Supplementary Material for Chemical Communications

Heavy metal boryl chemistry: complexes of cadmium, mercury and lead

Andrey V. Protchenko, Deepak Dange, Andrew D. Schwarz, Christina Y. Tang, Nicholas Phillips, Philip Mountford, Cameron Jones and Simon Aldridge

Supporting Information (12 pages)

1. General methods and instrumentation

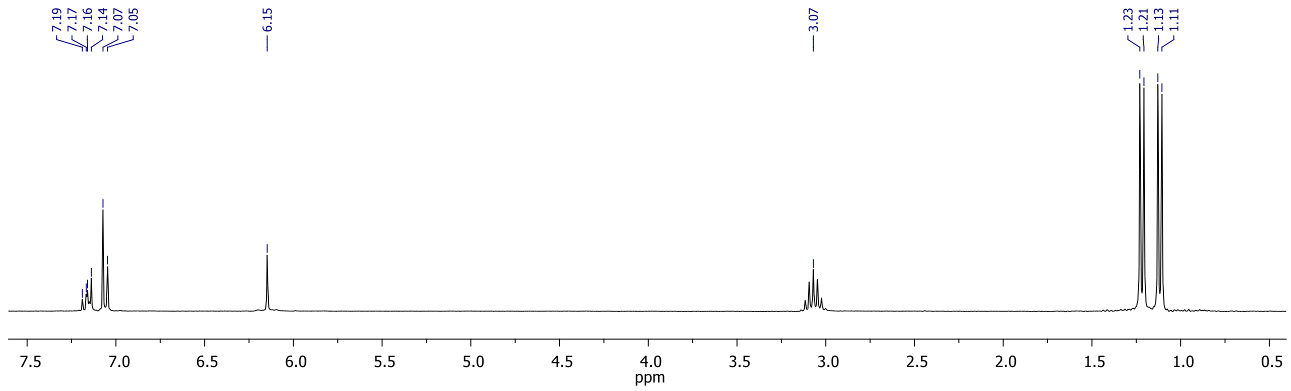
All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. Deuterated solvents were refluxed over the appropriate drying agent, distilled and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, ^{13}C, ^{11}B and ^{199}Hg NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 or Bruker AVIII 500 spectrometers and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). ^{11}B and ^{199}Hg NMR spectra were referenced to external $Et_2O{\cdot}BF_3$ and $HgMe_2$, respectively. Assignments were confirmed as necessary with the use two dimensional ^{1}H–^{1}H and ^{13}C–^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Mass spectra were recorded by the mass spectrometry service of Oxford University's Department of Chemistry. Elemental analyses were carried out by Stephen Boyer at London Metropolitan University.

Starting materials: commercial $HgBr_2$ was used as received, while $CdBr_2{\cdot}4H_2O$ was dehydrated first in air at 150 ºC then dried under vacuum at 200 ºC; CdI_2(tmeda),[s1] $\{(HCNDipp)_2B\}Li(thf)_2$,[s2] $[\{(HCNDipp)_2Ga\}K(tmeda)]_2$,[s3] $[Ga(NDippCH)_2K(OEt_2)]_2(OEt_2)$[s3] and $(HCNDipp)_2GaI_2$[s3] were prepared by literature procedures. $\{(HCNDipp)_2Ga\}_2$[s4] was prepared by reduction of $(HCNDipp)_2GaI_2$ with strictly stoichiometric amount of potassium metal. Thus, a solution of $(HCNDipp)_2GaI_2$ (0.912 g, 1.30 mmol) in thf (20 mL) was added to K metal (0.103 g, 2.63 mmol) and the mixture was sonicated until all potassium was consumed (*ca*. 3 h). The solution was filtered, the residue was washed with thf (2×5 mL) and the combined extract was evaporated *in vacuo* yielding red crystalline material (0.493 g, 0.55 mmol, 85%), which was >95% pure by ^{1}H-NMR[s4] and used without further purification.

2. Syntheses of new compounds

*Hg{B(NDippCH)$_2$}Br (**1**).* A solution of {(HCNDipp)$_2$B}Li(thf)$_2$ (150 mg, 0.28 mmol) in benzene (3 mL) was added to a suspension of HgBr$_2$ (120 mg, 0.33 mmol) in benzene (3 mL) at room temperature and the mixture sonicated until the crystals of HgBr$_2$ disappeared (~5 min). Volatiles were removed *in vacuo* and the gray residue was extracted with hexane (2×10 mL). The filtered extract was concentrated until a microcrystalline solid was formed, warmed up to dissolve the precipitate and left at room temperature overnight yielding colourless block crystals of **1** (67 mg, 0.10 mmol, 36%); further crystallisation from the mother liquor resulted in a mixture of **1** and (HCNDipp)$_2$BBr. Clear crystals of **1** turned white and crumbled upon freezing to 210-220 K, thus the X-ray data were collected at 230 K. Anal. Calc. for $C_{26}H_{36}BBrN_2Hg$: C, 46.76; H, 5.43; N, 4.19. Found: C, 46.70, H, 5.55, N, 4.24%.

