Supplementary Material (ESI) for Chemical Communications

Abstractions of β-hydrogen vs. alkyl groups in reactions of dialkylzinc compounds and bis(oxazolinyl)borane

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Experimental details.

General Procedures. All reactions were carried out under an inert atmosphere using standard Schlenk techniques or in a glovebox. All solvents were dried and degassed unless otherwise indicated. $PhB(Ox^{Me2})_2$,[1] Ph_2Zn, *n*-Pr_2Zn, *i*-Bu_2Zn, Bn_2Zn,[2] and DPE[3] were prepared according to reported procedures. Me_2Zn (2 M in toluene), Et_2Zn, BnMgBr (1 M in Et_2O), PhMgBr (3 M in Et_2O), *i*-BuMgCl (2 M in Et_2O), and *n*-PrMgBr (2 M in Et_2O) were purchased from Aldrich and used as received. TMEDA was purchased from Aldrich and distilled from Na. All NMR spectra were obtained at room temperature using a Bruker DRX-400 spectrometer, Bruker Avance II-700 spectrometer, or Agilent MR400 spectrometer. ^{15}N NMR chemical shifts were determined by ^{1}H-^{15}N HMBC experiments recorded on an Avance II-700 spectrometer; the chemical shift values are reported relative to CH_3NO_2. ^{11}B NMR spectra chemical shifts are reported relative to $BF_3{\cdot}Et_2O$. Elemental analyses were obtained at the Iowa State Chemical Instrumentation Facility using a Perkin-Elmer 2400 Series II CHN/S.

{κ²-PhMeB(Ox^{Me2})$_2$}ZnMe (1). $PhB(Ox^{Me2})_2$ (0.590 g, 2.09 mmol) was dissolved in 15 mL of benzene. A 2 M toluene solution of Me_2Zn (1.05 mL, 2.09 mmol) was added to the mixture via syringe to give a yellow solution. This solution was stirred for 24 h and then filtered to remove a white precipitate that slowly formed over time. The benzene filtrate was evaporated under reduced pressure to give a yellow solid. The crude solid was washed with 10 mL of pentane and dried under vacuum to give pale yellow, analytically pure {κ²-PhMeB(Ox^{Me2})$_2$}ZnMe (0.587 g, 1.55 mmol, 73.9%). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.78 (d, $^{3}J_{HH}$ = 7.3 Hz, 2 H, *ortho*-C_6H_5), 7.42 (t, $^{3}J_{HH}$ = 7.5 Hz, 2 H, *meta*-C_6H_5), 7.23 (t, $^{3}J_{HH}$ = 7.3 Hz, 1 H, *para*-C_6H_5), 3.32 (d, $^{2}J_{HH}$ = 8.6 Hz, 2 H, $CNCMe_2CH_2O$), 3.24 (d, $^{2}J_{HH}$ = 8.6 Hz, 2 H, $CNCMe_2CH_2O$), 0.94 (s br, 3 H, B*Me*), 0.862 (s, 6 H, $CNCMe_2CH_2O$), 0.859 (s, 6 H, $CNCMe_2CH_2O$), -0.18 (s, 3 H, Zn*Me*). $^{13}C\{^{1}H\}$ NMR (benzene-d_6, 125 MHz): δ 198.81 (br, $CNCMe_2CH_2O$), 151.92 (*ipso*-C_6H_5), 132.87 (*ortho*-C_6H_5), 128.29 (*meta*-C_6H_5), 125.85 (*para*-C_6H_5), 78.67 ($CNCMe_2CH_2O$), 65.29 ($CNCMe_2CH_2O$),

