Neutral Bis(imino)-1,4-dihydropyridinate and Cationic Bis(imino)pyridine σ-Alkylzinc(II) Complexes as Hydride Exchange Systems: Classic Organometallic Chemistry Meets Ligand-Centered, Biomimetic Reactivity.

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SUPPORTING INFORMATION (ESI): Full experimental details and characterization data for protonated ligands and ionic complexes **3-10**

PROTONATED LIGANDS:

Synthesis of $[H(4\text{-Bn-}^{iPr}BIP)]^+[BAr^F{}_4]^-$. A solution of $[H(OEt_2)_2][BAr^F{}_4]$ (974 mg; 0.96 mmol) in 10 mL of Et_2O was added to an equal volume of a cooled solution of 4-Bn-^{iPr}BIP containing 522 mg (0.91 mmol) in the same solvent, stirred at - 60°C. The stirring was maintained for 30 min and then for 1 h at the room temperature. Then, the volatiles were removed under reduced pressure. The orange, oily residue solidified when it was stirred with three portions of hexane (3 x 10 mL). The product was dried under vacuum, resulting in an orange powder, which was recrystallized from a 2:1 mixture of diethylether/hexane at the freezer temperature (-20 ºC), affording the title product as a microcrystalline orange solid. Yield: 1.08 g, 82 %. ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ 1.15 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CHMe*Me*), 1.20 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*Me), 2.48 (s, 6H, *Me*-CN), 2.62 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 4.41 (s, 2H, CH_2Ph), 7.10-7.40 (m, 5H, CH$_2$*Ph*), 7.32 (d, 4H, $^3J_{HH}$ = 7.1 Hz, *m*-C$H_{\text{N-Ar}}$), 7.42 (t, 2H, $^3J_{HH}$ = 7.1 Hz, *p*-C$H_{\text{N-Ar}}$), 7.61 (s, 4H, *p*-CH_{Ar} $BAr^F{}_4$), 7.80 (s, 8H, *o*-CH_{Ar} $BAr^F{}_4$), 8.39 (s, 2H, 3-CH_{Py}). ^{11}B{^{1}H} NMR (128 MHz, 25 ºC, CD_2Cl_2): δ - 6.60. ^{19}F{^{1}H} NMR (376 MHz, 25 ºC, CD_2Cl_2): δ - 62.8.

Synthesis of $[H^{Mes}BIP]^+[BAr^F{}_4]^-$. The synthesis of this salt was carried out following the procedure described above, starting from: 6.06 g (6.0 mmol) of $[H(OEt_2)_2][BAr^F{}_4]$ and 2.16 g (5.45 mmol) of ^{Mes}BIP. An orange microcrystalline solid was isolated after recrystallization from a 2:1 mixture of diethylether/hexane. Yield: 6.37 g, 92%. ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ 2.13 (s, 12H, *o-Me*$_{\text{N-Ar}}$), 2.38 (s, 6H, *p-Me*$_{\text{N-Ar}}$), 2.57 (s, 6H, *Me*-CN), 7.09 (s, 4H, *m*-C$H_{\text{N-Ar}}$), 7.59 (s, 4H, *p*-CH_{Ar} $BAr^F{}_4$), 7.76 (s, 8H, *o*-CH_{Ar} $BAr^F{}_4$), 8.37 (t, 1H, $^3J_{HH}$ = 7.9 Hz, 4-CH_{Py}), 8.68 (d, 2H, $^3J_{HH}$ = 7.9 Hz, 3-CH_{Py}). ^{13}C {^{1}H}-NMR (CD_2Cl_2, 25 °C, 100 MHz): δ 16.6 (*Me*-CN), 17.7 (*o-Me*$_{\text{N-Ar}}$), 20.7 (*p-Me*$_{\text{N-Ar}}$), 117.5 (s, *p*-*C*H$_{Ar}$ $BAr^F{}_4$), 124.6 (q, $^1J_{CF}$ = 272 Hz, *C*F$_3$ $BAr^F{}_4$), 128.6 (*p*-$C_{\text{N-Ar}}$), 128.9 (q, $^2J_{CF}$ = 31 Hz, *C*-CF$_3$ $BAr^F{}_4$), 129.4 (3-*C*H$_{Py}$), 129.8 (*m*-CH$_{\text{N-Ar}}$), 134.8 (s, *o*-*C*H$_{Ar}$ $BAr^F{}_4$), 138.2 (*o*-$C_{\text{N-Ar}}$), 140.8 (4-*C*H$_{Py}$), 140.9 (*i*-$C_{\text{N-Ar}}$), 149.6 (2-C_{Py}), 161.8 (q, $^1J_{CB}$ = 50 Hz, *i*-C_{Ar} $BAr^F{}_4$), 172.2 (Me-*C*N). ^{11}B{^{1}H} NMR (128 MHz, 25 ºC, CD_2Cl_2): δ - 6.60. ^{19}F{^{1}H} NMR (376 MHz, 25 ºC, CD_2Cl_2): δ - 62.8.

