Inorganic Chemistry © Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Destabilizing Character of a π -Conjugated Boron Center in **Bisphenol Radicals**

Ming-Han Chung, Isaac Furay Yu, Yi-Hung Liu, Tien-Sung Lin, Shie-Ming Peng, and Ching-Wen Chiu*

Department of Chemistry, National Taiwan University, No. 1, Section 4, Roosevelt Road, Taipei 10617, Taiwan

Supporting Information

ABSTRACT: Although boron-containing radicals are promising materials for molecular electronic devices, the electronic effect of the σ -donating yet π -accepting boron center on the stability of open-shell species has been less discussed. In this work, the role of a tricoordinate boron center in π -conjugated radicals was explored through electron paramagnetic resonance measurement of several boron-linked bisphenol radicals and diradicals. Replacing the bridging methine fragment of a neutral Galvinoxyl radical with an arylboryl group led to the corresponding boron-linked radical anion that requires excessive steric protection at the boron center to be persistent in solution. Experimental and theoretical investigations



revealed that the introduction of boron would diminish the quinoidal character of the phenoxyl radical and increase both the electrophilicity and nucleophilicity of the open-shell species. Therefore, it is important to consider the steric protection of the boron center in boron-containing π -conjugated organic radicals.

INTRODUCTION

Stable organic free radicals are fascinating because of their own unique electronic and magnetic properties and have emerged as promising materials for spintronic devices,¹ field-effect transistors,² organic light-emitting diodes,³ and radical batteries.⁴ While most of the electronic applications of organic radicals have focused on chlorinated trityl radicals, nitroxide radicals, and phenoxyl radicals, boron-centered radicals have also received considerable attention.⁵ In addition to the welldocumented boron radical anions, neutral⁶ and cationic boron radicals have been realized and structurally characterized in the past few years.⁷ Diradicals and diradicaloids featuring two boron radical centers have also been reported.⁸ However, the incorporation of a boron atom onto π -conjugated organic radicals is less explored.⁹ Taking into account the σ -donating and π -withdrawing character of the boron atom, the electronic effect of the boryl functional group on the stability of organic free radicals remains obscure. To investigate the role of the boron atom in π -conjugated radicals, we decided to replace the central sp² carbon of the Galvinoxyl radical and Yang's biradical with an arylboryl group. The Galvinoxyl radical,¹⁰ a commercially available radical scavenger having an unpaired electron fully delocalized over the two phenol rings, is one of the most stable noncoordinated phenoxyl radicals. On the other hand, the C_3 -symmetric Yang's biradical is a classical non-Kekulé system featuring a triplet ground state with a singlet-triplet energy gap of 5.86 kJ/mol.¹¹ To our surprise, the incorporation of a boron atom in the bisphenol radical and diradical significantly destabilizes the open-shell molecule,

leading to fast decomposition of the radical species. The generation and decomposition of the boryl-functionalized bisphenol radical and diradical are summarized herein.

RESULTS AND DISCUSSION

The preparation of boron-linked bisphenol derivatives is straightforward and is summarized in Scheme S1. The Grignard reagent prepared from silyl-protected 4-bromo-2,6di--tert-butylphenol was allowed to react with Me₃SnCl to yield the corresponding stannane. Subsequent exchange with 0.5 equiv of BCl₃ in dichloromethane (DCM) resulted in a bisphenol-chloroborane, which was subjected to nucleophilic substitution with the appropriate aryllithium in toluene. Subsequent desilylation with tetra-n-butylammonium fluoride afforded the anticipated bisphenol derivatives 1 [R = Me (1a)]^tBu (1b)]. For both compounds, symmetrical ¹H NMR spectra were observed, indicating that all B-C bonds can freely rotate in solution. The ¹¹B resonances recorded as broad signals at 69.8 ppm for 1a and 67.6 ppm for 1b are slightly upfieldshifted compared to that of Mes₃B because of the presence of two π -donating *p*-hydroxyl groups. Structural characterizations of 1a and 1b were also realized with single-crystal X-ray diffraction analysis (Figures S1 and S2). 1a crystallizes in the C2/c space group from the slow evaporation of a DCM/ ethanol solution of 1a under ambient conditions. The trigonalplanar geometry at boron is confirmed with the sum of the C-

Received: July 5, 2018

B–C angles of 359.9°. All B–C bond distances fall within the typical range of B–C single bonds (1.56–1.62 Å). Compound **1b** adopts the $P2_1/c$ unit cell with two independent molecules in an asymmetric unit. The bond distances of **1b** resemble that observed for **1a**, except the slightly elongated C_{aryl} –B bonds [1.574(4) Å in **1a** and 1.602(3) Å in **1b**]. A noticeable reduction in the dihedral angle between the two phenol rings from 55.5° in **1a** to 39.7° and 38.7° in **1b** can be attributed to the increased steric congestion at the boron center upon the replacement of mesityl with a supermesityl group.

