Acyclic 1,2-Dimagnesioethanes/-ethene Derived from Magnesium(I) Compounds: Multipurpose Reagents for Organometallic Synthesis

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Supplementary Information (30 pages)

Contents

1. Experimental

General considerations.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Pentane was distilled over Na/K alloy (25:75), while THF, hexane and toluene were distilled over molten potassium. ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H} and ^{11}B{^{1}H} NMR spectra were recorded on either Bruker DPX300 or Bruker AvanceIII 400 spectrometers and were referenced to the resonances of the solvent used, external $SiMe_4$, or external $BF_3.OEt_2$. Mass spectra were recorded on an Agilent Technologies 5975D inert MSD with a solid state probe. IR spectra were recorded as Nujol mulls, using a Agilent Cary 630 spectrometer operating in attenuated total reflectance (ATR) or transmission modes. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. Microanalyses were carried out at the Science Centre, London Metropolitan University. The compounds [{(^{Ar}Nacnac)Mg–}$_2$] (Ar = Xyl,[1] Mes[2] or Dep[3]), [{(^{Mes}Nacnac)Mg}$_2$(μ-DPE)],[4] [L*ZnBr],[5] [^{TBo}LZnBr],[6] K[^{PhBo}L],[7] [(L†MgI)$_2$][8] and [L*GeCl][9] were prepared by literature procedures. All other reagents were used as received.

Synthesis of [{(^{Xyl}Nacnac)Mg}$_2$(μ-DPE)] (5). To a stirred solution of [{(^{Xyl}Nacnac)Mg}$_2$] (0.40 g, 0.605 mmol) in toluene (60 mL) at -40 °C was added neat 1,1-diphenylethylene (0.22 mL, 1.21 mmol) via a microsyringe. The yellow solution became deep red upon addition, and was then warmed to room temperature. Volatiles were removed *in vacuo* and the residue taken up in hexane (*ca.* 20 mL) and stored at -30 °C overnight, yielding deep red blocks of **5**. Isolation of the crystals and further evaporation of the filtrate gave a second crop of crystals (0.40 g, 78%). N.B. **5** may be cleanly prepared *in situ* for further reactions, by the addition of one equivalent of 1,1-diphenylethylene to a stirred solution of [{(^{Xyl}Nacnac)Mg}$_2$] in toluene at room temperature. M.p. 97-101 °C; ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ = 0.37 (s, 2H; MgCH_2CPh$_2$), 1.42 (s, 12H; NCCH_3), 1.86 (s, 24H; ArCH_3), 4.70 (s, 2H; NCC*H*), 6.23-6.35 (m, 4H; Ar*H*), 6.46-6.49 (m, 2H; Ar*H*), 6.74-6.78 (m, 4H; Ar*H*), 6.88 (br. s, 12H; Ar*H*); ^{13}C{^{1}H} NMR (100 MHz, 298 K, C_6D_6) δ = 11.9 (*C*H$_2$CPh$_2$), 18.8 (NC*C*H3), 22.8 (Ar*C*H3), 51.8 (CH$_2$*C*Ph$_2$), 94.8 (NC*C*H), 116.2, 117.7, 124.5, 128.5, 130.4, 131.8, 147.0, 147.4 (Ar*C*), 168.5 (N*C*CH3); IR ν/cm^{-1} (ATR) = 1522(s), 1474(s), 1448(s), 1145(m), 1182(s), 847(m), 761(m), 738(s), 696(s); EI/MS (70eV): *m/z* (%): 329.1 (^{Xyl}NacnacMg^{+}, 68); anal. calc. for $C_{56}H_{62}Mg_2N_4$: C, 80.10 %; H, 7.44 %; N, 6.67 %; found: C, 80.03 %; H,7.52 %; N, 6.70 %.

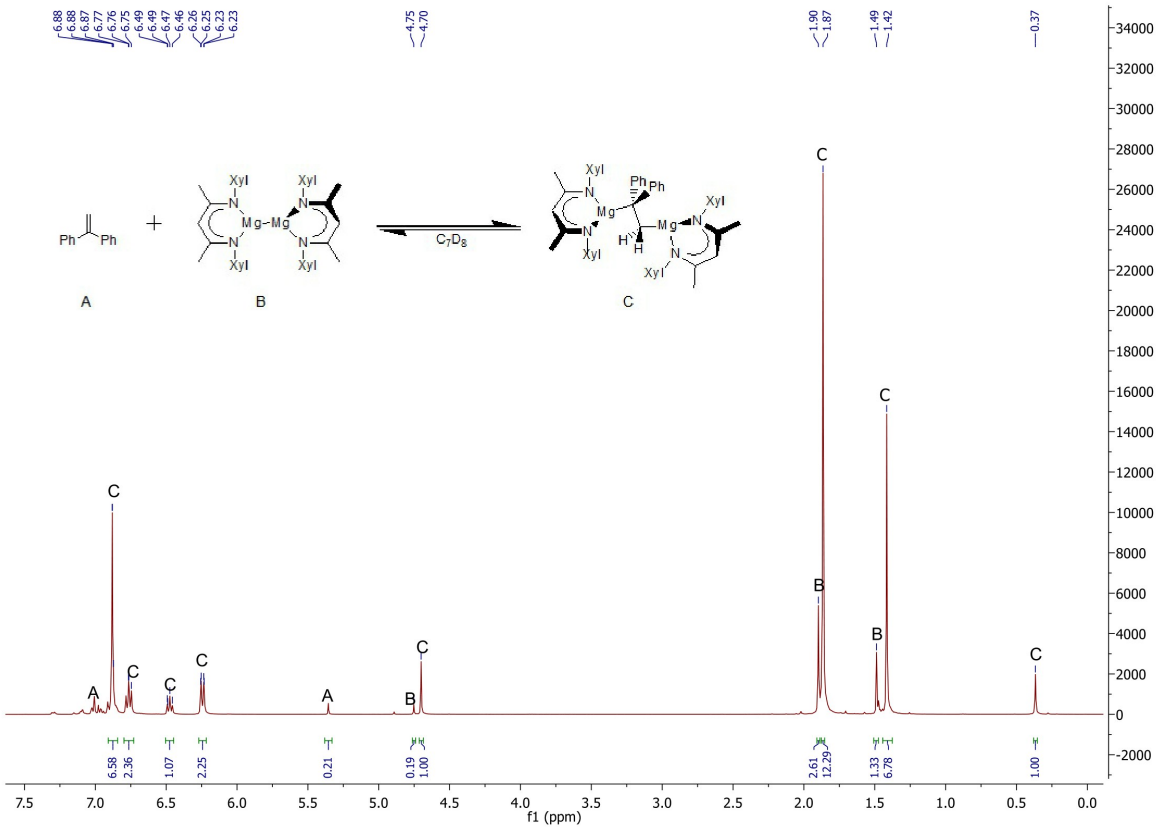


Figure S1. ^{1}H NMR spectrum (400 MHz, C_6D_6) of an equilibrium mixture of **5**, [{(^{Xyl}Nacnac)Mg}$_2$] and DPE at 298 K.

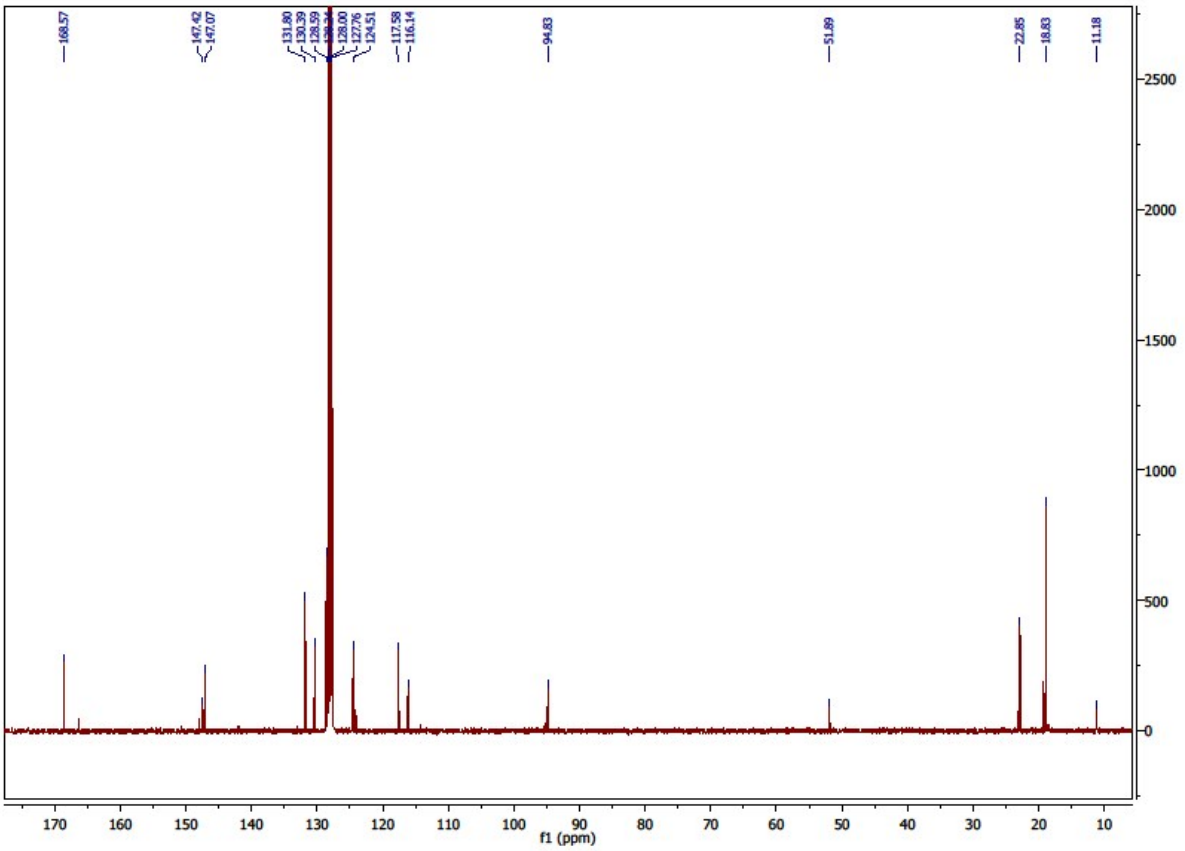


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, C_6D_6) of an equilibrium mixture of **5**, [{(^{Xyl}Nacnac)Mg}$_2$] and DPE at 298 K.

Synthesis of [{(^{Dep}Nacnac)Mg}$_2$(μ-MS)] (6). To a stirred solution of [{(^{Dep}Nacnac)Mg}$_2$] (0.50 g, 0.624 mmol) in toluene (40 mL) at -40 °C was added neat α-methyl styrene (0.16 mL, 1.24 mmol) via a microsyringe. The yellow solution became deep red upon addition, and was then warmed to room temperature. Volatiles were removed *in vacuo* and the residue taken up in hexane (*ca.* 20 mL) and stored at -30 ºC overnight, yielding deep red blocks of **6**. Isolation and further evaporation of the filtrate gave a second crop of crystals (0.35 g, 64 %). N.B. **6** may be cleanly prepared *in situ* for further reactions, by the addition of one equivalent of α-methyl styrene to a stirred solution of [{(^{Dep}Nacnac)Mg}$_2$] in toluene at room temperature. M.p. 139-143 °C. ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ = 0.16 (s, 2H; MgCH_2CPhCH$_3$), 1.09-1.14 (m, 27H; CH$_2$CH_3 and CH$_2$CPhCH_3), 1.50 (s, 12H; NCCH_3), 2.13 (m, 8H; CH_2CH$_3$), 2.40 (m, 8H; CH_2CH$_3$), 4.78 (s, 2H; NCC*H*), 6.41-6.46 (m, 1H; Ar*H*), 6.77-6.83 (m, 2H; Ar*H*), 7.04-7.07 (m, 14H; Ar*H*); $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) δ = 13.8 (*C*H$_2$CPhCH$_3$), 14.4 (CH$_2$*C*H$_3$), 21.8 (CPh*C*H$_3$), 23.2 (NC*C*H$_3$), 25.2 (*C*H$_2$CH$_3$), 94.8 (NC*C*H), 112.4 (CH$_2$*C*PhCH$_3$), 124.9, 125.8, 127.6, 128.5, 137.0, 141.6 143.6, 146.2 (Ar*C*), 168.7 (N*C*CH3); IR ν/cm^{-1} (ATR) = 1516(s), 1439(s), 1264(s), 1178(s), 1028(s), 978(m), 801(m), 748(s), 695(s); EI/MS (70eV): *m/z* (%): 174.1 (MeCNDep$^+$, 100), 385.3 (^{Dep}NacnacMg$^+$, 35); anal. calc. for $C_{59}H_{76}Mg_2N_4$: C, 79.63 %; H, 8.61 %; N, 6.30 %; found: C, 78.66 %; H,7.96 %; N, 6.39 %.

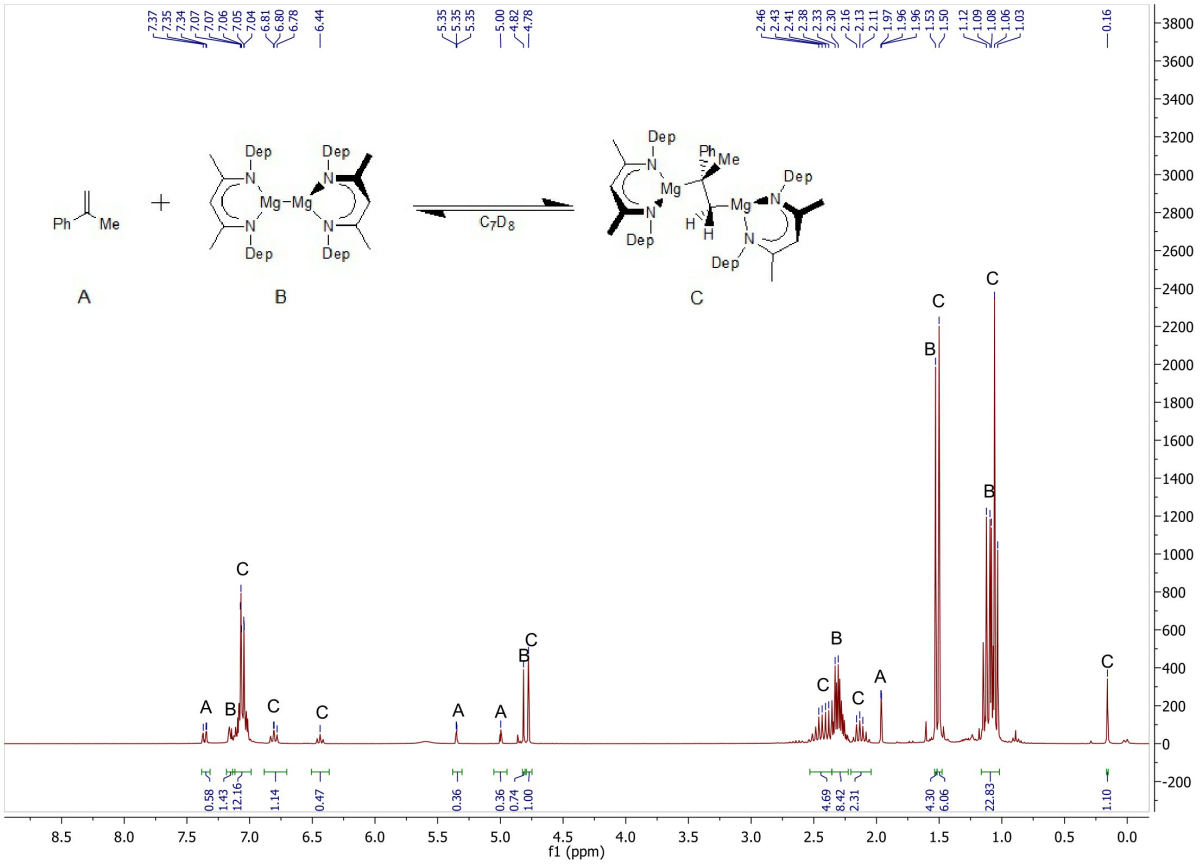


Figure S3. ^{1}H NMR spectrum (400 MHz, C_6D_6) of an equilibrium mixture of **6**, [{(^{Dep}Nacnac)Mg}$_2$] and α-methyl styrene at 298 K.

