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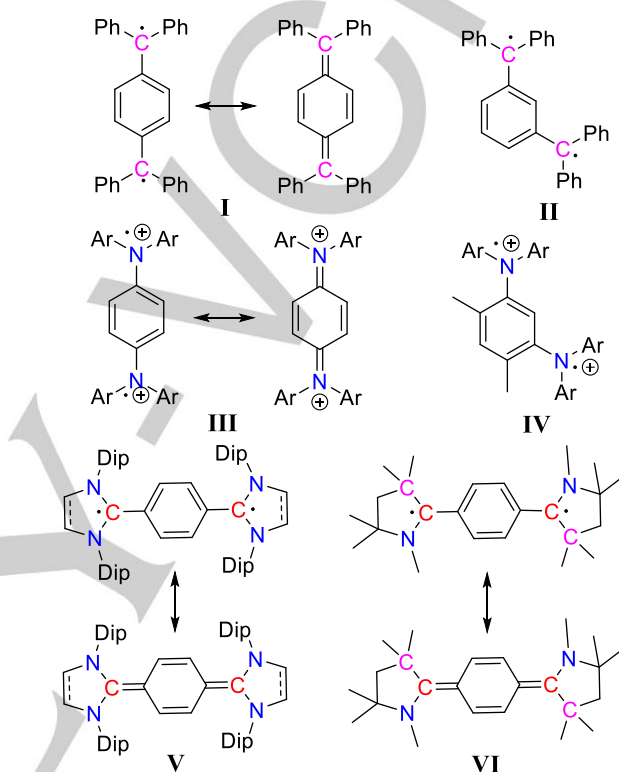
CAAC-Based Thiele and Schlenk Hydrocarbons

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Dedicated to Professor Dr. Herbert W. Roesky on the occasion of his 85th birthday.

Abstract: Diradicals have been of tremendous interest for over a century ever since the first reports of *p*- and *m*-phenylene-bridged diphenylmethylradicals in 1904 by Thiele and 1915 by Schlenk. Herein, we report the first examples of cyclic(alkyl)(amino)carbene (CAAC)-analogues of Thiele's hydrocarbon, a Kekulé diradical, and Schlenk's hydrocarbon, a non-Kekulé diradical *without* using CAAC as a precursor. The CAAC analogue of Thiele's hydrocarbon has a singlet ground state, whereas the CAAC analogue of Schlenk's hydrocarbon contains two unpaired electrons. The latter forms a dimer, by an intermolecular double head-to-tail dimerization. Our disclosed straightforward synthetic methodology is modular and can be extended for the generation of redox-active organic compounds.

Diradicals, are a class of intriguing reactive compounds having two unpaired electrons.^[1] Such compounds have been of considerable interest for several reasons. Firstly, their design and assembly have been a challenge to the synthetic chemists.^[2] Secondly, their structural and spectroscopic properties have been of interest both from a theoretical and an experimental point of view.^[3] And thirdly, open-shell compounds in general as well as diradicals that fall into this category have been of significant importance for the design of novel functional materials with applications in a variety of areas including molecular electronics.^[4] Considering their assembly, the two radical centres in reported diradicals have been connected via different types of motifs.^[5] Following the landmark report on the formation of the triphenylmethyl radical in 1900 by Gomberg,^[6] Thiele *et al.* reported in 1904 their diradical **I** (Scheme 1), aka Thiele's hydrocarbon, in which the two radical centres are connected through the *p*-phenylene bridge.^[7] In 1915, Schlenk *et al.* reported the diradical **II**, aka Schlenk's hydrocarbon, in which the two radical centres are connected through the *m*-phenylene bridge.^[8] This system constitutes an open-shell triplet diradical (non-Kekulé diradical) since a direct communication between the two radical centers of **II** is not possible in contrast to diradical **I**.



Scheme 1. Chemical structures **I-VI** (Ar = 4-MeOC₆H₅, Dip = 2,6-*i*-Pr₂C₆H₃).

