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Cross-Coupling of NHC/CAAC-Based Carbodicarbene: Synthesis of Electron-Deficient Diradicaloids

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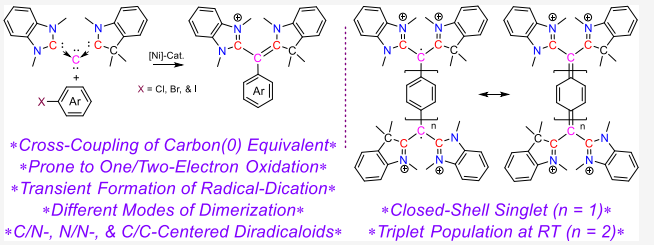
ABSTRACT: Herein, we report nickel(0)-catalyzed cross-coupling reactions of NHC/CAAC-based carbodicarbene (NHC = *N*-heterocyclic carbene and CAAC = cyclic(alkyl)(amino)carbene) with different aryl chlorides, bromides, and iodides. The resulting aryl-substituted cationic carbodicarbene derivatives are prone to one-electron oxidation yielding radical-dications, which, depending on the aryl motif employed, follow different modes of radical−radical dimerization and constitute an entry point to carbon/nitrogen- and nitrogen/nitrogen-centered diradicaloids. Subsequently, this coupling strategy was strategically applied to the synthesis of *p*-phenylene- and *p*,*p*′-biphenylene-bridged carbon/carbon-centered electron-deficient diradicaloids. The employed *π*-conjugated spacer plays a crucial role in determining the triplet population at room temperature by modulation of the singlet−triplet gap: EPR inactive for *p*-phenylene vs EPR active for *p*,*p*′-biphenylene. Nearly two decades after the disclosure of carbodicarbenes as donor-stabilized atomic carbon equivalents by Tonner and Frenking in 2007, we demonstrate their cross-couplings with a series of aryl halides/dihalides and, based on this, developed a modular methodology for the systematic synthesis of various electron-deficient diradicaloids.



INTRODUCTION

Transition metal-catalyzed cross-coupling reactions between functionalized aryl compounds have been, and still are, critically important in the synthesis of a variety of functional molecules ranging from pharmaceuticals to polymers (**I**, Scheme 1).[1] Such cross-coupling reactions were also known for the buildup of various alkyl-, vinyl-, and alkynyl-functional molecules.[2] Furthermore, carbon(II)-centers of *N*-heterocyclic carbenes (NHCs) were coupled to various aryl halides, resulting in the formation of (dihydro)-imidazolium cations (**II**, Scheme 1), which were then utilized as synthons for the generation of radicals under one-electron reduction.[3] Following the discovery of the concept of carbodicarbene as a donor-stabilized atomic carbon equivalent,[4] various functionalizations of carbodicarbenes have been reported, primarily harnessing the nucleophilic properties of the carbon(0)-center.[5] These findings inspired us to investigate the feasibility of cross-coupling reactions of the carbonic carbon(0)-center. Herein, the successful cross-coupling of an NHC/CAAC-based carbodicarbene (NHC = *N*-heterocyclic carbene and CAAC = cyclic(alkyl)(amino)carbene)[6] with different aryl chlorides, bromides, and iodides is reported (**III**, Scheme 1). The resulting aryl-functionalized cationic carbodicarbene derivatives are able to undergo one-electron oxidation under the formation of radical-dications, which then follow different modes of radical−radical dimerization based on the nature of the aryl groups employed. Furthermore, we also considered the use of *π*-conjugated diiodoaryls as coupling partners, and the resulting dicationic bis-carbodicarbene derivatives undergo reversible two-electron oxidation, yielding electron-deficient diradicaloids. Please note that NHC/CAAC-based carbodicarbene can be depicted in various forms **A**−**D**, considering different concepts of bonding and representation (Scheme 1).[7] We have opted to represent it here as the mono-zwitterionic form **C** by taking into account the different electronic natures of NHC and CAAC; specifically, NHC is relatively less nucleophilic and less electrophilic in nature than CAAC,[8] which is also reflected in the solid-state molecular structure of NHC/CAAC-based carbodicarbene.[6]

RESULTS AND DISCUSSION

The cross-coupling reactions of NHC/CAAC-based carbodicarbene **1** with phenyl chloride/bromide/iodide or 4-*tert*-butyl-phenyl bromide/iodide in the presence of a catalytic amount of $Ni(COD)_2/PPh_3$ led to the isolation of yellow

