A crystalline radical cation derived from Thiele’s hydrocarbon with redox range beyond 1 V

Ying Kai Loh1, Petra Vasko2, Caitilín McManus1, Andreas Heilmann1, William K. Myers1 & Simon Aldridge1✉

Thiele’s hydrocarbon occupies a central role as an open-shell platform for new organic materials, however little is known about its redox behaviour. While recent synthetic approaches involving symmetrical carbene substitution of the CPh2 termini yield isolable neutral/dicationic analogues, the intervening radical cations are much more difficult to isolate, due to narrow compatible redox ranges (typically < 0.25 V). Here we show that a hybrid BN/carbene approach allows access to an unsymmetrical analogue of Thiele’s hydrocarbon 1, and that this strategy confers markedly enhanced stability on the radical cation. 1+ is stable across an exceptionally wide redox range (> 1 V), permitting its isolation in crystalline form. Further single-electron oxidation affords borenium dication 12+, thereby establishing an organoboron redox system fully characterized in all three redox states. We perceive that this strategy can be extended to other transient organic radicals to widen their redox stability window and facilitate their isolation.
Shortly after Gomberg’s pioneering discovery of the persistent triphenylmethyl radical in 1900, Thiele reported the first stable organic diradical (‘Thiele’s hydrocarbon’; Fig. 1)\textsuperscript{2}, derived from \textit{p}-quinodimethane. Thiele’s hydrocarbon, which can attain aromaticity in its central ring, can be described by both closed-shell quinoidal (Kekulé) and open-shell diradical (non-Kekulé) resonance forms, accounting for its inherently high reactivity. Subsequently, its X-ray structure was determined, confirming its diradicaloid character\textsuperscript{3}. Since then, Thiele’s hydrocarbon has been widely exploited and integrated into the design of new organic materials with small HOMO – LUMO energy gaps\textsuperscript{4}.

Organic molecules that can reversibly access three stable redox states have received considerable recent attention\textsuperscript{5–14}, reflecting applications as super-electron donors\textsuperscript{15}, photo-/electro-catalysts\textsuperscript{16}, redox switches\textsuperscript{17}, or in redox-flow batteries etc\textsuperscript{18}. However, such systems are rarely isolated, due to the redox instability of the intervening radical species\textsuperscript{19}. Thiele’s hydrocarbon, which can gain aromaticity upon successive one-electron oxidations, presents itself as a privileged platform for such applications. However, its redox properties are far less studied, restricted by the transient nature of its radical monocation (\(t_{1/2} \approx 3\) s), and structural information for both its mono- and dication are unknown (Fig. 1)\textsuperscript{19}.

Carbenes have recently emerged as highly efficient ligands to stabilize organic radicals\textsuperscript{20–27}, and have granted access to simple non-annulated versions of Thiele’s hydrocarbon (Method A, Fig. 1)\textsuperscript{28–31}. This strategy contrasts with traditional (synthetically challenging) approaches which necessitate the use of multiple planar-fused \(\pi\)-conjugated rings to facilitate spin delocalization\textsuperscript{4}. Importantly, the diverse library of available carbenes also allows for modular tuning of the CPh\(_2\) termini\textsuperscript{32}. That said, recently reported analogues based on N-heterocyclic carbene (NHCs) by Ghadwal et al., cyclic (alkyl)amino(carbenes) (CAACs) and acyclic diaminocarbenes (ADCs) by Jana et al. are characterized either by two single-electron transfer events at potentials which are very close (\(\Delta E < 0.25\) V)\textsuperscript{28–29}, or by a single two-electron redox wave\textsuperscript{30–31}, alluding to the instability of the respective mixed-valence radical cations towards disproportionation\textsuperscript{1,33–35}. As such, these systems are typically limited to only two stable redox states, viz. the neutral and dicationic forms. Most recently, Jana et al. pushed this strategy further, reporting that symmetrical CH(NDippMe) disubstitution accesses a more stable radical cation with a redox range extended to 0.48 V\textsuperscript{34}.

