Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for:

A Facile and Selective Route to Monocyclic NHC-stabilized Boriranes

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Experimental Section

General considerations:

Unless otherwise stated, all reactions were accomplished under an atmosphere of dry argon using standard Schlenk line and glovebox techniques. Deuterated solvents as well as fluorobenzene were degassed by three freeze-pump-thaw cycles and dried over molecular sieves. Other solvents were dried by storage over, and distillation from, sodium (diethyl ether), potassium (benzene) or Na/K alloy (all other solvents) under an argon atmosphere. The solvents were then stored under argon over 4 Å molecular sieves. NMR spectra were obtained from a Bruker Avance 500 NMR spectrometer (^{1}H: 500.13 MHz, ^{11}B: 160.46 MHz, ^{13}C{^{1}H}: 125.76 MHz, ^{31}P: 202.5 MHz) at room temperature. Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR spectra were referenced to external standards [$BF_3{\cdot}OEt_2$] or 85% H_3PO_4, respectively. For the compounds **3** and **5** the assignments were supported by COSY, HMBC and HCQC NMR experiments. Microanalyses (C, H, N) were performed on an Elementar vario MICRO cube elemental analyzer. *I*Me,[1] *I*Me^{Me},[2] $PhBCl_2$,[3] $Na_2[C_{14}H_{12}]$[4] and $[Pt(PEt_3)_4]$[5] were synthesized according to literature procedures.

Preparation of *I*Me·BPhCl$_2$ (1):

A solution of *I*Me (4.13 g, 43.0 mmol) in toluene (50 mL) was added dropwise to a solution of $PhBCl_2$ (8.14 g, 51.2 mmol) in toluene (25 mL) at –78 °C. The mixture was stirred for one hour at this temperature and then for an additional 16 hours at room temperature. The resulting solid was filtered, washed with hexane (4 × 20 mL) and dried *in vacuo*. Crystallization from boiling toluene afforded **1** as colorless crystals at –30 °C, which were washed with pentane and dried *in vacuo* (9.30 g, 36.5 mmol, 85 %).

^{1}H NMR (500.13 MHz, C_6D_6) δ = 8.07-8.00 (m, 2H, *m*-$C_{ar}H$), 7.33-7.27 (m, 2H, *o*-$C_{ar}H$), 7.22-7.17 (m, 1H, *p*-$C_{ar}H$), 5.37 (s, 2H, NC*H*), 3.02 (s, 6H, NCH_3).

^{11}B NMR (160.46 MHz, C_6D_6): δ = 0.9 (s).

^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6): δ = 133.36, 127.94, 127.21 (C_{ar}H), 121.75 (N*C*H), 38.21 (N*C*H_3).

Elemental analysis: calculated for $C_{11}H_{13}BCl_2N_2$: C 51.82; H 5.14; N 11.0; found: C 51.93; H 5.32; N 11.29.

Preparation of *I*Me^{Me}·BPhCl$_2$ (2):

A solution of $PhBCl_2$ (954 mg, 6.00 mmol) in toluene (20 mL) was added dropwise to a suspension of *I*Me^{Me} (744 mg, 5.99 mmol) in toluene (25 mL)) at –78 °C. The mixture was then allowed to reach ambient temperature and was stirred for three hours at this temperature, whereas a brown solid occured. The supernatant was removed with a syringe from the brown residue. From the removed

supernatant the solvent was removed *in vacuo* and the resulting residue was washed with hexane (3 × 20 mL) and dried *in vacuo* to afford **2** as colorless solid (1.12 g, 3.96 mmol, 66 %).

^{1}H NMR (500.13 MHz, C_6D_6) δ = 8.22-8.16 (m, 2H, *m*-$C_{ar}H$), 7.40-7.34 (m, 2H, *o*-$C_{ar}H$), 7.27-7.22 (m, 1H, *p*-$C_{ar}H$), 3.04 (s, 6H, NCH_3), 1.03 (s, 6H, NCCH_3).

