

PAPER

[View Article Online](#)
[View Journal](#) | [View Issue](#)

Cite this: *Dalton Trans.*, 2023, **52**, 668

Received 15th November 2022,
Accepted 9th December 2022

DOI: 10.1039/d2dt03672j

rsc.li/dalton

Probing borafluorene B–C bond insertion with gold acetylide and azide†

Yijie Li,^a Yu-Hsuan Shen,^b Alec M. Esper,^b John R. Tidwell,^a
Adam S. Veige^{*b} and Caleb D. Martin^{†a}

The reaction of Ph_3PAuN_3 with 9-Ph-9-borafluorene resulted in complexation of the azide to boron while a gold acetylide reacted with 9-Ph-9-borafluorene to insert the acetylide carbon to access a six-membered boracycle with an exocyclic double bond.

Introduction

9-Borafluorenes are analogues of boroles that contain a biphenyl backbone.^{1–4} The reactivity of 9-borafluorenes often mirrors that of boroles but there are some different reaction outcomes attributed to the diminished Lewis acidity at boron or the lack of a true diene that renders the BC_4 unit resilient to Diels–Alder chemistry.^{5–22} Both boroles and 9-borafluorenes have been recognized as effective reagents for accessing boracycles larger than five atoms *via* intermolecular ring expansion reactions.^{22–41}

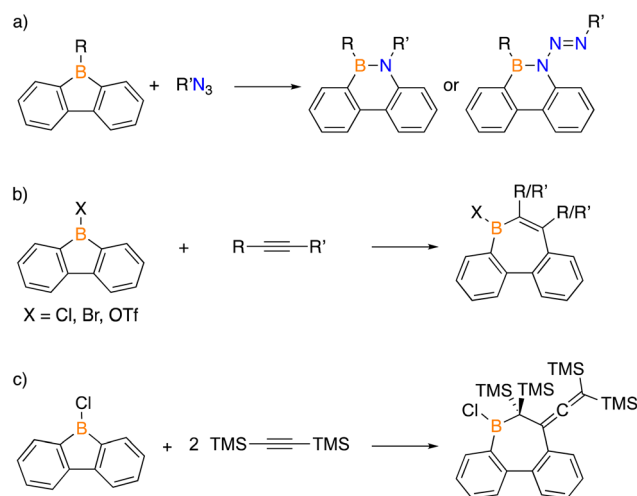
Two widely investigated reactions with 9-borafluorenes have been with organic azides and alkynes.^{42–45} The reactions of organic azides with 9-borafluorenes are effective to access 9,10-*B,N*-phenanthrenes (Scheme 1a).^{46,47} The expulsion of N_2 occurs in all examples but one, in which 9-Ph-9-borafluorene reacts with phenylazide to insert the γ -nitrogen atom and form the diazene.⁴⁶ Fukushima and coworkers reported the reactions of 9-borafluorenes featuring a halide or pseudo-halide on boron with a wide variety of alkynes that primarily underwent 1,2-carboboration to access borepin species with a biphenyl framework (Scheme 1b).^{43,45} In the case of bis(trimethylsilyl) acetylene, two equivalents of alkyne reacted to furnish a seven membered ring system with an exocyclic allene (Scheme 1c).⁴³

While organic substrates have been studied extensively, there has not been a report of a reaction of a metal-acetylide or metal-azide with a borole species. Aside from the reactions of boroles with metal precursors to form polyhaptic

complexes^{48–52} or Z-type donor–acceptor complexes,^{53,54} their chemistry with metal reagents has been neglected. Gold acetylides or gold azides are known to engage in similar reactions to their organic counterparts and accordingly, have been labeled as “iClick” reagents.^{55–66} In this work, we examine the reactivity of 9-phenyl-9-borafluorene with gold(i) reagents that feature acetylide and azide ligands.

Results and discussion

The reaction of 9-phenyl-9-borafluorene (**1**) and Ph_3PAuN_3 in benzene results in a color change from yellow to colorless within 1 h and after work up, the product was isolated in 96% yield (Scheme 2). The ^{11}B NMR resonance at 4.7 ppm is diagnostic of a tetracoordinate boron species and a single crystal X-ray diffraction study revealed the identity as the azide adduct coordinated *via* the α -nitrogen to the boron center (Fig. 1). The

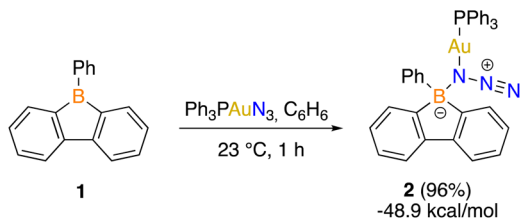


Scheme 1 Reactions of 9-borafluorenes with azides and alkynes.

^aBaylor University, Department of Chemistry and Biochemistry, One Bear Place #97348, Waco, TX 76798, USA. E-mail: caleb_d_martin@baylor.edu

^bUniversity of Florida, Department of Chemistry, Center for Catalysis, Gainesville, FL 32611, USA

†Electronic supplementary information (ESI) available: NMR spectra, FT-IR spectra, X-ray crystallographic table, and computational details (PDF). CCDC 2219219–2219221. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2dt03672j>



Scheme 2 Reaction between **1** and Ph_3PAuN_3 to access **2**. The energy of **2** is relative to the starting materials (298 K and 1 atm; calculated at B3LYP-D0(SMD)/TZ//B3LYP/DZ level of theory).