Main group heteroatoms have been introduced to modify the electronic properties of \(\pi\)-conjugated organic molecules\textsuperscript{35,36}, leading to the synthesis of silicon\textsuperscript{37}, mono-/dianionic boron\textsuperscript{38,39}, and dicationic nitrogen analogues of Thiele’s hydrocarbon\textsuperscript{40}. In regards to anionic boron analogues, three-state redox systems have been reported very recently, but the redox ranges associated with the intermediate radicals are also very narrow (\(\Delta E = 0.20\) V), thus limiting the stability of these radicals.

An attractive strategy to incorporate boron while still maintaining charge neutrality is to exploit the isoelectronic B=N/C=C relationship\textsuperscript{41}. Interestingly, this approach has recently been shown to enhance the electronic coupling in electron-rich olefins, leading to isolable olefin radical cations, albeit at the expense of decreasing the stability of the dicaticonic species, meaning that a three-state redox system could not be achieved\textsuperscript{42}. In the context of systems based on Thiele’s hydrocarbon, replacement of both exocyclic C=C double bonds with B=N successfully delivers isolable BN analogues, as reported by the groups of Piers, Yamashita and Ye (Method B, Fig. 1)\textsuperscript{13–16}. However, in stark contrast to their all-carbon counterparts, these bis-BN analogues are only stable in their neutral states. Cyclic voltammetry reveals irreversible one-electron oxidations, hinting at the generation of extremely reactive radical cations and dications derived from these systems that contain a pair of highly electron-deficient boron atoms.

Inspired by these reports, we hypothesized that an unsymmetrical mono-BN analogue of Thiele’s hydrocarbon featuring isoelectronic NHC and N-heterocyclic boryl (NHB)\textsuperscript{47–54} substituents might allow access to an isolable radical cation with a significantly enhanced redox range, within an overall three-state system (Method A + B, Fig. 1). Importantly, B=N substitution (Method B) would be expected to render the intervening radical cation stable across a wide redox range by disfavouring the second oxidation step (cf. bis-BN systems), albeit moderated somewhat by the presence of the opposing NHC function (Method A) which would mitigate the enhanced electrophilicity at boron in the doubly oxidized dication\textsuperscript{55}.

**Results and discussion**

**Syntheses of neutral organoboron analogues of Thiele’s hydrocarbon.** The large steric profile inherent in both trflate-substituted borane (HCDippN)\(_2\)BOTf and IDipp leads to the formation of a B/C frustrated Lewis pair (FLP) system (Fig. 2a)\textsuperscript{56}. Upon exposure to pyridine at room temperature, a red solution of a B/C frustrated Lewis pair (FLP) system (Fig. 2a)\textsuperscript{56}. Upon exposure to pyridine at room temperature, a red solution forms upon exposure to pyridine at room temperature, a red solution forms. However, this system was unstable, decomposing upon standing.

**Fig. 1 Systems derived from Thiele’s hydrocarbon.** Thiele’s hydrocarbon, its radical cation and dication; previous modification methods A, B and present work. (Dipp = 2,6-diisopropylphenyl, NHC = N-heterocyclic carbene, CAAC = cyclic (alkyl)amino(carbenes), ADC = acyclic diaminocarbanes).
the NHB unit displays a broad signal at 19.9 ppm in the $^{11}$B{1H} NMR spectrum. However, single crystals of 1 gave weak diffraction patterns, and an X-ray structure could not be obtained. As a surrogate for 1, we synthesized IMes-containing analogues via the same procedure. 2 gives rise to a similar $^{11}$B NMR signal ($\delta_B = 19.0$ ppm), and in this case crystallographic study unambiguously confirms the identity of 2 (and provides credence to 1) as the target unsymmetrical organoboron analogue of Thiele's hydrocarbon.

Structurally, 2 adopts a curved shape (Fig. 2b). The exocyclic $\text{B}-\text{N}$ bond (1.424(4) Å) is shorter than the endocyclic $\text{B}-\text{N}$ bonds (mean: 1.445(4) Å), consistent with a degree of double bond character, and the exocyclic $\text{C}-\text{C}$ bond (1.356(4) Å) is slightly shorter than those of Thiele's hydrocarbon and related bis-carbene derivatives (1.365(4) Å – 1.381(3) Å)$^{28-31}$. DFT analyses of 1 and 2 show no significant geometric deviations between them and confirm the closed-shell nature of their ground states implied spectroscopically, in line with symmetrical bis-carbene and bis-BN analogues$^{28-31}$. In the case of 1, the calculated singlet-triplet gap is calculated to be 1.76 eV (169.4 kJ mol$^{-1}$). Moreover, consideration of the natural bond orders obtained from NRT (natural resonance theory) calculations, suggests that the predominant resonance structure features exocyclic $\text{B}-\text{N}$ single and $\text{C}=\text{C}$ double bonds (Fig. 2a and Supporting Information Table S4). The localization of a lone pair at nitrogen implied by this resonance structure is consistent with the curved structure of 2.$^{12}$