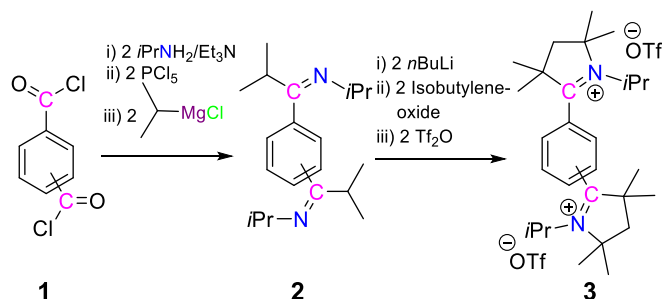
Following the initial synthesis of **I** and **II**, a variety of other derivatives^[9] including nitrogen analogues such as **III**^[10] and **IV**^[11] (Scheme 1) were prepared and studied.^[12] Ghadwal *et al.* reported the *N*-heterocyclic carbene (NHC)-analogue of Thiele's hydrocarbons, **V**.^[13] Recent theoretical studies by Munz and coworkers pointed to CAAC-analogues of Thiele's hydrocarbon, **VI** (Scheme 1) as excellent candidates for opto-electronic applications.^[14] However, the synthesis and properties of such a system has not been reported yet. It has already been noticed that replacing the Ph₂C/Ph₂C-scaffolds in **I** and **II** with isoelectronic Ar₂N⁺/Ar₂N⁺ as in **III** and **IV** and with isoelectronic NHC as in **V** results in distinct changes in their electronic and consequently in their spectroscopic properties. Given this realization, along with the theoretical calculations and, even more importantly, the wide use of CAAC-scaffolds for the isolation of a variety of open-shell compounds,^[15] we were interested in designing diradicals containing CAAC-motifs.

Employing the corresponding pyrrolinium salts as precursors constitutes one of the routes toward CAAC-scaffold based carbon centred radicals. In order to get the requisite bis-pyrrolinium salts a strategy based on our recent report^[16] was applied (Scheme 2).^[17] The three sequential reactions of **1^p** or **1^m**

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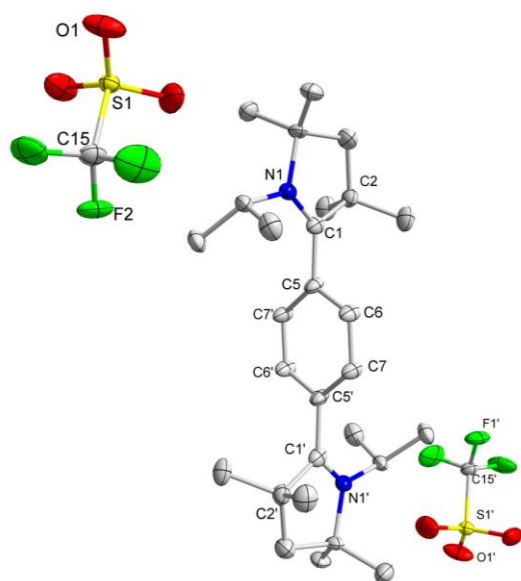
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with two equivalents of *i*PrNH₂/Et₃N, PCl₅, and *i*PrMgCl afforded the bisimines, **2^p** and **2^m**. The final cyclization step of bisimines, **2^p** and **2^m** to the corresponding *p*- and *m*-phenylene-bridged pyrrolinium cations, **3^p** and **3^m** was accomplished in a one-pot reaction involving two equivalents of *n*BuLi, isobutylene oxide, and Tf₂O (Scheme 2).^[17]



Scheme 2. Synthesis of *p*- and *m*-phenylene bridged pyrrolinium cations **3^p** and **3^m**.

Compounds **3^p** and **3^m** were characterized by multi-nuclear solution NMR spectroscopy (¹H, ¹³C{¹H}, and ¹⁹F{¹H}) as well as by solid state single crystal X-ray diffraction analysis.^[18] The ¹H NMR spectra of **3^p** and **3^m** exhibit only one set of septet at $\delta = 4.33$ and 4.32 ppm, respectively and this indicates the fast rotation of pyrrolinium-scaffold in the NMR-time scale even at lower temperature (-35 °C). The four aromatic C-H of **3^p** give rise to a singlet at $\delta = 7.69$ while the corresponding aromatic C-H of **3^m** result in three resonances in a 1:1:2 ratio at $\delta = 7.89$, 7.79, and 7.72 ppm. These results indicate that in solution compounds **3^p** and **3^m** have a symmetric structure with a C₂-axis. This has also been reflected in their corresponding solid state structures determined through single crystal X-ray diffraction (*vide infra*).



