Anionic *N*-Heterocyclic Carbenes (NHCs): A Versatile Route to Saturated NHCs Bearing Pendant Weakly Coordinating Anions

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Supplementary Information (7 pages total)

1. General details of synthetic procedures and instrumentation

All reactions involving air- or moisture-sensitive compounds were carried out under an inert atmosphere by using Schlenk-type glassware or in a glovebox. Solvents were dried using an MBraun SPS800 prior to use. NMR-solvents were dried over potassium or molecular sieves and degassed before use. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves when necessary. ^{1}H and ^{13}C NMR spectra were measured on Bruker Ascend-400 or AVII-500 spectrometer 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 ^{19}F spectra are referenced with respect to $BF_3{\cdot}OEt_2$ and $CFCl_3$, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out by London Metropolitan University. Unless otherwise noted, all starting materials were commercially available and used without further purification. The following compounds were prepared via literature methods: *N*,*N′*-di*iso*propylphenyl-*N*-allylformamidine (**1a**),[s1] $B(C_6F_5)_3$,[s2] $[Rh(COD)Cl]_2$,[s3] and (THT)AuCl.[s4]

2. Syntheses and characterizing data for new compounds

***N,N'-bis*(di*iso*propylphenyl)-*N*-(1-butenyl)formamidine, 1b and *N,N'-bis*(di*iso*propylphenyl)-*N*-(1-pentenyl) formamidine, 1c**: A common method was used for the synthesis of these two precursors, exemplified here for **1b**. A mixture of *N,N'-bis*(2,6-diisopropylphenyl)formamidine (2.7 g, 7.4 mmol), 4-bromo-1-butene (1.0 g, 7.4 mmol) and K_2CO_3 (0.5 g, 3.7 mmol) were suspended in acetonitrile (150 cm^3). The reaction mixture was then refluxed in the dark for 4 d. After cooling, volatiles were removed under vacuum and the residue was dissolved in CH_2Cl_2 (80 cm^3). This solution was filtered through a pad of silica gel after which the solvent was removed. Recrystallisation of the crude product from hexane at -30 °C gave colourless crystals in 26% yield (0.80 g). The corresponding synthesis of **1c** from 5-bromo-1-pentene gave the product as colourless crystals in 68% yield (2.50 g).

Spectroscopic data: (for **1b**) ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ_H 7.39 – 7.02 (7H, m, CH Dipp and NCHN), 5.91 (1H, m, CH alkene), 5.12 (2H, m, CH_2 alkene), 3.86 (2H, m, NCH_2), 3.29 (2H, overlapping m, CH ^{i}Pr), 3.28 (2H, overlapping m, CH ^{i}Pr), 2.58 (2H, m, NCH_2CH_2), 1.36 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.25 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.18 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ_C 151.0 (NCHN), 148.0, 147.4 (NC Dipp), 139.8, 138.7 (*ortho*-C Dipp), 135.6 (CH alkene), 128.6 (*para*-CH Dipp), 124.3, 122.6 (*meta*-CH Dipp), 116.4 (CH_2 alkene), 49.5 (NCH_2), 31.7 (NCH_2CH_2), 28.2, 27.8 (CH ^{i}Pr), 25.3, 24.1, 23.5 (CH_3 ^{i}Pr). MS (EI +ve): *m/z* 418.3 (M^+). Accurate mass ($[C_{29}H_{42}N_2]^+$): 418.3341(meas.), 418.3348(calc.). (For **1c**) ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ_H 7.36 – 7.01 (7H, m, CH Dipp and NCHN), 5.84 (1H, m, CH alkene), 5.02 (2H, m, CH_2 alkene), 3.79 (2H, m, NCH_2), 3.27 (4H, app sept, $^3J_{HH}$ = 6.7 Hz, CH ^{i}Pr), 2.16 (2H, app qt, $CH_2CH{=}CH_2$), 1.87 (2H, m, NCH_2CH_2), 1.34 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.23 (12H, d, $^3J_{HH}$ = 7.2 Hz, CH_3 ^{i}Pr), 1.16 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ_C 151.1 (NCHN), 148.0, 147.4 (NC Dipp), 139.9, 138.7 (*ortho*-C Dipp), 137.9 (CH alkene, 128.5 (*para*-CH Dipp), 124.3, 122.6 (*meta*-CH Dipp), 114.8 (CH_2 alkene), 49.6 (NCH_2), 31.5 ($CH_2CH{=}CH_2$), 28.2, 27.8 (CH ^{i}Pr), 26.3 (NCH_2CH_2), 25.3, 24.1, 23.5 (CH_3 ^{i}Pr). MS (EI +ve): *m/z* 432.4 (M^+). Accurate mass ($[C_{30}H_{44}N_2]^+$): 432.3515(meas.), 432.3505(calc.). Elemental analysis: calc. for $C_{30}H_{44}N_2$: C 83.28, H 10.25, N 6.47, meas. C 82.76, H 10.54, N 6.68.