Cyclic voltammetry was used to elucidate the redox properties of 1, revealing two reversible single-electron oxidations, consistent with the targeted three-state redox nature (Fig. 3a). The first oxidation wave ($E_1 = -1.47$ V) falls within the range of bis-carbene systems ($-1.42$ to $-0.95$ V; Fig. 1)$^{28-31}$, suggesting that 1 shares similarly strong reducing properties to its all-carbon congeners. Strikingly, the second oxidation wave ($E_2 = -0.39$ V) occurs at a much more positive potential, leading to a markedly wider separation ($\Delta E = 1.08$ V) between the two redox events.

The redox range associated with radical cation $^{1+}$ not only greatly exceeds that of the elusive radical cations of bis-carbene analogues ($\Delta E < 0.25$ V; Fig. 1)$^{28-31}$ but also other related structurally characterized radicals (Hansmann et al. reported in ref. 12 that a related radical cation [(MeCMesN)$_2$C(C$_6$H$_4$)Trip]$^{+}$ has redox range $\Delta E = 0.72$ V, but this species has not been structurally characterized).

**Synthesis of a radical cationic organoboron analogue of Thiele's hydrocarbon**. With this in mind, the cationic mono-radical species, $^{1+}$, was targeted on a preparative scale by chemical oxidation. Treatment of 1 with Ag[SbF$_6$] (1 equiv.) results in the immediate formation of an NMR-silent dark-brown solution (Fig. 4a). X-ray crystallography confirms its identity as the target mixed-valence radical cation $^{1+}$[SbF$_6$] (Fig. 4b). Mono-nuclear boron radical cations are an extremely rare class of boron radical species$^{37-39}$, in sharp contrast to their neutral and anionic counterparts$^{60}$, presumably due to a confluence of the strong electrophilicity of a boron cation and the high reactivity of an open-shell species. Hence, $^{1+}$ represents a rare example of an isolable boron-containing radical cation.

EPR analysis of $^{1+}$ (which is in good agreement with simulation) confirms the presence of an unpaired electron centred at $g = 2.0021$, which exhibits hyperfine couplings to B1 [$a(\text{^{14}B}) = 3.32$ G], N1 [$a(\text{^{14}N}) = 3.14$ G], N2'/N3' [$a(\text{^{14}N}) = 2.25$ G] and C3H/C4H [$a(\text{^{14}H}) = 3.18$ G], hinting at the fully delocalized nature of the radical across the entire $\pi$ system.
Informatively, the spin population across the B ligands is lower than the C bond, reflecting the more localized nature of the B=N (15%) bond compared to the C=C (27%) bond in the range of mononuclear boron radical cations (2.10 – 6.43 G)\(^{57,59}\), suggesting boron radical character in \(1^{+}\).

Spin-density analysis confirms delocalization, with a significant contribution on the central pyridyl ring (65%; Fig. 5b). Informatively, the spin population across the B=N (15%) bond is lower than the C=C (27%) bond, reflecting the more localized nature of the B=N (as opposed to C=C) bridge and resulting in an unsymmetrical distribution of the remaining spin density from the central ring onto the peripheral NHB (6%) and NHC (27%) ligands. As such, \(1^{+}\) can be described by several contributing resonance forms (Fig. 4a): (i) C-centred pyridyl radical \(1^{+}\); (ii) N-centred pyridyl radical \(1^{+}\); and (iii) NHC-centred radical \(1^{+}\). Contributions from these three resonance structures account for (i) the majority of the unpaired spin density being located on the pyridyl and NHC heterocycles; and (ii) for NRT-derived natural bond order data for \(1^{+}\) which shows reduced bond order alternation in the central pyridyl ring compared to \(1\) (but greater than in \(1^{2+}\); see below), and an exocyclic C=C bond order which is also between those determined for \(1\) and \(1^{2+}\). It is also noteworthy that in metal-free radical borylations catalyzed by 4-substituted pyridines, a pyridine-stabilized boryl radical has been invoked as the key reactive intermediate\(^{63-65}\). \(1^{+}\) can be regarded as a crystalline analogue of this boryl radical species.

