Supporting Information for:

CuOTf-mediated intramolecular diborene hydroarylation

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Experimental Details

General information

All reactions were performed under an atmosphere of dry argon using standard Schlenk line or glovebox techniques. Deuterated benzene and dichloromethane were degassed by three freeze-pump-thaw cycles and dried over molecular sieves. Other solvents were dried by storage over, and distillation from, potassium (benzene, THF) or P₂O₅ (dichloromethane) under an argon atmosphere. The solvents were then stored under argon over activated 4 Å molecular sieves. Diborene **1** was synthesized according to a literature procedure.¹ Anhydrous CuCl, [CuOTf]₂·toluene and all other chemicals were purchased either from Aldrich, Acros or TCI Chemical Co. and used as received unless otherwise specified.

NMR spectra were obtained from a Bruker Avance 500 NMR spectrometer (¹H: 500.1 MHz, ¹³C{¹H}: 125.8 MHz, ³¹P{¹H}: 202.5 MHz) or a Bruker Avance 400 (¹H and ¹H{¹¹B}: 400.1 MHz, ¹³C{¹H}: 100.6 MHz; ¹¹B and ¹¹B{¹H}: 128.4 MHz, ³¹P{¹H}: 162.0 MHz, ¹⁹F: 376.5 MHz) at 298 K. Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei (¹³C{¹H}) or residual protons (¹H) of the solvent. ¹¹B, ³¹P{¹H} and ¹⁹F{¹H} NMR spectra were referenced to external standard [BF₃·OEt₂], 85% H₃PO₄, or CFCl₃, respectively. Microanalyses (C, H, N) were performed on an Elementar vario MICRO cube elemental analyzer. High-resolution mass spectrometry was obtained from a Thermo Scientific Exactive Plus spectrometer.

Synthesis of CuCl complex 4



A mixture of diborene 1 (26.4 mg, 0.05 mmol) and finely powdered CuCl (20.0 mg, 0.2 mmol) was suspended in C₆H₆ (1.0 mL) and stirred for ca. 10 min at RT. Once the green color had diminished, the excess CuCl was then filtered off and washed with benzene (0.5 mL \times 3) in a glovebox. The combined bright yellow solution was then dried *in vivo* and washed with pentane (1 mL \times 3) to give a yellow solid. Yield: 30.1 mg, 95%. Yellow needles suitable for X-ray crystallography were obtained from a THF solution stored at –30 °C.

¹**H** NMR (400.1 MHz, C₆D₆): $\delta = 10.21$ (d, J = 8.8 Hz, 2H, C_{Ar}H), 9.57 (d, J = 8.8 Hz, 2H, C_{Ar}H), 8.33 (s, 2H, C_{Ar}H), 8.01-7.93 (m, 6H, C_{Ar}H), 7.60 (dd, J = 7.6, 7.2 Hz, 2H, C_{Ar}H), 7.44 (dd, J = 7.6, 7.2 Hz, 4H, C_{Ar}H), 0.27 (vt, J = 5.2 Hz, 18H, PCH₃). ¹³C{¹H} NMR (100.6 MHz, C₆D₆): $\delta = 137.3$ (t, J = 3 Hz), 137.2 (t, J = 3 Hz), 134.4, 133.0 (t, J = 2 Hz), 133.3 (t, J = 2 Hz), 129.6, 129.2, 128.6, 126.6 (t, J = 3 Hz), 126.0, 124.9, 124.7, 122.6, 12.3 (vt, J = 19 Hz). ¹¹B NMR (128.4 MHz, C₆D₆): $\delta = 17.1$. ³¹P{¹H} NMR (162.0 MHz, C₆D₆): $\delta = -19.0$ (br).

Elemental Analysis: calculated for $C_{38}H_{44}B_2OP_2CuCl (M + THF)$: C 65.26; H 6.34; found: C 65.29; H 6.75.

Synthesis of boryl boronium triflate salt 7



A mixture of diborene **1** (21.7 mg, 0.04 mmol) and (CuOTf)₂-toluene (12.5 mg, 0.024 mmol) was disolved in benzene (1.0 mL). After stirring for 5 min at RT with the precipitation of a black solid, the reaction mixture was filtered off and washed with benzene (0.5 mL \times 3) to give a red solution. ¹¹B and ³¹P{¹H} NMR analysis indicated that the major product in the red solution was the diborene-CuOTf complex. After storing at RT for several days in a glovebox, orange crystals formed and were collected, and were found to be suitable for X-ray diffraction analysis. Yield: 7.2 mg, 36%.