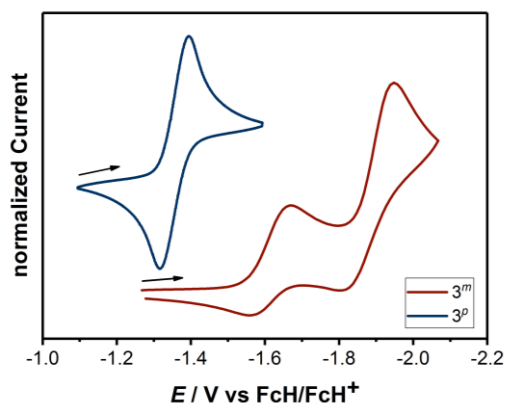


Figure 3. Cyclic voltammograms of 3^P (blue), with 0.1 M $\text{NBu}_4\text{BARf}_4$, and 3^m (red), with 0.1 M NBu_4PF_6 , in MeCN at $100 \text{ mV}\cdot\text{s}^{-1}$.

Additionally, proof for the two-electron nature of this wave was generated by performing CV and differential potential voltammogram (DPV) measurements on an equimolar solution of 3^P and 3^m . (Figure 4 and see below). The comparative current heights also imply the two-electron nature of the reduction wave of 3^P . This implies that the electronic coupling between the two redox centres is very small in the case of the CAAC-scaffold and that it is motif dependent. The case of the NHC analogue of the Thiele hydrocarbons **V** ($\Delta E_{1/2} = 0.25 \text{ V}$ for unsaturated NHC-motif and $\Delta E_{1/2} = 0.15 \text{ V}$ for saturated NHC-motif) supports this reasoning.^[13]

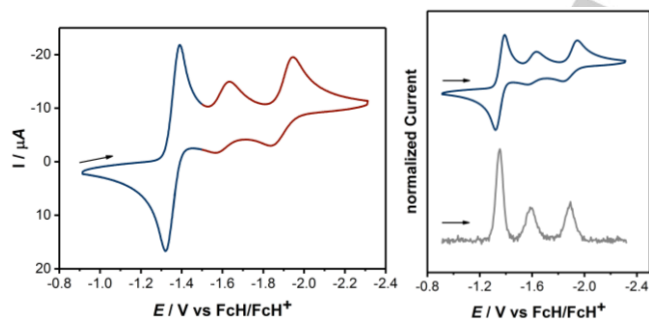


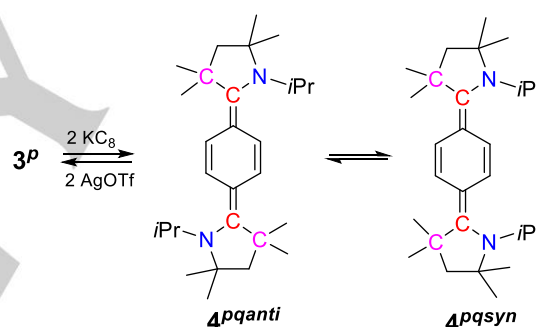
Figure 4. Left: Cyclic Voltammogram of a 0.1 M solution of 3^P (blue part) and 3^m (red part) with 0.05 M $\text{NBu}_4\text{BARf}_4$ in MeCN at $100 \text{ mV}\cdot\text{s}^{-1}$. Right: Cyclic voltammogram (top) and differential potential voltammogram (DPV) (bottom) of a 0.1 M solution of 3^P and 3^m in MeCN at $100 \text{ mV}\cdot\text{s}^{-1}$ (CV) and $20 \text{ mV}\cdot\text{s}^{-1}$ (dpv) with 0.05 M $\text{NBu}_4\text{BARf}_4$.

3^P displays a single absorption band at $\lambda_{\text{max}} = 267 \text{ nm}$ consistent with its colorless nature. Vis/NIR spectroelectrochemical measurements showed a clean conversion of this compound to a new species with an absorption maximum at $\lambda_{\text{max}} = 431 \text{ nm}$ (Figure S41) and this is very similar to the spectrum of the isolated two-electron reduced quinoidal form 4^P ($\lambda_{\text{max}}(\epsilon) = 429 (54062) \text{ nm} (\text{Lmol}^{-1}\text{cm}^{-1})$).^[17]

In accordance with the cyclic voltammetry experiments, the reduction of 3^P with two equivalents of KC_8 leads to 4^P in about 70 % yield as a thermally stable but highly air and moisture sensitive yellow solid (Scheme 3).^[17] At room temperature a well resolved ^1H NMR spectrum was obtained, which is consistent with a diamagnetic singlet ground state. 4^P consists of a mixture

of two-isomers (4^{psyn} and 4^{panti}). Calculations at TPSSh/def2-TZVP level of theory point to strong antiferromagnetic coupling of the spins, leading to a singlet ground state which is stabilized with respect to the triplet excited state by more than 2000 cm^{-1} .^[17] Accordingly, no EPR signals were observed for the two-electron reduced compound 4^P . When a crystalline sample of 4^P was dissolved in C_6D_6 and a ^1H NMR spectrum immediately recorded, we observed the presence of 4^{panti} as the major isomer as in the solid state molecular structure (*vide infra*). Time-dependent ^1H NMR shows that the 4^{panti} isomer reached an equilibrium with 4^{psyn} isomer in about 190 minutes (Figures S16 and S17).^[17]