Compound 1 can be deprotonated with 2 equiv of sodium bis(trimethylsilyl)amide in tetrahydrofuran (THF) to yield the corresponding bisphenoxides (Na₂[2]; Scheme 1). Upon

Scheme 1. Synthesis and Decomposition of the Boryl-Functionalized Radical and Diradical



deprotonation, the aromatic proton of phenol became upfield-shifted compared to that of 1, which is consistent with the formation of phenoxide. However, no obvious shift in the ¹¹B resonance was detected, suggesting the low contribution of the quinoidal canonical structure in the solution. Molecular structures of $[2a,2b]^{2-}$ were further corroborated with X-ray diffraction analysis (Figures S3 and S4). While Na₂[2a] crystallizes with six coordinating THF molecules in the C2/c space group, $[2b]^{2-}$ forms a onedimensional coordination polymer in the solid state through [Na₂O₂] linkages (Figure S5). Nevertheless, the two bisphenoxide salts share similar structural parameters around the boron atom, including the C_{phenol} -B bond distances [1.550(3) Å in $[2a]^{2-}$ and 1.545(4) and 1.561(4) Å in $[2b]^{2-}]$ and the dihedral angle between two phenol rings $(40.9^{\circ} \text{ in } [2a]^{2-} \text{ and }$ 43.7° in $[2b]^{2-}$).

With neutral bisphenols (1a and 1b) and dianionic bisphenoxides $(Na_2[2a,2b])$ in hand, we then carried out the generation of the corresponding mono- and diradical derivatives and investigated the role of boron in the π -

conjugated open-shell species. Initial attempts in generating the boron-linked diradical from the oxidation of 1 with PbO₂ were not successful. The reaction between 1a and PbO₂ in DCM led to the decomposition of 1a to 2,2',6,6'-tetra-*tert*butyl-4,4'-biphenylquinone (3). On the other hand, the oxidation of 1b with PbO₂ led to the formation of a neutral phenolphenoxyl radical 4b[•] (Figure 1). The electron para-



Figure 1. Top: Experimental and simulated EPR spectrum of $4b^{\bullet}$ in hexane. Bottom: Molecular structure of $4b^{\bullet}$ with thermal ellipsoids set at 50% probability and *tert*-butyl groups displayed in a wireframe style for clarity.

magnetic resonance (EPR) signal of $4b^{\bullet}$ centered at $g_{iso} =$ 2.0054 features a nine-line pattern. Using the EasySpin package,¹² the signal could be satisfactorily simulated with hyperfine coupling constants of 1.81 and 3.64/1.22 G to ¹H and ¹¹B/¹⁰B nuclei, respectively. The coupling of the unpaired electron with two hydrogen atoms suggests localization of the spin density in one of the phenol rings with substantial population at the boron center. The identity of 4b° was further verified with an independent generation of the radical from the reaction of 1b and 2,2-diphenyl-1-picrylhydrazyl radical (DPPH), which serves as a hydrogen-atom abstractor. Structural determination on dark-purple crystals obtained from a concentrated pentane solution of 4b° supports the assignment of the structure (Figure 1). $4b^{\bullet}$ crystallizes as a pentane solvate in a triclinic $P\overline{1}$ space group with the observed C_{phenol} -B distance [1.566(4) and 1.578(4) Å] comparable to that of 1b.

To achieve the boryl-substituted analogue of the Galvinoxyl radical, we then focused on the controlled chemical oxidation of the bisphenoxides $(Na_2[2a,2b])$. $[5b]^{\bullet-}$ can be generated

from one-electron oxidation of Na₂[**2b**] with silver trifluoromethanesulfonate (AgOTf) in acetonitrile (CH₃CN) or THF (Scheme 1). In CH₃CN, the detection of a well-resolved quintet-of-quartet signal centered at $g_{iso} = 2.0051$ is consistent with the formation of phenoxide–phenoxyl radical anion [**5b**]^{•–} (Figure 2a). Simulation of the EPR spectrum suggests



Figure 2. EPR spectra of $[5b]^{\bullet-}$ in CH3CN (a) and DCM (b).

