Electronic Supplementary Material (ESI) for Dalton Transactions.

Magnesium, Calcium and Zinc [N_2N'] Heteroscorpionate Complexes

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SUPPORTING INFORMATION

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General considerations

All manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or drybox procedures. Solvents were pre-dried over activated 4 Å molecular sieves and refluxed over sodium (toluene), sodium/potassium (pentane, diethyl ether), or calcium hydride (dichloromethane) under a dinitrogen atmosphere and collected by distillation. Alternatively, solvents were degassed by sparging with dinitrogen and dried by passing through a column of activated alumina. Deuterated solvents were dried over potassium (C_6D_6) or P_2O_5 (CD_2Cl_2), distilled under reduced pressure, and stored under dinitrogen in J. Young Teflon valve ampoules. Solution NMR samples were prepared under a dinitrogen atmosphere in a drybox, in 5 mm Wilmad NMR tubes possessing Young's Teflon valves. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer or a Bruker AVII 500 spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). ^{7}Li NMR spectra are referenced relative to LiCl. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Where necessary, ^{1}H and ^{13}C assignments were assisted by the use of two-dimensional ^{1}H-^{1}H and ^{1}H-^{13}C correlation experiments. IR spectra were recorded on a Perkin-Elmer 1710 or Nicolet magna 560 FTIR spectrometer. Samples were prepared in a drybox as Nujol mulls between NaCl plates. IR data are quoted as wavenumbers (cm^{-1}) within the range 4000−400 cm^{-1}. Mass spectra were recorded by the mass spectrometry service of the University of Oxford Inorganic Chemistry Laboratory. Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University. The compounds $H_2C(^tBu_2pz)_2$,[1] $HC(Me_2pz)_2SiMe_2N(H)^iPr$,[2] $Ca\{N(SiMe_3)_2\}(thf)_2$,[3] $Mg\{N(SiMe_3)_2\}_2$[3] and $Mg\{N(SiHMe_2)_2\}_2$[3] were prepared according to literature procedures. ε-Caprolactone was dried over freshly ground CaH_2, stored over molecular sieves (4 Å)at 4 °C and distilled before use. *rac*-lactide was recrystallized twice from toluene and subsequently sublimed twice prior to use. All other reagents were purchased and used without further purification. All other reagents were purchased and used without further purification. Polymer molecular weights (M_n, M_w) were determined by GPC using a Polymer Laboratories Plgel Mixed-D column (300 mm length, 7.5 mm diameter) and a Polymer Laboratories PL-GPC50 Plus instrument equipped with a refractive index detector. Tetrahydrofuran (HPLC grade) was used as an eluent at 30 °C with a rate of 1 mL min^{-1}. Linear polystyrenes were used as primary calibration standards, and Mark-Houwink corrections for poly(ε-CL) or poly(*rac*-LA) in thf were applied for the experimental samples.[4]

Additional synthetic details

HC(Me$_2$pz)$_2$SiMe$_2$N(H)^{t}Bu

To a stirred solution of HC(Me$_2$pz)$_2$SiMe$_2$Cl (4.00 g, 13.5 mmol) in Et$_2$O (60 mL) at 0 °C, was added NH$_2$^{t}Bu (4.25 mL, 40.4 mmol). The resultant white suspension was stirred for 4 h at 0 °C, filtered, dried under reduced pressure and extracted into pentane (3 x 20 mL). The volatiles were removed under reduced pressure to afford HC(Me$_2$pz)$_2$SiMe$_2$N(H)^{t}Bu as a clear yellow oil. Yield: 3.82 g (85%). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 6.06 (1 H, s, HC(Me$_2$pz)$_2$), 5.65 (2 H, s, N$_2$C$_3$HMe$_2$), 2.17 (6 H, s, 3-N$_2$C$_3$HMe$_2$), 1.89 (6 H, s, 5-N$_2$C$_3$HMe$_2$), 1.12 (9 H, s, CMe$_3$), 0.45 (6 H, s, SiMe). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 293 K): δ 146.5 (3-N$_2$C$_3$HMe$_2$), 140.1 (5-N$_2$C$_3$HMe$_2$), 106.4 (4-N$_2$C$_3$HMe$_2$), 69.6 (HC(Me$_2$pz)$_2$), 49.6 (CMe$_3$), 33.9 (CMe$_3$), 13.7 (3-N$_2$C$_3$HMe$_2$), 10.9 (5-N$_2$C$_3$HMe$_2$), 1.7 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 3368 (m), 2959 (s), 2867 (s), 1551 (m), 1463 (s), 1417 (s) 1358 (m), 1322 (m), 1274 (m), 1246 (m), 1226 (m), 1027 (m), 972 (w), 860 (m), 800 (s), 777 (m), 691 (s). EI-MS: *m/z* = 333 (100%) [M]$^+$, 238 (15%) [M-Me$_2$pz]$^+$. Anal. found (calcd. for C$_{17}$H$_{31}$N$_5$Si): C, 60.6 (61.2); H, 9.4 (9.4); N, 21.0 (20.4)%.

HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)^{t}Bu

To a stirred solution of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl (4.00 g, 8.60 mmol) in Et$_2$O (60 mL) at 0 °C, was added NH$_2$^{t}Bu (2.71 mL, 25.8 mmol). The resultant colourless suspension was stirred at 40 °C for 6 days. The suspension was filtered, dried under reduced pressure and extracted into pentane (3 x 20 mL). The volatiles were removed under reduced pressure to afford HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)^{t}Bu as a thick, colourless oil. Yield: 4.27 g (99%). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 7.07 (1 H, s, HC(^{t}Bu$_2$pz)$_2$), 6.03 (2 H, s, N$_2$C$_3$H^{t}Bu$_2$), 2.14 (1 H, s, NH), 1.42 (9 H, s, CMe$_3$), 1.17 (18 H, s, 3-N$_2$C$_3$H^{t}Bu$_2$), 1.16 (18 H, s, 5-N$_2$C$_3$H^{t}Bu$_2$), 0.50 (6 H, s, SiMe). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 293 K): δ 158.2 (3-N$_2$C$_3$H^{t}Bu$_2$), 154.2 (5-N$_2$C$_3$H^{t}Bu$_2$), 102.5 (4-N$_2$C$_3$H^{t}Bu$_2$), 76.1-(HC(^{t}Bu$_2$pz)$_2$), 49.8 (CMe$_3$), 34.1 (CMe$_3$), 32.4 (3-N$_2$C$_3$H(CMe$_3$)$_2$), 32.4 (5-N$_2$C$_3$H(CMe$_3$)$_2$), 30.9 (3-N$_2$C$_3$H(CMe$_3$)$_2$), 30.5 (5-N$_2$C$_3$H(CMe$_3$)$_2$), 3.5 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 3335 (w), 2710 (w), 2600 (w), 1536 (s), 1360 (s), 1343 (s), 1318 (w), 1275 (s), 1234 (s), 1177 (w), 1157 (w), 1067 (m), 1021 (s), 1003 (s), 931 (w), 868 (m). EI-MS: *m/z* = 501 (6%) [M]$^+$, 444 (100%) [M-^{t}Bu]$^+$, 429 (6%) [M-N(H)^{t}Bu]$^+$. Anal. found (calcd. for C$_{29}$H$_{55}$N$_5$Si): C, 69.5 (69.4); H, 11.0 (11.1); N, 14.0 (14.0)%.

HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)Ph

To a stirred solution of NH$_2$Ph (0.78 mL, 8.60 mmol) in Et$_2$O (20 mL), was added NEt$_3$ (2.40 mL, 17.2 mmol). This mixture was slowly added to a stirred solution of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl (4.00 g, 8.60 mmol) in Et$_2$O (50 mL). The resultant white suspension was stirred for 20 days. The suspension was filtered, the solid washed with Et$_2$O (3 x 10 mL) and the volatiles removed under reduced pressure to afford a colourless, oily solid which was extracted into pentane (3 x 10 mL) and dried under reduced pressure. The colourless solid was recrystallised from pentane (20 mL) at -30 °C, filtered and dried under reduced pressure to afford HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)Ph as a colourless solid. Yield: 4.40 g (98%). Diffraction-quality crystals were grown from a saturated pentane solution at -30 °C. ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 7.17−7.12 (3 H, overlapping t and s, 3-C$_6$H$_5$ and HC(^{t}Bu$_2$pz)$_2$), 6.82 (2 H, d, $^3J_{HH}$ = 8.2 Hz, 2-C$_6$H$_5$), 6.76 (1 H, t, $^3J_{HH}$ = 7.3 Hz, 4-C$_6$H$_5$), 6.02 (2 H, s, N$_2$C$_3$H^{t}Bu$_2$), 5.03 (1 H, s, NH), 1.40 (18 H, s, 3-N$_2$C$_3$H^{t}Bu$_2$), 1.10 (18 H, s, 5-N$_2$C$_3$H^{t}Bu$_2$), 0.52 (6 H, s, SiMe). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 293 K): δ 158.9 (3-N$_2$C$_3$H^{t}Bu$_2$), 154.3 (5-N$_2$C$_3$H^{t}Bu$_2$), 147.5

(1-C_6H_5), 129.6 (3-C_6H_5), 118.2 (4-C_6H_5), 117.1 (2-C_6H_5), 102.7 (4-$N_2\underline{C}_3H{}^t Bu_2$), 74.6 ($H\underline{C}({}^t Bu_2pz)_2$), 32.2 (3-$N_2C_3H(\underline{C}Me_3)_2$), 32.2 (5-$N_2C_3H(\underline{C}Me_3)_2$), 30.7 (3-$N_2C_3H(C\underline{Me}_3)_2$), 30.3 (5-$N_2C_3H(C\underline{Me}_3)_2$), 0.0 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 3315 (w), 1602 (m), 1586 (w), 1535 (m), 1499 (s), 1398 (m), 1342 (m), 1319 (m), 1298 (s), 1238 (m), 1212 (m), 1177 (w), 1153 (w), 1069 (m), 1004 (m), 996 (m), 904 (m), 882 (w), 868 (w), 750 (m), 690 (w). EI-MS: *m/z* = 429 (66%) $[M\text{-}N(H)Ph]^+$. Anal. found (calcd. for $C_{31}H_{51}N_5Si$): C, 71.3 (71.4); H, 9.8 (9.9); N, 13.3 (13.4)%.

$[Li\{HC({}^t Bu_2pz)_2SiMe_2N{}^i Pr\}]_n$ (1)

$HC({}^t Bu_2pz)_2SiMe_2N(H){}^i Pr$ (0.970 g, 2.00 mmol) was dissolved in pentane (60 mL) and cooled to -78 °C. ^{n}BuLi (1.5 mL, 2.4 mmol; 1.6 M in hexanes) was diluted with pentane (10 mL), similarly cooled and then added dropwise to the pro-ligand solution to afford a clear, colourless solution. The reaction mixture was stirred for 6 h, during which time a colourless precipitate formed. The reaction mixture was allowed to stand overnight before the solid was filtered off, washed with cold (-78 °C) pentane (3 x 10 mL) and dried under reduced pressure. NMR spectral analysis showed the presence of a small amount of protio ligand. ^{n}BuLi (1.25 mL, 2.00 mmol; 1.6 M in hexanes) was added to reaction mixture, redissolved in pentane (60 mL) at -78 °C. This was allowed to stir for 6 h, concentrated to 40 mL and allowed to stand overnight before the colourless solid was filtered off, washed with cold (-78 °C) pentane (3 x 5 mL) and dried under reduced pressure to yield complex **1** as a colourless powder. Yield: 0.05 g (5%).^{1}H NMR (C_5D_5N, 299.9 MHz, 293 K): 6.73 (1 H, s, $\underline{H}C({}^t Bu_2pz)_2$, 6.22 (2 H, s, $N_2C_3\underline{H}{}^t Bu_2$), 3.74 (1 H, m, $\underline{H}CMe_2$), 1.46 (18 H, s, 3-$N_2C_3H{}^t\underline{Bu}_2$), 1.35 (18 H, s, 5-$N_2C_3H{}^t\underline{Bu}_2$), 1.18 (6 H, d, $^3J_{HH}$ = 6.2 Hz, $HC\underline{Me}_2$), 0.32 (6 H, s, SiMe) ppm. IR (NaCl plates, Nujol): 1536 (w), 1461 (s), 1365 (m), 1319 (w), 1249 (w), 1235 (w), 1211 (w), 1157 (w), 1113 (w), 1025 (m), 881 (w), 795 (m) cm^{-1}. Anal. Found (calcd for $C_{28}H_{52}LiN_5Si$): C, 67.9 (68.1); H, 10.6 (10.6); N, 14.2 (14.2)%.

$[Li\{HC({}^t Bu_2pz)_2SiMe_2N{}^t Bu\}]_n$ (2)

$HC({}^t Bu_2pz)_2SiMe_2N(H){}^t Bu$ (0.60 g, 1.20 mmol) was dissolved in pentane (40 mL) and cooled to -78 °C. ^{n}BuLi (0.74 mL, 1.5 mmol; 1.6 M in hexanes) was diluted with pentane (10 mL), similarly cooled and then added dropwise to the pro-ligand solution to afford a clear, colourless solution. The reaction mixture was stirred for 6 h and was then concentrated under reduced pressure to the point of the precipitation of a colourless solid. The reaction mixture was allowed to stand overnight, whereby crystallisation occurred. The colourless solid was filtered off, washed with cold (-78 °C) pentane (3 x 10 mL) and dried under reduced pressure to afford complex **2** as a colourless powder. Yield: 0.08 g (13%). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): 6.44 (1 H, s, $\underline{H}C({}^t Bu_2pz)_2$, 5.93 (2 H, s, $N_2C_3\underline{H}{}^t Bu_2$), 1.60 (18 H, s, 3-$N_2C_3H{}^t\underline{Bu}_2$), 1.30 (9 H, s, $HNC\underline{Me}_3$), 1.27 (18 H, s, 5-$N_2C_3H{}^t\underline{Bu}_2$), 0.25 (6 H, s, SiMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K): 152.8 (3-$N_2\underline{C}_3H{}^t Bu_2$), 150.9 (5-$N_2\underline{C}_3H{}^t Bu_2$), 110.3 (4-$N_2\underline{C}_3H{}^t Bu_2$), 100.9 ($\underline{H}C({}^t Bu_2pz)_2$), 52.2 ($HN\underline{C}Me_3$), 39.2 ($HNC\underline{Me}_3$), 32.8 (5-$N_2C_3H\underline{C}(CMe_3)_2$), 32.2 (3-$N_2C_3H\underline{C}(CMe_3)_2$), 31.9 (5-$N_2C_3H\underline{C}(CMe_3)_2$), 30.5 (3-$N_2C_3H\underline{C}(CMe_3)_2$), 5.5 (SiMe). IR (NaCl plates, Nujol): 1536 (w), 1342 (m), 1303 (w), 1247 (m), 1227 (m), 1109 (m), 1064 (w), 1023 (w), 855 (w), 751 (w) cm^{-1}. EI-MS: *m/z*: 429 $[M\text{-}LiN{}^t Bu]^+$ (35%). Anal. Found (calcd for $C_{29}H_{54}LiN_5Si$): C, 68.6 (68.6); H, 10.8 (10.7); N, 13.7 (13.8)%.