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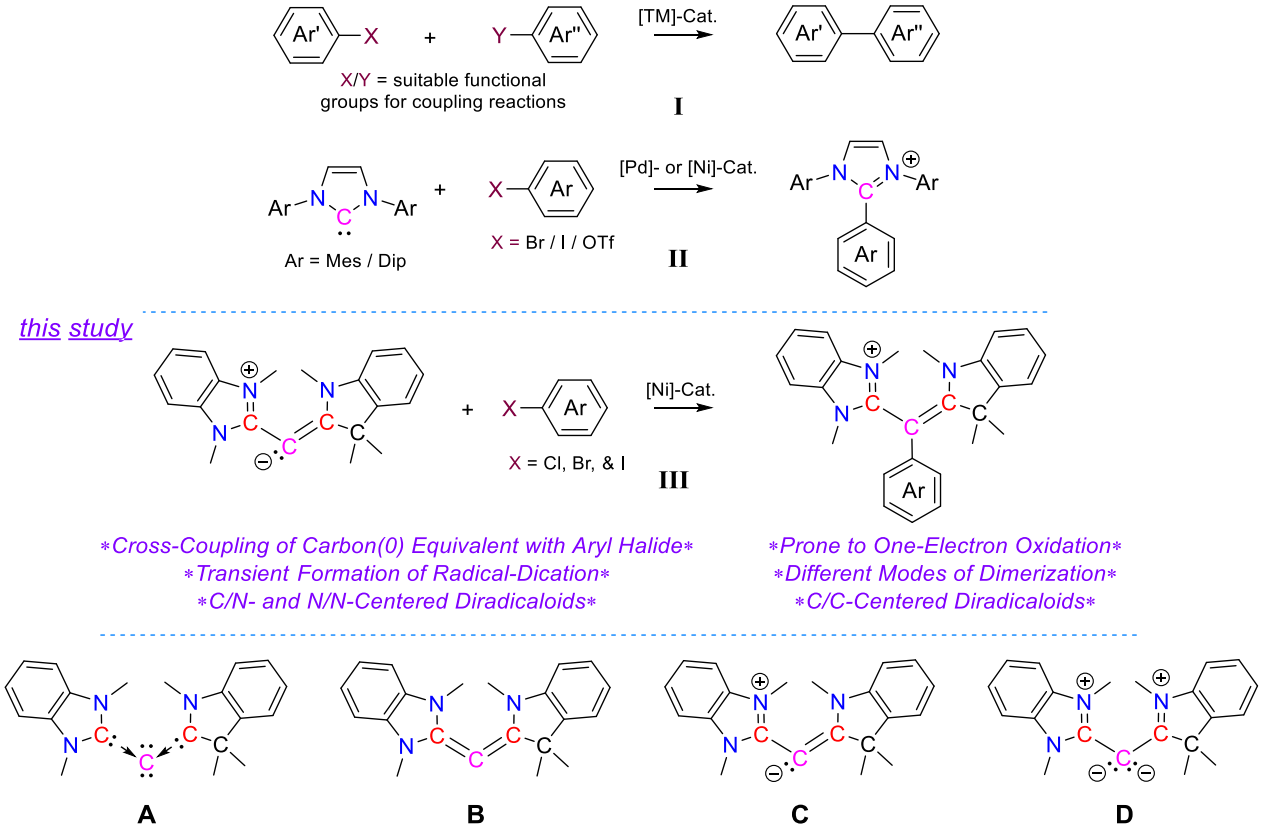
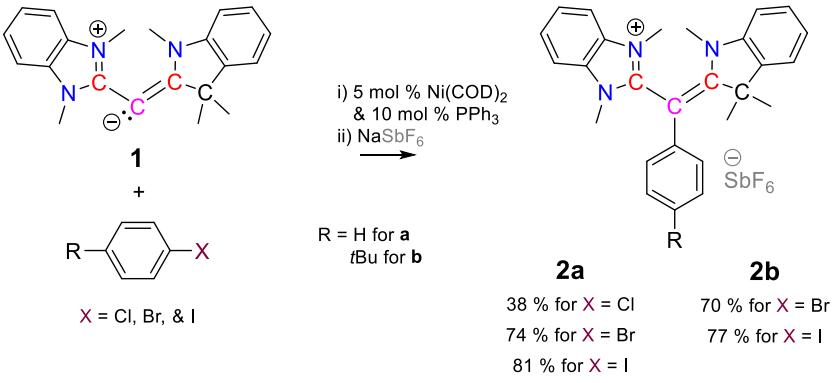
Scheme 1. Schematic Representation of Reactions I–III (Corresponding Counter Anions of Ionic Compounds Are Omitted for Clarity) and Four Possible Representations of NHC/CAAC-Based Carbodicarbene A–D



Scheme 2. Synthesis of 2a/2b



crystalline **2a**/**2b** (Scheme 2).[9] In the $^{13}C\{^1H\}$ NMR spectra of **2a** and **2b**, the resonances at δ = 88.80 and 88.66 ppm are assigned to the aryl-functionalized carbonic carbon, respectively. The single-crystal X-ray diffraction analyses of **2a** and **2b** reveal that the C1–C3 bond lengths (1.454(4)/1.436(5) Å) are longer than the C1–C2 distance (1.368(4)/1.363(5) Å), reflecting the different electronic natures of NHC and CAAC (Figure 1).

With cyclic voltammetry, it was shown that both compounds **2a** and **2b** are prone to oxidation at $E_{1/2}$ = 0.71[10] and 0.58 V vs Fc/Fc^+, respectively (Figure 2).

Subsequent chemical oxidation of **2a**/**2b** with $[NO][SbF_6]$ in CH_3CN led to an immediate visible color change from yellow to blue and red, respectively. In the case of **2a**, compound **4** was obtained along with its two-electron oxidized form **5** (Scheme 3). The formation of **4**/**5** indicates that the initially formed radical-dication **3a** undergoes heteroleptic dimerization[11] between the *para*-position of the phenyl group and the *para*-position of the benzannulated CAAC-motif (relative to the *N*-substituent). This dimerization is also supported by the spin-density analysis of **3a** at the UB3LYP-D3/Def2-SVP(CH_3CN-SMD) level of theory,[9] which indicates that the unpaired spin is mostly delocalized over the carbonic carbon, *ortho*- and *para*-positions of the phenyl group, and nitrogen/benzene-ring (*ortho*- and *para*-positions with respect to the *N*-substituent) of the CAAC-motif (Figure 3 - left). Reduction of the crude reaction mixture with elemental zinc led to the pure crystalline compound **4** in 28% yield. The single-crystal X-ray diffraction analysis unambiguously confirmed the formation of **4**, proving the bond-connectivity to be the result of heteroleptic dimerization of radical-dication **3a** (Figure 4).

