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Electronic Supporting Information

Molecular Magnesium Hydrides Supported by an Anionic Triazacyclononane-Type Ligand

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General experimental remarks

All manipulations were performed under argon atmosphere using standard Schlenk or glove box techniques. Solvents (THF, *n*-pentane) were purified using a *MB SPS-800* solvent purification system or distilled under argon (benzene, THF-d_8, C_6D_6) from sodium/benzophenone ketyl prior to use. The starting materials Mg*i*Bu_2[S1] and (*i*Pr_2TACN)H[S2] were prepared according to literature procedures. All other chemicals were commercially available and used after appropriate purification. NMR measurements were recorded on a *Bruker Avance II 400* and a *Bruker Avance III HD 400* spectrometer at 23 °C in J. Young type NMR tubes. The chemical shifts (δ ppm) in ^{1}H NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane. Combustion analyses were performed with an *elementar vario EL* machine. For **2**, **6** and **8** despite repeated recrystallizations, the analytical results were outside acceptable limits. The problem of low carbon content is probably due to incomplete combustion as the result of metal carbide formation during combustion. Similar problems are known in the literature.[S3] Metal contents were determined by inductively coupled plasma mass spectrometry using *ICP Spectroflame* by *Spectro*. A defined amount of sample was dissolved in 8 mL of 40% hydrofluoric acid, 2 mL of conc. sulfuric acid, and 40 mL of water. For **3** and **6**, despite repeated recrystallizations, the aluminum contents were outside the acceptable limits, possible due to incomplete dissolution of the aluminum-containing sample.

Synthetic Procedures

[Mg(*i*Pr$_2$TACN)(η^1-C$_3$H$_5$)]$_2$ (1). A solution of (*i*Pr$_2$TACN)H (0.100 g, 0.47 mmol) in 1 mL of THF was layered on top of a solution of Mg(C$_3$H$_5$)$_2$ (0.050 g, 0.47 mmol) in 0.5 mL of THF. The reaction mixture was allowed to stand at –30 °C for 1 h, during which time colorless crystals precipitated from the solution. The crystals were isolated, washed with cold *n*-pentane, and dried under reduced pressure to give [Mg(*i*Pr$_2$TACN)(η^1-C$_3$H$_5$)]$_2$ (**1**) as a colorless solid; yield: 0.082 g (0.15 mmol, 63%). Single crystals suitable for X-ray diffraction were obtained from the reaction mixture. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 6.34 (quint, $^3J_{\mathrm{HH}}$ = 11.5 Hz, 2H, CH$_2$C*H*CH$_2$), 3.85 (br, 8H, CH_2CHCH_2), 3.30 (sept, $^3J_{\mathrm{HH}}$ = 6.7 Hz, 4H, C*H* (*i*Pr$_2$TACN)), 2.77-2.91 (m, 8H, CH_2 (*i*Pr$_2$TACN)), 2.48-2.66 (m, 12H, CH_2 (*i*Pr$_2$TACN)), 2.35-2.41 (m, 4H, CH_2 (*i*Pr$_2$TACN)), 1.26 (d, $^3J_{\mathrm{HH}}$ = 6.7 Hz, 12H, CH_3 (*i*Pr$_2$TACN)), 1.00 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, 12H, CH_3 (*i*Pr$_2$TACN)); ^{1}H NMR (400 MHz, THF-d_8, –30 °C): δ 6.26-6.37 (m, 2H, CH$_2$C*H*CH$_2$), 3.81 (dd, $^3J_{\mathrm{HH}}$ = 16.4, 3.4 Hz, 2H, MgCH_2CHCH_2), second resonance for MgCH_2CHCH_2 obscured by THF resonances, 3.27 (sept, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 4H, C*H* (*i*Pr$_2$TACN)), 2.77-2.86 (m, 8H, CH_2 (*i*Pr$_2$TACN)), 2.48-2.64 (m, 12H, CH_2 (*i*Pr$_2$TACN)), 2.35-2.41 (m, 4H, CH_2 (*i*Pr$_2$TACN)), 1.27 (d, $^3J_{\mathrm{HH}}$ = 6.7 Hz, 12H, CH_3 (*i*Pr$_2$TACN)), 1.00 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, 12H, CH_3 (*i*Pr$_2$TACN)), 0.97 (d, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 4H, MgCH_2CHCH_2); ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 25 °C): δ 153.0 (CH$_2$*C*HCH$_2$), resonance for MgCH$_2$*C*HCH_2 not detected, 54.4 (*C*H (*i*Pr$_2$TACN)), 51.6 (*C*H$_2$ (*i*Pr$_2$TACN)), 51.3 (*C*H$_2$ (*i*Pr$_2$TACN)), 45.9 (*C*H$_2$ (*i*Pr$_2$TACN)), 23.0 (*C*H$_3$ (*i*Pr$_2$TACN)), 14.3 (*C*H$_3$ (*i*Pr$_2$TACN)); ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, –30 °C): δ 153.1 (CH$_2$CH*C*H$_2$), 88.6 (MgCH$_2$*C*H*C*H$_2$), 54.3 (*C*H (*i*Pr$_2$TACN)), 51.1 (*C*H$_2$ (*i*Pr$_2$TACN)), 45.6 (*C*H$_2$ (*i*Pr$_2$TACN)), 27.2 (Mg*C*H$_2$CHCH$_2$), 22.9 (*C*H$_3$ (*i*Pr$_2$TACN)), 14.2 (*C*H$_3$ (*i*Pr$_2$TACN)). Analysis (%) Calcd for C$_{30}$H$_{62}$N$_6$Mg$_2$ (555.46 g·mol^{-1}): C 64.87, H 11.25, N 15.13, Mg 8.75; found: C 64.46, H 11.20, N 15.47, Mg 7.84.

[Mg(*i*Pr$_2$TACN)*i*Bu]$_2$ (2). Neat (*i*Pr$_2$TACN)H (0.085 g, 0.40 mmol) was added to a solution of Mg*i*Bu$_2$ (0.055 g, 0.40 mmol) in 2 mL of THF. The reaction mixture was allowed to stand at –30 °C for 24 h, during which time colorless crystals precipitated from the solution. The crystals were collected, washed with cold *n*-pentane (2 x 1 mL), and dried under reduced pressure to give the product as a colorless solid; yield: 0.075 g (0.13 mmol, 64%). ^{1}H NMR (400 MHz, THF-d_8): δ 3.22 (sept, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 4H, C*H* (*i*Pr$_2$TACN)), 2.96-3.02 (m, 4H, CH_2 (*i*Pr$_2$TACN)), 2.73-2.80

(m, 4H, CH_2 (iPr$_2$TACN)), 2.55-2.68 (m, 8H, CH_2 (iPr$_2$TACN)), 2.47-53 (m, 4H, CH_2 (iPr$_2$TACN)), 2.34-2.40 (m, 4H, CH_2 (iPr$_2$TACN)), 1.89-1.99 (m, 2H, MgCH$_2$CH(CH$_3$)$_2$), 1.24 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH_3 (iPr$_2$TACN)), 1.00 (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH_3 (iPr$_2$TACN)), 0.91 (d, $^3J_{HH}$ = 6.3 Hz, 12H, MgCH$_2$CH(CH_3)$_2$), –0.54 (d, $^3J_{HH}$ = 6.0 Hz, 4H, MgCH_2CH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 54.67 (CH (iPr$_2$TACN)), 51.89 (CH$_2$ (iPr$_2$TACN)), 51.31 (CH$_2$ (iPr$_2$TACN)), 46.04 (CH$_2$ (iPr$_2$TACN)), 31.94 (CH$_3$ MgCH$_2$CH(CH$_3$)$_2$), 31.35 (CH MgCH$_2$CH(CH$_3$)$_2$), 23.25 (CH$_3$ (iPr$_2$TACN)), 14.53 (CH$_3$ (iPr$_2$TACN)) ppm; the carbon signal for CH$_2$ (MgCH$_2$CH(CH$_3$)$_2$) was not reliably assigned due to overlap with the solvent signals. Analysis (%) Calcd for $C_{32}H_{70}N_6Mg_2$ (586.54 g·mol^{-1}): C 65.41, H 12.01, N 14.30, Mg 8.27; found: C 64.02, H 12.19, N 14.34, Mg 8.08.

[Mg(iPr$_2$TACN·AliBu$_3$)iBu] (3). Neat (iPr$_2$TACN)H (0.213 g, 1.00 mmol) and neat AliBu$_3$ (0.198 g, 1.00 mmol) were added to a solution of MgiBu$_2$ (0.139 g, 1.00 mmol) in 6 mL of THF. The reaction mixture was stirred at 25 °C for 24 h. After all volatiles were removed *in vacuo*, the residue was washed with cold *n*-pentane (2 x 2 mL) and dried under reduced pressure to give the product as a colorless solid; yield: 0.363 g (0.74 mmol, 74%). ^{1}H NMR (400 MHz, THF-d_8): δ 3.13 (sept, $^3J_{HH}$ = 6.6 Hz, 4H, CH (iPr$_2$TACN)), 3.02-3.09 (m, 2H, CH_2 (iPr$_2$TACN)), 2.72-2.86 (m, 6H, CH_2 (iPr$_2$TACN)), 2.56-2.69 (m, 4H, CH_2 (iPr$_2$TACN)), 1.94-2.03 (m, 1H, MgCH$_2$CH(CH$_3$)$_2$), 1.82-1.92 (m, 3H, AlCH$_2$CH(CH$_3$)$_2$), 1.24 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH_3 (iPr$_2$TACN)), 1.21 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH_3 (iPr$_2$TACN)), 0.95 (d, $^3J_{HH}$ = 6.4 Hz, 6H, MgCH$_2$CH(CH_3)$_2$), 0.92 (d, $^3J_{HH}$ = 6.5 Hz, 18H, AlCH$_2$CH(CH_3)$_2$), –0.12 (d, $^3J_{HH}$ = 6.9 Hz, 6H, AlCH_2CH(CH$_3$)$_2$), –0.26 (d, $^3J_{HH}$ = 6.0 Hz, 2H, MgCH_2CH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 57.0 (CH (iPr$_2$TACN)), 50.4 (CH$_2$ (iPr$_2$TACN)), 50.0 (CH$_2$ (iPr$_2$TACN)), 49.4 (CH$_2$ (iPr$_2$TACN)), 31.4 (CH$_3$ MgCH$_2$CH(CH$_3$)$_2$), 29.7 (CH$_3$ AlCH$_2$CH(CH$_3$)$_2$), 29.7 (CH MgCH$_2$CH(CH$_3$)$_2$), 28.4 (CH AlCH$_2$CH(CH$_3$)$_2$), 23.8 (CH$_2$ MgCH$_2$CH(CH$_3$)$_2$), 19.8 (CH$_3$ (iPr$_2$TACN)), 18.3 (CH$_3$ (iPr$_2$TACN)) ppm; the carbon signal for CH$_2$ (AlCH$_2$CH(CH$_3$)$_2$) was not reliably assigned due to overlap with the solvent signals; ^{27}Al NMR (100 MHz, THF-d_8): δ 161.8 ppm. Analysis (%) Calcd for $C_{28}H_{62}N_3AlMg$ (491.46 g·mol^{-1}): C 68.34, H 12.70, N 8.54, Al 5.48 Mg 4.94; found: C 68.01, H 13.50, N 8.55, Al 4.31, Mg 5.13.