$[Li\{HC({}^t Bu_2pz)_2SiMe_2NPh\}]_n$ (3)

$HC({}^t Bu_2pz)_2SiMe_2N(H)Ph$ (0.50 g, 0.96 mmol) was dissolved in pentane (40 mL) and cooled to -78 °C. ^{n}BuLi (0.750 mL, 1.20 mmol; 1.6 M in hexanes) was diluted with pentane (10 mL), similarly cooled and then added

dropwise to the pro-ligand solution to afford a colourless precipitate and pale-yellow solution. The reaction mixture was stirred for 6 h. The reaction mixture was allowed to stand overnight, whereby crystallisation occurred. The white solid was filtered off, washed with cold (-78 °C) pentane (3 x 10 mL) and dried under reduced pressure to afford complex **3** as a colourless powder. Yield: 0.04 g (8%). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): 7.35 (2 H, app. t, app. $^{3}J_{HH}$ = 7.2 and 7.7 Hz, 3-C_6H_5), 6.89 (2 H, dd, $^{3}J_{HH}$ = 7.2 Hz and $^{4}J_{HH}$ = 1.1 Hz, 2-C_6H_5), 6.72 (1 H, tt, $^{3}J_{HH}$ = 7.7 Hz and $^{4}J_{HH}$ = 1.1 Hz, 4-C_6H_5), 6.50 (1 H, s, H$\underline{C}$(^{t}Bu$_2$pz)$_2$), 5.92 (2 H, s, $N_2C_3\underline{H}$^{t}Bu$_2$), 1.22 (18 H, s, 3-$N_2C_3H$$^{t}\underline{Bu}_2$), 1.19 (18 H, s, 5-$N_2C_3H$$^{t}\underline{Bu}_2$), 0.24 (6 H, s, SiMe) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): 160.9 (1-C_6H_5), 159.9 (3-$N_2\underline{C}_3H$^{t}Bu$_2$), 153.4 (5-$N_2\underline{C}_3H$^{t}Bu$_2$), 129.7 (3-C_6H_5), 121.8 (2-C_6H_5), 111.8 (4-C_6H_5), 101.4 (4-$N_2\underline{C}_3H$^{t}Bu$_2$), 71.4 (H$\underline{C}$(^{t}Bu$_2$pz)$_2$), 32.8 (5-$N_2C_3H(\underline{C}Me_3)_2$), 32.1 (3-$N_2C_3H(\underline{C}Me_3)_2$), 31.7 (3-$N_2C_3H(C\underline{Me}_3)_2$), 30.2 (5-$N_2C_3H(C\underline{Me}_3)_2$), 0.39 (SiMe). IR (NaCl plates, Nujol): 1587 (m), 1535 (m), 1363 (m), 1320 (m), 1237 (s), 1209 (m), 1171 (w), 1028 (w), 1011 (m), 998 (s), 883 (w), 849 (w), 823 (m), 749 (w), 699 (m), 641 (w), 571 (w) cm^{-1}. EI-MS: *m/z*: 430 [M-LiNPh]$^{+}$ (100%), 371 [M-$SiMe_2N(Li)Ph]^{+}$ (32%). Anal. Found (calcd for $C_{31}H_{50}LiN_5Si$): C, 70.6 (70.6); H, 9.6 (9.6); N, 13.2 (13.3)%.

Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}Me (6)

To a stirred solution of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)Ph (0.50 g, 0.96 mmol) in benzene (30 mL), was added MeMgCl (0.96 mL, 2.87 mmol; 3.0 M in thf). The resultant yellow solution was stirred for 30 h. Volatiles were removed under reduced pressure to afford a colourless solid, which was extracted into pentane (3 x 10 mL) and dried under reduced pressure. The solid was recrystallised from pentane (15 mL) at -80 °C, filtered and dried under reduced pressure to afford complex **6** as a colourless solid. Yield = 0.36 g (67%). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.34−7.27 (4 H, overlapping 2 x m, 2-C_6H_5 and 3-C_6H_5), 6.77 (1 H, m, 4-C_6H_5), 6.52 (1 H, s, H$\underline{C}$(^{t}Bu$_2$pz)$_2$), 5.96 (2 H, s, $N_2C_3\underline{H}$^{t}Bu$_2$), 1.46 (18 H, s, 3-$N_2C_3H$$^{t}\underline{Bu}_2$), 1.10 (18 H, s, 5-$N_2C_3H$$^{t}\underline{Bu}_2$), 0.17 (6 H, s, SiMe), -0.11 (3 H, s, MgMe). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 164.1 (3-$N_2\underline{C}_3H$^{t}Bu$_2$), 157.1 (1-C_6H_5), 153.9 (5-$N_2\underline{C}_3H$^{t}Bu$_2$), 129.2 (3-C_6H_5), 123.3 (2-C_6H_5), 115.4 (4-C_6H_5), 103.4 (4-$N_2\underline{C}_3H$^{t}Bu$_2$), 69.3 (H$\underline{C}$(^{t}Bu$_2$pz)$_2$), 33.0 (3-$N_2C_3H(\underline{C}Me_3)_2$), 32.3 (5-$N_2C_3H(\underline{C}Me_3)_2$), 31.5 (3-$N_2C_3H(C\underline{Me}_3)_2$), 30.7 (5-$N_2C_3H(C\underline{Me}_3)_2$), 0.1 (SiMe), -4.8 (MgMe). IR (NaCl plates, Nujol mull, cm^{-1}): 1587 (m), 1543 (w), 1491 (m), 1367 (m), 1355 (m), 1281 (s), 1245 (s), 1209 (m), 1183 (w), 1056 (m), 1025 (m), 991 (m), 949 (s), 867 (m), 831 (m), 766 (m), 754 (m). EI-MS: *m/z* = 429 (35%) [HC(^{t}Bu$_2$pz)$_2$SiMe$_2$]$^{+}$. Anal. found (calcd. for $C_{32}H_{53}MgN_5Si$): C, 68.2 (68.6); H, 9.4 (9.5); N, 12.2 (12.5)%.

Mg{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}^{n}Bu (7)

To a stirred solution of HC(Me$_2$pz)$_2$SiMe$_2$N(H)^{i}Pr (0.500 g, 1.56 mmol) in benzene (30 mL), was added Mg^{n}Bu$_2$ (1.56 mL, 1.56 mmol; 1.0 M in heptanes). The resultant orange solution was stirred for 12 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 x 5 mL, -78 °C) and dried under reduced pressure to afford complex **7** as a bright orange solid. Yield = 0.41 g (66%). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 5.29 (2 H, s, $N_2C_3\underline{H}Me_2$), 5.10 (1 H, s, H$\underline{C}$(Me$_2$pz)$_2$), 3.66 (1 H, sept, $^{3}J_{HH}$ = 6.1 Hz, $\underline{H}CMe_2$), 2.33 (2 H, m, 2-Mg^{n}Bu), 2.15 (6 H, s, 3-$N_2C_3H\underline{Me}_2$), 1.95 (2 H, sext, $^{3}J_{HH}$ = 7.3 Hz, 3-Mg^{n}Bu), 1.61 (6 H, s, 5-$N_2C_3H\underline{Me}_2$), 1.54 (6 H, d, $^{3}J_{HH}$ = 6.3 Hz, HC$\underline{Me}_2$), 1.35 (3 H, t, $^{3}J_{HH}$ = 7.3 Hz, 4-Mg^{n}Bu), 0.41 (2 H, m, 1-Mg^{n}Bu), 0.00 (6 H, s, SiMe). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 150.2 (3-$N_2\underline{C}_3HMe_2$), 139.0 (5-$N_2\underline{C}_3HMe_2$), 105.5 (4-$N_2\underline{C}_3HMe_2$), 63.8 (H$\underline{C}$(Me$_2$pz)$_2$), 46.9 (H$\underline{C}Me_2$), 33.8 (2-Mg^{n}Bu), 33.0 (3-Mg^{n}Bu), 32.3 (HC$\underline{Me}_2$), 14.7 (1-Mg^{n}Bu), 13.0 (3-$N_2C_3H\underline{Me}_2$), 10.4 (5-$N_2C_3H\underline{Me}_2$), 8.9 (4-Mg^{n}Bu), 0.13 (SiMe). IR

(NaCl plates, Nujol mull, cm^{-1}): 2361 (m), 1558 (s), 1533 (w), 1521 (m), 1457 (s), 1377 (s), 1309 (m), 1282 (w), 1259 (m), 1239 (m), 1189 (m), 1162 (m), 1043 (s), 978 (m), 902 (s), 817 (w), 801 (m), 755 (w), 723 (m). EI-MS: *m/z* = 356 (40%) $[M\text{-}^{i}Pr]^{+}$, 203 (20%) $[HC(Me_2pz)_2]^{+}$. Anal. found (calcd. for $C_{20}H_{37}MgN_5Si$): C, 59.9 (60.0); H, 9.3 (9.3); N, 17.4 (17.5)%.

Mg{HC(Me$_2$pz)$_2$SiMe$_2$N^{t}Bu}^{n}Bu (8)

To a stirred solution of HC(Me$_2$pz)$_2$SiMe$_2$N(H)^{t}Bu (0.500 g, 1.49 mmol) in benzene (30 mL), was added Mg^{n}Bu$_2$ (1.49 mL, 1.49 mmol; 1.0 M in heptanes). The resultant yellow solution was stirred for 16 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 x 5 mL, -78 °C) and dried under reduced pressure to afford complex **8** as a thick, orange oil. Yield = 0.25 g (41%). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 5.30 (2 H, s, $N_2C_3\underline{H}Me_2$), 5.02 (1 H, s, $\underline{H}C(Me_2pz)_2$), 2.26 (2 H, m, 2-Mg^{n}Bu), 2.18 (6 H, s, 3-$N_2C_3H\underline{Me}_2$), 1.91 (2 H, app. sext, app. $^3J_{HH}$ = 7.5 Hz, 3-Mg^{n}Bu), 1.63 (6 H, s, 5-$N_2C_3H\underline{Me}_2$), 1.61 (9 H, s, $C\underline{Me}_3$), 1.32 (3 H, t, $^3J_{HH}$ = 7.3 Hz, 4-Mg^{n}Bu), 0.36 (2 H, m, 1-Mg^{n}Bu), 0.05 (6 H, s, SiMe). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 149.3 (3-$N_2\underline{C}_3HMe_2$), 138.9 (5-$N_2\underline{C}_3HMe_2$), 105.6 (4-$N_2\underline{C}_3HMe_2$), 64.5 ($H\underline{C}(Me_2pz)_2$), 51.6 ($\underline{C}Me_3$), 37.9 ($C\underline{Me}_3$), 33.7 (2-Mg^{n}Bu), 33.1 (3-Mg^{n}Bu), 14.6 (1-Mg^{n}Bu), 12.9 (3-$N_2C_3H\underline{Me}_2$), 10.4 (5-$N_2C_3H\underline{Me}_2$), 9.6 (4-Mg^{n}Bu), 3.4 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2357 (m), 1562 (s), 1501 (s), 1441 (m), 1352 (s), 1301 (s), 1224 (m), 1208 (w), 1177 (m), 1130 (m), 1031 (m), 915 (m), 897 (m), 858 (w), 814 (m), 763 (m), 744 (m). EI-MS: *m/z* = 413 (40%) $[M]^{+}$. Anal. found (calcd. for $C_{21}H_{39}MgN_5Si$): C, 60.7 (60.9); H, 9.5 (9.5); N, 17.1 (16.9)%.

Mg{HC(Me$_2$pz)$_2$SiMe$_2$NAd}^{n}Bu (9)

To a stirred solution of HC(Me$_2$pz)$_2$SiMe$_2$N(H)Ad (0.500 g, 1.21 mmol) in benzene (30 mL), was added Mg^{n}Bu$_2$ (1.21 mL, 1.21 mmol; 1.0 M in heptanes). The resultant orange solution was stirred for 16 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 x 5 mL, -78 °C) and dried under reduced pressure to afford complex **9** as a thick, dark orange oil. Yield = 0.32 g (54%). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 5.30 (2 H, s, $N_2C_3\underline{H}Me_2$), 5.02 (1 H, s, $\underline{H}C(Me_2pz)_2$), 2.26 (2 H, m, 2-Mg^{n}Bu), 2.19 (6 H, s, 3-$N_2C_3H\underline{Me}_2$), 2.07 (6 H, m, Ad), 1.93 (2 H, app. sext, app. $^3J_{HH}$ = 7.2 Hz, 3-Mg^{n}Bu), 1.82 (3 H, m, Ad), 1.70 (6 H, m, Ad) 1.64 (6 H, s, 5-$N_2C_3H\underline{Me}_2$), 1.33 (3 H, t, $^3J_{HH}$ = 7.2 Hz, 4-Mg^{n}Bu), 0.36 (2 H, m, 1-Mg^{n}Bu), 0.08 (6 H, s, SiMe). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 149.3 (3-$N_2\underline{C}_3HMe_2$), 138.9 (5-$N_2\underline{C}_3HMe_2$), 105.6 (4-$N_2\underline{C}_3HMe_2$), 64.7 ($H\underline{C}(Me_2pz)_2$), 52.0 (Ad, 3 C, 6 H), 51.7 (Ad, 1 C, 0 H), 37.3 (Ad, 3 C, 6 H), 33.9 (2-Mg^{n}Bu), 33.0 (3-Mg^{n}Bu), 31.5 (Ad, 3 C, 3 H), 14.7 (1-Mg^{n}Bu), 13.0 (3-$N_2C_3H\underline{Me}_2$), 10.4 (5-$N_2C_3H\underline{Me}_2$), 9.8 (4-Mg^{n}Bu), 4.1 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2312 (m), 1570 (m), 1416 (m), 1374 (s), 1261 (s), 1190 (m), 1161 (w), 1076 (w), 1016 (m), 954 (m), 871 (w), 812 (s), 781 (m), 739 (w). EI-MS: *m/z* = 342 (30%) $[M\text{-}NAd]^{+}$, 275 (10%) $[HC(Me_2pz)_2SiMe_2]^{+}$. Anal. found (calcd. for $C_{27}H_{45}MgN_5Si$): C, 65.8 (65.9); H, 9.2 (9.2); N, 14.1 (14.2)%.

Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N^{i}Pr}^{n}Bu (11)

To a stirred solution of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)^{i}Pr (0.500 g, 1.02 mmol) in benzene (30 mL), was added Mg^{n}Bu$_2$ (2.04 mL, 2.04 mmol; 1.0 M in heptanes). The resultant yellow solution was stirred for 4 days. Volatiles were removed under reduced pressure to afford a colourless solid, which was washed with cold pentane (3 x 5 mL, -78 °C) and dried under reduced pressure. The solid was recrystallised from pentane (15 mL) at -80 °C, filtered and dried under reduced pressure to afford complex **11** as a colourless solid. Yield = 0.27 g (47%). ^{1}H NMR

(C_6D_6, 299.9 MHz, 293 K): δ 6.48 (1 H, s, H<u>C</u>(^{t}Bu$_2$pz)$_2$), 5.94 (2 H, s, N$_2$C$_3$H^{t}Bu$_2$), 3.66 (1 H, sept, $^3J_{HH}$ = 6.2 Hz, H<u>C</u>Me$_2$), 2.27 (2 H, m, 2-Mg^{n}Bu), 2.00 (2 H, m, 3-Mg^{n}Bu), 1.54 (6 H, d, $^3J_{HH}$ = 6.2 Hz, HC<u>Me</u>$_2$), 1.50 (18 H, s, 3-N$_2$C$_3$H^t<u>Bu</u>$_2$), 1.26 (3 H, m, 4-Mg^{n}Bu), 1.14 (18 H, s, 5-N$_2$C$_3$H^t<u>Bu</u>$_2$), 0.47 (2 H, m, 1-Mg^{n}Bu), 0.06 (6 H, s, SiMe). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 165.2 (3-N$_2$<u>C</u>$_3$H^{t}Bu$_2$), 154.1 (5-N$_2$<u>C</u>$_3$H^{t}Bu$_2$), 103.8 (4-N$_2$<u>C</u>$_3$H^{t}Bu$_2$), 67.8 (H<u>C</u>(^{t}Bu$_2$pz)$_2$), 48.1 (H<u>C</u>Me$_2$), 33.5 (HC<u>Me</u>$_2$), 33.3 (3-N$_2$C$_3$H(<u>C</u>Me$_3$)$_2$), 33.1 (2-Mg^{n}Bu), 32.9 (3-Mg^{n}Bu), 32.6 (5-N$_2$C$_3$H(<u>C</u>Me$_3$)$_2$), 31.8 (3-N$_2$C$_3$H(C<u>Me</u>$_3$)$_2$), 30.9 (5-N$_2$C$_3$H(C<u>Me</u>$_3$)$_2$), 16.1 (1-Mg^{n}Bu), 14.9 (4-Mg^{n}Bu), 0.42 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 1543 (s), 1363 (m), 1312 (s), 1229 (s), 1206 (w), 1134 (w), 1023 (w), 1003 (w), 967 (w), 930 (w), 774 (s), 686 (w). EI-MS: *m/z* = 429 (80%) [HC(^{t}Bu$_2$pz)$_2$SiMe$_2$]$^+$. Anal. found (calcd. for $C_{32}H_{61}MgN_5Si$): C, 67.1 (67.6); H, 10.8 (10.8); N, 12.3 (12.3)%.

Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}{N(SiHMe$_2$)$_2$} (15)

To a stirred solution of Mg{N(SiHMe$_2$)$_2$}$_2$ (0.400 g, 1.41 mmol) in benzene (20 mL), was added a solution of HC(Me$_2$pz)$_2$SiMe$_2$N(H)Ph (0.500 g, 1.41 mmol) in benzene (20 mL). The resultant orange solution was stirred for 16 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 x 5 mL, -78 °C) and dried under reduced pressure to afford complex **15** as an orange solid. Yield = 0.51 g (71%). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.32 (2 H, app. t, app. $^3J_{HH}$ = 7.8 Hz, 3-C$_6$H$_5$), 7.01 (2 H, app. d, app. $^3J_{HH}$ = 7.5 Hz, 2-C$_6$H$_5$), 6.82 (1 H, app. t, app. $^3J_{HH}$ = 7.2 Hz, 4-C$_6$H$_5$), 5.34−5.30 (4 H, overlapping m and s, N(Si<u>H</u>Me$_2$)$_2$ and N$_2$C$_3$<u>H</u>Me$_2$), 4.99 (1 H, s, <u>H</u>C(Me$_2$pz)$_2$), 2.38 (6 H, s, 3-N$_2$C$_3$H<u>Me</u>$_2$), 1.49 (6 H, s, 5-N$_2$C$_3$H<u>Me</u>$_2$), 0.52 (12 H, d, $^3J_{HH}$ = 3.0 Hz, N(SiH<u>Me</u>$_2$)$_2$), -0.09 (6 H, s, SiMe). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 156.8 (1-C$_6$H$_5$), 150.8 (3-N$_2$<u>C</u>$_3$HMe$_2$), 139.9 (5-N$_2$<u>C</u>$_3$HMe$_2$), 129.2 (3-C$_6$H$_5$), 124.1 (2-C$_6$H$_5$), 116.4 (4-C$_6$H$_5$), 106.2 (4-N$_2$<u>C</u>$_3$HMe$_2$), 63.0 (H<u>C</u>(Me$_2$pz)$_2$), 13.8 (3-N$_2$C$_3$H<u>Me</u>$_2$), 10.3 (5-N$_2$C$_3$H<u>Me</u>$_2$), 4.0 (N(SiHMe$_2$)$_2$), -1.2 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2960 (w), 2361 (m), 2099 (s), 2040 (m), 1587 (s), 1556 (s), 1464 (s), 1419 (m), 1378 (m), 1312 (m), 1281 (s), 1240 (s), 1172 (m), 1150 (w), 1017 (s), 995 (w), 930 (m), 889 (s), 832 (m), 794 (m), 770 (m), 690 (m). EI-MS: *m/z* = 508 (85%) [M]$^+$, 376 (70%) [M-N(SiHMe$_2$)$_2$]$^+$. Anal. found (calcd. for $C_{23}H_{40}MgN_6Si_3$): C, 54.1 (54.2); H, 7.8 (7.9); N, 16.4 (16.5)%.

Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (19)

To a stirred solution of Mg{N(SiMe$_3$)$_2$}$_2$ (0.480 g, 1.41 mmol) in benzene (20 mL), was added a solution of HC(Me$_2$pz)$_2$SiMe$_2$N(H)Ph (0.500 g, 1.41 mmol) in benzene (20 mL). The resultant yellow solution was stirred for 14 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 x 5 mL, -78 °C) and dried under reduced pressure to afford complex **19** as an light orange solid. Yield = 0.58 g (77%). Diffraction-quality crystals were grown from slow diffusion of diethyl ether into a concentrated toluene solution.^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.30 (2 H, t, $^3J_{HH}$ = 7.6 Hz, 3-C$_6$H$_5$), 6.98 (2 H, d, $^3J_{HH}$ = 7.5 Hz, 2-C$_6$H$_5$), 6.83 (1 H, t, $^3J_{HH}$ = 7.2 Hz, 4-C$_6$H$_5$), 5.37 (2 H, s, N$_2$C$_3$<u>H</u>Me$_2$), 4.99 (1 H, s, <u>H</u>C(Me$_2$pz)$_2$), 2.42 (6 H, s, 3-N$_2$C$_3$H<u>Me</u>$_2$), 1.49 (6 H, s, 5-N$_2$C$_3$H<u>Me</u>$_2$), 0.41 (18 H, s, N(SiMe$_3$)$_2$), -0.13 (SiMe). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 157.0 (1-C$_6$H$_5$), 150.6 (3-N$_2$<u>C</u>$_3$HMe$_2$), 140.0 (5-N$_2$<u>C</u>$_3$HMe$_2$), 129.2 (3-C$_6$H$_5$), 125.3 (2-C$_6$H$_5$), 117.0 (4-C$_6$H$_5$), 106.2 (4-N$_2$<u>C</u>$_3$HMe$_2$), 62.9 (H<u>C</u>(Me$_2$pz)$_2$), 14.1 (3-N$_2$C$_3$H<u>Me</u>$_2$), 10.4 (5-N$_2$C$_3$H<u>Me</u>$_2$), 6.3 (N(SiMe$_3$)$_2$), -1.1 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2972 (w), 2728 (m), 1581 (s), 1521 (s), 1419 (m), 1377 (s), 1312 (s), 1243 (s), 1172 (m), 1096 (s), 1005 (s), 959 (m), 882 (m), 826 (s), 773 (m). EI-MS: *m/z* = 536 (40%) [M]$^+$, 376 (85%) [M-N(SiMe$_3$)$_2$]$^+$. Anal. found (calcd. for $C_{25}H_{44}MgN_6Si_3$): C, 55.8 (55.9); H, 8.3 (8.3); N, 15.6 (15.7)%.

Ca{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}{N(SiMe$_3$)$_2$}(thf) (21)

To a stirred solution of Ca{N(SiMe$_3$)$_2$}$_2$(thf$_2$) (0.780 g, 1.56 mmol) in benzene (20 mL), was added a solution of HC(Me$_2$pz)$_2$SiMe$_2$N(H)^{i}Pr (0.500 g, 1.56 mmol) in benzene (20 mL). The resultant orange solution was stirred for 12 h. Volatiles were removed under reduced pressure, the solid washed with cold pentane (3 x 5 mL, -78 °C) and dried under reduced pressure to afford complex **21** as a light orange solid. Yield = 0.63 g (63%). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 5.46 (2 H, s, N$_2$C$_3$HMe$_2$), 5.12 (1 H, s, HC(Me$_2$pz)$_2$), 3.90 (4 H, br s, OCH$_2$CH$_2$), 3.80 (1 H, sept, $^3J_{HH}$ = 6.3 Hz, HCMe$_2$), 2.36 (6 H, s, 3-N$_2$C$_3$HMe$_2$), 1.70 (6 H, s, 5-N$_2$C$_3$HMe$_2$), 1.43 (4 H, br s, OCH$_2$CH$_2$), 1.42 (6 H, d, $^3J_{HH}$ = 6.3 Hz, HCMe$_2$), 0.45 (18 H, s, N(SiMe$_3$)$_2$), 0.03 (SiMe). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 293 K): δ 153.6 (3-N$_2$C$_3$HMe$_2$), 139.3 (5-N$_2$C$_3$HMe$_2$), 105.8 (4-N$_2$C$_3$HMe$_2$), 69.2 (OCH$_2$CH$_2$), 65.7 (HC(Me$_2$pz)$_2$), 48.4 (HCMe$_2$), 32.0 (HCMe$_2$), 25.2 (OCH$_2$CH$_2$), 14.2 (3-N$_2$C$_3$HMe$_2$), 11.0 (5-N$_2$C$_3$HMe$_2$), 6.2 (N(SiMe$_3$)$_2$), 3.3 (SiMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2965 (w), 1557 (m), 1456 (s), 1376 (s), 1316 (s), 1285 (w), 1234 (m), 1177 (m), 1042 (s), 979 (w), 879 (m), 816 (m), 785 (w), 746 (w), 726 (m). EI-MS: *m/z* = 357 (30%) [M-(N(SiMe$_3$)$_2$)(thf)]$^+$. Anal. found (calcd. for C$_{26}$H$_{53}$CaN$_6$OSi$_3$): C, 52.8 (52.9); H, 8.9 (9.0); N, 14.0 (14.2)%.

Zn{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (25)

To a stirred solution of HC(Me$_2$pz)$_2$SiMe$_2$N(H)^{i}Pr (0.500 g, 1.56 mmol) in benzene (30 mL), was added ZnMe$_2$ (2.34 mL, 1.56 mmol; 2.0 M in toluene). The resultant clear, colourless solution was stirred for 15 h. Volatiles were removed under reduced pressure, the solid washed with cold hexanes (3 x 5 mL, -78 °C) and dried under reduced pressure to afford complex **25** as a colourless solid. Yield = 0.43 g (70%). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 5.35 (2 H, s, N$_2$C$_3$HMe$_2$), 5.11 (1 H, s, HC(Me$_2$pz)$_2$), 3.70 (1 H, sept, $^3J_{HH}$ = 6.2 Hz, HCMe$_2$), 2.14 (6 H, s, 3-N$_2$C$_3$HMe$_2$), 1.66 (6 H, s, 5-N$_2$C$_3$HMe$_2$), 1.49 (6 H, sept, $^3J_{HH}$ = 6.0 Hz, HCMe$_2$), 0.04 (3 H, s, ZnMe), -0.18 (6 H, s, SiMe). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 293 K): δ 149.5 (3-N$_2$C$_3$HMe$_2$), 138.1 (5-N$_2$C$_3$HMe$_2$), 105.4 (4-N$_2$C$_3$HMe$_2$), 63.0 (HC(Me$_2$pz)$_2$), 47.7 (HCMe$_2$), 31.5 (HCMe$_2$), 12.9 (3-N$_2$C$_3$HMe$_2$), 10.4 (5-N$_2$C$_3$HMe$_2$), -0.16 (SiMe), -9.3 (ZnMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2920 (w), 2361 (m), 1555 (s), 1521 (w), 1458 (s), 1419 (w), 1377 (s), 1314 (m), 1241 (m), 1170 (m), 1136 (s), 1098 (m), 1040 (s), 996 (m), 898 (s), 827 (m), 780 (m), 763 (m), 667 (m). EI-MS: *m/z* = 281 (20%) [M-SiMe$_2$N^{i}Pr]$^+$. Anal. found (calcd. for C$_{17}$H$_{31}$N$_5$SiZn): C, 51.1 (51.2); H, 7.8 (7.8); N, 17.5 (17.5)%.

Zn{HC(Me$_2$pz)$_2$SiMe$_2$N^{t}Bu}Me (26)

To a stirred solution of HC(Me$_2$pz)$_2$SiMe$_2$N(H)^{t}Bu (0.500 g, 1.49 mmol) in benzene (30 mL), was added ZnMe$_2$ (2.25 mL, 4.49 mmol; 2.0 M in toluene). The resultant clear solution was stirred for 15 h. Volatiles were removed under reduced pressure, the solid washed with cold hexanes (3 x 5 mL, -78 °C) and dried under reduced pressure to afford complex **26** as a colourless solid. Yield = 0.47 g (77%). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 5.34 (2 H, s, N$_2$C$_3$HMe$_2$), 5.03 (1 H, s, HC(Me$_2$pz)$_2$), 2.15 (6 H, s, 3-N$_2$C$_3$HMe$_2$), 1.66 (6 H, s, 5-N$_2$C$_3$HMe$_2$), 1.63 (9 H, s, CMe$_3$), 0.12 (3 H, s, ZnMe), 0.10 (6 H, s, SiMe). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 293 K): δ 148.3 (3-N$_2$C$_3$HMe$_2$), 137.9 (5-N$_2$C$_3$HMe$_2$), 105.3 (4-N$_2$C$_3$HMe$_2$), 64.0 (HC(Me$_2$pz)$_2$), 52.5 (CMe$_3$), 37.3 (CMe$_3$), 12.9 (3-N$_2$C$_3$HMe$_2$), 10.6 (5-N$_2$C$_3$HMe$_2$), 3.2 (SiMe), -10.8 (ZnMe). IR (NaCl plates, Nujol mull, cm^{-1}): 2924 (w), 2361 (m), 1521 (s), 1506 (w), 1463 (w), 1419 (m), 1377 (s), 1314 (s), 1207 (s), 1225 (m), 1137 (s), 1101 (w), 1081 (m), 979 (m), 867 (s), 824 (m), 784 (m), 761 (m), 727 (m), 661 (w). EI-MS: *m/z* = 411

(60%) $[M]^+$, 396 (100%) $[M\text{-}Me]^+$. Anal. found (calcd. for $C_{18}H_{33}N_5SiZn$): C, 52.2 (52.3); H, 8.0 (8.0); N, 17.0 (17.0)%.

Representative NMR spectra

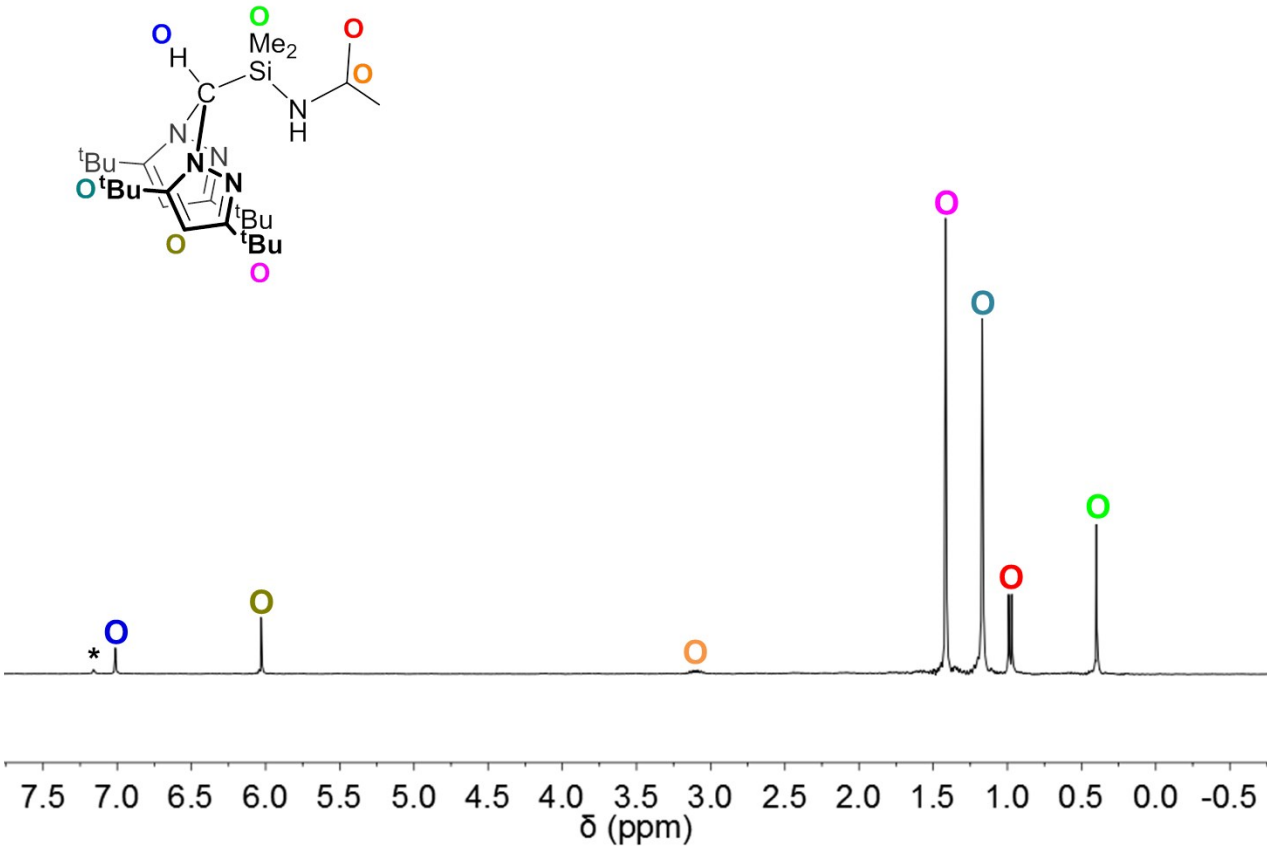

Figure S1. ^{1}H NMR spectrum (C_6D_6, 299.9 MHz, 293 K) of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)^{i}Pr. * denotes residual protio solvent.