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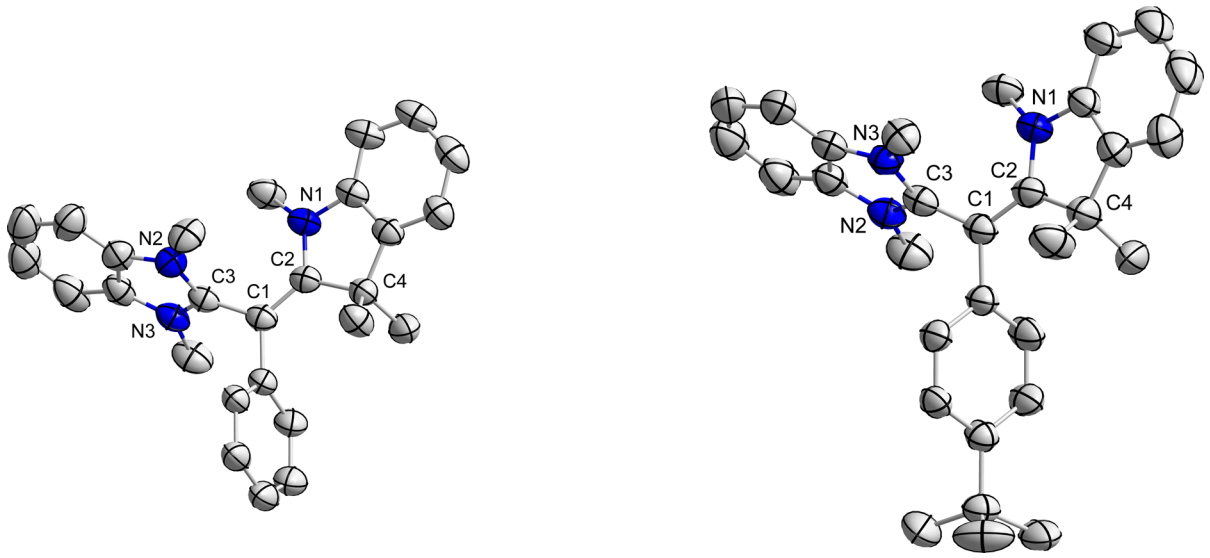

Figure 1. Molecular structures of **2a** and **2b** at 40 and 50% probability levels, respectively. All hydrogens and counteranions are omitted for clarity. Selected bond lengths (Å) and bond angles (°) for **2a**: C1−C2 1.368(4), C1−C3 1.454(4), C1−C5 1.534(11); C2−C1−C3 121.8(2), C2−C1−C5 125.7(12), C3−C1−C5 111.5(11); and for **2b**: C1−C2 1.363(5), C1−C3 1.436(5), C1−C5 1.502(5); C2−C1−C3 120.9(3), C2−C1−C5 124.3(3), C3−C1−C5 114.7(3).

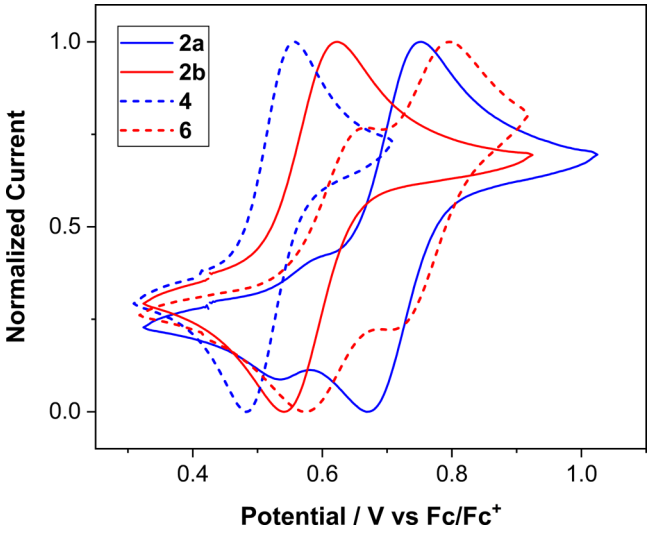

Figure 2. Cyclic voltammograms of **2a**, **2b**, **4**, and **6** at a 100 mV/s scan rate in CH_3CN (0.1 mol/L Bu_4NPF_6) at room temperature.

A cyclic voltammetry study confirmed that compound **4** can be subjected to a single two-electron oxidation at $E_{1/2}$ = 0.52 V vs Fc/Fc^+ (Figure 2), resulting in the formation of tetracation **5**; this also supports the co-formation of **5** along with the initially formed **4** during the oxidation of **2a** using $[NO][SbF_6]$ ($E_{1/2}$ = 0.87 V vs Fc/Fc^+ in CH_3CN).[12] Subsequent chemical oxidation of **4** with two equivalents of $[NO][SbF_6]$ indeed leads to **5**.[13] The UV/vis/NIR spectrum of the solution resulting from the chemical oxidation shows the longest wavelength absorption at λ_{max} = 686 nm for **5** (Figure S47), which is considerably red-shifted in comparison to that of **4** (λ_{max} = 393 nm) (Figure S41). However, due to its limited stability in CH_3CN, it could not be crystallized, even after several attempts.