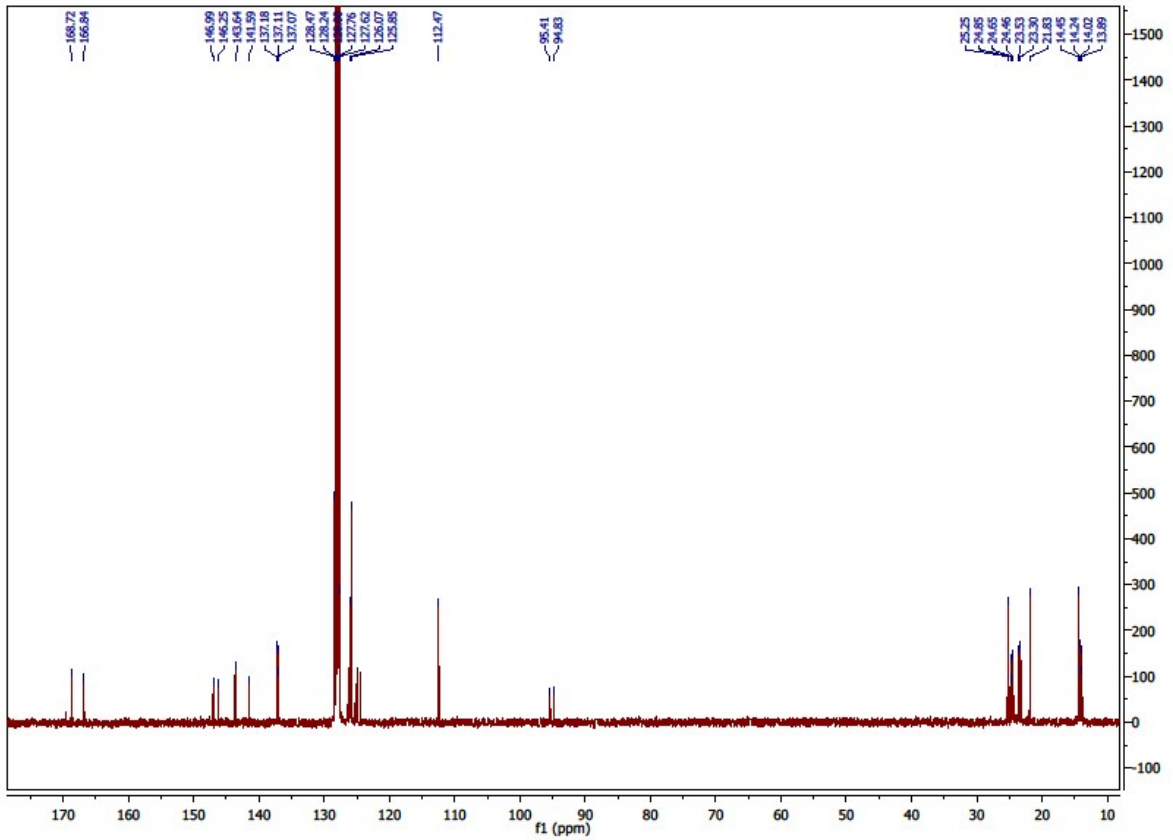


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, C_6D_6) of an equilibrium mixture of **6**, [{(^{Dep}Nacnac)Mg}$_2$] and α-methyl styrene at 298 K.

Synthesis of [{(^{Mes}Nacnac)Mg}$_2$(μ-TS)] (7). [{(^{Mes}Nacnac)Mg}$_2$] (300 mg, 0.419 mmol) and *trans*-stilbene (84 mg, 0.466 mmol) were dissolved in toluene (15mL) and stirred at room temperature, affording an orange solution after 1h. The mixture was then stirred overnight, after which time volatiles were removed *in vacuo* and the residue extracted with pentane (*ca.* 5mL). The extract was stored at -30 °C overnight, yielding red crystals of **7** (216 mg, 57 %). NMR spectra of analytically pure crystalline samples showed one other significant product, in addition to **7**. This is thought to be a diastereomer, which co-crystallises with **7** and cannot be separated. The NMR assignments below are only tentative. M.p. 130-133°C (decomp); ^{1}H NMR (400 MHz, 298 K, C_6D_6); δ = 1.48 (s, 12H; NCCH_3), 1.64 (broad, 12H; ArCH_3), 2.08-2.16 (2 broad overlapping signals, 24H; ArCH_3), 2.50 (s, 2H, MgC(Ph)*H*), 4.72 (s, 2H, NCC*H*), 6.49-7.34 (m, 18H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, C_6D_6); δ = 18.9 (Ar*C*H$_3$), 21.0 (Ar*C*H$_3$), 23.0 (NC*C*H$_3$), 46.0 (Mg*C*H(Ph), 95.0 (NC*C*H), 116.3, 127.0, 128.9, 129.1, 129.3, 131.5, 133.1, 157.0 (Ar*C*), 168.2 (N*C*CH$_3$); IR ν/cm^{-1} (ATR): 1654 (w), 1597 (m), 1541 (m), 1508(m), 1474 (m), 1446 (m), 1366 (s), 1313 (w), 1256 (m), 1197 (m), 1161 (m), 1106 (w), 1052 (m) 848 (w), 793 (m), 763 (m), 741 (m), 697 (s); EI/MS (70eV) *m/z* (%): 357.3 (^{Mes}NacnacMg$^+$, 100); anal. calc. for $C_{60}H_{70}Mg_2N_4$: C, 80.44 %; H, 7.88 %; N, 6.25 %; found: C, 80.32 %; H, 8.06 %; N, 6.39 %.

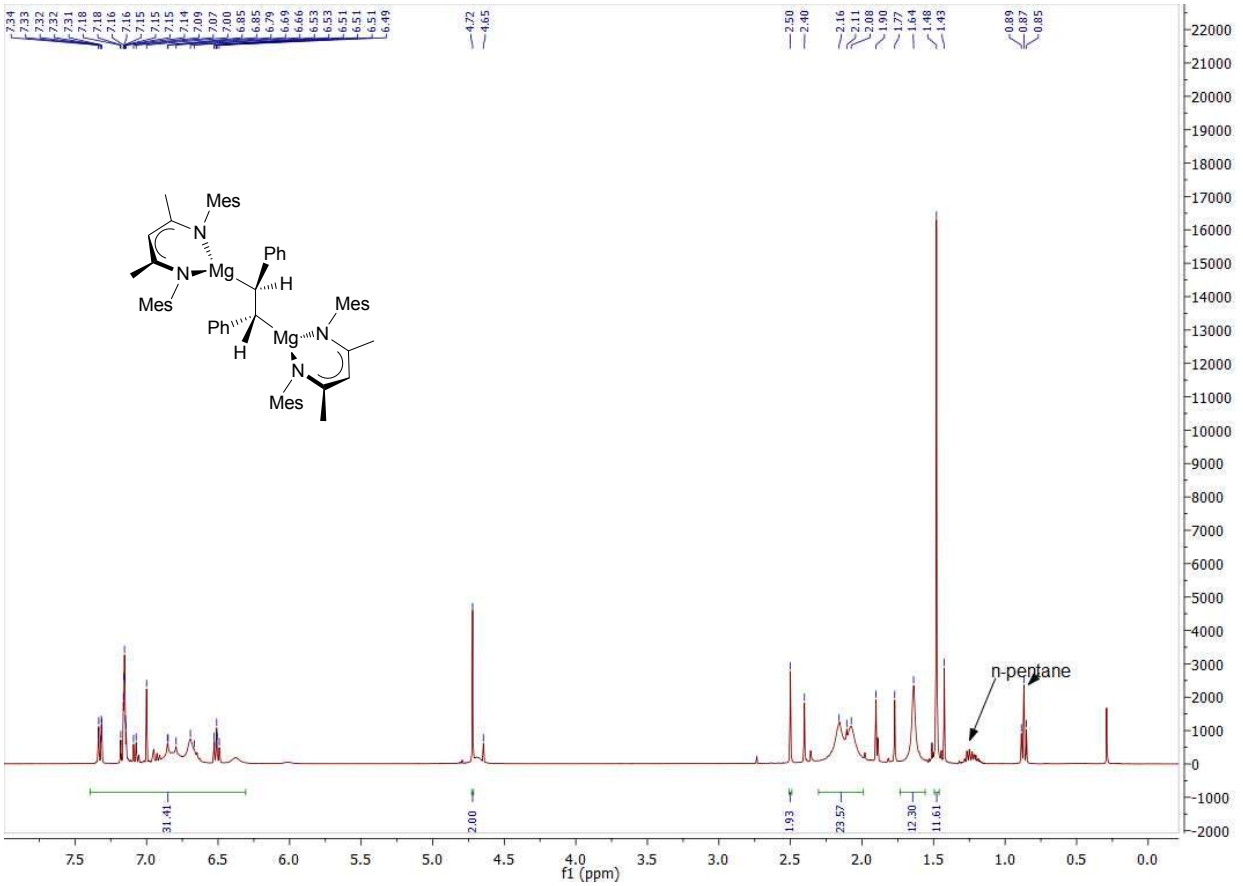


Figure S5. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of a compound mixture containing **7**.

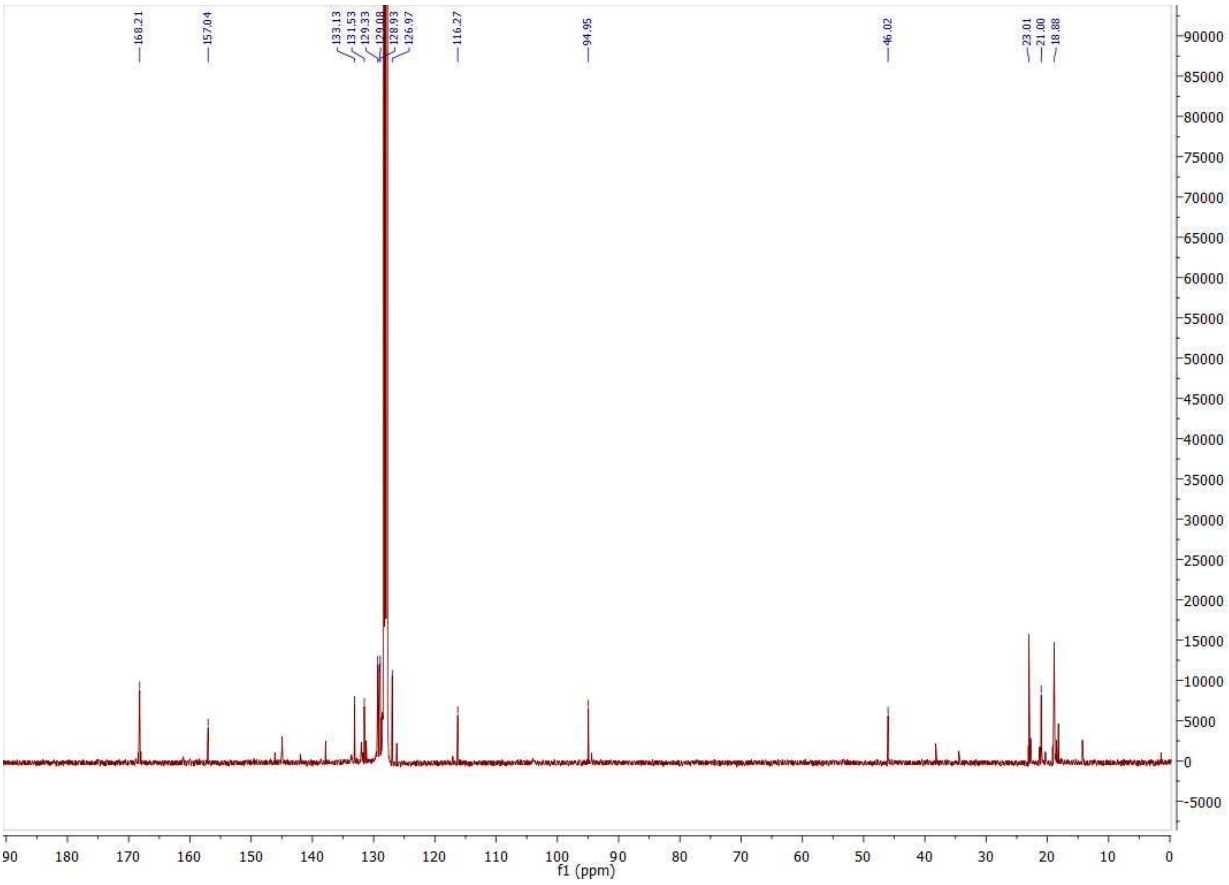


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, 298 K, C_6D_6) of a compound mixture containing **7**.

Synthesis of [{(DepNacnac)Mg}$_2$(μ-TS)] (8). [{(DepNacnac)Mg}$_2$] (100 mg, 0.130 mmol) and *trans*-stilbene (25 mg, 0.139 mmol) were dissolved in toluene (10mL) and stirred at room temperature, affording an orange solution after 1h. The mixture was then stirred for 72h, after which time volatiles were removed *in vacuo* and the residue extracted with pentane (*ca.* 5mL). The extract was stored at -30 °C overnight, yielding red crystals of red crystals of **8** (60 mg, 49 %). NMR spectra of analytically pure crystalline samples showed one other significant product, in addition to **8**. This is thought to be a diastereomer, which co-crystallises with **8** and cannot be separated. The NMR assignments below are only tentative. M.p. 186-189 °C; ^{1}H NMR (400 MHz, 298K, C_6D_6); δ = 1.00-1.23 (m of overlapping signals, ArCH$_2$C*H*$_3$), 1.48 (s, 12H, NCC*H*$_3$), 2.04-2.66 (m of overlapping signals, ArC*H*$_2$CH$_3$), 2.39 (s, 2H, MgC(Ph)*H*) 4.71 (s, 2H, NCC*H*), 6.38-7.27 (m, 22H, Ar*H*); ^{13}C{^{1}H} NMR spectra could not be assigned confidently due to two sets of signals observed; IR ν/cm^{-1} (ATR): 1619 (w), 1544 (s), 1516 (m), 1443 (m), 1395 (m), 1329 (m), 1263 (m), 1176 (m), 1104 (m), 1063 (w), 1020 (m), 929 (w), 861 (w), 795 (m), 760 (s), 697 (s); EI/MS (70eV) *m/z* (%): 174.1 (MeCNDep$^+$, 100), 333.2 (DepNacnacH-CH$_2$CH$_3^+$, 18), 347.3 (DepNacnacH-CH$_3^+$, 26), 385.3 (DepNacnacMg$^+$, 17); anal. calc. for $C_{64}H_{78}Mg_2N_4$: C, 80.75 %; H, 8.26 %; N, 5.89 %; found: C, 80.57 %; H, 8.40 %; N, 6.04 %.