28.66 (CNC*Me*$_2$CH$_2$O), 28.47 (CNC*Me*$_2$CH$_2$O), 14.76 (br, B*Me*), 5.53 (br, Zn*Me*). ^{11}B NMR (benzene-d_6, 128 MHz): δ -16.7. ^{15}N NMR (benzene-d_6, 71 MHz): -174.3. IR (KBr, cm^{-1}): 3065 m, 3046 m, 2967 s, 2930 s, 2899 s, 1948 vw, 1887 vw, 1817 vw, 1569 vs (CN), 1462 s, 1431 s, 1367 s, 1272 s, 1196 s, 1158 s, 1081 s, 1011 s, 976 s, 891 m, 836 m, 774 w, 740 m, 713 s, 703 s. Calcd. for $C_{18}H_{27}BN_2O_2Zn$: C, 56.95; H, 7.17; N, 7.38. Found: C, 57.30; H, 7.08; N, 7.01. mp 166-168 °C (dec.).

{κ^2-Ph$_2$B(Ox^{Me2})$_2$}ZnPh (2). PhB(Ox^{Me2})$_2$ (0.749 g, 2.65 mmol) was dissolved in 15 mL of benzene. A yellow solution formed upon addition of solid Ph$_2$Zn (0.582 g, 2.65 mmol), and this solution was stirred for 24 hours. A white precipitate slowly formed, and the reaction mixture was filtered removed this white solid. The benzene filtrate was evaporated under reduced pressure to give a yellow solid. The crude solid was washed with 10 mL of pentane and dried under reduced pressure giving the phenyl-abstracted product **2** (0.975 g, 1.94 mmol, 72.9%). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.82 (d, $^3J_{HH}$ = 7.3 Hz, 4 H, *ortho*-C$_6$H$_5$B), 7.61 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, *ortho*-C$_6$H$_5$Zn), 7.44 (t, $^3J_{HH}$ = 7.4 Hz, 4 H, *meta*-C$_6$H$_5$B), 7.35 (t, $^3J_{HH}$ = 7.1 Hz, 2 H, *meta*-C$_6$H$_5$Zn), 7.27 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, *para*-C$_6$H$_5$B), 7.22 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, *para*-C$_6$H$_5$Zn), 3.28 (s, 4 H, CNCMe$_2$C*H*$_2$O), 0.84 (s, 12 H, CNC*Me*$_2$CH$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6, 125 MHz): δ 197.81 (br, *C*NCMe$_2$CH$_2$O), 150.93 (*ipso*-C$_6$H$_5$B), 150.40 (*ipso*-C$_6$H$_5$Zn), 138.96 (*ortho*-C$_6$H$_5$Zn), 134.96 (*ortho*-C$_6$H$_5$B), 128.92 (*meta*-C$_6$H$_5$Zn), 128.03 (*meta*-C$_6$H$_5$B), 127.77 (*para*-C$_6$H$_5$Zn), 126.14 (*para*-C$_6$H$_5$B), 78.89 (CNCMe$_2$*C*H$_2$O), 65.52 (CN*C*Me$_2$CH$_2$O), 28.63 (CNC*Me*$_2$CH$_2$O). ^{11}B NMR (benzene-d_6, 128 MHz): δ -12.4. ^{15}N NMR δ (benzene-d_6, 71 MHz): -172.7. IR (KBr, cm^{-1}): 3042 m, 2995 m, 2966 s, 2928 m, 2895 m, 2870 m, 1946 w, 1871 w, 1813 w, 1554 vs br (CN), 1462 m, 1424 m, 1369 s, 1354 s, 1278 s, 1197 s, 1159 s, 1076 m, 1032 m, 969 vs, 892 m, 743 s, 735 s, 724 s, 701 vs. Calcd. for $C_{28}H_{31}BN_2O_2Zn$: C, 66.76; H, 6.20; N, 5.56. Found: C, 66.63; H, 6.17; N, 5.07. mp 126-130 °C.