H(5-Dipp^{BArF}), 2a: *Tris*(pentafluorophenyl)borane (154 mg, 0.3 mmol) was added to a stirred solution of **1a** (121 mg, 0.3 mmol) in toluene (15 cm^3). The reaction mixture was then allowed to stir for 1 h, after which volatiles were removed *in vacuo*. Washing with hexanes and drying *in vacuo* yielded the crude product as a white powder. X-ray quality crystals were obtained in 62% yield (0.17 g) from a concentrated solution of toluene stored at -30 °C.

Spectroscopic data: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.32-7.04 (7H, m, CH Dipp and NCHN), 4.34 (1H, m, NCH), 3.80 (1H, apparent tr, $^2J_{HH}$ = 10.8 Hz, NCH_2), 3.61 (1H, apparent tr, $^2J_{HH}$ = 10.8 Hz, NCH_2), 3.15 (1H, sept, $^3J_{HH}$ = 5.9 Hz, CH-^{i}Pr), 2.80 (1H, sept, $^3J_{HH}$ = 5.9 Hz, CH ^{i}Pr), 2.62 (1H, sept, $^3J_{HH}$ = 6.7 Hz, CH ^{i}Pr), 2.48 (1H, sept, $^3J_{HH}$ = 5.3 Hz, CH ^{i}Pr), 2.16 (1H, apparent tr, $^2J_{HH}$ = 14.7 Hz, CH_2-B), 1.51 (1H, apparent d, $^2J_{HH}$ = 12.3 Hz, CH_2-B), 1.33 (3H, d, $^3J_{HH}$ = 6.9 Hz, CH_3 ^{i}Pr), 1.20 (3H, d, $^3J_{HH}$ = 6.9 Hz, CH_3 ^{i}Pr), 1.13 (3H, overlapping d, CH_3 ^{i}Pr), 1.11 (3H, overlapping d, CH_3 ^{i}Pr), 1.00 (12H, overlapping d, CH_3 ^{i}Pr). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 155.6 (NCHN), 148.0 (dm, $^1J_{CF}$ = 240.1 Hz, *ortho*-CF), 147.6, 146.4 (NC Dipp), 146.0, 146.0 (*ortho*-C Dipp), 138.2 (dm, $^1J_{CF}$ = 243.0 Hz, *para*-CF), 136.6 (dm, $^1J_{CF}$ = 245.0 Hz, *meta*-CF), 131.7, 131.6 (*para*-CH Dipp), 127.4, 125.1, 125.0, 124.8 (*meta*-CH Dipp), 71.0 (NCH), 58.8 (NCH_2), 29.5, 29.4, 29.3, 29.0 (CH ^{i}Pr), 26.4, 25.2, 24.9, 24.8, 24.0, 23.6, 22.6 (CH_3 ^{i}Pr), (CH_2B not observed). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ -14.65 (s). ^{19}F NMR ($CDCl_3$, 282 MHz, 298 K): δ -131.44 (d, $^3J_{FF}$ = 28.8 Hz, *ortho*-F), -161.64 (tr, $^3J_{FF}$ = 21.3 Hz, *para*-F), -165.36 (m, *meta*-F). MS (EI +ve): *m/z* 403.3 ($[M\text{-}BCF]^+$, 100%), 512.0 ($[BCF]^+$, 30%). Elemental analysis: calcd. for $C_{46}H_{40}BF_{15}N_2$: C 60.28, H 4.40, N 3.06, meas. C 61.12, H 4.22, N 3.58.

Crystallographic data: **2a**·C_7H_8, $C_{53}H_{48}BF_{15}N_2$, M_r = 1008.76, monoclinic, *C* 2/*c*, a = 35.4499(3), b = 11.1438(1), c = 25.1650(2) Å, β = 104.2861(3)°, V = 9633.92(14) Å^3, Z = 8, ρ_c = 1.391 Mg m^{-3}, T = 150 K, λ = 0.710730 Å, 21331 reflections collected, 10963 independent [R(int) = 0.027], which were used in calculations. R_1 = 0.0603, wR_2 = 0.1340 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.0875, wR_2 = 0.1603 for all unique reflections. Max. and min. residual electron densities 0.89 and -0.52 e Å^{-3}. CCDC 1006573.