In the solid state molecular structure only the *anti*-isomer, 4^{panti} , is present (Figure 5).^[18] The distance between C1-C5 is $1.381(2) \text{ \AA}$ which is similar to that observed in Thiele's hydrocarbon, **I** (1.381 \AA)^[19] but longer than that found in **V** (1.375 \AA for unsaturated NHC and 1.371 \AA for saturated NHC).^[13] The C-C bond lengths in the central phenyl ring reveal an alternation of short and long bond lengths consistent with the chemical structure. The sum of the bond angles around C1 and C1' is 359.54° . Both N1 and N1' also adopt an almost planar geometry ($\Sigma\text{N} = 358.16^\circ$). Compound 4^P could be reversibly oxidized to 3^P by two equivalents of AgOTf in a 78 % isolated yield (Scheme 3).



Scheme 3. Synthesis of 4^P .

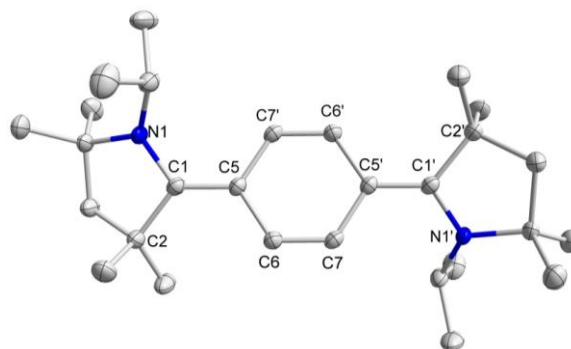


Figure 5. Molecular structure of 4^{panti} with thermal ellipsoids at 50 %. All hydrogen atoms are omitted for clarity. Selected bond lengths [\AA] and bond angle [$^\circ$]: N1–C1 $1.395(2)$, C1–C5 $1.381(2)$, C5–C6 $1.452(2)$, C6–C7 $1.352(2)$, C7–C5' $1.453(2)$; N1–C1–C2 $108.15(10)$.

In contrast to 3^P , the meta-substituted compound, 3^m displays two one-electron reduction steps at $E_{1/2} = -1.61 \text{ V}$ and -1.88 V in $\text{CH}_3\text{CN}/0.1 \text{ M}$ Bu_4NPF_6 or $\text{Bu}_4\text{NBARf}_4$ ($[\text{BARf}_4]^- = [3,5-$

(CF₃)₂-C₆H₃4B⁻), the first of which is completely reversible (Figures 3 and S34-S35).^[17] The difference between the two reduction waves of 270 mV points to a reasonable thermodynamic stability for the one-electron reduced mixed-valence species. However, the second reduction is not reversible in CH₃CN solvent. The native form of **3^m** in solution displays absorption bands only in the UV region. Upon one-electron reduction new bands appear in the visible region with maxima at λ_{max} = 364 and λ_{max} = 493 nm (Figure 6). Reversing the potential to the starting potential led to the quantitative regeneration of the spectrum corresponding to **3^m**, thus proving the reversible nature of the first reduction wave on the Vis-NIR spectroelectrochemical timescale. The second reduction turned out to be irreversible in CH₃CN as the starting spectrum of the compound could not be regenerated once two electrons were added. This implies that **4^m**, the 2-e reduced compound, reacts with CH₃CN. This was confirmed by an independent reaction of **4^m** and CH₃CN. This is in contrast to the stability of **4^m** in hexane (Figure S32).^[17] However, the initial changes in the UV/vis spectrum upon the second reduction of **3^m** are very similar to those observed for the one-electron reduced species (Figure 6). This suggests that there is no electronic coupling between the two reduced centers in the two-electron reduced form, and the differences in the redox potentials between the two reduction waves should be largely assigned to coulombic interactions. No further bands at longer wavelengths were observed either for the one- or the two-electron reduced compounds. It was not possible to investigate the one-electron reduced form of **3^m** by EPR spectroscopy. Both EPR spectroelectrochemistry (longer electrolysis times compared to Vis-NIR spectroelectrochemistry because of different cell designs), and chemical reduction proved unsuccessful for this purpose.