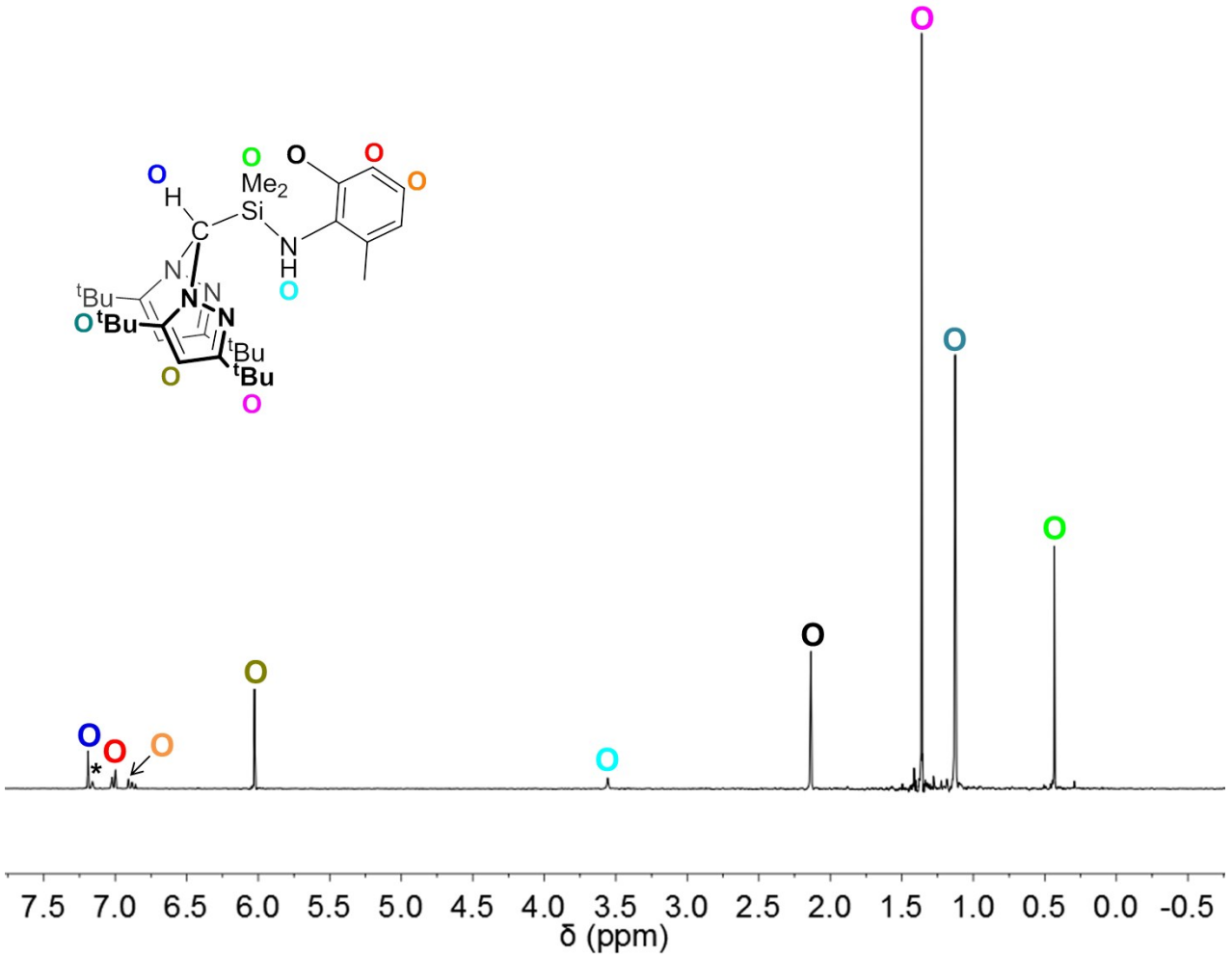

Figure S2. ^{1}H NMR spectrum (C_6D_6, 299.9 MHz, 293 K) of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)Xyl. * denotes residual protio solvent.

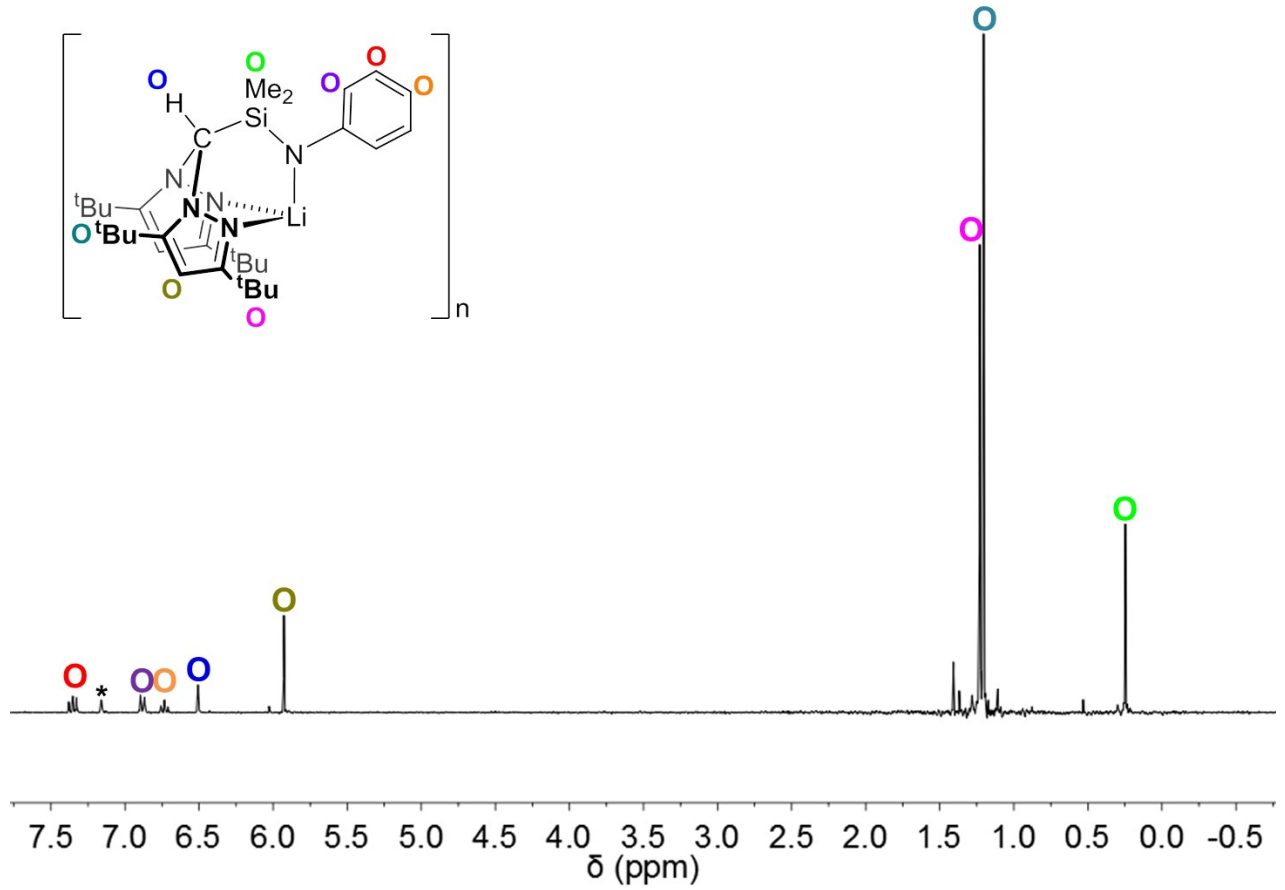

Figure S3. ^{1}H NMR spectrum (C_6D_6, 299.9 MHz, 293 K) of [Li{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}]$_n$ (**3**). * denotes residual protio solvent.

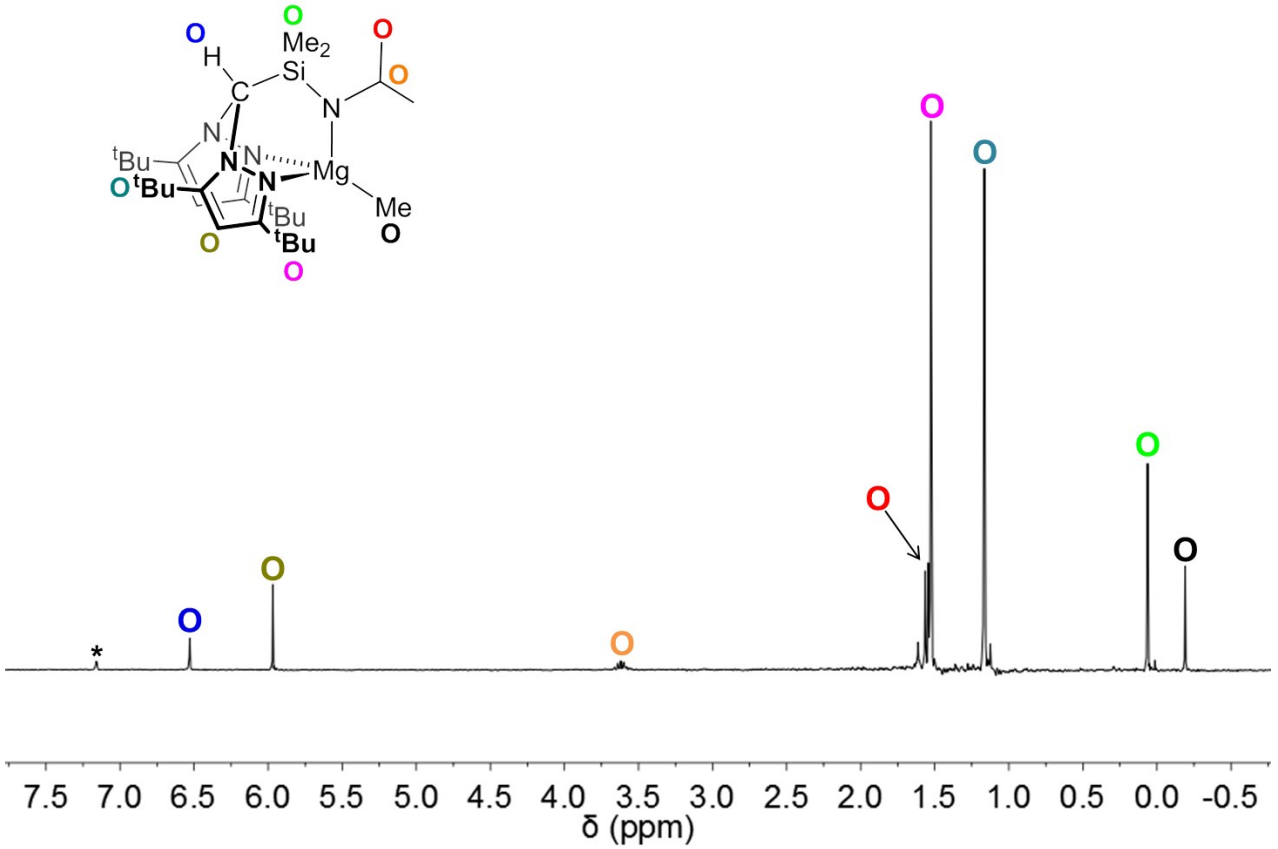

Figure S4. ^{1}H NMR spectrum (C_6D_6, 299.9 MHz, 293 K) of Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**5**). * denotes residual protio solvent.

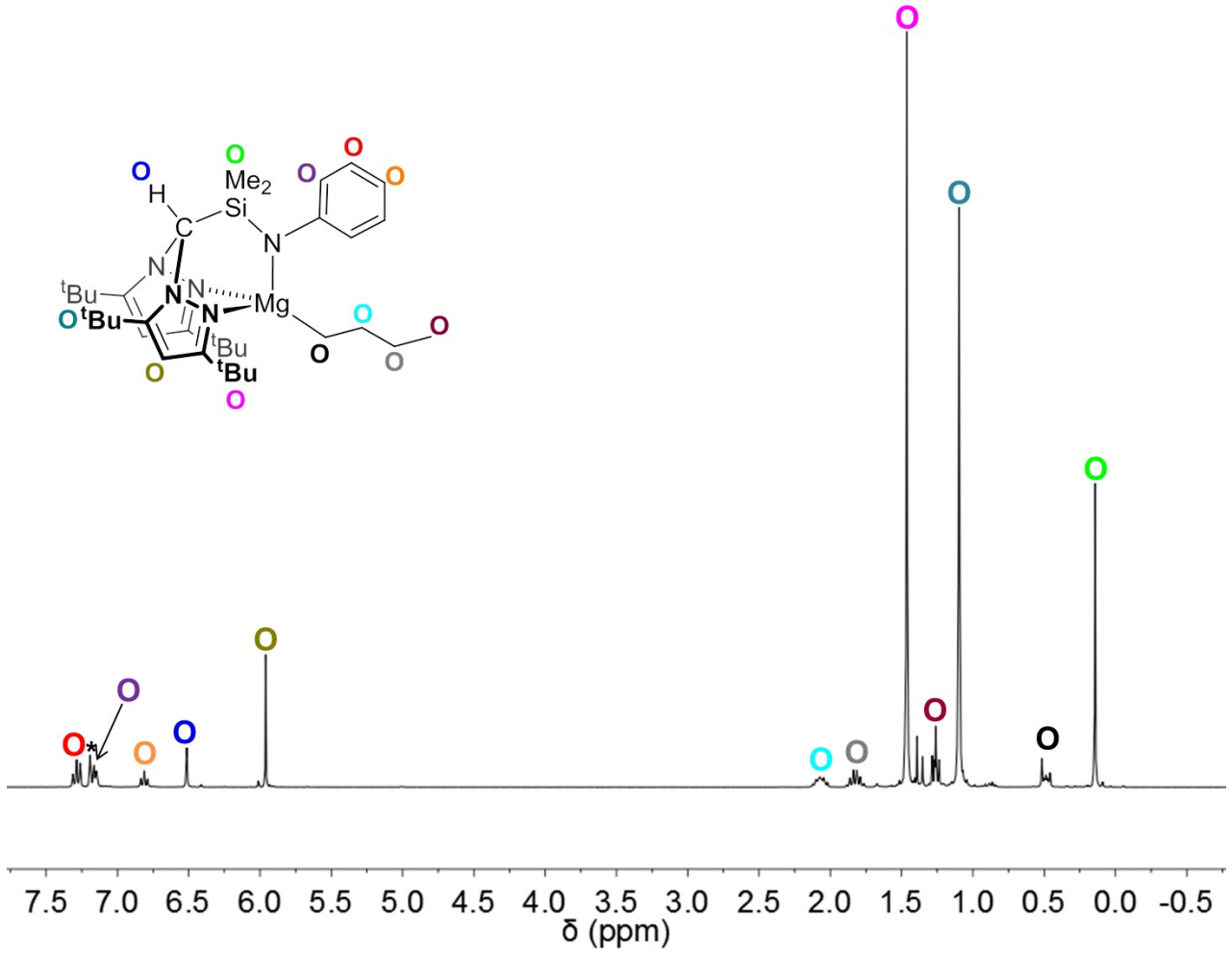

Figure S5. ^{1}H NMR spectrum (C_6D_6, 299.9 MHz, 293 K) of Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}^{n}Bu (**12**). * denotes residual protio solvent.