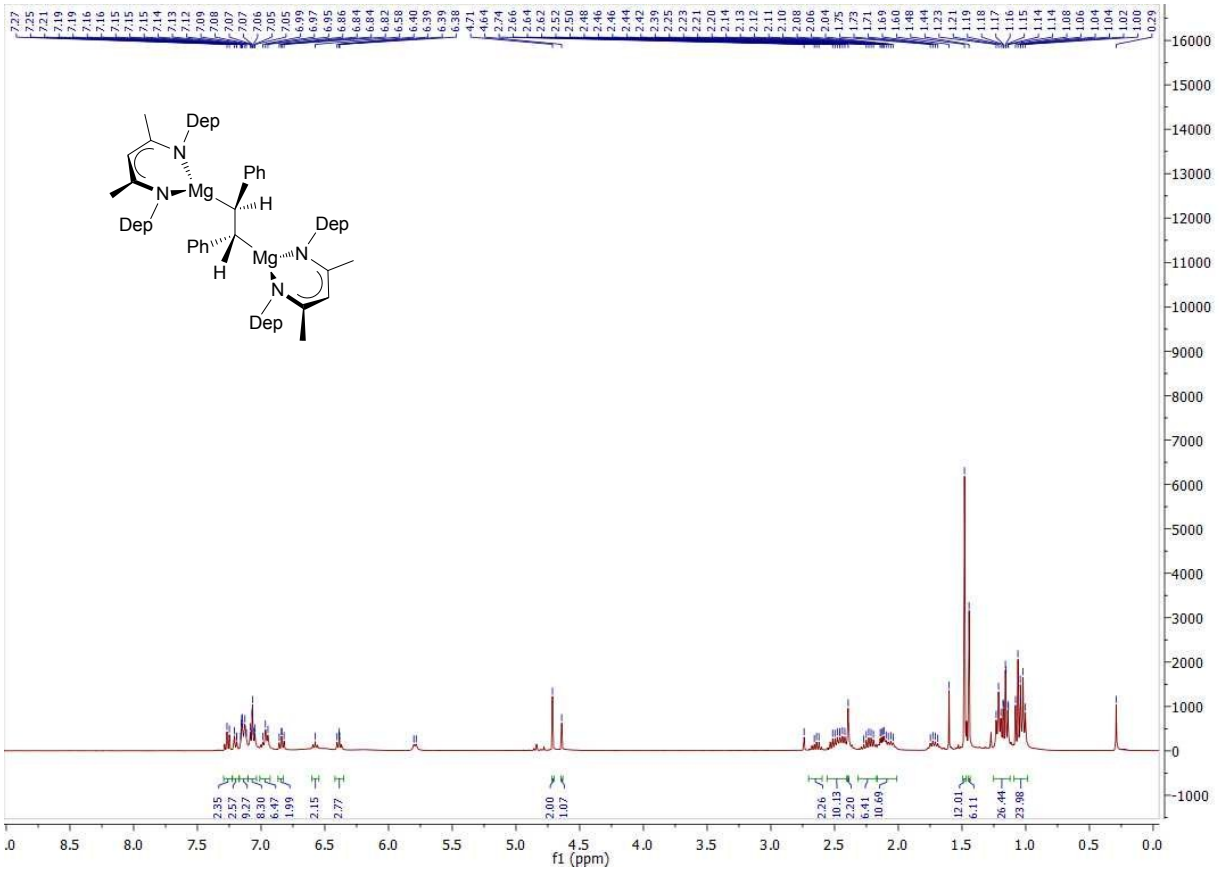


Figure S7. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of a compound mixture containing **8**.

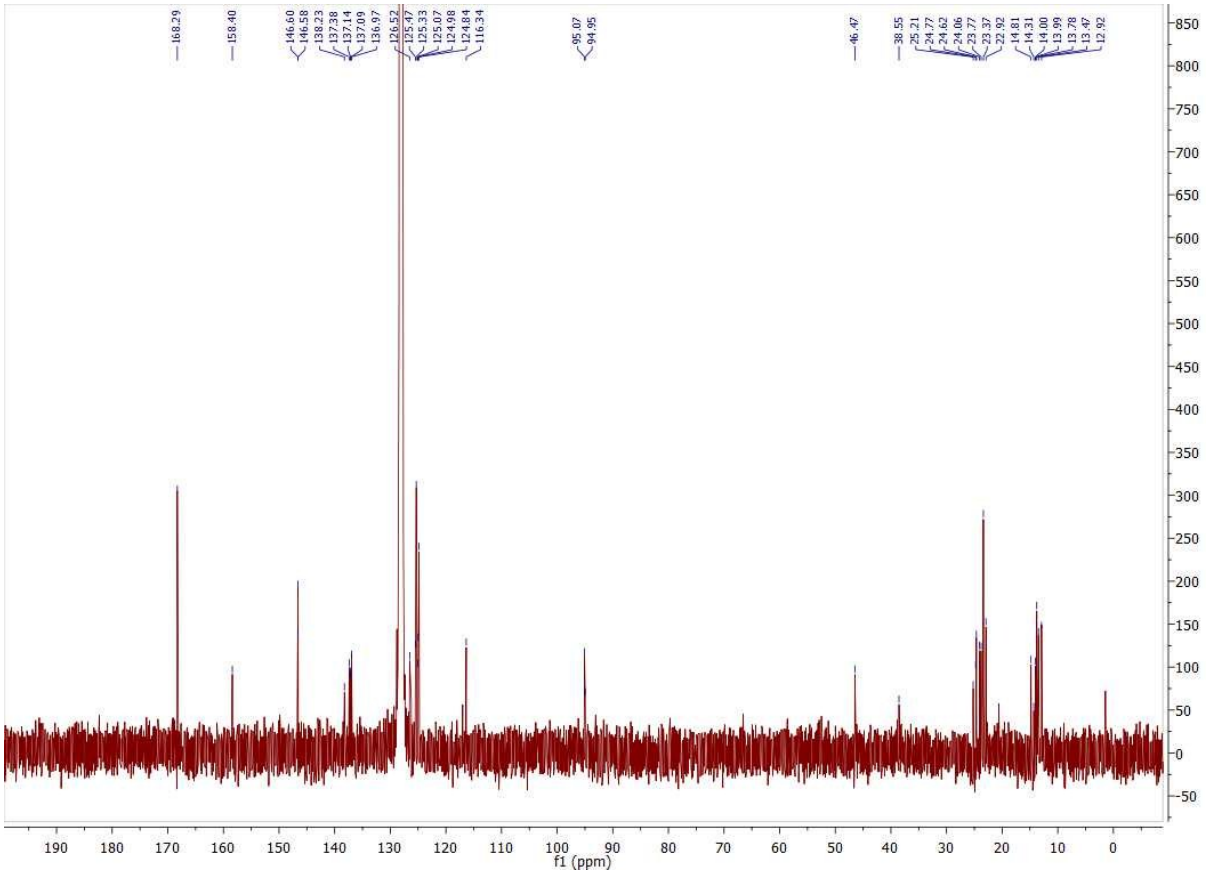


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, 298 K, C_6D_6) of a compound mixture containing **8**.

Synthesis of [{(^Mes^Nacnac)Mg}$_2$(μ-DPA)] (9). [{(^Mes^Nacnac)Mg}$_2$] (500 mg, 0.698 mmol) and diphenylacetylene (131 mg, 0.735 mmol) were dissolved in toluene (15mL) and stirred at room temperature for 6 hours, during which time the reaction mixture became an orange solution. This was concentrated *in vacuo* (to *ca.* 5mL) and stored at -30 °C to give orange block like crystals of **9** overnight (429 mg, 69% yield). Crystals suitable for x-ray diffraction were grown from a saturated hexane solution stored at -30°C overnight. M.p. 203-206 °C; ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ = 1.49 (s, 12H, ArCH_3) 1.89 (s, 24H, ArCH_3), 2.29 (s, 12H, NCCH_3), 4.72 (s, 2H, NCC*H*), 6.41-6.43 (m, 4H, Ar*H*), 6.78 (s, 8H, Mes Ar*H*), 6.91-6.94 (m, 4H, Ar*H*), 7.02-7.05 (m, 2H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, C_6D_6): δ = 19.0 (Ar*C*H_3), 21.1 (Ar*C*H_3), 22.9 (NC*C*H_3), 94.9 (NC*C*H), 122.9, 123.6, 129.2, 130.4, 131.6, 132.8, 144.8 (Ar*C*), 160.2 (Mg*C*(Ph)), 168.1 (N*C*CH$_3$); IR ν/cm^{-1} (ATR): 1584 (w), 1542 (m), 1521 (m), 1449 (m), 1389 (s), 1365 (s), 1260 (m), 1196 (m), 1196 (m), 1016 (w), 854 (w), 767 (m), 756 (m), 742 (m), 705 (s); EI/MS (70eV) *m/z* (%): 119.1 (Mes$^+$, 40), 160.1 (MeCNMes$^+$, 82), 357.3 (^Mes^NacnacMg$^+$, 100); anal. calc. for $C_{60}H_{68}Mg_2N_4$: C, 80.62 %; H, 7.67 %; N, 6.27 %; found: C, 80.47 %; H, 7.78 %; N, 6.17 %.

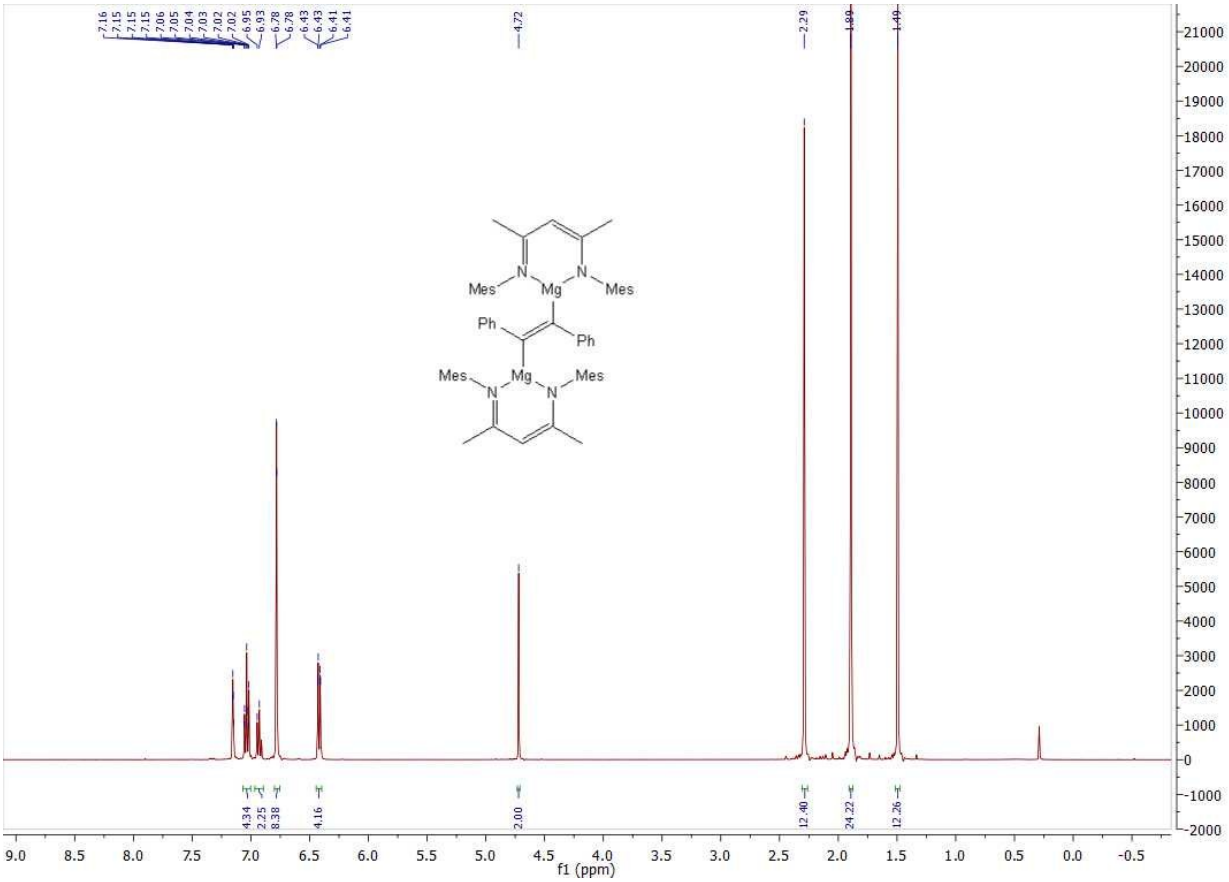


Figure S9. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **9**.

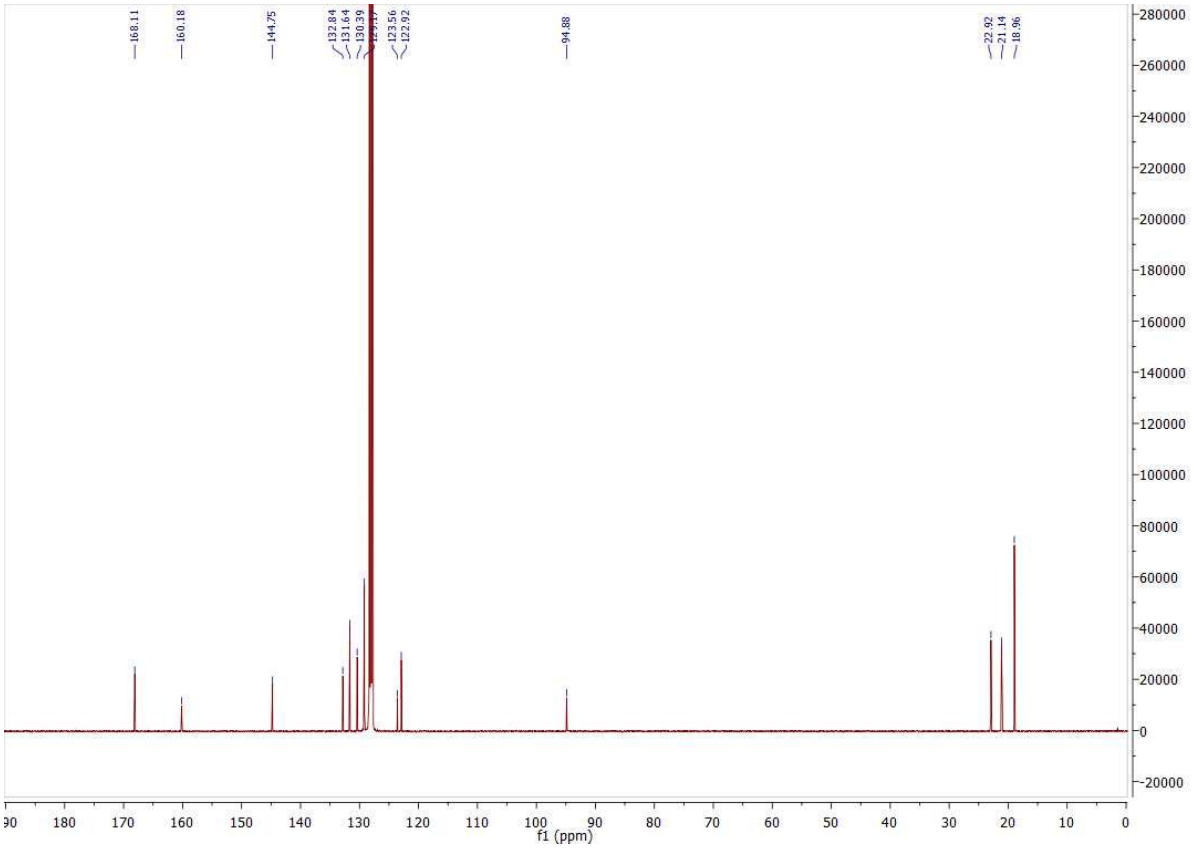


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, 298 K, C_6D_6) of **9**.