[Mg(iPr$_2$TACN·AliBu$_3$)(µ-HAliBu$_3$)] (4). Neat AlHiBu$_2$ (0.051 g, 0.36 mmol) was added to a solution of [Mg(iPr$_2$TACN·AliBu$_3$)iBu] (**3**) (0.150 g, 0.36 mmol) in 3 mL of benzene. The reaction mixture was stirred at 25 °C for 24 h. After all volatiles were removed *in vacuo*, the residue was washed with cold *n*-pentane (2 x 2 mL) and dried under reduced pressure to give the product as a colorless oil which always contained traces of unidentified impurities; yield: 0.180 g (0.28 mmol, 28%). ^{1}H NMR (400 MHz, C_6D_6): *δ* 2.82-2.92 (m, 4H, C*H*, C*H*$_2$ (*i*Pr$_2$TACN)), 2.58 (s, 1H, Mg*H*Al), 2.22-2.32 (m, 3H, AlCH$_2$C*H*(CH$_3$)$_2$), 2.21-2.31 (m, 3H, AlCH$_2$C*H*(CH$_3$)$_2$), 2.14-2.20 (m, 2H, C*H*$_2$ (*i*Pr$_2$TACN)), 1.89-2.01 (m, 4H, C*H*$_2$ (*i*Pr$_2$TACN)), 1.44-1.61 (m, 4H, C*H*$_2$ (*i*Pr$_2$TACN)), 1.38 (d, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 18H, AlCH$_2$CH(C*H*$_3$)$_2$), 1.35 (d, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 18H, AlCH$_2$CH(C*H*$_3$)$_2$), 0.99 (d, $^3J_{\mathrm{HH}}$ = 6.7 Hz, 6H, C*H*$_3$ (*i*Pr$_2$TACN)), 0.54 (d, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 6H, C*H*$_3$ (*i*Pr$_2$TACN)), 0.39 (d, $^3J_{\mathrm{HH}}$ = 7.0 Hz, 6H, AlC*H*$_2$CH(CH$_3$)$_2$), 0.14 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 6H, AlC*H*$_2$CH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): *δ* 55.5 (*C*H (*i*Pr$_2$TACN)), 50.0 (*C*H$_2$ (*i*Pr$_2$TACN)), 48.3 (*C*H$_2$ (*i*Pr$_2$TACN)), 46.5 (*C*H$_2$ (*i*Pr$_2$TACN)), 29.7 (*C*H$_3$ AlCH$_2$CH(CH$_3$)$_2$), 29.6 (*C*H$_3$ AlCH$_2$CH(CH$_3$)$_2$), 28.4 (*C*H AlCH$_2$CH(CH$_3$)$_2$), 28.3 (*C*H AlCH$_2$CH(CH$_3$)$_2$), 26.3 (*C*H$_2$ (AlCH$_2$CH(CH$_3$)$_2$), 25.0 (*C*H$_2$ (AlCH$_2$CH(CH$_3$)$_2$), 21.9 (*C*H$_3$ (*i*Pr$_2$TACN)), 15.8 (*C*H$_3$ (*i*Pr$_2$TACN)); ^{27}Al NMR (100 MHz, THF-*d*$_8$): *δ* 172.2 ppm.

[Mg(*i*Pr$_2$TACN·Al*i*Bu$_3$)H] (5). Neat AlH*i*Bu$_2$ (0.027 g, 0.19 mmol) was added to a solution of [Mg(*i*Pr$_2$TACN·Al*i*Bu$_3$)*i*Bu] (0.095 g, 0.19 mmol) in 2 mL of benzene. The reaction mixture was stirred at 25 °C for 24 h. After the volatiles were removed *in vacuo*, the residue was dissolved in 0.5 mL of THF and 2 mL of *n*-pentane. The solution was allowed to standing at –78 °C for 4 days, during which time colorless crystals precipitated; yield: 0.011 g (0.03 mmol, 14%). ^{1}H NMR (400 MHz, THF-*d*$_8$): *δ* 4.15 (s, 1H, Mg*H*), 3.37 (sept, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 2H, C*H* (*i*Pr$_2$TACN)), 3.06-3.12 (m, 2H, C*H*$_2$ (*i*Pr$_2$TACN)), 2.79-2.86 (m, 2H, C*H*$_2$ (*i*Pr$_2$TACN)), 2.69-2.76 (m, 6H, C*H*$_2$ (*i*Pr$_2$TACN)), 2.56-2.62 (m, 2H, C*H*$_2$ (*i*Pr$_2$TACN)), 1.81-1.91 (m, 3H, AlCH$_2$C*H*(CH$_3$)$_2$), 1.28 (d, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 6H, C*H*$_3$ (*i*Pr$_2$TACN)), 1.22 (d, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 6H, C*H*$_3$ (*i*Pr$_2$TACN)), 0.91 (d, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 18H, AlCH$_2$CH(C*H*$_3$)$_2$), –0.15 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 6H, AlC*H*$_2$CH(CH$_3$)$_2$) ppm. The product was isolated only once, and the yield was insufficient for ^{13}C{^{1}H} NMR spectroscopy and elemental analysis.

[Mg(*i*Pr$_2$TACN·AlH*i*Bu$_2$)(*μ*-H)]$_2$ (6). Neat AlH*i*Bu$_2$ (0.142 g, 1.00 mmol) was added to a solution of [Mg(*i*Pr$_2$TACN·Al*i*Bu$_3$)*i*Bu] (0.492 g, 1.00 mmol) in 2 mL of benzene. The reaction mixture was stirred at 25 °C for 24 h. After the volatiles were removed *in vacuo*, the residue was dissolved in 0.4 mL of THF and 4 mL of *n*-pentane. The solution was allowed to stand at –30 °C for 4 d, during which time colorless crystals precipitated. These were isolated, washed with cold *n*-pentane and dried under reduced pressure to give the product as a colorless solid; yield: 0.089 g (0.12 mmol, 35%). Recrystallization from THF/toluene/*n*-pentane (1:1:3) at –30 °C gave colorless crystals suitable for X-ray diffraction. ^{1}H NMR (400 MHz, THF-d_8): δ 3.34 (sept, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 4H, C*H* (*i*Pr$_2$TACN)), 3.29 (br s, 2H, Mg*H*Mg), 3.06-3.13 (m, 4H, C*H*$_2$ (*i*Pr$_2$TACN)), 2.68-2.75 (m, 4H, C*H*$_2$ (*i*Pr$_2$TACN)), 2.66 (br s, 8H, C*H*$_2$ (*i*Pr$_2$TACN)), 2.54-2.61 (m, 4H, C*H*$_2$ (*i*Pr$_2$TACN)), 2.44-2.51 (m, 4H, C*H*$_2$ (*i*Pr$_2$TACN)), 1.83-1.93 (m, 4H, MgCH$_2$C*H*(CH$_3$)$_2$), 1.36 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 12H, C*H*$_3$ (*i*Pr$_2$TACN)), 1.16 (d, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 12H, C*H*$_3$ (*i*Pr$_2$TACN)), 0.94 (d, $^3J_{\mathrm{HH}}$ = 3.4 Hz, 12H, AlCH$_2$CH(C*H*$_3$)$_2$), 0.92 (d, $^3J_{\mathrm{HH}}$ = 3.3 Hz, 12H, AlCH$_2$CH(C*H*$_3$)$_2$), –0.11-0.10 (m, 8H, AlC*H*$_2$CH(CH$_3$)$_2$) ppm; the proton signal for Al*H* was not reliably assigned due to overlap with the (*i*Pr$_2$TACN) ligand signals; ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 55.9 (*C*H (*i*Pr$_2$TACN)), 50.0 (*C*H$_2$ (*i*Pr$_2$TACN)), 49.2 (*C*H$_2$ (*i*Pr$_2$TACN)), 48.8 (*C*H$_2$ (*i*Pr$_2$TACN)), 30.0 (*C*H$_3$ AlCH$_2$CH(CH$_3$)$_2$), 29.1 (*C*H$_3$ AlCH$_2$CH(CH$_3$)$_2$), 28.4 (*C*H AlCH$_2$CH(CH$_3$)$_2$), 24.0 (*C*H$_2$ AlCH$_2$CH(CH$_3$)$_2$), 19.7 (*C*H$_3$ (*i*Pr$_2$TACN)), 18.5 (*C*H$_3$ (*i*Pr$_2$TACN)); ^{27}Al NMR (100 MHz, THF-d_8): δ 150.9 ppm. Analysis (%) Calcd for $C_{40}H_{92}N_6Al_2Mg_2$ (758.67 g·mol^{-1}): C 63.23, H 12.21, N 11.06, Al 7.10 Mg 6.40; found: C 61.92, H 12.21, N 10.90, Al 4.92, Mg 5.31.