SYNTHESES OF CATIONIC COMPLEXES 3 - 10

Synthesis of $[(4\text{-Bn-}^{iPr}BIP)Zn(CH_2SiMe_3)]^+[BAr^F{}_4]^-$ (3). A 0.52 M toluene solution of $Zn(CH_2SiMe_3)_2$ (1mL, 0.52 mmol) was slowly added *via* cannula to a gas-tight centrifuge cone loaded with a solution of 741 mg of $[4\text{-Bn-H}^{iPr}BIP]^+[BAr^F{}_4]^-$ (0.52 mmol) in 10 mL of CH_2Cl_2, magnetically stirred at -60 °C. The mixture was stirred at that temperature for 20 min and then at the room temperature for 2h. The volatiles were evaporated under reduced pressure. Next, the solid residue was treated as described for **2**·BAr^F_4, leaving 504 mg (0.34 mmol, 65 % yield) of compound **3** as an orange powder. ^{1}H NMR (CD_2Cl_2, 25 °C, 500 MHz): δ -0.73 (s, 9H, $ZnCH_2Si\mathit{Me}_3$), 0.01 (s, 2H, $ZnC\mathit{H}_2SiMe_3$), 1.10 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CHMe*Me*), 1.22 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*Me*)*, 2.43 (s, 6H, *Me*-CN), 2.51 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me_2), 4.38 (s, 2H, CH_2 Py-Bn), 7.27 - 7.40 (m, 5H, CH_{Ar} Py-Bn), 7.29 (d, 4H, $^3J_{HH}$ = 7.4 Hz, *m*-C$\mathit{H}_{N\text{-}Ar}$), 7.42 (t, 2H, $^3J_{HH}$ = 7.3 Hz, *p*-C$\mathit{H}_{N\text{-}Ar}$), 7.55 (s, 4H, *p*-CH_{Ar} BAr^F_4), 7.72 (s, 8H, *o*-CH_{Ar} BAr^F_4), 8.21 (s, 2H, 3-CH_{Py}). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 25 ºC, 125 MHz): δ –4.8 (Zn*C*H_2SiMe_3), 1.5 ($ZnCH_2Si\mathit{Me}_3$), 18.7 (*Me*-CN), 23.5 (CHMe*Me*), 23.9 (CH*Me*Me), 29.1 (*C*HMe_2), 42.1 (*C*H_2 Py-Bn), 117.6 (s, *p*-*C*H_{Ar} BAr^F_4), 124.7 (*m*-*C*$H_{N\text{-}Ar}$), 124.7 (q, $^1J_{CF}$ = 272 Hz, *C*F_3 BAr^F_4), 127.8 (3-*C*H_{Py}), 127.9 (*m*-*C*H_{Ar} Py-Bn), 128.2 (*p*-*C*H_{Ar} Py-Bn), 128.9 (q, $^2J_{CF}$ = 31 Hz, *C*-CF_3 BAr^F_4), 129.2 (*o*-*C*H_{Ar} Py-Bn), 129.7 (*p*-*C*$H_{N\text{-}Ar}$), 134.9 (s, *o*-*C*H_{Ar} BAr^F_4), 135.9 (*i*-*C*$_{Ar}$ Py-Bn), 137.7 (*o*-*C*$_{N\text{-}Ar}$), 140.8 (*i*-*C*$_{N\text{-}Ar}$), 148.6 (2-*C*$_{Py}$), 162.1 (c, $^1J_{CB}$ = 50 Hz, *i*-*C*$_{Ar}$ BAr^F_4), 163.0 (4-*C*$_{Py}$), 166.9 Me-*C*N). ^{11}B{^{1}H} NMR (128 MHz, 25 ºC, CD_2Cl_2): δ -6.60. ^{19}F{^{1}H} NMR (376 MHz, 25 ºC, CD_2Cl_2): δ -62.8 IR (Nujol, cm^{-1}): 1609, ν (C=N, BIP); 1278, 1125 and 887 ν (B-C) for $[BAr^F_4]^-$. Anal. Calcd for $C_{76}H_{72}BF_{24}N_3SiZn$: C, 57.49; H, 4.57; N, 2.65. Found: C, 57.14; H, 4.40; N, 2.46 %.