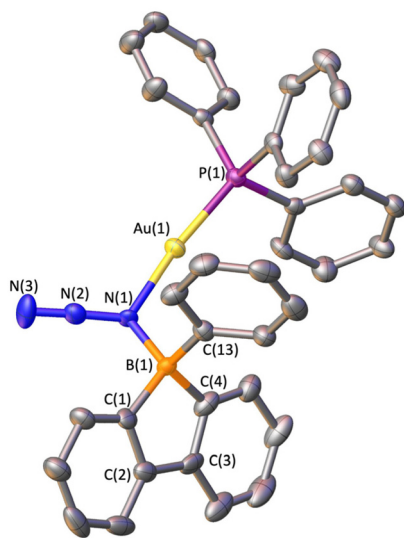


Fig. 1 Solid-state structure of **2**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) of **2**: B(1)–C(13) 1.621(14), B–C 1.636(13), C(4)–B 1.621(14), B–N 1.647(12), N(1)–N(2) 1.228(11), N(2)–N(3) 1.119(12), N(1)–Au(1) 2.074(7), Au–P 2.219(2), P(1)–Au(1)–N(1) 171.6(2), N(1)–N(2)–N(3) 177.8(11).

$^{31}\text{P}\{^1\text{H}\}$ NMR signal for Ph_3PAuN_3 at 30.4 ppm⁶⁷ disappeared with a new peak emerging slightly downfield at 31.2 ppm. The B–N bond distance [1.647(12) Å] is shorter than that of the tris(pentafluorophenyl)borane [$\text{B}(\text{C}_6\text{F}_5)_3$] adduct of phenyl azide [1.678(2) Å], but similar to that of the $\text{B}(\text{C}_6\text{F}_5)_3$ adduct of trimethylsilyl azide [1.648(2) Å].⁶⁸ The geometry at the β -nitrogen is essentially linear [N–N–N angle = 177.8(11)°] and the N_α – N_β bond elongates upon coordination [1.228(11) Å *cf.* Ph_3PAuN_3 : 1.181(4) Å] while the N_β – N_γ bond shortens [1.119(12) Å *cf.* Ph_3PAuN_3 : 1.168(4) Å]. The diagnostic azide stretching frequency appears at 2110 cm^{-1} , red-shifted compared to Ph_3PAuN_3 (2053 cm^{-1}).⁶⁷ DFT calculations at the B3LYP-D0 (SMD)/TZ//B3LYP/DZ level of theory (see ESI for details)^{69–84} indicates coordination through the α -nitrogen is extremely exothermic (–48.9 kcal mol^{-1}) and favored over γ -nitrogen coordination by 7.2 kcal mol^{-1} (–41.7 kcal mol^{-1}). These values greatly exceed that of the previously reported value for the trimethylsilylazide adduct of pentaphenylborole of –3.1 kcal mol^{-1} (ref. 27) and –14.6 kcal mol^{-1} (ref. 31) that

could not be isolated. An azide adduct has been proposed as an intermediate in reaction sequences of borole species with azides, but never isolated.^{27,29,31} Thermochemical calculations on a model system of HN_3 in place of Ph_3PAuN_3 reveals that adduct formation is unfavorable by 2.8 kcal mol^{-1} , suggesting the gold phosphine unit is important for the isolation of the adduct. Attempts to transform **2** thermally (heating at 50 °C) or photochemically ($h\nu = 254 \text{ nm}$) resulted in mixtures that we were unable to identify (ESI: Fig. S7–10†). However, the isolation of **2** gives credence to it being a viable intermediate in other transformations and is the first species isolated from a borafuorene reaction with an azide that is not an azaborine compound.

Combining **1** with $\text{Ph}_3\text{PAu-C}\equiv\text{C-}p\text{-tol}$ in C_6D_6 resulted in an instant color change from yellow to orange/red. The reaction was kept in the dark and monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR signals for $\text{Ph}_3\text{PAu-C}\equiv\text{C-}p\text{-tol}$ disappeared within 15 min with concomitant formation of a major species and a minor species (major: $^{31}\text{P}\{^1\text{H}\}$: $\delta = 41.3 \text{ ppm}$, $p\text{-methyl } ^1\text{H}$: $\delta = 2.10 \text{ ppm}$; minor: $^{31}\text{P}\{^1\text{H}\}$: $\delta = 41.9 \text{ ppm}$, $p\text{-methyl } ^1\text{H}$: $\delta = 1.97 \text{ ppm}$). The integration ratio of the methyl peaks of the two products is ~20 : 1 at 15 min and changed to 6.7 : 1 at 1 h, then to 1.7 : 1 at 3 h, and 1 : 1.1 at 45 h (Fig. S7–S10†). Attributed to decomposition, a black precipitate began forming after 21 h along with signals emerging in the ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra that did not belong to either species. Monitoring was stopped after 69 h as the ratio was unchanged from 45 h and the amount of black precipitate increased and the decomposition signals in the ^1H NMR spectrum became more prevalent. Heating the reaction at 50 °C resulted in the equilibrium being reached in 30 min, albeit with the same decomposition signatures based on ^1H NMR spectroscopy and the black precipitate. Unfortunately, we were unable to isolate either compound due to decomposition. We postulated that their adducts might be more stable and accordingly, one equivalent of 4-dimethylaminopyridine (DMAP) was added to the solution at specific reaction times. After stirring the reaction for 1 min, DMAP was added resulting in an immediate change from orange/red to yellow/orange. Upon workup, a pale-yellow powder was isolated with a single resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (41.9 ppm) and a ^{11}B resonance in the tetra-coordinate region at 1.3 ppm. The molecular structure was determined by a single crystal X-ray diffraction study as the acetylide carbon insertion product with an exocyclic alkene (Fig. 2, **3Z-DMAP**). The complex is the result of a gold migration to the adjacent carbon atom of the acetylide, with *Z* stereochemistry of the exocyclic alkene. This 1,1-carbo-boration product contrasts the 1,2-carbo-boration with 9-borafuorenes that Fukushima observed with organic alkynes (Scheme 1b).⁴⁴ To sequester the second product, DMAP was added at 45 h giving a dark red solution. A pale-yellow powder was isolated after workup with slightly different NMR spectroscopic signatures than **3Z-DMAP** ($^{31}\text{P}\{^1\text{H}\} = 39.8 \text{ ppm}$ and $^{11}\text{B} = 1.5 \text{ ppm}$ *cf.* **3Z-DMAP** $^{31}\text{P}\{^1\text{H}\} = 41.9 \text{ ppm}$ and $^{11}\text{B} = 1.3 \text{ ppm}$). An X-ray diffraction experiments confirmed the identity to be the *E*-isomer (**3E-DMAP**, Fig. 2).