^{11}B NMR (160.46 MHz, C_6D_6): δ = 1.3 (s).

^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6): δ = 133.53, 127.96, 127.06 (C_{ar}H), 124.90 (NCCH$_3$), 34.09 (NCH$_3$), 7.84 (NCCH$_3$).

Elemental analysis: calculated for $C_{13}H_{17}BCl_2N_2$: C 55.17; H 6.06; N 9.90; found: C 55.58; H 6.15; N 9.47.

Preparation of *I*Me·BPh($C_{14}H_{12}$) (3):

A solution of $Na_2[C_{14}H_{12}]$ in THF (20 mL, 2.5 mmol, 0.13 M) was added slowly over a period of ten minutes to a solution of *I*Me·PhBCl$_2$ (**1**) (647 mg, 2.54 mmol) in THF (20 mL) at –78 °C. After the addition the mixture was stirred for 15 minutes at this temperature. The mixture was then allowed to reach ambient temperature and was stirred for one hour. The solvent was removed *in vacuo* and the resulting residue was washed with toluene (2 × 10 mL), diethyl ether (3 × 5 mL) and then extracted with dichloromethane (4 × 10 mL). The solution was stored at –30 °C to afford **3** after three crystallization cycles as a pale yellow solid, which was dried *in vacuo* (495 mg, 1.36 mmol, 54 %).

^{1}H NMR (500.13 MHz, CD_2Cl_2): δ = 7.12-6.92 (m, 12H, *o/m*-$C_{ar}H$), 6.87-6.78 (m, 3H *p*-$C_{ar}H$), 6.66-6.61 (m, 2H, NCH), 4.23, 3.03 (br s, 6H, NCH_3), 2.52, 2.17 (d, $^3J_{HH}$ = 7.50 Hz, 2H, BCH).

^{11}B NMR (160.46 MHz, CD_2Cl_2): δ = –20.0 (s).

^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2): δ = 151.28, 148.80, 134.11, 127.94, 127.62, 127.19, 126.91, 124.55, 124.02, 122.33, 121.38 (C_{ar}H), 121.11 (NCH), 35.56, 33.57 (br, NCH$_3$).

Elemental analysis: calculated for $C_{25}H_{25}BN_2$: C 82.43; H 6.92; N 7.69; found: C 82.49; H 6.86; N 7.87.

Preparation of *I*Me^{Me}·BPh($C_{14}H_{12}$) (4):

A THF solution of $Na_2[C_{14}H_{12}]$ (9.8 mL, 1.11 mmol, 0.11 M) was added dropwise to a solution of *I*Me^{Me}·PhBCl$_2$ (**2**) (311 mg, 1.10 mmol) in THF (20 mL) at –78 °C. After the addition the mixture was stirred for ten minutes at this temperature and then was allowed to reach room temperature and stirred for 1.5 h at ambient temperature. The solvent was removed *in vacuo* and the resulting residue was washed over celite with diethyl ether (2 × 10 mL) and then extracted with dichloromethane (3 × 10 mL). The solvent was removed *in vacuo* and the resulting residue was washed with pentane (3 × 10 mL) and dried *in vacuo* to afford **4** as a colorless solid (170 mg, 0.433 mmol, 39 %).

^{1}H NMR (500.13 MHz, CD_2Cl_2): δ = 7.46-7.43 (m, 2H, $C_{ar}H$), 7.29-7.24 (m, 4H, $C_{ar}H$), 7.16-7.12 (m, 1H, $C_{ar}H$), 7.11-7.07 (m, 2H, $C_{ar}H$), 7.07-7.02 (m, 1H, $C_{ar}H$), 6.94-6.90 (m, 1H, $C_{ar}H$), 6.83-6.79 (m,

2H, $C_{ar}H$), 3.43 (v br, 3H, NCH_3), 2.92 (d, $^3J_{HH}$ = 7.25 Hz, 1H, BCH), 2.57 (v br, 3H, NCH_3), 2.33 (d, $^3J_{HH}$ = 7.25 Hz, 1H, BCH), 1.19, 0.99 (v br, 6H, NCCH_3).