{κ^2-PhCH$_2$PhB(Ox^{Me2})$_2$}ZnCH$_2$Ph (3). PhB(Ox^{Me2})$_2$ (0.449 g, 1.59 mmol) was dissolved in 15 mL of benzene and Bn$_2$Zn (0.394 g, 1.59 mmol) was added. After 24 h, the mixture was filtered to remove a white precipitate. The benzene filtrate was evaporated under reduced pressure to give a yellow solid. The crude solid was washed with 10 mL of pentane and dried (0.658 g, 1.24 mmol, 77.9%). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.70 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, *ortho*-C$_6$H$_5$),

7.41 (t, $^{3}J_{HH}$ = 7.2 Hz, 2 H, *meta*-C_6H_5), 7.24 (t, $^{3}J_{HH}$ = 7.6 Hz, 1 H, *para*-C_6H_5), 7.20-7.09 (m, 4 H, *ortho*-$C_6H_5CH_2Zn$ and *ortho*-$C_6H_5CH_2B$) 7.07-6.97 (m, 4 H, *meta*-$C_6H_5CH_2Zn$ and *meta*-$C_6H_5CH_2B$), 6.96-6.88 (m, 2 H, *para*-$C_6H_5CH_2Zn$ and *para*-$C_6H_5CH_2B$), 3.38 (d, $^{3}J_{HH}$ = 8.8 Hz, 2 H, $CNCMe_2CH_2O$), 3.25 (d, $^{3}J_{HH}$ = 8.8 Hz, 2 H, $CNCMe_2CH_2O$), 2.92 (s br, 2 H, BCH_2Ph), 2.00 (s, 2 H, $ZnCH_2Ph$), 0.73 (s, 6 H, $CNCMe_2CH_2O$), 0.71 (s, 6 H, $CNCMe_2CH_2O$). $^{13}C\{^{1}H\}$ NMR (benzene-d_6, 125 MHz): δ 196.98 (br, $CNCMe_2CH_2O$), 150.49 (br, *ipso*-C_6H_5B), 148.42 (*ipso*-$C_6H_5CH_2B$), 148.24 (*ipso*-$C_6H_5CH_2Zn$), 133.34 (*ortho*-C_6H_5B), 129.05 (*meta*-$C_6H_5CH_2B$), 128.65 (*ortho*-$C_6H_5CH_2B$), 128.33 (*meta*-$C_6H_5CH_2Zn$), 128.15 (*meta*-C_6H_5B), 127.72 (*ortho*-$C_6H_5CH_2Zn$), 126.10 (*para*-C_6H_5B), 123.91 (*para*-$C_6H_5CH_2Zn$), 122.56 (*para*-$C_6H_5CH_2B$), 78.82 ($CNCMe_2CH_2O$), 65.30 ($CNCMe_2CH_2O$), 32.79 (BCH_2), 28.73 ($CNCMe_2CH_2O$), 28.23 ($CNCMe_2CH_2O$), 20.15 ($ZnCH_2$). ^{11}B NMR (benzene-d_6, 128 MHz): δ -14.9. ^{15}N NMR (benzene-d_6, 71 MHz): δ -170.5. IR (KBr, cm^{-1}): 3066 m, 3017 m, 2970 s, 2928 m, 2897 m, 1938 w, 1866 w, 1798 w, 1595 s (CN), 1572 vs (CN), 1488 vs, 1461 s, 1450 m, 1432 m, 1368 m, 1279 m, 1208 s, 1148 m, 1074 m, 1063 m, 997 m, 970 s, 799 m, 753 s 770 vs. Calcd for $C_{30}H_{35}BN_2O_2Zn$: C, 67.75; H, 6.63; N, 5.27. Found: C, 67.94; H, 6.55; N, 4.88. mp 140-143 °C.