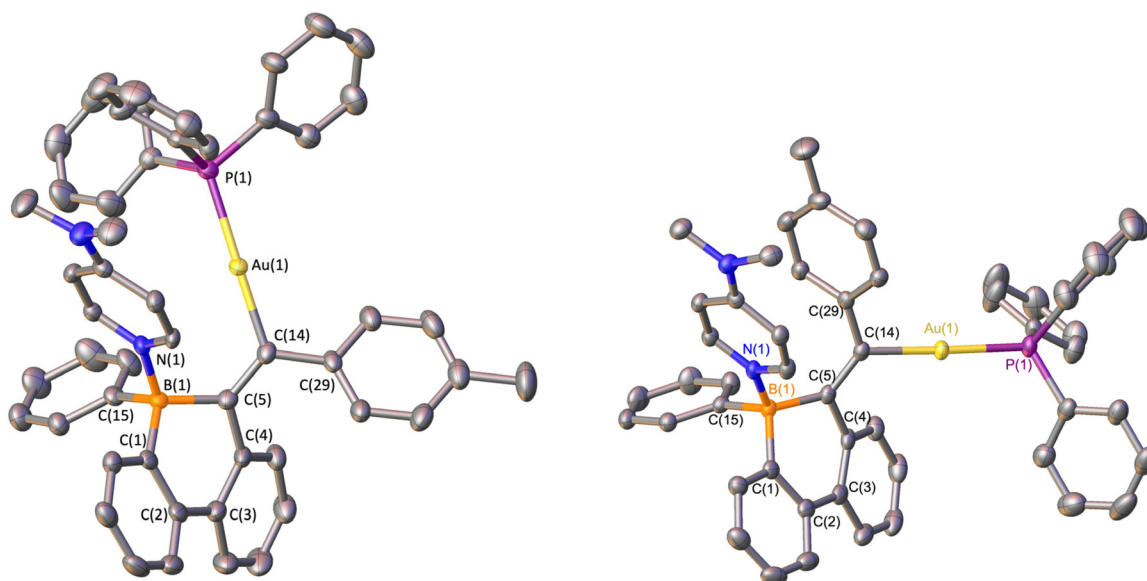
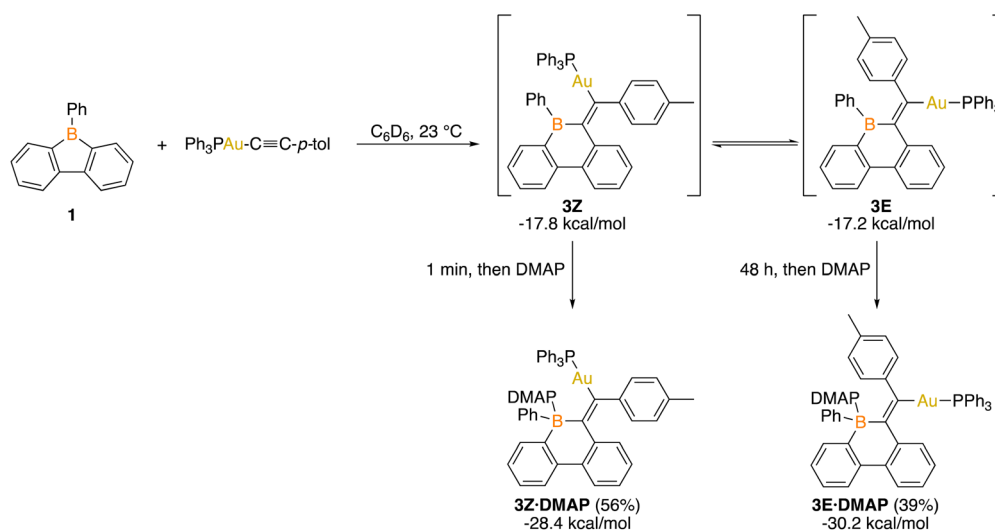