^{1}H-NMR (C_6D_6): δ 1.12 (d, ^3J(H,H) = 6.94 Hz, 12H, CH*Me*$_2$), 1.22 (d, ^3J(H,H) = 6.94 Hz, 12H, CH*Me*$_2$), 3.07 (sept, ^3J(H,H) = 6.94 Hz, 4H, C*H*Me$_2$), 6.15 (s, 2H, NCH), 7.06 (d, ^3J(H,H) = 7.7 Hz, 4H, *m*-H of Ar), 7.17 (dd, ^3J(H,H) = 6.4 and 8.6 Hz, 2H, *p*-H of Ar). ^{13}C-NMR (C_6D_6): δ 24.38 and 24.98 (CH*Me*$_2$), 28.56 (*C*HMe$_2$), 121.35 (NCH), 123.95 (*m*-CH of Ar), 128.64 (*p*-CH of Ar), 137.95 (*ipso*-C of Ar), 146.01 (*o*-C of Ar). ^{11}B-NMR (C_6D_6): δ 32.3 (br, $\Delta w_{1/2}$ = 187 Hz, with satellites $^1J(^{11}B, ^{199}Hg)$ = 2750 Hz). ^{199}Hg-NMR (C_6D_6): δ −692 (quartet, $^1J(^{199}Hg, ^{11}B)$ = 2778 Hz).



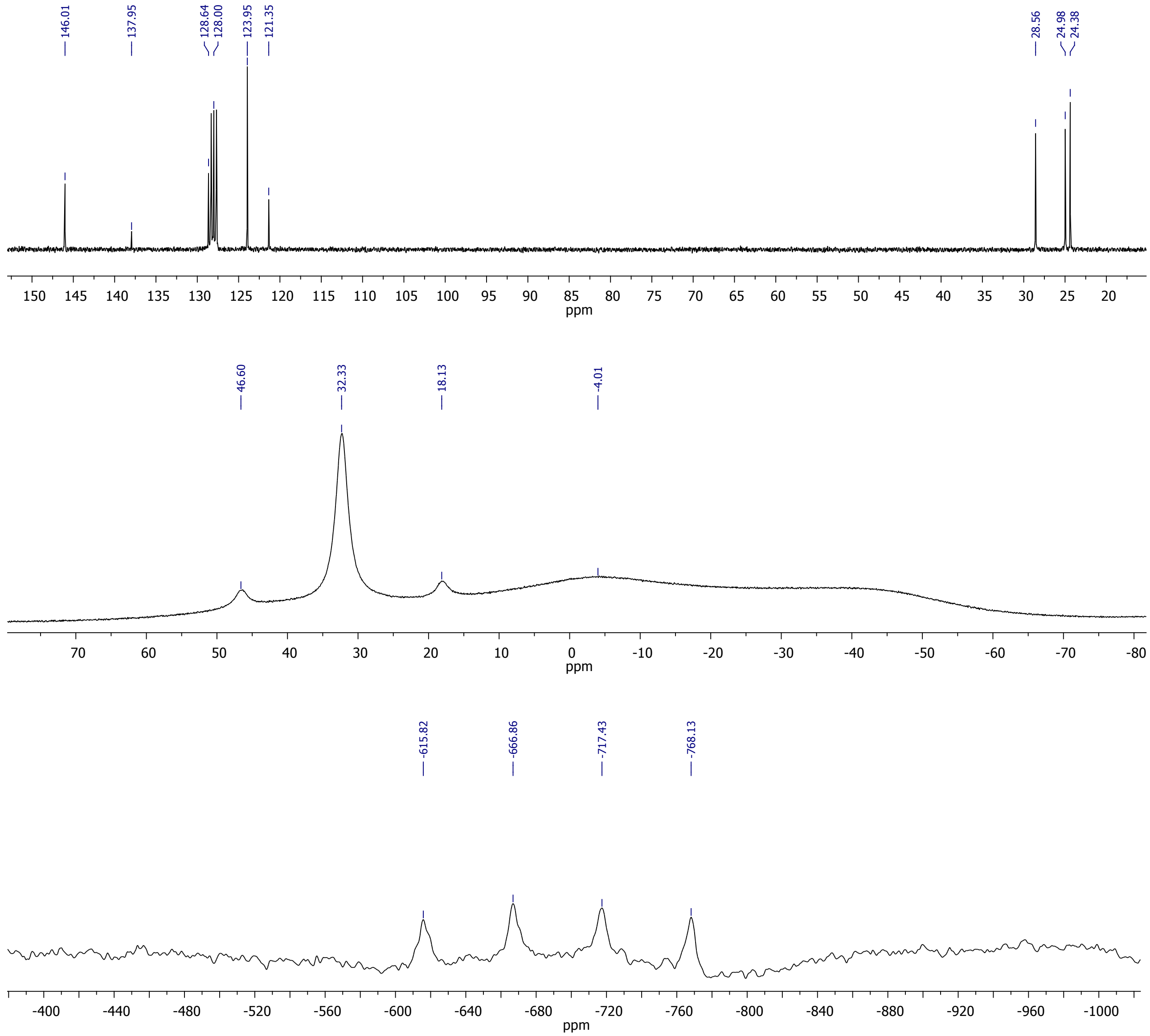


Fig. s1 ^{1}H-, ^{13}C-, ^{11}B- and ^{199}Hg-NMR spectra of crystalline **1** in C_6D_6