H(6-Dipp^{BArF}), 2b: A solution of $B(C_6F_5)_3$ (0.650 g, 1.3 mmol) in toluene (10 cm^3) was added to a stirred solution of **1b** (0.542 g, 1.3 mmol) also in toluene (10 cm^3). After stirring for 1 h under inert atmosphere conditions, the reaction mixture can be opened to the air and volatiles removed under vacuum. The white residue was washed with hexane (30 cm^3) and dissolved in toluene (30 cm^3). This solution was concentrated and stored at -30 °C to afford colourless crystals of the product in 66% yield (0.78 g). Crystals suitable for X-ray crystallography were obtained from layering a CH_2Cl_2 solution with hexane and storage at 20 °C.

Spectroscopic data: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ_H 7.35 (1H, tr, $^3J_{HH}$ = 7.8 Hz, *para*-CH), 7.27 (1H, tr, $^3J_{HH}$ = 7.8 Hz, *para*-CH), 7.20 – 7.02 (5H, m, *meta*-CH and NCHN), 4.07 (1H, m, NCH_2), 3.37 (1H, d m, $^2J_{HH}$ = 14.0 Hz, NCH_2), 3.17 (1H, br m, NCH), 2.98 (2H, sept, $^3J_{HH}$ = 6.5 Hz, CH ^{i}Pr), 2.65 (1H, sept, $^3J_{HH}$ = 6.8 Hz, CH ^{i}Pr), 2.37 (1H, sept, $^3J_{HH}$ = 6.6 Hz, CH ^{i}Pr), 2.35 (1H, m, BCH_2), 2.23 (2H, m, NCH_2CH_2), 2.20 (1H, m, BCH_2), 1.35 (3H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.24 (3H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.20 (3H, d, $^3J_{HH}$ = 6.4 Hz, CH_3 ^{i}Pr), 1.19 (3H, d, $^3J_{HH}$ = 6.4 Hz, CH_3 ^{i}Pr), 1.05 (3H, d, $^3J_{HH}$

= 6.8 Hz, CH_3 ^{i}Pr), 1.01 (3H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 0.98 (3H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 0.96 (3H, d, $^{3}J_{HH}$ = 7.2 Hz, CH_3 ^{i}Pr). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ_C 152.6 (NCHN), 148.0 (br d, $^{1}J_{CF}$ = 240 Hz, *ortho*-CF), 146.3, 146.0 (NC Dipp), 145.0, 144.9 (*ortho*-C Dipp), 138.0 (br d, $^{1}J_{CF}$ = 244 Hz, *para*-CF), 136.6 (br d, $^{1}J_{CF}$ = 262 Hz, *meta*-CF), 135.5, 134.3, 131.4, 130.9 (*para*-CH Dipp), 128.2, 125.3, 125.1, 124.8 (*meta*-CH Dipp), 63.2 (NCH), 46.8 (NCH_2), 29.2, 29.0, 28.9 (CH ^{i}Pr), 26.8, 25.6, 25.5, 24.7, 24.3, 24.2 (CH_3 ^{i}Pr), 23.9 (br, CH_2B), 23.2, 22.2 (CH_3 ^{i}Pr), 21.4 (NCH_2CH_2). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ_B -14.47 (s, $CBAr^F_3$). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ_F -131.19 (d, $^{3}J_{FF}$ = 20.3 Hz, *ortho*-F), -162.1 (tr, $^{3}J_{FF}$ = 20.5 Hz, *para*-F), -165.48 (m, *meta*-F). Elemental analysis: calc. for $C_{47}H_{42}N_2BF_{15}$: C 60.66, H 4.55, N 3.01, meas. C 60.63, H 4.64, N 3.34.

Crystallographic data: **2b**, $C_{47}H_{42}N_2BF_{15}$, M_r = 930.64, monoclinic, $P2_1/n$, a = 10.4429(1), b = 32.1025(5), c = 12.9291(2) Å, β = 100.0078(12) °, V = 4268.44(10) Å^3, Z = 4, ρ_c = 1.448 Mg m^{-3}, T = 150 K, λ = 1.54180 Å, 25214 reflections collected, 8853 independent [R(int) = 0.049], which were used in calculations. R_1 = 0.0471, wR_2 = 0.1258 for observed unique reflections [I > 2σ(I)] and R_1 = 0.0492, wR_2 = 0.1281 for all unique reflections. Max. and min. residual electron densities 0.40 and -0.29 e Å^{-3}. CCDC 1006574.