Synthesis of a dicaticonic organoboron analogue of Thiele’s hydrocarbon. Completion of the redox triad was accomplished by synthesis of the corresponding dication. Treatment of \(1\) with Ag\(\text{SbF}_6\) (2 equiv.) results in successive colour changes from deep red to dark brown and ultimately to a persistent deep purple solution (Fig. 6a). The product is NMR-active and the \(^{1}H\) spectrum reveals a marked downfield shift of the pyridyl ring protons, suggesting increased aromaticity within the central ring, while the boron signal of the NHB unit is essentially unchanged (\(\delta_B = 20.1\) ppm). X-ray crystallography confirms its identity as the target doubly oxidized dication \(1^{2+}\) (Fig. 6b). Three-coordinate borenium dications are extremely rare\(^{66,67}\), and no further redox chemistry has been reported for the isolated systems, possibly due to the presence of strongly \(\pi\)-donating ligands tailoring the stability of these highly electron-deficient species\(^{68-70}\). Hence, \(1^{2+}\) together with \(1^{+}\) and \(1\) constitutes an isolable organoboron redox triad which can reversibly shuttle between dicaticonic, radical cationic and neutral states.

With regard to \(1^{2+}\), NPA analysis reveals the two positive charges to be highly delocalized, with boron bearing the greatest share of positive charge (+0.94). This value is larger than that determined for bis(carbodicarbene)\([\text{BH}]^{2+}\) system (+0.36) reported by Ong et al.\(^{66}\), but close to that of bis(imino)\([\text{BPh}]^{2+}\) dication (+1.02) reported by Inoue et al.\(^{67}\). As such, \(1^{2+}\) can be described by several contributing resonance forms (Fig. 6a): (i) pyridinium–imidazolium \(1^{2+}\); (ii) borenium–imidazolium \(1^{2+}\); or (iii) borenium dication \(1^{2+}\). NICS calculations are consistent with the aromatic character of the central ring suggested by the NMR measurements (NICS(0) = –7.55; NICS(1) = –8.99), and contrast with the non-aromatic character for \(1^{+}\) (NICS(0) = 1.52; NICS(1) = –0.87) and anti-aromatic character for \(1\) (NICS(0) = 6.67; NICS(1) = 4.14). Moreover, the natural bond orders obtained from NRT calculations (Supporting Information Table S4), suggest that \(1^{2+}\) represent the overwhelmingly dominant resonance structures (exocyclic B-N/C-C single bonds; equivalent bonds within the central heterocycle).

In the solid state, both \(1^{+}\) and \(1^{2+}\) sit on a crystallographic inversion centre (Figs. 4b and 6b). Hence, the BN- and CC-
containing halves in each structure are modelled as identical fragments, and geometric discussions of $1^{+}$ and $1^{2+}$ are based upon the mean values for each. Upon successive single-electron oxidations, the exocyclic carbon–boron and carbon–nitrogen linkages lengthen, with accompanying reduction of the bond length alternation (BLA) in the pyridyl ring, consistent with diminishing exocyclic double-bond character and concomitant aromaticity enhancement (Table 1). This is also reflected in the progressive twisting of the central ring away from coplanarity with the peripheral NH and NHC ligands.

The UV–vis spectra (and associated TD-DFT calculations) show a gradual red-shifting of the prominent absorption bands from $1^{+}$ ($\lambda_{\text{max}} = 342$ nm; HOMO → LUMO) to $1^{2+}$ ($\lambda_{\text{max}} = 442$ nm; SOMO(\(\pi\)) → LUMO(\(\pi\))) (Fig. 7). Interestingly, the very broad absorption band of $1^{2+}$ (range: 400–700 nm) arising from the charge transfer from the NHB ligand to the central pyridyl ring, stretches across the visible region. This is in contrast to dications derived from wholly carbon systems which are typically restricted to absorptions in the UV region6–13, and hints at potential applications of all three states of this organoboron redox system in visible light photoredox catalysis.

