

Supplementary Material (ESI) for Chemical Communications

Divergent reaction pathways of tris(oxazolinyl)borato zinc and magnesium silyl compounds

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Experimental details.

General Procedures. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox, unless otherwise indicated. Benzene, toluene, pentane, diethyl ether, and tetrahydrofuran were dried and deoxygenated using an IT PureSolv system. Benzene-*d*₆ was heated to reflux over Na/K alloy and vacuum-transferred. The starting materials (TMEDA)MgMeBr,¹ H[To^M],² To^MMgMe,³ To^MZnCl,⁴ Si(SiHMe₂)₄,⁵ and KSi(SiMe₃)₃⁶ were synthesized according to literature procedures. ¹H, ¹³C{¹H}, ²⁹Si and ¹¹B NMR spectra were collected on Agilent MR-400, Bruker DRX400 or AVIII 600 spectrometers. ¹¹B NMR spectra were referenced to an external BF₃OEt₂ standard. ²⁹Si NMR spectra were acquired with INEPT sequences and referenced to an external SiMe₄ standard. ¹⁵N chemical shifts were determined by ¹H-¹⁵N HMBC experiments on a Bruker AVII 600 spectrometer with a Bruker Z-gradient inverse TXI ¹H/¹³C/¹⁵N 5mm cryoprobe; ¹⁵N chemical shifts were originally referenced to an external liquid NH₃ standard and recalculated to the CH₃NO₂ chemical shift scale by adding -381.9 ppm. Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHN/S by the Iowa State Chemical Instrumentation Facility. X-ray diffraction data was collected on a Bruker APEX II diffractometer.

Caution! High-pressure glass apparatuses must be handled with care. Thick-walled NMR tubes equipped with J. Young-style resealable Teflon valves (pressured to 100 psi with CO₂) were obtained from Wilmad-Labglass and attached to a high-pressure steel manifold through commercial Swagelock fittings. The pressurized NMR tubes were handled in protective jackets.

To^MMgBr(THF)₂, H[To^M] (0.100 g, 4.25 mmol) and (TMEDA)MgMeBr (0.163 g, 4.25 mmol) were dissolved in THF and stirred for 30 min at ambient temperature. The volatile materials were

evaporated, the residue was washed with pentane (3×5 mL), and the resulting white solid was dried under vacuum to provide $\text{To}^{\text{M}}\text{MgBr}(\text{THF})_2$ (0.230 g, 0.365 mmol, 85.8%). Analytically pure $\text{To}^{\text{M}}\text{MgBr}(\text{THF})_2$ and X-ray quality single crystals were obtained from a concentrated THF solution of $\text{To}^{\text{M}}\text{MgBr}(\text{THF})_2$ at -30 °C. Additionally, the quantity of THF in the product can vary from zero to two equivalents; the data is given for a batch isolated with two equivalents of THF. ^1H NMR (400 MHz, benzene- d_6): δ 1.06 (s, 18 H, $\text{CNCMe}_2\text{CH}_2\text{O}$), 1.42 (t, $^3J_{\text{HH}} = 6.6$ Hz, 8 H, β -THF), 3.36 (s, 6 H, $\text{CNCMe}_2\text{CH}_2\text{O}$), 3.58 (t, $^3J_{\text{HH}} = 6.6$ Hz, 8 H, α -THF), 7.36 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1 H, *para*- C_6H_5), 7.53 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, *meta*- C_6H_5), 8.23 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, *ortho*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 175 MHz): δ 26.15 (β -THF), 28.44 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 65.64 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 68.17 (α -THF), 80.80 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 126.54 (*para*- C_6H_5), 127.32 (*meta*- C_6H_5), 136.32 (*ortho*- C_6H_5), 142.84 (br, *ipso*- C_6H_5), 191.30 (br, $\text{CNCMe}_2\text{CH}_2\text{O}$). ^{11}B NMR (128 MHz, benzene- d_6): δ -18.2 . ^{15}N NMR: δ -160.9 . IR (KBr, cm^{-1}): 3050 (m), 2972 (s), 2873 (m), 1599 (s, ν_{CN}), 1492 (w), 1462 (s), 1433 (m), 1389 (m), 1371 (s), 1354 (m), 1303 (m), 1273 (s), 1253 (m), 1197 (s), 1155 (s), 1047 (s), 995 (s), 966 (s), 939 (m), 890 (m), 843 (m), 822 (w), 777 (w), 708 (m), 695 (s), 685 (w), 666 (w), 649 (w). Anal. Calcd. for $\text{C}_{29}\text{H}_{45}\text{BBrMgN}_3\text{O}_5$: C, 55.23; H, 7.19; N, 6.66. Found: C, 54.75; H, 6.70; N, 6.58. Mp: 251-253 °C.