In the case of **2b**, compound **6** was obtained along with its one- and two-electron oxidized compounds **7** and **8**, respectively (Scheme 4). The formation of **6**/**7**/**8** indicates that the initially formed radical-dication **3b** undergoes homoleptic dimerization[14] between the *para*-positions of the benzannulated CAAC-motif (relative to the *N*-substituent). This is also supported by the spin density plot[9] of **3b**, in which the unpaired spin is delocalized as in the case of **3a** (Figure 3 - right); however, here the *t*Bu-substituent blocks the *para*-position carbon of the phenyl group from partaking in the dimerization. The strikingly distinct modes of dimerization observed for radical-dications **3a** and **3b** are hence defined by the *para*-substituent of the phenyl ring: H vs *t*Bu. Such kind of substituent-dependent dimerization mode is well-known in the case of triarylmethyl radicals.[15] From the crude reaction mixture, radical-trication **7** was obtained after the workup. Compound **7** exhibits a broad EPR signal with unresolved hyperfine couplings, reflecting a highly delocalized spin system (Figure S133). Subsequently, compound **6** can be isolated by the reduction of **7** with elemental zinc. Compound **6** undergoes two separate one-electron oxidations at $E_{1/2}$ = 0.62 and 0.75 V vs Fc/Fc^+ (Figure 2), resulting in the sequential formation of radical-trication **7** and tetracation **8**;[16] this also supports the co-formation of **7** and **8** along with the initially formed **6** during the oxidation of **2b** with $[NO][SbF_6]$. Compounds **6**/**7**/**8** exhibit the longest wavelength absorptions in their UV/vis/NIR spectra at λ_{max} = 412 (ε = 38200 L $mol^{-1}cm^{-1}$), 1510 (ε = 36700 L $mol^{-1}cm^{-1}$), and 896 nm, respectively (Figure S61). Single-crystal X-ray analyses of **6**/**7**/**8**[17] unambiguously confirmed their formation, corroborating the bond-connectivity and, hence, homoleptic dimerization of radical-dication **3b** (Figures 5, S87, and S88). The bond distance between the two phenylene rings of the central *p*-biphenylene bridge gradually decreases from 1.498(7) to 1.460(10) to 1.431(12) Å, indicating a progressive development of double-bond character upon sequential oxidation.

Subsequently, to realize the tetracationic Thiele's[18] and Chichibabin's[19] hydrocarbon analogues of carbon-centered diradicaloids, the cross-coupling reactions of NHC/CAAC-based carbodicarbene **1** were strategically performed with 1,4-diiodobenzene and 4,4′-diiodobiphenyl in the presence of catalytic amounts of $Ni(COD)_2/PPh_3$, obtaining **9a**/**9b** in 75

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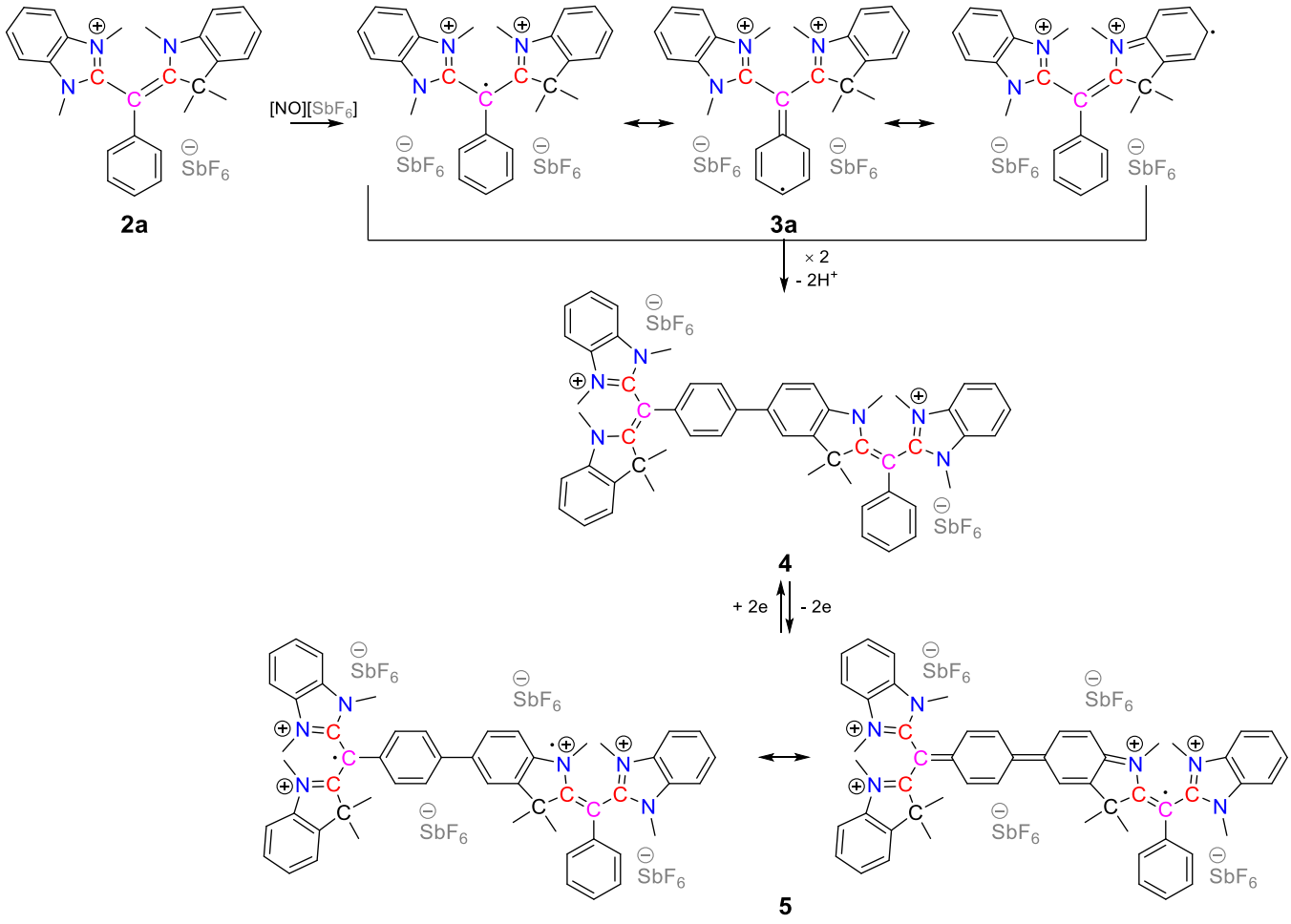
Scheme 3. Oxidation of 2a