To conclude, we disclose an unsymmetrically organoboron analogue of Thiele’s hydrocarbon 1, derived from isoelectronic NHB and NHC ligands. We demonstrate that B=N substitution confers an electronic coupling enhancement of $> 1$ V, enabling the isolation of a boron-containing radical cation $1^{+}$ related to Thiele’s hydrocarbon. Further single-electron oxidation affords borenium dication $1^{2+}$, thereby establishing a new organoboron reversible redox triad featuring $1$, $1^{+}$ and $1^{2+}$. We propose that this hypothesis accounts for the stability of $1^{+}$ over an unprecedented redox range, and is consistent with the experimental observation that dicaticionic species derived from doubly BN-substituted systems (Fig. 1, Method B) are too oxidizing to be experimentally accessible. As such, we perceive that our present strategy can be extended to other transient organic radicals to imbue maximal stability and facilitate their isolation.

### Methods

#### General considerations

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent. NMR spectra were measured in benzene-$d_6$ (which was dried over potassium), with the solvent then being distilled under reduced pressure and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with $J$. Young Teflon valves. $1^H$, $13^C$-$[H]$, $1^9^F$-$[H]$ NMR spectra were recorded on Bruker Avance III HD nanobay 400 MHz or Bruker Avance 500 MHz spectrometer at ambient temperature and referenced internally to residual protio-solvent ($^1H$) or solvent ($^{13}C$) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). $^{19}F$ resonances are referenced externally to CFC$_3$. Assignments were confirmed using two-dimensional $^1H$-$^1H$ and $^{13}C$-$^1H$ NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out by London Metropolitan University. (HCDipp)N$_2$BBr was prepared by the literature method (see Supplementary Information S1). All other reagents were used as received.

#### Preparation of (HCDippN)$_2$BOTf

To a mixture of (HCDippN)$_2$BBr (2.00 g, 4.28 mmol) and AgOTf (1.65 g, 6.42 mmol) was added CHCl$_3$ (3 mL) and stirred for 3 days at 60°C in an ampoule. To the suspension was added benzene (20 mL) and filtered. The filtrate was dried under vacuum to yield a solid covered in a tar-like substance. To this was added n-hexane (250 mL) and benzene (10 mL) to disdissolve the tar-like substance and filtered. The filtrate was dried under vacuum to yield a solid covered in a tar-like substance. This was added n-hexane (250 mL) and benzene (10 mL) to disdissolve the tar-like substance and filtered. The filtrate was dried under vacuum to yield a solid covered in a tar-like substance. This was added n-hexane (250 mL) and benzene (10 mL) to disdissolve the tar-like substance and filtered. The filtrate was dried under vacuum to yield a solid covered in a tar-like substance.

### Table 1 Mean distances (Å) and angles (°) between BN- and CC-containing fragments (DFT-calculated exocyclic bond lengths given in square parentheses).

|          | B1–N1/Ct–C2’ | BLA (pyridyl) | Twist (pyridyl) |
|----------|---------------|---------------|-----------------|
| $1^{+}$  | 1.430(4), 1.356(4) | 0.072(4) | 10.7 |
| $1^{2+}$ | 1.465(4), 1.469(4), 1.416 | 0.029(4) | 16.4 |
| $2$      | 1.495(3), 1.499, 1.453 | 0.005(3) | 46.7 |

#### Fig. 6 Synthesis and characterization of dicationic organoboron analogue of Thiele’s hydrocarbon.

*a* Synthesis of $1^{2+}$, showing contributing resonance structures. *b* Solid-state structure of $1^{2+}$ [SbF$_6$]$^{2-}$ with side view. For clarity, [SbF$_6$]$^{2-}$ counter-anions and H atoms omitted, Dipp groups simplified as wireframes. Thermal ellipsoids set at 50% probability. Key bond lengths given in square parentheses.

