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A Novel Transformation of a Zirconium Imido Compound and the Development of a New Class of N_3 Donor Heteroscorpionate Ligand

Robert G. Howe, Cara S. Tredget, Sally C. Lawrence, Suparabhorn Subongkoj, Andrew R. Cowley and Philip Mountford

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Electronic supporting information: characterising data

[Zr(N-2,6-$C_6H_3{}^iPr_2$){MeSi(3,5-$Me_2pz)_2$}Cl_3] (1)

^{1}H NMR Data (CD_2Cl_2, 300 MHz, 298 K): 7.10 (3H, s, *m*- and *p*-$C_6\underline{H}_3{}^iPr$), 6.03 (2H, s, 4-$N_2C_3Me_2\underline{H}$), 3.06 (2H, sept, ^3J = 6.9 Hz $C_6H_3(C\underline{H}Me_2)_2$), 2.62 (6H, s, 3-$N_2C_3\underline{Me}_2H$), 2.37 (6H, s, 5-$N_2C_3\underline{Me}_2H$), 1.17 (6H, d, ^3J = 6.9 Hz$C_6H_3(CH\underline{Me}_2)_2$dn), 0.90 (3H, s, Si$\underline{Me}$), 0.84 (6H, d, ^3J = 6.6 Hz $C_6H_3(CH\underline{Me}_2)_2$ up). ^{13}C-{^{1}H} NMR data (CD_2Cl_2, 125.7 MHz, 298 K): 158.5 (*ipso*-$\underline{C}_6H_3{}^iPr_2$), 147.5(3-$N_2\underline{C}_3Me_2H$), 144.3 (5-$N_2\underline{C}_3Me_2H$), 125.5 (*m*- or *p*-$\underline{C}_6H_3{}^iPr_2$), 124.5 (*o*-$\underline{C}_6H_3{}^iPr_2$), 110.2 (4-$N_2\underline{C}_3Me_2H$), 28.4 {$C_6H_3(\underline{C}HMe_2)_2$}, 25.9 {$C_6H_3(CH\underline{Me}_2)_2$ u}, 23.8 {$C_6H_3(CH\underline{Me}_2)_2$ dn}, 15.4 (3-$N_2C_3\underline{Me}_2H$), 13.0 (5-$N_2C_3\underline{Me}_2H$), -3.9 (SiMe). IR data (NaCl plates, Nujol, cm^{-1}): 2360(w), 1543(m), 1418(w), 1338(w), 1316(w), 1273(m), 1262(m), 1242(w), 1184(w), 1099(m), 1041(m), 938(w), 834(m), 801(s), 739(w), 590(w), 501(w). Anal. found: calculated for ($C_{23}H_{34}Cl_3N_5SiZr\cdot 1.25CH_2Cl_2$) C, 41.0 (40.7); N, 10.0 (9.8); H, 4.7 (5.1) %.EI^+ MS: *m/z* = 603 [Zr(N-2,6-$C_6H_3{}^iPr_2$){MeSi(3,5-$Me_2pz)_2$}Cl_3], 35%, *m/z* = 509 [Zr(N-2,6-$C_6H_3{}^iPr_2$){MeSi(3,5-$Me_2pz)Cl_3$}], 80%, *m/z* = 313 [Zr(N-2,6-$C_6H_3{}^iPr_2$)(SiMe)], 100%.

[$HC(Me_2pz)_2SiMe_2Cl$] (2)