Synthesis of [(L*Zn)$_2$(μ-DPE)] (10). To a stirred solution of [{(^{Mes}Nacnac)Mg}$_2$] (0.20 g, 0.278 mmol) in toluene (30 mL) was added neat 1,1-diphenylethylene (0.054 mL, 0.306 mmol) *via* a microsyringe, and the reaction mixture was then cooled to -80 °C. To this was added a solution of [L*ZnBr], (0.410 g, 0.556 mmol) in toluene (20 mL), whereupon the reaction mixture darkened slightly. After warming to room temperature, the orange-red colour of the solution faded to pale orange. After stirring for a further 1 h, volatiles were removed *in vacuo*. The residue was extracted into pentane (15 mL) and stored at -30 °C overnight, yielding colourless crystals of **10** (0.21 g, 51 %). M.p.= 202-206 °C; ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 0.65 (s, 2H, CH_2CPh$_2$), 0.86-1.06 (m, 42H, CH(CH_3)$_2$), and CH(CH$_3$)$_2$), 1.81 (s, 3H, ArCH_3), 1.85 (s, 3H, ArCH_3), 6.20 (s, 2H, CHPh$_2$), 6.22 (s, 2H, CHPh$_2$), 6.50-7.43 (m, 54H, ArH); ^{13}C{^{1}H} NMR (400 MHz, 298 K, C_6D_6): δ = 14.3 (CH(*C*H$_3$)$_2$), 14.9 (CH(*C*H$_3$)$_2$), 15.6 (*C*H$_2$CPh$_2$), 19.3 (*C*H(CH$_3$)$_2$), 19.5 (*C*H(CH$_3$)$_2$), 21.0 (Ar*C*H$_3$), 21.1 (Ar*C*H$_3$), 51.3 (*C*HPh$_2$), 52.6 (*C*HPh$_2$), 55.5 (CH$_2$*C*Ph$_2$), 124.5, 126.5, 126.6, 126.6, 126.9, 127.2, 127.6, 128.5, 128.6, 128.8, 128.9, 129.2, 129.4, 129.5, 129.9, 130.1, 130.3, 130.5, 130.6, 131.4, 141.0, 144.9, 145.5, 146.0, 146.1, 146.5, 146.7, 146.9 (Ar-*C*); ^{29}Si{^{1}H} NMR (400 MHz, 298 K, C_6D_6): δ = -21.9, 2.8; IR υ/cm^{-1} (Nujol): 1597 (m), 1491 (s), 1458 (s), 1377 (s), 1228 (m), 1210 (m), 1127 (m), 1075 (m), 1030 (m), 879 (s), 858 (m), 820 (m), 744 (s), 661 (s); MS/EI *m/z* (%): 157.4 (SiPr$^i_3$$^+$, 65), 167.1 (Ph$_2CH^+$, 100), 595.4 (L*$^+$, 15); anal. calc. for $C_{98}H_{108}N_2Si_2Zn_2$: C, 78.43 %; H, 7.25 %; N, 1.87 %; found: C, 78.22 %; H, 7.31 %; N, 1.94 %.

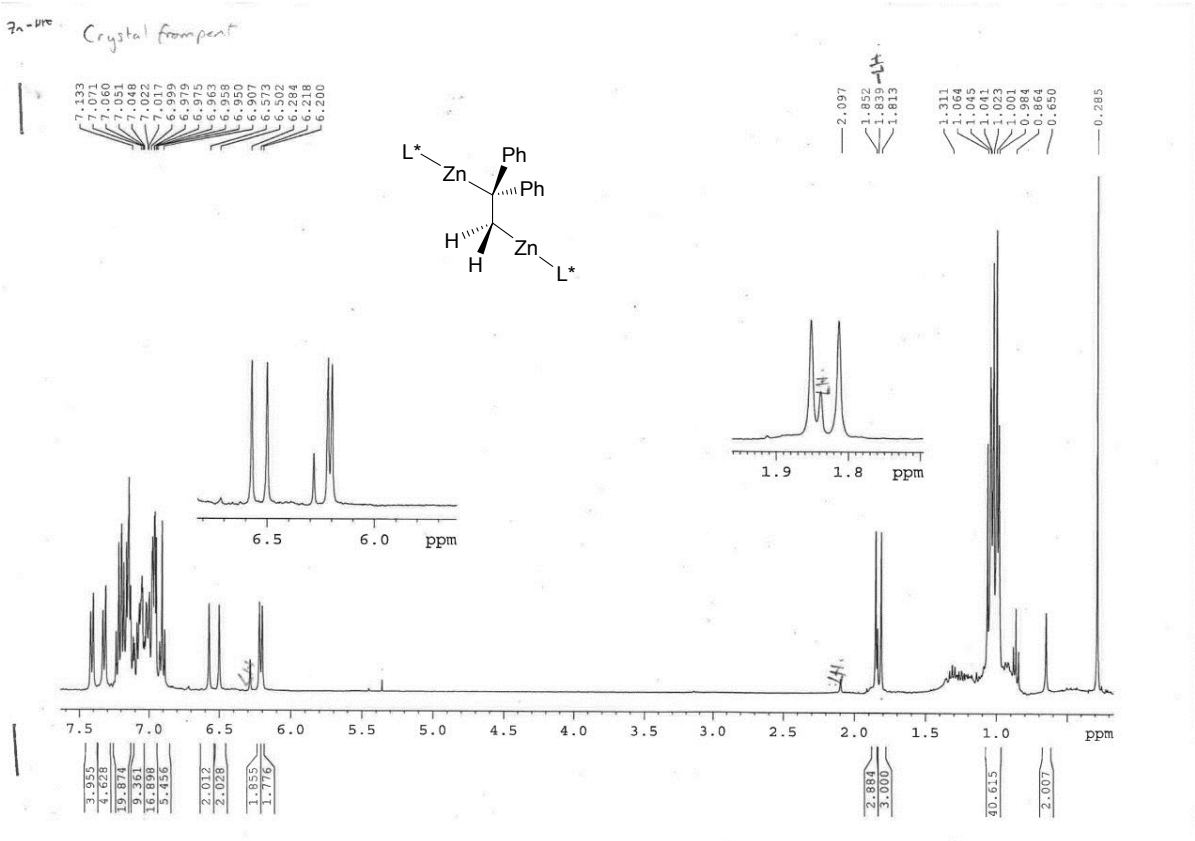


Figure S11. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **10**.

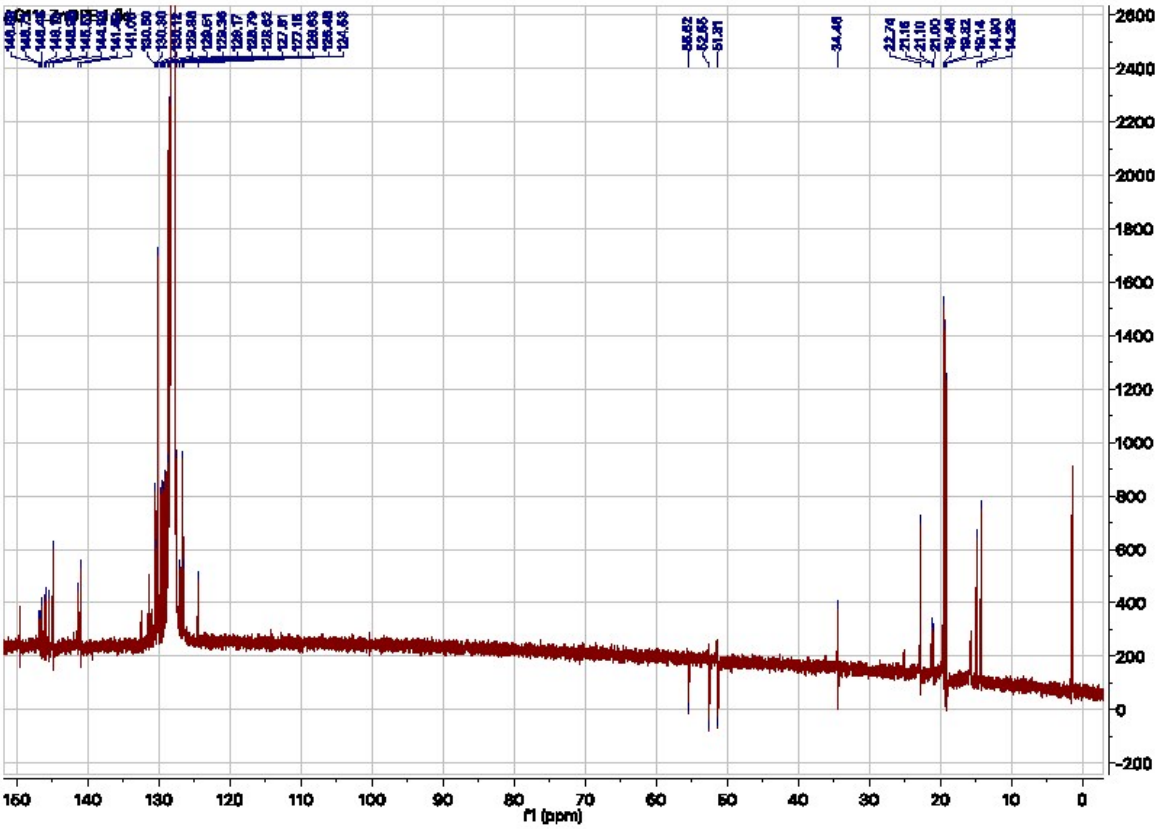


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, 298 K, C_6D_6) of **10**.

Synthesis of [(^{TBo}LZn)$_2$(μ-DPA)] (11). To a stirred solution of [^{TBo}LZnBr(THF)] (150mg, 0.217 mmol) in toluene (20mL) at -78 °C, was added [{(^{Mes}Nacnac)Mg}$_2$(μ-DPA)] (97 mg, 0.108 mmol) dissolved in toluene (10mL). The reaction mixture was warmed to room temperature over the course of an hour and stirred overnight, during which time a colourless precipitate formed The reaction solution was filtered, and volatiles removed *in vacuo*. The residue was taken up in hexane (*ca.* 20mL) and stored at -30°C overnight, yielding colourless crystals of **11** (85mg, 62 %). M.p. 120-123 °C (decomp); ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ = 0.03 (s, 18H, Si(CH_3)$_3$) 1.12-1.14 (d, $^{3}J_{HH}$ = 6.9 Hz, 24H, CH(CH_3)$_2$), 1.22-1.23 (d, $^{3}J_{HH}$ = 6.9 Hz, 24H, CH(CH_3)$_2$), 3.33 (sept, $^{3}J_{HH}$ = 6.9Hz, 8H, C*H*(CH$_3$)$_2$), 5.96 (s, 4H, NC*H*), 6.89-7.20 (m, 22H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, C_6D_6): δ = 4.9 (Si(*C*H$_3$)$_3$), 23.7 (CH(*C*H$_3$)$_2$), 25.8 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 118.0 (N*C*H), 124.5, 127.1, 129.3, 139.7, 147.1, 151.8, (Ar*C*), 168.8 (Zn*C*(Ph)); $^{11}B\{^{1}H\}$ NMR (128 MHz, 298 K, C_6D_6): δ = 23.4; $^{29}Si\{^{1}H\}$ NMR (80 MHz, 298 K, C_6D_6): δ = -1.1; IR ν/cm^{-1} (ATR): 1599 (w), 1466 (m), 1388 (m), 1365 (s), 1228 (m), 1111 (w), 1074 (w), 880 (w), 830 (w), 799 (w), 756 (m), 698 (s); EI/MS (70eV) *m/z* (%): 475.4 (^{TBo}LH^{+} , 100); a reproducible microanalysis could not be obtained as the compound presistently co-crystallised with a small amount (*ca.* 3%) of the pro-ligand, ^{TBo}LH.

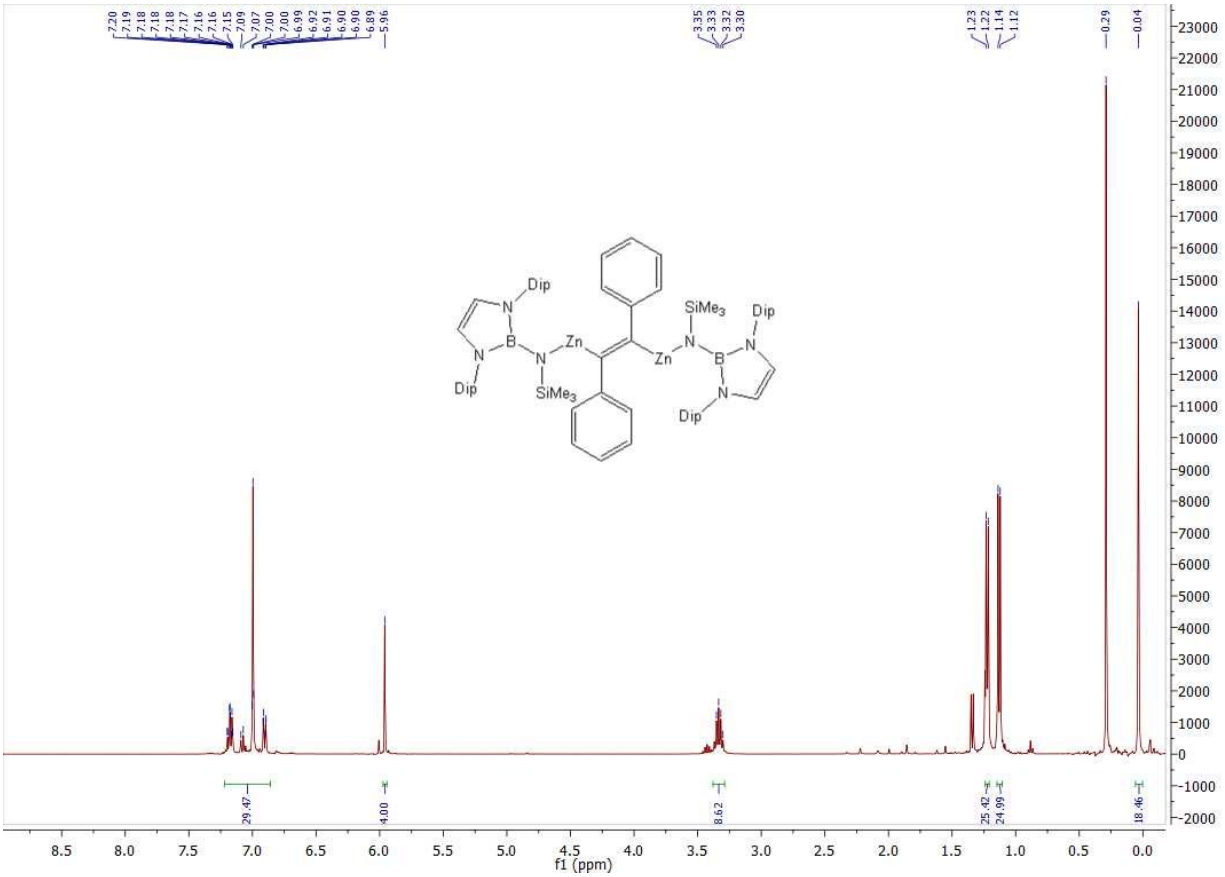


Figure S13. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **11**.

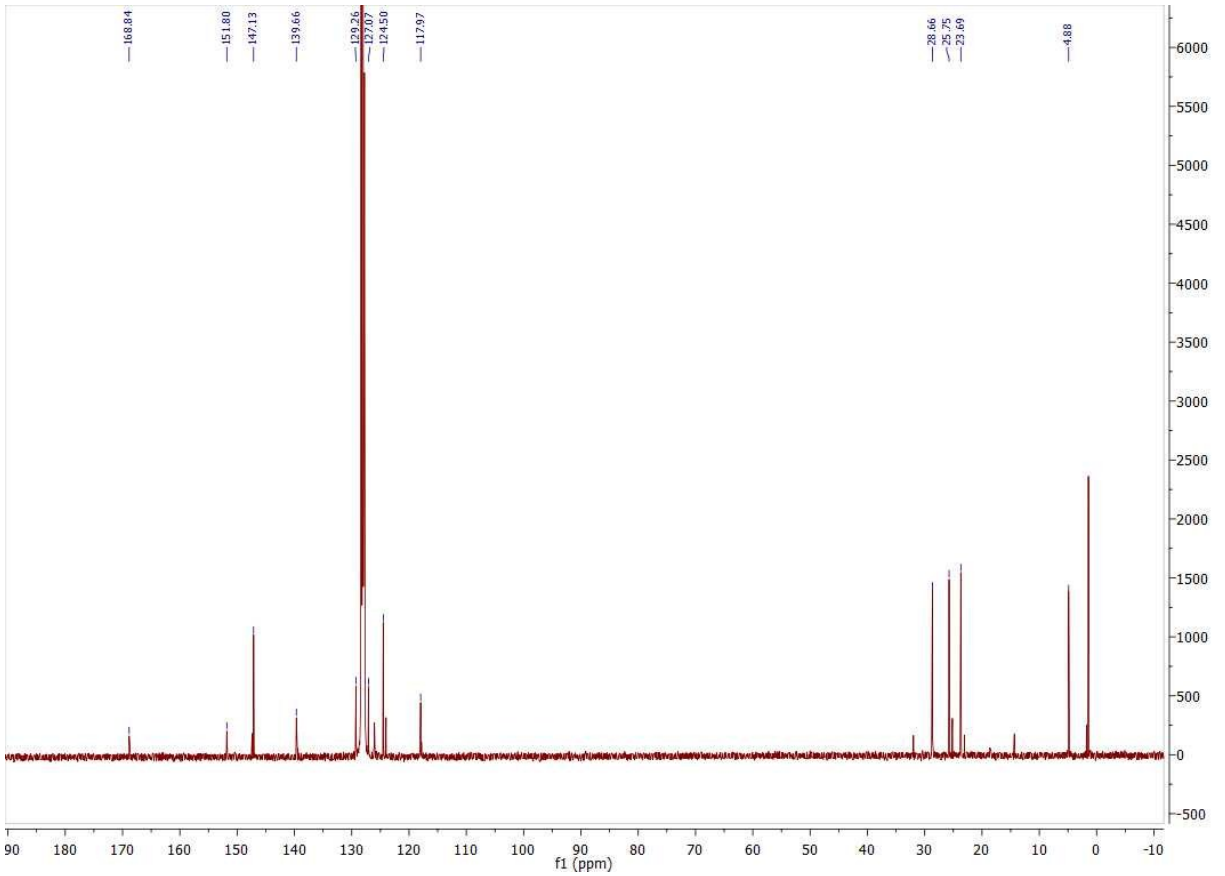


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, 298 K, C_6D_6) of **11**.