{κ^2-PhHB(Ox^{Me2})$_2$}ZnEt (5). $PhB(Ox^{Me2})_2$ (0.220 g, 0.781 mmol) was dissolved in 15 mL of THF. Et_2Zn (80.0 µl, 0.781 mmol) was added to the mixture via syringe to give a yellow solution. This solution was stirred for 24 h, and then the volatile materials were removed under reduced pressure. The residue was then extracted with benzene and the benzene was evaporated. The solid residue was then washed with 10 mL of pentane and dried (0.251 g, 0.662 mmol, 84.8%). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.87 (d, $^{3}J_{HH}$ = 7.2 Hz, 2 H, *ortho*-C_6H_5), 7.42 (t, $^{3}J_{HH}$ = 7.2 Hz, 2 H, *meta*-C_6H_5), 7.23 (t, $^{3}J_{HH}$ = 7.2 Hz, 1 H, *para*-C_6H_5), 3.36 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H, $CNCMe_2CH_2O$), 3.53 (1 H, BH), 3.29 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H, $CNCMe_2CH_2O$), 1.51 (t, $^{3}J_{HH}$ = 8 Hz, 3 H, $ZnCH_2CH_3$), 0.87 (s, 6 H, $CNCMe_2CH_2O$), 0.86 (s, 6 H, $CNCMe_2CH_2O$), 0.62 (q, $^{3}J_{HH}$ = 8.0 Hz, 2 H, $ZnCH_2CH_3$). $^{13}C\{^{1}H\}$ NMR (benzene-d_6, 125 MHz): δ 196.88 (br, $CNCMe_2CH_2O$), 149.46 (*ipso*-C_6H_5), 135.39 (*ortho*-C_6H_5), 128.92 (*meta*-C_6H_5), 125.82 (*para*-C_6H_5), 78.72 ($CNCMe_2CH_2O$), 65.10 ($CNCMe_2CH_2O$), 28.78 ($CNCMe_2CH_2O$), 28.38 ($CNCMe_2CH_2O$), 13.35 ($ZnCH_2CH_3$), 1.63 ($ZnCH_2CH_3$). ^{11}B NMR (benzene-d_6, 128 MHz): δ -19.1 (d, $^{1}J_{BH}$ = 88 Hz). ^{15}N NMR (benzene-d_6, 71 MHz): δ -172.8. IR (KBr, cm^{-1}): 3066 w, 3044 w, 2965 s, 2931 s, 2896 s, 2871 s, 2342 w br (BH), 1945 vw, 1879 vw, 1813 vw, 1563 s (CN),

1462 s, 1432 m, 1368 s, 1273 s, 1196 s, 1156 s, 1082 s, 1028 s, 966 s, 889 m, 840 m, 802 m, 744 m, 704 s. Calcd. for $C_{18}H_{27}BN_2O_2Zn$: C, 56.95; H, 7.17; N, 7.38. Found: C, 56.87; H, 7.30; N, 6.97. mp 146-150 °C.