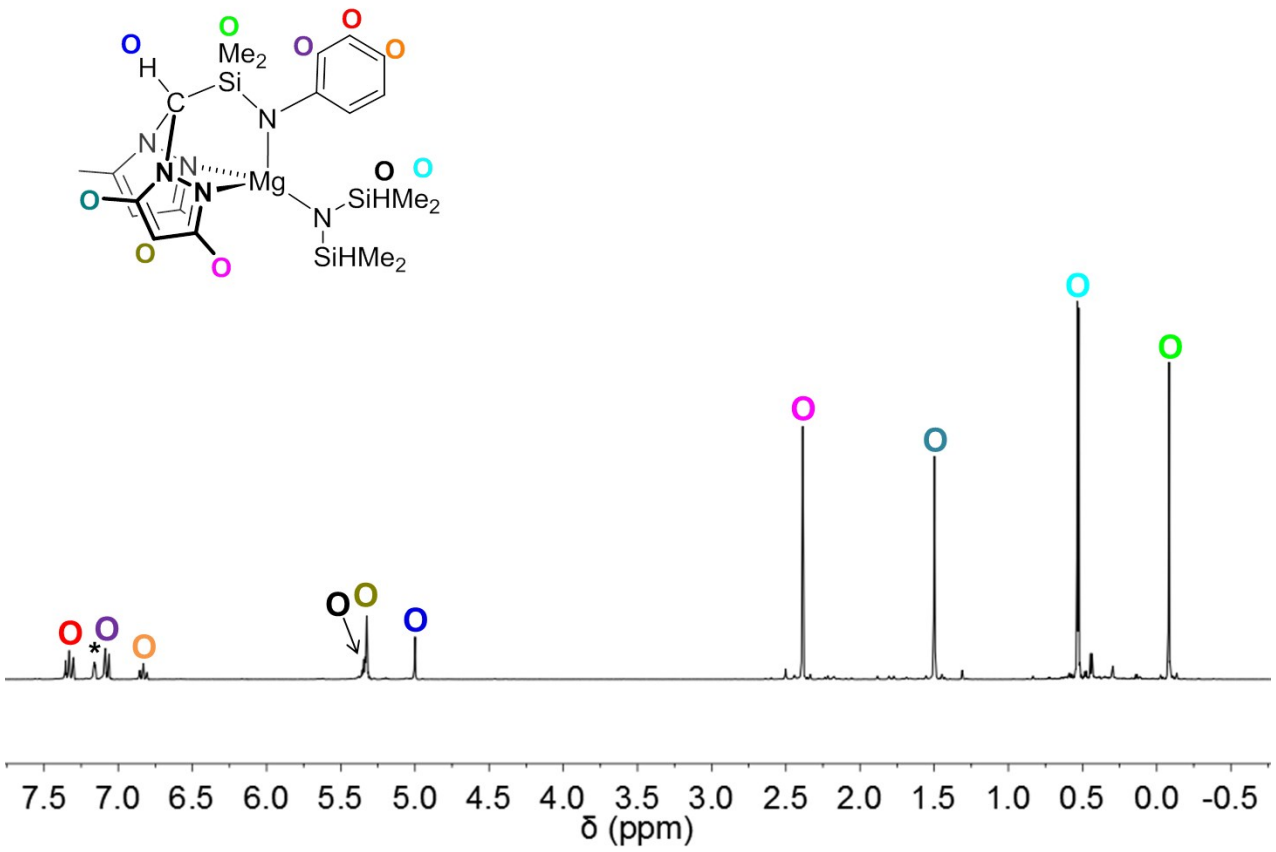

Figure S6. ^{1}H NMR spectrum (C_6D_6, 299.9 MHz, 293 K) of Mg{HC(Me_2pz)$_2$SiMe_2NPh}{N(SiHMe_2)$_2$} (**15**). * denotes residual protio solvent.

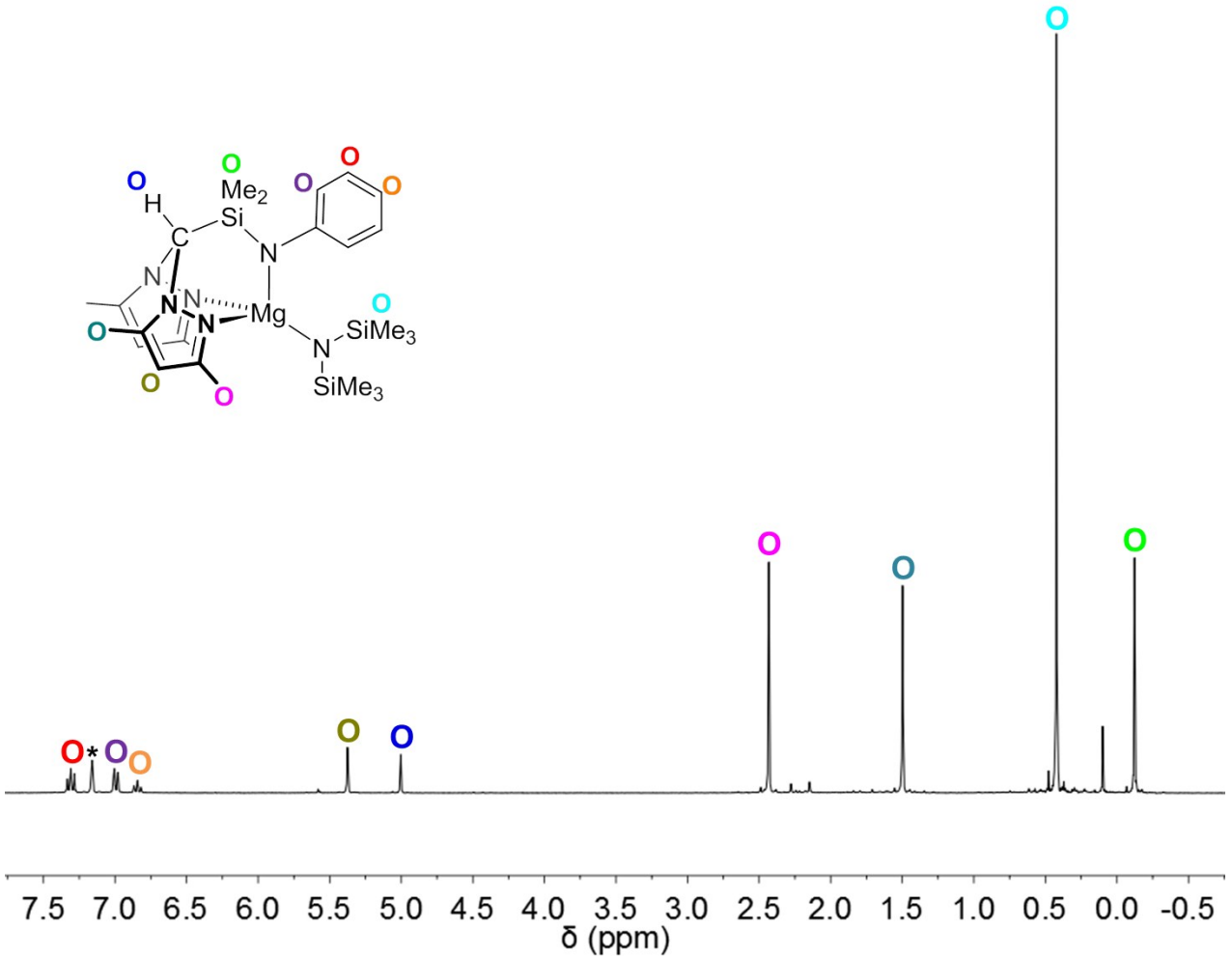

Figure S7. ^{1}H NMR spectrum (C_6D_6, 299.9 MHz, 293 K) of Mg{HC(Me_2pz)$_2$SiMe_2NPh}{N($SiMe_3$)$_2$} (**19**). * denotes residual protio solvent.

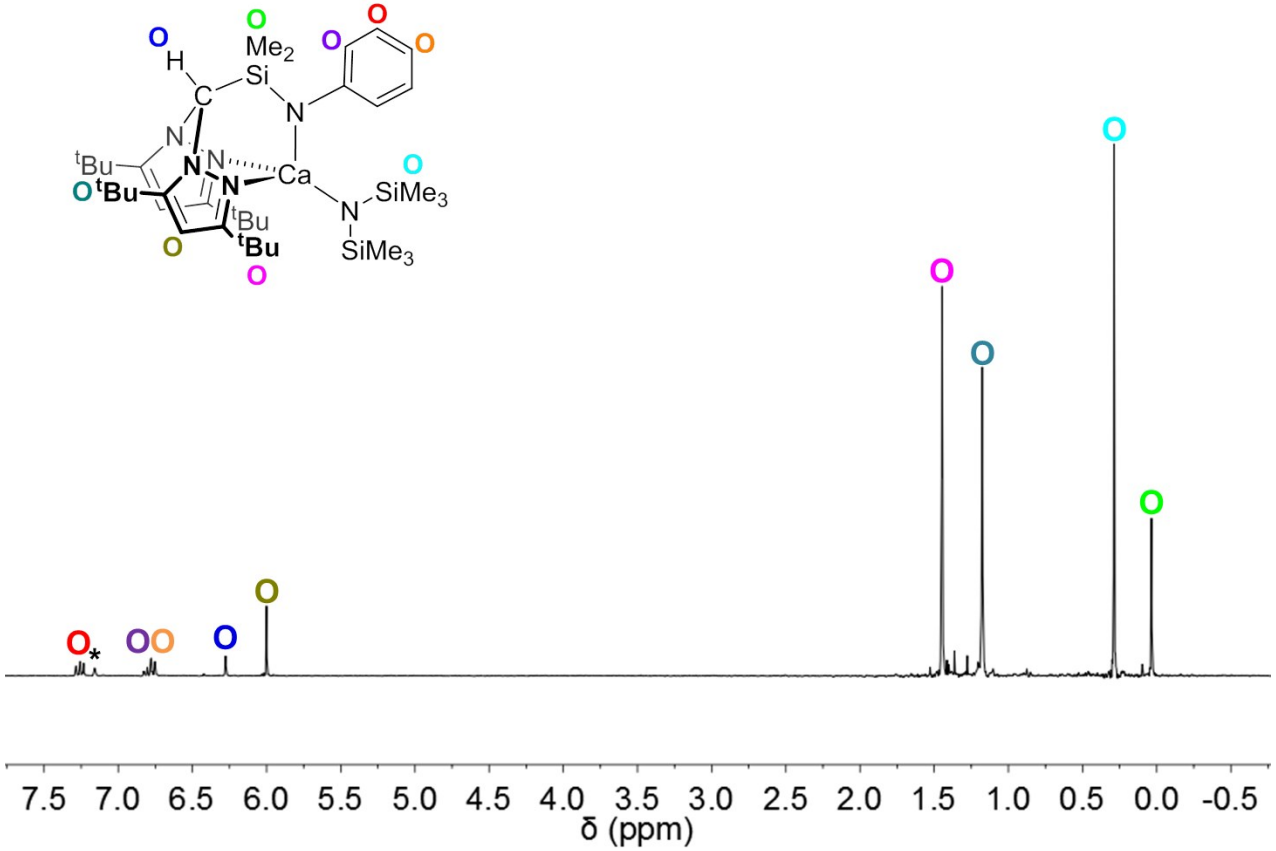

Figure S8. ^{1}H NMR spectrum (C_6D_6, 299.9 MHz, 293 K) of Ca{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**24**). * denotes residual protio solvent.

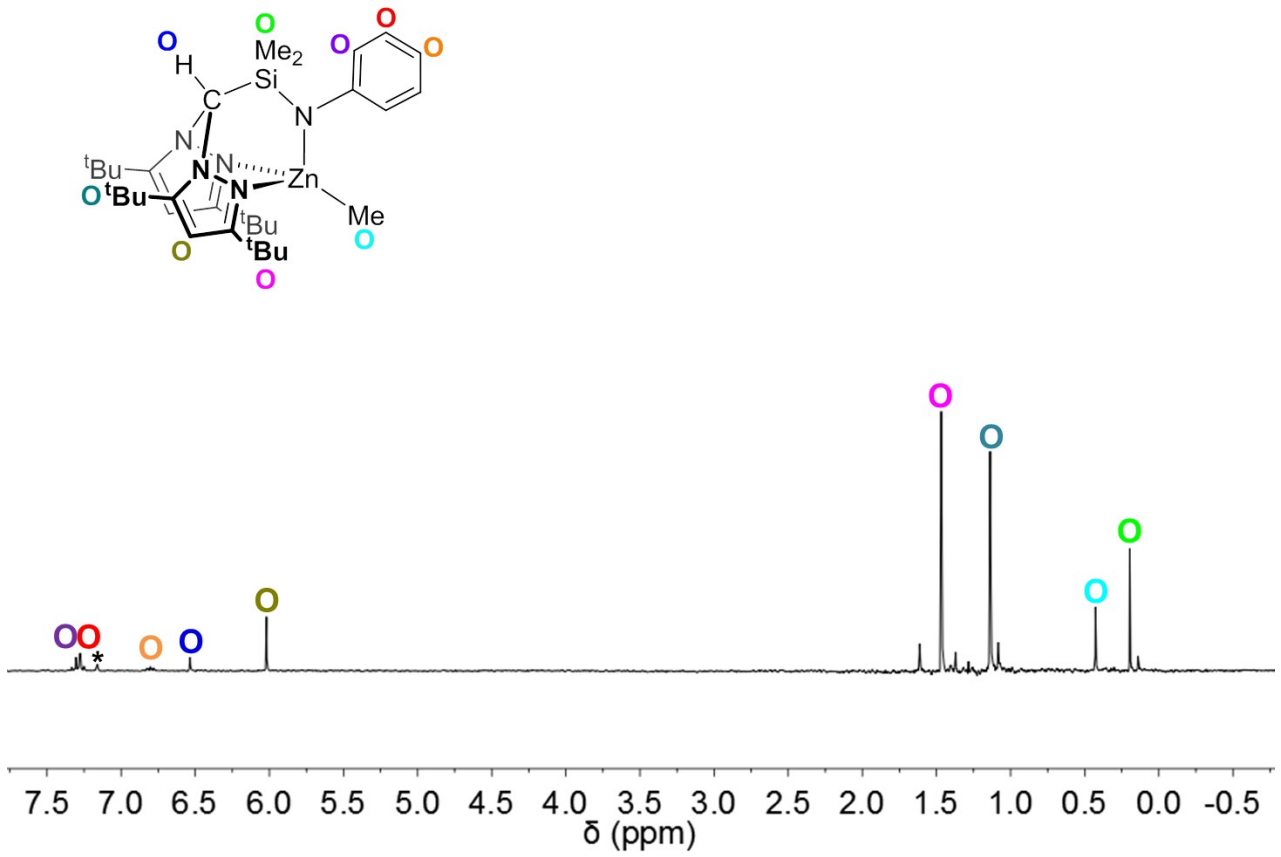

Figure S9. ^{1}H NMR spectrum (C_6D_6, 299.9 MHz, 293 K) of Zn{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}Me (**28**). * denotes residual protio solvent.

Additional X-ray Crystallographic data

HC(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl

Single crystals of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl suitable for an X-ray diffraction study were grown from a saturated pentane solution at 23 °C.

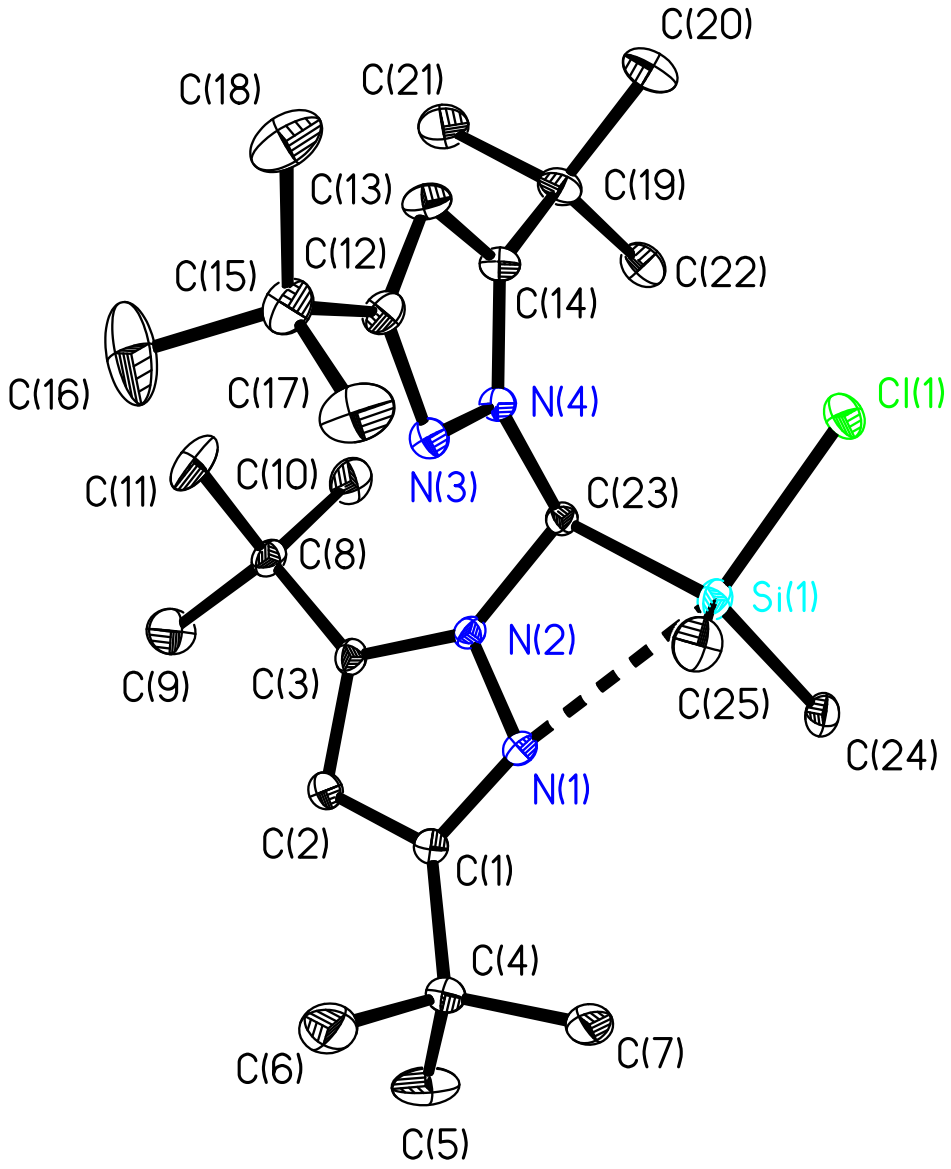

Figure S10. Thermal displacement ellipsoid drawing (23% probability ellipsoids) of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl. Hydrogen atoms have been omitted for clarity.

HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)Ph

Single crystals of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)Ph suitable for an X-ray diffraction study were grown from a saturated pentane solution at -30 °C.

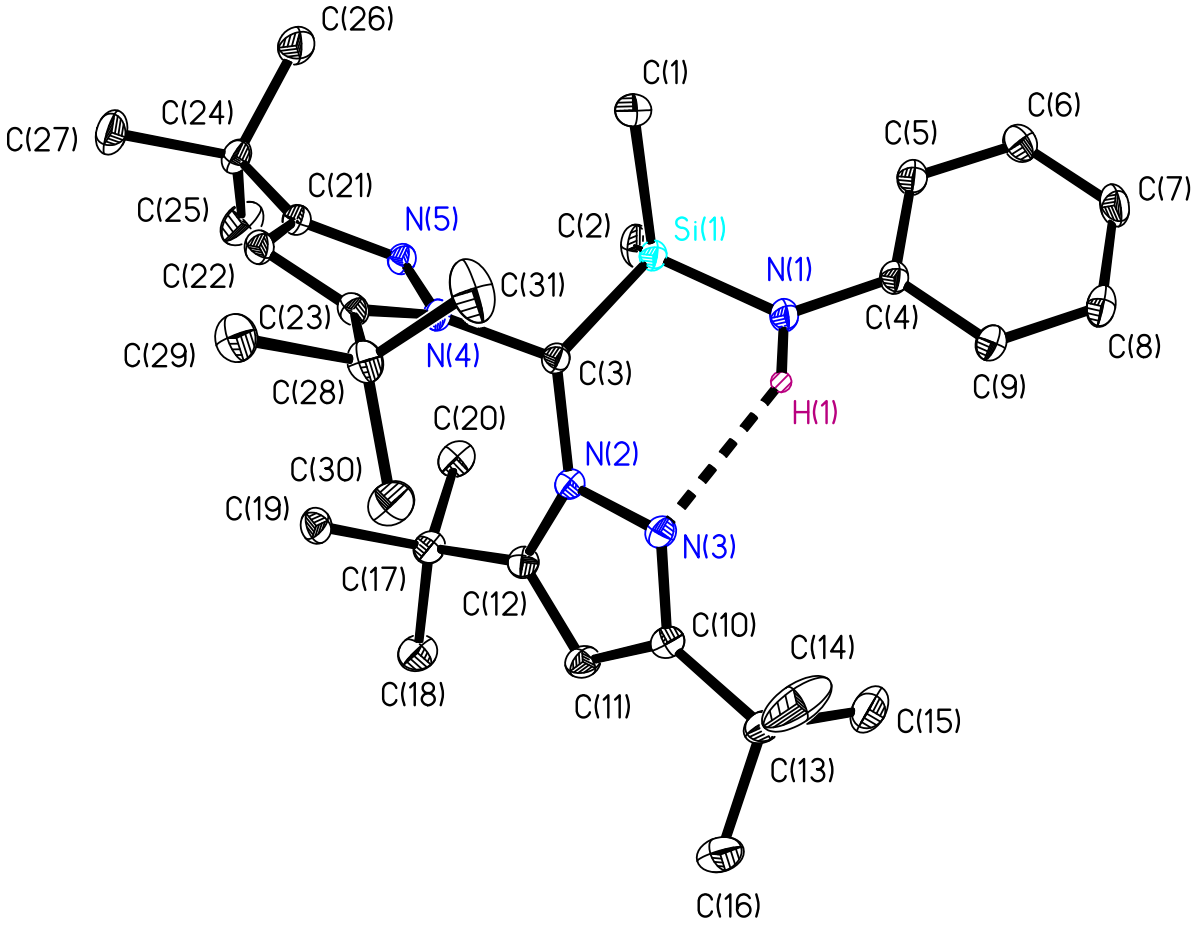

Figure S11. Thermal displacement ellipsoid drawing (25% probability ellipsoids) of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)Ph. Hydrogen atoms, apart from H(1), have been omitted for clarity. H(1) drawn as a sphere of arbitrary radius.

Table S1. Selected bond lengths (Å) and angles (°) for HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N(H)Ph.

H(1)-N(3)	2.286
N(4)-N(5)	1.3656(15)
N(2)-N(3)	1.3771(15)
Si(1)-N(1)	1.7326(12)
C(3)-Si(1)	1.9228(13)
N(4)-C(23)	1.3767(16)
N(3)-C(10)	1.3277(17)
N(4)-C(3)-N(2)	116.65(10)
N(4)-C(3)-Si(1)	116.65(10)
N(5)-N(4)-C(3)	116.36(10)
N(2)-C(3)-Si(1)	117.74(8)
N(3)-N(2)-C(3)	110.30(10)

Like HC(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl, this structure shows an intramolecular interaction; a hydrogen bond between H(1) and N(3) in the pyrazole ring, over a length of 2.286 Å. This interaction is likely to have an effect on the

orientation of the pyrazole rings with the interplane angle now being only 76.0 °. Bond lengths within the pyrazole rings and the distance C(3)-Si(1) are all comparable to those in compound $HC(^tBu_2pz)_2SiMe_2Cl$.

$Mg\{HC(Me_2pz)_2SiMe_2NPh\}_2$

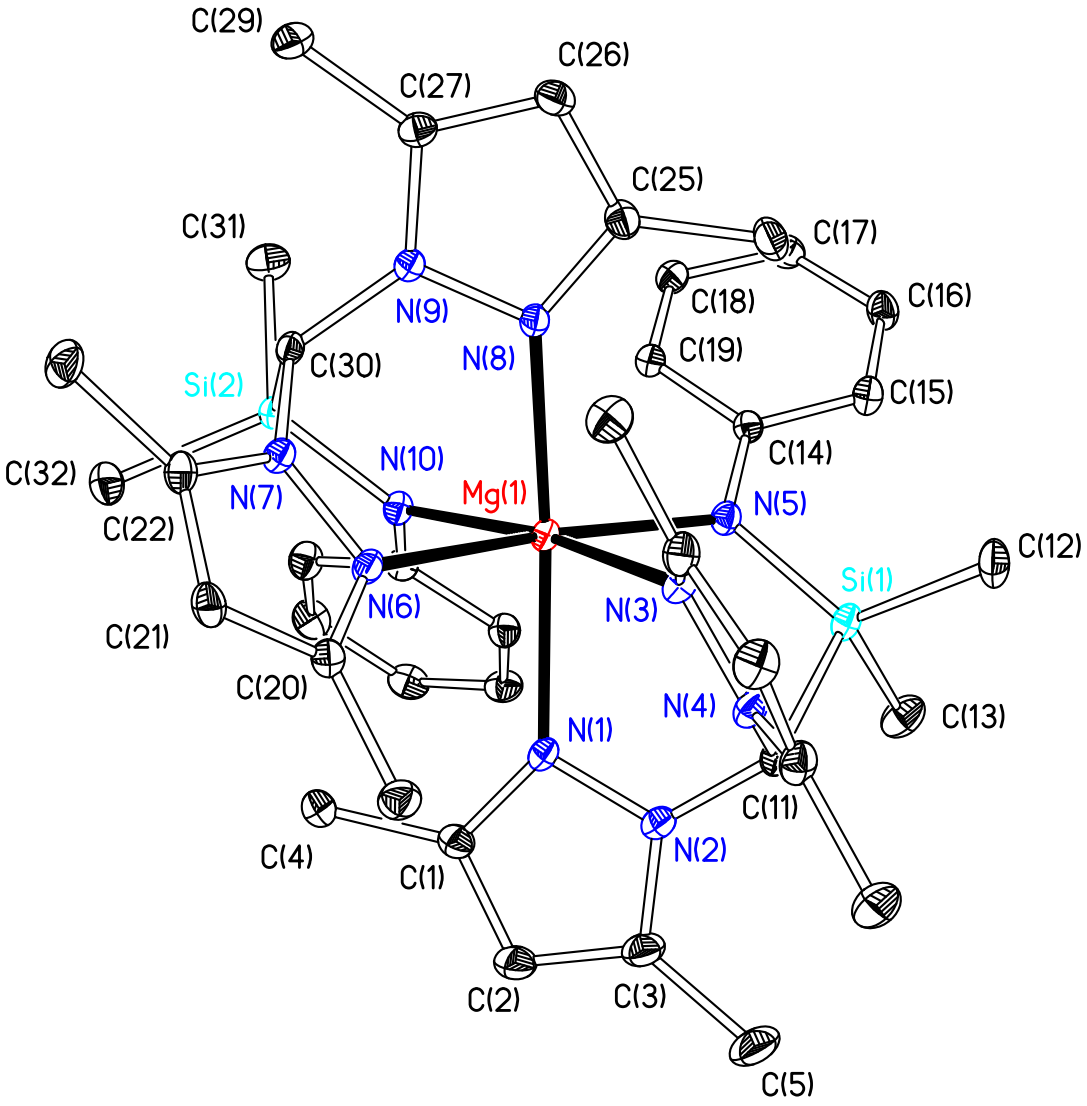

Figure S12. Thermal displacement ellipsoid drawing (25% probability ellipsoids) of $Mg\{HC(Me_2pz)_2SiMe_2NPh\}_2$. Hydrogen atoms are omitted for clarity.

Mg{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}{N(SiMe$_3$)$_2$} (17)

Single crystals of Mg{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}{N(SiMe$_3$)$_2$} (**17**) suitable for an X-ray diffraction study were grown by slow diffusion of diethyl ether into a saturated toluene solution of **17** at 23 °C.

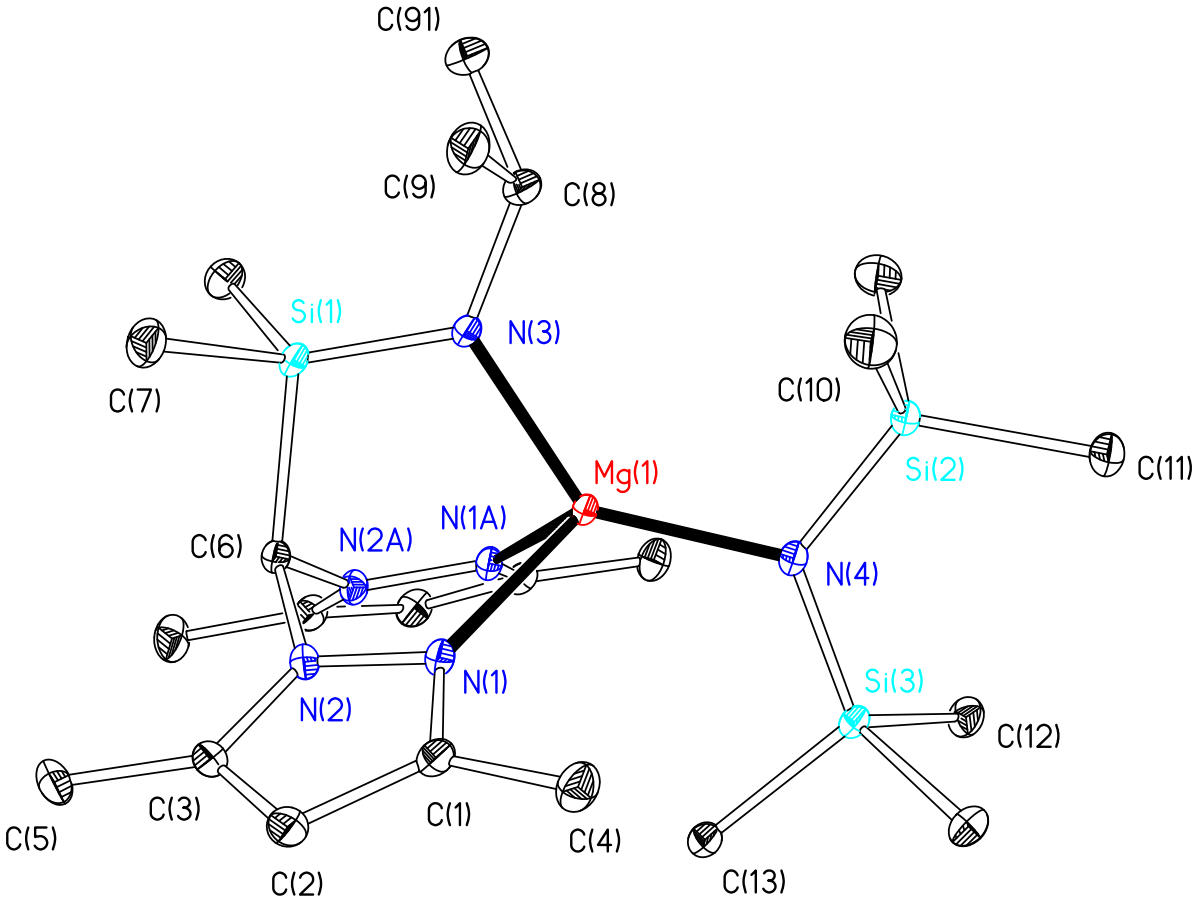

Figure S13. Thermal displacement ellipsoid drawing (20% probability ellipsoids) of Mg{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}{N(SiMe$_3$)$_2$} (**17**). Hydrogen atoms and minor disorder omitted for clarity. Atoms carrying the suffix 'A' are related to their counterparts by the symmetry operator x,-y+3/2,z.

Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (19)

Single crystals of Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**19**) suitable for an X-ray diffraction study were grown by slow diffusion of diethyl ether into a saturated toluene solution of **19** at 23 °C.

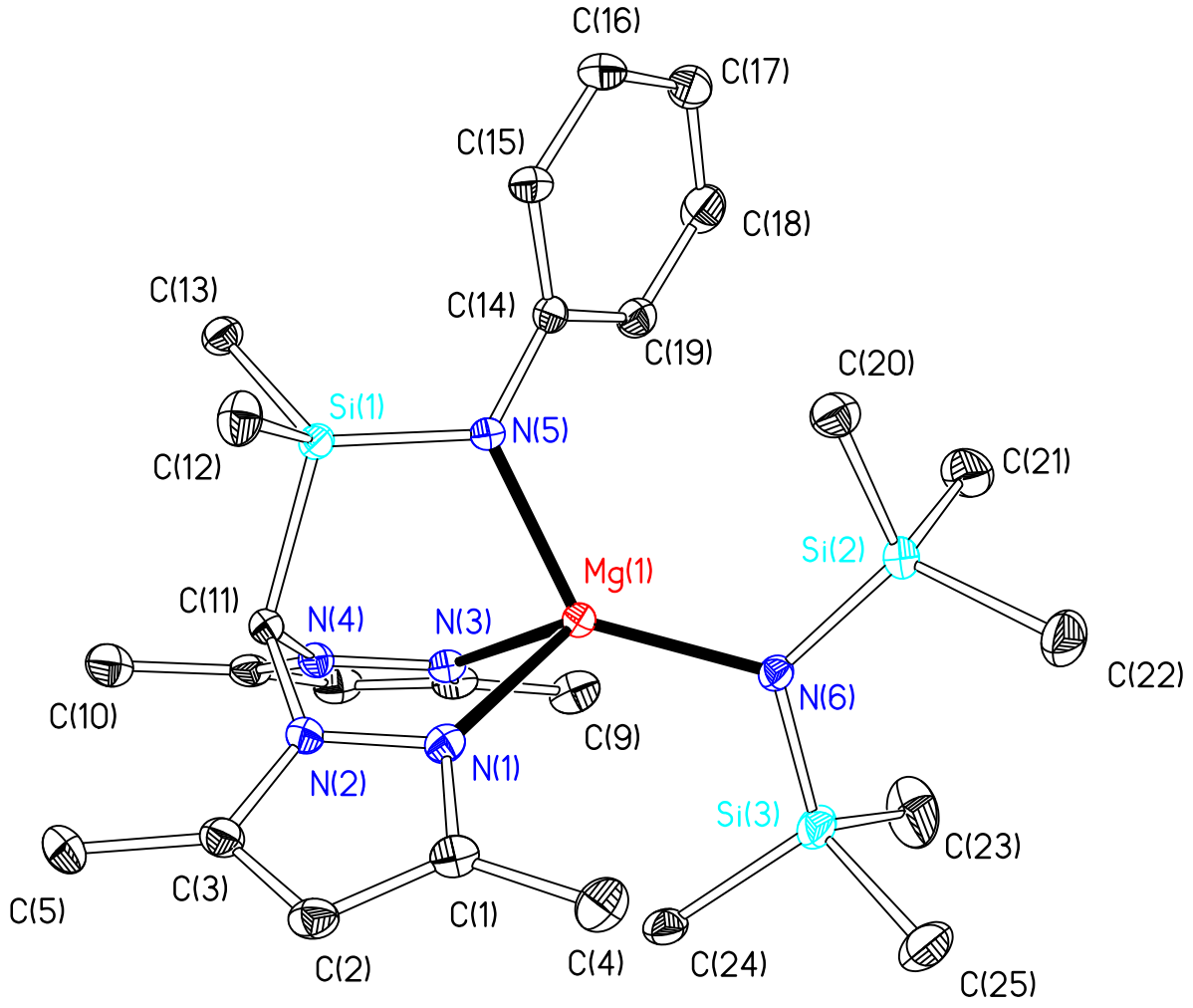

Figure S14. Thermal displacement ellipsoid drawing (20% probability ellipsoids) of Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**19**).