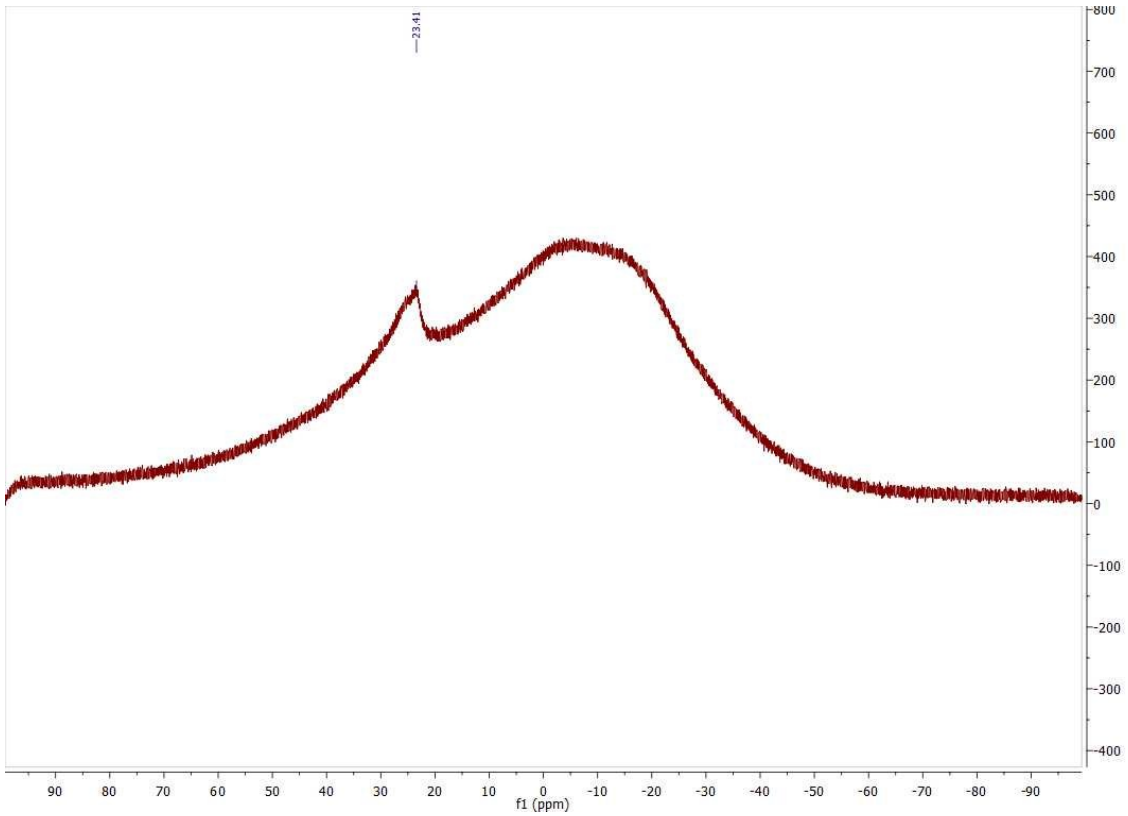


Figure S15. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, 298 K, C_6D_6) of **11**.

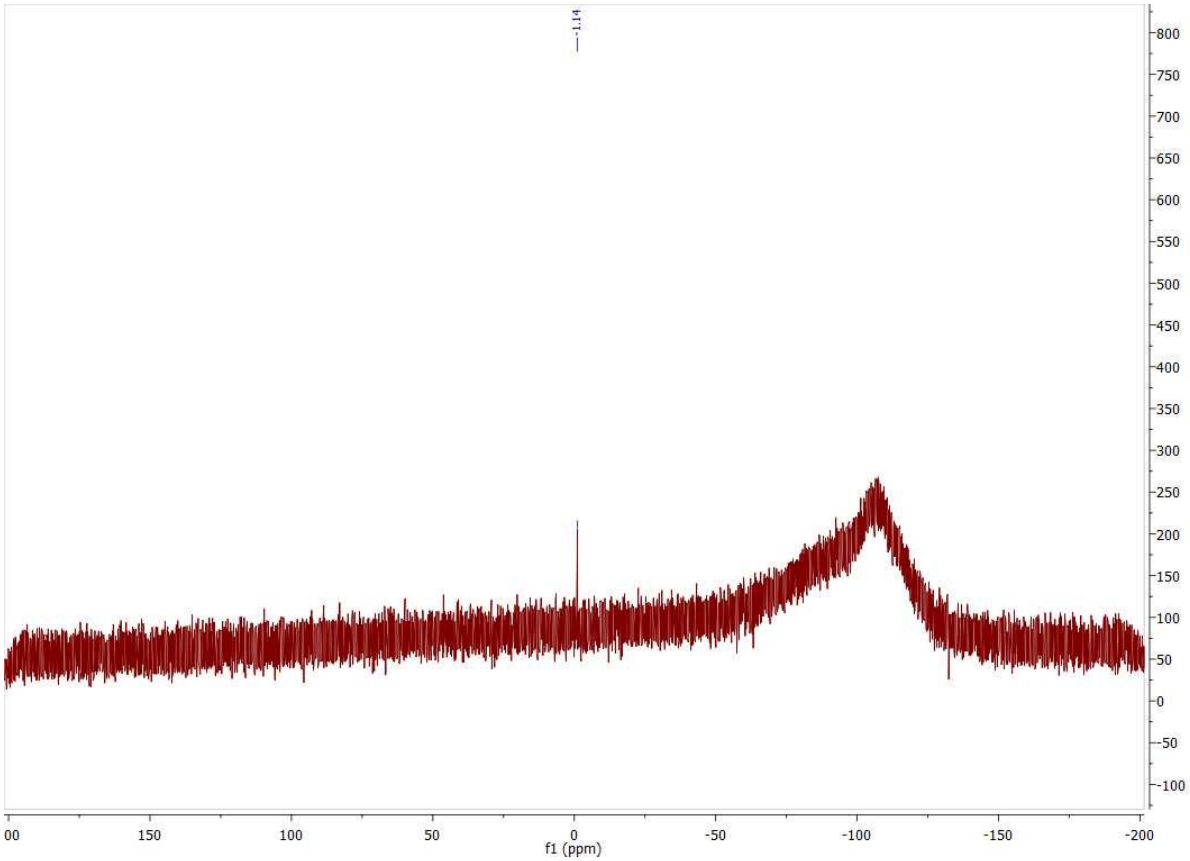


Figure S16. $^{29}Si\{^{1}H\}$ NMR spectrum (80 MHz, 298 K, C_6D_6) of **11**.

Synthesis of [(^{PhBo}LCdI)$_2$]. K[^{PhBo}L] (0.70 g, 1.00 mmol) was dissolved in THF (30 mL) and the solution was added to a suspension of CdI_2 (403 mg, 1.10 mmol) in THF (20 mL) at -80 °C. The reaction mixture was warmed to room temperature and stirred for 12 hrs, affording a bright yellow solution. Volatiles were removed *in vacuo* and the residue was extracted with hexane (30 mL). The bright yellow extract was filtered and the filtrate concentrated to *ca.* 10 mL, affording bright yellow crystals of the title compound overnight (0.76 g, 85 %). M.p. 221-224 °C; ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 1.11 (d, J = 6.8 Hz, 24H, CH(CH_3)$_2$), 1.15 (d, J = 6.8 Hz, 24H, CH(CH_3)$_2$), 3.49 (sept, J = 6.8 Hz, 8H, CH(CH$_3$)$_2$), 5.96 (s, 4H, NCH), 6.98-7.56 (m, 42H, ArH); ^{13}C{^{1}H} NMR (75 MHz, 298 K, C_6D_6): δ = 23.6 (CH(CH$_3$)$_2$), 25.6 (CH(CH$_3$)$_2$), 28.7 (CH(CH$_3$)$_2$), 118.1 (NCH), 125.7, 128.7, 129.7, 130.0, 135.5, 135.8, 138.8, 139.4, 147.6 (ArC); ^{29}Si{^{1}H} NMR (80 MHz, 298 K, C_6D_6): δ = -19.5; ^{11}B{^{1}H} NMR (128 MHz, 298 K, C_6D_6): δ = 24.2; no signal was observed in the ^{113}Cd{^{1}H} NMR spectrum; IR ν/cm^{-1} (Nujol): 2921 (s), 2853 (s), 1738 (m), 1574 (w), 1456 (s), 1401 (m), 1375 (s), 1353 (s), 1227 (m), 1146 (w), 1103 (m), 1070 (m), 984 (m), 932 (w), 894 (m), 800 (m) 758 (m), 725 (m), 697 (s); MS/EI *m/z* (%): 901.5 (^{PhBo}LCdI$^+$, 20.3), 661.5 (^{PhBo}LH$^+$, 78.2), 583.4 (^{PhBo}LH$^+$-Ph, 100), 259.1 (Ph_3Si^+, 93.5); anal. calc. for $C_{88}H_{102}B_2I_2N_6Si_2Cd_2$: C, 58.71 %; H, 5.71 %; N, 4.67 %; found: C, 58.60 %; H, 5.73 %; N, 4.52 %.

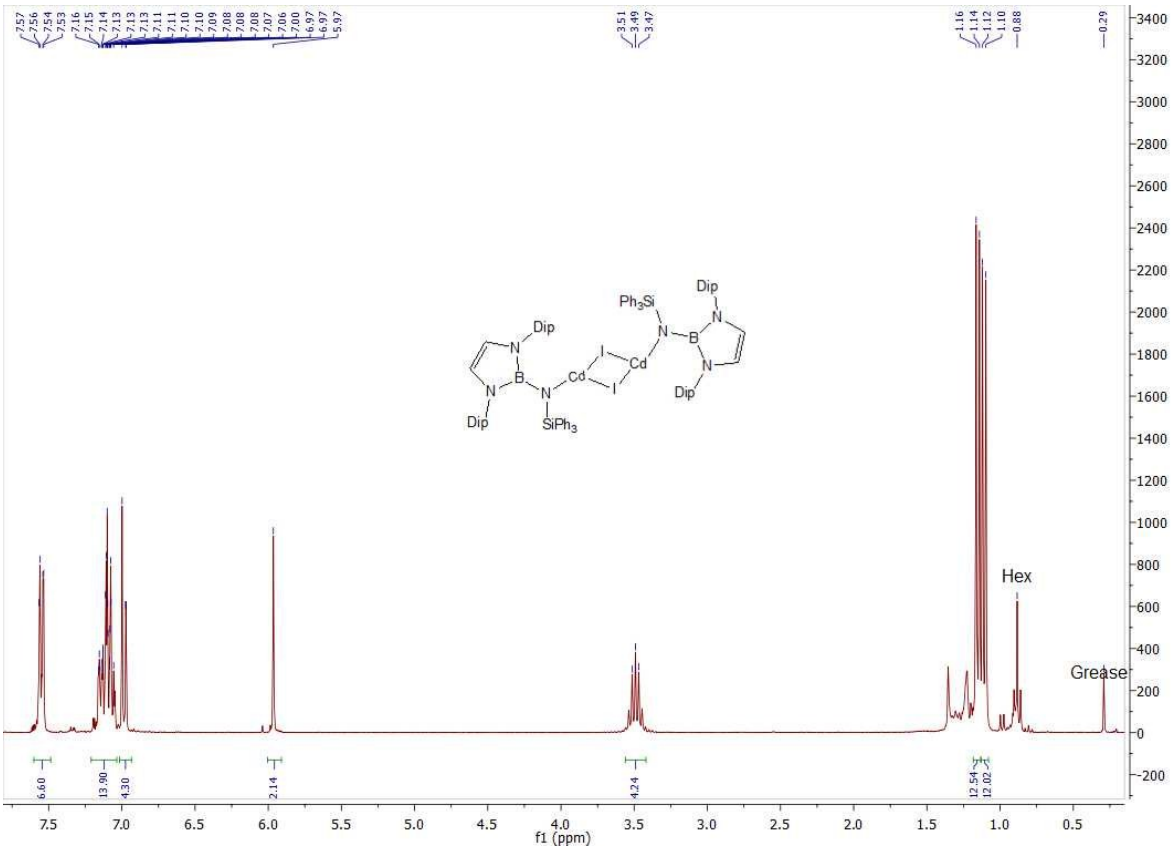


Figure S17. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of [(^{PhBo}LCdI)$_2$].

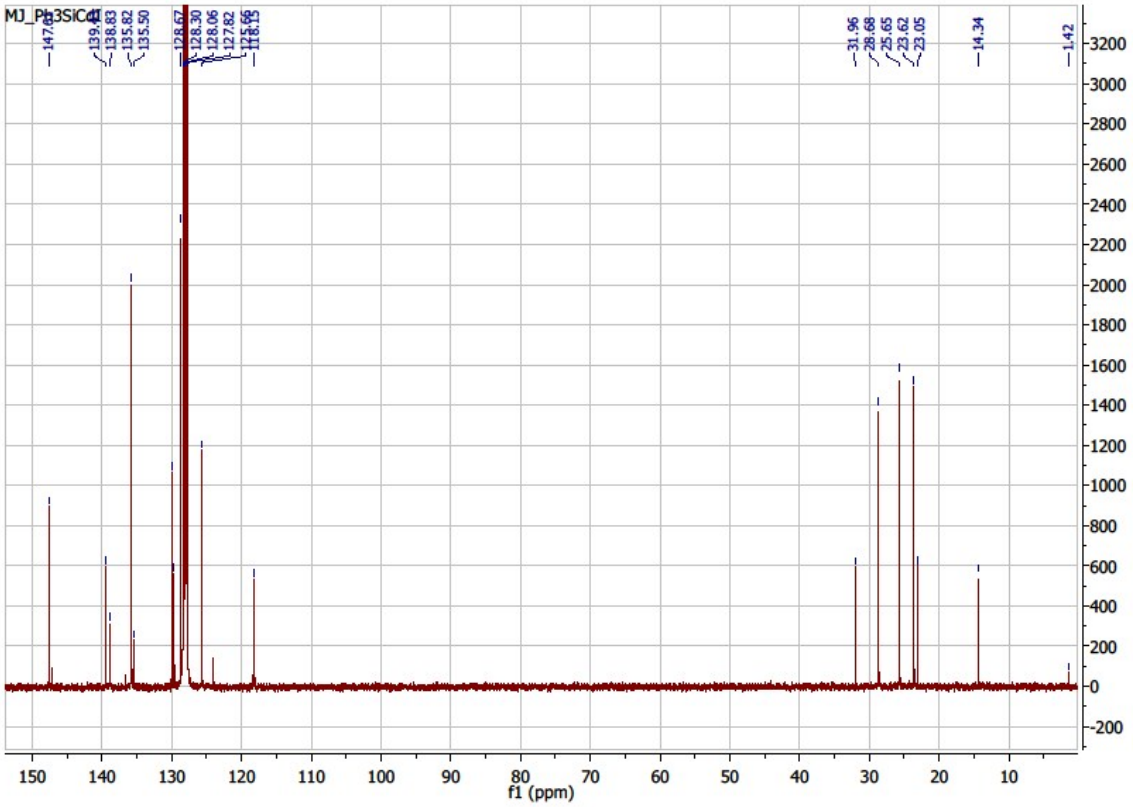


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, 298 K, C_6D_6) of [(^{PhBo}LCdI)$_2$].