{κ^2-PhHB(Ox^{Me2})$_2$}Zn(*n*-Pr) (7). PhB(Ox^{Me2})$_2$ (0.269 g, 0.952 mmol) was dissolved in 15 mL of THF. A yellow solution was obtained upon addition of *n*-Pr$_2$Zn (0.145 g, 0.952 mmol), which was stirred for 24 h and then evaporated. The residue was then extracted with benzene. After evaporation of the benzene extracts, the resulting solid was washed with 10 mL of pentane and dried (0.273 g, 0.693 mmol, 72.8%). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.82 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, *ortho*-C$_6$H$_5$), 7.41 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *meta*-C$_6$H$_5$), 7.22 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, *para*-C$_6$H$_5$), 3.47 (1 H, BH), 3.36 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 3.28 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 1.84 (m, 2 H, $^3J_{HH}$ = 7.6 Hz, ZnCH$_2$C*H*$_2$CH$_3$), 1.21 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, ZnCH$_2$CH$_2$C*H*$_3$), 0.88 (s, 6 H, CNC*Me*$_2$CH$_2$O), 0.87 (s, 6 H, CNC*Me*$_2$CH$_2$O), 0.70 (t, $^3J_{HH}$ = 8.0 Hz, 2 H, ZnC*H*$_2$CH$_2$CH$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125 MHz): δ 196.75 (br, *C*NCMe$_2$CH$_2$O), 148.67 (*ipso*-C$_6$H$_5$), 135.35 (*ortho*-C$_6$H$_5$), 128.19 (*meta*-C$_6$H$_5$), 125.86 (*para*-C$_6$H$_5$), 78.75 (CNCMe$_2$*C*H$_2$O), 65.14 (CN*C*Me$_2$CH$_2$O), 28.78 (CNC*Me*$_2$CH$_2$O), 28.41 (CNC*Me*$_2$CH$_2$O), 22.75 (ZnCH$_2$*C*H$_2$CH$_3$), 22.43 (ZnCH$_2$CH$_2$*C*H$_3$), 14.03 (Zn*C*H$_2$CH$_2$CH$_3$). ^{11}B NMR (benzene-d_6, 128 MHz): δ -19.5 (d, $^1J_{BH}$ = 89 Hz). ^{15}N NMR (benzene-d_6, 71 MHz): δ -172.7. IR (KBr, cm^{-1}): 3065 m, 3048 m, 2917 s, 2849 m, 2260 w (BH), 1563 s (CN), 1463m, 1432 m, 1386 m, 1368 m, 1279 m, 1262 m, 1199 m, 1029 s, 991 m, 956 m, 803 m, 718 m, 704 m. Calcd. for $C_{19}H_{29}BN_2O_2Zn$: C, 57.97; H, 7.43; N, 7.12. Found: C, 57.57; H, 7.30; N, 7.02. mp 122-128 °C.

{κ^2-PhHB(Ox^{Me2})$_2$}Zn*i*-Bu (9). PhB(Ox^{Me2})$_2$ (0.247 g, 0.875 mmol) was dissolved in 15 mL of THF and *i*-Bu$_2$Zn (0.157 g, 0.875 mmol) was added. This solution was stirred for 3 days, and then the volatile materials were removed in vacuo. The residue was then extracted with benzene. After evaporation of the benzene extracts, the resulting residue was washed with 10 mL of pentane and dried under reduced pressure (0.181 g, 0.445 mmol, 50.8%). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.82 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, *ortho*-C$_6$H$_5$), 7.41 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *meta*-C$_6$H$_5$), 7.22 (t, $^3J_{HH}$ = 7.3 Hz, 1 H, *para*-C$_6$H$_5$), 3.35 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 3.27 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 2.17 (m, 1 H, $^3J_{HH}$ = 6.8 Hz, ZnCH$_2$C*H*Me$_2$), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 2 H, ZnCH$_2$CH*Me*$_2$), 0.91 (s, 6 H, CNC*Me*$_2$CH$_2$O), 0.89 (s, 6 H, CNC*Me*$_2$CH$_2$O), 0.74

(d, $^{3}J_{HH}$ = 7.6 Hz, 2 H, ZnC*H*$_2$CHMe$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 125 MHz): δ 197.16 (br, *C*NCMe$_2$CH$_2$O), 148.83 (br, *ipso*-C$_6$H$_5$), 135.30 (*ortho*-C$_6$H$_5$), 128.02 (*meta*-C$_6$H$_5$, overlapped by C$_6$D$_6$, assigned by ^{1}H-^{13}C HMQC experiment), 125.90 (*para*-C$_6$H$_5$), 78.80 (CNCMe$_2$*C*H$_2$O), 65.20 (CN*C*Me$_2$CH$_2$O), 30.10 (ZnCH$_2$CH*Me*$_2$), 29.20 (ZnCH$_2$*C*HMe$_2$) 28.80 (CNC*Me*$_2$CH$_2$O), 28.45 (CNC*Me*$_2$CH$_2$O), 24.00 (Zn*C*H$_2$CHMe$_2$). ^{11}B NMR (benzene-d_6, 128 MHz): δ -20.0 (d, $^{1}J_{BH}$ = 87 Hz). ^{15}N NMR (benzene-d_6, 71 MHz): δ -172.8. IR (KBr, cm^{-1}): 3066 m, 3047 m, 2943 s, 2874 s, 2258 m br (BH), 2052 vw, 1948 vw, 1876 vw, 1818 vw, 1564 s (CN), 1461 s, 1432 s, 1386 s, 1361 s, 1282 s, 1197 s, 1159 s, 1028 s, 984 s, 956 s, 836 m, 741 w, 716 s, 704 s. Calcd. for C$_{20}$H$_{31}$BN$_2$O$_2$Zn: C, 58.92; H, 7.66; N, 6.87. Found: C, 59.13; H, 7.46; N, 6.51. mp 212-213 °C (dec.).