H(7-Dipp^{BArF}) 2c: A solution of $B(C_6F_5)_3$ (0.400 g, 0.9 mmol) in toluene (20 cm^3) was added to a stirred solution of **1c** (0.474 g, 0.9 mmol) also in toluene (10 cm^3). After stirring for 2 h under inert atmosphere conditions, the reaction mixture can be opened to the air and the solvent was removed under vacuum. The white residue was washed with hexane (30 cm^3) and dissolved in Et_2O (20 cm^3). This solution was concentrated and stored at -30 °C to afford colourless crystals of the product in 59% yield (0.51 g). Crystals suitable for X-ray crystallography were obtained from an Et_2O solution at -30 °C.

Spectroscopic data: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ_H 7.41 (2H, overlapping tr, $^{3}J_{HH}$ = 7.8 Hz, *para*-CH), 7.25 (3H, m, *meta*-CH), 7.17 (1H, s, NCHN), 7.16 (1H, m, *meta*-CH), 4.18 (1H, br m, NCH), 4.05 (1H, m, NCH_2), 3.70 (1H, m, NCH_2), 3.19 (1H, sept, $^{3}J_{HH}$ = 6.9 Hz, CH ^{i}Pr), 2.98 (1H, sept, $^{3}J_{HH}$ = 6.7 Hz, CH ^{i}Pr), 2.92 (1H, sept, $^{3}J_{HH}$ = 6.8 Hz, CH ^{i}Pr), 2.53 (1H, sept, $^{3}J_{HH}$ = 6.8 Hz, CH ^{i}Pr), 2.47 (1H, m, NCH_2CH_2), 2.31 (1H, m, $NCHCH_2$), 2.20 (1H, m, $NCHCH_2$), 2.15 (1H, m, NCH_2CH_2), 1.48 (3H, d, $^{3}J_{HH}$ = 6.4 Hz, CH_3 ^{i}Pr), 1.32 (3H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.31 (3H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.25 (3H, d, $^{3}J_{HH}$ = 6.0 Hz, CH_3 ^{i}Pr), 1.23 (3H, d, $^{3}J_{HH}$ = 6.0 Hz, CH_3 ^{i}Pr), 1.17 (3H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.13 (3H, d, $^{3}J_{HH}$ = 7.2 Hz, CH_3 ^{i}Pr), 0.97 (3H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ_C 158.0 (NCHN), 148.0 (br d, $^{1}J_{CF}$ = 236 Hz, *ortho*-CF), 145.7, 145.3 (NC Dipp), 144.8, 143.7, 138.9 (*ortho*-C Dipp), 138.0 (br d, $^{1}J_{CF}$ = 235 Hz, *para*-CF), 136.5 (br d, $^{1}J_{CF}$ = 253 Hz, *meta*-CF), 135.9 (*ortho*-C Dipp), 131.0, 130.7 (*para*-CH Dipp), 125.6, 125.2, 125.0, 124.8 (*meta*-CH Dipp), 69.7 (NCH), 56.0 (NCH_2), 29.3, 29.3 (CH ^{i}Pr), 29.2 ($NCHCH_2$), 28.9 (CH ^{i}Pr), 26.2, 25.8, 25.1, 25.1 (CH_3 ^{i}Pr), 24.1 (NCH_2CH_2), 24.0, 23.6, 22.8, 22.8 (CH_3 ^{i}Pr). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ_B -14.28 (s, $CBAr^F_3$). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ_F -130.80 (d, $^{3}J_{FF}$ = 21.8 Hz, *ortho*-F), -162.1 (tr, $^{3}J_{FF}$ = 20.5 Hz, *para*-F), -165.55 (m, *meta*-F). Elemental analysis: calc. for $C_{48}H_{44}N_2BF_{15}$: C 61.02, H 4.69, N 2.96, meas. C 60.51, H 4.59, N 2.99.

Crystallographic data: **2c**·2(Et_2O), $C_{56}H_{64}N_2BF_{15}O_2$, M_r = 1092.92, triclinic, *P*-1, a = 12.3124(4), b = 15.5237(5), c = 15.6860(4) Å, α = 66.407(3), β = 100.0078(12), γ = 89.507(3) °, V = 2704.24 (16) Å^3, Z = 2, ρ_c = 1.342 Mg m^{-3}, T = 150 K, λ = 1.54180 Å, 28501 reflections collected, 11217 independent [R(int) = 0.019], which were used in calculations. R_1 = 0.0347, wR_2 = 0.0873 for observed unique reflections [I > 2σ(I)] and R_1 = 0.0372, wR_2 = 0.0893 for all unique reflections. Max. and min. residual electron densities 0.31 and -0.26 e Å^{-3}. CCDC 1006575.

