and DFT calculations.

The dimerization of stable singlet carbenes has been a matter of controversy for decades.[23] Because of lone pair repulsion, the dimerization is associated with a considerable energy barrier,[22] which can usually only be overcome by acid catalysis.[24,25] We therefore reasoned that addition of an NHC to a cyclic iminium salt should give rise to the corresponding adduct. As expected, the reaction of the CAAC conjugate acid **1** with the NHC dimer **2**, which is known to stand in equilibrium with its monomers **3** in solution,[26] led to the precipitation of **4** as a colorless solid (Scheme 2). The ^{1}H and ^{13}C NMR spectra revealed characteristic signals for the central C–H unit (^{1}H: 5.4 ppm; ^{13}C: 74.2 ppm). Addition of

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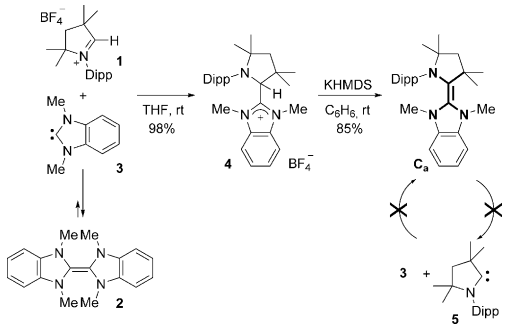
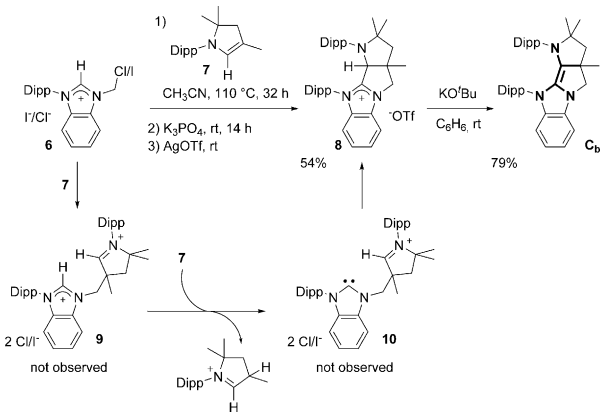


Scheme 2. Synthesis of triazaolefin $\mathbf{C_a}$. Dipp = 2,6-Diisopropylphenyl.

KHMDS to a benzene suspension of salt **4** led after work-up to the isolation of the desired triazaolefin $\mathbf{C_a}$ as a colorless solid (85% yield). Its structure was unambiguously established by NMR spectroscopy and a single-crystal X-ray diffraction study (see below). $\mathbf{C_a}$ is indefinitely stable under inert atmosphere, both in the solid state (m.p.: 182 °C) and in solution, and thus does not dissociate into the corresponding carbenes **3** and **5**. Of note, no reaction occurred when free CAAC **5** was reacted with NHC dimer **2**, underlining the high reaction barrier for this cross-carbene dimerization and the crucial role of the iminium proton in the coupling reaction.

We then turned our attention to the preparation of the tethered carbene heterodimer $\mathbf{C_b}$ using the synthetic strategy recently reported for the preparation of bidentate CAACs.[27] Accordingly, benzimidazolium salt **6** was reacted with an excess of cyclic enamine **7** in acetonitrile (Scheme 3). To our



Scheme 3. Synthesis of tethered triazaolefin $\mathbf{C_b}$.

surprise, we observed the formation of the mono-cationic polycycle **8**. The latter probably results from the deprotonation of the first formed bis(cation) **9** by the cyclic enamine **7**, which gives intermediate **10**; lastly, addition of the carbene center to the iminium carbon leads to the observed product **8**. After alkaline workup to eliminate the protonated enamine, and salt metathesis with AgOTf, compound **8** was isolated in 54% yield. Addition of potassium *tert*-butoxide[28] to a suspension of **8** in benzene led to clean formation of the polycyclic olefin $\mathbf{C_b}$, which was isolated as a bright yellow solid (79% yield, m.p.: 235 °C).