$\text{KSi}(\text{SiHMe}_2)_3$. $\text{Si}(\text{SiHMe}_2)_4$ (6.00 g, 0.027 mol) and KO^tBu (3.95 g, 0.027 mol) were dissolved in benzene (25 mL). The solution was allowed to stir for 30 min, and the product precipitated as a white solid during this time. The solid was isolated by filtration, washed with pentane, and recrystallized from toluene at -30 °C to give a white crystalline solid (5.99 g, 0.024 mol, 90.7%). ^1H NMR (benzene- d_6 , 600 MHz): δ 0.559 (d, 18 H, $^3J_{\text{HH}} = 4.5$ Hz, SiHMe_2), 4.22 (sept, 3 H, $^3J_{\text{HH}} = 4.5$ Hz, $^1J_{\text{SiH}} = 151.8$ Hz, SiHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 150 MHz): δ 2.47 (SiHMe_2). ^{29}Si (benzene- d_6 , 119.3 MHz) δ -23.8 (SiHMe_2), -202.3 ($\text{Si}(\text{SiHMe}_2)_3$). IR (KBr, cm^{-1}): 2959 (s), 2894 (s), 2020 (s, ν_{SiH}), 1419 (m), 1242 (s), 1041 (s), 872 (s), 766 (m), 685 (m), 645 (m). Anal. Calcd. for $\text{C}_6\text{H}_{21}\text{KSi}_4$: C, 29.45; H, 8.65. Found C, 29.20; H, 8.51. Mp 123-125 °C.

$\text{To}^{\text{M}}\text{ZnSi}(\text{SiHMe}_2)_3$ (1). $\text{To}^{\text{M}}\text{ZnCl}$ (0.235 g, 0.486 mmol) and $\text{KSi}(\text{SiHMe}_2)_3$ (0.119 g, 0.486 mmol) were dissolved in benzene, and the reaction mixture was stirred for 30 min. The reaction mixture was filtered to remove KCl, the filtrate was evaporated, and the resulting solid residue was washed with pentane and dried under vacuum to afford $\text{To}^{\text{M}}\text{ZnSi}(\text{SiHMe}_2)_3$ (0.303 g, 0.464

mmol, 95.5%) as an analytically pure white solid. X-ray quality single crystals were grown by slow pentane diffusion into a concentrated toluene solution of $\text{To}^{\text{M}}\text{ZnSi}(\text{SiHMe}_2)_3$ at $-30\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, benzene- d_6): δ 0.57 (d, $^3J_{\text{HH}} = 4.4$ Hz, 18 H, SiHMe_2), 1.14 (s, 18 H, $\text{CNCMe}_2\text{CH}_2\text{O}$), 3.45 (s, 6 H, $\text{CNCMe}_2\text{CH}_2\text{O}$), 4.64 (sept, $^3J_{\text{HH}} = 4.4$ Hz, 3 H, SiHMe_2), 7.35 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1 H, *para*- C_6H_5), 7.53 (vt, $^3J_{\text{HH}} = 7.6$ Hz, 2 H, *meta*- C_6H_5), 8.31 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, *ortho*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, benzene- d_6): δ 0.16 (SiHMe_2), 28.76 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 66.08 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 81.06 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 126.37 (*para*- C_6H_5), 127.30 (*meta*- C_6H_5), 136.46 (*ortho*- C_6H_5), 142.30 (br, *ipso*- C_6H_5), 190.18 (br, $\text{CNCMe}_2\text{CH}_2\text{O}$). ^{11}B NMR (128 MHz, benzene- d_6): δ -18.5 . ^{29}Si NMR (120 MHz, benzene- d_6): δ -28.3 ($^1J_{\text{SiH}} = 172.2$ Hz, $\text{Si}(\text{SiHMe}_2)_3$), -171.3 ($\text{Si}(\text{SiHMe}_2)_3$). ^{15}N NMR (59.2 MHz, benzene- d_6): δ -157.4 . IR (KBr, cm^{-1}): 3079 (w), 2967 (s), 2897 (m), 2064 (s, ν_{SiH}), 1591 (s, ν_{CN}), 1495 (w), 1462 (m), 1431 (w), 1387 (m), 1368 (m), 1276 (s), 1241 (s), 1195 (s), 1158 (s), 961 (s), 867 (s), 747 (m), 703 (s). Anal. Calcd. for $\text{C}_{27}\text{H}_{50}\text{BSi}_4\text{N}_3\text{O}_3\text{Zn}$: C, 49.64; H, 7.71; N, 6.43. Found: C, 49.21; H, 7.58; N, 6.37. Mp: 208-210 $^\circ\text{C}$.