^{11}B NMR (160.46 MHz, C_6D_6): δ = –19.4 (s).

^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6): δ = 152.33, 149.21, 134.56, 127.93, 127.77, 127.72, 127.51, 124.86, 124.56 (C_{ar}H), 123.41 (br) (NCCH_3), 122.80, 121.11 (C_{ar}H), 36.60, 35.52 (br, BCH(Ph)), 32.85, 31.73 (br, NCH_3), 7.72 (br, NCCH_3).

Elemental analysis: calculated for $C_{27}H_{29}BN_2$: C 82.65, H 7.45, N 7.14; found: C 81.90, H 7.48, N 6.90.

Preparation of *trans*-[$(Et_3P)_2$HPt{C=CH$(NMe)_2$C·BPh$(C_{14}H_{12})$}] (5):

In a J. Young NMR tube [$Pt(PEt_3)_4$] (196.6 mg, 294.4 μmol) was heated for 6 h at 60 °C under vacuum ($1\cdot10^{-3}$ mbar) to remove one phosphine and form the reactive tris(phosphine) species [$Pt(PEt_3)_3$] in situ. The remaining oil was dissolved in C_6H_5F (0.7 mL) and *I*Me·BPh($C_{14}H_{12}$) (**3**) (106.0 mg, 291.2 μmol) was added. The suspension was heated for 5 weeks at 60 °C. The volatiles were then removed *in vacuo* and the resulting solid was dissolved in C_6H_6 (0.7 mL) and heated for a further two weeks at 60 °C. The volatiles were removed *in vacuo* and the resulting solid was washed with hexane (2 × 1 mL). The residue was dissolved in toluene (1 mL) and after slow evaporation at room temperature, colorless crystals of **5** were obtained, which were washed with pentane (2 × 1 mL) and dried *in vacuo* (115 mg, 112 μmol, 38 %).

^{1}H NMR (500.13 MHz, C_6D_6): δ = 7.69-6.94 (br m, 30H, $C_{ar}H$, R1, R2), 5.92 (br s, 1H, NCH, R1), 5.69 (br s, 1H, NCH, R2), 4.11 (s, 3H, NCH_3, R2), 3.77 (s, 3H, NCH_3, R1), 3.16 (s, 3H, NCH_3, R1), 3.04 (br m, 2H, BCH, R1, R2), 2.82 (s, 3H, NCH_3, R2), 2.65 (d, $^3J_{HH}$ = 7.40 Hz, 2H, BCH, R1, R2), 1.57-1.12 (br m, 24H, PCH_2CH_3, R1, R2), 0.96-0.60 (br m, 36H, PCH_2CH_3, R1, R2), –6.53 ppm (t, $^2J_{HP}$ = 17.9 Hz, $^1J_{HPt}$ = 699 Hz, 1H, PtH, R2), –6.74 (t, $^2J_{HP}$ = 16.9 Hz, $^1J_{HPt}$ = 698 Hz, 1H, PtH, R1).

^{11}B NMR (160.46 MHz, C_6D_6): δ = –18.7 (s, R1), –19.1 (s, R2).

^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6): δ = 153.61, 153.48, 150.54, 150.18, 149.86, 149.57 (*i*-C_{ar}, R1, R2), 134.27, 134.01, 127.59, 127.17, 127.03, 124.77, 124.29, 124.07, 122.72, 122.48 (C_{ar}H, R1, R2), 122.24 (NCH, R1, R2), 120.73, 120.46 (C_{ar}H, R1, R2), 39.69 (br, NCH_3, R2), 38.00 (br, NCH_3, R1), 37.17 (br, BCH, R1, R2), 36.09, 34.82 (br, BCH(Ph) R1, R2), 35.40 (NCH_3, R1), 34.03 (NCH_3, R2), 19.04 (br, PCH_2CH_3, R1, R2), 8.66 (br, PCH_2CH_3, R1, R2).