Synthesis of $[(4\text{-Bn-}^{iPr}BIP)Zn(CH_2CMe_2Ph)]^+[BAr^F_4]^-$ (4). A 0.5 M solution of $Zn(CH_2CMe_2Ph)_2$ (0.8 mL, 0.40 mmol) was slowly added to a gas-tight centrifuge cone loaded with a solution of 538.0 mg (0.40 mmol) of $[4\text{-Bn-H}^{iPr}BIP]^+[BAr^F_4]^-$ in 15 mL Et_2O, magnetically stirred at -60 ºC. The mixture was stirred at room temperature for 2 h and taken to dryness under reduced pressure. The residue was processed in the same way described for **2**·BAr^F_4 and 3, leaving 487 mg (0.32 mmol, 79 % yield) of **4** as a microcrystalline orange solid. ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ 0.56 (s, 6H, $ZnCH_2C\mathit{Me}_2Ph$), 0,92 (s, 2H, Zn*C*H_2CMe_2Ph), 1.09 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CHMe*Me*), 1.18 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*Me), 2.46 (s, 6H, *Me*-CN), 2.50 (sept, 4H, $^3J_{HH}$ = 7.3 Hz, C*H*Me_2), 4.39 (s, 2H, CH_2 Py-Bn), 6.77 (d, 2H, $^3J_{HH}$ = 7.1 Hz, o-CH_{Ar} $ZnCH_2CMe_2\mathit{Ph}$), 6.96 (t, 1H, $^3J_{HH}$ = 7.2 Hz, *p*-CH_{Ar} $ZnCH_2CMe_2\mathit{Ph}$), 7.03 (t, 2H, $^3J_{HH}$ = 7.3 Hz, *m*-CH_{Ar} $ZnCH_2CMe_2\mathit{Ph}$), 7.25-7.41 (m, 5H, CH_{Ar} Py-Bn), 7.32 (d, 4H, $^3J_{HH}$ = 7.1 Hz, *m*-C$\mathit{H}_{N\text{-}Ar}$), 7.43 (t, 2H, $^3J_{HH}$ = 7.1 Hz, *p*-C$\mathit{H}_{N\text{-}Ar}$), 7.55 (s, 4H, *p*-CH_{Ar} BAr^F_4), 7.72 (s, 8H, *o*-CH_{Ar} BAr^F_4), 8.21 (s, 2H, 3-CH_{Py}). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 25 ºC, 100 MHz): δ 19.1 (*Me*-CN), 23.1 (CHMe*Me*), 24.2 (CH*Me*Me), 29.3 (*C*HMe_2), 33.2 (Zn*C*H_2CMe_2Ph), 33.8 ($ZnCH_2C\mathit{Me}_2Ph$), 37.4 ($ZnCH_2$*C*Me_2Ph), 42.0 (*C*H_2 Py-Bn), 117.5 (s, *p*-*C*H_{Ar} BAr^F_4), 124.6 (q, $^1J_{CF}$ = 272 Hz, *C*F_3 BAr^F_4), 124.7 (*o*-*C*H_{Ar} $ZnCH_2CMe_2\mathit{Ph}$), 124.7 (*m*-*C*$H_{N\text{-}Ar}$), 125.3 (*p*-*C*H_{Ar} $ZnCH_2CMe_2\mathit{Ph}$), 127.6 (*m*-*C*H_{Ar} Py-Bn), 127.8 (*m*-*C*H_{Ar} $ZnCH_2CMe_2\mathit{Ph}$), 128.0 (*p*-*C*H_{Ar} Py-Bn), 128.1 (3-*C*H_{Py}), 128.9 (q, $^2J_{CF}$ = 31 Hz, *C*-CF_3 BAr^F_4), 129.2 (*o*-*C*H_{Ar} Py-Bn), 129.7 (*p*-*C*$H_{N\text{-}Ar}$), 134.9 (s, *o*-*C*H_{Ar} BAr^F_4), 135.9 (*i*-*C*$_{Ar}$ Py-Bn), 137.8 (*o*-*C*$_{N\text{-}Ar}$), 141.0 (*i*-*C*$_{N\text{-}Ar}$), 149.1 (2-*C*$_{Py}$), 153.5 (*i*-*C*$_{Ar}$ $ZnCH_2CMe_2\mathit{Ph}$), 161.8 (q, $^1J_{CB}$ = 50 Hz, *i*-*C*$_{Ar}$ BAr^F_4), 166.9 (Me-*C*N). ^{11}B{^{1}H} NMR (128 MHz, 25 ºC, CD_2Cl_2): δ -6.60. ^{19}F{^{1}H} NMR (376 MHz, 25 ºC, CD_2Cl_2): δ -62.8 IR (Nujol, cm^{-1}): 1609, ν

(C=N) in $[Zn(CH_2CMe_2Ph)(4\text{-Bn-}^{iPr}BIP)]^+$; 1278, 1125 and 886 ν (B-C) for $[BAr^F{}_4]^-$. Anal. Calcd for $C_{82}H_{74}BF_{24}N_3Zn$: C, 60.29; H, 4.57; N, 2.57. Found C, 60.59; H, 4.71; N, 2.16 %.