that the unpaired electron is coupled to one ${}^{11}B/{}^{10}B$ (4.77/ 1.59 G) and four ¹H nuclei (0.78 G), confirming delocalization of the π -radical through the empty 2p orbital at boron. The observed $a(^{11}\text{B})$ of 4.77 G is considerably smaller than that of $[\text{BMes}_3]^{\bullet-}$ $[a(^{11}\text{B}) = 10.32 \text{ G}].^{13}$ Besides, the hyperfine coupling constant of *m*-CH is also markedly smaller than that of the Galvinoxyl radical (1.4 G).^{10b} Both values suggest that the majority of the spin density resides on the oxygen atoms. Interestingly, by replacement of the coordinating CH₃CN with less coordinating THF (Figure S14) and DCM, a distinct change in the EPR pattern was observed (Figure 2b). The EPR signal of [5b]^{•-} in THF and DCM can be satisfactorily simulated with hyperfine coupling to one boron atom [THF, $a({}^{11}\text{B})/a({}^{10}\text{B}) = 4.48/1.43$ G; DCM, $a({}^{11}\text{B})/a({}^{10}\text{B}) = 4.10/100$ 1.19 G] and two hydrogen atoms [THF, $a(^{1}H) = 1.50$ G; DCM, $a({}^{1}\text{H}) = 1.75 \text{ G}$, implying that the unpaired electron is now localized on one of the phenol moieties because of coordination of the sodium cation at the phenoxide fragment.

On the other hand, chemical oxidation of $[2a]^{2-}$ can only be carried out in cold CH₃CN because of the poor solubility of Na₂[2a] in THF and the instability of the resulting radical anion at ambient temperature. The observed EPR signal of $[5a]^{\bullet-}$ in CH₃CN is reminiscent of that of $[5b]^{\bullet-}$ with $a(^{11}B)/a(^{10}B)$ of 4.93/1.62 G and $a(^{1}H)$ of 0.82 G (Figure S9). However, while $[5b]^{\bullet-}$ is persistent in solution, the EPR signal of $[5a]^{\bullet-}$ decreased dramatically at room temperature and reached an EPR-silent state within a few minutes (Figure 3). Furthermore, continuous monitoring of the spectrum



Figure 3. Time-delay EPR spectrum of $[5a]^{\bullet-}$ in CH₃CN at (a) 1, (b) 500, (c) 1035, (d) 1570, and (e) 2107 s.

revealed the formation of a new radical species in the solution. The new resonance signal centered at $g_{iso} = 2.0043$ features a quintet line structure in relative intensities of 1:4:6:4:1 with a coupling constant of 0.46 G. The observed EPR signal suggests the formation of the 2,2',6,6'-tetra-*tert*-butyl-4,4'-biphenylse-miquinone radical anion ([3]^{•-}), which was later confirmed by the independent generation of [3]^{•-} from the one-electron reduction of 3 (Figure S11).

Although the observation of an EPR-silent period (Figure 3c) during the transformation may suggest the formation of a diamagnetic dimer of $[5a]^{\bullet-}$ ($[(5a)_2]^{2-}$), monitoring of the evolution of the EPR signal during the process revealed that the disappearance of $[5a]^{\bullet-}$ follows first-order kinetics with respect to $[5a]^{\bullet-}$ (Figure S13). Unfortunately, all attempts at the isolation and characterization of the short-lived diamagnetic intermediate were unsuccessful. Therefore, the exact decomposition pathway of $[5a]^{\bullet-}$ to $[3]^{\bullet-}$ remains unresolved at the moment. Nevertheless, the observed rapid decomposition of the mesityl-subsituted boryl-linked phenoxide—phenoxyl radical anion in stark contrast to the supermesityl derivative implies that the nucleophilic attack at boron potentially initiates the decomposition of $[5a]^{\bullet-}$.

The presence of a bulky supermesityl group at boron turned out to be essential in realizing the boron-linked diradical (**6b**^{••}). The neutral diradical species could be generated by adding 2 equiv of AgOTf to the THF/hexane (1:3) solution of [**2b**]^{2–} at 195 K. After stirring for 30 min, the solvents were removed under vacuum at a temperature below 240 K. The resulting dark-blue solid mixture was then redissolved in hexane for EPR measurement. At room temperature, the EPR spectrum of the blue residue is essentially identical with that of **4b**[•]. However, upon cooling of the sample to 77 K, a weak but noticeable signal centered at 1694 G ($\Delta m_s = 2$ transition) was observed, indicating the presence of a triplet diradical in the mixture. The half-field signal becomes much more intense at temperatures below 77 K (Figure 4). The temperature dependence of the doubly integrated $\Delta m_s = 2$ signal (I_{EPR})