#### Fig. 7 UV–vis studies. UV–vis spectra of $1$, $1^{+}$ and $1^{2+}$ in CH$_2$Cl$_2$: key absorption assignments by TD-DFT.
Preparation of 1. To a mixture of (HC)DippβNBTOT (200 mg, 0.37 mmol) and (HC)DippβPC (145 mg, 0.37 mmol) in benzene (1 mL) was added pyridine (0.1 mL, 1.24 mmol) and stirred for 5 min at room temperature to form a red solution. To the solution was added K[N(SiMe3)2] (75 mg, 0.38 mmol) at room temperature and stirred for 5 min at room temperature to form a deep red solution. Volatiles were removed under vacuum. To the residue was added benzene (5 mL) and the mixture filtered. The filtrate was dried under vacuum to yield 1 (264 mg, 83% yield) as a red-brown powder. Single crystals (yellow plates) suitable for X-ray crystallography were obtained by slow evaporation of a concentrated solution of 1 in n-pentane at room temperature.

Preparation of 2. To a mixture of (HC)DippβNBTOT (200 mg, 0.37 mmol) and (HCMeNC)2 (114 mg, 0.37 mmol) in benzene (1 mL) was added pyridine (0.1 mL, 1.24 mmol) and stirred for 5 min at room temperature to form a red solution. To the solution was added K[N(SiMe3)2] (75 mg, 0.38 mmol) at room temperature and stirred for 5 min at room temperature to form a deep red solution. Volatiles were removed under vacuum. To the residue was added n-hexane (25 mL) and the mixture filtered. The filtrate was dried under vacuum to yield 2 (159 mg, 56% yield) as an orange-red powder. Single crystals (brown rods and plates) suitable for X-ray crystallography were obtained by slow evaporation of a concentrated solution of 2 in n-pentane at room temperature.