$\text{To}^{\text{M}}\text{MgSi}(\text{SiHMe}_2)_3$ (2). $\text{To}^{\text{M}}\text{MgBr}(\text{THF})_2$ (0.706 g, 1.12 mmol) and $\text{KSi}(\text{SiHMe}_2)_3$ (0.275 g, 1.12 mmol) were dissolved in benzene (12 mL) and stirred for 30 min at ambient temperature. The reaction mixture was filtered, and evaporation of the filtrate gave a white solid. The solid was washed with pentane (3×5 mL) and dried under vacuum providing crystalline, analytically pure $\text{To}^{\text{M}}\text{MgSi}(\text{SiHMe}_2)_3$ (0.630 g, 1.03 mmol, 91.5%). X-ray quality single crystals were obtained from a concentrated toluene solution cooled to $-30\text{ }^\circ\text{C}$. ^1H NMR (600 MHz, benzene- d_6): δ 0.61 (d, $^3J_{\text{HH}} = 4.2$ Hz, 18 H, SiHMe_2), 1.13 (s, 18 H, $\text{CNCMe}_2\text{CH}_2\text{O}$), 3.38 (s, 6 H, $\text{CNCMe}_2\text{CH}_2\text{O}$), 4.71 (sept, $^3J_{\text{HH}} = 4.2$ Hz, 3 H, SiHMe_2), 7.36 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1 H, *para*- C_6H_5), 7.53 (vt, $^3J_{\text{HH}} = 7.6$ Hz, 2 H, *meta*- C_6H_5), 8.26 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, *ortho*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, benzene- d_6): δ 0.76 (SiHMe_2), 28.89 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 65.91 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 80.65 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 126.42 (*para*- C_6H_5), 127.27 (*meta*- C_6H_5), 136.41 (*ortho*- C_6H_5), 142.30 (br, *ipso*- C_6H_5), 192.83 (br, $\text{CNCMe}_2\text{CH}_2\text{O}$). ^{11}B NMR (128 MHz, benzene- d_6): δ -18.2 . ^{29}Si NMR (120 MHz, benzene- d_6): δ -27.2 ($^1J_{\text{SiH}} = 169.7$ Hz, $\text{Si}(\text{SiHMe}_2)_3$), -186.8 ($\text{Si}(\text{SiHMe}_2)_3$). ^{15}N NMR (59.2 MHz, benzene- d_6): δ -161.9 . IR (KBr, cm^{-1}): 3078 (w), 3048 (w), 2966 (s), 2054 (s, ν_{SiH}), 1582 (s, ν_{CN}), 1495 (w), 1463 (m), 1432 (w), 1387 (w), 1369 (m), 1352 (m), 1274 (s), 1246 (m), 1194 (s), 1160 (m), 963 (s), 894 (s), 861 (s), 832 (s), 747 (m),

703 (m), 689 (m), 670 (m), 650 (m), 639 (m). Anal. Calcd. for $C_{27}H_{50}BN_3O_3Si_4Mg$: C, 52.98; H, 8.23; N, 6.86. Found: C, 53.14; H, 8.35; N, 6.91. Mp: 201-203 °C.

To^MZnSi(SiMe₃)₃ (3). To^MZnCl (0.310 g, 0.642 mmol) and KSi(SiMe₃)₃ (0.184 g, 0.642 mmol) were dissolved in benzene (12 mL), and the reaction mixture was stirred for 2 h at ambient temperature. Filtration and evaporation of the benzene provided a white solid. The solid was washed with pentane (3 × 5 mL) and further dried under vacuum to obtain crystalline, analytically pure To^MZnSi(SiMe₃)₃ (0.420 g, 0.604 mmol, 94.1%). X-ray quality single crystals were grown from a concentrated toluene solution of To^MZnSi(SiMe₃)₃ at -30 °C. ¹H NMR (600 MHz, benzene-*d*₆): δ 0.53 (SiMe₃), 1.14 (s, 18 H, CNCMe₂CH₂O), 3.43 (s, 6 H, CNCMe₂CH₂O), 7.36 (t, ³J_{HH} = 7.2 Hz, 1 H, *para*-C₆H₅), 7.55 (vt, ³J_{HH} = 7.6 Hz, 2 H, *meta*-C₆H₅), 8.33 (d, ³J_{HH} = 7.2 Hz, 2 H, *ortho*-C₆H₅). ¹³C{¹H} NMR (175 MHz, benzene-*d*₆): δ 6.22 (SiHMe₂), 29.47 (CNCMe₂CH₂O), 66.23 (CNCMe₂CH₂O), 81.08 (CNCMe₂CH₂O), 126.28 (*para*-C₆H₅), 127.22 (*meta*-C₆H₅), 136.54 (*ortho*-C₆H₅), 140.55 (br, *ipso*-C₆H₅), 190.21 (br, CNCMe₂CH₂O). ¹¹B NMR (128 MHz, benzene-*d*₆): δ -18.7. ²⁹Si{¹H} NMR (120 MHz, C₆D₆): δ -8.1 (SiMe₃), -162.4 (Si(SiMe₃)₃). ¹⁵N NMR (59.2 MHz, benzene-*d*₆): δ -157.4. IR (KBr, cm⁻¹): 3078 (w), 3039 (w), 2968 (m), 2893 (m), 1591 (s, ν_{CN}), 1496 (w), 1462 (m), 1432 (w), 1386 (w), 1367 (m), 1355 (m), 1277 (s), 1241 (s), 1196 (s), 1162 (s), 1022 (s), 978 (s), 961 (s), 896 (w), 862 (m), 828 (s), 746 (m), 733 (w), 703 (s), 676 (s), 634 (m), 623 (s). Anal. Calcd. for C₃₀H₅₆BSi₄N₃O₃Zn: C, 51.82; H, 8.12; N, 6.04. Found: C, 51.43; H, 7.88; N, 6.01. Mp: 254-258 °C (dec)