¹**H NMR** (500.1 MHz, CD₂Cl₂): $\delta = 8.69$ (s, 1H, C_{Ar}*H*), 8.54 (s, 1H, C_{Ar}*H*), 8.43 (d, *J* = 8.5 Hz, 1H, C_{Ar}*H*), 8.28 (d, *J* = 8.5 Hz, 1H, C_{Ar}*H*), 8.14 (d, *J* = 8.5 Hz, 2H, C_{Ar}*H*), 7.92 (d, *J* = 8.5 Hz, 1H, C_{Ar}*H*), 7.76 (d, *J* = 6.0 Hz, 1H, C_{Ar}*H*), 7.69 (dd, *J* = 8.5, 6.5 Hz, 1H, C_{Ar}*H*), 7.65 (dd, *J* = 8.5, 6.5 Hz, 1H, C_{Ar}*H*), 7.61 (t, *J* = 7.5 Hz, 1H, C_{Ar}*H*), 7.49 (dd, *J* = 8.5, 7.0 Hz, 2H, C_{Ar}*H*), 7.26 (dt, *J* = 8.0, 1.0 Hz, 2H, C_{Ar}*H*), 7.15 (d, *J* = 9.0 Hz, 2H, C_{Ar}*H*), 1.44 (d, *J* = 11.0 Hz, 18H, PCH₃). ¹³C{¹H} **NMR** (125.8 MHz, CD₂Cl₂): $\delta = 152.0$ (t, *J* = 9 Hz), 151.3 (br), 144.9 (br), 135.5, 134.6 (t, *J* = 2 Hz), 134.3, 134.1 (t, *J* = 2 Hz), 131.8, 131.3, 131.1, 130.7, 130.1, 129.0, 128.25, 128.17 (dd, *J* = 23, 25 Hz), 127.6 (t, *J* = 2.3 Hz), 127.4, 127.3, 127.0, 125.9, 125.7, 125.3, 121.3 (q, *J* = 321 Hz, CF₃SO₃), 13.3 (dd, *J* = 43, 4 Hz).

¹¹**B** NMR (128.4 MHz, CD₂Cl₂): δ = 103.1 (br s), -20.5 (s).

³¹P{¹H} NMR (202.5 MHz, CD_2Cl_2): $\delta = -10.8$ (br m).

¹⁹**F NMR** (376.5 MHz, CD_2Cl_2): $\delta = -79.0$ (s).

HRMS (LIFDI): calculated for $C_{34}H_{35}B_2P_2^+$: 527.2395; found: 527.2390.



Figure S1. ¹¹B NMR of the reaction mixture of 1 with (CuOTf)₂-toluene in benzene.



Figure S2. ³¹P{¹H} NMR of the reaction mixture of **1** with (CuOTf)₂·toluene in benzene.



Figure S4. ³¹P{¹H} NMR of the reaction mixture of **1** with (CuOTf)₂·toluene in benzene after heating at 60 °C for 4-5 h.

X-ray Crystallographic Details

Crystal structure determination

The crystal data of **4** were collected on a BRUKER SMART-APEX II equipped with a CCD area detector and graphite monochromated $Mo_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,² refined with the SHELXL program³ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystal data for 4: $C_{38}H_{44}B_2ClCuOP_2$, $M_r = 699.28$, yellow block, 0.026×0.0235×0.0325 mm³, orthorhombic space group $P2_12_12_1$, a = 10.7014(4) Å, b = 17.5374(7) Å, c = 18.6212(8) Å, V = 3494.7(2) Å³, Z = 4, $\rho_{calcd} = 1.329$ g·cm⁻³, $\mu = 0.823$ mm⁻¹, F(000) = 1464, T = 296(2) K, $R_I = 0.0335$, $wR^2 = 0.0734$, 7157

independent reflections $[20 \le 52.744^\circ]$ and 413 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1575190. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Crystal structure determination

The crystal data of 7 were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,² refined with the SHELXL program³ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

 $M_{\rm r} = 832.46$ Crystal data for 7: $C_{47}H_{47}B_2F_3O_3P_2S$, yellow block, $0.34 \times 0.24 \times 0.14 \text{ mm}^3$, monoclinic space group $P2_{1}/c$, a = 11.0551(4) Å, b = 13.8648(6) Å, c = 28.6834(11) Å, $\beta = 99.6580(10)$ °, V = 4334.2(3) Å³, Z = 4, $\rho_{calcd} = 1.276 \text{ g} \cdot \text{cm}^{-3}, \ \mu = 0.202 \text{ mm}^{-1}, \ F(000) = 1744, \ T = 100(2) \text{ K}, \ R_I = 0.0651,$ $wR^2 = 0.1083$, 8535 independent reflections [2 $\theta \le 52.044^\circ$] and 529 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1575191. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif







Figure S8. ${}^{31}P{}^{1}H$ NMR of compound 4 in C₆D₆.







Figure S12. ${}^{31}P{}^{1}H$ NMR of compound 7 in CD₂Cl₂.



Figure S13. ¹⁹F NMR of compound 7 in CD₂Cl₂.

References

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