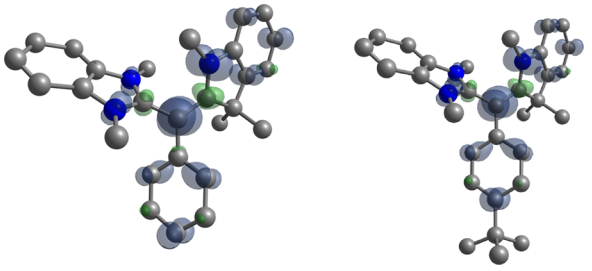


Figure 3. Spin density plots of radical-dications **3a** and **3b** (isovalue of 0.004) computed at the UB3LYP-D3/Def2-SVP(CH_3CN-SMD) level of theory. Two hexafluoroantimonate as counteranions and all hydrogens of both the radical-dications were omitted for clarity.

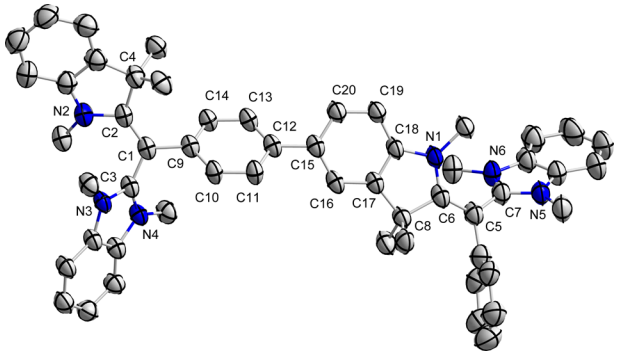


Figure 4. Molecular structure of **4** at 50% probability level. All hydrogens, counteranions, and Et_2O lattice solvent are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: C1−C2 1.382(7), C1−C3 1.440(6), C1−C9 1.492(6), C12−C15 1.481(6), C5−C6 1.369(7), C5−C7 1.448(7); C5−C21 1.496(8); and C2−C1−C3 121.4(4), C2−C1−C9 123.0(4), C3−C1−C9 115.5(4), C6−C5−C7 122.0(5), C6−C5−C21 122.0(5), C7−C5−C21 115.3(4).

and 76% yields as yellow and orange−yellow crystalline solids, respectively (Scheme 5). The single-crystal X-ray diffraction analyses unambiguously proved their formation (Figures S89 and S90).

Cyclic voltammograms of **9a** and **9b** are overall chemically reversible in nature. However, in the case of **9a**, from the second scan onward, two additional oxidative waves were observed at E_{pa} = 0.36 and 0.45 V, apart from E_{pa} = 0.60 V vs Fc/Fc^+, after the follow-up reduction at E_{pc} = 0.32 V vs Fc/Fc^+ (Figure 6). In the case of **9b**, there was only one oxidative wave at E_{pa} = 0.63 V vs Fc/Fc^+ and one reductive wave at E_{pc} = 0.48 V vs Fc/Fc^+. The additional oxidative waves for **9a** are most likely due to the conformational change of the NHC/CAAC-carbone scaffolds during its two-electron oxidation that is reflected in their solid-state molecular structures (vide infra). However, the impact of a similar conformational change of the NHC/CAAC-carbone scaffolds is not observable in the case of **9b** (E_{pa} = 0.63 V and E_{pc} = 0.48 V vs Fc/Fc^+).

The two-electron reversible chemical oxidation of **9a**/**9b** using two equivalents of [NO][SbF_6] then led to the isolation