Synthesis of $[(^{iPr}BIP)Zn(Bn)]^+[BAr^F{}_4]^-$ (5). 5 mL of a CH_2Cl_2 solution of $[H^{iPr}BIP]^+[BAr^F{}_4]^-$ (258 mg; 0.20 mmol) were were carefully added to 5 mL of dichloromethane solution of $Zn(CH_2Ph)_2$ (containing 49.7 mg; 0.20 mmol) that was stirred at -60 °C in a gas-tight centrifuge cone. The reaction mixture was stirred at -60 °C for 20 min and then at the room temperature for 2 h after which time it was taken to dryness under reduced pressure. The work-up was carried out as described for the preceding complexes. Compound 5 was isolated as a microcrystalline orange solid. Yield 248 mg, 86 %. Good quality crystals could not be grown, in spite our efforts. ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ 1.09 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CHMe*Me*), 1.09 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*Me), 1.76 (s, 2H, CH_2 Zn-Bn), 2.48 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me_2), 2.50 (s, 6H, *Me*-CN), 5.59 (m, 2H, *o*-CH_{Ar} Zn-Bn), 6.58 (m, 2H, *m*-CH_{Ar} Zn-Bn), 6.59 (m, 1H, *p*-CH_{Ar} Zn-Bn), 7.39 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *m*-C$H_{N\text{-}Ar}$), 7.44 (t, 2H, $^3J_{HH}$ = 7.3 Hz, *p*-C$H_{N\text{-}Ar}$), 7.56 (s, 4H, *p*-CH_{Ar} $BAr^F{}_4$), 7.73 (s, 8H, *o*-CH_{Ar} $BAr^F{}_4$), 8.41 (d, 2H, $^3J_{HH}$ = 7.9 Hz, 3-CH_{Py}), 8.58 (t, 1H, $^3J_{HH}$ = 7.9 Hz, 4-CH_{Py}). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 25 ºC, 100 MHz): δ 18.3 (*Me*-CN), 18.6 (CH_2 Zn-Bn), 22.9 (CHMe*Me*), 23.9 (CH*Me*Me), 29.2 (*C*HMe_2), 117.6 (s, *p*-CH_{Ar} $BAr^F{}_4$), 121.3 (*p*-CH_{Ar} Zn-Bn), 124.6 (q, $^1J_{CF}$ = 272 Hz, *C*F_3 $BAr^F{}_4$), 124.7 (*m*-C$H_{N\text{-}Ar}$), 126.4 (*o*-CH_{Ar} Zn-Bn), 127.7 (3-CH_{Py}), 127.9 (*m*-CH_{Ar} Zn-Bn), 128.1 (*p*-C$H_{N\text{-}Ar}$), 128.9 (q, $^2J_{CF}$ = 31 Hz, *C*-CF_3 $BAr^F{}_4$), 134.8 (s, *o*-CH_{Ar} $BAr^F{}_4$), 137.8 (*o*-$C_{N\text{-}Ar}$), 141.0 (*i*-$C_{N\text{-}Ar}$), 145.4 (*i*-C_{Ar} Zn-Bn), 146.0 (4-CH_{Py}), 148.7 (2-C_{Py}), 161.8 (q, $^1J_{CB}$ = 50 Hz, *i*-C_{Ar} $BAr^F{}_4$), 166.8 (Me-*C*-N). $^{11}B\{^1H\}$ NMR (128 MHz, 25 ºC, CD_2Cl_2): δ -6.60. $^{19}F\{^1H\}$ NMR (376 MHz, 25 ºC, CD_2Cl_2): δ -62.8 IR (Nujol, cm^{-1}): 1609, 1596, ν(C=N) BIP; 1276, 1127 and 888, ν(B-C) $[BAr^F{}_4]^-$. Anal. Calcd for $C_{72}H_{62}BF_{24}N_3Zn$: C, 57.60; H, 4.16; N, 2.80. Found: C, 57.46; H, 4.15; N, 2.63 %.