[(*i*Pr$_2$TACN)H·BH$_3$] (7). Neat (*i*Pr$_2$TACN)H (0.500 g, 2.34 mmol) was added to a THF solution of BH$_3$(thf) (1.0 molar, 2.6 mL, 2.58 mmol). The reaction mixture was stirred at 25 °C for 24 h. After the volatiles were removed *in vacuo*, the residue was washed with cold *n*-pentane and dried under reduced pressure to give the product as a colorless solid; yield: 0.415 g (1.83 mmol, 77%). ^{1}H NMR (400 MHz, THF-d_8): δ 6.64 (br s, 1H, N*H* (*i*Pr$_2$TACN)H), 2.91 (sept, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 2H, C*H* (*i*Pr$_2$TACN)), 2.46-2.78 (m, 10H, C*H*$_2$ (*i*Pr$_2$TACN)), 2.34-2.42 (m, 2H, C*H*$_2$ (*i*Pr$_2$TACN)), 1.57 (t, $^3J_{\mathrm{HB}}$ = 81.2 Hz, 3H, B*H*$_3$), 1.05 (d, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 6H, C*H*$_3$ (*i*Pr$_2$TACN)), 1.03 (d, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 6H, C*H*$_3$ (*i*Pr$_2$TACN)), ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 53.3 (*C*H (*i*Pr$_2$TACN)), 53.3 (*C*H$_2$ (*i*Pr$_2$TACN)), 47.7 (*C*H$_2$ (*i*Pr$_2$TACN)), 44.4 (*C*H$_2$ (*i*Pr$_2$TACN)), 19.52 (*C*H$_3$ (*i*Pr$_2$TACN)), 18.9 (*C*H$_3$ (*i*Pr$_2$TACN)); ^{11}B{^{1}H} NMR (128 MHz, THF-d_8): δ –15.88 ppm. Analysis (%) Calcd for $C_{12}H_{30}N_3B$ (227.27 g·mol^{-1}): C 63.44, H 13.31, N 18.49; found: C 63.10, H 13.05, N 18.19.

[Mg(*i*Pr$_2$TACN·BH$_3$)*i*Bu] (8). Solid Mg*i*Bu$_2$ (0.174 g, 0.44 mmol) was added to a solution of [(*i*Pr$_2$TACN)H·BH$_3$] (0.285 g, 1.25 mmol) in 5 mL of THF. The reaction mixture was stirred at

25 °C for 24 h. After all volatiles were removed *in vacuo*, the residue was washed with cold *n*-pentane and dried under reduced pressure to give the product as a colorless solid: yield: 0.342 g (1.11 mmol, 89%). ^{1}H NMR (400 MHz, THF-d_8): δ 3.08 (sept, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, 2H, CH (*i*Pr$_2$TACN)), 2.87-2.94 (m, 2H, CH_2 (*i*Pr$_2$TACN)), 2.68-2.80 (m, 4H, CH_2 (*i*Pr$_2$TACN)), 2.64-2.53 (m, 4H, CH_2 (*i*Pr$_2$TACN)), 2.37-2.44 (m, 2H, CH_2 (*i*Pr$_2$TACN)), 1.91-2.01 (m, 1H, MgCH$_2$CH(CH$_3$)$_2$), 1.25 (d, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, 6H, CH_3 (*i*Pr$_2$TACN)), 1.14 (d, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, 6H, CH_3 (*i*Pr$_2$TACN)), 0.94 (d, $^{3}J_{\mathrm{HH}}$ = 6.4 Hz, 6H, MgCH$_2$CH(CH_3)$_2$), –0.39 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 2H, MgCH_2CH(CH$_3$)$_2$) ppm; the proton signals for BH_3 were not reliably assigned due to overlap with the (*i*Pr$_2$TACN) ligand signals; ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 56.3 (CH (*i*Pr$_2$TACN)), 54.4 (CH$_2$ (*i*Pr$_2$TACN)), 51.0 (CH$_2$ (*i*Pr$_2$TACN)), 47.5 (CH$_2$ (*i*Pr$_2$TACN)), 30.97 (CH$_3$ MgCH$_2$CH(CH$_3$)$_2$), 30.1 (CH MgCH$_2$CH(CH$_3$)$_2$), 23.6 (CH$_2$ MgCH$_2$CH(CH$_3$)$_2$), 20.8 (CH$_3$ (*i*Pr$_2$TACN)), 17.1 (CH$_3$ (*i*Pr$_2$TACN)); ^{11}B{^{1}H} NMR (128 MHz, THF-d_8): δ –17.51 ppm. Analysis (%) Calcd for $C_{16}H_{38}N_3BMg$ (307.62 g·mol^{-1}): C 62.47, H 12.45, N 13.66, Mg 7.90; found: C 60.49, H 12.43, N 11.93 Mg 8.44.

NMR spectra

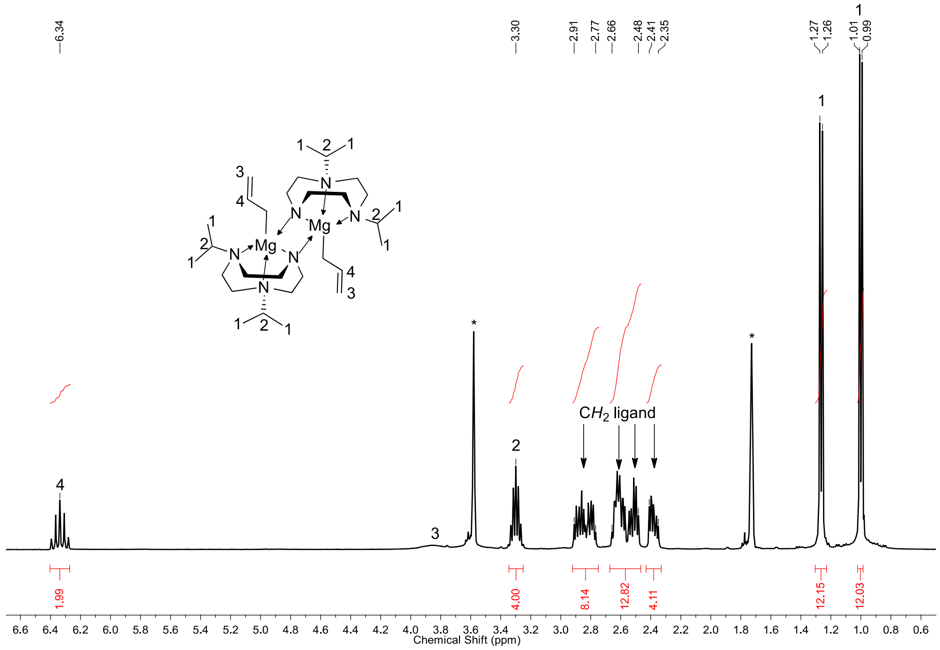

Figure S1. ^{1}H NMR Spectrum of **1** in THF-d_8 (*) at 23 °C.

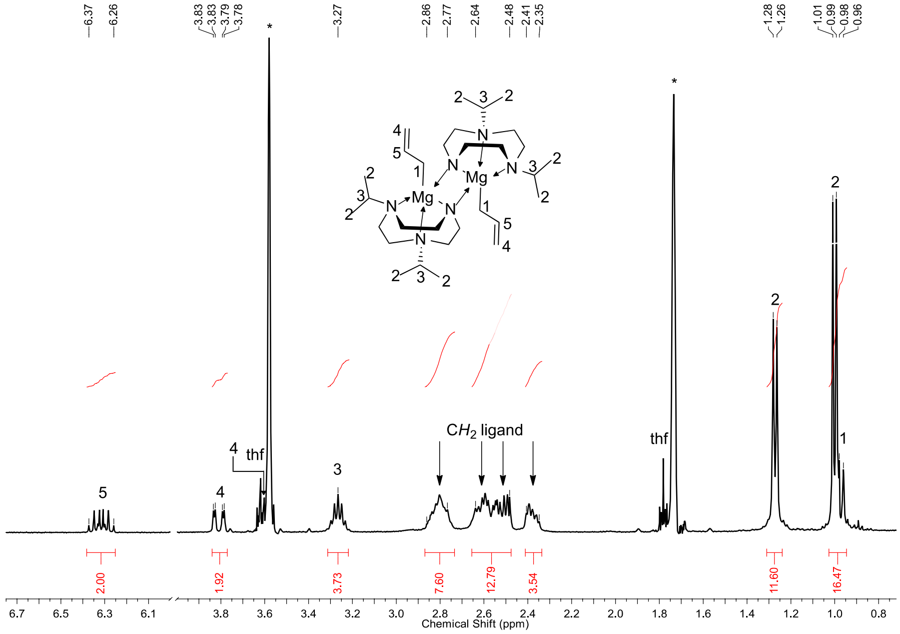

Figure S2. ^{1}H NMR spectrum of **1** in THF-d_8 (*) at –30 °C.

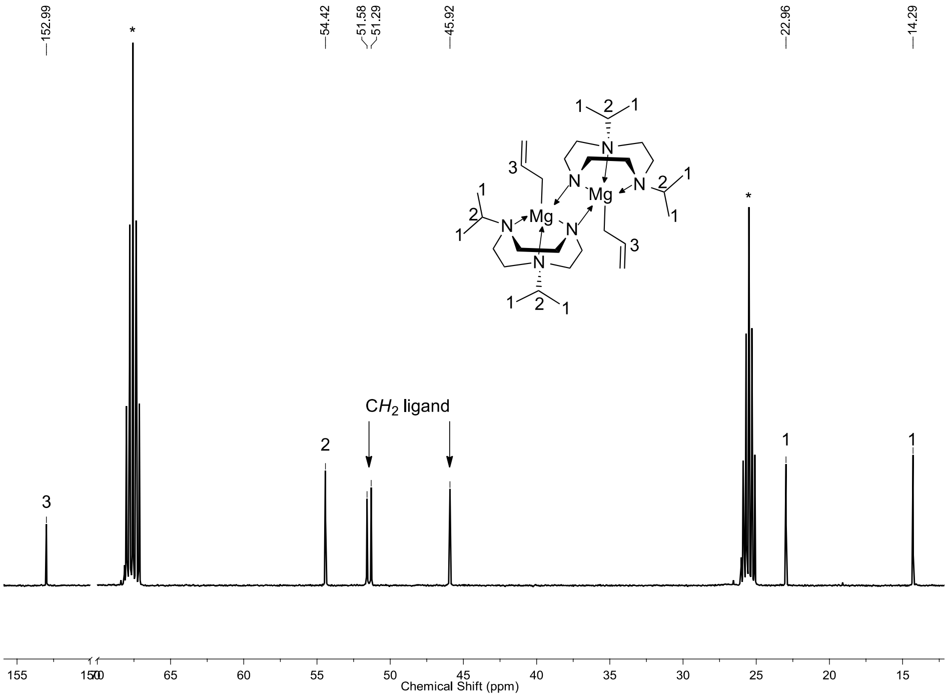

Figure S3. $^{13}C\{^1H\}$ NMR spectrum of **1** in THF-d_8 (*) at 23 °C.