[K(18-crown-6)][(5-Dipp^{BArF})], 3: K[N(SiMe$_3$)$_2$] (0.024 g, 0.12 mmol) in THF (10 cm^3) was added to a stirred solution of **2a** (0.100 g, 0.11 mmol) also in THF (15 cm^3). The mixture was allowed to stir for 30 min, then the mixture transferred onto 18-crown-6 (0.029 g, 0.11 mmol) and stirred for a further 10 min. Removal of the volatiles under vacuum and washing with hexanes yielded product as a white powder. Green oil can form on the surface of the product, which can be washed away using diethyl ether. X-ray quality crystals were obtained in 54% yield (0.07 g) from a concentrated solution in THF layered with pentane and stored at 20 °C.

Spectroscopic data: ^{1}H NMR ($C_6D_5CD_3$, 400 MHz, 298 K): δ_H 7.11-6.76 (6H, m, CH Dipp), 4.45 (1H, m, NCH), 4.19 (1H, tr, $^{2}J_{HH}$ = 12.6 Hz, NCH_2), 3.61 (1H, tr, $^{2}J_{HH}$ = 11.4 Hz, NCH_2), 3.26 (1H, sept, $^{3}J_{HH}$ = 7.0 Hz, CH ^{i}Pr), 2.75 (1H, sept, $^{3}J_{HH}$ = 6.8 Hz, CH ^{i}Pr), 2.68 (1H, overlapping tr, $^{2}J_{HH}$ = 13.2 Hz, CH_2-B), 2.56 (1H, sept, $^{3}J_{HH}$ = 6.6 Hz, CH ^{i}Pr), 2.43 (1H, sept, $^{3}J_{HH}$ = 6.8 Hz, CH ^{i}Pr), 1.72 (1H, br d, $^{2}J_{HH}$ = 13.6 Hz, CH_2-B), 1.44 (3H, d, $^{3}J_{HH}$ = 6.9 Hz, CH_3 ^{i}Pr), 1.18 (3H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.08 (3H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.01, 0.99 (3H, overlapping d, CH_3 ^{i}Pr), 0.91 (6H, overlapping d, CH_3 ^{i}Pr), 0.89 (3H, overlapping d, CH_3 ^{i}Pr). ^{13}C NMR ($C_6D_5CD_3$, 125 MHz, 298 K): δ_C 165.5 (NCN), 148.8 (dm, $^{1}J_{CF}$ = 236.9 Hz, *ortho*-CF), 147.8, 146.3 (NC Dipp), 146.1, 146.0, 143.7, 141.5 (*ortho*-C Dipp), 138.6 (dm, $^{1}J_{CF}$ = 240.6 Hz, *para*-CF), 137.3 (dm, $^{1}J_{CF}$ = 194.1 Hz, *meta*-CF), 131.7, 129.6 (*para*-CH Dipp), 125.6, 124.8, 123.8 (*meta*-CH Dipp), 71.5 (NCH), 58.8 (NCH_2), 30.4, 29.7, 29.5, 29.1 (CH ^{i}Pr), 27.8 (CH_2B), 26.2, 25.9, 24.4, 23.8, 23.5, 23.1, 22.8 (CH_3 ^{i}Pr). ^{11}B NMR ($C_6D_5CD_3$, 128 MHz, 298 K): δ -14.4 (s). ^{19}F NMR ($C_6D_5CD_3$, 376 MHz, 298 K): δ -130.89 (d, $^{3}J_{FF}$ = 21.8 Hz, *ortho*-F), -161.24 (tr, $^{3}J_{FF}$ = 20.3 Hz, *para*-F), -165.09 (m, *meta*-F). MS (ESI -ve): *m/z* 933.3 ([M+H_2O]$^-$, 100%). The extremely air-sensitive nature of **3** prevented reproducible elemental microanalysis.

Crystallographic data: **3**, $C_{58}H_{63}BF_{15}N_2KO_6$, M_r = 1219.03, monoclinic, *P* $2_1/n$, a = 10.5956(2), b = 22.6260(3), c = 24.4132(4) Å, β = 98.9391(6)°, V = 5781.64(16) Å^3, Z = 4, ρ_c = 1.400 Mg m^{-3}, T = 150 K, λ = 0.710730 Å, 70863 reflections collected, 13012 independent [R(int) = 0.037], which were used in calculations. R_1 = 0.0689, *w*R_2 = 0.1251 for observed unique reflections [I > 2σ(I)] and R_1 = 0.1062, *w*R_2 = 0.1453 for all unique reflections. Max. and min. residual electron densities 1.01 and -0.69 e Å^{-3}. CCDC 1006576.