The cyclic voltammograms showed two reversible one-electron redox processes at −0.01 V and +0.33 V for $\mathbf{C_a}$ and −0.46 V and +0.41 V vs. SCE for $\mathbf{C_b}$ (Figure 1). For comparison, the voltammogram of the parent TTF **A** displays two waves at $E_{1/2} = +0.32$ V and +0.71 V vs. SCE,[11b] and

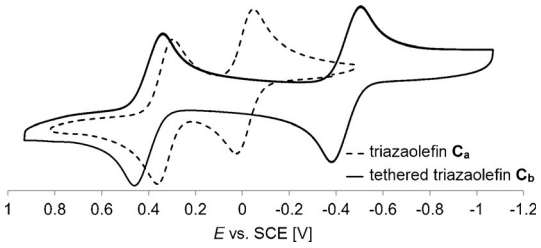
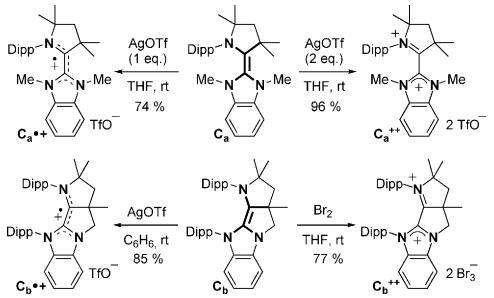


Figure 1. Cyclic voltammograms of olefins $\mathbf{C_a}$ and $\mathbf{C_b}$ (nBu$_4$NPF$_6$ 0.1 M in THF, 100 mV s^{-1}, vs. SCE).

tetraazafulvalenes **B** display overlapping or very close redox waves centered at more reductive potentials, typically around −1.00 V vs. SCE.[11] Similarly to the NHC dimers **B**, the electronic coupling in the tethered system $\mathbf{C_b}$ is much larger than in $\mathbf{C_a}$ with $\Delta[E_{1/2}(\mathbf{C_b})] = 0.87$ V and $\Delta[E_{1/2}(\mathbf{C_a})] = 0.34$ V.

In agreement with the oxidation potentials, compound $\mathbf{C_a}$ was chemically oxidized with one equivalent of silver trifluoromethanesulfonate in THF. After workup, $\mathbf{C_a}^{\bullet+}\cdot\mathrm{TfO}^-$ was isolated in 74% yield as an NMR-silent brownish solid. When two equivalents of silver trifluoromethanesulfonate were used, bis(cation) $\mathbf{C_a}^{2+}\cdot 2\,\mathrm{TfO}^-$ was formed and after workup isolated as a colorless solid in 96% yield (Scheme 4).



Scheme 4. Synthesis of mono-cationic radicals $\mathbf{C_a}^{\bullet+}$ and $\mathbf{C_b}^{\bullet+}$ and bis(cation)s $\mathbf{C_a}^{2+}$ and $\mathbf{C_b}^{2+}$.

Similarly, addition of silver trifluoromethanesulfonate or an excess of iodine to a benzene solution of olefin $\mathbf{C_b}$ allowed for the formation of the radical cation $\mathbf{C_b}^{\bullet+}\cdot\mathrm{TfO}^-$ and $\mathbf{C_b}^{\bullet+}\cdot\mathrm{I_3}^-$, which precipitated from the reaction solution as bright yellow single crystals. Lastly, addition of excess bromine to a THF solution of $\mathbf{C_b}$ induced the crystallization of red single crystals of $\mathbf{C_b}^{2+}\cdot 2\,\mathrm{Br_3}^-$. The solid-state structures of all six compounds are depicted in Figure 2.[29]

Comparison of the solid-state structures of the olefins (Figure 2 a and d) reveals that both internal C=C bonds are of comparable length [$\mathbf{C_a}$ 1.3459(16) Å, $\mathbf{C_b}$ 1.344(2) Å]. These values are close to those found in the parent TTF [1.349-(3) Å][30] and in benzimidazolylidene dimer **2** [1.343(4) Å].[31]

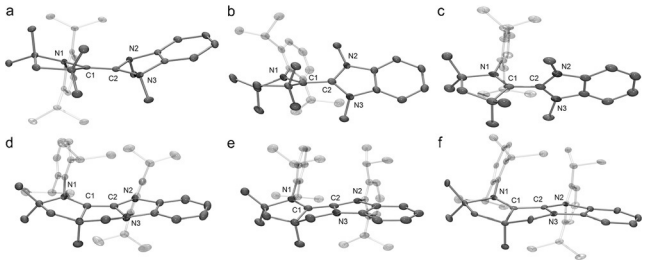


Figure 2. Solid-state structures of $\mathbf{C_a}$ (a), $\mathbf{C_a}^{\bullet+}$ (b), $\mathbf{C_a}^{2+}$ (c), $\mathbf{C_b}$ (d), $\mathbf{C_b}^{\bullet+}$ (e), and $\mathbf{C_b}^{2+}$ (f). Hydrogen atoms, solvent molecules, and counter-anions are omitted for clarity.[29]