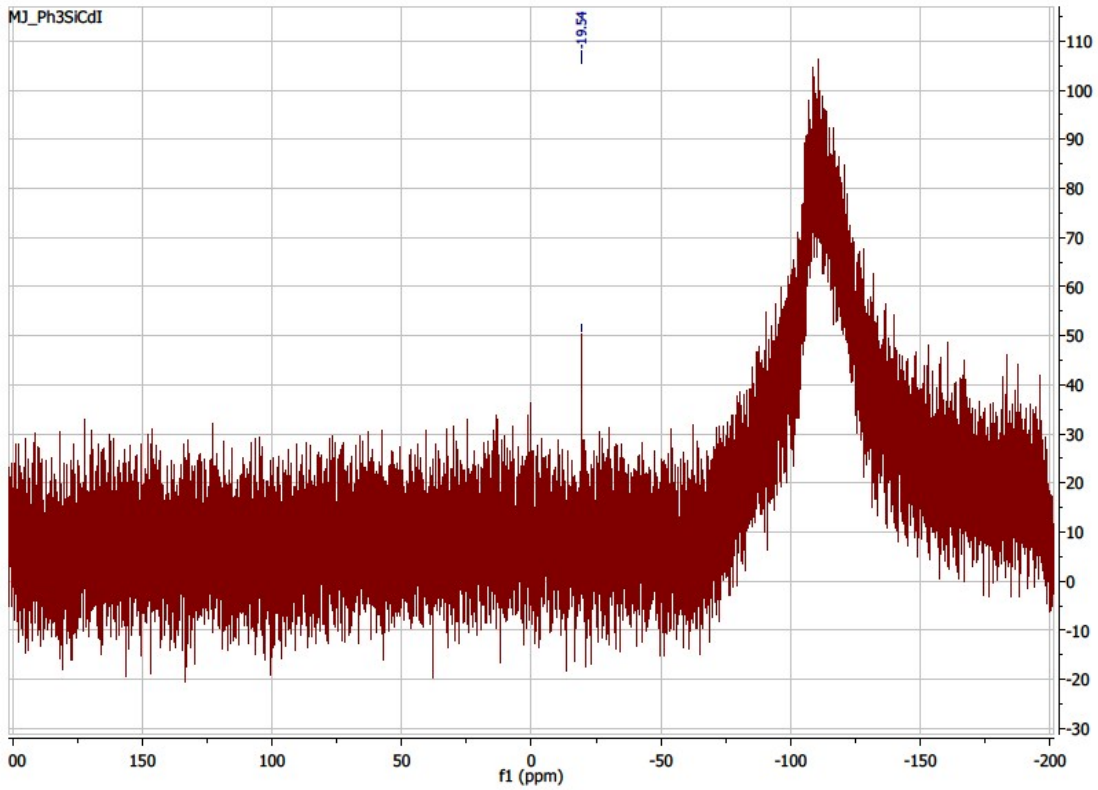


Figure S19. $^{29}Si\{^{1}H\}$ NMR spectrum (80 MHz, 298 K, C_6D_6) of [(^{PhBo}LCdI)$_2$].

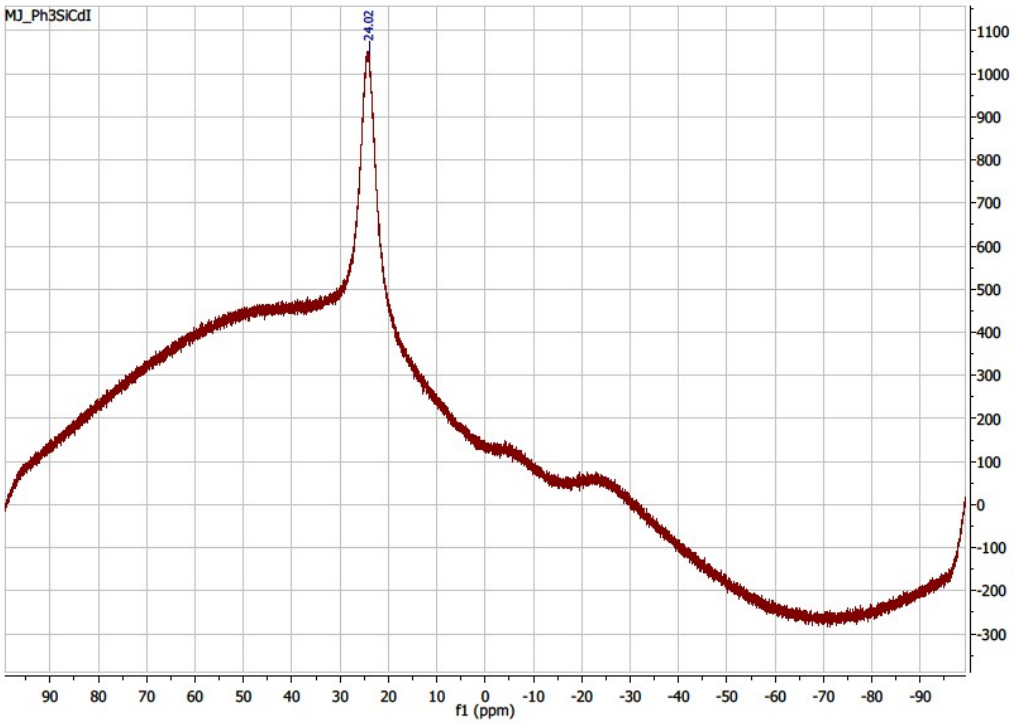


Figure S20. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, 298 K, C_6D_6) of [(^{PhBo}LCdI)$_2$].

Synthesis of [^{PhBo}LCdCd^{PhBo}L] (12). To a stirred solution of [{(^{Mes}Nacnac)Mg}$_2$] (0.082 g, 0.114 mmol) in hexane (30 mL) was added neat 1,1-diphenylethylene (0.022 mL, 0.125 mmol) *via* a microsyringe, and the reaction mixture cooled to -80 °C. A solution of [(^{PhBo}LCdI)$_2$] (0.206 g, 0.114 mmol) in hexane (20 mL) was then added, whereupon the reaction mixture darkened slightly. After warming to room temperature, the orange-red colour of the solution faded to pale yellow. After stirring for a further 1 h, volatiles were removed *in vacuo*. The residue was extracted into hexane (15 mL) and stored at -30 °C overnight, yielding yellow crystals of **12** (0.081 g, 46 %). M.p. = 124-128 °C (decomposition); ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 1.08 (d, $^{3}J_{H,H}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.23 (d, $^{3}J_{H,H}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 3.54 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 6.12 (s, 4H, NC*H*), 6.87-7.48 (m, 42H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (75 MHz, 298 K, C_6D_6): δ = 23.0 (CH(*C*H$_3$)$_2$), 25.6 (CH(*C*H$_3$)$_2$), 28.6 (*C*H(CH$_3$)$_2$), 118.4 (N*C*H), 128.6, 129.9, 135.4, 135.8, 136.0, 139.4, 140.1, 147.5 (Ar*C*); $^{29}Si\{^{1}H\}$ NMR (80 MHz, 298 K, C_6D_6): δ = -20.7; $^{11}B\{^{1}H\}$ NMR (128 MHz, 298 K, C_6D_6): δ = 24.2; no signal was observed in the $^{113}Cd\{^{1}H\}$ NMR spectrum; IR υ/cm^{-1} (Nujol): 1623 (m), 1551 (m), 1457 (m), 1440 (m), 1401 (s), 1354 (s), 1259 (s), 1188 (m), 1148 (m), 1101 (s), 1071 (m), 1019 (m), 984 (m), 801 (s), 759 (m), 737 (m); MS/EI *m/z* (%): 259.1 ($SiPh_3^+$, 72), 386.2 (B{N(Dip)CH}$_2^+$, 11), 661.5 (^{PhBo}LH$^+$, 100), 774.5 ({(HC(Dip)N)$_2$B}(Ph$_2$Si)NCd$^+$, 2); a reproducible microanalysis could not be obtained as the compound presistently co-crystallised with a small amount (*ca.* 3%) of the pro-ligand, ^{PhBo}LH.

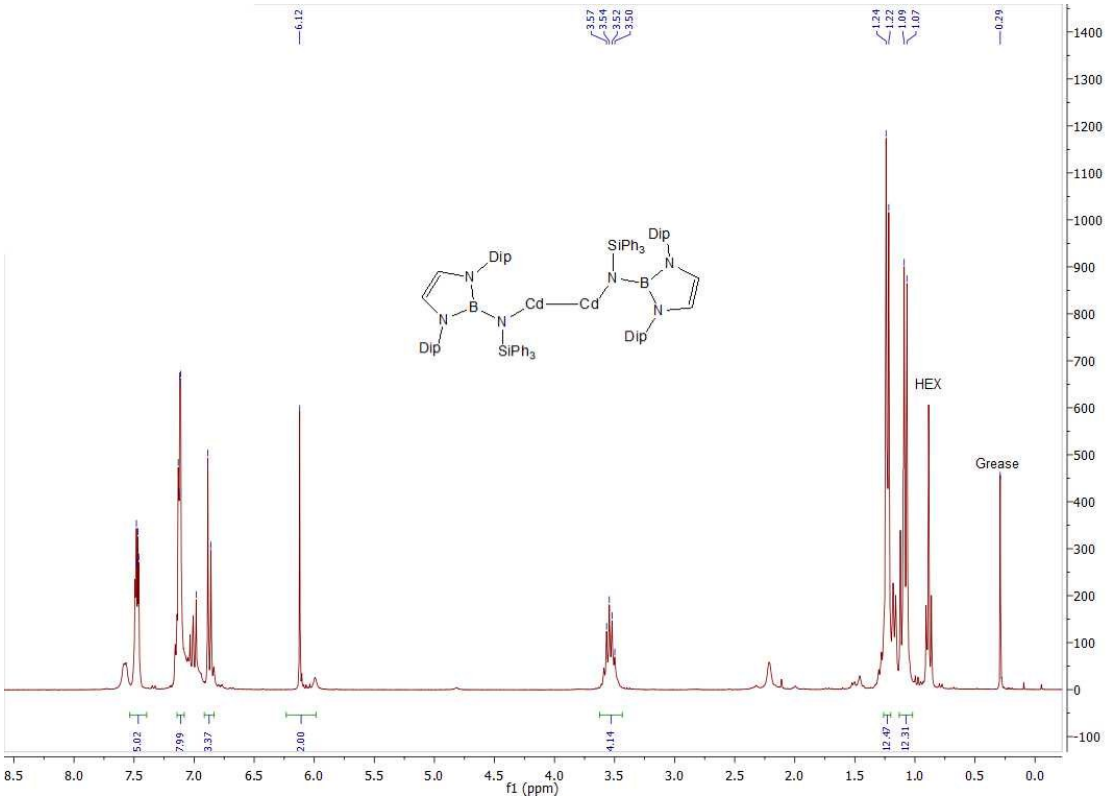


Figure S21. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **12**.

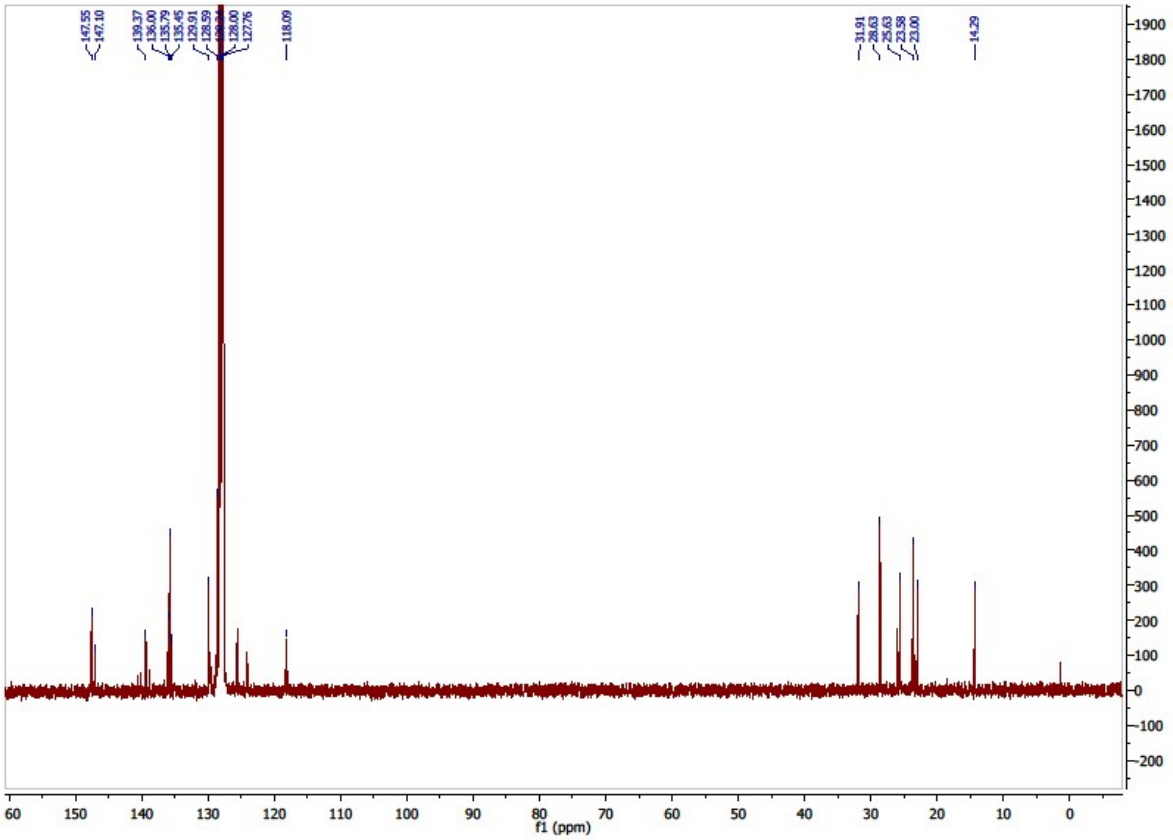


Figure S22. ^{13}C{^{1}H} NMR spectrum (75 MHz, 298 K, C_6D_6) of **12**.