Figure 4. EPR signal of **6b**^{••} at the half-field region ($\Delta m_s = 2$ transition). The inset is the temperature-dependent EPR intensity. The dotted line was generated by setting $C = 1.9 \times 10^7$ and J = 38 cm⁻¹.

can be fitted according to the Bleaney and Bowers equation, where *C* is a constant and *J* is the exchange integral.¹⁴ The fitting result gives a positive *J* value of $38 \pm 5 \text{ cm}^{-1}$, confirming the ferromagnetically coupled ground triplet state with a $\Delta E_{\rm ST}$ value of 0.91 kJ/mol (2*J*). In comparison, a weak antiferromagnetic coupling was observed in a boron-linked trisnitroxide triradical, which features an energy gap of 0.082 kJ/mol.^{9b,c} Unfortunately, the zero-field splitting *D* and *E* parameters of **6b**^{••} derivable from the $\Delta m_s = 1$ transition or susceptibility measurement could not be evaluated because of the presence of **4b**[•] in large quantity, which obscured the triplet signal. However, the appearance of an almost Gaussian line shape of the half-field transition would render a very small *E* value, which is similar to that observed in Yang's biradical.¹⁵

Radical $6b^{\bullet\bullet}$ was found to be reactive toward THF, tetrahydropyran, and CH₃CN. $6b^{\bullet\bullet}$ obtains a hydrogen atom from solvent molecules to form the phenolphenoxyl radical $4b^{\bullet}$, which then further decomposes to 1b (Scheme 1). Unfortunately, such an undesired decomposition pathway could not be avoided because of the poor solubility of Na₂[2b] and Na[5b] in solvents other than THF and CH₃CN.

The instability of $[5a]^{\bullet-}$ is rather peculiar given the fact that the Galvinoxyl radical features merely a methine group between the two phenol rings. Apparently, the electronic property of the bridging fragment plays a determinant role in the stability of the radical. We postulate that the instability of the radical might have resulted from the lack of quinoidal contribution in [5a]^{•-}, leading to an electron-deficient neutral boron atom and a nucleophilic phenoxide anion. To have a better understanding of the effect of sp² boron on π -conjugated organic radicals, theoretical computations on a simplified Galvinoxyl radical (7[•]) and its isoelectronic boron-linked radical anion $([8]^{\bullet-})$ were performed with the density functional theory method at the uB3LYP/6-311+G** level of theory using the Gaussian 09 program.¹⁶ Geometry optimization suggests the presence of a partial π bond between the central atom and phenol rings (Figure 5). However, the B–C π -bonding extent in [8]^{•–} is obviously lower than that of the C–C bond in 7^{\bullet} . While the calculated B–C bond distance of 1.533 Å is 2.8% shorter than that of Ph₃B (1.577 Å), the $C_{bridge}-C_{phenol}$ bond (1.408 Å) has shrunk about 8.6% in 7[•] compared to the typical C-C single bond (1.54 Å). In accordance, the calculated spin distribution is more polarized



Figure 5. Optimized geometry of 7[•] and $[8]^{•-}$ with the spin-density distribution (isovalue = 0.003). The percentage of spin-density distribution is presented using the square of the Mulliken spin density.

in $[8]^{\bullet-}$ with significant unpaired electron densities accumulated at the oxygen atoms (avg. 7.85% in 7°; 11.04% in $[8]^{\bullet-}$) and the *ipso*-carbon atoms (avg. 17.15% in 7°; 21.38% in $[8]^{\bullet-}$). Overall, substitution of the *p*-quinone methide fragment with *p*-quinone borataalkene not only introduces an electrophilic site to the molecule but also enhances the nucleophilicity of the oxygen atoms. Therefore, $[5]^{\bullet-}$ is considerably more reactive than the carbon analogue of the Galvinoxyl radical.

CONCLUSION

In summary, radicals having two phenol groups connected by a trivalent boron center were prepared and investigated with EPR spectroscopy. The extent of delocalization of an unpaired electron in monoradicals was found to be associated with the availability of phenoxide lone pairs. A localized spin distribution was observed when the phenoxide moiety is protonated (4b°) or coordinated by a sodium cation ([5b]^{•-} in DCM and THF). In addition, the ferromagnetic coupling of the two phenoxyl radicals in 6b^{••} results in a triplet ground state of the diradical with a ΔE_{ST} value of 0.91 kJ/mol, which is consistent with the small gap between the two highest singly occupied orbitals (-6.02 and -6.36 eV; Figure S21). Unlike the stable Yang's biradical, 6b^{••} decomposes rapidly via stepwise hydrogen-atom abstraction to yield 4b[•] and the corresponding bisphenol (1b).