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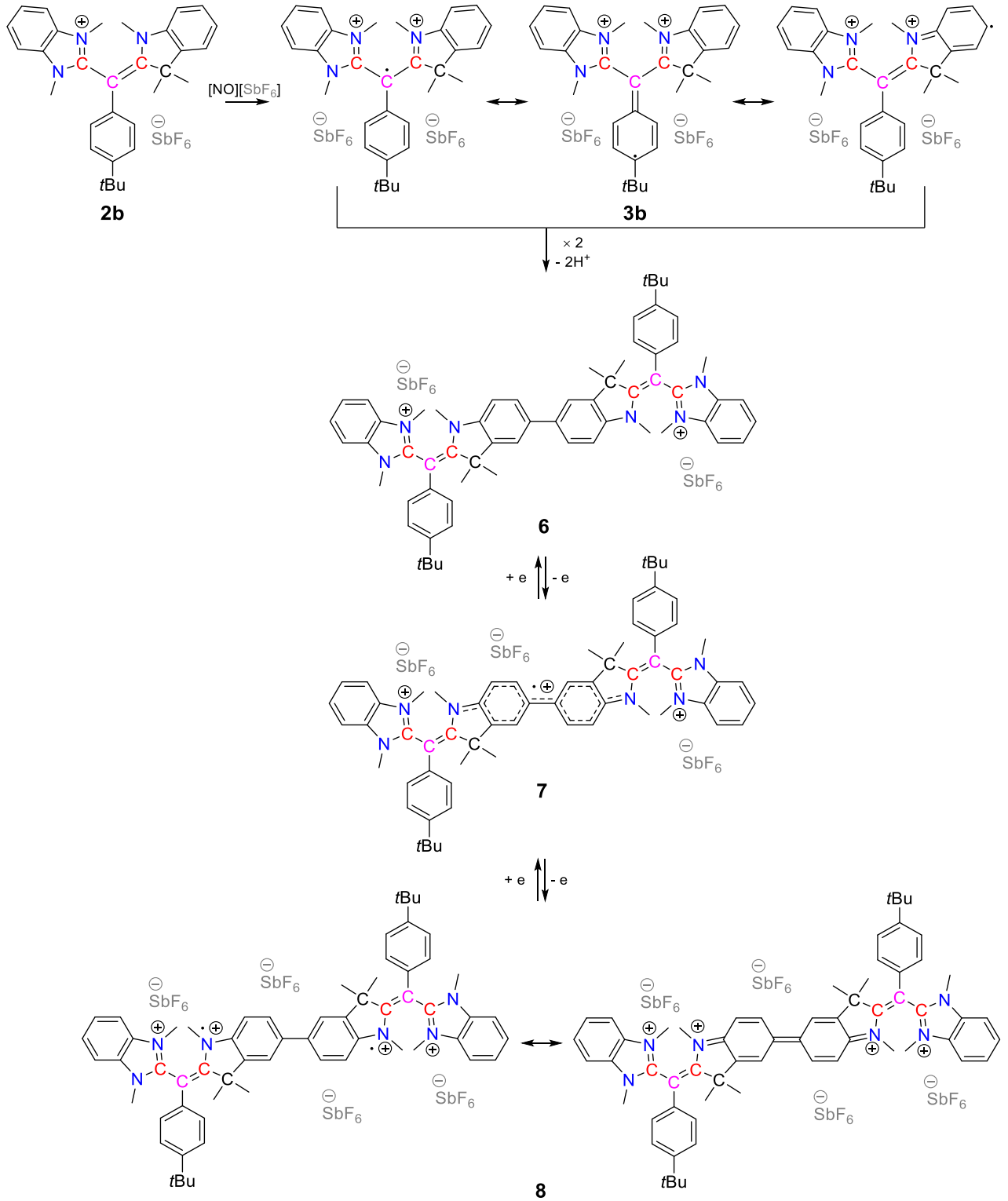
Scheme 4. Oxidation of 2b



of **10a**/**10b** as dark-red and dark-blue crystalline solids in 65 and 60% yields, respectively (Scheme 5). The analyses of the molecular structures of **9a**/**10a** (Figures S89 and 7 - left) revealed a decreasing C1−C5 distance from 1.513(9) to 1.380(16) Å due to the essentially quinoidal form of **10a**. The bond length alternation (BLA) value of the central *p*-phenylene bridge in **10a** is calculated to be 0.087 Å, compared to 0.10 Å in the case of the Thiele hydrocarbon.[20] Due to the substantial disorder in both the cationic and the anionic parts of **10b** (Figure 7 - right), we abstain from discussing its metrical parameters. Notably, upon two-electron oxidation, we have observed a change in the NHC/CAAC-carbone scaffold's orientation in the solid-state molecular structures. In the case of **9a**/**9b**, the "CMe_2" units of the CAAC-motifs appear inward relative to the central π-conjugated spacer (*p*-phenylene/*p*,*p*′-biphenylene bridge), whereas the orientation of the "CMe_2"

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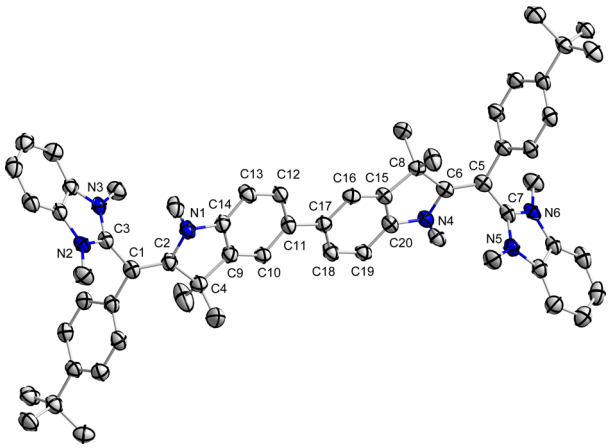


Figure 5. Molecular structure of **6** at 50% probability level. All hydrogens, counteranions, and CH_3CN lattice solvent are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **6**: C1−C2 1.372(8), C1−C3 1.462(8), C1−C21 1.489(8), N1−C14 1.407(7), C11−C17 1.498(7); C20−N4 1.406(7); C2−C1−C3 120.6(5), C3−C1−C21 113.5(4), C2−C1−C21 125.3(5).