**References**

1. Gomberg, M. An instance of trivalent carbon: triphenylmethyl. *J. Am. Chem. Soc.* 72, 757–771 (1950).
2. Thiele, J. & Ballhorn, H. Ueber einen chinoïden kohlenwasserstoff. *Ber. Dtsch. Chem. Ges.* 37, 1463–1470 (1904).
3. Montgomery, L. K., Huffman, J. C., Jurczak, E. A. & Grendze, M. P. The molecular structures of Thiele’s and Chichibabin’s hydriodic acids. *J. Am. Chem. Soc.* 108, 6004–6011 (1986).
4. Chen, Z. X., Li, Y. & Huang, F. Persistent and stable organic radicals: design, synthesis, and applications. *Chem. https://doi.org/10.1016/j.jchemp.2020.09.024 (2020).
5. Deuchert, K. & Hüning, M. Multistage organic redox systems—a general structural principle. *Angew. Chem. Int. Ed. Engl.* 17, 875–886 (1978).
6. Li, Y. et al. Cu-Camulene and the corresponding air-stable radical cation and dication. *Angew. Chem. Int. Ed.* 53, 4168–4172 (2014).
7. Jin, L., Melaimi, M., Liu, L. & Bertrand, G. Sinletar carbenes as mimics for transition metals: synthesis of an air-stable organic mixed valence compound [M(C5H5)2]+ = cyclic[alkyl](amino)carbene. *Org. Chem. Front.* 1, 351–354 (2014).
8. Munz, D., Chu, J., Melaimi, M. & Bertrand, G. NHC-CAAC heterodimers with three stable oxidation states. *Angew. Chem. Int. Ed.* 55, 12886–12890 (2016).
9. Hansmann, M. M., Melaimi, M., Munz, D. & Bertrand, G. Modular approach to Kekulé diradicaloids derived from cyclic (aryl)(amino)carbenes. *J. Am. Chem. Soc.* 140, 2546–2554 (2018).
10. Hansmann, M. M., Melaimi, M. & Bertrand, G. Organic mixed valence compounds derived from cyclic (aryl)(amino)carbenes. *J. Am. Chem. Soc.* 140, 2206–2213 (2018).
11. Antoni, P. W. & Hansmann, M. M. Pyrylenes: a new class of tunable, redox-switchable, photoexcitable pyrylium—carbene hybrids with three stable redox-states. *J. Am. Chem. Soc.* 140, 14832–14835 (2018).
12. Antoni, P. W., Bruckhoff, T. & Hansmann, M. M. Organic redox systems based on pyridinium—carbene hybrids. *J. Am. Chem. Soc.* 141, 9701–9711 (2019).
13. Messelberger, I. et al. Aromaticity and steric control whether a cationic olefin radical is resistant to disproportionation. *Chem. Sci.* 11, 4138–4149 (2020).
14. Freeman, L. A. et al. Soluble, crystalline, and thermally stable alkali CO2− clusters supported by cyclic[alkyl](amino)carbenes. *Chem. Sci.* 12, 3544–3550 (2021).
15. Broggi, J., Terme, T. & Vanelle, P. Organic electron donors as powerful single-electron reducing agents in organic synthesis. *Angew. Chem. Int. Ed.* 53, 384–413 (2014).
16. Romerero, N. A. & Nieczwicz, D. A. Organic photoredox catalysis. *Chem. Rev.* 116, 10075–101166 (2016).
17. Schroder, H. V. & Schalley, C. A. Tetraphenylvalenene—a redox-switchable building block to control motion in mechanically interlocked molecules. *Beilstein J. Org. Chem.* 14, 2163–2185 (2018).
18. Luo, J., Hu, B., Hu, M., Zhao, Y. & Liu, T. L. Status and prospects of organic redox flow batteries toward sustainable energy storage. *ACS Energy Lett.* 4, 2220–2240 (2019).
19. Hart, H., Fleming, J. S. & Dye, J. L. One-electron transfer from an olefin to a dicarbonyl ion. *J. Am. Chem. Soc.* 86, 2079–2080 (1964).
20. Kato, K. & Osuka, A. Platforms for stable carbon-centered radicals. *Angew. Chem. Int. Ed.* 58, 8978–8986 (2019).
21. Kundu, S., Sinhababu, S., Chandrasekhar, V. & Roecky, H. W. Stable cyclic[alkyl](amino)carbene (cAAC) radicals with main group substituents. *Chem. Sci.* 10, 4727–4741 (2019).
22. Ghadwal, R. S. Stable carbon-centered radicals based on N-heterocyclic carbenes. *Synthet.* 30, 1765–1775 (2019).
23. Nesterov, V. et al. NHCs in main group chemistry. *Chem. Rev.* 118, 9678–9842 (2018).
24. Kim, Y. & Lee, E. Stable organic radicals derived from N-heterocyclic carbenes. *Chem. Eur. J.* 24, 19110–19121 (2018).
25. Melaimi, M., Jazzer, R., Soleilhavoup, M. & Bertrand, G. Cyclic[alkyl](amino)carbenes (CAACs): recent developments. *Angew. Chem. Int. Ed.* 56, 10046–10068 (2017).
26. Soleilhavoup, M. & Bertrand, G. Cyclic[alkyl](amino)carbenes (CAACs): stable carbene on the rise. *Acc. Chem. Res.* 48, 256–266 (2015).
27. Martin, C. D., Soleilhavoup, M. & Bertrand, G. Carbone-stabilized main group radicals and radical ions. *Chem. Sci.* 4, 3020–3030 (2013).
28. Rottschäfer, D. et al. N-Heterocyclic carbene analogues of Thiele and Chichibabin hydrocarbons. Angew. Chem. Int. Ed. 57, 5838–5842 (2018).