To^MMgSi(SiMe₃)₃ (4). The preparation of To^MMgSi(SiMe₃)₃ follows the method used for To^MMgSi(SiHMe₂)₃ given above. To^MMgBr (0.151 g, 0.24 mmol) and KSi(SiMe₃)₃ (0.068 g, 0.24 mmol) afforded To^MMgSi(SiMe₃)₃ (0.145 g, 0.22 mmol, 91.7%) as an analytically pure white solid. X-ray quality single crystals were grown from a concentrated toluene solution of To^MMgSi(SiMe₃)₃ at -30 °C. ¹H NMR (600 MHz, benzene-*d*₆): δ 0.55 (SiMe₃), 1.15 (s, 18 H, CNCMe₂CH₂O), 3.38 (s, 6 H, CNCMe₂CH₂O), 7.35 (t, ³J_{HH} = 7.2 Hz, 1 H, *para*-C₆H₅), 7.53 (vt, ³J_{HH} = 7.6 Hz, 2 H, *meta*-C₆H₅), 8.26 (d, ³J_{HH} = 7.2 Hz, 2 H, *ortho*-C₆H₅). ¹³C{¹H} NMR (175 MHz, benzene-*d*₆): δ 6.42 (SiMe₃), 29.41 (CNCMe₂CH₂O), 66.02 (CNCMe₂CH₂O), 80.67 (CNCMe₂CH₂O), 126.37 (*para*-C₆H₅), 127.27 (*meta*-C₆H₅), 136.48 (*ortho*-C₆H₅), 141.30 (br, *ipso*-C₆H₅), 192.61 (br, CNCMe₂CH₂O). ¹¹B NMR (128 MHz, benzene-*d*₆): δ -18.5. ²⁹Si NMR

(120 MHz, benzene-*d*₆): δ -6.8 (SiMe₃), -179.7 (Si(SiMe₃)₃). ¹⁵N NMR (59.2 MHz, benzene-*d*₆): δ -155.8. IR (KBr, cm⁻¹): 3082 (w), 3044 (w), 2965 (s), 2894 (s), 1582 (s, ν_{CN}), 1496 (w), 1463 (m), 1433 (w), 1387 (w), 1368 (m), 1355 (m), 1369 (m), 1275 (s), 1239 (s), 1192 (s), 1162 (s), 1020 (s), 960 (s), 895 (w), 830 (s), 747 (m), 702 (s), 675 (s), 640 (s), 619 (s), 415 (s). Anal. Calcd. for C₃₀H₅₆BN₃O₃Si₄Mg: C, 61.80; H, 6.53; N, 8.01. Found: C, 61.25; H, 6.30; N, 8.01. Mp: 215-217 °C.

(To^MMgOMe)₂ (5). A benzene solution of To^MMgMe (0.300 g, 0.712 mmol) was exposed to O₂ (1 atm) for 5 minutes in a 100 mL Schlenk flask. The flask was sealed and then allowed to stand for 1 h at room temperature to form crystals. White, X-ray quality crystals were isolated by cannula filtration. The crystals were washed with pentane (3 × 5 mL) and dried under vacuum providing analytically pure To^MMgOMe (0.225 g, 0.514 mmol, 72.2%). ¹H NMR (400 MHz, benzene-*d*₆): δ 1.16 (s, 18 H, CNCMe₂CH₂O), 3.54 (s, 6 H, CNCMe₂CH₂O), 3.57 (s, 3 H, OMe), 7.29 (t, ³J_{HH} = 7.2 Hz, 1 H, *para*-C₆H₅), 7.49 (t, ³J_{HH} = 7.2 Hz, 2 H, *meta*-C₆H₅), 8.20 (d, ³J_{HH} = 7.2 Hz, 2 H, *ortho*-C₆H₅). ¹³C{¹H} NMR (175 MHz, benzene-*d*₆): δ 28.71 (CNCMe₂CH₂O), 52.51 (OMe), 66.68 (CNCMe₂CH₂O), 79.10 (CNCMe₂CH₂O), 125.96 (*para*-C₆H₅), 127.47 (*meta*-C₆H₅), 135.29 (*ortho*-C₆H₅), 151.90 (br, *ipso*-C₆H₅), 189.99 (br, CNCMe₂CH₂O). ¹¹B NMR (128 MHz, benzene-*d*₆): δ -17.6. ¹⁵N NMR (71 MHz, benzene-*d*₆): δ -154.9. IR (KBr, cm⁻¹): 3047 (w), 2965 (s), 2884 (s), 1595 (s, ν_{CN}), 1496 (w), 1465 (m), 1434 (w), 1383 (w), 1365 (m), 1349 (m), 1267 (s), 1198 (s), 1153 (s), 1024 (w), 966 (s), 934 (w), 892 (w), 837 (w), 810 (w), 748 (w), 702 (s), 658 (s), 638 (s). Anal. Calcd. for C₂₂H₃₂BN₃O₄Mg: C, 60.38; H, 7.37; N, 9.60. Found: C, 59.95; H, 6.95; N, 9.77. Mp 275-280 °C (dec).

To^MZnOCHO (6). A 100 mL sealable reaction flask with a Teflon valve was charged with To^MZnH (0.450 g, 1.00 mmol) dissolved in benzene (15 mL). The solution was degassed, the flask was cooled to -78 °C, and excess, dry CO₂ was condensed into the flask. The reaction was allowed to warm to room temperature, and the resulting mixture was stirred for 30 min. The volatile materials were evaporated, and the white residue was washed with pentane (3 × 5 mL) and subsequently dried under vacuum to provide analytically pure To^MZnOCHO as a white powder. X-ray quality single crystals were grown from a concentrated toluene solution of To^MZnOCHO at -35 °C (0.463 g, 0.940, 93.7%). ¹H NMR (600 MHz, benzene-*d*₆): δ 1.13 (s, 18