Fig. 2 Solid-state structures of **3Z·DMAP** (left), and **3E·DMAP** (right). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) of **3Z·DMAP**: B(1)–C(15) 1.631(8), B(1)–C(1) 1.636(8), B(1)–C(5) 1.618(7), B(1)–N(1) 1.634(7), C(5)–C(14) 1.365(7), C(14)–Au(1) 2.050(5), Au(1)–P(1) 2.2917(13), B(1)–C(5)–C(14) 127.5(4), C(5)–C(14)–C(29) 122.0(4), C(5)–C(14)–Au(1) 122.1(4), C(29)–C(14)–Au(1) 115.7(4), C(14)–Au(1)–P(1) 173.72(15); **3E·DMAP**: B(1)–C(15) 1.637(3), B(1)–C(1) 1.634(3), B(1)–C(5) 1.624(3), B(1)–N(1) 1.614(2), C(5)–C(14) 1.358(3), C(14)–C(29) 1.484(3), C(14)–Au(1) 2.0626(19), Au(1)–P(1) 2.2753(5), B(1)–C(5)–C(14) 132.06(17), C(5)–C(14)–C(29) 124.65(17), C(5)–C(14)–Au(1) 123.55(14), C(29)–C(14)–Au(1) 111.80(12), P(1)–Au(1)–C(14) 178.37(5).

Theoretical geometry optimizations of **3Z·DMAP** and **3E·DMAP** match well with their experimental solid-state parameters (ESI: Tables S2–S4[†]). The DFT calculations reveal that forming the uncoordinated alkyne insertion products (both *Z* and *E* isomers) is exothermic (**3Z**: -17.8 kcal mol^{−1} and **3E**: -17.2 kcal mol^{−1}), matching the experimental observations (Scheme 3). Clearly, from the experimental data, **3Z** is the kinetic product as it is dominant upon mixing **1** and the Ph₃PAu–C≡C–*p*-tol in a 20 : 1 ratio with a small amount of **3E**,

but after 45 h, the ration changes to 1 : 1.1, respectively. A ground state energy difference of 0.6 kcal mol^{−1} between **3Z/3E** is within the error limit of the computation, supporting the observed equilibrium from the experiment. Preventing decomposition with DMAP is also predicted by DFT. The calculations predict a significant stabilization upon DMAP coordination (**3Z·DMAP**: -28.4 kcal mol^{−1}, **3E·DMAP**: -30.4), thus allowing their isolation. Replacing Ph₃PAu–C≡C–*p*-tol with HC≡C–*p*-tol also gives energetically favored products, albeit



Scheme 3 Reactions between **1**, Ph₃PAu–C≡C–*p*-tol, and DMAP to yield **3Z·DMAP** and **3E·DMAP**. Yields in parentheses.

with lower relative energies (lower than both **3E/Z** by ~ 10 kcal mol⁻¹ and both **3E/Z-DMAP** by 15 kcal mol⁻¹). The relative energy between the two isomers remains similar (0.5 kcal mol⁻¹ difference for **3E/Z** and 2.5 kcal mol⁻¹ for **3E/Z-DMAP**).

Conclusion

The reactions of 9-Ph-9-borafluorene with a gold acetylide and a gold azide yield an adduct and insertion product, respectively. Adding Ph₃PAuN₃ to 9-Ph-9-borafluorene generates a gold azido-borafluorene adduct coordinated to boron through the α -nitrogen that was computed to be notably downhill (-48.9 kcal mol⁻¹), rationalizing its isolation. Azide adducts have been previously proposed as intermediates in transformations of borole species with organic azides, yet had never been isolated. The reaction between Ph₃PAu-C $\equiv$ C-*p*-tol and 9-Ph-9-borafluorene results in a 1,1-carboboration reaction, producing two unstable isomers of a six-membered boracycle featuring an exocyclic vinyl gold moiety. Treating these complexes *in situ* with DMAP at 1 min and 45 h traps the compounds enabling the isolation of the *Z* and *E* isomers. In the acetylide insertion into 9-Ph-9-borafluorene, the DFT predicted product distribution matches the experiment within the margin of the error of the calculations. These are the first reactions of a metal acetylide or azide with 9-phenylborafluorene and provide a foundation for a new class of Au(I) organoboron compounds.

Experimental section

General considerations

All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Unilab glove box or using standard Schlenk techniques unless specified. Solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over molecular sieves. The reagents 9-Ph-9-borafluorene,⁵⁰ Ph₃PAu-C $\equiv$ C-*p*-tol,^{85,86} and Ph₃PAuN₃⁸⁷ were prepared according to literature methods. Chloroform-*d* and C₆D₆ for NMR spectroscopy was purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH₂, distilled, and stored over 4 Å molecular sieves. Multinuclear NMR spectra were recorded on Bruker 400 or 600 MHz spectrometers. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. High Resolution mass spectra (HRMS) were obtained in the Baylor University Mass Spectrometry Center on a Thermo Orbitrap Q-exactive Focus spectrometer. Melting points were measured with a Thomas Hoover Uni-melt capillary melting point apparatus and are uncorrected. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-K α radiation ($\lambda = 0.71073$ Å). Crystals were selected under paratone oil, mounted on micromounts,

and placed in a cold stream of N₂ immediately. Structures were solved and refined using SHELXTL and figures produced using OLEX2.^{88,89}