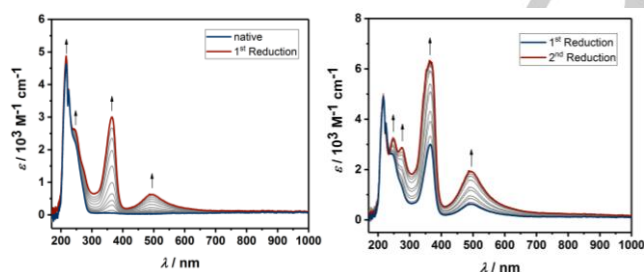
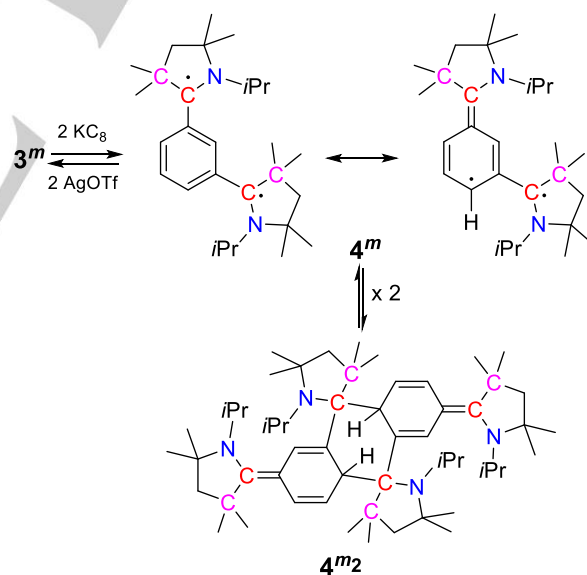


Figure 6. Changes in UV/vis spectrum of **3^m** in MeCN with 0.1 M Bu₄NPF₆ during the first reversible (left) and second irreversible (right) reduction.

When the reduction of **3^m** was carried out with two equivalents of KC₈ in hexane, the formation of a deep-red coloured solution was observed (Scheme 4). After work up, the resulting red colored sticky compound was crystallized from benzene/hexane solution and after one week very few yellow crystals of **4^{m2}** could be isolated in a reproducible manner, the molecular structure of which was confirmed by single crystal X-ray diffraction analysis (Figure 7).^[18] Compound **4^{m2}** is the dimer of the initially formed diradical **4^m** and is possibly formed by an intermolecular double head-to-tail dimerization. **4^m** can be reversibly “re-oxidized” back to **3^m** by two equivalents of AgOTf in hexane in a 58% isolated yield, indirectly indicating the existence of a di-radical centre in **4^m** (Scheme 4). *m*-Quinodimethane, the parent hydrocarbon of the *m*-quinonoid or

dimethyl substituted *m*-quinodimethane is also known to dimerize in an intermolecular double head-to-head fashion under the formation of *m*-cyclophane.^[20] In benzene, **4^{m2}** dissociates to **4^m**, a process that can be followed by a slow color change from light yellow to red.

The chemically isolated two-electron reduced compound **4^m** was investigated both as the red sticky compound as well as in solution in hexane via EPR spectroscopy. In both cases, strong EPR responses were observed with signals centered at *g*-values of 2.0032 and 2.0042 respectively (Figure 7).^[17] The spectrum in solution was nicely simulated by considering hyperfine coupling to one ¹⁴N and to five different ¹H nuclei (Table S2).^[17] These findings support a diradical nature of **4^m** as required for the subsequent dimerization reaction. Additionally, the EPR data indicate the existence of two uncoupled electron spins in **4^m**. This fact is also supported indirectly by the Vis-NIR spectroelectrochemistry data, where the “attempted” generation of the two-electron reduced species delivered a spectrum that just displayed a doubling of intensity of the spectrum of the one-electron reduced form (see above). Calculations at TPSSh/def2-TZVP level of theory indicate a triplet ground state for **4^m** with the excited singlet state lying at least 400 cm⁻¹ higher in energy.^[17] A likely explanation for the observation of two uncoupled spins could be the orthogonal twist of the spin-containing peripheral groups with respect to the central phenylring. The spin-spin coupling in this case is likely to be highly sensitive to the aforementioned twist, and DFT calculations probably overestimate the coupling because of this sensitivity.



Scheme 4. Synthesis of **4^m** and **4^{m2}**.