H, $\text{CNCMe}_2\text{CH}_2\text{O}$), 3.46 (s, 6 H, $\text{CNCMe}_2\text{CH}_2\text{O}$), 7.37 (m, $^3J_{\text{HH}} = 7.2$ Hz, 1 H, *para*- C_6H_5), 7.55 (m, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, *meta*- C_6H_5), 8.31 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, *ortho*- C_6H_5), 8.76 (s, 1 H, OCHO). $^{13}\text{C}\{^1\text{H}\}$ NMR (175 HMz, benzene- d_6): δ 27.95 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 65.84 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 81.36 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 126.54 (*para*- C_6H_5), 127.37 (*meta*- C_6H_5), 136.37 (*ortho*- C_6H_5), 140.90 (br, *ipso*- C_6H_5), 169.18 (ZnOCHO), 189.80 (br, $\text{CNCMe}_2\text{CH}_2\text{O}$). ^{11}B NMR (128 MHz, benzene- d_6): δ -18.1. ^{15}N NMR (59.2 MHz, benzene- d_6): δ -160.3. IR (KBr, cm^{-1}): 3072 (w), 2965 (s), 2923 (w), 1629 (s, ν_{CO}), 1595 (s, ν_{CN}), 1461 (m), 1423 (m), 1389 (m), 1370 (m), 1351 (m), 1307 (s, ν_{CO}), 1273 (s), 1197 (s), 1163 (m), 1124 (m), 1033 (w), 1019 (m), 996 (m), 957 (s), 946 (s), 893 (m), 871 (m), 844 (w), 819 (m). Anal. Calcd. For $\text{C}_{22}\text{H}_{30}\text{BZnN}_3\text{O}_5$: C, 53.63; H, 6.14; N, 8.53. Found C, 53.91; H, 6.19; N, 8.49. Mp 207-213 °C.

To^MMgO₂CSi(SiHMe₂)₃ (7). A 15 mL benzene solution of To^MMgSi(SiHMe₂)₃ (0.230 g, 0.376 mmol) was degassed and stirred under CO₂ (1 atm) for 24 h at ambient temperature. The volatile components were evaporated, and the white residue was washed with pentane (3 × 5 mL). Vacuum drying provided analytically pure To^MMgO₂CSi(SiHMe₂)₃ (0.226 g, 0.344 mmol, 91.5%). ^1H NMR (600 MHz, benzene- d_6): δ 0.48 (d, $^3J_{\text{HH}} = 4.4$ Hz, 18 H, SiHMe₂), 1.16 (s, 18 H, $\text{CNCMe}_2\text{CH}_2\text{O}$), 3.46 (s, 6 H, $\text{CNCMe}_2\text{CH}_2\text{O}$), 4.45 (sept, $^3J_{\text{HH}} = 4.4$ Hz, 3 H, SiHMe₂) 7.37 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1 H, *para*- C_6H_5), 7.55 (vt, $^3J_{\text{HH}} = 7.8$ Hz, 2 H, *meta*- C_6H_5), 8.36 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, *ortho*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (175 HMz, benzene- d_6): δ -3.65 (SiHMe₂), 28.20 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 65.87 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 80.63 ($\text{CNCMe}_2\text{CH}_2\text{O}$), 126.16 (*para*- C_6H_5), 127.16 (*meta*- C_6H_5), 136.57 (*ortho*- C_6H_5), 191.65 (br, $\text{CNCMe}_2\text{CH}_2\text{O}$), 202.61 (MgO₂CSi). ^{11}B NMR (128 MHz, benzene- d_6): δ -18.1. ^{29}Si NMR (120 MHz, benzene- d_6): δ -35.51 (d, $^1J_{\text{SiH}} = 169.7$ Hz, SiHMe₂), -86.34 (Si(SiHMe₂)₃). ^{15}N NMR (59.2 MHz, benzene- d_6): δ -157.4. IR (KBr, cm^{-1}): 3076 (w), 3046 (w), 2965 (s), 2928 (w), 2897 (w), 2101 (s, ν_{SiH}), 1593 (s, ν_{CN}), 1463 (s), 1389 (w), 1366 (s), 1272 (s), 1248 (s), 1195 (s), 1161 (m), 963 (s), 888 (s), 859 (s), 838 (s), 705 (m), 672 (m), 639 (w), 619 (w), 514 (m). Anal. Calcd. for $\text{C}_{28}\text{H}_{50}\text{BSi}_4\text{N}_3\text{O}_5\text{Mg}$: C, 51.25; H, 7.68; N, 6.40. Found: C, 51.25; H, 7.39; N, 6.46. Mp: 190-193 °C.

HO₂CSi(SiHMe₂)₃ (8). Tetrakis(dimethylsilyl)silane (2.00 g, 7.56 mmol) was dissolved in THF (20 mL). Methyllithium (7.08 mL, 11.3 mmol, 1.6 M in ether) was added. The reaction was stirred at room temperature for 3 days, and then the mixture was poured into a slurry of dry ice in

ether. After excess CO₂ had evaporated, the reaction mixture was washed with 2% HCl (3 × 50 mL), and the ether layer was collected and dried over Na₂SO₄. The ether was evaporated to give a colorless oil (0.697 g, 2.78 mmol, 36.9%). ¹H NMR (benzene-*d*₆, 600 MHz): δ 0.297 (br, 18 H, SiHMe₂), 4.27 (sept, 3 H, ³J_{HH} = 4.5 Hz, SiHMe₂), 11.67 (br, 1 H, HO₂CSi). ¹³C{¹H} NMR (benzene-*d*₆, 175 MHz): δ 195.22 (HO₂CSi), 1.76 (SiHMe₂). ²⁹Si (benzene-*d*₆, 120 MHz) δ -26.1 (d, ¹J_{SiH} = 180.6 Hz, SiHMe₂), -85.2 (Si(SiHMe₂)₃). HRMS Calcd. For C₇H₂₂O₂Si₄: (M⁺-1), 249.0619. Found: *m/z*, 249.0974 (M⁺-1).