Synthesis of 2. In the dark at 23 °C, a benzene solution of 9-Ph-9-borafluorene (14.2 mg, 0.059 mmol, 2 mL) was added dropwise to a vial wrapped with aluminum foil in the dark containing a benzene solution of Ph₃PAuN₃ (30.0 mg, 0.058 mmol, 3 mL) and the mixture stirred for 1 h. The volatiles were removed *in vacuo* and the residue washed with *n*-pentane (3 $\times$ 1 mL) to give a white powder. Single crystals for X-ray diffraction studies were grown by vapor diffusion of dichloromethane solution of **2** into toluene. Yield: 42.8 mg, 96%. d.p.: 128 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.45–7.38 (m, 3H), 7.32 (td, *J* = 8.0, 4.0 Hz, 6H), 7.19–7.04 (m, 11H), 6.94 (t, *J* = 6.0 Hz, 2H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 149.58, 134.19 (d, *J* = 13.1 Hz), 133.33, 132.21 (d, *J* = 2.0 Hz), 131.37, 129.42 (d, *J* = 12.1 Hz), 128.31, 128.0 (d, *J* = 99.0 Hz), 127.69, 127.42, 126.44, 126.16, 119.32. ¹¹B NMR (128 MHz, CDCl₃): δ 4.7 ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 31.2 ppm. FT-IR (ranked intensity): 2110(3), 1480(13), 1435(1), 1245(9), 1181(14), 1101(7), 997(15), 887(12), 739(4), 704(11), 690(1), 640(8), 617(10), 545(2), 504(5). We were unable to detect ions corresponding to the molecular ion, or fragments, of **2** by HRMS using CI and ESI techniques. Since **2** has an intact azide, we did not submit a sample for combustion analysis. The purity of **2** was established by multinuclear NMR spectroscopy.

Synthesis of 3Z-DMAP. In the dark at 23 °C, a toluene solution of 9-Ph-9-borafluorene (24.0 mg, 0.100 mmol, 0.2 mL) was transferred into a vial wrapped in aluminum foil containing a suspension of Ph₃PAu-C $\equiv$ C-*p*-tol (57.4 mg, 0.100 mmol) in toluene (0.3 mL) and stirred for 1 min to give an orange/red solution. Solid DMAP was then added (12.2 mg, 0.100 mmol) and stirred for 1 min to give an orange/yellow solution. The mixture was cooled to -35 °C for 30 min which induced the precipitation of a solid. The supernatant was decanted, and the solids washed with *n*-pentane (3 $\times$ 1 mL) and dried to give **3Z-DMAP** as a yellow powder. Single crystals for X-ray diffraction studies were grown by vapor diffusion of dichloromethane solution of **3Z-DMAP** into toluene. Yield: 52.8 mg, 56%. d.p.: 126 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.05 (br, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.36–7.32 (m, 3H), 7.28–7.14 (m, 15H), 7.08 (d, *J* = 4.0 Hz, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.79–6.71 (m, 6H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.52–6.45 (m, 2H), 6.06 (br, 2H), 2.79 (s, 6H), 2.15 (s, 3H) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 154.34, 153.81, 146.48, 145.19 (d, *J* = 12.1 Hz), 142.74, 139.40, 135.86, 135.03 (d, *J* = 13.6 Hz), 133.78, 132.82, 132.52, 131.08, 130.80, 130.44 (d, *J* = 1.5 Hz), 128.61 (d, *J* = 10.6 Hz), 127.18, 126.79, 126.56, 125.27, 125.16 (d, *J* = 78.5 Hz), 124.51, 124.04, 105.51, 37.98, 21.23 ppm. ¹¹B NMR (128 MHz, C₆D₆): δ 1.3 ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 41.9 ppm. FT-IR (cm⁻¹, ranked intensity): 1626(1), 1549(11), 1436(9), 1392(15), 1225(8), 1101(14), 1084(7), 1035(12), 816(5), 756(13), 740(1), 710(10), 691(3), 532(4), 500(2). HRMS(+ESI): calcd 937.3157 for C₅₂H₄₅AuBN₂P [M + H]⁺ found 937.3148.

Synthesis of 3E-DMAP. In the dark at 23 °C, a C₆D₆ solution of 9-Ph-9-borafluorene (24.1 mg, 0.100 mmol, 0.6 mL) was transferred into a vial wrapped in aluminum foil containing a suspension of Ph₃PAu-C≡C-*p*-tol (57.4 mg, 0.100 mmol) and stirred for 45 h. To the resulting orange/red solution, solid DMAP was added (12.2 mg, 0.100 mmol) and stirred for 5 min to give a dark red solution. The volatiles were removed *in vacuo* and the remaining solid was washed with benzene (3 × 2 mL) and dried to give a pale-yellow powder. Single crystals for X-ray diffraction studies were grown by vapor diffusion of dichloromethane solution of 3E-DMAP into hexanes. Yield: 36.8 mg, 39%. d.p.: 125 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.18 (d, *J* = 6.0 Hz, 1H), 7.86 (br, 1H), 7.73 (d, *J* = 6.0 Hz, 1H), 7.49 (d, *J* = 12 Hz, 3H), 7.40–7.32 (m, 15H), 7.14 (t, *J* = 6.0 Hz, 3H), 7.09 (t, *J* = 6.0 Hz, 2H), 7.00 (t, *J* = 6.0 Hz, 2H), 6.96 (t, *J* = 6.0 Hz, 1H), 6.72 (t, *J* = 6 Hz, 1H), 6.6 (br, 3H), 6.28 (br, 1H), 5.99 (br, 2H), 5.78 (br, 1H), 2.92 (s, 6H), 2.06 (s, 3H) ppm. ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 154.82, 150.53, 149.49 (d, *J* = 7.4 Hz), 141.12, 137.01, 135.95, 134.50 (d, *J* = 13.6 Hz), 132.30, 131.99, 131.40, 130.57 (d, *J* = 1.5 Hz), 130.29, 129.98, 128.73 (d, *J* = 10.4 Hz), 128.49, 126.92, 125.46 (d, *J* = 86.8 Hz), 125.29, 124.88, 123.10, 122.91, 39.26, 20.77 ppm. ¹¹B{¹H} NMR (128 MHz, C₆D₆): δ 1.5 ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 39.8 ppm. FT-IR (cm⁻¹, ranked intensity): 1632(5), 1546(9), 1480(15), 1434(7), 1389(14), 1225(8), 1091(4), 1040(11), 815(1), 737(3), 708(12), 691(1), 620(13), 530(2), 496(10) HRMS(+ESI): calcd 937.3157 for C₅₂H₄₅AuBN₂P [M + H]⁺ found 937.3199.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to the Welch Foundation (Grant No. AA-1846) and the National Science Foundation (Award No. 1753025) for supporting this work. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences Energy Frontier Research Centers program under Award Number DE-SC-0020008.