29. Reisner, D.; Negri-Russo, B.; Staimler, H.-G.; Andrade, D. M. & Ghadwal, R. S. Kekulé diradicaloids derived from a classical N-heterocyclic carbene. Chem. Sci. 9, 4970–4976 (2018).
30. Maiti, A. et al. Anionic boron- and carbon-based hetero-diradicaloids spanned beyond diaminocarbenes. Angew. Chem. Int. Ed. 59, 6729–6734 (2020).
31. Maiti, A.; Changara, S.; Sarkar, R. & Jana, A. Acyclic diaminocarbone-based Thiele, Chichibabin, and Müller hydrocarbons. Chem. Sci. 11, 11827–11833 (2020).
32. Melaimi, M.; Soleilhavou, M. & Bertrand, G. Stable cyclic carbones and related species beyond diaminocarbenes. Angew. Chem. Int. Ed. 49, 8810–8849 (2010).
33. Hankace, J. & Weng, O. S. Organic mixed valence. Chem. Rev. 111, 5138–5178 (2011).
34. Mahata, A. et al. o-diamo-p-quinodimethinates with three stable oxidation states. Org. Lett. 22, 8332–8336 (2020).
35. Loh, Y. K. & Aldridge, S. Acid base free main group carbonyl analogues. Angew. Chem. Int. Ed. 60, 8626–8648 (2021).
36. Fischer, R. C. & Power, P. P. n-Bonding and the lone pair effect in multiple bonds involving heavier main group elements: developments in the new millennium. Chem. Rev. 110, 3877–3923 (2010).
37. Nozawa, T., Nagata, M., Ichinohe, M. & Sekiguchi, A. Isolable p- and m-([Bu2MeSi]2Si)2C6H4 disilaquinodimethane vs triplet bis(silyl radical). J. Am. Chem. Soc. 133, 5773–5775 (2011).
38. Zheng, Y., Xiong, J., Sun, Y., Pan, X. & Wu, J. Stepwise reduction of 9,10-bis(trialkylsilyl)anthracene. Angew. Chem. Int. Ed. 54, 1293–12936 (2015).
39. Mati, A. et al. Anionic boron- and carbon-based hetero-diradicaloids spanned by a p-phenylene bridge. J. Am. Chem. Soc. 143, 3687–3692 (2021).
40. Su, Y. et al. Nitrogen analogues of Thiele’s hydrocarbon. Angew. Chem. Int. Ed. 54, 1634–1635 (2015).
41. Campbell, P. G., Marzitzen, J. C. & Liu, S.-Y. Recent advances in azaborine chemistry. Angew. Chem. Int. Ed. 51, 6074–6092 (2012).
42. Su, Y., Li, Y., Ganguly, R. & Kinjo, R. Crystalline boron-linked tetraminoethylenyl radical cations. Chem. Sci. 8, 7419–7423 (2017).
43. Morgan, M. M. et al. Zirconocene-based methods for the preparation of BN-intermediates: application to the synthesis of 1,5-dibora-4a,8a-diaza-1,2,3,5,6,7-hexaxynyl-8-b-dimethyl-s-indacenes. Organometallics 36, 2541–2551 (2017).
44. Noguchi, M. et al. Planar and bent BN-embedded p-quinodimethinates synthesized by transmetallation of bis(trimethylsilyl)-1,4-dihydropyrazines with chloroborane. Organometallics 37, 1833–1836 (2018).
45. Katsuma, Y., Asakawa, H. & Yamashita, M. Reactivity of highly Lewis acidic diboran(4) towards pyridine and isocyanide: formation of boraalkene–pyridine complex and ortho-functionalized pyridine derivatives. Chem. Sci. 9, 1301–1310 (2018).
46. Baer, L. et al. Reactions of dihaloboranes with electron-rich 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadienides. Molecules 25, 2875 (2020).
47. Weber, L. Recent progress in 1,3,2-diazaborole chemistry. Coord. Chem. Rev. https://doi.org/10.1016/j.ccr.2021.213667 (2021).
48. Stephan, D. A tale of two elements: the Lewis acidity/basicity umpolung of boron and phosphorus. Angew. Chem. Int. Ed. 56, 5984–5992 (2017).
49. Proctenkon, A. V. et al. Stable GaX2, InX2 and TlX2 radicals. Nat. Chem. 6, 315–319 (2014).
50. Asami, S., Iishida, S., Ishiwato, T., Suzuki, K. & Yamashita, M. Isolation and characterization of radical anions derived from a boryl-substituted N-heterocyclic boryloxy ligand isoelectronic with N-heterocyclic imines: facile access and transfer of a terminal B–N bond by the cooperative catalysis of two Lewis bases: computational design and experimental verification. Angew. Chem. Int. Ed. 55, 5985–5989 (2016).
51. Chen, W.-C. et al. The elusive three-coordinate dicationic hydridro boron complex. J. Am. Chem. Soc. 136, 914–917 (2014).
52. Francz, D.; Šízlívási, T.; Požih, A.; Deiser, F. & Inoue, S. Three-coordinate boron(III) and diboron(II) dications. Chem. Eur. J. 24, 4283–4288 (2018).
53. Lin, Y. & Chiu, C. Mono- and polynuclear boron dications. Chem. Lett. 46, 913–922 (2017).
54. Piers, W. E., Bourke, S. C. & Conroy, K. B. Borinum, borenium, and boronium ions: synthesis, reactivity, and applications. Angew. Chem. Int. Ed. 44, 5016–5036 (2005).