*Hg{B(NDippCH)$_2$}$_2$ (**2**)*. Solid $HgBr_2$ (11.2 mg, 0.031 mmol) was added to a solution of {(HCNDipp)$_2$B}Li(thf)$_2$ (33.6 mg, 0.062 mmol) in C_6D_6 (0.5 mL) at room temperature forming a light yellow solution with a grey precipitate; the ^{1}H-NMR spectrum showed the presence of both the starting boryllithoum reagent (6.71 ppm) and the product **2** (6.16 ppm). The ^{11}B-NMR spectrum showed a new signal at 68 ppm, as well as signals of the starting boryllithium at 44 ppm and the side products: (HCNDipp)$_2$BH (23 ppm) and (HCNDipp)$_2$BBr (20 ppm). The mixture was sonicated until the crystals of $HgBr_2$ disappeared (~5 min), while ^{1}H- and ^{11}B-NMR spectra showed that the starting boryllithium disappeared and the signals of **2** increased. The solution was decanted into a λ-tube;

evaporation of the solvent gave a tacky colourless crystalline residue which was extracted with warm hexane (insoluble white powder was also formed) into the second leg of the tube; crystallisation at −30 °C yielded colourless crystals of **2** (13.0 mg, 0.013 mmol, 43%). Anal. Calc. for $C_{52}H_{72}B_2N_4Hg$: C, 64.03; H, 7.44; N, 5.74. Found: C, 64.23, H, 7.56, N, 5.83%.

^{1}H-NMR (C_6D_6): δ 0.96 (d, ^3J(H,H) = 6.95 Hz, 24H, CH*Me*$_2$), 1.15 (d, ^3J(H,H) = 6.95 Hz, 24H, CH*Me*$_2$), 3.05 (sept, ^3J(H,H) = 6.95 Hz, 8H, C*H*Me$_2$), 6.16 (s, 4H, NCH), 7.07 (d, ^3J(H,H) = 7.6 Hz, 8H, *m*-H of Ar), 7.22 (dd, ^3J(H,H) = 7.0 and 8.2 Hz, 4H, *p*-H of Ar). ^{13}C-NMR (C_6D_6): δ 24.25 and 25.01 (CH*Me*$_2$), 28.39 (*C*HMe$_2$), 120.79 (NCH), 123.26 (*m*-CH of Ar), 127.42 (*p*-CH of Ar), 140.43 (*ipso*-C of Ar), 146.30 (*o*-C of Ar). ^{11}B-NMR (C_6D_6): δ 68.6 (v br, $\Delta w_{1/2}$ = 675 Hz, satellites not clearly separated from the main peak).

*Alternative synthesis of **1**.* The direct reaction between $HgBr_2$ and {(HCNDipp)$_2$B}Li(thf)$_2$ yields a substantial amount of (HCNDipp)$_2$BBr side-product (along with metallic Hg), thereby lowering the yield of **1**. An alternative synthetic procedure was therefore developed. Thus, to a solution of **2** (34.0 mg, 0.035 mmol) in C_6D_6 (0.5 mL) was added $HgBr_2$ (12.6 mg, 0.035 mmol) and the mixture sonicated for 5 min showing clean formation of **1**. To this solution {(HCNDipp)$_2$B}Li(thf)$_2$ (38.2 mg, 0.071 mmol) was added; the ^{1}H-NMR spectrum showed that compound **2** was present in solution. Then $HgBr_2$ (25.6 mg, 0.071 mmol) was added and the mixture was sonicated for 10 min. All volatiles were removed *in vacuo*, the residue was extracted with benzene into the crystallisation tube, evaporated to dryness and recrystallised from hexane yielding colourless crystals of **1** (91.0 mg, 0.136 mmol, 96%).

Hg{B(NDippCH)$_2$}{Ga(NDippCH)$_2$} (3). Method A: NMR scale reaction. Solid [{(CHNDipp)$_2$Ga}K(tmeda)]$_2$ (19.6 mg, 0.033 mmol of the monomer) was added to a solution of **1** (21.8 mg, 0.033 mmol of the monomer) in C_6D_6 (0.5 mL) at room temperature producing a red solution with a gel-like precipitate. ^{1}H NMR showed two new sets of signals of (CHNDipp)$_2$E ligands and free tmeda. The volatiles were removed *in vacuo* and the residue was extracted with hexane (0.5 mL); slow evaporation of the solvent at room temperature gave a sticky crystalline material from which an X-ray quality crystal was separated manually.