References

- 1 R. Köster and G. Benedikt, *Angew. Chem.*, 1963, **75**, 419–419.
- 2 P. A. Chase, W. E. Piers and B. O. Patrick, *J. Am. Chem. Soc.*, 2000, **122**, 12911–12912.
- 3 X. Su, T. A. Bartholome, J. R. Tidwell, A. Pujol, S. Yruegas, J. J. Martinez and C. D. Martin, *Chem. Rev.*, 2021, **121**, 4147–4192.
- 4 J. He, F. Rauch, M. Finze and T. B. Marder, *Chem. Sci.*, 2021, **12**, 128–147.
- 5 J. J. Eisch, N. K. Hota and S. Kozima, *J. Am. Chem. Soc.*, 1969, **91**, 4575–4577.
- 6 J. J. Eisch, J. E. Galle, B. Shafii and A. L. Rheingold, *Organometallics*, 1990, **9**, 2342–2349.
- 7 A. P. Sadimenko, *Adv. Heterocycl. Chem.*, 2001, **79**, 115–200.
- 8 A. Steffen, R. M. Ward, W. D. Jones and T. B. Marder, *Coord. Chem. Rev.*, 2010, **254**, 1950–1976.
- 9 C. Fan, W. E. Piers, M. Parvez and R. McDonald, *Organometallics*, 2010, **29**, 5132–5139.
- 10 H. Braunschweig and T. Kupfer, *Chem. Commun.*, 2011, **47**, 10903–10914.
- 11 H. Braunschweig, I. Krummenacher and J. Wahler, in *Adv. Organomet. Chem*, ed. A. F. Hill and M. J. Fink, Academic Press, 2013, vol. 61, pp. 1–53.
- 12 J. H. Barnard, S. Yruegas, S. A. Couchman, D. J. D. Wilson, J. L. Dutton and C. D. Martin, *Organometallics*, 2016, **35**, 929–931.
- 13 W. Zhang, B. Zhang, D. Yu and G. He, *Sci. Bull.*, 2017, **62**, 899–900.
- 14 Z. Wang, Y. Zhou, K.-H. Lee, W. H. Lam, R. D. Dewhurst, H. Braunschweig, T. B. Marder and Z. Lin, *Chem. – Eur. J.*, 2017, **23**, 11587–11597.
- 15 S. Yruegas, J. H. Barnard, K. Al-Furaiji, J. L. Dutton, D. J. D. Wilson and C. D. Martin, *Organometallics*, 2018, **37**, 1515–1518.
- 16 Z. Wang, Y. Zhou, J.-X. Zhang, I. Krummenacher, H. Braunschweig and Z. Lin, *Chem. – Eur. J.*, 2018, **24**, 9612–9621.
- 17 J. J. Baker, K. H. M. Al Furaiji, O. T. Liyanage, D. J. D. Wilson, J. L. Dutton and C. D. Martin, *Chem. – Eur. J.*, 2019, **25**, 1581–1587.
- 18 W. Yang, K. E. Krantz, L. A. Freeman, D. A. Dickie, A. Molino, A. Kaur, D. J. D. Wilson and R. J. Gilliard Jr., *Chem. – Eur. J.*, 2019, **25**, 12512–12516.
- 19 W. Yang, K. E. Krantz, L. A. Freeman, D. A. Dickie, A. Molino, G. Frenking, S. Pan, D. J. D. Wilson and R. J. Gilliard Jr., *Angew. Chem., Int. Ed.*, 2020, **59**, 3850–3854.
- 20 F. Lindl, X. Guo, I. Krummenacher, F. Rauch, A. Rempel, V. Paprocki, T. Dellermann, T. E. Stennett, A. Lamprecht, T. Brückner, K. Radacki, G. Bélanger-Chabot, T. B. Marder, Z. Lin and H. Braunschweig, *Chem. – Eur. J.*, 2021, **27**, 11226–11233.
- 21 K. K. Hollister, W. Yang, R. Mondol, K. E. Wentz, A. Molino, A. Kaur, D. A. Dickie, G. Frenking, S. Pan, D. J. D. Wilson and R. J. Gilliard Jr., *Angew. Chem., Int. Ed.*, 2022, **61**, e202202516.
- 22 J. H. Barnard, S. Yruegas, K. Huang and C. D. Martin, *Chem. Commun.*, 2016, **52**, 9985–9991.
- 23 J. J. Eisch and J. E. Galle, *J. Am. Chem. Soc.*, 1975, **97**, 4436–4437.