^{31}P NMR (202.5 MHz, C_6D_6): δ = 17.2 ppm (m, $^1J_{PPt}$ = 2653 Hz, R1, R2).

Elemental analysis: calculated for $C_{37}H_{56}BN_2P_2Pt$: C 55.85; H 6.97; N 3.52; found: C 55.80; H 6.88; N 3.46.

Crystal structure determination

The crystal data of *I*Me·PhBCl$_2$ (**1**), *I*Me^{Me}·PhBCl$_2$ (**2**), *I*Me·B(Ph)C$_{14}$H$_{12}$ (**3**), *I*Me^{Me}·BPh(C$_{14}$H$_{12}$) (**4**) and *trans*-[(Et$_3$P)$_2$HPt{C=CH(NMe)$_2$C·BPh(C$_{14}$H$_{12}$)}] (**5**) were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo$_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the Shelx software package[6] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations.

Crystal data for **1**: $C_{11}H_{13}BCl_2N_2$, M_r = 254.94, colorless plate, 0.48×0.18×0.05 mm^3, monoclinic space group $P2_1/n$, a = 7.8390(6) Å, b = 16.0342(12) Å, c = 9.5567(7) Å, β = 96.056(3)°, V = 1194.50(15) Å^3, Z = 4, ρ_{calcd} = 1.418 g·cm^{-3}, μ = 0.514 mm^{-1}, F(000) = 528, T = 100(2) K, R_1 = 0.0393, wR^2 = 0.0981, 2521 independent reflections [2θ≤53.5°] and 147 parameters.

Crystal data for **2**: $C_{13}H_{17}BCl_2N_2$, M_r = 283.00, colorless plate, 0.41×0.21×0.035 mm^3, monoclinic space group Cc, a = 15.0371(15) Å, b = 7.5273(8) Å, c = 13.1615(14) Å, β = 108.431(4)°, V = 1413.3(3) Å^3, Z = 4, ρ_{calcd} = 1.330 g·cm^{-3}, μ = 0.442 mm^{-1}, F(000) = 592, T = 103(2) K, R_1 = 0.0312, wR^2 = 0.0729, 2891 independent reflections [2θ≤52.74°] and 167 parameters.

Crystal data for **3**: $C_{25}H_{25}BN_2$, M_r = 364.28, colorless block, 0.23×0.16×0.11 mm^3, monoclinic space group $P2_1/n$, a = 10.6800(12) Å, b = 14.1175(15) Å, c = 13.6179(15) Å, β = 93.975(4)°, V = 2048.3(4) Å^3, Z = 4, ρ_{calcd} = 1.181 g·cm^{-3}, μ = 0.068 mm^{-1}, F(000) = 776, T = 100(2) K, R_1 = 0.0593, wR^2 = 0.1024, 4364 independent reflections [2θ≤53.5°] and 255 parameters.

Crystal data for **4**: $C_{27}H_{29}BN_2$, M_r = 392.33, colorless needle, 0.342×0.085×0.017 mm^3, monoclinic space group $P2_1/n$, a = 11.205(4) Å, b = 13.058(4) Å, c = 16.087(7) Å, β = 106.498(14)°, V = 2257.0(14) Å^3, Z = 4, ρ_{calcd} = 1.155 g·cm^{-3}, μ = 0.066 mm^{-1}, F(000) = 840, T = 100(2) K, R_1 = 0.1249, wR^2 = 0.1267, 4609 independent reflections [2θ≤52.72°] and 283 parameters.