Generation and *in situ* characterization of [Li(thf)*$_n$*][(6-Dipp^{BArF})]: **2b** (0.040 g, 0.04 mmol) contained within a J. Young's NBMR tube was dissolved in THF-d_8 (1 cm^3) and the solution cooled to -78 °C. A solution of ^{n}BuLi in hexane (0.03 cm^3, 1.6 M, 0.04 mmol) was then added and the mixture allowed to warm to room temperature. After sonication for 30 min to ensure that the reaction had gone to completion, ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were measured. Conversion appeared to be quantitative by ^{1}H NMR.

Spectroscopic data: ^{1}H NMR (C_4D_8O, 400 MHz, 298 K): δ_H 7.20 – 6.89 (6H, m, CH Dipp), 3.65 (1H, m, NCH_2), 3.63 (2H, m, CH ^{i}Pr), 3.29 (1H, sept, $^3J_{HH}$ = 6.9 Hz, CH ^{i}Pr), 2.86 (1H, m, CH ^{i}Pr), 2.83 (1H, m, NCH_2), 2.57 (1H, m, BCH_2), 2.55 (1H, m, NCH), 2.44 (1H, br m, BCH_2), 2.10 (1H, m, NCH_2CH_2), 1.99 (1H, m, NCH_2CH_2), 1.37 (3H, d, $^3J_{HH}$ = 7.2 Hz, CH_3 ^{i}Pr), 1.23 (3H, d, $^3J_{HH}$ = 7.2 Hz, CH_3 ^{i}Pr), 1.22 (3H, d, $^3J_{HH}$ = 6.4 Hz, CH_3 ^{i}Pr), 1.20 (3H, d, $^3J_{HH}$ = 6.4 Hz, CH_3 ^{i}Pr), 1.09 (3H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.05 (3H, d, $^3J_{HH}$ = 6.4 Hz, CH_3 ^{i}Pr), 1.05 (3H, d, $^3J_{HH}$ = 6.4 Hz, CH_3 ^{i}Pr), 1.01 (3H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr). ^{13}C NMR (C_4D_8O, 100 MHz, 298 K): δ_C 243.1 (NCN), 149.2 (br d, $^1J_{CF}$ = 238 Hz, *ortho*-CF), 148.1, 147.9 (NC Dipp), 146.9, 146.5, 146.4, 145.5 (*ortho*-C Dipp), 138.5 (br d, $^1J_{CF}$ = 255 Hz, *para*-CF), 137.3 (br d, $^1J_{CF}$ = 242 Hz, *meta*-CF), 127.2, 126.6 (*para*-CH Dipp), 126.2, 124.1, 124.0, 123.1 (*meta*-CH Dipp), 56.3 (NCH), 43.3 (NCH_2), 29.4, 29.3, 28.9, 28.7 (CH ^{i}Pr), 27.4 (NCH_2CH_2), 27.2, 26.4, 25.1 (CH_3 ^{i}Pr), 24.7 (br, CH_2B), 24.4, 23.5, 22.4 (CH_3 ^{i}Pr). ^{11}B NMR (C_4D_8O, 128 MHz, 298 K): δ_B -13.86 (s, $CBAr^F_3$). ^{19}F NMR (C_4D_8O, 376 MHz, 298 K): δ_F -130.42 (d, $^3J_{FF}$ = 19.2 Hz, *ortho*-F), -166.25 (tr, $^3J_{FF}$ = 20.3 Hz, *para*-F), -168.28 (m, *meta*-F).

(5-Dipp^{BArF})Rh(COD), 4: **2a** (0.222 g, 0.24 mmol) was dissolved in THF (15 cm^3) and cooled to -78 °C. A 1.6M solution of ^{n}BuLi in hexane (0.15 cm^3, 0.24 mmol) was added and the reaction mixture allowed to warm to room temperature and stirred for 30 min. The mixture was then transferred onto a stirred solution of $[Rh(COD)Cl]_2$ (0.060 mg, 0.12 mmol) also in THF (10 cm^3). The reaction mixture was stirred for 2 h before volatiles were removed under vacuum. Washing the yellow residue with hexane (2 x 15 cm^3) yielded the product in 51% yield (0.14 g). Crystals suitable for X-ray crystallography were obtained from a layering of a CH_2Cl_2 solution with hexane and storage at 20 °C.