{κ^2-PhEtB(Ox^{Me2})$_2$}AlEt$_2$ (10). PhB(Ox^{Me2})$_2$ (0.241 g, 0.856 mmol) was dissolved in 15 mL of benzene. AlEt$_3$ (117 µl, 0.856 mmol) was added to the mixture via syringe giving a yellow solution. This solution was stirred for 24 h and then filtered. The benzene filtrate was evaporated under reduced pressure to give a yellow solid. The crude solid was washed with 10 mL of pentane and dried (0.210 g, 0.527 mmol, 61.6%). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.71 (d, $^{3}J_{HH}$ = 7.2 Hz, 2 H, *ortho*-C$_6$H$_5$), 7.39 (t, $^{3}J_{HH}$ = 7.2 Hz, 2 H, *meta*-C$_6$H$_5$), 7.20 (t, $^{3}J_{HH}$ = 7.2 Hz, 1 H, *para*-C$_6$H$_5$), 3.28 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 3.15 (d, $^{3}J_{HH}$ = 8.8 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 1.56 (s br, 2 H, BC*H*$_2$CH$_3$), 1.34 (t, $^{3}J_{HH}$ = 8.0 Hz, 3 H, AlCH$_2$C*H*$_3$), 1.29 (t, $^{3}J_{HH}$ = 8.0 Hz, 3 H, AlCH$_2$C*H*$_3$), 1.13 (t, $^{3}J_{HH}$ = 7.6 Hz, 3 H, BCH$_2$C*H*$_3$), 1.02 (s, 6 H, CNC*Me*$_2$CH$_2$O), 0.96 (s, 6 H, CNC*Me*$_2$CH$_2$O), 0.23 (m, $^{3}J_{HH}$ = 8.8 Hz, 4 H, AlC*H*$_2$CH$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 125 MHz): δ 200.98 (br, *C*NCMe$_2$CH$_2$O), 134.55 (*ipso*-C$_6$H$_5$), 133.26 (*ortho*-C$_6$H$_5$), 127.91 (*meta*-C$_6$H$_5$), 126.18 (*para*-C$_6$H$_5$), 79.58 (CNCMe$_2$*C*H$_2$O), 66.02 (CN*C*Me$_2$CH$_2$O), 27.42 (CNC*Me*$_2$CH$_2$O), 26.88 (CNC*Me*$_2$CH$_2$O), 13.18 (BCH$_2$*C*H$_3$), 10.12 (AlCH$_2$*C*H$_3$), 9.97 (AlCH$_2$*C*H$_3$), 9.86 (br, B*C*H$_2$CH$_3$, overlapped by AlCH$_2$*C*H$_3$, assigned by ^{1}H-^{13}C HMQC experiment) 3.30 (br, Al*C*H$_2$CH$_3$). ^{11}B NMR (benzene-d_6, 128 MHz): δ -14.3. ^{15}N NMR (benzene-d_6, 71 MHz): δ -186.5. IR (KBr, cm^{-1}): 3047 m, 3066 m, 2934 s, 2898 s, 2861 s, 2793 m, 2724 w, 1952 w, 1882 w, 1823 w, 1609 s (CN) 1464 s, 1432 m, 1411 m, 1372 w, 1297 s, 1201 s, 1162 s, 1042 s, 1026 s, 986 s, 965 s, 886 m, 845 m, 763 m, 712 s, 703 s. Calcd. for