Crystal data for **5**: $C_{37}H_{55}BN_2P_2Pt$, M_r = 795.67, colorless block, 0.34×0.23×0.15 mm^3, triclinic space group P-1, a = 15.9324(7) Å, b = 15.9875(7) Å, c = 16.3672(7) Å, α = 63.872(2)°, β = 87.926(2)°, γ = 79.834(2)°, V = 3680.2(3) Å^3, Z = 4, ρ_{calcd} = 1.436 g·cm^{-3}, μ = 3.927 mm^{-1}, F(000) = 1616, T = 100(2) K, R_1 = 0.0554, wR_2 = 0.1164, 15049 independent reflections [2θ≤52.744°] and 799 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1029521 (**1**), CCDC-1029522 (**2**), CCDC-1029523 (**3**), CCDC-

1029524 (**4**) and CCDC-1029525 (**5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

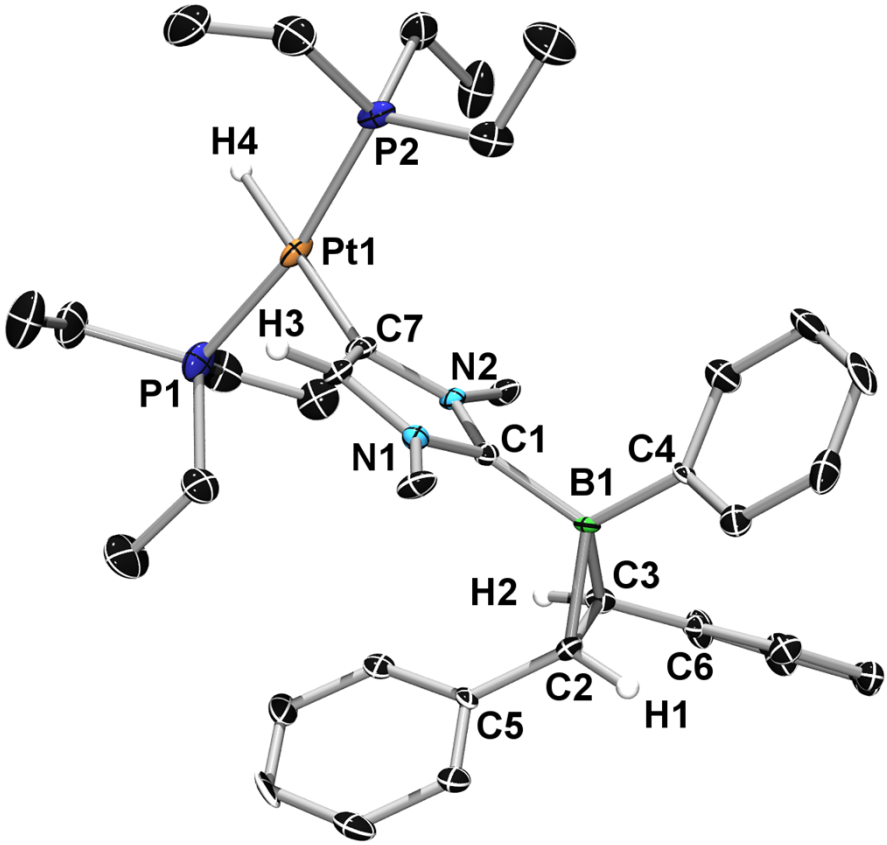

Figure S1: Molecular structure of *trans*-[$(Et_3P)_2PtH\{C{=}CH(NMe)_2C{\cdot}BPh(C_{14}H_{12})\}$] (**5**). For clarity, only the borirene, carbene and hydride hydrogen atoms are shown.

References

1 T. Schaub, M. Backes and U. Radius, *Organometallics*, 2006, **25**, 4196-4206.
2 N. Kuhn and T. Kratz, *Synthesis*, 1993, **1993**, 561-562.
3 D. Kaufmann, *Chem. Ber.*, 1987, **120**, 853-854.
4 U. Azzena, G. Dettori, C. Lubinu, A. Mannu and L. Pisano, *Tetrahedron*, 2005, **61**, 8663-8668.
5 T. Yoshida, T. Matsuda and S. Otsuka, *Inorg. Synth.*, 1990, **28**, 122-123.
6 G. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.