Method B: Solution of **1** (94.1 mg, 0.14 mmol of the monomer) in C_6H_6 (1 mL) was added to a solution/suspension of [Ga(NDippCH)$_2$K(OEt$_2$)]$_2$(OEt$_2$) (83.5 mg, 0.14 mmol of the monomer) in

C_6H_6 (1 mL) at room temperature producing a bright red solution with a gel-like precipitate. The volatiles were removed *in vacuo* and the residue was extracted with pentane (1 mL) into a crystallisation tube. Storing the concentrated solution at −30 °C did not produce any crystals, but slow evaporation of the solvent at room temperature gave a sticky crystalline material, from which clean red blocks (bright crimson when powdered) were separated manually, as attempted washing with cold pentane led to very rapid dissolution (51 mg, 0.049 mmol, 35%). Anal. Calc. for $C_{52}H_{72}BGaN_4Hg$: C, 60.39; H, 7.02; N, 5.42. Found: C, 60.53, H, 7.18, N, 5.48%.

^{1}H-NMR (C_6D_6): δ 1.04 (two overlapping d, ^3J(H,H) = 6.9 Hz, 24 H, CH*Me*$_2$), 1.11 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH*Me*$_2$), 1.24 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH*Me*$_2$), 3.03 (sept, ^3J(H,H) = 6.9 Hz, 4 H, C*H*Me$_2$), 3.47 (sept, ^3J(H,H) = 6.9 Hz, 4 H, C*H*Me$_2$), 6.13 (s, 2 H, NCH), 6.40 (s, 2 H, NCH), 7.03 (d, ^3J(H,H) = 7.7 Hz, 4 H, *m*-H of Ar), 7.14-7.18 (m, 8 H, H of Ar + C_6D_5H). ^{13}C-NMR (C_6D_6): δ 24.12, 24.24, 25.00 and 26.04 (CH*Me*$_2$), 28.05 and 28.46 (*C*HMe$_2$), 120.82 and 122.00 (NCH), 123.01 and 123.55 (*m*-CH of Ar), 125.46 and 128.00 (*p*-CH of Ar), 138.78 and 144.67 (*ipso*-C of Ar), 145.42 and 146.05 (*o*-C of Ar). ^{11}B-NMR (C_6D_6): δ 56.4 (br, $\Delta w_{1/2}$ ~ 430 Hz, with satellites $^1J(^{11}B, ^{199}Hg)$ = 1900 Hz). EI MS *m/z* (%, assignment): 1034.3 (70, $[M]^+$), 445.2 (20, $[(CHNDipp)_2Ga]^+$), 387.3 (100, $[(CHNDipp)_2B]^+$).

Attempted preparation of Hg{Ga(NDippCH)$_2$}$_2$. A solution of lithium gallyl was prepared *in situ* by reacting the digallane(4) $\{(HCNDipp)_2Ga\}_2$ (525 mg, 0.59 mmol) with a rolled piece of Li metal (12 mg, 1.73 mmol) in thf (20 mL) overnight with stirring (^{1}H NMR of an aliquot showed complete disappearance of the starting material and formation of a single new product); the solution was decanted from the remaining lithium and dried under vacuum yielding a yellow-brown oil (slowly crystallising at room temperature), which corresponded to $Li(thf)_4[Ga(NDippCH)_2]$ by ^{1}H NMR (C_6D_6): δ 1.30 (m, 16 H, thf), 1.36 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH*Me*$_2$), 1.43 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH*Me*$_2$), 3.35 (m, 16 H, thf), 4.08 (sept, ^3J(H,H) = 6.9 Hz, 4 H, C*H*Me$_2$), 6.62 (s, 2 H, NCH), 7.14-7.19 (m, *p*-H of Ar + C_6D_5H), 7.27 (d, ^3J(H,H) = 7.8 Hz, 4 H, *m*-H of Ar).

Addition of toluene gave a cloudy solution, which was diluted to 20 mL in a measuring ampoule. A part of this solution (15.9 mL, 0.94 mmol) was added to a suspension of $HgBr_2$ (170 mg, 0.47 mmol) in toluene (5 mL) at −30 °C with vigorous stirring. The mixture was allowed to warm to room temperature (1 h) and evaporated to dryness. The residue was extracted with hexane (2×20 mL); the solvent from the filtered extract was removed *in vacuo* and red crystalline material identified as $\{(HCNDipp)_2Ga\}_2$ by ^{1}H-NMR (350 mg, 0.39 mmol of the monomer, 83%).