Synthesis of $[(^{iPr}BIP)Zn(CH_2SiMe_3)]^+[BAr^F{}_4]^-$ (6). A 0.5 M toluene solution of $Zn(CH_2SiMe_3)_2$ (1mL 0.5 mmol) was slowly added *via* cannula to a small gas-tight centrifuge cone loaded with a solution of 622 mg of $[H^{iPr}BIP]^+[BAr^F{}_4]^-$ (0.5 mmol) in 10 mL of CH_2Cl_2, magnetically stirred at -60 °C. The mixture was stirred at that temperature for 20 min and then at the room temperature for 2h. The volatiles were evaporated under reduced pressure. The residue was washed with hexane 2 x 5 mL, and the washings were removed by centrifugation, and dried under vacuum as described before, leaving complex 6 as a yellow solid. This solid was dissolved in 5 mL of Et_2O and hexane was carefully added until one single drop turns the solution slightly turbid. The mixture was allowed to rest at -20 °C for 48 h, after which time yellow prismatic crystals were formed. Crystals for X-ray diffraction studies were selected at this point, before the overlying liquor was filtered out. Then the crystals were washed with a cold (-30 ºC) mixture of diethylether/hexane (1:10) and dried for 6 hours under vacuum. Yield: 328 mg (0.22 mmol), 48 %. ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ -0.69 (s, 9H, $ZnCH_2Si$*Me*$_3$), 0.62 (s, 2H, ZnCH_2SiMe_3), 1.11 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CHMe*Me*), 1.23 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*Me), 2.48 (s, 6H, *Me*-CN), 2.52 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me_2), 7.31 (m, 6H, *m*, *p*-C$H_{N\text{-}Ar}$), 7.56 (s, 4H, *p*-CH_{Ar} $BAr^F{}_4$), 7.72 (s, 8H, *o*-CH_{Ar} $BAr^F{}_4$), 8.39 (d, 2H, $^3J_{HH}$ = 7.9 Hz, 3-CH_{Py}), 8.57 (t, 1H, $^3J_{HH}$ = 7.9 Hz, 4-CH_{Py}). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 25 ºC, 100 MHz): δ -4.8 (Zn*C*H_2SiMe_3), 1.5 ($ZnCH_2Si$*Me*$_3$), 18.7 (*Me*-CN), 23.5 (CHMe*Me*), 23.9 (CH*Me*Me), 29.2 (*C*HMe_2), 117.6 (s, *p*-CH_{Ar} $BAr^F{}_4$), 124.6 (q, $^1J_{CF}$ = 272 Hz, *C*F_3 $BAr^F{}_4$), 124.7 (*m*-*C*$H_{N\text{-}Ar}$), 127.8 (3-*C*H_{Py}), 127.9 (*p*-*C*$H_{N\text{-}Ar}$), 128.9 (q, $^2J_{CF}$ = 31 Hz, *C*-CF_3 $BAr^F{}_4$), 134.9 (s, *o*-*C*H_{Ar} $BAr^F{}_4$), 137.7 (*o*-$C_{N\text{-}Ar}$), 140.6 (*i*-$C_{N\text{-}Ar}$), 146.3 (4-CH_{Py}), 148.5 (2-C_{Py}), 161.8 (q, $^1J_{CB}$ = 50 Hz, *i*-C_{Ar} $BAr^F{}_4$), 166.8 (Me-*C*N). $^{11}B\{^1H\}$ NMR (128 MHz, 25 ºC, CD_2Cl_2): δ -6.60. $^{19}F\{^1H\}$ NMR (376 MHz, 25 ºC, CD_2Cl_2): δ -62.8 IR (Nujol, cm^{-1}): 1609, 1595, ν(C=N) (BIP); 1278, 1122 and 887, ν(B-C) $[BAr^F{}_4]^-$. Anal. Calcd for $C_{68}H_{65}BF_{24}N_3SiZn$: C, 55.02; H, 4.41; N, 2.83. Found: C, 54.94, H, 4.64, N, 3.01 %.

Synthesis of $[(^{iPr}BIP)Zn(CH_2CMe_2Ph)]^+[BAr^F{}_4]^-$ (7). 0.9 mL of a 0.5 M solution in toluene of $Zn(CH_2CMe_2Ph)_2$ (0.45 mmol) was slowly added to a gas-tight centrifuge cone containing a stirred solution of $[H^{iPr}BIP]^+[BAr^F{}_4]^-$ (525 mg; 0.42 mmol) in 20 mL of Et_2O, cooled at -60 ºC. After 20 min, then the cooling bath was removed the stirring was continued at the room temperature for 1 h. The mixture was taken to dryness, and the residue was washed thrice with hexane (3 x 5 mL), removing each time the washing liquor by centrifugation. The residue was dried under the line vacuum, leaving 431 mg (0.30 mmol, 72 % yield) of compound **7** as a yellow microcrystalline solid. ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ 0.56 (s, 6H, $ZnCH_2C$*Me*$_2$Ph), 0,94 (s, 2H, Zn*C*H_2CMe_2Ph), 1.11 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CHMe*Me*), 1.19 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*Me), 2.52 (h, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me_2), 2.52 (s, 6H, *Me*-CN), 6.78 (d, 2H, $^3J_{HH}$ = 7.2 Hz, *o*-CH_{Ar} $ZnCH_2CMe_2$*Ph*), 6.97 (t, 1H, $^3J_{HH}$ = 7.2 Hz, *p*-CH_{Ar} $ZnCH_2CMe_2$*Ph*), 7.03 (t, 2H, $^3J_{HH}$ = 7.3 Hz, *m*-CH_{Ar} $ZnCH_2CMe_2$*Ph*), 7.33 (d, 4H, $^3J_{HH}$ = 6.9 Hz, *m*-$CH_{N\text{-}Ar}$), 7.39 (t, 2H, $^3J_{HH}$ = 7.6 Hz, *p*-$CH_{N\text{-}Ar}$), 7.55 (s, 4H, *p*-CH_{Ar} $BAr^F{}_4$), 7.72 (s, 8H, *o*-CH_{Ar} $BAr^F{}_4$), 8.42 (d, 2H, $^3J_{HH}$ = 7.9 Hz, 3-CH_{Py}), 8.61 (t, 1H, $^3J_{HH}$ = 7.9 Hz, 4-CH_{Py}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 ºC, 100 MHz): δ 19.2 (*Me*-CN), 23.1 (CHMe*Me*), 24.2 (CH*Me*Me), 29.3 (*C*HMe_2), 33.2 (Zn*C*H_2CMe_2Ph), 33.8 ($ZnCH_2C$*Me*$_2$Ph), 117.6 (s, *p*-CH_{Ar} $BAr^F{}_4$), 124.7 (*m*-*C*$H_{N\text{-}Ar}$), 124.7 (c, $^1J_{CF}$ = 272 Hz, *C*F_3 $BAr^F{}_4$), 124.7 (solap. *o*-*C*H_{Ar} $ZnCH_2CMe_2$*Ph*), 125.2 (*p*-CH_{Ar} $ZnCH_2CMe_2$*Ph*), 127.7 (*m*-*C*H_{Ar} $ZnCH_2CMe_2$*Ph*), 127.9 (3-*C*H_{Py}), 128.0 (*p*-*C*$H_{N\text{-}Ar}$), 128.9 (q, $^2J_{CF}$ = 31 Hz, *C*-CF_3 $BAr^F{}_4$), 134.9 (s, *o*-*C*H_{Ar} $BAr^F{}_4$), 137.9 (*o*-$C_{N\text{-}Ar}$), 140.9 (*i*-$C_{N\text{-}Ar}$), 146.2 (4-*C*H_{Py}), 149.1 (2-C_{Py}), 153.4 (*i*-C_{Ar} $ZnCH_2CMe_2$*Ph*), 161.8 (q, $^1J_{CB}$ = 50 Hz, *i*-C_{Ar} $BAr^F{}_4$), 166.9 (Me-*C*N). $^{11}B\{^1H\}$ NMR (128 MHz, 25 ºC, CD_2Cl_2): δ -6.60. $^{19}F\{^1H\}$ NMR (376 MHz, 25 ºC, CD_2Cl_2): δ -62.8. IR (Nujol, cm^{-1}): 1609, 1596, ν(C=N) (BIP); 1276, 1127 and 888, ν(B-C) in $[BAr^F{}_4]^-$**.** Anal. Calcd for $C_{75}H_{68}BF_{24}N_3Zn$: C, 58.36; H 4.44; N, 2.72. Found: C, 58.27; H, 4.59; N, 2.80 %**.**

Synthesis of $[(^{Mes}BIP)Zn(Bn)]^+[BAr^F{}_4]^-$ (8). 15 mL of a Et_2O solution containing 807.0 mg (0.69 mmol) of $[H^{Mes}BIP]^+[BAr^F{}_4]^-$ were stirred in a gas-tight centrifuge cone at – 60 °C while a 1 M solution of $Zn(CH_2Ph)_2$ in toluene (0.70 mL, 0.70 mmol) of was added dropwise. The stirring was continued for 20 min at this temperature and then at the room temperature for 2h. Next, it was taken to dryness, the residue was washed thrice with 10 mL of hexane for 30 min and the washings were removed by centrifugation. The microcrystalline orange solid was dried under vacuum. Yeld, 630 mg, 0.47 mmol, 69 % yield. ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ 1.62 (s, 2H, C*H*$_2$ Zn-Bn), 1.93 (s, 12H, *o-Me*$_{N-Ar}$), 2.37 (s, 6H, *p-Me*$_{N-Ar}$), 2.42 (s, 6H, *Me*-CN), 6.52 (d, 2H, $^3J_{HH}$ = 6.6 Hz, *o*-C*H*$_{Ar}$ Zn-Bn), 6.68 (m, 3H, *m*-C*H*$_{Ar}$, *p*-C*H*$_{Ar}$ Zn-Bn), 7.03 (s, 4H, *m*-C*H*$_{N-Ar}$), 7.56 (s, 4H, *p*-C*H*$_{Ar}$ BAr$^F{}_4$), 7.73 (s, 8H, *o*-C*H*$_{Ar}$ BAr$^F{}_4$), 8.32 (d, 2H, $^3J_{HH}$ = 7.9 Hz, 3-C*H*$_{Py}$), 8.51 (t, 1H, $^3J_{HH}$ = 7.9 Hz, 4-C*H*$_{Py}$). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 25 ºC, 100 MHz): δ 16.8 (*Me*-CN), 18.0 (*o-Me*$_{N-Ar}$), 19.3 (*C*H$_2$ Zn-Bn), 20.6 (*p-Me*$_{N-Ar}$), 117.6 (s, *p-C*H$_{Ar}$ BAr$^F{}_4$), 121.5 (*p-C*H$_{Ar}$ Zn-Bn), 124.7 (c, $^1J_{CF}$ = 272 Hz, *C*F$_3$ BAr$^F{}_4$), 126.0 (*o-C*H$_{Ar}$ Zn-Bn), 127.3 (3-*C*H$_{Py}$), 127.4 (*p-C*$_{N-Ar}$), 127.9 (*m-C*H$_{Ar}$ Zn-Bn), 128.9 (q, $^2J_{CF}$ = 31 Hz, *C*-CF$_3$ BAr$^F{}_4$), 129.8 (*m-C*H$_{N-Ar}$), 134.9 (s, *o-C*H$_{Ar}$ BAr$^F{}_4$), 137.2 (*o-C*$_{N-Ar}$), 140.7 (*i-C*$_{N-Ar}$), 144.8 (*i-C*$_{Ar}$ Zn-Bn), 145.9 (4-*C*H$_{Py}$), 148.6 (2-*C*$_{Py}$), 161.8 (q, $^1J_{CB}$ = 50 Hz, *i-C*$_{Ar}$ BAr$^F{}_4$), 166.9 (Me-*C*N). ^{11}B{^{1}H} NMR (128 MHz, 25 ºC, CD_2Cl_2): δ -6.60. ^{19}F{^{1}H} NMR (376 MHz, 25 ºC, CD_2Cl_2): δ -62.8. IR (Nujol, cm^{-1}): 1593, ν(C=N) BIP; 1277, 1128 and 887, ν(B-C) for [BAr$^F{}_4$]$^-$. Anal. Calcd. for $C_{66}H_{50}BF_{24}N_3Zn$: C, 55.93; H, 3.56; N, 2.96. Found: C, 55.71; H, 3.48; N, 2.42 %.