Spectroscopic data: ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ_H 7.55 – 7.27 (4H, m, CH-Dipp), 7.17 (2H, app tr, $^3J_{HH}$ = 8.0 Hz, *meta*-CH Dipp), 4.13 (1H, br q, $^3J_{HH}$ = 11.9 Hz, NCH), 3.71 (1H, sept, $^3J_{HH}$ = 6.9 Hz, CH ^{i}Pr), 3.57 (3H, br m, 1H NCH_2 and 2H CH=CH), 3.39 (1H, br, CH=CH), 3.28 (1H, tr, $^3J_{HH}$ = 10.4 Hz, NCH_2), 3.07 (1H, br, CH=CH), 2.97 (3H, m, CH ^{i}Pr), 2.06 (1H, br, CH_2B), 2.05 (3H, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 2.00 (3H, m, CH_2 COD), 1.95 (1H, m, CH_2 COD), 1.84 (3H, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.63 (1H, br d, $^3J_{HH}$ = 12.4 Hz, CH_2B), 1.52 (4H, m, CH_2 COD), 1.47 (3H, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.45 (3H, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.35 (3H, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.23 (3H, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.14 (3H, $^3J_{HH}$ = 6.8 Hz, CH_3 ^{i}Pr), 1.13 (3H, $^3J_{HH}$ = 7.2 Hz, CH_3 ^{i}Pr). ^{13}C NMR (CD_2Cl_2, 100 MHz, 298 K): δ_C 176.9 (d, $^1J_{CRh}$ = 40.9 Hz, NCN), 150.8, 150,1 (NC Dipp), 148.7 (br d, $^1J_{CF}$ = 231 Hz, *ortho*-CF), 147.0 (*ortho*-C Dipp), 138.6 (br d, $^1J_{CF}$ = 248 Hz, *para*-CF), 137.1 (br d, $^1J_{CF}$ = 239 Hz, *ortho*-CF), 131.9, 130.7 (*para*-CH Dipp), 127.7, 127.1, 125.2, 124.9 (*meta*-CH Dipp), 105.5 (d, $^1J_{CRh}$ = 6.8 Hz, CH=CH), 140.5 (d, $^1J_{CRh}$ = 5.9 Hz, CH=CH), 69.7 (d, $^1J_{CRh}$ = 16.6 Hz, CH=CH), 69.5 (d, $^1J_{CRh}$ = 17.4 Hz, CH=CH), 69.3 (NCH), 61.6 (NCH_2), 33.2, 33.1 (CH_2 COD), 30.7, 29.3 (CH ^{i}Pr), 28.3, 26.6, 26.6 (CH_3 ^{i}Pr), 26.4 (CH_2 COD), 25.8, 24.5, 24.0, 23.5, 23.2 (CH_3 ^{i}Pr). ^{11}B NMR (CD_2Cl_2, 128 MHz, 298 K): δ_B -14.53 ($CBAr^F_3$). ^{19}F NMR (CD_2Cl_2, 376 MHz, 298 K): δ_F -131.39 (d, $^3J_{FF}$ = 22.9 Hz, *ortho*-F), -163.1 (tr, $^3J_{FF}$ = 20.5 Hz, *para*-F), -166.46 (m, *meta*-F). Elemental analysis: calc. for $C_{54}H_{51}BF_{15}RhN_2$: C 57.56, H 4.56, N 2.49, meas. C 57.60, H 4.80, N 2.19.

Crystallographic data: **4**·C_6H_{14}, $C_{60}H_{65}N_2RhBF_{15}$, M_r = 1212.87, monoclinic, *P*$2_1/n$, a = 10.3204(1), b = 23.3192(2), c = 23.4928(2) Å, β = 98.6503(8) °, V = 5589.54(9) Å^3, Z = 4, ρ_c = 1.441 Mg m^{-3}, T = 150 K, λ = 1.54180 Å, 57957 reflections collected, 11714 independent [R(int) = 0.031], which were used in calculations. R_1 = 0.0297, *w*R_2 = 0.0773 for observed unique reflections [I > 2σ(I)] and R_1 = 0.0312, *w*R_2 = 0.0784 for all unique reflections. Max. and min. residual electron densities 0.74 and -0.62 e Å^{-3}. CCDC 1006577.

[Li(THF)$_4$][(6-Dipp^{BArF})AuCl], 5: **2b** (0.058 g, 0.06 mmol) was dissolved in THF (15 cm^3) and cooled to -78 °C. A 1.6M solution of ^{n}BuLi in hexane (0.04 cm^3, 0.06 mmol) was added and the reaction mixture allowed to warm to room temperature and stirred for 30 min. The mixture was then transferred onto a solution of (THT)AuCl (20 mg, 0.06 mmol) also in THF (10 cm^3) in the dark at 0 °C. Stirring in the dark was continued for 2 h resulting in a dark blue solution. Filtration through Celite and removal of volatiles under vacuum yielded the crude white product which was washed with hexane (2 x 15 cm^3). Crystals suitable for X-ray crystallography were obtained from layering a concentrated THF solution with hexane and storage at 20 °C.