Synthesis of Cd{B(NDippCH)₂}₂ (**5**). Solid $CdBr_2$ (0.0136 g, 0.050 mmol) was added to a solution of $\{(HCNDipp)_2B\}Li(thf)_2$ (0.0540 g, 0.100 mmol) in C_6D_6 (0.6 mL) at R.T. The tube was placed into an ultrasonic bath and treated for 30 min until $CdBr_2$ had disappeared forming a light-grey suspension. Next day the solution was decanted into a λ-tube; evaporation of the solvent gave tacky off-white crystalline residue which was extracted with warm hexane (insoluble white powder was also formed) into the second leg of the tube; crystallisation at −30 °C yielded colourless crystals (0.040 g, 0.045 mmol, 90%). X-ray-quality crystals were obtained by slow evaporation of hexane solution at room temperature. Anal. Calc. for $C_{52}H_{72}B_2N_4Cd$: C, 70.40; H, 8.18; N, 6.32. Found: C, 70.22, H, 8.26, N, 6.45%.

^{1}H-NMR (C_6D_6): δ 0.94 (d, ^3J(H,H) = 6.9 Hz, 24 H, CH*Me*₂), 1.16 (d, ^3J(H,H) = 6.9 Hz, 24 H, CH*Me*₂), 3.06 (sept, ^3J(H,H) = 6.9 Hz, 8 H, C*H*Me₂), 6.17 (s, 4 H, NCH), 7.07 (d, ^3J(H,H) = 7.6 Hz, 8 H, *m*-H of Ar), 7.22 (t, ^3J(H,H) = 7.7 Hz, 4 H, *p*-H of Ar). ^{13}C-NMR (C_6D_6): δ 24.27 and 25.15 (CH*Me*₂), 28.34 (*C*HMe₂), 120.33 (NCH), 123.25 (*m*-CH of Ar), 127.35 (*p*-CH of Ar), 141.07 (*ipso*-C of Ar), 146.29 (*o*-C of Ar). ^{11}B-NMR (C_6D_6): δ 41.3 (v br, $\Delta w_{1/2} \sim 900$ Hz).

Cd{B(NDippCH)₂}I(tmeda) (**5**): To a stirred solution of CdI_2(tmeda) (0.18 g, 0.37 mmol) in thf (10 mL) at −78 °C was added a solution of $\{(HCNDipp)_2B\}Li(thf)_2$ (0.20 g, 0.37 mmol) also in thf (10 mL). The resultant solution was slowly warmed to 0 °C over a period of 5 h, whereupon volatiles were removed *in vacuo*. The resulting solid was extracted into pentane (2 x 8 mL) and filtered. The extracts were concentrated to *ca.* 10 mL and stored at −30 °C overnight to give colorless crystals of **5** (yield: 0.126 g, 46%). M.p. = 124-126 ˚C (dec.). ^{1}H NMR (C_6D_6, 400 MHz, 296 K): δ_H 1.22 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*), 1.41 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*), 1.60 (br s, 4H, NC*H₂*), 1.72 (br s, 12H, N*CH₃*), 3.53 (sept, 4H, $^3J_{HH}$ = 7.2 Hz, C*H*Me₂), 6.48 (s, 2H, NC*H*), 7.15-7.20 (m, 6H, *m*- and *p*-H of Ar). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 296 K): δ_C 24.2 (CH*Me₂*), 25.9 (CH*Me₂*), 28.4 (*C*HMe₂), 47.8 (br, N*C*H₃), 56.7 (N*C*H₂), 121.7 (N*C*H), 123.3 (*m*-CH of Ar), 127.1 (*p*-CH of Ar), 146.6 (*o*-C of Ar); ^{11}B{^{1}H} NMR (C_6D_6, 128 MHz, 296 K): δ_B 38.3 (br s). IR (Nujol) *v*/cm^{-1}: 1585(w), 1326(w), 1260(m), 1163(w), 1059(m), 933(m), 805(s), 790(s). EI MS *m/z* (%, assignment): 627.1 (68,

[{$(HCNDipp)_2B$}CdI]$^+$), 387.2 (100, [$(HCNDipp)_2B$]$^+$). Reproducible microanalyses were not obtained as a small amount of $(HCNDipp)_2BI$ consistently co-crystallized with the product.