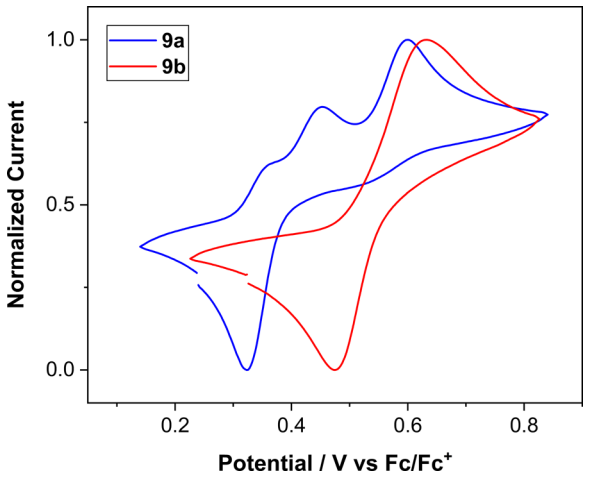


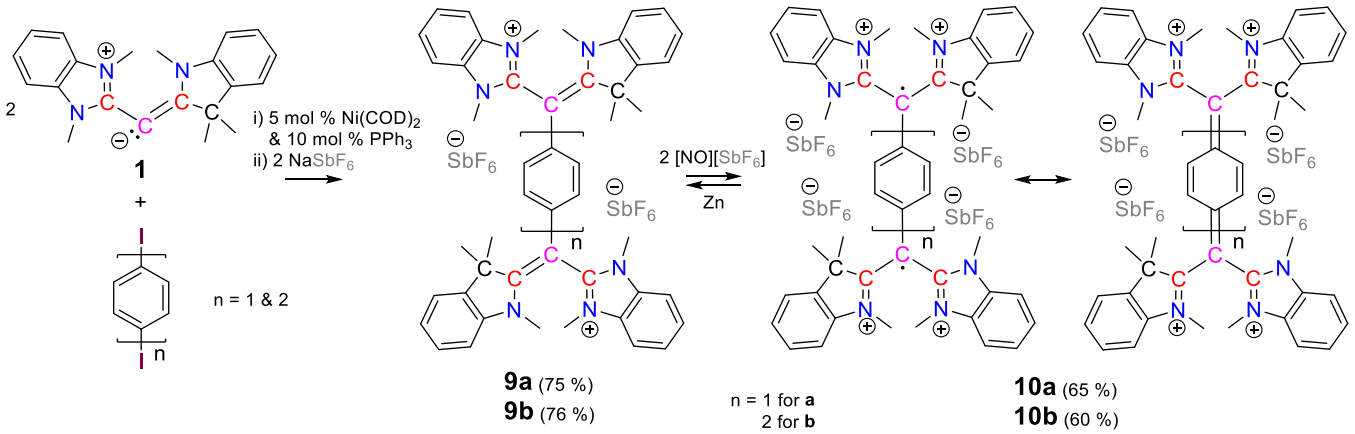
Figure 6. Cyclic voltammograms of **9a** and **9b** at a 100 mV/s scan rate in CH_3CN (0.1 mol/L Bu_4NPF_6) at room temperature.

units of the CAAC-motifs of **10a**/**10b** is outward relative to the central *p*-phenylene bridge.

Bands in the UV/vis/NIR absorption spectra of compounds **10a**/**10b** are red-shifted (λ_{max} = 497 nm (ε = 38700 L $mol^{-1}cm^{-1}$) and λ_{max} = 668 nm (ε = 53300 L $mol^{-1}cm^{-1}$)) (Figure 8 - left) in comparison to **9a**/**9b** (λ_{max} = 385 nm (ε = 38300 L $mol^{-1}cm^{-1}$) and λ_{max} = 368 nm (ε = 39900 L $mol^{-1}cm^{-1}$)), respectively (Figure S79). The resonances in the ^{1}H NMR spectrum of **10a** are well resolved at room temperature, including those of the central *p*-phenylene ring (Figure S25). In contrast, for **10b**, the resonances of the central *p*,*p*′-biphenylene ring are broad at room temperature and become sharper at lower temperatures (Figure S30). This indicates the presence of a thermally excited triplet-state population at room temperature for **10b**. Indeed, compound **10a** is EPR silent, as are the Thiele's hydrocarbon[20] and TCNQ.[21] Compound **10b**, in contrast, shows an increasing EPR signal intensity with rising temperature (Figure 8-center). Fitting of the temperature-dependent double-integral intensity to the Bleaney−Bowers model gives a singlet−triplet gap of $2J$ = −1250 cm^{-1} ($\Delta E_{S\text{-}T}$ = −14.9 kJ/mol) (Figure 8 - right), suggesting a singlet ground state.

This is also supported by the quantum chemical calculations at the UB3LYP-D3/Def2-SVP (CH_3CN-SMD) level of theory; it reveals a closed-shell singlet ground state for **10a** with $\Delta E_{S\text{-}T}$ = −30.9 kJ/mol, whereas **10b** has an open-shell singlet ground state with a close-lying triplet at $\Delta E_{S\text{-}T}$ = −4.9 kJ/mol (Table S12).[9] This kind of discrepancy, the calculated singlet−triplet gap, which is underestimated compared to the results obtained by VT-EPR spectroscopy ($\Delta E_{S\text{-}T}$ = −14.9 kJ/mol), has been previously known for the ionic diradicaloid systems.[22] Notably, the calculated biradical character index (γ) of **10b** is 0.40, which is higher than that of **8** (0.34) and **5** (0.36).[23] Compound **10b** is quite stable, with a half-life of 19 days in CH_3CN under ambient air conditions (Figures S81 and S82); however, this is shorter than that of the oxindolyl-based Chichibabin's analogue (highly stable, no indication of degradation even after 7 days)[19d] and sulfone-functionalized Chichibabin's analogues ($t_{1/2}$ = 41, 52, and 70 days)[19f] but significantly longer than that of the acyclic diaminocarbene-based Chichibabin's hydrocarbon ($t_{1/2}$ < 1 min).[19g] Compounds **10a**/**10b** exhibit a chemically reversible redox behavior and are reduced to **9a**/**9b**, respectively, upon treatment with elemental zinc, showcasing their electron-deficient nature.[24]