^{1}H NMR data (C_6D_6, 300.0 MHz, 298 K): 5.69 (1 H, s, $\underline{H}C(3,5\text{-}Me_2pz)_2(SiMe_2Cl)$), 5.62 (2 H, s, 4-$\underline{H}$-pz), 2.08 (6 H, s, 5-$\underline{Me}$-pz), 1.76 (6 H, s, 3-$\underline{Me}$-pz), 0.97 (6 H, s, Si$\underline{Me}_2$). ^{13}C-{^{1}H} NMR data (C_6D_6, 75.0 MHz, 298 K): 147.4 (5-pz), 139.3 (3-pz), 106.1 (4-pz), 66.4 ($H\underline{C}(3,5\text{-}Me_2pz)_2(SiMe_2Cl)$), 13.6 (5-$\underline{Me}$-pz), 10.7 (3-$\underline{Me}$-pz), 3.9 (Si$\underline{Me}_2$). I.R. data (NaCl plates, Nujol mull, cm^{-1}): 1558 (s), 1414 (s), 1381 (m), 1352 (m), 1324 (m), 1245 (s), 1031 (m), 975 (w), 882 (m), 752 (w), 711 (w), 673 (m). Anal. found: (calculated for $C_{13}H_{21}ClN_4$): C, 53.2 (52.6); N, 19.1 (18.9); H, 7.1 (7.1) %. EI^+ MS: *m/z* = 296 $[HC(3,5\text{-}Me_2pz)_2(SiMe_2Cl)]^+$, 80%, *m/z* = 261 $[HC(3,5\text{-}Me_2pz)_2(SiMe_2)]^+$, 100%.

[HC(Me$_2$pz)$_2$SiMe$_2$N(H)^{i}Pr] (3)

^{1}H NMR data (C_6D_6, 300.0 MHz, 298 K): 5.96 (1 H, s, HC(3,5-Me$_2$pz)$_2$(SiMe$_2$NH^{i}Pr), 5.65 (2 H, s, 4-H-pz), 3.11 (1 H, sept, ^{3}J = 6.0 Hz, HCMe$_2$), 2.15 (6 H, s, 5-Me-pz), 1.83 (6 H, s, 3-Me-pz), 0.97 (6 H, d, ^{3}J = 6.3 Hz, HCMe$_2$), 0.38 (6 H, s, SiMe$_2$).^{13}C-{^{1}H} NMR data (C_6D_6, 75 MHz, 298 K): 146.5 (5-pz), 139.9 (3-pz), 106.3 (4-pz), 69.8 (HC(3,5-Me$_2$pz)$_2$(SiMe$_2$NH^{i}Pr)), 43.5 (HCMe$_2$), 28.0 (HCMe$_2$), 13.7 (5-Me-pz), 10.9 (3-Me-pz), -0.8 (SiMe$_2$). I.R. data (NaCl plates, Nujol mull, cm^{-1}): 2960 (s), 1554 (m), 1358 (m), 1320 (w), 1259 (s), 1167 (w), 1023 (s), 881 (w).Anal. found: (calculated for $C_{16}H_{29}N_5Si$) C, 60.0 (60.1); N, 21.9 (21.9); H, 9.0 (9.2) %.EI$^+$ MS: *m/z* = 289 [HC(3,5-Me$_2$pz)$_2$(SiNH^{i}Pr)]$^+$, 30%, *m/z* = 261 [HC(3,5-Me$_2$pz)$_2$(SiMe$_2$)]$^+$, 20%, *m/z* = 224 [HC(3,5-Me$_2$pz)(SiMe$_2$NH^{i}Pr)]$^+$, 52%.

[Zr{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}(CH$_2$SiMe$_3$)$_3$] (4)