Strikingly, the nitrogen centers of the NHC moiety in $\mathbf{C_a}$ are considerably pyramidalized [Σ(CN2C) = 328.85°; Σ(CN3C) = 330.66°] thereby decreasing the conjugation between the olefinic π-orbitals and p(N) lone pairs. Due to the polycyclic nature of $\mathbf{C_b}$, the pyramidalization is much smaller, which explains the more negative first oxidation potential observed for $\mathbf{C_b}$.

As expected, upon oxidation of $\mathbf{C_a}$ to the cations $\mathbf{C_a}^{\bullet+}$ and $\mathbf{C_a}^{2+}$ (Figure 2a–c), the central C–C bond elongates from 1.3459(16) to 1.439(3) and 1.491(4) Å. Simultaneously, the torsion angle between the two heterocycles increases [$\mathbf{C_a}$: 12.9; $\mathbf{C_a}^{\bullet+}$: 56.5; $\mathbf{C_a}^{2+}$: 87.5°][32] and the geometry around the nitrogen atoms of the benzimidazole moiety become more planar [$\Sigma(\mathrm{CNC})_{av}$: $\mathbf{C_a}$ 329.76; $\mathbf{C_a}^{\bullet+}$ 358.53; $\mathbf{C_a}^{2+}$ 358.09°]. Along the tethered series $\mathbf{C_b}$, $\mathbf{C_b}^{\bullet+}$, and $\mathbf{C_b}^{2+}$ (Figure 2d–f), less variation of geometric parameters are again observed due to the rigidity of the system.

X-band EPR measurements of both radical cations $\mathbf{C_a}^{\bullet+}\cdot\mathrm{TfO}^-$ and $\mathbf{C_b}^{\bullet+}\cdot\mathrm{TfO}^-$ in THF show that in both cases the unpaired electron couples with all three nitrogen atoms (Figure 3). Simulation[33] of the spectra allowed for the

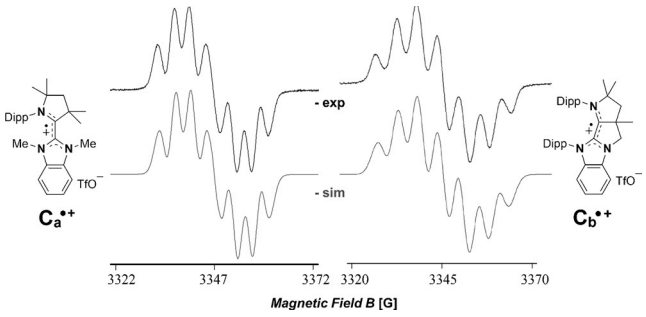


Figure 3. Experimental and simulated room-temperature EPR spectra of $\mathbf{C_a}^{\bullet+}\cdot\mathrm{TfO}^-$ and $\mathbf{C_b}^{\bullet+}\cdot\mathrm{TfO}^-$ in THF.

extraction of the isotropic hyperfine couplings with each nitrogen atom ($\mathbf{C_a}^{\bullet+}$ 15.6, 11.2, and 10.6 MHz; $\mathbf{C_b}^{\bullet+}$ 18.0, 14.7, and 13.1 MHz). These coupling constants confirm that there is no significant contribution from atomic s(N) orbitals in the SOMO of either $\mathbf{C_a}^{\bullet+}$ and $\mathbf{C_b}^{\bullet+}$ (< 1%).[34] Unrestricted DFT calculations at the B3LYP-D3(COSMO,ZORA)/def2-TZVPP//B3LYP-D3(COSMO,ZORA)/def2-TZVP level of theory reproduced the hyperfine couplings well. Of particular interest, the Löwdin population analysis confirms that the spin density is polarized toward the CAAC fragment of the carbene heterodimer with a larger hyperfine coupling constant with the CAAC nitrogen atom (Figure 4).