Synthesis of [(^{Mes}BIP)Zn(CH$_2$SiMe$_3$)]$^+$[BAr$^F{}_4$]$^-$ (9). 1.0 mL (0.52 mmol) of a 0.52 M solution of $Zn(CH_2SiMe_3)_2$ in toluene was added to 20 mL Et_2O solution of [H^{Mes}BIP]$^+$[BAr$^F{}_4$]$^-$ (609.0 mg, 0.48 mmol) while stirring at -60 ºC. The stirring was continued for 20 min and then at the room temperature for 2h. The solution was evaporated until 1/4 of the initial volume, and 10 mL of hexane were added until the product crystallizes spontaneously. The mother liquor was removed by filtration and the crystals were washed with hexane. After drying under vacuum, 403 mg (0.31 mmol, 64 % yield) of compound **9** were obtained as yellow crystals. ^{1}H NMR (CD_2Cl_2, 25 °C, 500 MHz): δ -0.87 (s, 2H, ZnC*H*$_2$SiMe$_3$), 0.65 (s, 9H, ZnCH$_2$Si*Me*$_3$), 2.0 (s, 12H, *o-Me*$_{N-Ar}$), 2.31 (s, 6H, *p-Me*$_{N-Ar}$), 2.42 (s, 6H, *Me*-CN), 7.01 (s, 4H, *m*-C*H*$_{N-Ar}$), 7.56 (s, 4H, *p*-C*H*$_{Ar}$ BAr$^F{}_4$), 7.73 (s, 8H, *o*-C*H*$_{Ar}$ BAr$^F{}_4$), 8.33 (d, 2H, $^3J_{HH}$ = 7.9 Hz, 3-C*H*$_{Py}$), 8.52 (t, 1H, $^3J_{HH}$ = 7.9 Hz, 4-C*H*$_{Py}$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 ºC, 100 MHz): δ -5.6 (Zn*C*H$_2$SiMe$_3$), 1.8 (ZnCH$_2$Si*Me*$_3$), 16.9 (*Me*-CN), 18.1 (*o-Me*$_{N-Ar}$), 20.5 (*p-Me*$_{N-Ar}$), 117.6 (s, *p-C*H$_{Ar}$ BAr$^F{}_4$), 124.7 (c, $^1J_{CF}$ = 272 Hz, *C*F$_3$ BAr$^F{}_4$), 127.1 (3-*C*H$_{Py}$), 127.2 (*p-C*$_{N-Ar}$), 128.9 (q, $^2J_{CF}$ = 31 Hz, *C*-CF$_3$ BAr$^F{}_4$), 129.7 (*m-C*H$_{N-Ar}$), 134.8 (s, *o-C*H$_{Ar}$ BAr$^F{}_4$), 137.1 (*o-C*$_{N-Ar}$), 140.3 (*i-C*$_{N-Ar}$), 145.9 (4-*C*H$_{Py}$), 148.5 (2-*C*$_{Py}$), 161.8 (c, $^1J_{CB}$ = 50 Hz, *i-C*$_{Ar}$ BAr$^F{}_4$), 166.6 (Me-*C*N). ^{11}B{^{1}H} NMR (128 MHz, 25 ºC, CD_2Cl_2): δ□-6.60. ^{19}F{^{1}H} NMR (376 MHz, 25 ºC, CD_2Cl_2): δ□-62.8. IR (Nujol, cm^{-1}): 1610, 1594, ν(C=N) (BIP); 1277, 1123 and 888, ν(B-C) for [BAr$^F{}_4$]$^-$, Anal. Calcd for $C_{63}H_{54}BF_{24}N_3SiZn$: C, 53.54; H, 3.85; N, 2.97. Found C, 53.10; H, 3.57; N, 2.34 %.