Scheme 5. Syntheses of 9a/9b and 10a/10b



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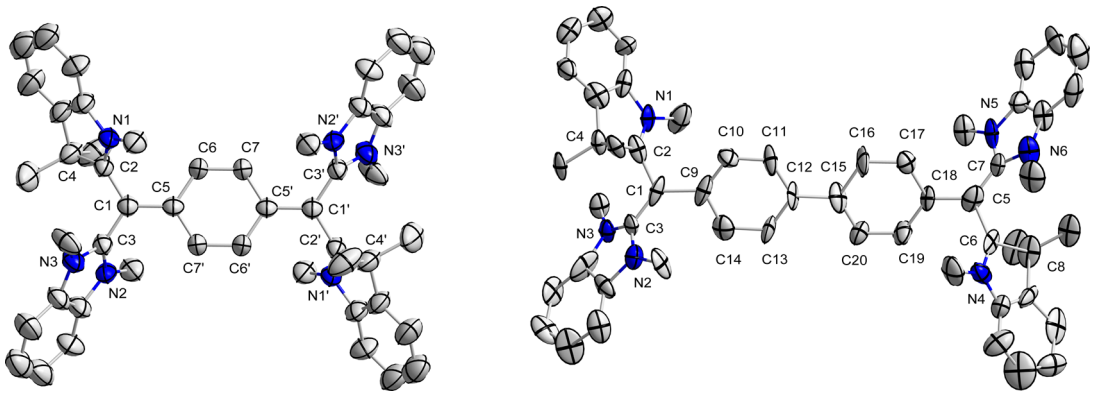

Figure 7. Molecular structures of **10a** (left) and **10b** (right) at 50 and 40% probability levels, respectively. All hydrogens and counteranions are omitted for clarity.

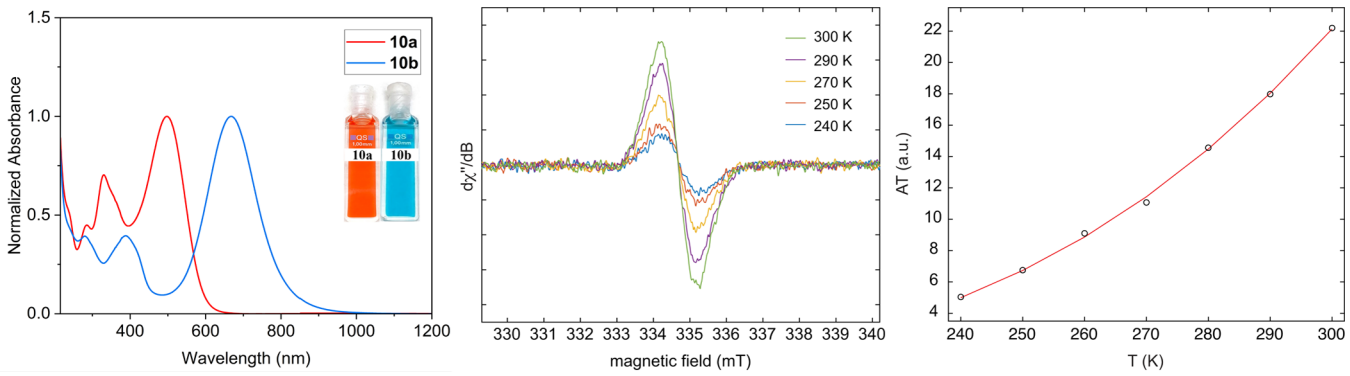

Figure 8. UV/vis/NIR spectra of **10a** and **10b** in CH_3CN at room temperature (left). Variable temperature X-band EPR spectra of **10b** in acetonitrile between 240 and 300 K (center) and temperature dependence of the double-integral EPR intensity (right). Circles (◯) represent the experimental results, and the red line corresponds to the fit with the Bleaney−Bowers equation. The EPR signal is centered around a *g* value of 2.0027.

CONCLUSIONS

In conclusion, we have developed a nickel(0)-catalyzed cross-coupling of NHC/CAAC-carbodicarbene as a donor-stabilized atomic carbon equivalent with aryl chlorides/bromides/iodides. The resulting aryl-functionalized cationic carbodicarbene derivatives are notably electron-rich and prone to one-electron oxidation under the formation of radical-dications, which results in distinct modes of radical−radical dimerization based on the aryl substituents. Moreover, this led to the synthesis of carbon- and nitrogen/nitrogen-centered diradicaloids. Based on these findings, we have also rationally synthesized *p*-phenylene- and *p*,*p*′-biphenylene-bridged tetracationic carbon/carbon-centered electron-deficient diradicaloids. The electronic structure is tuned by the substantial influence of the *π*-conjugated spacer mirrored in the presence/absence of a triplet population. The results emphasize the unique reactivity of carbodicarbenes, specifically herein with regard to their cross-coupling with different aryl halides. The developed procedures constitute a modular methodology for the synthesis of various electron-deficient diradicaloids. This study will thus enrich the diradicaloid chemistry in general, and we are, in this context, currently engaged in developing these concepts further. Moreover, all these electron-deficient diradicaloids have potential to be used as *p*-dopants in organic semiconductors.[25]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c08876.

Experimental section, plots of NMR spectra for new compounds, and complete details of computational calculations (PDF)

Accession Codes

CCDC 2333307−2333314 and 2340820−2340821 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare the following competing financial interest(s): We are working to file a patent related to the findings of this manuscript.

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■ DEDICATION

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(10) The cyclic voltammogram of **2a** is the average of the second and third scans at 100 mV/s at room temperature, where the presence of shoulder peaks at E_{pc} = 0.53 and E_{pa} = 0.60 V vs Fc/Fc^+ most likely represent the redox behavior of in situ formed **4**, originating from the oxidation of **2a**. In the first cycle, no such shoulder peak is observed at E_{pa} = 0.60 V vs Fc/Fc^+ (Figure S94).

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(16) Compound **8** represents the nitrogen analogue of Chichibabin's hydrocarbon.[27] It exhibits triplet population at room temperature, and the variable temperature-EPR study reveals a singlet ground state with $\Delta E_{S\text{-}T}$ = −10.9 kJ/mol (Figure S134). This is also supported by the quantum chemical calculations which suggest singlet as the ground state with an underestimated[22] close-lying triplet state at $\Delta E_{S\text{-}T}$ = −3.7 kJ/mol (Table S12).[9]

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