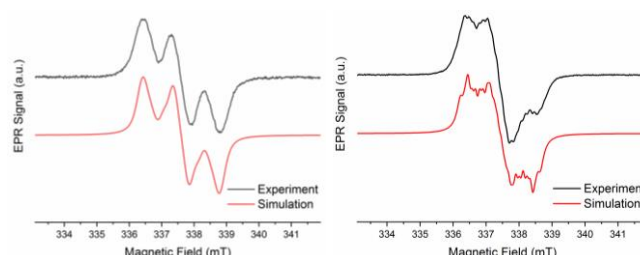


Figure 7. EPR spectra at 25 °C of 4^m as a sticky red oil (left) and 4^m in hexane solution (by dissolving the sticky red oil) (right)

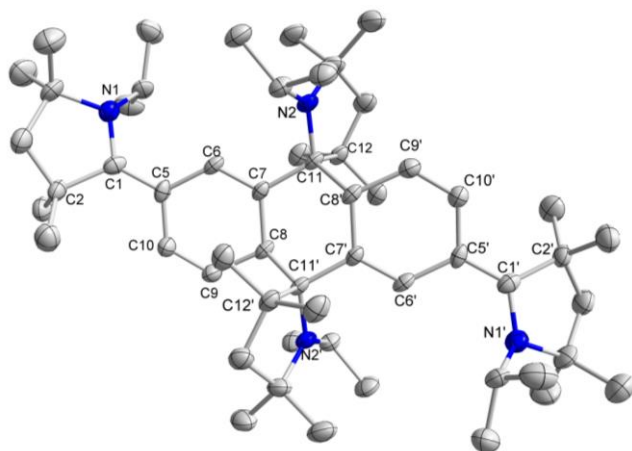


Figure 8. Molecular structure of 4^m_2 with thermal ellipsoids at 50 %. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: N1–C1 1.391(5), C1–C5 1.370(6), C5–C6 1.465(6), C6–C7 1.341(5), C7–C8 1.512(6), C8–C9 1.501(6), C9–C10 1.336(6), C10–C5 1.443(6), C7–C11 1.535(6), C8–C11' 1.594(5), C11–N2 1.478(5); N1–C1–C2 109.33(30), N2–C11–C12 103.00(26).

In 4^m_2 , the sum of the bond angles around C1 ($\Sigma C1 = 359.9^\circ$) and C11 ($\Sigma C11 = 325.84^\circ$) indicate that the respective centres adopt a planar and a pyramidal geometry, respectively. The C1–C5 bond distance is 1.370(6) Å whereas the C7–C11 bond distance is 1.535(6) Å. The six-membered ring (C8–C7–C11–C8'–C7'–C11') in the dimer adopts a chair conformation (Figure 8).^[18] Theoretical calculations show that dimerization of 4^m to form 4^m_2 is favored, with $\Delta G_{298} = -10.4$ kcal/mol.^[17]

In conclusion, we have designed and synthesized the first CAAC-based Thiele and Schlenk hydrocarbons *without* the use of CAAC as a precursor. The CAAC analogue of the Thiele hydrocarbon displays a singlet ground state (Kekulé diradical) while the CAAC analogue of the Schlenk hydrocarbon shows two unpaired electrons (non-Kekulé diradical) and undergoes an intermolecular double head-to-tail dimerization. The straightforward synthetic methodology revealed in this study will be instrumental for generating new classes of carbon centres based di- and poly-radical systems^[21] and also for the synthesis of new class of organic redox systems.

Acknowledgements

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Keywords: carbenes • conjugation • diradicals • Thiele's hydrocarbon • Schlenk's hydrocarbon

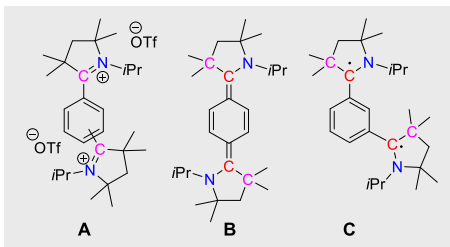
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COMMUNICATION

p- and *m*-phenylene bridged bis-pyrrolinium cations **A** provide access to CAAC-analogues of Thiele's hydrocarbon **B**, a Kekulé diradical, and to Schlenk's hydrocarbon **C**, a non-Kekulé diradical, respectively. Compound **B** has a singlet ground state. Compound **C** has two unpaired electrons in the ground state and forms a dimer by an intermolecular double head-to-tail dimerization.



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