Spectroscopic data: ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ_H 7.38 – 6.97 (6H, m, CH Dipp), 3.87 (1H, m, NCH_2), 3.57 (8H, m, OCH_2 THF), 3.29 (1H, m, NCH_2), 3.27 (1H, m, CH ^{i}Pr), 3.19 (1H, sept, $^3J_{HH}$ = 6.8 Hz, CH ^{i}Pr), 2.93 (1H, br d, $^3J_{HH}$ =

14.8 Hz, NCH), 2.65 (1H, sept, $^3J_{HH}$ = 6.9 Hz, CH ^{i}Pr), 2.39 (1H, m, BCH$_2$), 2.14 (2H, br, NCH$_2$CH$_2$), 1.82 (8H, m, CH$_2$ THF), 1.41 (3H, d, $^3J_{HH}$ = 6.4 Hz, CH$_3$ ^{i}Pr), 1.38 (3H, d, $^3J_{HH}$ = 6.4 Hz, CH$_3$ ^{i}Pr), 1.37 (3H, d, $^3J_{HH}$ = 6.4 Hz, CH$_3$ ^{i}Pr), 1.26 (6H, app tr, $^3J_{HH}$ = 6.8 Hz, CH$_3$ ^{i}Pr), 1.22 (1H, m, BCH$_2$), 1.18 (6H, app tr, $^3J_{HH}$ = 6.6 Hz, CH$_3$ ^{i}Pr), 0.98 (3H, d, $^3J_{HH}$ = 6.8 Hz, CH$_3$ ^{i}Pr). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz, 298 K): δ_C 188.5 (NCN), 148.5 (br d, $^1J_{CF}$ = 238 Hz, *ortho*-CF), 147.8, 147.5 (NC Dipp), 146.4, 146.2, 142.7, 141.7 (*ortho*-C Dipp), 138.4 (br d, $^1J_{CF}$ = 241 Hz, *para*-CF), 137.0 (br d, $^1J_{CF}$ = 234 Hz, *meta*-CF), 129.4, 128.9 (*para*-CH Dipp), 124.9, 124.9, 124.6, 124.5 (*meta*-CH Dipp), 68.9 (CH$_2$O THF), 62.2 (NCH), 46.5 (NCH$_2$), 32.2 (CH$_2$B), 29.3, 29.1, 29.0, 28.9 (CH ^{i}Pr), 25.9 (CH$_2$ THF), 25.9, 25.2, 25.1, 24.8, 24.7, 24.5, 23.9 (CH$_3$ ^{i}Pr), 23.2, (NCH$_2$CH$_2$), 22.8 (CH$_3$ ^{i}Pr). ^{11}B NMR (CD$_2$Cl$_2$, 128 MHz, 298 K): δ_B -14.35 (CBAr^F$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 376 MHz, 298 K): δ_F -131.20 (d, $^3J_{FF}$ = 20.3 Hz, *ortho*-F), -164.03 (tr, $^3J_{FF}$ = 20.3 Hz, *para*-F), -166.96 (m, *meta*-F). MS (ESI -ve): *m/z* 1161.25. Accurate mass ([C$_{47}$H$_{41}$N$_2$AuBClF$_{15}$]$^-$): 1161.2501 (meas.), 1161.2480 (calc.). While reproducible elemental microanalysis for **5** proved impossible to obtain, the corresponding [Ph$_3$PNPPh$_3$]$^+$ (PPN) salt can be obtained by simple metathesis with PPNCl and obtained as an analytically pure material. Elemental analysis: calc. for [Ph$_3$PNPPh$_3$][(6-Dipp^{BArF})AuCl]·2CH$_2$Cl$_2$, C$_{85}$H$_{75}$AuBCl$_5$F$_{15}$N$_3$P$_2$: C 54.58, H 4.04, N 2.25, meas. C 54.83, H 3.91, N 2.46.

Crystallographic data: **5**, C$_{63}$H$_{73}$N$_2$AuBClF$_{15}$LiO$_4$, M$_r$ = 1457.42, triclinic, *P*-1, a = 10.8473(3), b = 16.4395(4), c = 19.8987(4) Å, α = 69.270(2), β = 87.964(2), γ = 88.679(2) °, V = 3316.39(15) Å^3, Z = 2, ρ_c = 1.459 Mg m^{-3}, T = 150 K, λ = 1.54180 Å, 89243 reflections collected, 13788 independent [R(int) = 0.139], which were used in calculations. R$_1$ = 0.0839, *w*R$_2$ = 0.2025 for observed unique reflections [I > 2σ(I)] and R$_1$ = 0.1159, *w*R$_2$ = 0.2188 for all unique reflections. Max. and min. residual electron densities 3.25 and -2.64 e Å^{-3}. CCDC 1006578.

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