In general, the introduction of the tricoordinate boron atom increases the reactivity of the phenoxyl radical as a result of the reduced contribution of the quinoidal structure and more polarized spin distribution in the phenoxyl radical. Thus, kinetic protection of the electron-deficient boron center and the electron-rich oxyl radical plays a determinant role in the stability of these boron-linked π -conjugated radicals. However, the enhanced reactivity of radical species should be viewed as an opportunity to discover unusual reaction pathways of radicals. As shown in this work, the unexpected C-C coupling of phenol groups observed during the decomposition of $[5a]^{\bullet-}$ is an intriguing finding. Elucidating the reaction mechanism would potentially result in a new approach to the boronmediated C-C coupling reaction.¹⁷ A more detailed exploration of the decomposition of $[5a]^{\bullet-}$ to $[3]^{\bullet-}$ with theoretical calculation and a spin-trapping experiment is currently under investigation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b01865.

Syntheses and characterizations of 1a, 1b, $Na_2[2a]$, and $Na_2[2b]$, EPR spectra and simulation parameters of $[3]^{\bullet-}$, $4b^{\bullet}$, $[5a]^{\bullet-}$, $[5b]^{\bullet-}$, and $6b^{\bullet\bullet}$, orbital isosurface plot and spin density of $6b^{\bullet\bullet}$, and Cartesian coordinates of 7[•], $[8]^{\bullet-}$, and $6b^{\bullet\bullet}$ (PDF)

Accession Codes

CCDC 1823387–1823390 and 1843160 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.

AUTHOR INFORMATION

Corresponding Author

*E-mail: cwchiu@ntu.edu.tw.

ORCID 0

Ching-Wen Chiu: 0000-0001-7201-0943

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the Ministry of Science and Technology of Taiwan (Grants MOST 104-2113-M-002-018-MY3 and MOST 105-2119-M-002-031-MY2). T.-S.L. is grateful for a visiting professorship supported by MOST (Grant MOST 107-2811-M-002-001). We thank the Research Instrument Center of Taiwan located at the National Tsing Hua University for low-temperature EPR measurements.

REFERENCES

(1) (a) Mas-Torrent, M.; Crivillers, N.; Rovira, C.; Veciana, J. Attaching Persistent Organic Free Radicals to Surfaces: How and Why. *Chem. Rev.* **2012**, *112* (4), 2506–2527. (b) Ratera, I.; Veciana, J. Playing with organic radicals as building blocks for functional molecular materials. *Chem. Soc. Rev.* **2012**, *41* (1), 303–349.

(2) (a) Wang, Y.; Wang, H.; Liu, Y.; Di, C.-a.; Sun, Y.; Wu, W.; Yu, G.; Zhang, D.; Zhu, D. 1-Imino Nitroxide Pyrene for High Performance Organic Field-Effect Transistors with Low Operating Voltage. J. Am. Chem. Soc. 2006, 128 (40), 13058–13059. (b) Aoki, K.; Akutsu, H.; Yamada, J.-i.; Nakatsuji, S. i.; Kojima, T.; Yamashita, Y. The First Organic Radical Compounds Exhibiting n-Type FET Properties. Chem. Lett. 2009, 38 (2), 112–113. (c) Wei, P.; Oh, J. H.; Dong, G.; Bao, Z. Use of a 1H-Benzoimidazole Derivative as an n-Type Dopant and To Enable Air-Stable Solution-Processed n-Channel Organic Thin-Film Transistors. J. Am. Chem. Soc. 2010, 132 (26), 8852–8853. (d) Reig, M.; Gozálvez, C.; Jankauskas, V.; Gaidelis, V.; Grazulevicius, J. V.; Fajarí, L.; Juliá, L.; Velasco, D. Stable All-Organic Radicals with Ambipolar Charge Transport. Chem. - Eur. J. 2016, 22 (51), 18551–18558.