Zn{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (25)

Single crystals of Zn{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**25**) suitable for an X-ray diffraction study were grown by slow diffusion of diethyl ether into a saturated toluene solution of **25** at 23 °C.

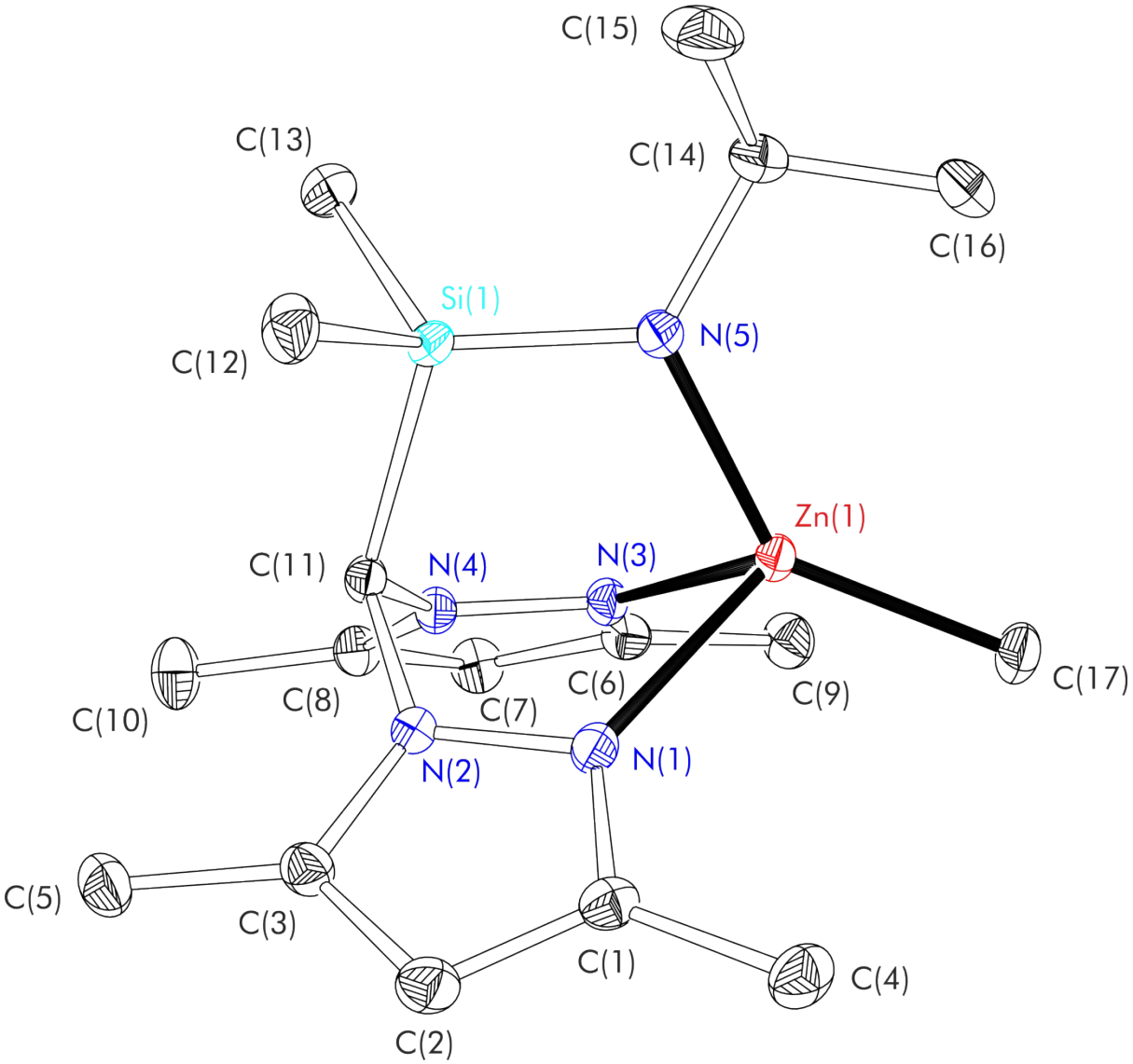

Figure S15. Thermal displacement ellipsoid drawing (30% probability ellipsoids) of Zn{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**25**). Hydrogen atoms are omitted for clarity.

Table S2. X-ray data collection and processing parameters for Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**5**), Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}^{n}Bu (**10**), Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiHMe$_2$)$_2$} (**16**), Mg{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}{N(SiMe$_3$)$_2$} (**17**), Mg{HC(Me$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**19**), Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}{N(SiMe$_3$)$_2$} (**20**).

	5	**10**	**16**	**17**	**19**	**20**
Chemical formula	$C_{29}H_{55}MgN_5Si$	$C_{23}H_{35}MgN_5Si$	$C_{35}H_{64}MgN_6Si_3 \cdot 0.75(C_5H_{12})$	$C_{22}H_{50}MgN_6Si_3$	$C_{25}H_{44}MgN_6Si_3$	$C_{37}H_{68}MgN_6Si_3$
M_r	526.18	433.96	731.61	507.24	537.23	705.55
Crystal system, space group	Orthorhombic, *Pbca*	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$	Monoclinic, $P12_1/m1$	Monoclinic, $P2_1/c$	Orthorhombic, $P2_12_12_1$
Temperature (K)	150	150	150	150	150	150
a, *b*, *c* (Å)	16.9775 (3), 19.4673 (3), 20.6194 (4)	8.7597 (2), 11.2019 (2), 25.3310 (6)	19.7490 (9), 11.0055 (5), 22.6313 (10)	10.3686 (2), 13.7276 (4), 11.7088 (3)	10.8767 (3), 17.7204 (5), 16.2958 (5)	13.9372 (2), 15.2750 (2), 20.1552 (2)
β (°)	90	90	110.253 (2)	113.6864 (15)	99.1999 (11)	90
V (Å^3)	6814.8 (2)	2485.61 (9)	4614.7 (4)	1526.19 (7)	3100.44 (16)	4290.85 (9)
Z	8	4	4	2	4	4
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.11	0.14	0.15	0.20	0.20	0.16
Crystal size (mm)	0.40 × 0.30 × 0.30	0.40 × 0.40 × 0.30	0.30 × 0.20 × 0.20	0.40 × 0.30 × 0.30	0.30 × 0.10 × 0.02	0.20 × 0.20 × 0.20
Diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer
Absorption correction	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.97, 0.97	0.95, 0.96	0.75, 0.97	0.93, 0.94	0.98, 1.00	0.97, 0.97
No. of measured, independent and observed [*I* >	15190, 7709, 4207	5198, 5174, 4225	31102, 10257, 4225	6618, 3604, 2428	12814, 7018, 3319	9765, 5371, 4450

$3.0\sigma(I)$] reflections						
R_{int}	0.044	0.000	0.116	0.025	0.061	0.022
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.649	0.649	0.648	0.650	0.649	0.649
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.043, 1.10	0.041, 0.038, 1.12	0.062, 0.059, 1.14	0.054, 0.061, 1.17	0.050, 0.050, 1.14	0.036, 0.037, 1.12
No. of reflections	4207	3875	4225	2428	3319	4450
No. of parameters	325	272	459	173	316	424
$(\Delta/\sigma)_{max}$	0.001	0.004	0.002	0.003	0.003	0.001
Δ_{max}, Δ_{min} ($e\ Å^{-3}$)	0.21, -0.26	0.24, -0.24	0.85, -0.41	0.94, -0.86	0.55, -0.43	0.25, -0.24
Absolute structure parameter	-	Flack, 0.03(13), 986 Friedel pairs	-	-	-	-

Table S3. X-ray data collection and processing parameters for Zn{HC(Me_2pz)$_2$SiMe_2N^{i}Pr}Me (**25**), Zn{HC(Me_2pz)$_2$SiMe_2NPh}Me (**27**), Zn{HC(^{t}Bu$_2$pz)$_2$SiMe_2NPh}Me (**28**), HC(^{t}Bu$_2$pz)$_2$SiMe_2Cl, HC(^{t}Bu$_2$pz)$_2$SiMe_2N(H)Ph and Mg{HC(Me_2pz)$_2$SiMe_2NPh}$_2$.

	25	**27**	**28**	HC(^{t}Bu$_2$pz)$_2$SiMe_2Cl	HC(^{t}Bu$_2$pz)$_2$SiMe_2N(H)Ph	Mg{HC(Me_2pz)$_2$SiMe_2NPh}$_2$
Chemical formula	$C_{17}H_{31}N_5SiZn$	$C_{20}H_{29}N_5SiZn$	$C_{32}H_{53}N_5SiZn$	$C_{25}H_{45}ClN_4Si$	$C_{31}H_{51}N_5Si$	$C_{38}H_{53}MgN_{10}Si_2$
M_r	398.93	432.95	601.27	465.20	521.86	730.38
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	150	150	150	150	150	150
a, b, c (Å)	8.1821 (3), 8.8902 (3), 14.2556 (5)	8.9736 (1), 25.8526 (5), 10.3274 (2)	25.4552 (2), 10.7201 (1), 25.4576 (2)	9.8478 (2), 16.9303 (3), 17.3365 (3)	8.8605 (1), 19.3115 (2), 19.2772 (2)	12.4038 (2), 18.3606 (3), 17.3649 (3)
β (°)	90.1009 (14), 93.1351 (14), 96.5529 (13)	110.1053 (8)	95.6052 (4)	100.7636 (7)	97.144 (1)	90.8103 (7)
V (Å^3)	1028.61 (6)	2249.86 (7)	6913.71 (10)	2839.59 (9)	3272.91 (6)	3954.31 (11)
Z	2	4	8	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.26	1.16	0.77	0.20	0.10	0.15
Crystal size (mm)	0.80 × 0.05 × 0.02	0.40 × 0.30 × 0.20	0.30 × 0.10 × 0.10	0.20 × 0.18 × 0.16	0.56 × 0.30 × 0.22	0.20 × 0.20 × 0.20
Diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer	Nonius KappaCCD diffractometer
Absorption correction	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.94, 0.98	0.71, 0.79	0.93, 0.93	0.97, 0.97	0.970, 0.980	0.97, 0.97
No. of measured, independent and	8057, 4627, 3962	9721, 5099, 2980	24102, 15388, 12573	16111, 8222, 4637	27112, 7443, 6307	17767, 9000, 5734

observed [$I > 3.0\sigma(I)$] reflections						
R_{int}	0.024	0.038	0.045	0.035	0.043	0.050
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.648	0.649	0.649	0.704	0.649	0.649
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.054, 1.09	0.031, 0.031, 1.12	0.045, 0.054, 0.99	0.040, 0.041, 1.12	0.046, 0.127, 1.02	0.050, 0.044, 1.13
No. of reflections	3962	2980	12573	4637	7443	5136
No. of parameters	217	244	704	280	348	460
$(\Delta/\sigma)_{max}$	0.001	0.002	0.003	0.001	< 0.001	0.001
Δ_{max}, Δ_{min} (e $Å^{-3}$)	0.70, -0.74	0.28, -0.22	0.83, -0.39	0.32, -0.32	0.29, -0.25	0.63, -0.55

Density Functional Theory Calculations

All DFT calculations were performed with the ORCA program package.[5] The geometry optimisations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level [6] of DFT. The def2-TZVP(-f) basis set in the scalar relativistic recontraction reported by Neese *et al.* (segmented all-electron relativistic basis sets, SARC) was applied.[7] For all elements up to bromine, the SARC basis sets are simply scalar relativistic recontractions of the basis sets developed by the Karlsruhe group,[8] while for heavier elements, the primitives and contraction patterns were designed in references [7a] and [7b]. The Coulomb fitting basis set of Weigend[9] was used in uncontracted form in all calculations. The RI[10] approximation was used to accelerate the calculations. Orbitals were generated with the program Chimera.[11]

Table S4. Comparison of experimental and calculated metrical parameters of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl

	Experimental	Calculated (B3LYP)
Si(1)-Cl(1)	2.1388 (6)	2.145
Si(1)-N(1)	2.4362 (14)	2.585
N(1)-C(1)	1.325 (2)	1.330
N(3)-C(12)	1.327 (2)	1.329
N(3)-N(4)	1.368 (2)	1.360
N(1)-N(2)	1.366 (2)	1.363
Cl(1)-Si(1)-N(1)	159.99 (4)	160.66
N(2)-C(23)-N(4)	112.04 (12)	115.27
N(2)-C(23)-Si(1)	102.93 (9)	105.87
N(1)-N(2)-C(23)	110.15 (11)	110.80
N(3)-N(4)-C(23)	114.34 (12)	116.13
N(4)-C(23)-Si(1)	112.14 (10)	112.20

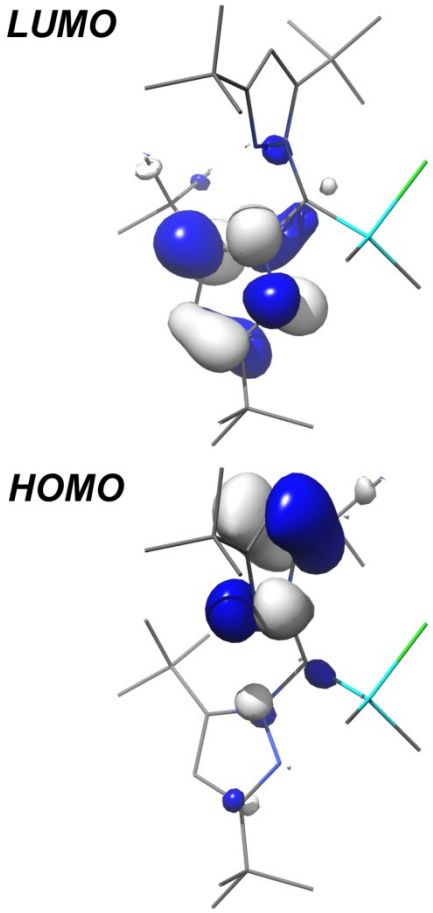

Figure S16. DFT-computed HOMO and LUMO of HC(^{t}Bu$_2$pz)$_2$SiMe$_2$Cl

Table S5. Comparison of experimental and calculated metrical parameters of Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**5**)

	Experimental	Calculated (B3LYP)
Mg(1)-N(1)	2.1799(16)	2.231
Mg(1)-N(3)	2.1911(16)	2.240
Mg(1)-N(5)	2.0083(17)	2.026
Mg(1)-C(29)	2.145(2)	2.135
N(1)-Mg(1)-C(29)	123.01(7)	123.40
N(3)-Mg(1)-C(29)	123.88(7)	121.89
N(5)-Mg(1)-C(29)	122.09(8)	124.08