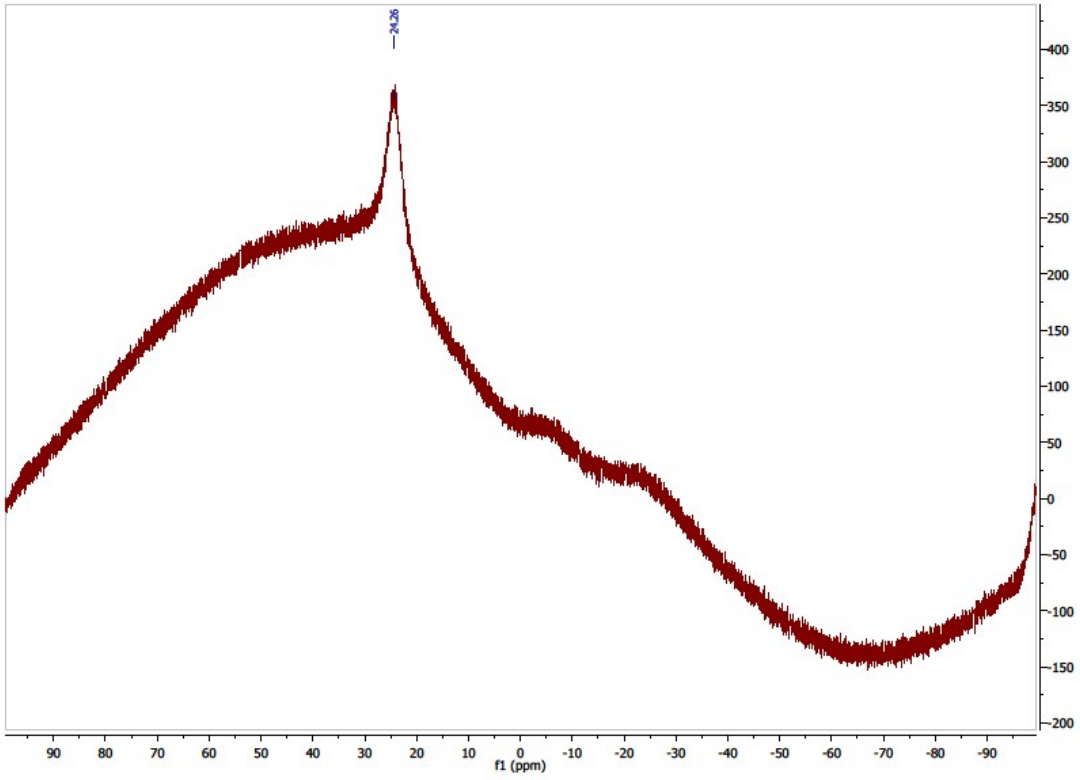


Figure S23. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, 298 K, C_6D_6) of **12**.

Synthesis of [L†MgMg L†]. To a stirred solution of [{(^{Mes}Nacnac)Mg}$_2$] (0.52g, 0.72 mmol) in toluene (40 mL) at room temperature was added neat 1,1-diphenylethylene (0.14 mL, 0.79 mmol) *via* a microsyringe. The yellow solution became red-orange and then red upon addition. The solution was then cooled to -78°C and to it was added dropwise solution of [(L†MgI)$_2$] (0.50g, 0.36 mmol) in toluene (40 mL). The reaction mixture was then slowly warmed to room temperature over 12 h whereupon volatiles were removed *in vacuo*. The residue was extracted into hexane (*ca.* 20 mL), filtered, and the filtrate concentrated to *ca.* 5 mL. This was stored at -30 °C overnight to give colorless crystals of the title compound (0.32 g, 80%). Spectroscopic data were identical to those previously reported.[8]

Synthesis of [GeH(κ^2-*N,C*-L*$^{-H}$){Mg(^{Mes}Nacnac)}] (13). To a stirred solution of [{(^{Mes}Nacnac)Mg}$_2$] (0.20g, 0.28 mmol) in toluene (40 mL) at room temperature was added neat 1,1-diphenylethylene (0.06 mL, 0.33 mmol) *via* a microsyringe. The yellow solution became red-orange and then red upon addition. The solution was then cooled to -78 °C and to it was added a solution of [L*GeCl] (0.20g, 0.28 mmol) in toluene (40 mL). The reaction mixture was warmed to room temperature over 12 h, whereupon volatiles were removed *in vacuo*. The residue was extracted into hexane (*ca.* 20 mL), filtered, and the filtrate concentrated to *ca.* 5 mL. This was stored at -30 ºC overnight to give colorless crystals of **13** (0.18 g, 56 %). M.p. 158-163 °C; ^{1}H NMR

(400 MHz, 298 K, C_6D_6) δ = 1.23 (br. s, 6H; ArCH_3), 1.30-1.34 (m, 18H, CH(CH_3)$_2$), 1.51 (s, 6H; ArCH_3), 1.62 (sept, $^3J_{HH}$= 7.5 Hz, 3H, CH(CH$_3$)$_2$), 2.15 (s, 3H; ArCH_3), 2.19 (s, 6H; ArCH_3), 2.29 (s, 6H; NCCH_3), 4.95 (s, 1H; NCCH), 6.40 cent. (m, 2H; ArH), 6.56 (s, 2H; CHPh$_2$), 6.72-7.90 (m, 23H; ArH), GeH resonance obscured; ^{13}C{^{1}H} NMR (100 MHz, 298 K, C_6D_6) δ = 14.2 (*C*H(CH$_3$)$_2$), 20.3 (Ar*C*H$_3$), 20.5 (Ar*C*H$_3$), 22.9 (Ar*C*H$_3$), 24.0 (NC*C*H$_3$), 48.0 (*C*HPh$_2$), 51.0 (*C*HPh$_2$), 95.3 (NC*C*H), 125.0, 125.8, 128.6, 129.3, 130.2, 131.4, 133.5, 133.8, 140.7, 142.0, 143.0, 145.4, 149.0,149.2, 149.6, 151.4 (Ar*C*), 168.5 (N*C*CH); ^{29}Si{^{1}H}NMR (C_6D_6, 296 K, 80 MHz): δ = 1.05; IR υ/cm^{-1} (Nujol): 1942 (s, Ge-H), 1509 (m), 1447 (s), 1255 (s), 1146 (s), 907 (s), 885 (s), 769 (m), 697 (s); EI/MS (70eV): *m/z* (%): 167.1 (CHPh$_2^+$, 100), 357.3 (^{Mes}NacnacMg$^+$, 50), 667.4 (L*-^{H}Ge$^+$, 10); anal. calc. for $C_{65}H_{77}GeMgN_3Si$: C, 76.14 %; H, 7.57 %; N, 4.10 %; found: C,75.94 %; H, 7.53 %; N,4.05 %.

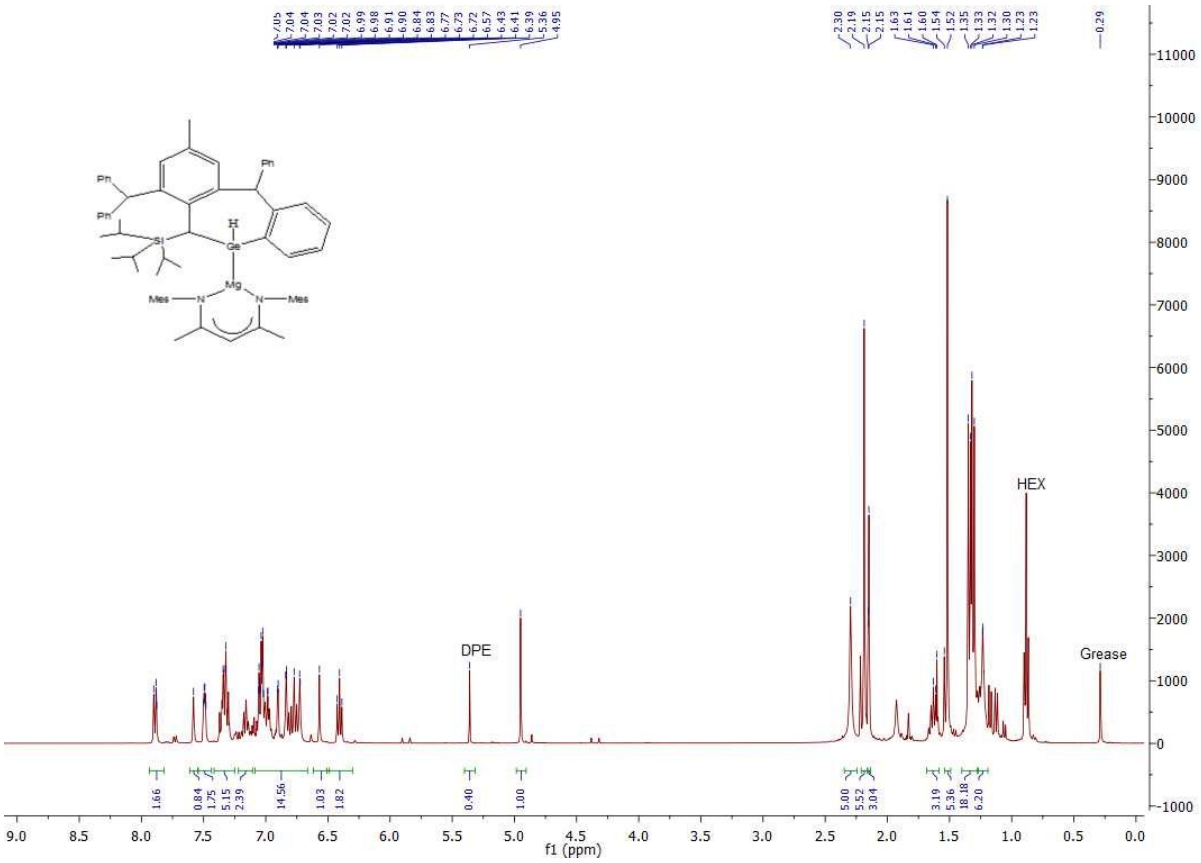


Figure S24. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **13**.

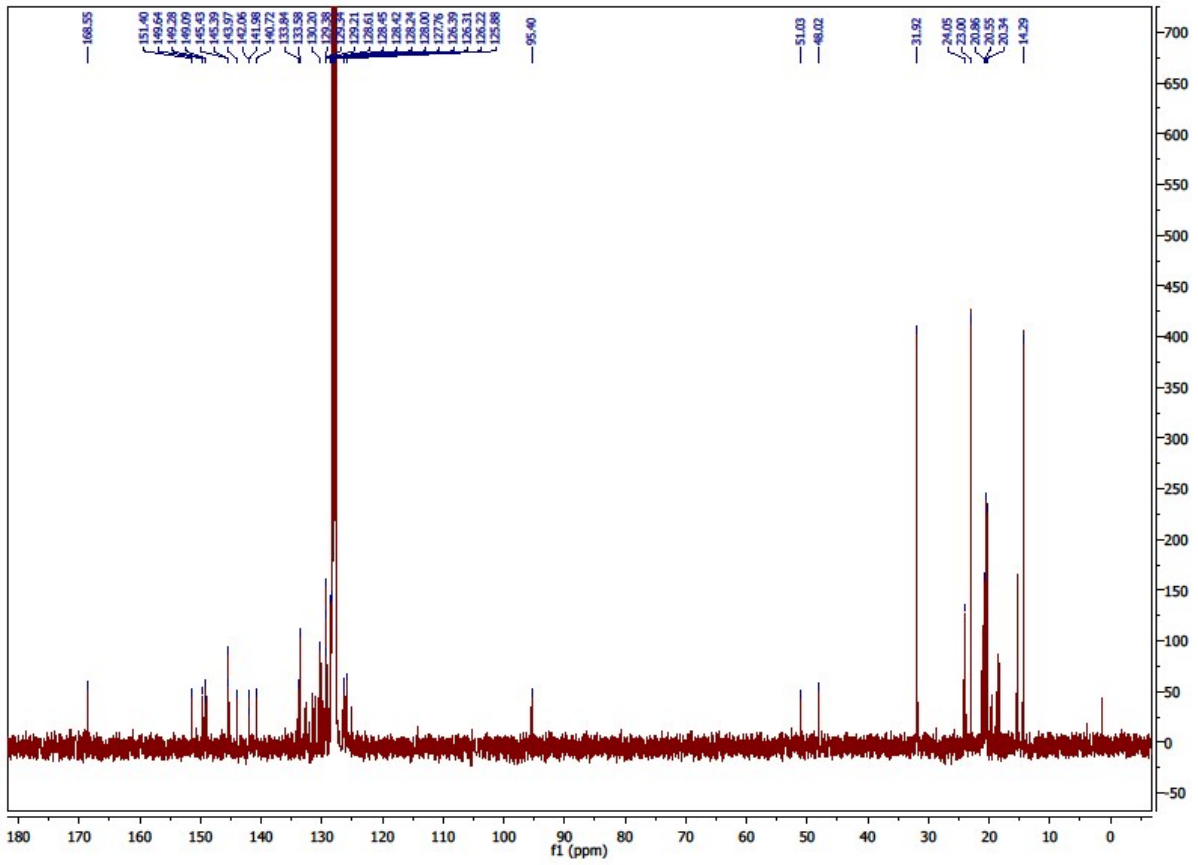


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, 298 K, C_6D_6) of **13**.

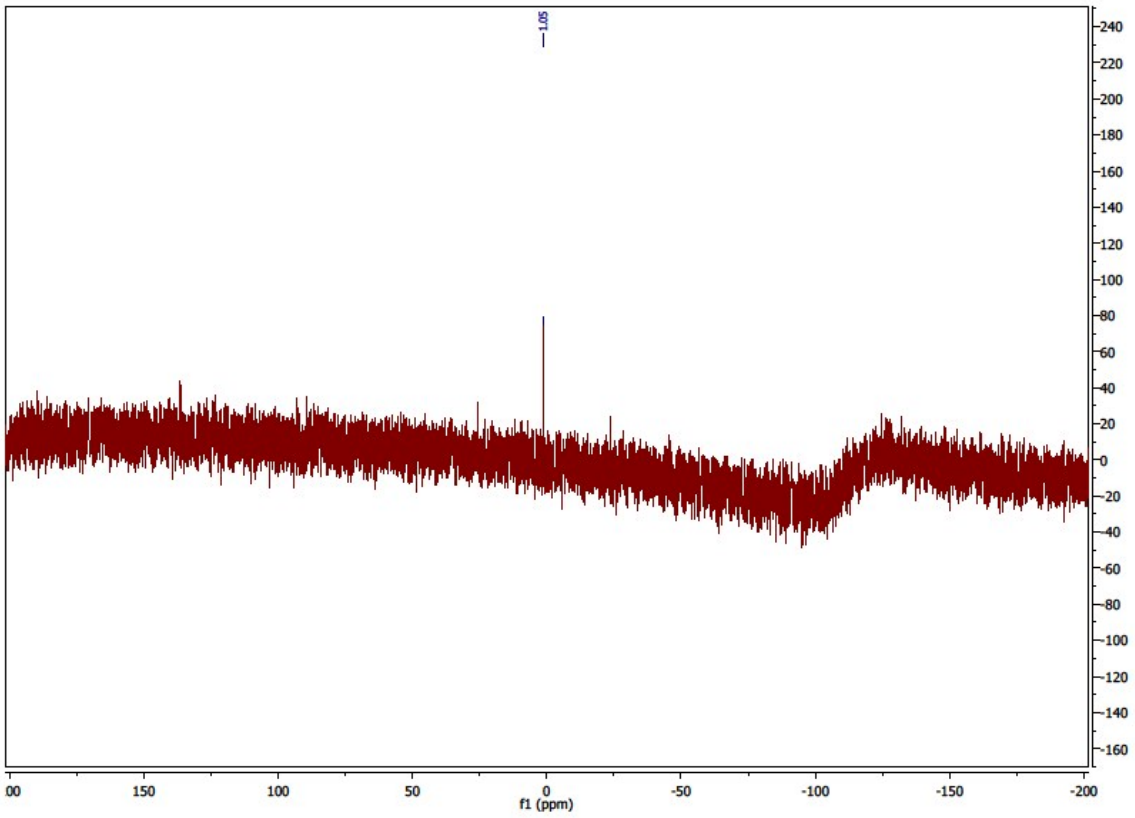
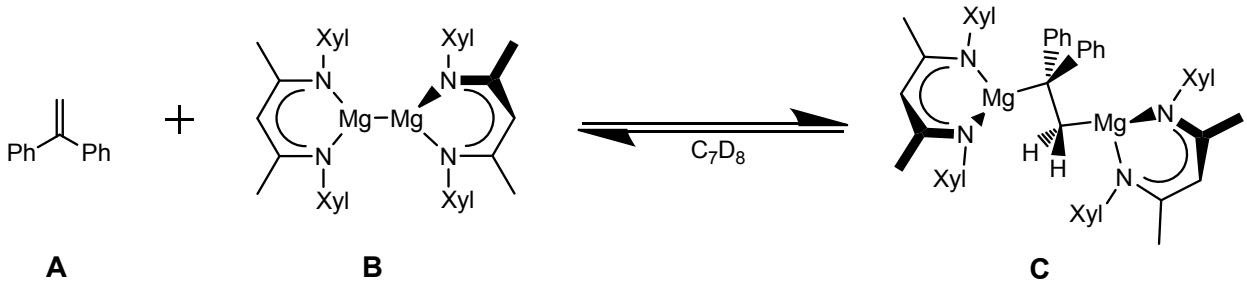


Figure S26. $^{29}Si\{^{1}H\}$ NMR spectrum (80 MHz, 298 K, C_6D_6) of **13**.