(3) (a) Obolda, A.; Zhang, M.; Li, F. Evolution of emission manners of organic light-emitting diodes: From emission of singlet exciton to emission of doublet exciton. *Chin. Chem. Lett.* **2016**, 27 (8), 1345–1349. (b) Obolda, A.; Ai, X.; Zhang, M.; Li, F. Up to 100% Formation Ratio of Doublet Exciton in Deep-Red Organic Light-Emitting Diodes Based on Neutral π -Radical. *ACS Appl. Mater. Interfaces* **2016**, 8 (51), 35472–35478. (c) Peng, Q.; Obolda, A.; Zhang, M.; Li, F. Organic Light-Emitting Diodes Using a Neutral π Radical as Emitter: The

Emission from a Doublet. Angew. Chem., Int. Ed. 2015, 54 (24), 7091–7095. (d) Bin, Z.; Duan, L.; Qiu, Y. Air Stable Organic Salt As an n-Type Dopant for Efficient and Stable Organic Light-Emitting Diodes. ACS Appl. Mater. Interfaces 2015, 7 (12), 6444–6450. (e) Hattori, Y.; Kusamoto, T.; Nishihara, H. Luminescence, Stability, and Proton Response of an Open-Shell (3,5-Dichloro-4-pyridyl)bis-(2,4,6-trichlorophenyl)methyl Radical. Angew. Chem., Int. Ed. 2014, 53 (44), 11845–11848.

(4) (a) Janoschka, T.; Hager, M. D.; Schubert, U. S. Powering up the Future: Radical Polymers for Battery Applications. *Adv. Mater.* 2012, 24 (48), 6397–6409. (b) Nevers, D. R.; Brushett, F. R.; Wheeler, D. R. Engineering radical polymer electrodes for electrochemical energy storage. *J. Power Sources* 2017, 352, 226–244.

(5) Su, Y.; Kinjo, R. Boron-containing radical species. *Coord. Chem. Rev.* 2017, 352, 346–378.

(6) (a) Aramaki, Y.; Omiya, H.; Yamashita, M.; Nakabayashi, K.; Ohkoshi, S.-i.; Nozaki, K. Synthesis and Characterization of B-Heterocyclic π -Radical and Its Reactivity as a Boryl Radical. J. Am. Chem. Soc. 2012, 134 (49), 19989-19992. (b) Bertermann, R.; Braunschweig, H.; Dewhurst, R. D.; Hörl, C.; Kramer, T.; Krummenacher, I. Evidence for Extensive Single-Electron-Transfer Chemistry in Boryl Anions: Isolation and Reactivity of a Neutral Borole Radical. Angew. Chem., Int. Ed. 2014, 53 (21), 5453-5457. (c) Bissinger, P.; Braunschweig, H.; Damme, A.; Krummenacher, I.; Phukan, A. K.; Radacki, K.; Sugawara, S. Isolation of a Neutral Boron-Containing Radical Stabilized by a Cyclic (Alkyl)(Amino)Carbene. Angew. Chem., Int. Ed. 2014, 53 (28), 7360-7363. (d) Dahcheh, F.; Martin, D.; Stephan, D. W.; Bertrand, G. Synthesis and Reactivity of a CAAC-Aminoborylene Adduct: A Hetero-Allene or an Organoboron Isoelectronic with Singlet Carbenes. Angew. Chem., Int. Ed. 2014, 53 (48), 13159-13163. (e) Rosenthal, A. J.; Devillard, M.; Miqueu, K.; Bouhadir, G.; Bourissou, D. A Phosphine-Coordinated Boron-Centered Gomberg-Type Radical. Angew. Chem., Int. Ed. 2015, 54 (32), 9198-9202. (f) Ledet, A. D.; Hudnall, T. W. Reduction of a diamidocarbene-supported borenium cation: isolation of a neutral boryl-substituted radical and a carbene-stabilized aminoborylene. Dalton Trans 2016, 45 (24), 9820-9826. (g) Silva Valverde, M. F.; Schweyen, P.; Gisinger, D.; Bannenberg, T.; Freytag, M.; Kleeberg, C.; Tamm, M. N-Heterocyclic Carbene Stabilized Boryl Radicals. Angew. Chem., Int. Ed. 2017, 56 (4), 1135-1140.