*Cd{B(NDippCH)$_2$}{Ga(NDippCH)$_2$}(tmeda) (**6**)*: To a stirred solution of **5** (0.15 g, 0.20 mmol) in thf (10 mL) at −78 °C was added a solution of {$(HCNDipp)_2Ga$}K(tmeda) (0.12 g, 0.20 mmol) also in thf (10 mL). The resulting solution was slowly warmed to room temperature over a period of 12 h, whereupon volatiles were removed *in vacuo.* The solid was extracted into pentane (2 x 8 mL) and filtered. The extracts were concentrated to *ca.* 10 mL and stored at −30 °C overnight to give colorless crystals of **6**. (yield: 0.16 g, 76%). M.p. = 148-152 °C (dec.). ^{1}H NMR (C_6D_6, 400 MHz, 296 K): δ_H 1.07 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me$_2$*), 1.19 (d, 12H, $^3J_{HH}$ = 5.7 Hz, CH*Me$_2$*), 1.25 (d, 12H, $^3J_{HH}$ = 7.2 Hz, CH*Me$_2$*), 1.36 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me$_2$*), 1.55 (s, 12H, NCH_3), 1.73 (s, 4H, NCH_2), 3.25 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$), 3.72 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$), 6.32 (s, 2H, NC*H*), 6.33 (s, 2H, NC*H*), 7.07-7.20 (m, 12H, *m*- and *p*-H of Ar). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 296 K): δ_C 23.7 (CH*Me$_2$*), 24.6 (CH*Me$_2$*), 25.9 (CH*Me$_2$*), 26.2 (CH*Me$_2$*), 28.2 (*C*HMe$_2$), 28.3 (*C*HMe$_2$), 47.6 (br, NCH_3), 57.6 (NCH_2), 121.6 (NCH), 121.7 (NCH), 123.0 (*m*-CH of Ar), 123.4 (*m*-CH of Ar), 124.7 (*p*-CH of Ar), 127.1 (*p*-CH of Ar), 145.8 (*o*-C of Ar), 146.5 (*o*-C of Ar). ^{11}B{^{1}H} NMR (C_6D_6, 128 MHz, 296 K): δ_B 39.6 (br s). IR (Nujol) *ν*/cm^{-1}: 1587(m), 1323(m), 1258(s), 1115(m), 1058(m), 933(m), 802(s), 760(s), 697(m); EI MS *m/z* (%, assignment): 946.4 (100, [M - tmeda]$^+$), 445.2 (65, [$(HCNDipp)_2Ga$]$^+$). Anal. Calc. for $C_{58}H_{88}BCdGaN_6$: C, 65.58; H, 8.35; N, 7.91. Found: C, 65.49; H, 8.46; N, 7.82%.

Isolation of Sn$_5${B(NDippCH)$_2$}$_4$ (7). In a typical synthesis of Sn{B(NDippCH)$_2$}$_2$ (from 0.27 mmol of $SnCl_2$, as described earlier[s5]), brown hexane washings were concentrated to ~ 1 mL and stored overnight at 0 °C yielding green crystals of Sn{B(NDippCH)$_2$}$_2$ (25 mg, 0.028 mmol, 10%); the remaining solution was stored at −30 °C for two weeks (in another preparation crystallization occurred at room temperature over a period of three months) yielding dark brown square blocks of **7** (~5 mg, ~0.002 mmol, 4%) suitable for X-ray diffraction. NMR was measured on a 2.6 mg sample showing signals for the highly asymmetric boryl moiety; the sample was too dilute for ^{119}Sn NMR.

^{1}H-NMR (C_6D_6): δ 0.76 (d, ^3J(H,H) = 6.6 Hz, 12H, CH*Me*$_2$), 0.88 (t, 6H, Me of hexane), 0.97 (d, ^3J(H,H) = 6.6 Hz, 12H, CH*Me*$_2$), 1.15 (two d, ^3J(H,H) = 6.6 Hz, 24H, CH*Me*$_2$), 1.22 and 1.26 (two d, ^3J(H,H) = 6.6 Hz, 24H, CH*Me*$_2$: + 8H, CH_2 of hexane), 1.49 (d, ^3J(H,H) = 6.6 Hz, 12H, CH*Me*$_2$), 1.61 (d, ^3J(H,H) = 6.6 Hz, 12H, CH*Me*$_2$), 2.47 (sept, ^3J(H,H) = 6.6 Hz, 4H, C*H*Me$_2$), 2.57 (sept, ^3J(H,H) = 6.6 Hz, 4H, C*H*Me$_2$), 2.62 (sept, ^3J(H,H) = 6.6 Hz, 4H, C*H*Me$_2$), 3.58 (sept, ^3J(H,H) = 6.6 Hz, 4H, C*H*Me$_2$), 6.04 (d, ^3J(H,H) = 1.8 Hz, 4H, NCH), 6.20 (d, ^3J(H,H) = 1.8 Hz, 4H, NCH), 7.15-7.19 (m, overlapping with C_6D_5H, CH of Ar), 7.27-7.33 (m, 16H, CH of Ar). ^{13}C-NMR (C_6D_6): δ 21.45, 23.77, 26.92, 26.98, 27.16, 27.50, 27.88, 28.14 (CH*Me*$_2$); 27.67, 27.92, 28.55, 28.93 (*C*HMe$_2$), 123.76 (NCH + CH of Ar), 124.16 (NCH), 124.57 (CH of Ar), 124.84 (CH of Ar), 128.29 (two CH of Ar), 139.79, 141.25 (*ipso*-C of Ar), 144.84, 145.72, 147.07, 148.46 (*o*-C of Ar).

^{11}B-NMR (C_6D_6): δ 46.8 (v br, $\Delta w_{1/2}$ = 950 Hz).