To^MZnO₂CSi(SiHMe₂)₃ (9). To^MZnEt (0.035 g, 0.073 mmol) and HO₂CSi(SiHMe₂)₃ (0.018 g, 0.073 mmol) were dissolved in benzene and stirred for 30 min. Evaporation of the volatile components under reduced pressure provided a white solid, which was washed with pentane (3 × 5 mL) and dried under vacuum to obtain analytically pure To^MZnO₂CSi(SiHMe₂)₃ (0.047 g, 0.067 mmol, 92.3%). ¹H NMR (400 MHz, benzene-*d*₆): δ 0.51 (d, ³J_{HH} = 4.3 Hz, 18 H, SiHMe₂), 1.18 (s, 18 H, CNCMe₂CH₂O), 3.48 (s, 6 H, CNCMe₂CH₂O), 4.46 (sept, ³J_{HH} = 4.3 Hz, 3 H, SiHMe₂), 7.35 (t, ³J_{HH} = 7.6 Hz, 1 H, *para*-C₆H₅), 7.53 (vt, ³J_{HH} = 7.4 Hz, 2 H, *meta*-C₆H₅), 8.31 (d, ³J_{HH} = 7.2 Hz, 2 H, *ortho*-C₆H₅). ¹³C{¹H} NMR (175 MHz, benzene-*d*₆): δ -3.75 (SiHMe₂), 28.00 (CNCMe₂CH₂O), 65.90 (CNCMe₂CH₂O), 81.30 (CNCMe₂CH₂O), 126.41 (*para*-C₆H₅), 127.30 (*meta*-C₆H₅), 136.42 (*ortho*-C₆H₅), 141.72 (br, *ipso*-C₆H₅), 190.19 (br, CNCMe₂CH₂O), 193.38 (ZnO₂CSi). ¹¹B NMR (128 MHz, benzene-*d*₆): δ -18.3. ²⁹Si NMR (120 MHz, benzene-*d*₆): δ -36.36 (d, ¹J_{SiH} = 169.7 Hz, ZnOC(O)Si(SiHMe₂)₃), -87.38 (s, ZnOC(O)Si(SiHMe₂)₃). ¹⁵N NMR (61 MHz, benzene-*d*₆): δ -158.0. IR (KBr, cm⁻¹): 3077 (w), 3049 (w), 2963 (s), 2928 (w), 2898 (w), 2103 (s, ν_{SiH}), 1598 (s, ν_{CN}), 1510 (m), 1464 (m), 1368 (m), 1352 (m), 1261 (s), 1196 (m), 961 (m), 907 (m), 838 (s), 813 (s), 777 (w), 704 (m), 687 (m), 639 (m), 624 (w). Anal. Calcd. for C₂₈H₅₀BSi₄N₃O₅Zn: C, 48.23; H, 7.23; N, 6.03. Found: C, 47.81; H, 7.38; N, 5.69. Mp: 218-220 °C.

Procedures for DOSY (Diffusion-Ordered Spectroscopy) experiment. All the measurements were performed on a Bruker DRX400 spectrometer using a DOSY stimulated spin-echo pulse program with bipolar gradients.⁷ Accurately known concentrations of the species in question, To^MMgSi(SiHMe₂)₃ (2), To^MMgO₂CSi(SiHMe₂)₃ (7), and To^MZnO₂CSi(SiHMe₂)₃ (9) were determined by integration of resonances corresponding to species of interest and integration of a

tetrakis(trimethylsilyl)silane standard of accurately known concentration. The temperature in the NMR probe was preset to 296 K, and the probe was maintained at a constant temperature for each experiment. The delay time in between pulses was set to 5 s in order to ensure the spins are fully relaxed to their ground states. During the experiments, a series of 1D ^1H NMR spectra were acquired at increasing gradient strength. The signal intensity decay was fit by non-linear least squares regression analysis to Equation 1 to obtain the diffusion coefficient D (Figure S-1, S-2, and S-3),⁷

$$\ln\left(\frac{I}{I_0}\right) = -(\gamma\delta)^2 G^2 \left(\Delta - \frac{\delta}{3}\right) D \quad (1)$$

where I is the observed intensity, D is the diffusion coefficient, γ is the gyromagnetic ratio of the nucleus, δ is the length of the gradient pulse, and Δ is the diffusion time. These experiments were performed on $\text{To}^{\text{M}}\text{MgSi}(\text{SiHMe}_2)_3$ ($6.945 \times 10^{-10} \text{ m}^2/\text{s}$), $\text{To}^{\text{M}}\text{MgO}_2\text{CSi}(\text{SiHMe}_2)_3$ ($6.849 \times 10^{-10} \text{ m}^2/\text{s}$), $\text{To}^{\text{M}}\text{ZnO}_2\text{CSi}(\text{SiHMe}_2)_3$ ($6.429 \times 10^{-10} \text{ m}^2/\text{s}$), and $\text{To}^{\text{M}}_2\text{Mg}$ ($6.00 \times 10^{-10} \text{ m}^2/\text{s}$). From this trend, we conclude that the silane carboxylate compounds are monomeric, as we would expect diffusion constants $< 6 \times 10^{-10} \text{ m}^2/\text{s}$ for dimeric compounds.