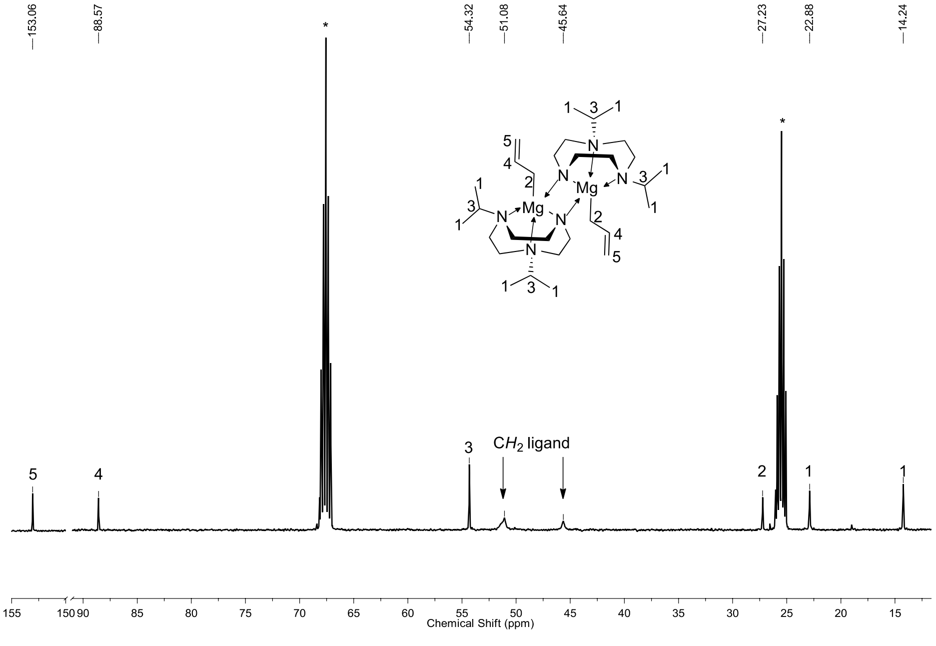

Figure S4. $^{13}C\{^1H\}$ NMR spectrum of **1** in THF-d_8 (*) at –30 °C.

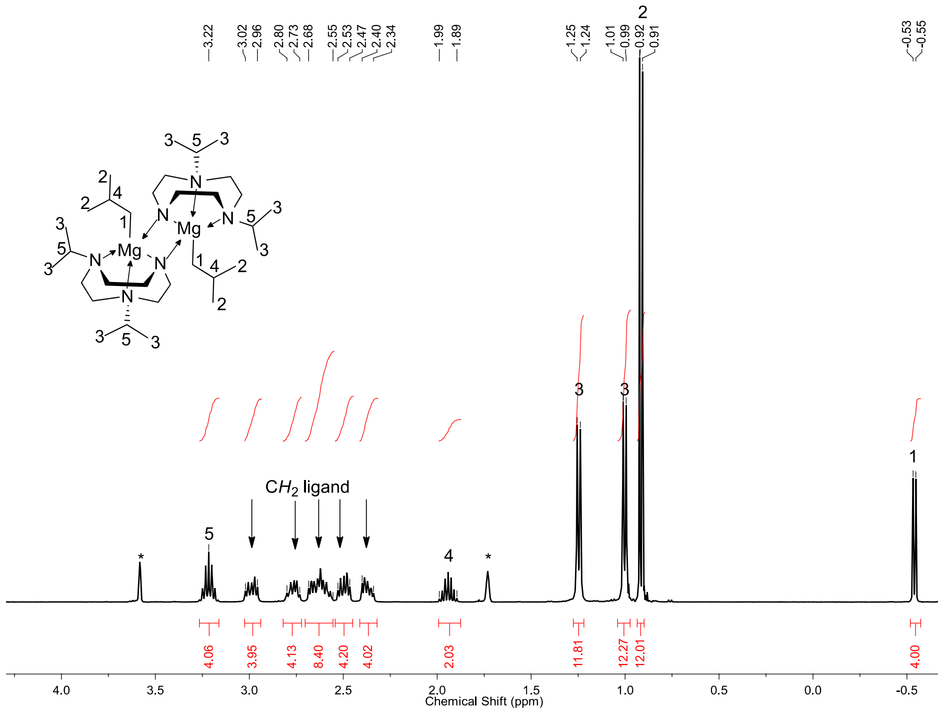

Figure S5. ${}^{1}H$ NMR spectrum of **2** in THF-d_8 (*) at 23 °C.

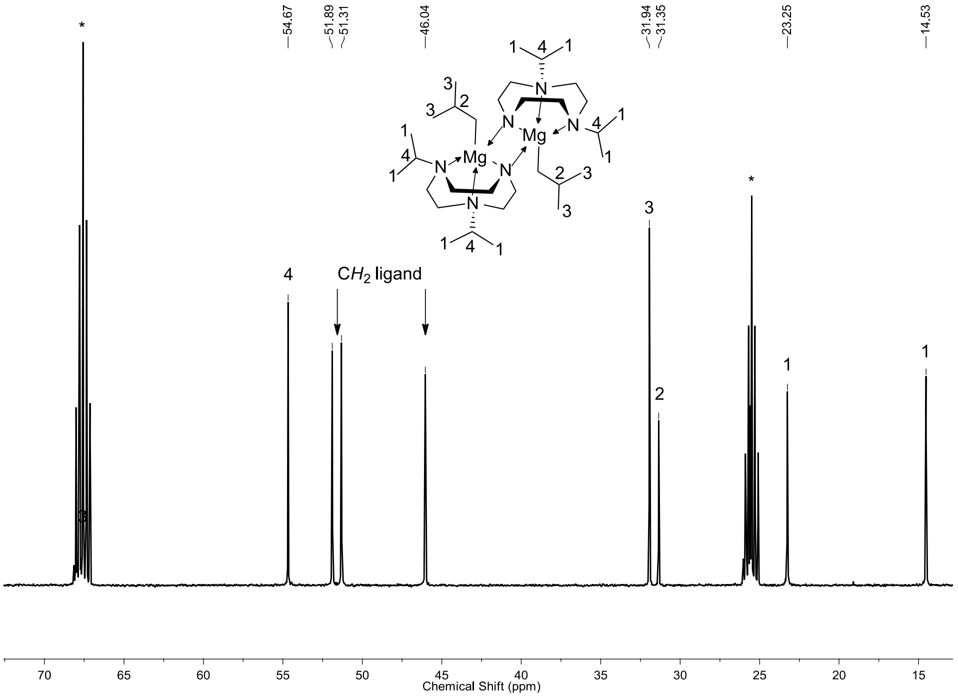

Figure S6. ${}^{13}C\{{}^{1}H\}$ NMR spectrum of **2** in THF-d_8 (*) at 23 °C.

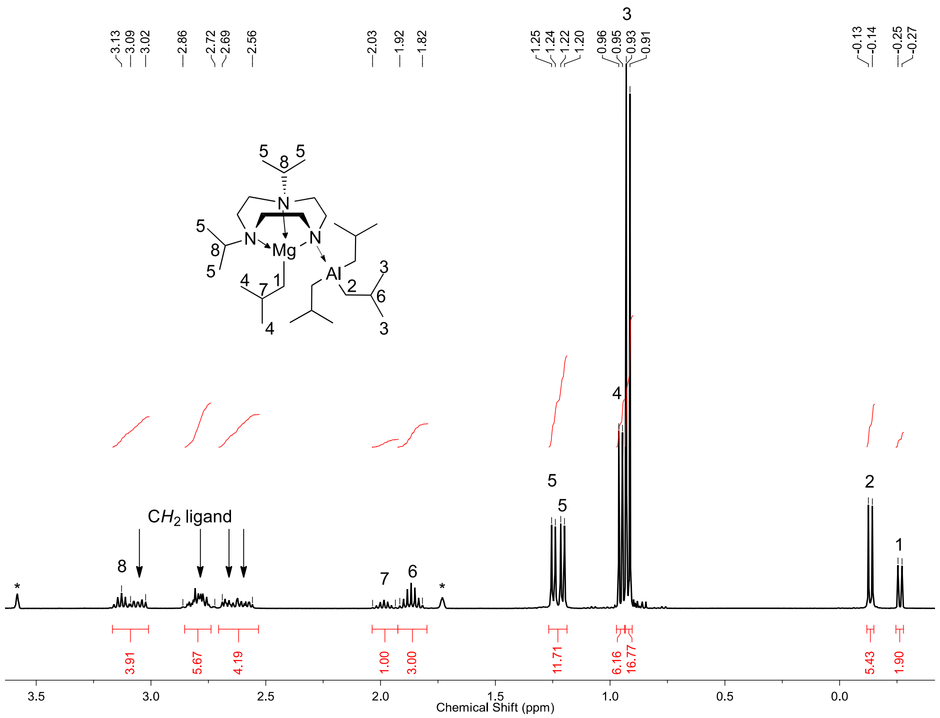

Figure S7. ^{1}H NMR spectrum of **3** in THF-d_8 (*) at 23 °C.