(7) (a) Kinjo, R.; Donnadieu, B.; Celik, M. A.; Frenking, G.; Bertrand, G. Synthesis and Characterization of a Neutral Tricoordinate Organoboron Isoelectronic with Amines. Science 2011, 333 (6042), 610. (b) Suzuki, S.; Yoshida, K.; Kozaki, M.; Okada, K. Syntheses and Structural Studies of Tris(N-phenothiazinyl)borane and Its Radical Cation. Angew. Chem., Int. Ed. 2013, 52 (9), 2499-2502. (c) Xie, X.; Adams, C. J.; Al-Ibadi, M. A. M.; McGrady, J. E.; Norman, N. C.; Russell, C. A. A polycyclic borazine radical cation: [1,2-B2{1,2-(MeN)2C6H4}2]+. Chem. Commun. 2013, 49 (88), 10364-10366. (d) Bissinger, P.; Braunschweig, H.; Damme, A.; Kupfer, T.; Krummenacher, I.; Vargas, A. Boron Radical Cations from the Facile Oxidation of Electron-Rich Diborenes. Angew. Chem., Int. Ed. 2014, 53 (22), 5689-5693. (e) Litters, S.; Kaifer, E.; Himmel, H.-J. A Radical Tricationic Rhomboid Tetraborane(4) with Four-Center, Five-Electron Bonding. Angew. Chem., Int. Ed. 2016, 55 (13), 4345-4347. (f) Wang, H.; Zhang, J.; Lin, Z.; Xie, Z. Synthesis and Structural Characterization of Carbene-Stabilized Carborane-Fused Azaborolyl Radical Cation and Dicarbollyl-Fused Azaborole. Organometallics 2016, 35 (16), 2579-2582. (g) Su, Y.; Li, Y.; Ganguly, R.; Kinjo, R. Crystalline boron-linked tetraaminoethylene radical cations. Chem. Sci. 2017, 8 (11), 7419-7423. (h) Taylor, J. W.; McSkimming, A.; Guzman, C. F.; Harman, W. H. N-Heterocyclic Carbene-Stabilized Boranthrene as a Metal-Free Platform for the Activation of Small Molecules. J. Am. Chem. Soc. 2017, 139 (32), 11032-11035. (i) Wang, B.; Li, Y.; Ganguly, R.; Webster, R. D.; Kinjo, R. A Crystalline Diazadiborinine Radical Cation and Its Boron-Centered Radical Reactivity. Angew. Chem., Int. Ed. 2018, 57 (26), 7826-7829. (8) (a) Rajca, A.; Rajca, S.; Desai, S. R. Boron-centred diradical dianion: a new triplet state molecule. J. Chem. Soc., Chem. Commun.

Ε

1995, 19, 1957-1958. (b) Scheschkewitz, D.; Amii, H.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. Singlet Diradicals: from Transition States to Crystalline Compounds. Science 2002. 295 (5561), 1880. (c) Braunschweig, H.; Dyakonov, V.; Engels, B.; Falk, Z.; Hörl, C.; Klein, J. H.; Kramer, T.; Kraus, H.; Krummenacher, I.; Lambert, C.; Walter, C. Multiple Reduction of 2,5-Bis(borolyl)thiophene: Isolation of a Negative Bipolaron by Comproportionation. Angew. Chem., Int. Ed. 2013, 52 (49), 12852-12855. (d) Ji, L.; Edkins, R. M.; Lorbach, A.; Krummenacher, I.; Brückner, C.; Eichhorn, A.; Braunschweig, H.; Engels, B.; Low, P. J.; Marder, T. B. Electron Delocalization in Reduced Forms of 2-(BMes2)pyrene and 2,7-Bis(BMes2)pyrene. J. Am. Chem. Soc. 2015, 137 (21), 6750-6753. (e) Wang, L.; Fang, Y.; Mao, H.; Qu, Y.; Zuo, J.; Zhang, Z.; Tan, G.; Wang, X. An Isolable Diboron-Centered Diradical with a Triplet Ground State. Chem. - Eur. J. 2017, 23 (28), 6930-6936. (f) Yuan, N.; Wang, W.; Fang, Y.; Zuo, J.; Zhao, Y.; Tan, G.; Wang, X. Bis(boryl anion)-Substituted Pyrenes: Syntheses, Characterizations, and Crystal Structures. Organometallics 2017, 36 (14), 2498-2501. (g) Wang, L.; Li, J.; Zhang, L.; Fang, Y.; Chen, C.; Zhao, Y.; Song, Y.; Deng, L.; Tan, G.; Wang, X.; Power, P. P. Isolable Borane-Based Diradical and Triradical Fused by a Diamagnetic Transition Metal Ion. J. Am. Chem. Soc. 2017, 139 (49), 17723-17726.