*Pb{B(NDippCH)$_2$}$_2$ (**8**). Method A.* A solution of {(HCNDipp)$_2$B}Li(thf)$_2$ (121 mg, 0.22 mmol) in Et_2O (5 mL) was added to a suspension of $PbBr_2$ (41 mg, 0.11 mmol) in Et_2O (10 mL) at −45 °C with stirring (when $PbCl_2$ was used, the reaction gave a yellow solution from which no crystalline product could be isolated). The colour immediately changed to dark red-brown and black precipitate appeared. The mixture was stirred at −45 to −30 °C for 1 h, while the colour turned to green-brown. The solvent was removed *in vacuo* and hexane (10 mL) was added producing brown solution with dark grey heavy precipitate. The solution was decanted via cannula and concentrated to ~1 mL when green microcrystalline solid was formed, together with brown tar and colourless crystals. The mixture was warmed up to dissolve the precipitate (*ca.* 40 °C) and left at RT for 1 h yielding bright green crystals of **8** suitable for X-ray diffraction.

Method B. Because extensive decomposition led to low yields of **8** in Et_2O solvent (which was successful in case of Sn boryl), the reaction was carried out in a less polar solvent. Solid {(HCNDipp)$_2$B}Li(thf)$_2$ (29.5 mg, 0.055 mmol) was added to a suspension of $PbBr_2$ (10.0 mg, 0.027 mmol) in C_6D_6 (0.5 mL) at room temperature. The mixture was sonicated for 5 min producing a dirty green suspension. The ^{1}H-NMR spectrum showed the formation of a new product together with some (HCNDipp)$_2$BH and (HCNDipp)$_2$BBr. The mixture was transferred into a λ-shaped crystallisation tube, the volatiles removed *in vacuo* and hexane (0.5 mL) was added. The product was extracted into the second leg of the tube, crystallised by slow evaporation at room temperature and washed with a small amount of cold hexane, yielding green crystals of **8** (11.2 mg, 0.011 mmol, 42%).

<u>Scale up procedure</u> from {(HCNDipp)$_2$B}Li(thf)$_2$ (269.7 mg, 0.50 mmol) and $PbBr_2$ (91.0 mg, 0.247 mmol) in C_6H_6 (3 mL) after similar work-up yielded Pb{B(NDippCH)$_2$}$_2$ (112 mg, 0.114 mmol, 46%). Anal. Calc. for $C_{52}H_{72}B_2N_4Pb$: C, 63.60; H, 7.39; N, 5.71. Found: C, 63.41, H, 7.41, N, 5.58%.

^{1}H-NMR (C_6D_6): δ 0.98 (d, ^{3}*J*(H,H) = 6.92 Hz, 24H, CH*Me*$_2$), 1.15 (d, ^{3}*J*(H,H) = 6.92 Hz, 24H, CH*Me*$_2$), 3.21 (sept, ^{3}*J*(H,H) = 6.92 Hz, 8H, C*H*Me$_2$), 6.80 (s, 4H, NCH), 6.98 (d, ^{3}*J*(H,H) = 7.8 Hz, 8H, *m*-H of Ar), 7.13 (t, ^{3}*J*(H,H) = 7.8 Hz, 4H, *p*-H of Ar). ^{13}C-NMR (C_6D_6): δ 25.23 and 27.00 (CH*Me*$_2$), 29.23 (*C*HMe$_2$), 123.83 (*m*-CH of Ar), 127.42 (*p*-CH of Ar), 132.00 (NCH), 140.03 (*ipso*-C of Ar), 146.00 (*o*-C of Ar). ^{11}B-NMR (C_6D_6): δ 261.4 (v br, $\Delta w_{1/2}$ = 520 Hz).