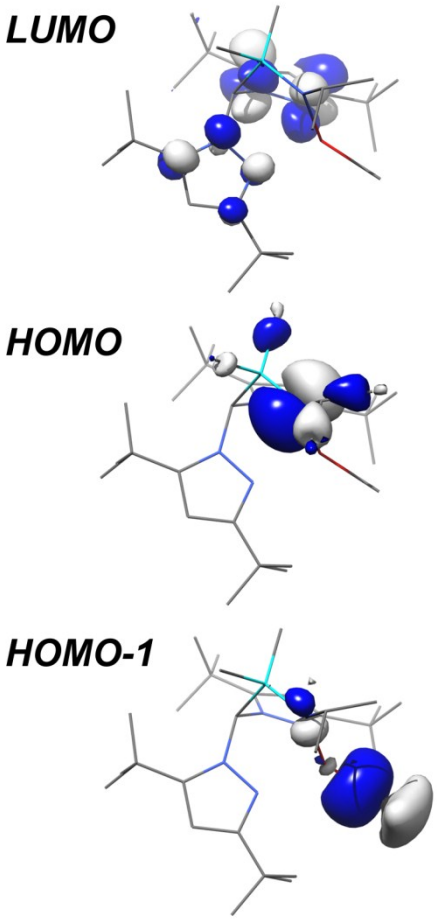

Figure S17. DFT-computed HOMO-1, HOMO and LUMO of Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**5**)

Table S6. Comparison of experimental and calculated metrical parameters of Zn{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}Me (**28**)

	Experimental	Calculated (B3LYP)
Zn(1)-N(1)	2.171(4)	2.359
Zn(1)-N(3)	2.202(4)	2.256
Zn(1)-N(5)	1.976(3)	1.998
Zn(1)-C(32)	2.041(3)	2.003
N(1)-Zn(1)-C(32)	122.59(14)	119.07
N(3)-Zn(1)-C(32)	120.12(14)	122.51
N(5)-Zn(1)-C(32)	125.94(14)	129.59

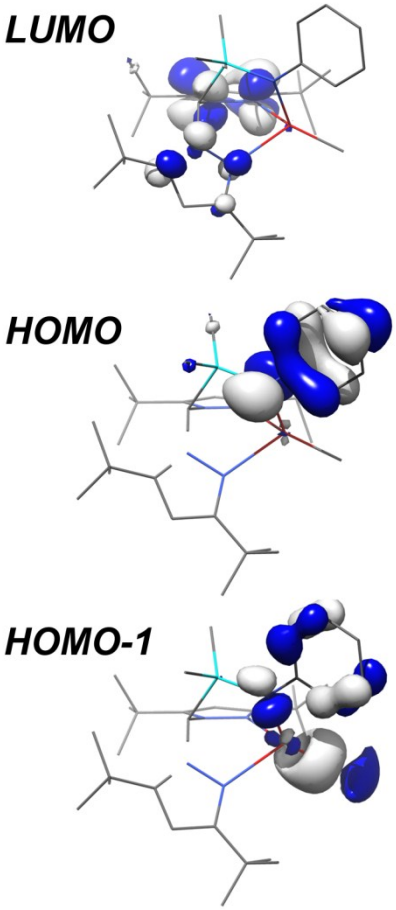

Figure S18. DFT-computed HOMO-1, HOMO and LUMO of Zn{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}Me (**28**)

Table S7. Cartesian coordinates for $HC(^tBu_2pz)_2SiMe_2Cl$

Si	0.144494	1.768334	-1.065887
Cl	2.151173	2.279894	-0.507738
N	-2.045036	0.419553	-1.331330
N	-1.283552	-0.570014	-0.785652
N	1.343695	-1.130110	-1.999550
N	1.176399	-0.856258	-0.677894
C	-3.270402	-0.068085	-1.501951
C	-3.297585	-1.410550	-1.062680
C	-2.025202	-1.717802	-0.592228
C	-4.404447	0.744925	-2.124510
C	-5.772393	0.185220	-1.682166
C	-4.313560	0.654661	-3.664600
C	-4.320445	2.221782	-1.693926
C	-1.589540	-3.047885	0.021416
C	-2.805529	-3.998417	0.068341
C	-1.106745	-2.837175	1.471589
C	-0.490728	-3.741020	-0.814589
C	2.523241	-1.732438	-2.109590
C	3.134861	-1.830830	-0.841078
C	2.271411	-1.238382	0.073254
C	3.055106	-2.207273	-3.457121
C	2.260184	-3.447441	-3.924183
C	2.913109	-1.079517	-4.500261
C	4.543133	-2.586588	-3.323583
C	2.624581	-1.049949	1.561619
C	4.000314	-0.334690	1.622156
C	2.772590	-2.448398	2.211134
C	1.649402	-0.213443	2.415010
C	0.018800	-0.040315	-0.332844
C	-0.828673	3.051452	-0.124689
C	0.187312	1.919457	-2.919030
H	-4.149087	-2.081858	-1.083629
H	-6.582646	0.781684	-2.131827
H	-5.891989	0.223277	-0.587551
H	-5.916343	-0.856512	-2.010009
H	-5.106492	1.259938	-4.133705
H	-4.434795	-0.384868	-4.009006
H	-3.343893	1.025004	-4.032023
H	-5.137073	2.797760	-2.157171
H	-4.409018	2.326815	-0.600300
H	-3.371225	2.678888	-2.007345
H	-2.500514	-4.953987	0.522752
H	-3.628890	-3.587900	0.672182
H	-3.191997	-4.218108	-0.938566
H	-0.900502	-3.809502	1.946584
H	-1.868456	-2.315834	2.073627
H	-0.179312	-2.254913	1.510025
H	-0.220230	-4.702456	-0.347753
H	0.417846	-3.135863	-0.896715
H	-0.848095	-3.948298	-1.835013
H	4.104203	-2.261547	-0.611213
H	2.658115	-3.820819	-4.883011
H	2.332164	-4.262980	-3.186181
H	1.195228	-3.205218	-4.063341
H	3.315480	-1.405763	-5.473804
H	3.464431	-0.178438	-4.186590
H	1.859447	-0.796106	-4.640365
H	4.939677	-2.923468	-4.294811

H	4.692812	-3.407773	-2.604135
H	5.149266	-1.729546	-2.988729
H	4.291800	-0.167505	2.672077
H	4.789290	-0.934520	1.146201
H	3.959685	0.638301	1.112470
H	3.144293	-2.351641	3.245169
H	1.811840	-2.983781	2.242541
H	3.485799	-3.072758	1.653583
H	2.064299	-0.125859	3.431493
H	0.659079	-0.679395	2.519453
H	1.529696	0.807824	2.024774
H	0.003566	0.039994	0.756618
H	-0.770412	2.872659	0.961791
H	-0.391243	4.045014	-0.315997
H	-1.884908	3.062557	-0.422216
H	0.885521	1.175396	-3.327363
H	0.550751	2.922047	-3.198495
H	-0.801715	1.747692	-3.364636

Table S8. Cartesian coordinates for Mg{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$N^{i}Pr}Me (**5**)

Mg	0.002068	0.069189	0.035113
N	-1.411667	-1.625345	-0.350074
N	-1.045756	-2.818420	0.219394
N	1.516778	-1.543022	-0.254210
N	1.360043	-2.617159	0.580527
N	-0.029243	0.026120	2.060712
Si	-0.355280	-1.494216	2.673829
C	-2.497618	-1.863952	-1.090982
C	-2.848475	-3.223304	-0.980361
C	-1.919789	-3.818272	-0.138378
C	-3.221129	-0.790484	-1.896619
C	-2.298019	-0.247741	-3.010841
C	-3.658601	0.351176	-0.953422
C	-4.479311	-1.392638	-2.555726
C	-1.889892	-5.290221	0.273938
C	-1.994257	-5.468082	1.806918
C	-0.625850	-5.973263	-0.296600
C	-3.118903	-6.005539	-0.331916
C	2.747464	-1.632712	-0.775961
C	3.395336	-2.755753	-0.241254
C	2.506256	-3.371445	0.634848
C	3.304315	-0.650651	-1.801910
C	2.388088	-0.636804	-3.045875
C	3.407431	0.766384	-1.194464
C	4.716779	-1.097408	-2.231188
C	2.932433	-4.557605	1.520055
C	1.865977	-5.183437	2.434413
C	3.486328	-5.672683	0.600904
C	4.076095	-4.045174	2.434300
C	0.035826	-2.786450	1.221694
C	-2.141842	-1.890928	3.152442
C	0.688726	-2.013166	4.162264
C	0.227111	1.158481	2.957814
C	-0.768477	2.302843	2.722137
C	1.678340	1.652547	2.832634
C	-0.042865	1.861136	-1.123901
H	-3.686461	-3.715617	-1.457217
H	-2.835812	0.503700	-3.611830
H	-1.979419	-1.058525	-3.685833
H	-1.403334	0.235933	-2.596087
H	-4.188614	1.131871	-1.522750
H	-4.340414	-0.025499	-0.173873
H	-2.799233	0.824344	-0.457971
H	-5.012630	-0.609480	-3.117247
H	-4.224880	-2.194498	-3.266534
H	-5.178394	-1.801535	-1.809560
H	-2.078495	-6.539028	2.051960
H	-1.128391	-5.081580	2.359155
H	-2.888879	-4.959799	2.197048
H	-0.542412	-7.005775	0.080595
H	-0.675978	-6.016250	-1.395684
H	0.296338	-5.437987	-0.037497
H	-3.100562	-7.068687	-0.044864
H	-3.124804	-5.957450	-1.431113
H	-4.060432	-5.574784	0.040643
H	4.407640	-3.082641	-0.448727
H	2.773530	0.071732	-3.796772
H	2.340430	-1.634971	-3.509972

H	1.365337	-0.328219	-2.786895
H	3.843042	1.460925	-1.931273
H	4.052330	0.768530	-0.301542
H	2.422395	1.163594	-0.913087
H	5.112425	-0.402073	-2.987803
H	4.712585	-2.104131	-2.679426
H	5.418725	-1.100281	-1.381869
H	2.344803	-5.970031	3.038172
H	1.057519	-5.667469	1.871855
H	1.435959	-4.456465	3.135733
H	3.880272	-6.502231	1.209937
H	4.302783	-5.310493	-0.040387
H	2.700613	-6.076373	-0.056262
H	4.470832	-4.874333	3.044136
H	4.907666	-3.625185	1.850854
H	3.714230	-3.260295	3.116166
H	0.054037	-3.769863	1.682843
H	-2.275851	-2.916631	3.535238
H	-2.836598	-1.736752	2.312364
H	-2.451380	-1.202377	3.957184
H	0.413278	-3.007142	4.551722
H	1.770519	-2.000033	3.953698
H	0.512498	-1.295782	4.982111
H	0.095352	0.853142	4.018611
H	-0.584759	3.150894	3.403729
H	-1.800501	1.949297	2.878914
H	-0.693999	2.675763	1.687002
H	1.890519	2.489902	3.519602
H	2.384657	0.837212	3.055326
H	1.880941	1.999860	1.804948
H	0.565645	2.632220	-0.610372
H	-1.063250	2.286814	-1.177632
H	0.324711	1.835829	-2.167489

Table S9. Cartesian coordinates for Zn{HC(^{t}Bu$_2$pz)$_2$SiMe$_2$NPh}Me (**28**)

Zn	-0.170953	-0.041310	-0.200738
N	-0.006399	-0.015254	2.152680
N	-0.138966	-1.253669	2.710081
N	1.590864	-1.424493	0.067319
N	1.552269	-2.172507	1.216138
N	-1.495364	-1.525456	-0.388371
Si	-1.124381	-2.909180	0.520075
C	-0.204799	0.871330	3.134923
C	-0.508735	0.186721	4.324677
C	-0.471623	-1.174719	4.044125
C	-0.086862	2.380589	2.956875
C	1.153929	2.721270	2.106596
C	-1.374367	2.921976	2.293191
C	0.085626	3.044738	4.339774
C	-0.891343	-2.246943	5.071404
C	-0.111072	-2.008087	6.387520
C	-2.402776	-2.048560	5.359600
C	-0.687703	-3.715018	4.663181
C	2.831567	-1.509553	-0.415775
C	3.607725	-2.323269	0.436045
C	2.783303	-2.732911	1.472911
C	3.306459	-0.796701	-1.679923
C	2.219604	-0.837899	-2.772233
C	3.664926	0.667999	-1.329256
C	4.575207	-1.489658	-2.223160
C	3.186032	-3.586797	2.672927
C	2.964965	-2.795919	3.982869
C	2.446486	-4.947159	2.684843
C	4.696709	-3.898123	2.583625
C	0.235926	-2.387290	1.840508
C	-2.612020	-3.548201	1.483482
C	-0.293249	-4.369019	-0.343342
C	-2.545078	-1.459465	-1.305820
C	-3.075990	-0.213599	-1.726385
C	-4.118297	-0.133548	-2.650102
C	-4.695019	-1.287724	-3.193815
C	-4.192954	-2.528754	-2.793138
C	-3.140290	-2.614443	-1.879278
C	-0.039623	1.687279	-1.204955
H	-0.755105	0.630226	5.282751
H	1.249378	3.813919	2.000565
H	2.071010	2.345347	2.588402
H	1.092334	2.283559	1.102693
H	-1.328917	4.018709	2.191095
H	-1.518007	2.491535	1.291666
H	-2.260160	2.672850	2.899412
H	0.270847	4.124043	4.217283
H	0.943438	2.616989	4.882996
H	-0.811369	2.931872	4.968761
H	-0.452696	-2.717248	7.158028
H	-0.271465	-0.993507	6.780102
H	0.972551	-2.150890	6.253117
H	-2.732852	-2.758612	6.135222
H	-2.617707	-1.031823	5.720067
H	-3.008379	-2.223670	4.457797
H	-1.062850	-4.363144	5.469771
H	0.370346	-3.968348	4.516942
H	-1.249298	-3.977141	3.758562

H	4.651965	-2.580943	0.307256
H	2.579740	-0.327555	-3.679809
H	1.297068	-0.336081	-2.453498
H	1.964665	-1.874918	-3.041925
H	4.040825	1.194495	-2.222478
H	2.789644	1.213747	-0.951946
H	4.450178	0.707989	-0.557079
H	4.896097	-0.993526	-3.152611
H	5.416122	-1.426091	-1.514677
H	4.394736	-2.552119	-2.453403
H	3.242003	-3.413353	4.853542
H	3.593550	-1.892671	3.994265
H	1.928939	-2.462696	4.116370
H	2.794658	-5.555721	3.535202
H	2.655430	-5.508593	1.760835
H	1.355227	-4.859318	2.773478
H	4.996186	-4.510135	3.448508
H	5.301147	-2.978734	2.596341
H	4.947848	-4.467140	1.675737
H	0.339344	-3.250187	2.494627
H	-2.445078	-4.522038	1.972594
H	-2.940588	-2.821182	2.242692
H	-3.452657	-3.672545	0.782750
H	0.130135	-5.080480	0.386224
H	0.520989	-4.037439	-1.005865
H	-1.012197	-4.931046	-0.961381
H	-2.653438	0.702030	-1.307542
H	-4.493924	0.849907	-2.950020
H	-5.516336	-1.218747	-3.911721
H	-4.619010	-3.448734	-3.205933
H	-2.755055	-3.602715	-1.617724
H	-0.769883	2.423283	-0.827881
H	0.947002	2.175385	-1.186962
H	-0.296953	1.502281	-2.262128

References

(1) Beck, A.; Weibert, B.; Burzlaff, N. *Eur. J. Inorg. Chem.* **2001**, *2001*, 521-527.

(2) Howe, R. G.; Tredget, C. S.; Lawrence, S. C.; Subongkoj, S.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2006**, 223-225.

(3) Westerhausen, M. *Inorg. Chem.* **1991**, *30*, 96-101.

(4) (a) Barakat, I.; Dubois, P.; Jérôme, R.; Teyssié, P. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 505-514; (b) Dorgan, J. R.; Janzen, J.; Knauss, D. M.; Hait, S. B.; Limoges, B. R.; Hutchinson, M. H. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 3100-3111.

(5) F. Neese, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2012, **2**, 73.

(6) (a) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524-4529; (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785-789; (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

(7) (a) Pantazis, D. A.; Chen, X.-Y.; Landis, C. R.; Neese, F. *J. Chem. Theory Comput.* **2008**, *4*, 908-919; (b) Pantazis, D. A.; Neese, F. *J. Chem. Theory Comput.* **2009**, *5*, 2229-2238.

(8) (a) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829-5835; (b) Weigend, F.; Ahlrichs, R. *PCCP* **2005**, *7*, 3297-3305.

(9) Weigend, F. *PCCP* **2006**, *8*, 1057-1065.

(10) (a) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119-124; (b) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283-290; (c) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652-660.

(11) Pettersen, E. F.; Goddard, T. D.; Huang, C. C.; Couch, G. S.; Greenblatt, D. M.; Meng, E. C.; Ferrin, T. E. *J. Comput. Chem.* **2004**, *25*, 1605-1612.