$C_{22}H_{36}AlBN_2O_2$: C, 66.34; H, 9.11; N, 7.03. Found: C, 66.06; H, 8.70; N, 6.55. mp 140-142 °C (dec.).

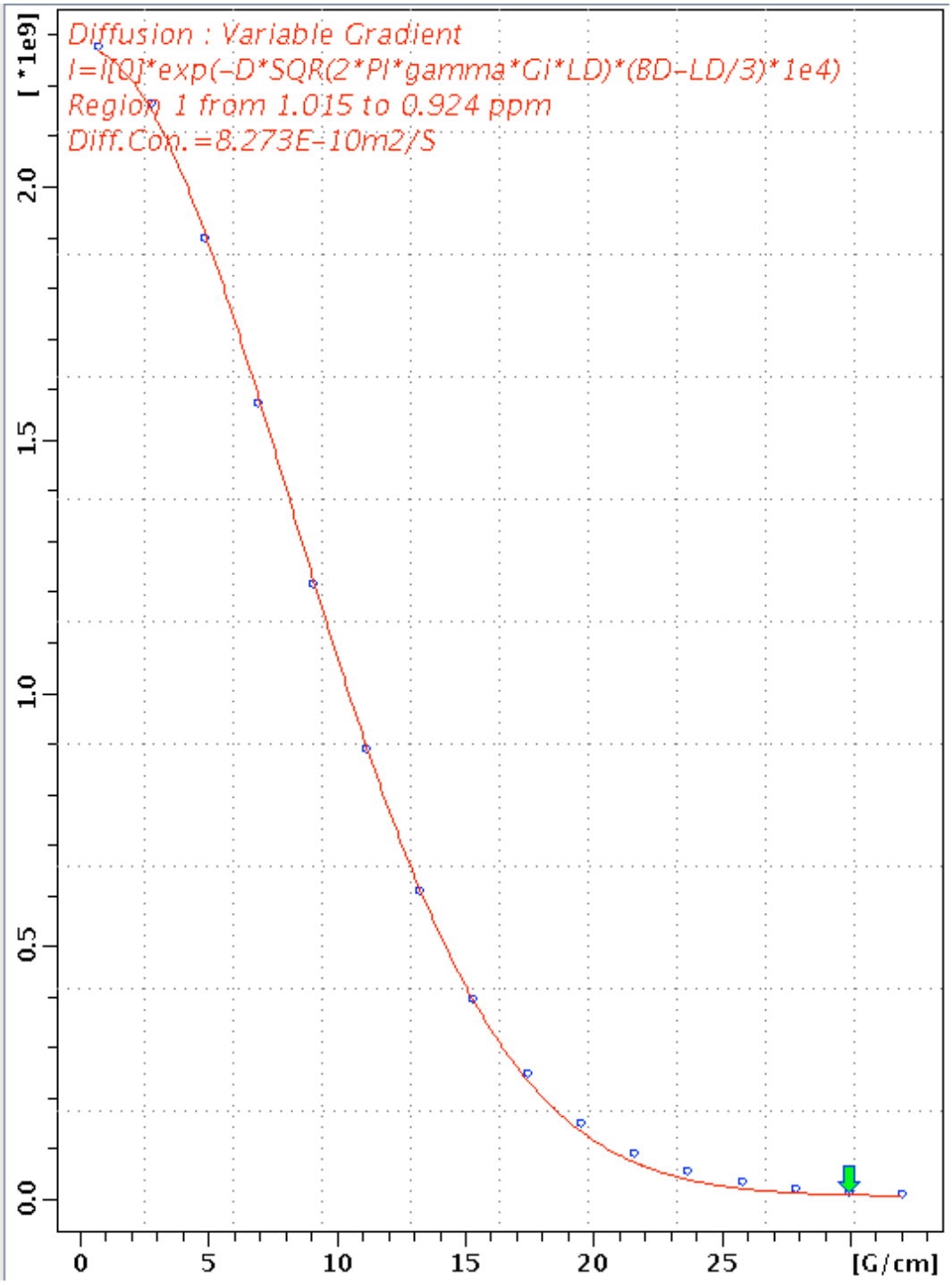
Et_2Zn(DPE). Et_2Zn (0.23 mL, 2.24 mmol) was added to a 12 mL benzene solution of dipyrrolidinylethane (0.335 g, 1.99 mmol), and the resulting solution was stirred for 1 h at room temperature. Evaporation of the volatile materials provided analytically pure Et_2Zn(DPE) (0.55 g, 1.88 mmol, 94.8 %). ^{1}H NMR (benzene-d_6, 400 MHz): δ 2.29 (s, br, 8 H, NCH_2CH$_2$CH$_2$CH_2), 2.01 (s, 4 H, N(CH_2)$_2$N), 1.80 (t, $^3J_{HH}$ = 8 Hz, 6 H, ZnCH$_2$CH_3), 1.603 (s, br, 8 H, NCH$_2$CH_2CH_2CH$_2$), 0.25 (q, $^3J_{HH}$ = 8 Hz, 4 H, ZnCH_2CH$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz): δ 55.64 (N*C*H$_2$CH$_2$CH$_2$*C*H$_2$), 55.39 (N(*C*H$_2$)$_2$N), 23.81 (NCH$_2$*C*H$_2$*C*H$_2$CH$_2$), 15.30 (ZnCH$_2$*C*H$_3$), 1.50 (Zn*C*H$_2$CH$_3$). ^{15}N NMR (benzene-d_6, 41 MHz): δ -127.9. IR (KBr, cm^{-1}): 2975 (m), 2927 (m), 2873 (s), 2846 (s), 2788 (m), 1458 (s, $\nu_{C\text{-}N}$), 1414 (w), 1345 (w), 1331 (m), 1299 (m), 1264 (m), 1226 (w), 1194 (w), 1123 (m), 1079 (w), 1035 (m), 980 (m), 947 (m), 903 (s), 866 (m), 607 (s), 