^{1}H NMR data (CD_2Cl_2, 300.0 MHz, 248 K): 5.90 (2 H, s, 4-H-pz), 5.43 (1 H, s, HC(Me$_2$pz)$_2$, 4.48 (1 H, sept., ^{3}J = 5.87, HCMe$_2$), 2.31 (overlapping, 12 H, s, 3,5-Me$_2$pz), 1.19 (6 H, d, ^{3}J = 5.86, HCMe$_2$), 0.78 (2 H, d, ^{2}J = 11.56, CH$_2$SiMe$_3$), 0.50 (2 H, d, ^{2}J= 11.56, CH$_2$SiMe$_3$), 0.02 (2 H, s, CH$_2$SiMe$_3$), -0.05 (18 H, s, CH$_2$SiMe$_3$), -0.11 (6 H, s, SiMe$_2$), -0.34 (9 H, s, SiMe$_3$) ppm. ^{13}C-{^{1}H} NMR data (CD_2Cl_2, 75 MHz, 248 K): 149.6 (3-pz), 138.9 (5-pz), 106.8 (4-pz), 62.2 (HC(pz)), 59.1 (CH$_2$SiMe$_3$), 44.7 (HCMe$_2$), 41.4 (CH$_2$SiMe$_3$), 28.2 (HCMe$_2$), 15.7 (3,5-Me$_2$pz), 11.4 (3,5-Me$_2$pz), 2.7 (SiMe$_3$), 2.63 (SiMe$_2$), 0.95 (SiMe$_3$) ppm. I.R. data (NaCl plates, Nujol mull, cm^{-1}): 1558 (w), 1418 (m), 1259 (s), 1241 (s), 1153 (m), 898 (s), 850 (s), 821 (s), 786 s). Anal. found: (calculated for $C_{28}H_{61}N_5Si_4Zr$): C, 46.8 (50.1); N, 10.0 (10.4); H, 9.1 (9.2) %. The low %C analysis of this spectroscopically pure sample is attributed to incomplete combustion (carbide formation) or thermal degradation (e.g., elimination of $SiMe_4$ and alkylidene formation) before combustion starts.

[Sc{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}(CH$_2$SiMe$_3$)$_2$] (5)

^{1}H NMR data (C_6D_6, 300.0 MHz, 298 K): 5.23 (2 H, s, 4-H-pz), 5.05 (1 H, s, HC(3,5-Me$_2$pz)$_2$(SiMe$_2$NH^{i}Pr)), 4.75 (1 H, sept, ^{3}J = 6.4 Hz, HCMe$_2$), 2.35 (6 H, s, 3-Me-pz), 1.50 (6 H, s, 5-Me-pz), 1.47 (6 H, d, ^{3}J = 6.5 Hz, HCMe$_2$), 0.54 (4 H, d, CH$_2$SiMe$_3$), 0.45 (18 H, s, SiMe$_3$), -0.01 (6 H, s, SiMe$_2$).^{13}C-{^{1}H} NMR data (C_6D_6, 75 MHz, 298 K): 150.8 (3-pz), 139.0 (5-pz), 107.0 (4-pz), 64.4 (HC(3,5-Me$_2$pz)$_2$(SiMe$_2$NH^{i}Pr)), 47.1 (SiMe$_2$), 36.8 (HCMe$_2$), 29.7 (HCMe$_2$), 15.0 (3-Me-pz), 10.4 (5-Me-pz), 4.5 (SiMe$_3$), 1.9 (CH$_2$SiMe$_2$). I.R. data (NaCl plates, Nujol mull, cm^{-1}): 2854 (s), 1556 (w), 1461 (s), 1376 (s), 1163 (w), 1023 (w), 856 (m). Anal. found: (calculated for $C_{24}H_{50}N_5Si_3Sc$): C, 53.5 (53.6); N, 13.0 (13.0); H, 9.5 (9.4) %.

[Y{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}(CH$_2$SiMe$_3$)$_2$(THF)] (6)

^{1}H NMR data (C_6D_6, 300.0 MHz, 298 K): 5.23 (2 H, s, 4-H-pz), 5.05 (1 H, s, HC(3,5-Me$_2$pz)$_2$(SiMe$_2$NH^{i}Pr)), 4.75 (1 H, sept, ^{3}J = 6.4 Hz, HCMe$_2$), 4.68 (4 H, m, OCH$_2$CH$_2$), 2.35 (6 H, s, 3-Me-pz), 1.50 (6 H, s, 5-Me-pz), 1.45 (6 H, d, ^{3}J = 6.2 Hz, HCMe$_2$), 1.19 (4 H, m, OCH$_2$CH$_2$) 0.44 (18 H, s, SiMe$_3$), 0.29 (6 H, s, SiMe$_2$), -0.01 (4 H, d, CH$_2$SiMe$_3$). ^{13}C-{^{1}H} NMR data (C_6D_6, 75.0 MHz, 298 K): 149.9 (3-pz), 139.0 (5-pz), 106.3 (4-pz), 69.6 (HCMe$_2$), 65.1 (HC(3,5-Me$_2$pz)$_2$(SiMe$_2$NH^{i}Pr)), 30.9 (HCMe$_2$), 28.6 (d, CH$_2$SiMe$_3$), 14.7 (3-Me-pz), 10.9 (5-Me-pz), 5.1 (SiMe$_3$), 2.9 (SiMe$_2$). I.R. data (NaCl plates, Nujol mull, cm^{-1}): 2924 (s), 2854 (s), 1555 (w), 1459 (s), 1376 (m), 1231 (m), 1178 (m), 862 (s), 792 (m), 770 (m), 756 (m), 727 (w). Elemental analysis for $C_{28}H_{50}N_5OSi_3Y$: Found (calculated): C, 51.3 (51.4); N, 10.6 (10.7); H, 8.8 (8.9) %.