- 24 S. Biswas, C. Maichle-Mössmer and H. F. Bettinger, *Chem. Commun.*, 2012, **48**, 4564–4566.
- 25 A. Fukazawa, J. L. Dutton, C. Fan, L. G. Mercier, A. Y. Houghton, Q. Wu, W. E. Piers and M. Parvez, *Chem. Sci.*, 2012, **3**, 1814–1818.
- 26 H. Braunschweig, J. Maier, K. Radacki and J. Wahler, *Organometallics*, 2013, **32**, 6353–6359.
- 27 S. A. Couchman, T. K. Thompson, D. J. D. Wilson, J. L. Dutton and C. D. Martin, *Chem. Commun.*, 2014, **50**, 11724–11726.
- 28 H. Braunschweig, C. Hörl, L. Mailänder, K. Radacki and J. Wahler, *Chem. – Eur. J.*, 2014, **20**, 9858–9861.
- 29 H. Braunschweig, M. A. Celik, F. Hupp, I. Krummenacher and L. Mailänder, *Angew. Chem., Int. Ed.*, 2015, **54**, 6347–6351.
- 30 H. Braunschweig, I. Krummenacher, L. Mailänder and F. Rauch, *Chem. Commun.*, 2015, **51**, 14513–14515.
- 31 H. Braunschweig, M. A. Celik, T. Dellermann, G. Frenking, K. Hammond, F. Hupp, H. Kelch, I. Krummenacher, F. Lindl, L. Mailänder, J. H. Müssig and A. Ruppert, *Chem. – Eur. J.*, 2017, **23**, 8006–8013.
- 32 Y. Li, R. K. Siwatch, T. Mondal, Y. Li, R. Ganguly, D. Koley and C.-W. So, *Inorg. Chem.*, 2017, **56**, 4112–4120.
- 33 K. R. Bluer, L. E. Laperriere, A. Pujol, S. Yruegas, V. A. K. Adiraju and C. D. Martin, *Organometallics*, 2018, **37**, 2917–2927.
- 34 F. Lindl, S. Lin, I. Krummenacher, C. Lenczyk, A. Stoy, M. Müller, Z. Lin and H. Braunschweig, *Angew. Chem., Int. Ed.*, 2019, **58**, 338–342.
- 35 J. Kashida, Y. Shoji and T. Fukushima, *Chem. – Asian J.*, 2019, **14**, 1879–1885.
- 36 T. A. Bartholome, K. R. Bluer and C. D. Martin, *Dalton Trans.*, 2019, **48**, 6319–6322.
- 37 T. A. Bartholome, A. Kaur, D. J. D. Wilson, J. L. Dutton and C. D. Martin, *Angew. Chem., Int. Ed.*, 2020, **59**, 11470–11476.
- 38 W. Yang, K. E. Krantz, D. A. Dickie, A. Molino, D. J. D. Wilson and R. J. Gilliard Jr., *Angew. Chem., Int. Ed.*, 2020, **59**, 3971–3975.
- 39 X. Su, J. J. Baker and C. D. Martin, *Chem. Sci.*, 2020, **11**, 126–131.
- 40 S. Fuchs, A. Jayaraman, I. Krummenacher, L. Haley, M. Bašćovanović, M. Fest, K. Radacki, H. Helten and H. Braunschweig, *Chem. Sci.*, 2022, **13**, 2932–2938.
- 41 M. O. Akram, J. R. Tidwell, J. L. Dutton, D. J. D. Wilson, A. Molino and C. D. Martin, *Inorg. Chem.*, 2022, **61**, 9595–9604.
- 42 M. Müller, C. Maichle-Mössmer and H. F. Bettinger, *Angew. Chem., Int. Ed.*, 2014, **53**, 9380–9383.
- 43 Y. Shoji, N. Tanaka, S. Muranaka, N. Shigeno, H. Sugiyama, K. Takenouchi, F. Hajjaj and T. Fukushima, *Nat. Commun.*, 2016, **7**, 12704.
- 44 Y. Shoji, N. Shigeno, K. Takenouchi, M. Sugimoto and T. Fukushima, *Chem. – Eur. J.*, 2018, **24**, 13223–13230.
- 45 Y. Murata, K. Matsunagi, J. Kashida, Y. Shoji, C. Özen, S. Maeda and T. Fukushima, *Angew. Chem., Int. Ed.*, 2021, **60**, 14630–14635.
- 46 S. Yruegas, J. J. Martinez and C. D. Martin, *Chem. Commun.*, 2018, **54**, 6808–6811.
- 47 W. Zhang, G. Li, L. Xu, Y. Zhuo, W. Wan, N. Yan and G. He, *Chem. Sci.*, 2018, **9**, 4444–4450.
- 48 G. E. Herberich, B. Hessner, M. Negele and J. A. K. Howard, *J. Organomet. Chem.*, 1987, **336**, 29–43.
- 49 G. E. Herberich, B. Hessner, H. Ohst and I. A. Raap, *J. Organomet. Chem.*, 1988, **348**, 305–316.
- 50 P. E. Romero, W. E. Piers, S. A. Decker, D. Chau, T. K. Woo and M. Parvez, *Organometallics*, 2003, **22**, 1266–1274.
- 51 D. V. Muratov, P. V. Petrovskii, Z. A. Starikova, G. E. Herberich and A. R. Kudinov, *J. Organomet. Chem.*, 2006, **691**, 3251–3259.
- 52 S. Yruegas, H. Tang, G. Z. Bornovski, X. Su, S. Sung, M. B. Hall, M. Nippe and C. D. Martin, *Inorg. Chem.*, 2021, **60**, 16160–16167.
- 53 S. Bontemps, G. Bouhadir, K. Miqueu and D. Bourissou, *J. Am. Chem. Soc.*, 2006, **128**, 12056–12057.
- 54 L. A. Essex, J. W. Taylor and W. H. Harman, *Tetrahedron*, 2019, **75**, 2255–2260.
- 55 D. V. Partyka, J. B. Updegraff, M. Zeller, A. D. Hunter and T. G. Gray, *Organometallics*, 2007, **26**, 183–186.
- 56 D. V. Partyka, L. Gao, T. S. Teets, J. B. Updegraff III, N. Deligonul and T. G. Gray, *Organometallics*, 2009, **28**, 6171–6182.
- 57 T. J. Del Castillo, S. Sarkar, K. A. Abboud and A. S. Veige, *Dalton Trans.*, 2011, **40**, 8140–8144.
- 58 J. E. Heckler, N. Deligonul, A. L. Rheingold and T. G. Gray, *Chem. Commun.*, 2013, **49**, 5990–5992.
- 59 T. J. Robilotto, N. Deligonul, J. B. Updegraff III and T. G. Gray, *Inorg. Chem.*, 2013, **52**, 9659–9668.
- 60 A. R. Powers, I. Ghiviriga, K. A. Abboud and A. S. Veige, *Dalton Trans.*, 2015, **44**, 14747–14752.
- 61 X. Yang, S. Wang, I. Ghiviriga, K. A. Abboud and A. S. Veige, *Dalton Trans.*, 2015, **44**, 11437–11443.
- 62 J. J. Mihaly, D. J. Stewart, T. A. Grusenmeyer, A. T. Phillips, J. E. Haley, M. Zeller and T. G. Gray, *Dalton Trans.*, 2019, **48**, 15917–15927.
- 63 C. C. Beto, C. J. I. V. Zeman, Y. Yang, J. D. Bullock, E. D. Holt, A. Q. Kane, T. A. Makal, X. Yang, I. Ghiviriga, K. S. Schanze and A. S. Veige, *Inorg. Chem.*, 2020, **59**, 1893–1904.
- 64 C. J. I. V. Zeman, Y.-H. Shen, J. K. Heller, K. A. Abboud, K. S. Schanze and A. S. Veige, *J. Am. Chem. Soc.*, 2020, **142**, 8331–8341.
- 65 Y.-H. Shen, A. M. Esper, I. Ghiviriga, K. A. Abboud, K. S. Schanze, C. Ehm and A. S. Veige, *Dalton Trans.*, 2021, **50**, 12681–12691.
- 66 J. J. Mihaly, S. M. Wolf, A. T. Phillips, S. Mam, Z. Yung, J. E. Haley, M. Zeller, K. de La Harpe, E. Holt, T. A. Grusenmeyer, S. Collins and T. G. Gray, *Inorg. Chem.*, 2022, **61**, 1228–1235.
- 67 R. K. Thomson, C. R. Graves, B. L. Scott and J. L. Kiplinger, *Eur. J. Inorg. Chem.*, 2009, **2009**, 1451–1455.
- 68 K. Bläsing, J. Bresien, R. Labbow, D. Michalik, A. Schulz, M. Thomas and A. Villinger, *Angew. Chem., Int. Ed.*, 2019, **58**, 6540–6544.
- 69 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone,