605 (s), 569 (m), 488 (s), 439 (m). Anal. Calc. for $C_{14}H_{30}N_2Zn$: C, 57.62; H, 10.36; N, 9.60. Found: C, 57.54; H, 9.70; N, 9.59. mp 103-105 °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.[4] Accurately known concentrations of the species in question were used. The concentrations of {κ^2-PhMeB(Ox^{Me2})$_2$}ZnMe (**1**) and To^{M}ZnMe 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 ^{1}H 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.[4]

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

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.

Figure S1. Plot of intensity versus gradient strength that was used to determine the diffusion coefficient for {κ^2-PhMeB(Ox^{Me2})$_2$}ZnMe (**1**).



References

1 J. F. Dunne, K. Manna, J. W. Wiench, A. Ellern, M. Pruski, A. D. Sadow, *Dalton Trans.*, 2010, **39**, 641–653.

2 A. Côté, A. B. Charette, *J. Am. Chem. Soc.* 2008, **130**, 2771-2773.

3 J. G. Noltes, J. Boersma, *J. Organomet. Chem.*, 1967, **9**, 1-4.

4 (a) P. S. Pregosin, E. Martínez-Viviente and P. G. A. Kumar, *Dalton Trans*., 2003, 4007-4014; (b) M. Valentini, P. S. Pregosin, H. Ruegger, *Organometallics*, 2000, **19**, 2551-2555.