[Zr{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}(CH$_2$SiMe$_3$)$_2$][B(Ar^F)$_4$] (7) (NMR tube scale)

^{1}H NMR (CD_2Cl_2, 300.0 MHz, 298 K). 6.12 (2 H, s, 4-H-pz), 5.86 (1 H, s, HCpz), 4.41 (1 H, sept., ^{3}J = 6.17 Hz, HCMe$_2$), 2.44 (6 H, s, 3,5-Me$_2$pz), 2.37 (6 H, s, 3,5-Me$_2$pz), 1.59 (2 H, d, ^{2}J = 11.45, CH$_2$SiMe$_3$), 1.51 (6 H, d, ^{3}J = 6.46 Hz, HCMe$_2$), 1.10 (2 H, d, ^{2}J = 11.16 Hz, CH$_2$SiMe$_3$), 0.08 (6H, s, SiMe$_2$), 0.03 (18 H, s, CH$_2$SiMe$_3$). ^{19}F NMR (CD_2Cl_2, 282.1 MHz, 298 K): -133.56 (*o*-C_6F_5), -164.11 (*p*-C_6F_5), -167.98 (*m*-C_6F_5).

[Sc{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}(CH$_2$SiMe$_3$)(THF)][B(Ar^F)$_4$] (8) (NMR tube scale)

^{1}H NMR data (CD_2Cl_2, 300.0 MHz, 298 K): 6.08 (2 H, s, 4-H-pz), 5.73 (1 H, s, HC(3,5-Me$_2$pz)$_2$(SiMe$_2$NH^{i}Pr)), 4.18 (4 H, br s, thf), 3.67 (1 H, sept, ^{3}J = 6.5 Hz, HCMe$_2$), 2.40 (6 H, s, 5-Me-pz), 2.38 (6 H, s, 3-Me-pz), 2.11 (4 H, br s, thf), 1.26 (6 H, d, ^{3}J = 6.5 Hz, HCMe$_2$), 0.35 (2 H, s, CH$_2$SiMe$_3$), 0.04 (6 H, s, SiMe$_2$), 0.00 (18 H, s, SiMe$_3$).^{19}F NMR data (CD_2Cl_2, 282.1 MHz, 298 K): -133.6 (*o*-C_6F_5), -164.1 (*p*-C_6F_5), -169.0 (*m*-C_6F_5).

Ethylene polymerisation data

[Zr(N-2,6-C$_6$H$_3$^{i}Pr$_2$){MeSi(3,5-Me$_2$pz)$_2$}Cl$_3$] (1). Evaluation of **1** with MAO cocatalyst in toluene gave a productivity in excess of 3120 kg(PE).mol^{-1}.h^{-1}.bar^{-1} (M_w = 336,000; M_w/M_n = 3.1).

[Zr{HC(Me$_2$pz)$_2$SiMe$_2$N^{i}Pr}(CH$_2$SiMe$_3$)$_3$] (4). Evaluation of **4** with [CPh$_3$][BAr$^F_4$] cocatalyst in toluene in the presence of Al^{i}Bu$_3$ gave an ethylene polymerisation productivity of 315 kg(PE).mol^{-1}.h^{-1}.bar^{-1} (M_w = 209,000; M_w/M_n = 2.8)