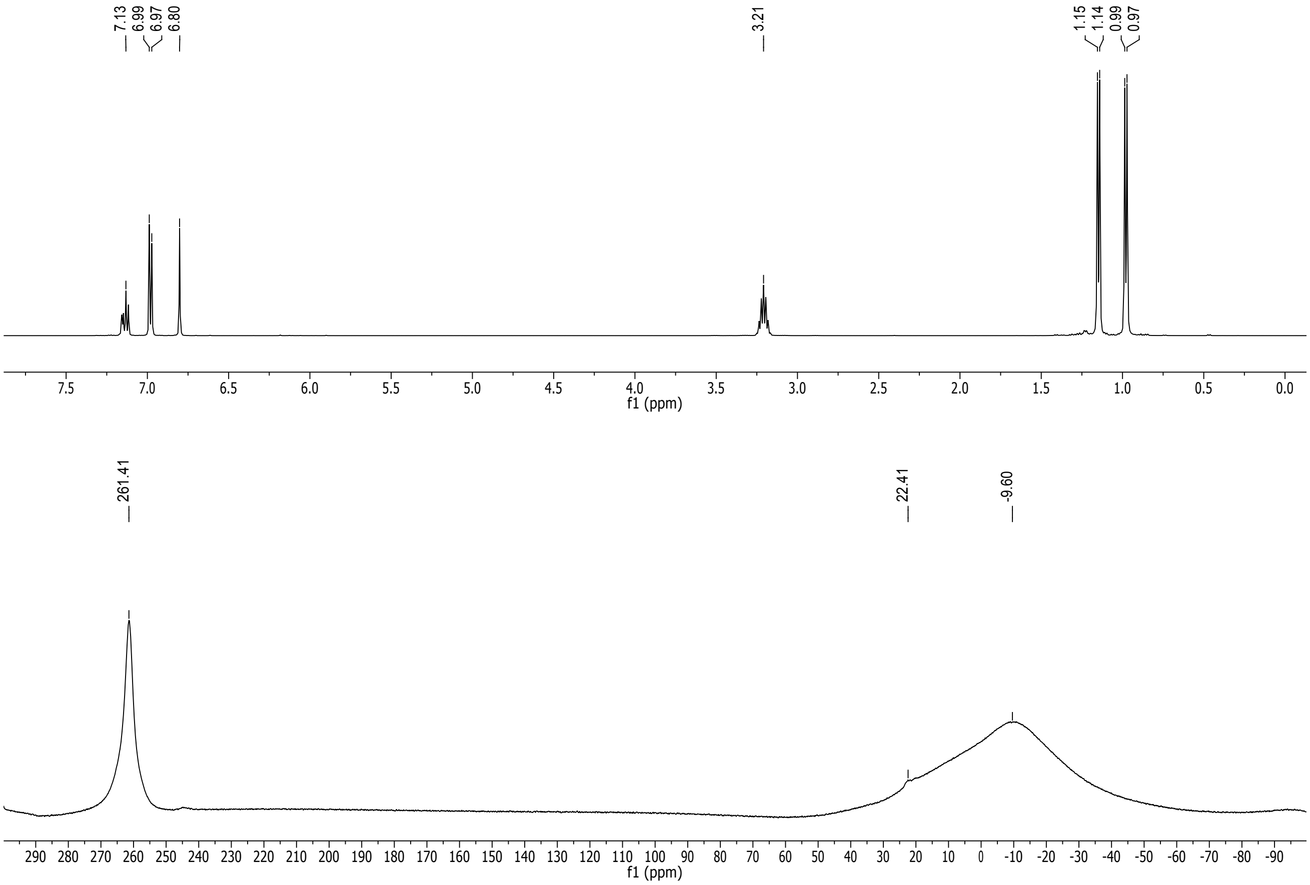


Fig. s2 ^{1}H- and ^{11}B-NMR spectra of the crystalline Pb{B(NDippCH)$_2$}$_2$ in C_6D_6 (group of small peaks in ^{11}B spectrum near 22 ppm correspond to minute impurities XB(NDippCH)$_2$, X = H, Br, OH)

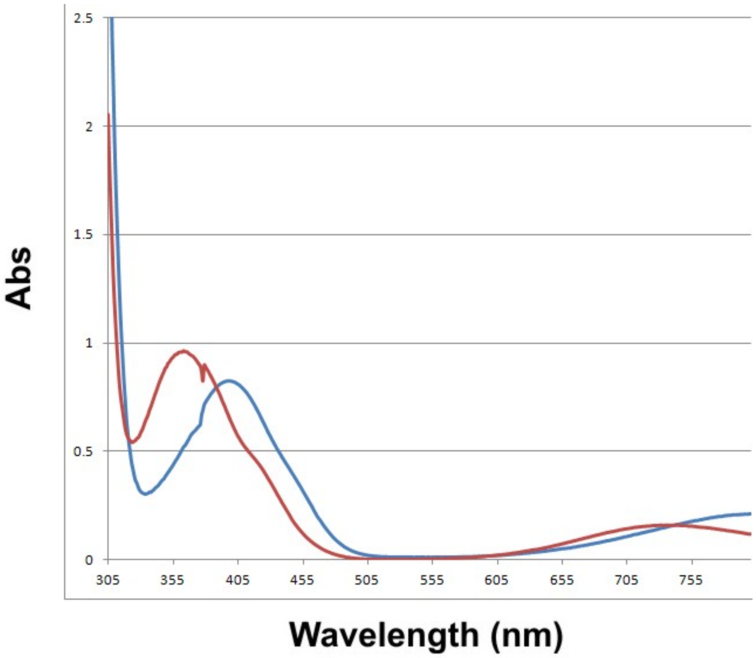


Fig. s3 UV-vis spectrum of a hexane solution (*ca*. 0.6 mM) of Pb$\{B(NDippCH)_2\}_2$ (**8**; red trace); the spectrum of Sn$\{B(NDippCH)_2\}_2$ (blue) is included for comparison at similar concentration, and the spike at 375 nm is an instrument artefact. The extinction coefficients associated with the principal features in these spectra are as follows: **8**: λ = 361 nm, ε = 1600 mol^{-1} dm^3 cm^{-1}, λ = 725 nm, ε = 300 mol^{-1} dm^3 cm^{-1}; Sn$\{B(NDippCH)_2\}_2$: λ = 404 nm, ε = 1300 mol^{-1} dm^3 cm^{-1}.

3. References for supporting information

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