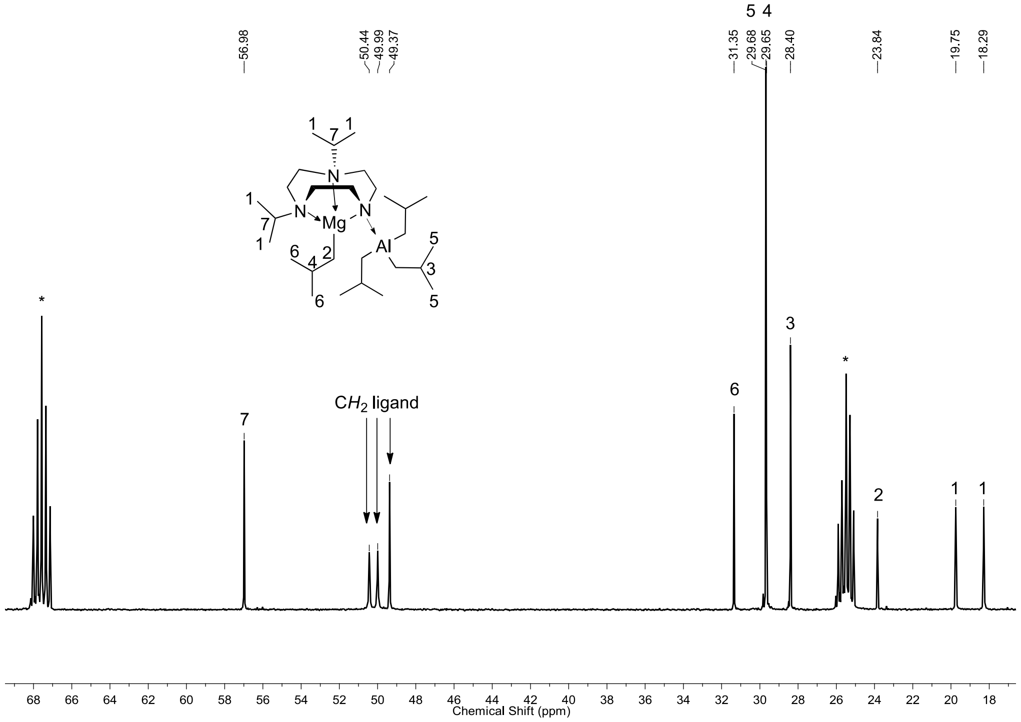

Figure S8. ^{13}C{^{1}H} NMR spectrum of **3** in THF-d_8 (*) at 23 °C.

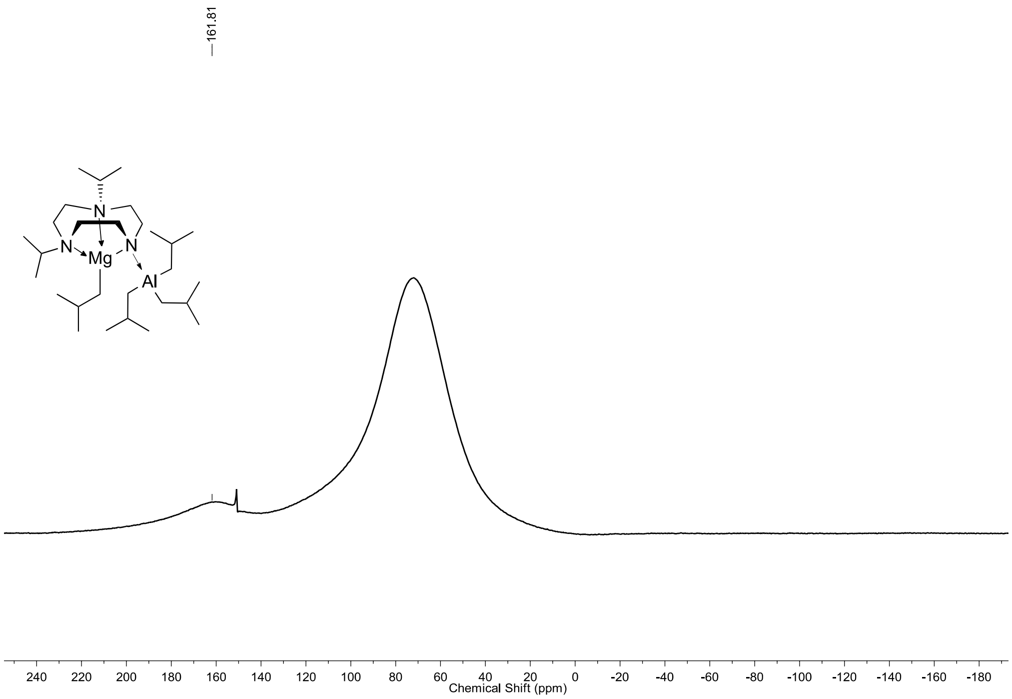

Figure S9. Baseline corrected ^{27}Al NMR spectrum of **3** in THF-d_8 (*) at 23 °C.

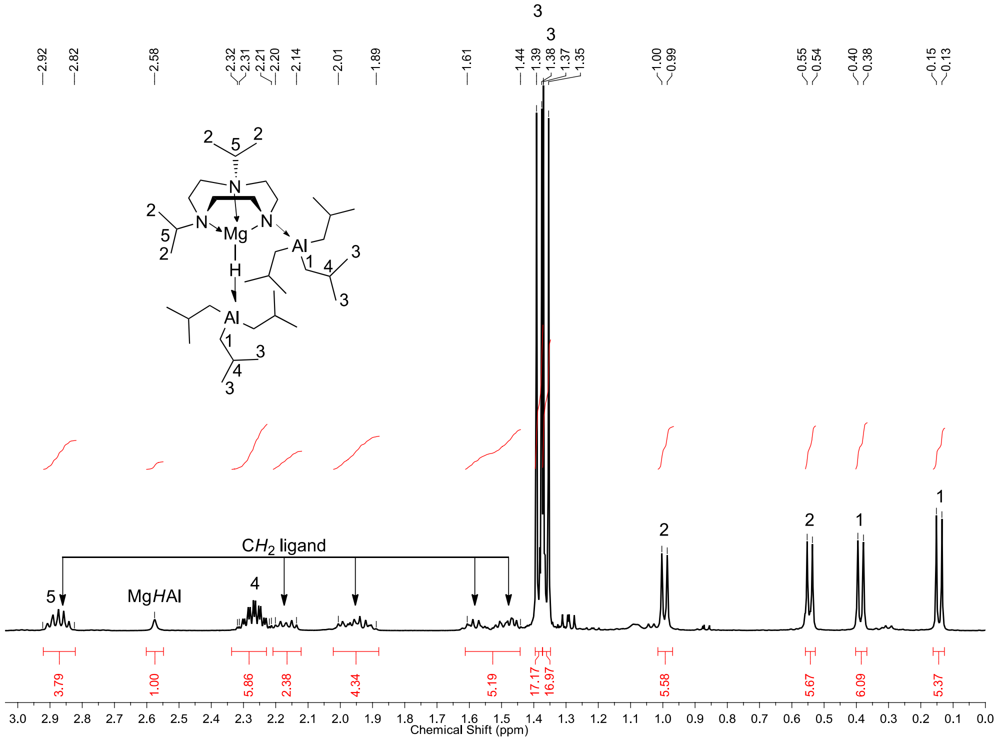

Figure S10. ^{1}H NMR spectrum of **4** in THF-d_8 (*) at 23 °C.

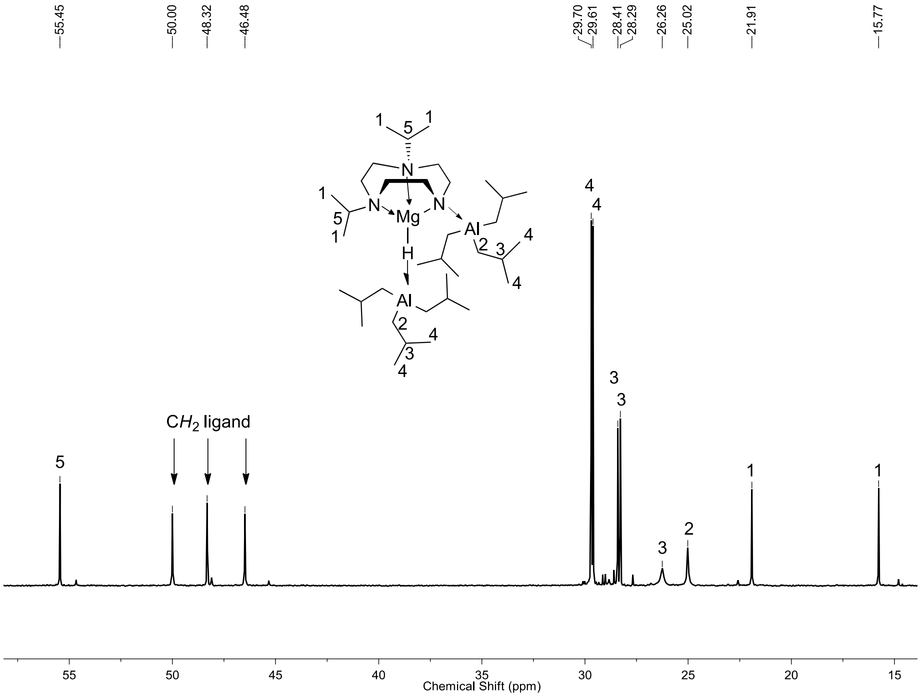

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in THF-d_8 (*) at 23 °C.

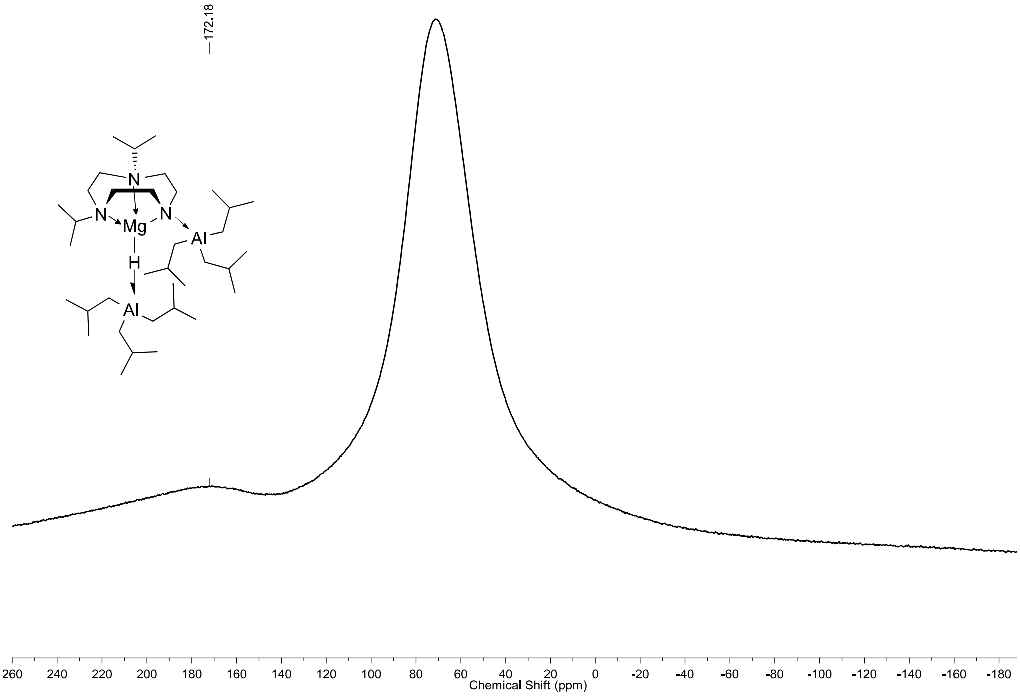

Figure S12. Baseline corrected ^{27}Al NMR spectrum of **4** in THF-d_8 (*) at 23 °C.