(9) (a) Feng, P.-Y.; Liu, Y.-H.; Lin, T.-S.; Peng, S.-M.; Chiu, C.-W. Redox Chemistry of a Hydroxyphenyl-Substituted Borane. Angew. Chem., Int. Ed. 2014, 53 (24), 6237-6240. (b) Itoh, T.; Matsuda, K.; Iwamura, H.; Hori, K. Tris[p-(N-oxyl-N-tert-butylamino)phenyl]amine, -methyl, and -borane Have Doublet, Triplet, and Doublet Ground States, Respectively. J. Am. Chem. Soc. 2000, 122 (11), 2567-2576. (c) Itoh, T.; Matsuda, K.; Iwamura, H.; Hori, K. The Ground Spin States of Tris[p-(N-oxyl-N-tert-butylamino)phenyl] amine, -Methyl, and -Borane. Prospects of Further Studies. J. Solid State Chem. 2001, 159 (2), 428-439. (d) Chiu, C.-W.; Gabbaï, F. P. A 9-Borylated Acridinyl Radical. Angew. Chem., Int. Ed. 2007, 46 (10), 1723-1725. (e) Kushida, T.; Shirai, S.; Ando, N.; Okamoto, T.; Ishii, H.; Matsui, H.; Yamagishi, M.; Uemura, T.; Tsurumi, J.; Watanabe, S.; Takeya, J.; Yamaguchi, S. Boron-Stabilized Planar Neutral π -Radicals with Well-Balanced Ambipolar Charge-Transport Properties. J. Am. Chem. Soc. 2017, 139 (41), 14336-14339.

(10) (a) Coppinger, G. M. A Stable Phenoxy Radical Inert to Oxygen. J. Am. Chem. Soc. **1957**, 79 (2), 501–502. (b) Steelink, C.; Fitzpatrick, J. D.; Kispert, L. D.; Hyde, J. S. Electron paramagnetic resonance and electron-nuclear double resonance studies of phenoxyl radicals derived from substituted diphenylmethanes. J. Am. Chem. Soc. **1968**, 90 (16), 4354–4361. (c) Ljubic, I.; Kivimaki, A.; Coreno, M.; Kazazic, S.; Novak, I. Characterisation of the electronic structure of galvinoxyl free radical by variable energy UPS, XPS and NEXAFS spectroscopy. Phys. Chem. Chem. Phys. **2018**, 20 (4), 2480–2491.

(11) (a) Yang, N. C.; Castro, A. J. Synthesis of a Stable Biradical. J. Am. Chem. Soc. 1960, 82 (23), 6208–6208. (b) Mukai, K.; Ishizu, K.; Deguchi, Y. Magnetic Susceptibility of Yang's a Biradical from 4.2 to 293 K. J. Phys. Soc. Jpn. 1969, 27 (3), 783–783. (c) Mukai, K.; Mishina, T.; Ishizu, K. ESR studies of Yang's biradical. J. Chem. Phys. 1977, 66 (4), 1680–1684. (d) Bock, H.; John, A.; Havlas, Z.; Bats, J. W. The Triplet Biradical Tris(3,5-di-tert-butyl-4-oxophenylene)methane: Crystal Structure, and Spin and Charge Distribution. Angew. Chem., Int. Ed. Engl. 1993, 32 (3), 416–418.

(12) All EPR simulations were run using the *EasySpin* software package. Stoll, S.; Schweiger, A. EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Reson.* **2006**, *178* (1), 42–55.

(13) Elschenbroich, C.; Kühlkamp, P.; Behrendt, A.; Harms, K. Metall- π -Komplexe von Benzolderivaten, 49. Halbsandwichkomplexe des Trimesitylborans Mes3B: Darstellung und Struktur von Mes2B-[(η 6-Mes)Cr(CO)3], MesB[(η 6-Mes)Cr(CO)3]2 und B[(η 6-Mes)-Cr(CO)3]3. Redoxverhalten und Fragen der intramolekularen Wechselwirkung. *Chem. Ber.* **1996**, *129* (7), 859–869.

(14) (a) Bleaney, B.; Bowers, K. D. Anomalous paramagnetism of copper acetate. *Proc. R. Soc. London, Ser. A* 1952, 214 (1119), 451.
(b) Abe, M. Diradicals. *Chem. Rev.* 2013, 113 (9), 7011–7088.

(15) Mukai, K.; Ishizu, K.; Nakahara, M.; Deguchi, Y. ESR Studies of Temperature Dependent Zero-field Splitting in Yang's Biradical. *Bull. Chem. Soc. Jpn.* **1980**, 53 (11), 3363–3364.

(16) All theoretical computations were performed using the Gaussian 09 program suite. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo. C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

(17) Shoji, Y.; Tanaka, N.; Muranaka, S.; Shigeno, N.; Sugiyama, H.; Takenouchi, K.; Hajjaj, F.; Fukushima, T. Boron-mediated sequential alkyne insertion and C–C coupling reactions affording extended π -conjugated molecules. *Nat. Commun.* **2016**, *7*, 12704.