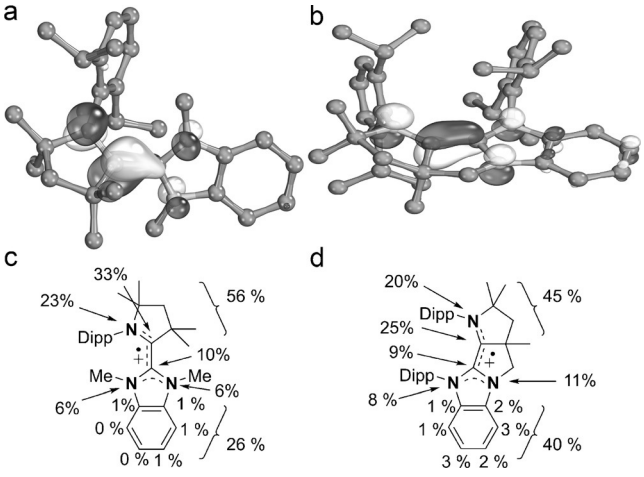


Figure 4. Representation[35] of SOMOs (α-spin) of $\mathbf{C_a}^{\bullet+}$ (a) and $\mathbf{C_b}^{\bullet+}$ (b). Spin densities as predicted by the Löwdin population analysis for $\mathbf{C_a}^{\bullet+}$ (c) and $\mathbf{C_b}^{\bullet+}$ (d).

Since the change of oxidation states in the $\mathbf{C_a}^{n+}$ series (n = 0, 1, 2) leads to greater structural and color changes than for the tethered $\mathbf{C_b}^{n+}$ series, we explored the electronic and intramolecular charge-transfer properties of $\mathbf{C_a}^{\bullet+}\cdot\mathrm{TfO}^-$. Olefin $\mathbf{C_a}$ and dication $\mathbf{C_a}^{2+}\cdot 2\,\mathrm{TfO}^-$ do not show any strong bands with a wavelength longer than 330 nm, whereas three broad absorption bands were observed for $\mathbf{C_a}^{\bullet+}\cdot\mathrm{TfO}^-$ (λ_{max} = 530 nm, 360–410 nm, 330 nm; Figure 5). TD-DFT calculations allowed the assignment of the absorption bands to specific electronic transitions (Supporting Information, Figure S18). All transitions S1–S9 correspond to π–π* transitions with considerable charge transfer character. The band observed at 530 nm corresponds to the S1 excitation of the unpaired electron residing in the α-spin HOSO (highest occupied spin orbital) to the α-spin LUSO (lowest unoccu-

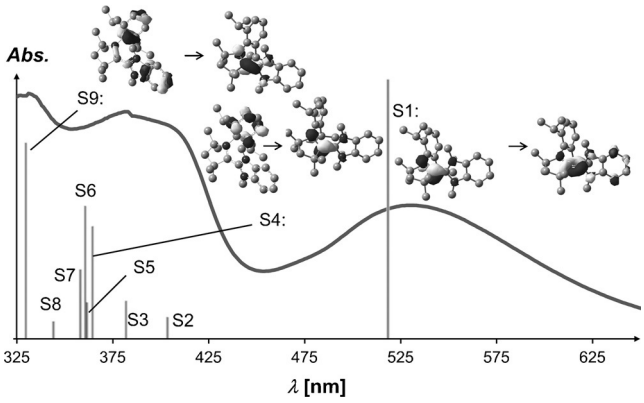


Figure 5. Normalized UV/Vis spectrum of $\mathbf{C_a}^{\bullet+}\cdot\mathrm{TfO}^-$ in THF (curve), and electronic transitions as modeled by TD-DFT (bars) with depiction of selected natural transition orbitals.

pied spin orbital), which expands over the olefin and benzimidazole π-system. The bands assigned to S4 and S9 feature transitions from a π-orbital located mainly on the diisopropylphenyl group (S4) and from the benzimidazole moiety (S9) to the central CC bond. The band at 330 nm and broad band extending from 360–410 nm are associated with charge transfer processes between the olefin, the diisopropylphenyl group, and the benzimidazole moiety.

In summary, tethered and non-tethered NHC-CAAC heterodimers are readily available via direct addition of an NHC onto a cyclic iminium salt, followed by deprotonation. The resulting triazaolefins display three isolable oxidation states, and therefore qualify as a new class of redox switch electron-rich olefins. On one hand, non-tethered triazaolefin family exhibits significant changes in their absorption spectra upon formation of each of the three oxidation states. On the other hand, the tethered series is characterized by a more delocalized unpaired electron with a very large electronic communication close to 0.9 V. By analogy with TTF derivatives, these carbene heterodimers hold promise for future applications.

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