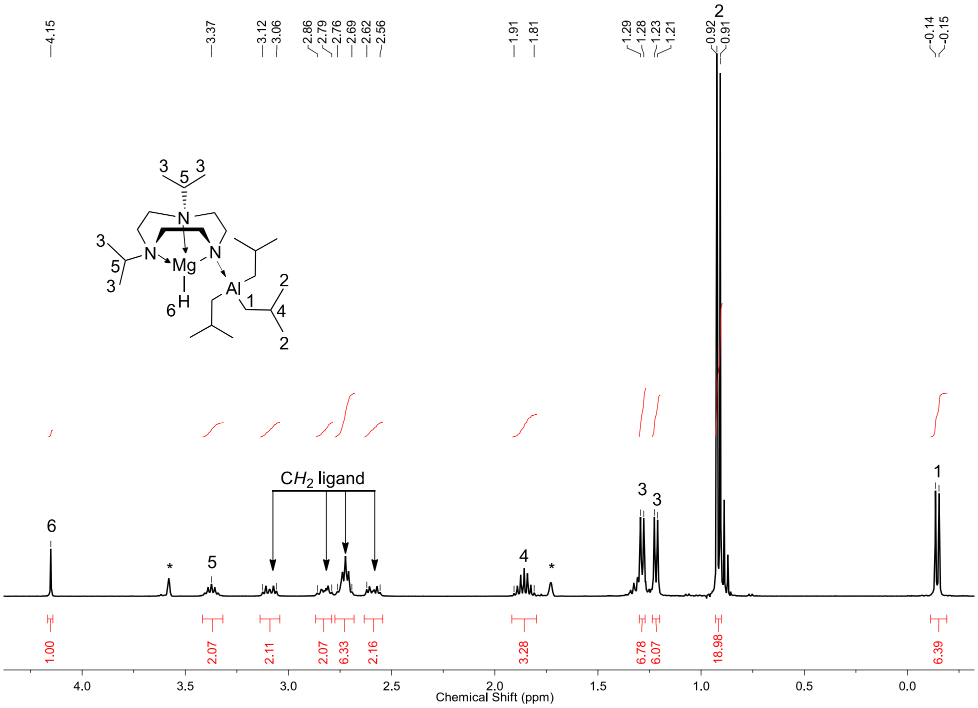

Figure S13. ^{1}H NMR spectrum of **5** in THF-d_8 (*) at 23 °C.

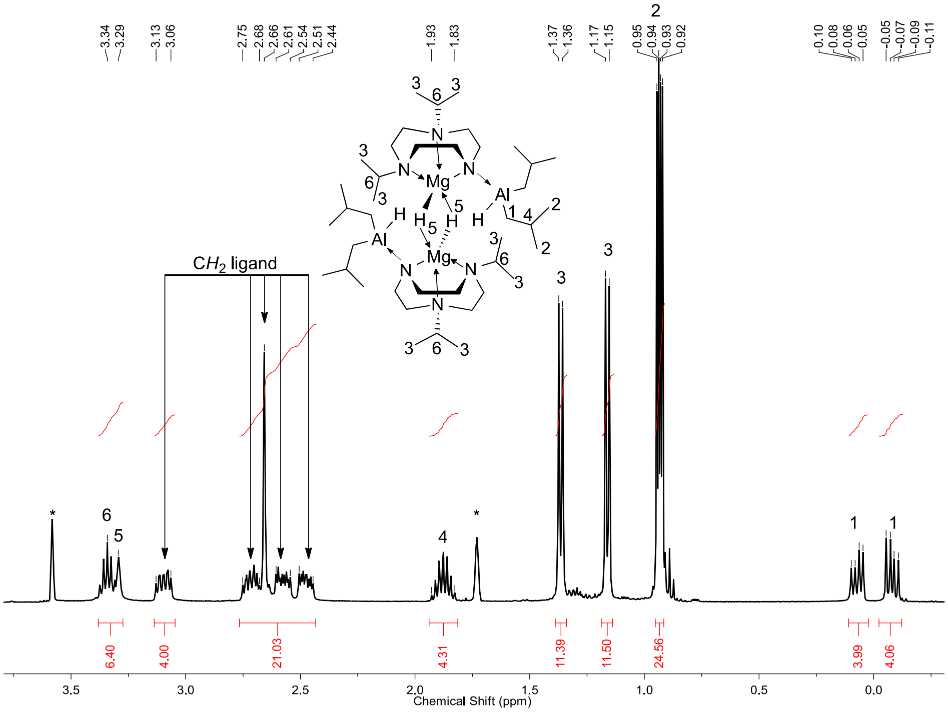

Figure S14. ^{1}H NMR spectrum of **6** in THF-d_8 (*) at 23 °C.

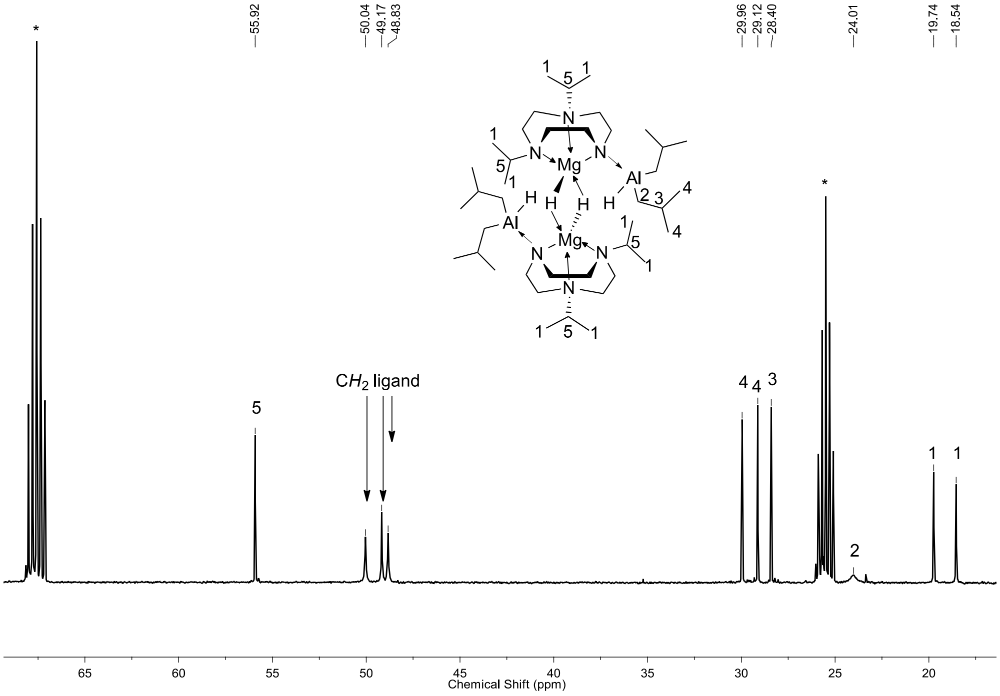

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in THF-d_8 (*) at 23 °C.

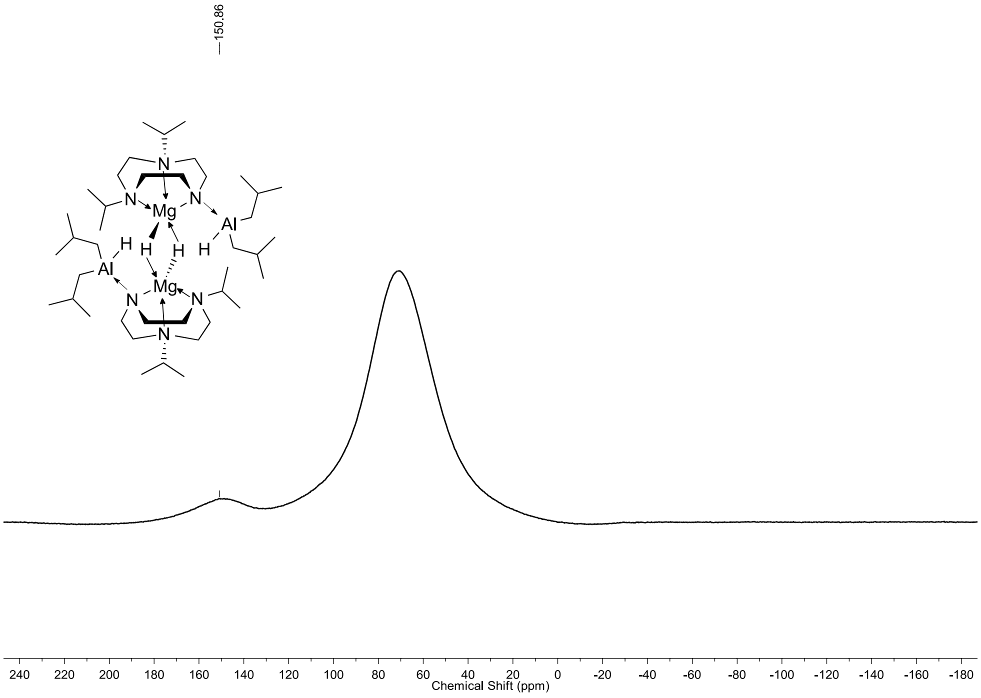

Figure S16. Baseline corrected ^{27}Al NMR spectrum of **6** in THF-d_8 (*) at 23 °C.