Figure S-1. Plot of intensity versus gradient strength that was used to determine the diffusion coefficient ($6.945 \times 10^{-10} \text{ m}^2/\text{s}$) for $\text{To}^{\text{M}}\text{MgSi}(\text{SiHMe}_2)_3$ (**2**).

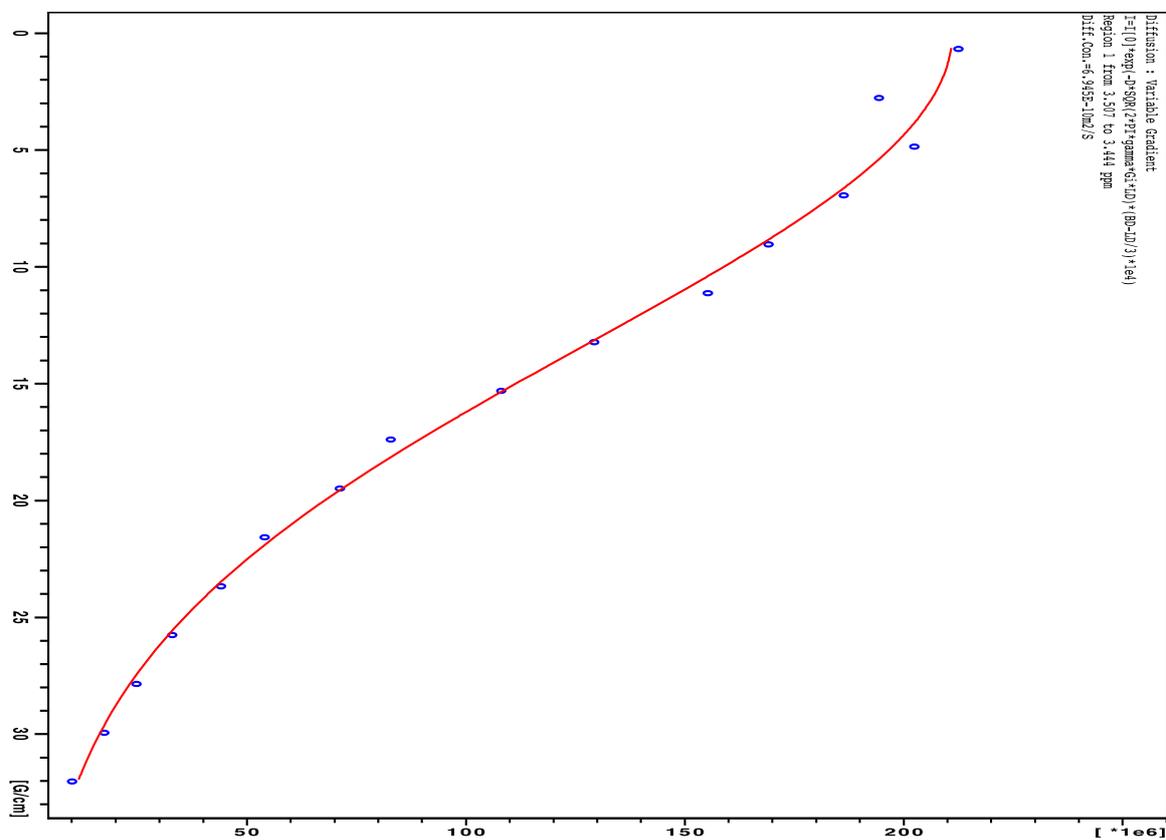


Figure S-2. Plot of intensity versus gradient strength that was used to determine the diffusion coefficient ($6.849 \times 10^{-10} \text{ m}^2/\text{s}$) for $\text{To}^{\text{M}}\text{MgO}_2\text{CSi}(\text{SiHMe}_2)_3$ (**7**).