- G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16, Revision C.01*, Gaussian Inc., Wallingford CT, 2016.
- 70 R. Dennington, T. A. Keith and J. M. Millam, *GaussView, Version 6.0.16*, Semichem Inc., Shawnee Mission KS, 2016.
- 71 E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41–51.
- 72 J. L. Whitten, *J. Chem. Phys.*, 1973, **58**, 4496–4501.
- 73 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785–789.
- 74 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- 75 M. Feyereisen, G. Fitzgerald and A. Komornicki, *Chem. Phys. Lett.*, 1993, **208**, 359–363.
- 76 O. Vahtras, J. Almlöf and M. W. Feyereisen, *Chem. Phys. Lett.*, 1993, **213**, 514–518.
- 77 S. Tobisch and T. Ziegler, *J. Am. Chem. Soc.*, 2004, **126**, 9059–9071.
- 78 N. B. Balabanov and K. A. Peterson, *J. Chem. Phys.*, 2005, **123**, 064107.
- 79 N. B. Balabanov and K. A. Peterson, *J. Chem. Phys.*, 2006, **125**, 074110.
- 80 K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorathi, J. Chase, J. Li and T. L. Windus, *J. Chem. Inf. Model.*, 2007, **47**, 1045–1052.
- 81 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.
- 82 S. Grimme, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2011, **1**, 211–228.
- 83 F. Zaccaria, C. Ehm, P. H. M. Budzelaar and V. Busico, *ACS Catal.*, 2017, **7**, 1512–1519.
- 84 F. Zaccaria, R. Cipullo, P. H. M. Budzelaar, V. Busico and C. Ehm, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 2807–2814.
- 85 S. Banerjee and N. T. Patil, *Chem. Commun.*, 2017, **53**, 7937–7940.
- 86 X.-K. Wan, X.-L. Cheng, Q. Tang, Y.-Z. Han, G. Hu, D.-e. Jiang and Q.-M. Wang, *J. Am. Chem. Soc.*, 2017, **139**, 9451–9454.
- 87 D. V. Partyka, J. B. Updegraff, M. Zeller, A. D. Hunter and T. G. Gray, *Organometallics*, 2007, **26**, 183–186.
- 88 G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
- 89 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.