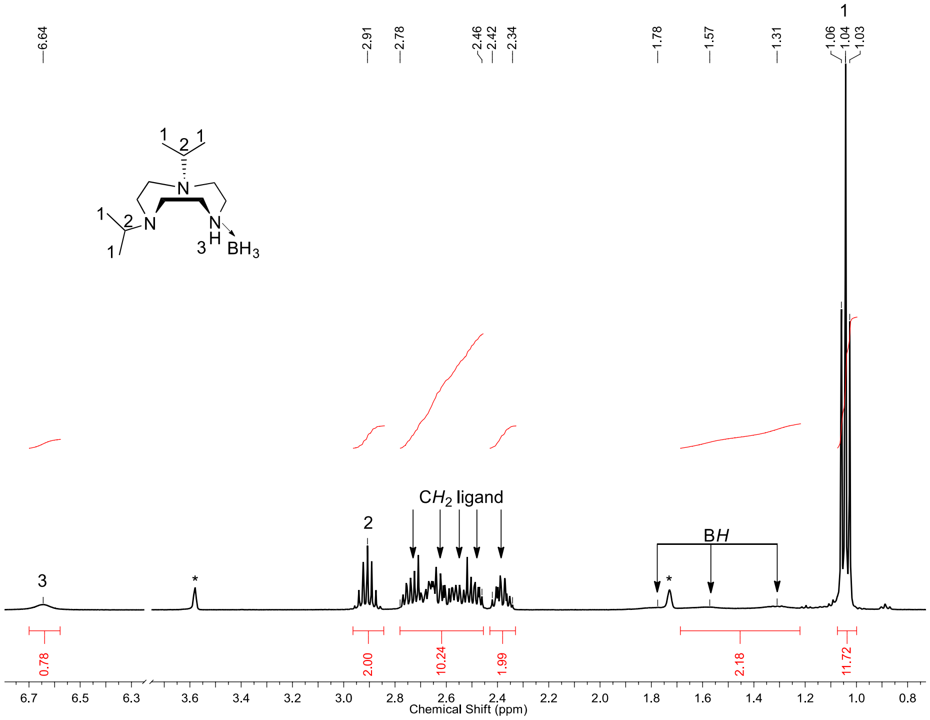

Figure S17. ^{1}H NMR spectrum of **7** in THF-d_8 (*) at 23 °C.

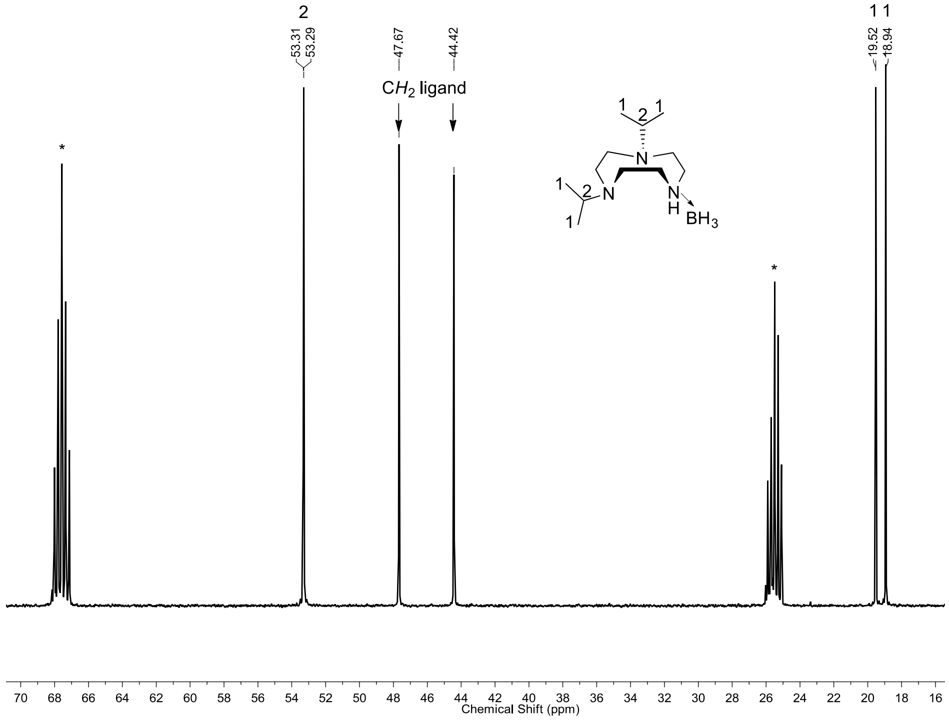

Figure S18. ^{13}C{^{1}H} NMR spectrum of **7** in THF-d_8 (*) at 23 °C.

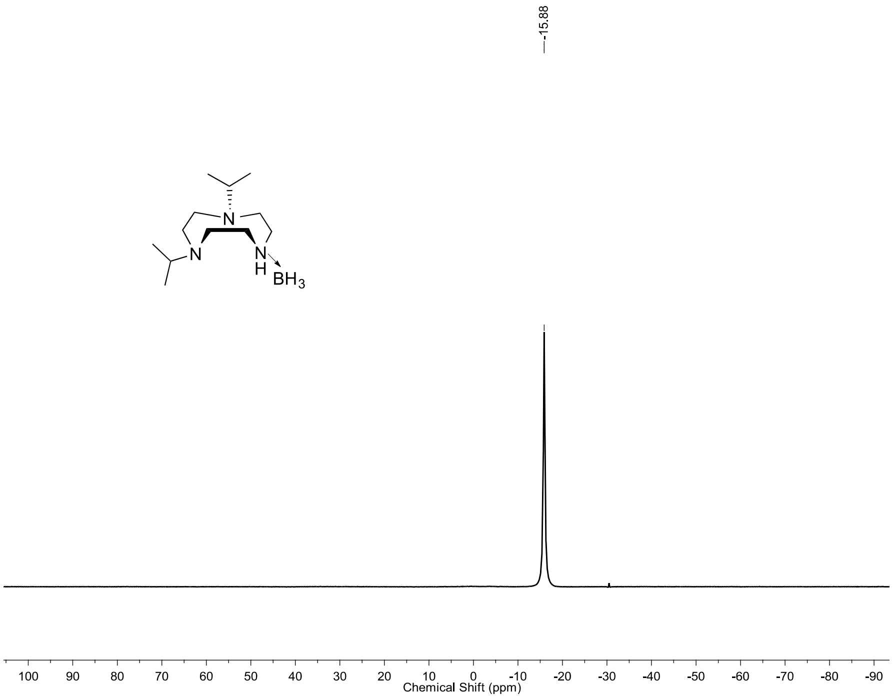

Figure S19. Baseline corrected $^{11}B\{^{1}H\}$ NMR spectrum of **7** in THF-d_8 (*) at 23 °C.

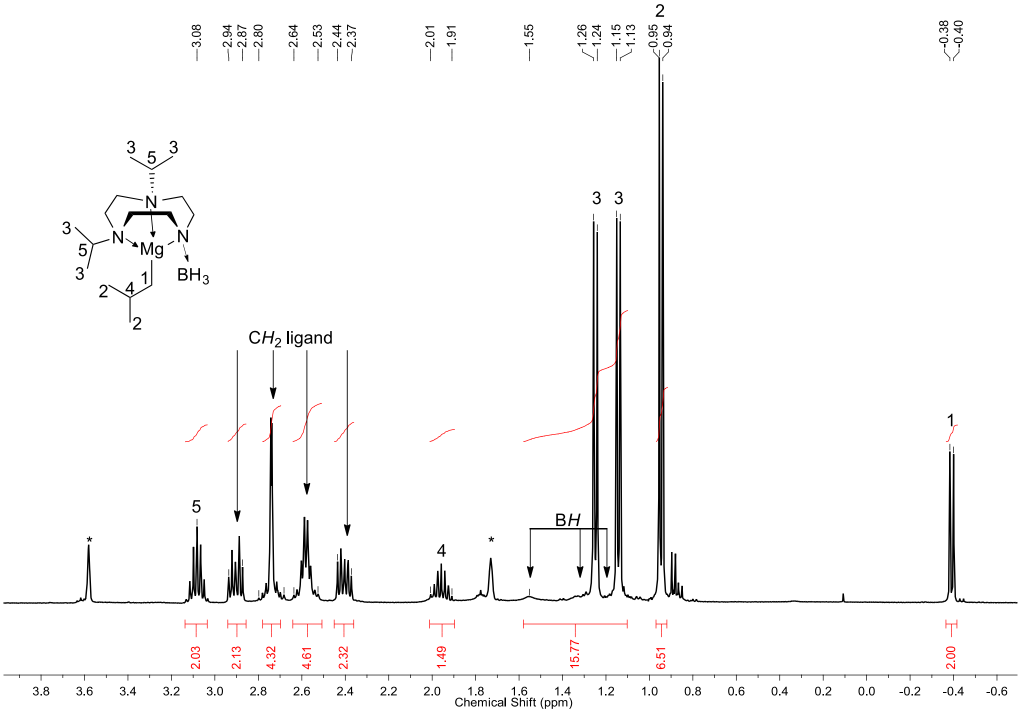

Figure S20. ^{1}H NMR spectrum of **8** in THF-d_8 (*) at 23 °C.

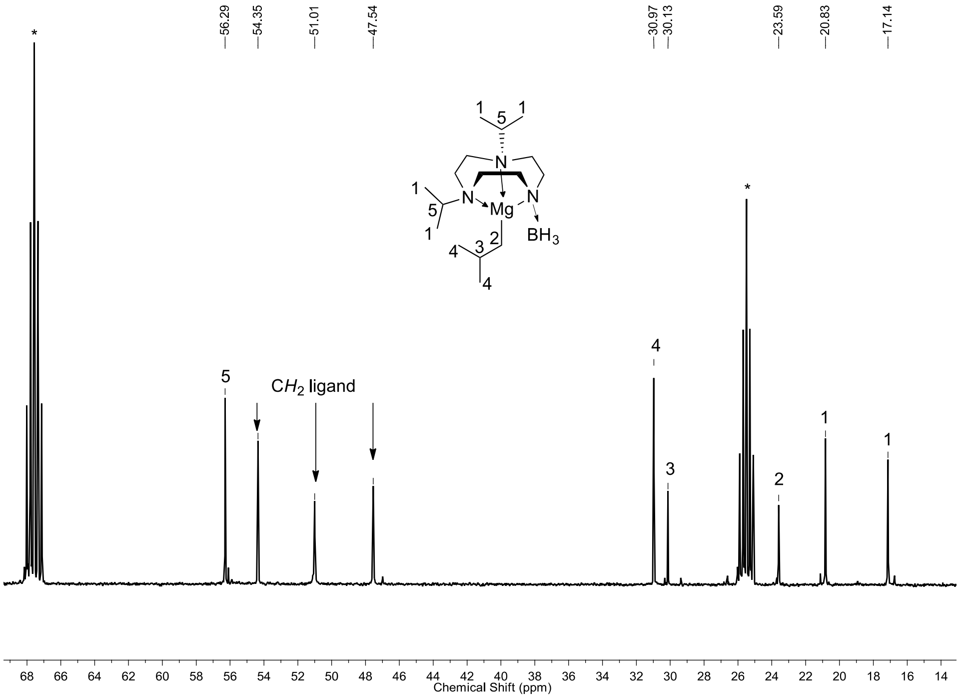

Figure S21. $^{13}C\{^1H\}$ NMR spectrum of **8** in THF-d_8 (*) at 23 °C.