Synthesis of [(^{Mes}BIP)Zn(CH$_2$CMe$_2$Ph)]$^+$[BAr$^F{}_4$]$^-$ (10). A 15 mL orange solution of 514 mg (0.41 mmol) of [H^{iMes}BIP]$^+$[BAr$^F{}_4$]$^-$ in Et_2O was loaded into a gas-tight centrifuge cone and stirred at - 60 °C. Next, 1.0 mL of $Zn(CH_2CMe_2Ph)_2$ (0.50 M solution in toluene, 0.50 mmol) was added dropwise, and the stirring was continued for 20 min. The cooling bath was removed and the stirring was continued for 2 h at the room temperature. Volatiles were evaporated under reduced pressure and the residue was washed with hexane (3 x 5 mL), removing the washing liquors by centrifugation. After filtration and drying, an orange solid (**10**) was isolated (476 mg, 0.35 mmol, 85 % yield). This solid was recrystallized by dissolving 300 mg of **10** in 5 mL of Et_2O and carefully adding pentane until the solution becomes slightly turbid. After 2 days at -20 ^oC, orange crystals suitable for x-ray diffraction studies were formed. These were isolated from the mother liquor and washed with a cold (-30 ^oC) 1/10 mixture of Et_2O and pentane. ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ0.69 (s, 6H, $ZnCH_2CMe_2Ph$), 0,81 (s, 2H, $ZnCH_2CMe_2Ph$), 1.95 (s, 12H, *o-Me*$_{N-Ar}$), 2.36 (s, 6H, *p-Me*$_{N-Ar}$), 2.40 (s, 6H, *Me*-CN), 6.73 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *o*-C*H*$_{Ar}$ $ZnCH_2CMe_2Ph$), 7.01 (m, 3H, *m*-C*H*$_{Ar}$ *p*-C*H*$_{Ar}$ $ZnCH_2CMe_2Ph$), 7.03 (s, 4H, *m*-C*H*$_{N-Ar}$), 7.55 (s, 4H, *p*-C*H*$_{Ar}$ $BAr^F{}_4$), 7.72 (s, 8H, *o*-C*H*$_{Ar}$ $BAr^F{}_4$), 8.32 (d, 2H, $^3J_{HH}$ = 7.9 Hz, 3-C*H*$_{Py}$), 8.51 (t, 1H, $^3J_{HH}$ = 7.9 Hz, 4-C*H*$_{Py}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 ºC, 100 MHz): δ 17.3 (*Me*-CN), 18.2 (*o-Me*$_{N-Ar}$), 20.6 (*p-Me*$_{N-Ar}$), 33.2 ($ZnCH_2CMe_2Ph$), 33.6 ($ZnCH_2CMe_2Ph$), 37.4 ($ZnCH_2CMe_2Ph$), 117.6 (s, *p*-*C*H$_{Ar}$ $BAr^F{}_4$), 124.3 (*o*-*C*H$_{Ar}$ $ZnCH_2CMe_2Ph$), 124.7 (c, $^1J_{CF}$ = 272 Hz, CF_3 $BAr^F{}_4$), 124.8 (*p*-*C*H$_{Ar}$ $ZnCH_2CMe_2Ph$), 127.4 (*m*-*C*H$_{Ar}$ $ZnCH_2CMe_2Ph$), 127.5 (*p*-*C*$_{N-Ar}$), 127.9 (3-*C*H$_{Py}$), 128.9 (c, $^2J_{CF}$ = 31 Hz, *C*-CF_3 $BAr^F{}_4$), 129.8 (*m*-*C*H$_{N-Ar}$), 134.9 (s, *o*-*C*H$_{Ar}$ $BAr^F{}_4$), 137.1 (*o*-*C*$_{N-Ar}$), 140.9 (*i*-*C*$_{N-Ar}$), 145.7 (4-*C*H$_{Py}$), 149.0 (2-*C*$_{Py}$), 154.5 (*i*-*C*$_{Ar}$ $ZnCH_2CMe_2Ph$), 161.8 (c, $^1J_{CB}$ = 50 Hz, *i*-*C*$_{Ar}$ $BAr^F{}_4$), 166.6 (Me-*C*N). $^{19}F\{^1H\}$ NMR (376 MHz, 25 ºC, CD_2Cl_2): δ -62.8. IR (Nujol, cm^{-1}): 1610, 1594, ν(C=N) in (BIP); 1279, 1118 and 886, ν(B-C) for $[BAr^F{}_4]^-$. Anal. Calcd for $C_{69}H_{56}BF_{24}N_3Zn$: C, 56.79; H, 3.87; N, 2.88. Found: C, 56.85; H, 3.93 N, 2.48 %.