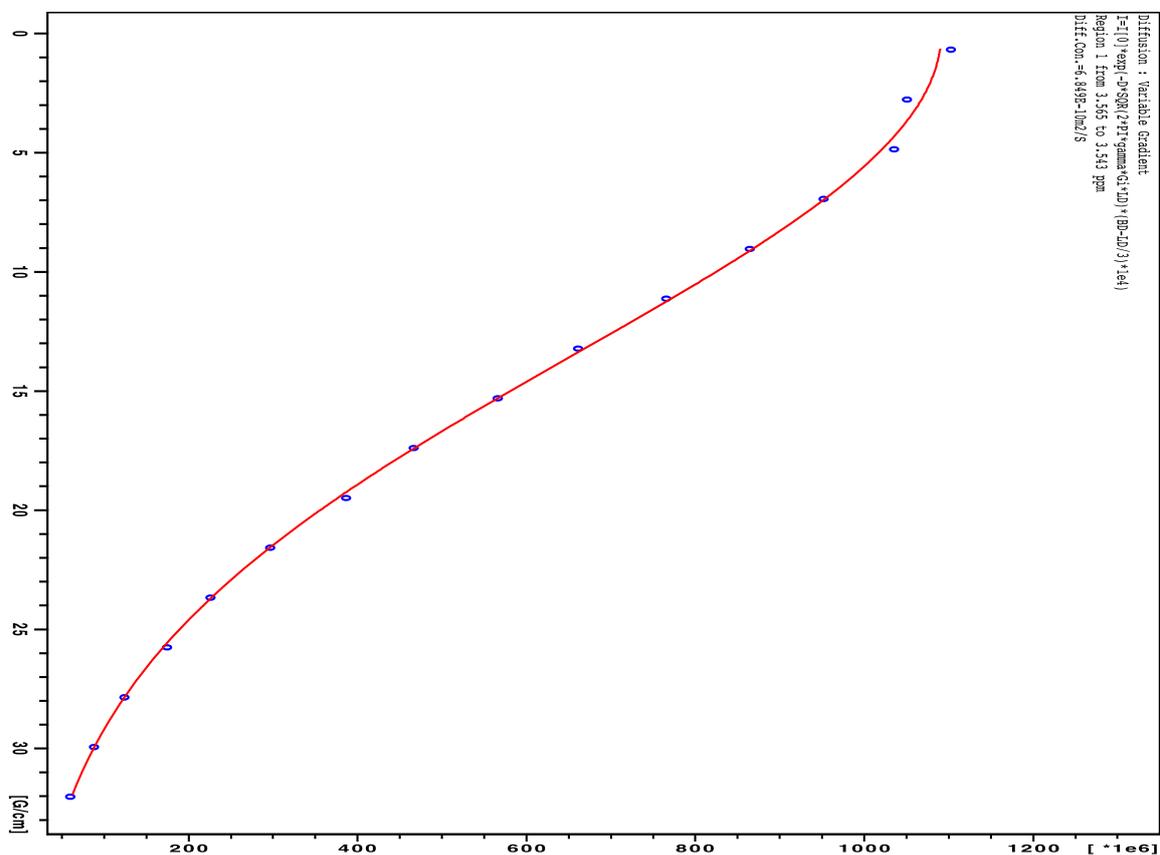
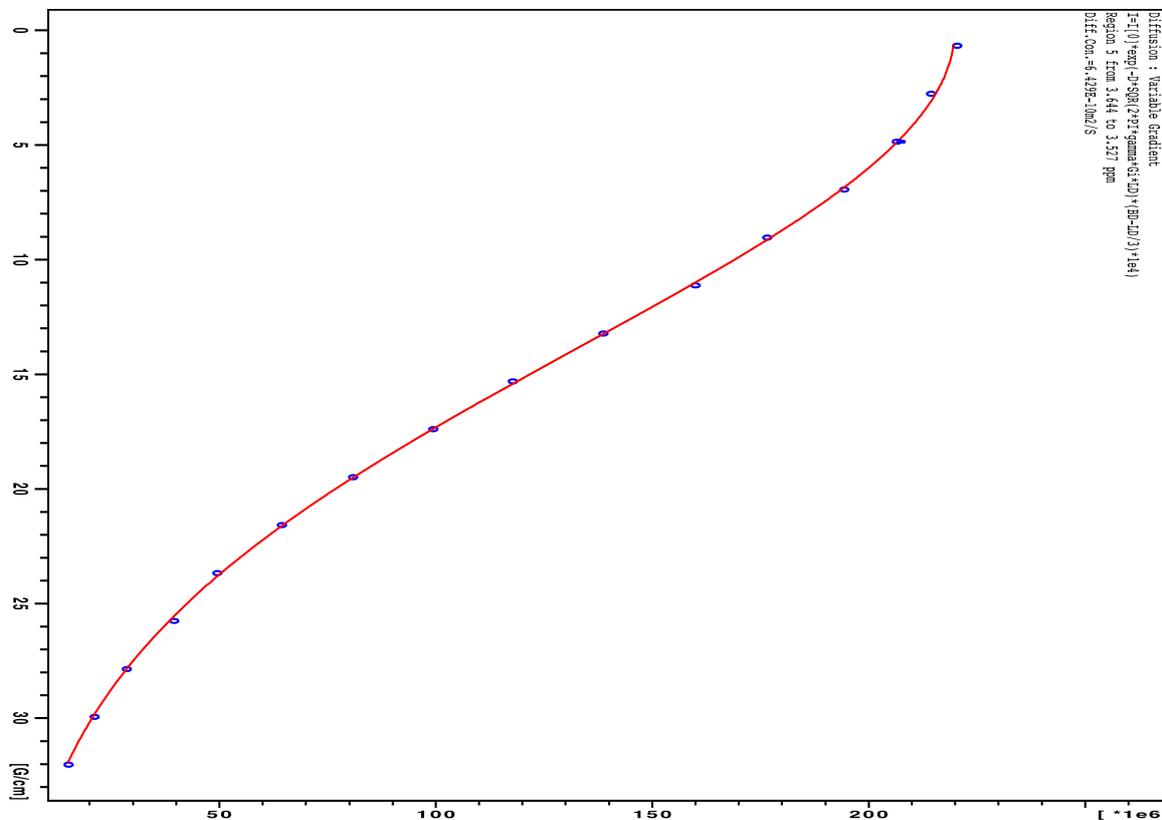


Figure S-3. Plot of intensity versus gradient strength that was used to determine the diffusion coefficient ($6.429 \times 10^{-10} \text{ m}^2/\text{s}$) for $\text{To}^{\text{M}}\text{ZnO}_2\text{CSi}(\text{SiHMe}_2)_3$ (**9**).



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