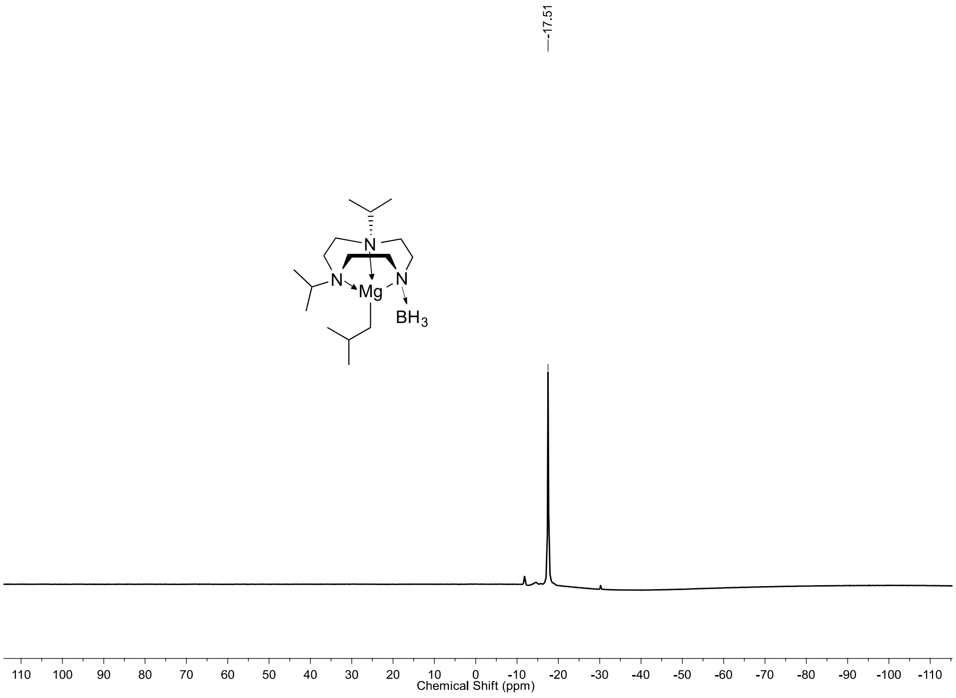

Figure S22. Baseline corrected $^{11}B\{^1H\}$ NMR spectrum of **8** in THF-d_8 (*) at 23 °C.

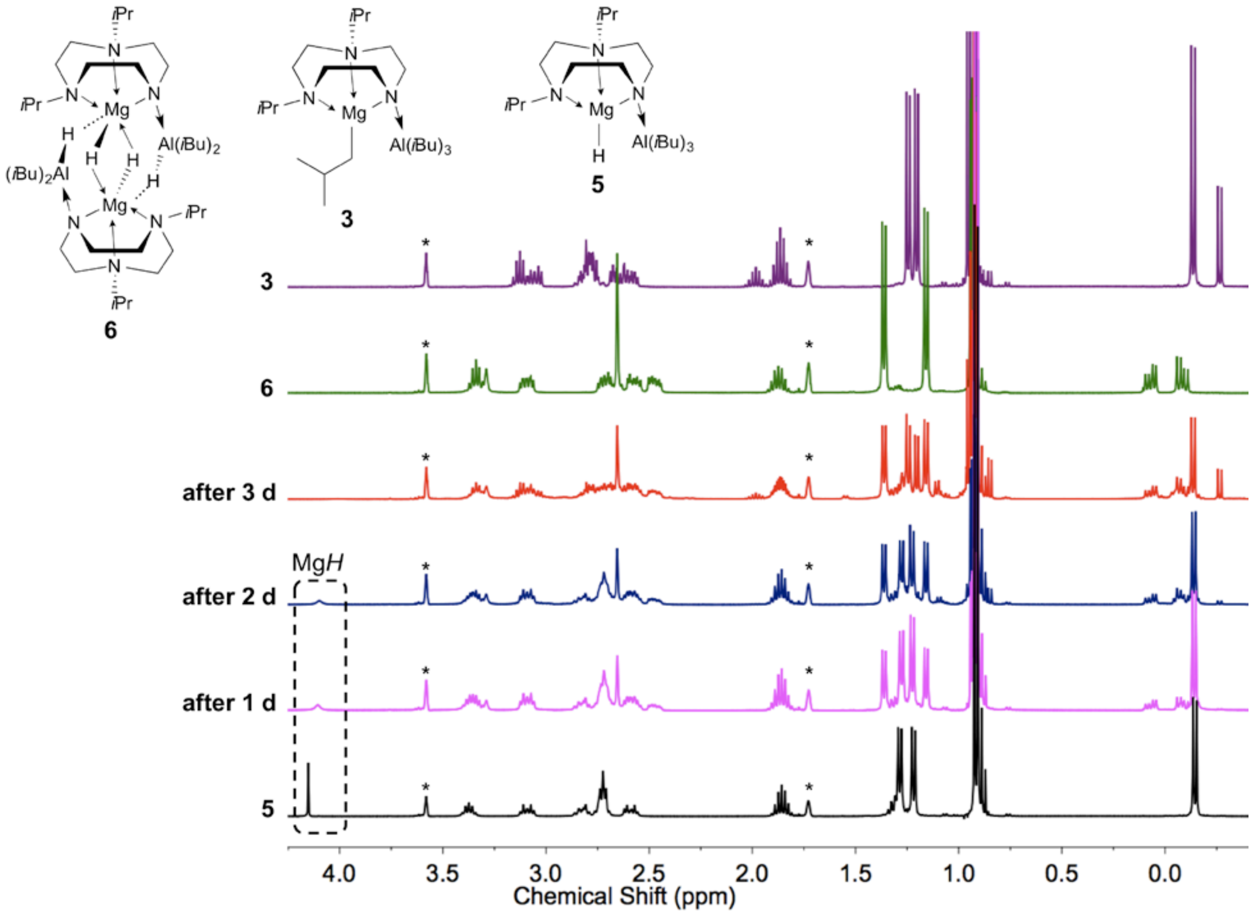

Figure S23. ^{1}H NMR spectra in THF-d_8 (*) at 23 °C. Rearrangement of **5** into **6** and **3** in the ratio 1:2.

X-ray Crystallography

X-ray diffraction data of **1** and **6** were collected on a Bruker D8 goniometer with APEX CCD area-detector with MoKα radiation (multilayer optics, λ = 0.71073 Å) using ω scans. Temperature control was achieved with an Oxford cryostream 700. The SMART program was used for data collection and unit cell determination; processing of the raw data frame was performed using SAINT+,[S4] multi scan absorption corrections were applied with SADABS.[S5] The structures were solved by direct methods (SHELXS).[S6] Refinements were performed against F^2 using all reflections with the program SHELXL-2013.[S6] Hydrogen atoms were included as riding on calculated positions with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq.}}$ or $1.5U_{\text{eq.}}$ (non-H), except for the hydride atoms H1 and H2 in **6**. These atoms were localized in difference Fourier maps and refined in their positions with isotropic displacement parameters. All non-hydrogen atoms were refined anisotropically. Structure **6** contains two crystallographically independent toluene molecules co-crystallized in the lattice. One is well ordered, aligned on a twofold axis and described by the five atoms C200 - C204. The other molecule of toluene is disordered around an inversion center and each atom was refined with an occupancy of 0.5. To allow for a stable refinement, the aromatic C–C distances were restrained to 1.38 Å and the C–C distance between the aromatic ring and the methyl group (C100–C101) to 1.5 Å. Additionally, these atoms were restrained within a common plane. The carbon atoms of the benzene ring (C101 – C106) were only refined isotropically. The overall toluene content corresponds to one molecule per formula unit of $C_{40}H_{90}Al_2Mg_2N_6$. Graphical representations were performed with the program DIAMOND.[7] CCDC reference numbers CCDC-1516409 (**1**), 1516410 (**6**). These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data and Structure Refinement.

	1	**6**
chemical formula	$C_{30}H_{62}Mg_2N_6$	$C_{40}H_{90}Al_2Mg_2N_6 \times 2(C_7H_8)$
fw (g·mol^{-1})	555.47	942.02
space group	$P\bar{1}$	$C2/c$
crystal size (mm)	0.12 × 0.16 × 0.21	0.32 × 0.39 × 0.48
unit cell parameters		
a (Å)	8.0801(11)	15.539(5)
b (Å)	9.6293(13)	15.329(5)
c (Å)	11.6216(15)	24.985(9)
α (°)	106.2030(19)	
β (°)	91.124(2)	101.664(7)
γ (°)	110.3937(19)	
V (Å^3)	807.00(19)	5828(4)
Z	1	4
T (K)	100(2)	100(2)
μ(Mo K_α) (mm^{-1})	0.103	0.109
reflns	11557	25137
independent reflns ($R_{int.}$)	4281 (0.0278)	5581 (0.0931)
observed reflns	3692	3625
parameters	296	310
goodness of fit on F^2	1.038	1.044
final R indices		
$R1$, $wR2$ [$I \geq 2\sigma(I)$]	0.0414, 0.1003	0.0628, 0.1568
$R1$, $wR2$ (all data)	0.0486, 0.1062	0.1068, 0.1787

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