Van't Hoff analysis of variable temperature ^{1}H NMR spectra of [(^{Xyl}Nacnac)Mg(μ-CH_2CPh_2)Mg(^{Xyl}Nacnac)].

In an NMR tube equipped with a J.Young stopper, a solution of [(^{Xyl}Nacnac)Mg(μ-CH_2CPh_2)Mg(^{Xyl}Nacnac)] **C** (40.00 mg, 0.0606 mmol) in toluene-d_8 (600 uL, 0.1010M) was subject to a variable temperature ^{1}H NMR spectroscopic analysis. The integrals for the signals of free diphenylethylene CPh_2CH_2 **A** protons, and NCCH protons of the ligands of both **C** and [{(^{Xyl}Nacnac)Mg}$_2$] **B** were used for the determination of the equilibrium constant of the reaction between **B** and **A** to give **C**. Temperatures between 20 ºC (293 K) to 60 ºC (343 K), at 10 K increments, were used for the van't Hoff analysis.



The equilibrium constant (K_{eq}) was calculated according to **Equation 1**:

$$K_{eq} = \frac{[C]}{[A][B]}$$

A van't Hoff plot of ln(K_{eq}) against 1/T was constructed for the above reaction. ΔS and ΔH were calculated using the slope and intercept of the plot (Figure S27) according to **Equation 2**:

$$ln(K_{eq}) = -\frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

The free energy ΔG of the reaction was calculated according to **Equation 3**:

$$\Delta G = \Delta H - T\Delta S$$

Tables of integrals and concentrations used to produce the van't Hoff plot are shown below.

Table S1. Integrations from VT-NMR studies

T (K)	A (DPE)	B (Mg Dimer)	C (Product 5)
293	10.88	10.77	78.05
303	15.09	15.60	69.3
313	19.49	20.21	60.28
323	24.07	24.09	51.83
333	28.41	29.51	42.06
343	35.53	35.75	28.71
353	Decomposition seen in the ^{1}H NMR spectrum above this temperature		

Table S2. Table of calculated concentrations (molar).

T (K)	[A]	[B]	[C]
293	1.23E-02	1.22E-02	8.87E-02
303	1.80E-02	1.86E-02	8.30E-02
313	2.46E-02	2.56E-02	7.63E-02
323	3.20E-02	3.20E-02	6.90E-02
333	4.07E-02	4.23E-02	6.03E-02
343	5.59E-02	5.62E-02	4.51E-02

Table S3. K_{eq} and 1/T values used for van't Hoff plot.

T (K)	K_{eq}	ln K_{eq}	1/T
293	5.87E+02	6.37E+00	3.41E-03
303	1.45E+02	5.50E+00	3.29E-03
313	1.20E+01	4.79E+00	3.19E-03
323	6.71E+01	4.20E+00	3.09E-03
333	3.49E+01	3.55E+00	3.00E-03
343	1.43E+01	2.66E+00	2.91E-03

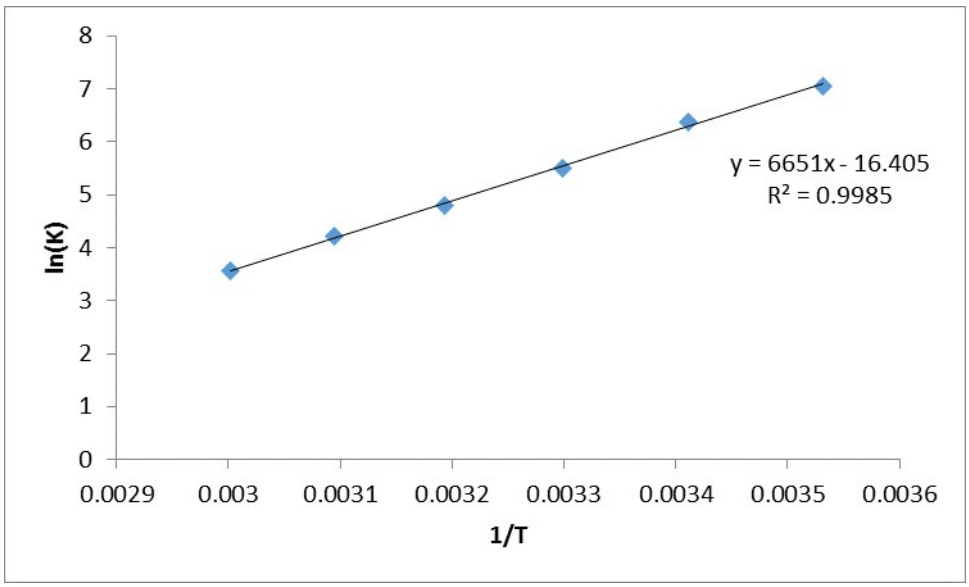


Figure S27. Van't Hoff plot of lnK against 1/T.

Table S4. Calculated ΔS and ΔH values.

Slope: 6651	**ΔS (J.mol^{-1}.K^{-1})**	**ΔS (kcal.mol^{-1}.K^{-1})**	**ΔH (J.mol^{-1})**	**ΔH (kcal.mol^{-1})**
Intercept: -16.405	-136.349	-0.03258	-55296.4	-13.2162

Table S5. Calculation of free enthalpy ΔG for varying temperatures.

T (K)	**ΔG (kcal.mol^{-1})**
293	-3.670
303	-3.344
313	-3.018
323	-2.693
333	-2.367
343	-2.041

Estimate of error: The uncertainty in integration was estimated to be 5%. The variable temperature NMR apparatus has an uncertainty of 1º. The uncertainty of the concentration of **C** in C_7D_8 is 3%. The overall uncertainty of the data is 10%.

2. X-Ray Crystallography

Crystals of **5-13**, [L†MgMgL†] and [(^{PhBo}LCdI)$_2$] suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using either an Oxford Gemini Ultra, or a Bruker X8 diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (1.54180 Å); or the MX1 beamline of the Australian Synchrotron (λ = 0.71090 Å). The software package Blu-Ice[10] was used for synchrotron data acquisition, while the program XDS[11] was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-16[12]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model). Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S6.

Table S6. Crystal data for **5-13**, [L†MgMg L†] and [(^{PhBo}LCdI)$_2$].

	5	**6**	**7**	**8**	**9**	**10**·(pentane)
empirical formula	$C_{56}H_{62}Mg_2N_4$	$C_{59}H_{76}Mg_2N_4$	$C_{60}H_{70}Mg_2N_4$	$C_{64}H_{78}Mg_2N_4$	$C_{60}H_{68}Mg_2N_4$	$C_{103}H_{120}N_2Si_2Zn_2$
formula weight	839.71	889.85	895.82	951.92	893.80	1572.92
crystal system	monoclinic	monoclinic	orthorhombic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	Cc	$Pbca$	P-1	P-1	Cc
a (Å)	18.7478(10)	19.9645(7)	15.3389(6)	8.6500(3)	13.659(4)	14.8102(4)
b (Å)	12.7752(9)	11.2773(4)	14.0741(5)	12.2882(5)	14.429(4)	18.8756(4)
c (Å)	20.4162(10)	22.9784(8)	23.7894(10)	13.5191(5)	15.718(5)	31.5018(9)
α (°)	90	90	90	108.311(4)	67.851(10)	90
β (°)	100.287(5)	93.089(3)	90	90.582(3)	79.390(10)	98.531(2)
γ (°)	90	90	90	100.254(3)	66.344(10)	90
V (Å^3)	4811.2(5)	5166.0(3)	5135.7(3)	1339.07	2626.1(13)	8755.1(4)
Z	4	4	4	1	2	4
T (K)	123(2)	123(2)	123(2)	123(2)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.159	1.144	1.159	1.180	1.130	1.193
μ (mm^{-1})	0.091	0.088	0.089	0.089	0.087	0.623
F(000)	1800	1928	1928	514	960	3360
reflns collected	28117	22426	75822	22800	16900	33281
unique reflns	8948	8241	5097	5809	16900	13774
R_{int}	0.0336	0.0989	0.1204	0.0777	0.0000	0.0481
R1 [I > 2σ(I)]	0.0399	0.0921	0.0712	0.0533	0.0916	0.0460
wR2 (all data)	0.1018	0.2705	0.2100	0.1501	0.2650	0.0917
largest peak and hole (e·Å^{-3})	0.265, -0.235	1.171, -0.601	1.125, -0.446	0.424, -0.418	0.481, -0.511	0.633, -0.370
CCDC no.	1890177	1890171	1890170	1890169	1890173	1890179

	11	**12**·(hexane)	**13**·(hexane)$_{1.5}$	$(L^{\dagger}Mg)_2$	$(^{PhBo}LCdI)_2$·(hexane)
empirical formula	$C_{72}H_{100}B_2N_6Si_2Zn_2$	$C_{93}H_{114}B_2Cd_2N_6Si_2$	$C_{74}H_{98}GeMgN_3Si$	$C_{76}H_{80}Mg_2N_2Si_2$	$C_{94}H_{116}B_2Cd_2I_2N_6Si_2$
formula weight	1258.11	1618.50	1154.54	1126.22	1886.32
crystal system	triclinic	orthorhombic	triclinic	monoclinic	monoclinic
space group	*P*-1	$P2_12_12$	*P*-1	$P2_1/c$	*C*2/*c*
a (Å)	10.9999(4)	14.733(3)	11.0530(7)	11.10040(10)	23.4536(17)
b (Å)	12.4537(5)	27.815(6)	12.9063(9)	16.2687(3)	11.0309(7)
c (Å)	13.2073(5)	11.021(2)	23.4106(16)	18.3324(2)	33.833(2)
α (º)	92.950(2)	90	99.680(6)	90	90
β (º)	90.257(2)	90	97.495(6)	103.1710(10)	92.003(3)
γ (º)	108.0410(10)	90	95.233(5)	90	90
V (Å^3)	1717.63(11)	4516.4(16)	3242.0(4)	3223.54(8)	8747.7(10)
Z	1	2	2	2	4
T (K)	123(2)	100(2)	123(2)	123(2)	150(2)
ρ_{calcd} (g·cm^3)	1.216	1.190	1.183	1.160	1.432
μ (mm^{-1})	0.778	0.543	0.544	1.017	1.268
F(000)	672	1696	1242	1204	3848
reflns collected	22529	29143	37790	33951	64001
unique reflns	6842	7903	12072	6726	6098
R_{int}	0.0396	0.0337	0.0827	0.0593	0.01006
R1 [I > 2σ(I)]	0.0365	0.0424	0.0748	0.0451	0.0676
wR2 (all data)	0.0825	0.1119	0.1982	0.1199	0.1299
largest peak and hole (e·Å^{-3})	0.417, -0.403	0.969, -1.271	1.631, -0.883	0.278, -0.357	0.693, -0.953
CCDC no.	1890174	1890172	1890176	1890178	1890175

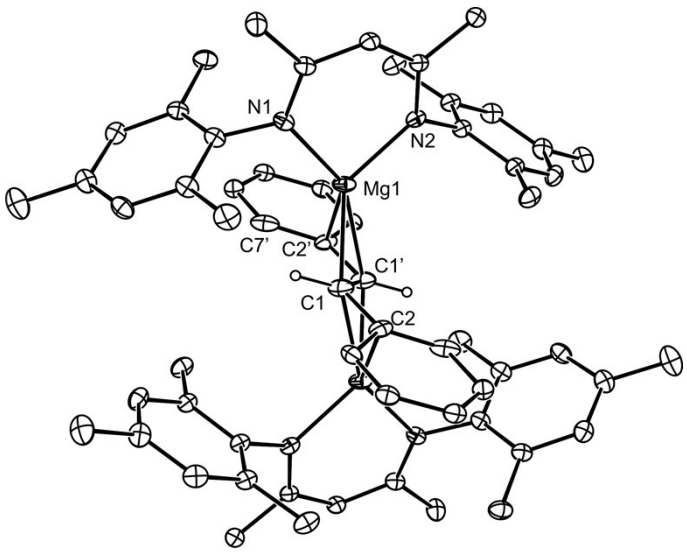


Figure S28. ORTEP diagram of compound **7** (25% thermal ellipsoids; hydrogen atoms, except alkenenic protons, omitted). See Table 1 in main text for metrical parameters.

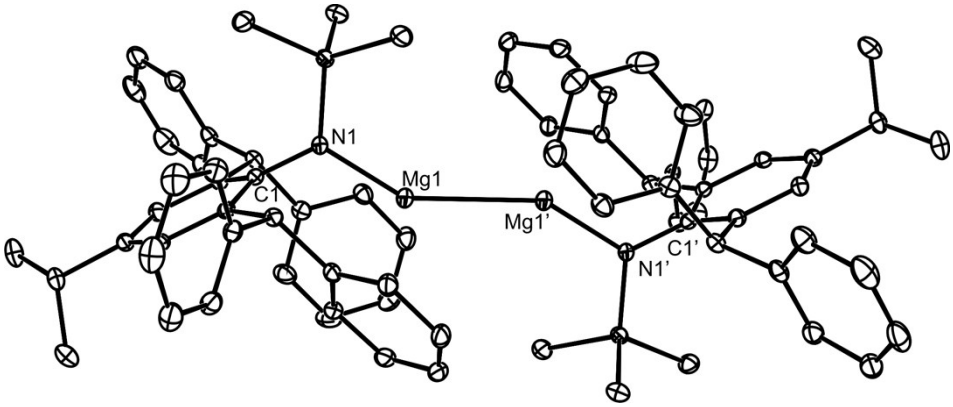


Figure S29. ORTEP diagram of compound [L†MgMgL†] (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Mg(1)-N(1) 1.9876(15), Mg(1)-Mg(1)' 2.8085(11), N(1)-Mg(1)-Mg(1)' 149.48(5).

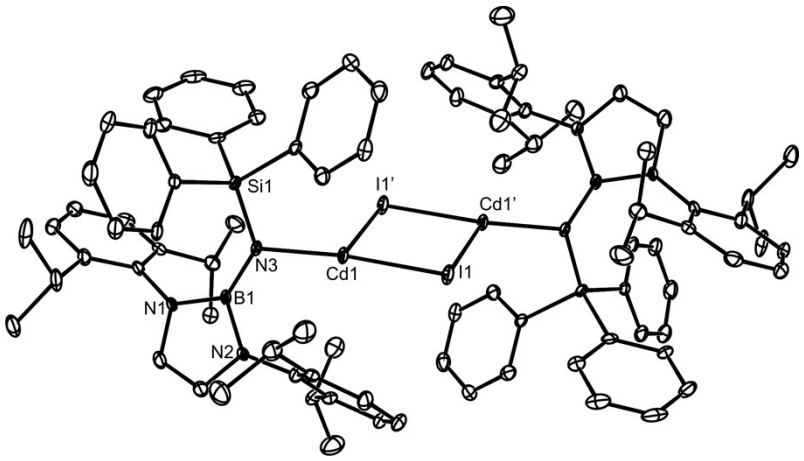


Figure S30. ORTEP diagram of compound [(^{PhBo}LCdI)$_2$] (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): I(1)-Cd(1) 2.7077(8), I(1)-Cd(1)' 2.9451(9), Cd(1)-N(3) 2.104(6), N(3)-Cd(1)-I(1) 155.48(19), N(3)-Cd(1)-I(1)' 111.03(17), I(1)-Cd(1)-I(1)' 92.52(2).

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