Cationic Magnesium Hydride \([\text{MgH}]^+\) Stabilized by an NNNN-Type Macrocycle

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General considerations

All operations were performed under inert atmosphere of dry argon using standard Schlenk techniques or glovebox techniques. THF, THP, Et₂O, n-pentane, n-hexane and toluene were purified using a MB SPS-800 solvent purification system or distilled under argon from sodium/benzophenone ketyl prior to use. Pyridine was dried over CaH₂ and distilled under argon prior to use. Deuterated solvents (THF-\(d₈\), benzene-\(d₆\)) were distilled under argon from sodium/benzophenone ketyl prior to use. The starting materials Me₄TACD[1] and [NEt₃H][B(3,5-Me₂-C₆H₃)₄][2] were prepared according to literature procedures. The starting material [Mg(HMDS)₂(THF)₂] were analogously prepared to [Mg(HMDS)₂(OEt)₂].[3] NMR spectra were recorded on a Bruker Avance II 400 or a Bruker Avance III HD 400 spectrometer at 25 °C in J. Young-type NMR tubes. Chemical shifts (\(\delta\) in ppm) in the \(^1\)H, \(^{13}\)C\{\(^1\)H\} and \(^{29}\)Si\{\(^1\)H\} NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane. The resonances in the \(^1\)H and \(^{13}\)C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HSQC, HMBC). Combustion analyses were performed with an Elementar Vario EL. The low carbon content for 3, 4, 6, 8a and 8b may be ascribed to incomplete combustion.[4] The magnesium contents were determined by complexometric titrations and were carried out according to the published procedure[5] or were determined by inductively coupled plasma mass spectrometry using a Spectro ICP Spectroflame D instrument. A defined amount of sample was dissolved in 8 mL of 40% hydrofluoric acid, 2 mL of concentrated sulfuric acid, and 40 mL of water.
[(Me₄TACD)Mg(µ-H)₂Mg(HMDS)₂] (1). A solution of Me₄TACD (114 mg, 0.5 mmol) and PhSiH₃ (216 mg, 2.0 mmol) in toluene (2mL) was added slowly to a solution of [Mg(HMDS)₂(THF)₂] (489 mg, 1.0 mmol) in toluene (2mL). The reaction mixture was left for 3 days at 25 °C and the product crystallized during that time. The mother liquor was decanted off. The crystals were washed with n-pentane (3 x 3 mL) and dried under reduced pressure to give [(Me₄TACD)Mg(µ-H)₂Mg(HMDS)₂] (1) (247 mg, 0.41 mmol) as slightly yellow crystals; yield: 82%. Single crystals suitable for X-ray analysis were obtained from toluene over a period of 72 h. 

¹H NMR (THF-d₈; 400.1 MHz): δ 0.05 (s, 36H, N{Si(CH₃)₃}), 2.58 (s, 12H, CH₃-Me₄TACD), 2.65 - 2.72 (m, 8H, CH₂-Me₄TACD), 2.75 - 2.82 (m, 8H, CH₂-Me₄TACD), 3.61 (s, 2H, MgH₂) ppm. ¹³C{¹H} NMR (THF-d₈; 100.6 MHz): δ 7.67 (N{Si(CH₃)₃}), 47.1 (CH₃-Me₄TACD), 56.4 (CH₂-Me₄TACD) ppm. ²⁹Si{¹H} NMR (THF-d₈; 79.5 MHz): δ -11.32 ppm. Anal. calc. for C₂₄H₆₆N₆Si₄Mg₂ (566.78 g∙mol⁻¹): C, 48.06; H, 11.09; N, 14.01; Mg, 8.10. Found: C, 47.30; H, 10.71; N, 14.05; Mg, 8.35%.

¹H, ¹³C{¹H} and ²⁹Si NMR spectra of [(Me₄TACD)Mg(µ-H)₂Mg(HMDS)₂] (1)

Figure S1. ¹H NMR spectrum of 1 in THF-d₈ (*) at 25 °C.
Figure S2. \( ^{13}\text{C}\{^1\text{H}\} \) NMR spectrum of 1 in THF-\( d_8 \) (*) at 25 °C (# unidentified species, $ TMS $).

Figure S3. \( ^{29}\text{Si}\{^1\text{H}\} \) NMR spectrum of 1 in THF-\( d_8 \) at 25 °C.
[(Me₄TACD)Mg(μ-D)₂Mg(HMDS)₂] (1-d₂). A solution of Me₄TACD (46 mg, 0.2 mmol) and PhSiD₃ [6] (89 mg, 0.8 mmol) in toluene (2mL) was added slowly to a solution of [Mg(HMDS)₂(THF)₂] (196 mg, 1.0 mmol) in toluene (2mL). The reaction mixture was left for 3 days at 25 °C and the product crystallized during that time. The solution was decanted off. The crystals were washed with n-pentane (3 x 3 mL) and dried under reduced pressure. [(Me₄TACD)Mg(μ-D)₂Mg(HMDS)₂] (1-d₂) (78 mg, 0.13 mmol) was obtained as slightly yellow crystals in 65% yield. ¹H NMR (THF-d₈; 400.1 MHz): δ 0.05 (s, 36H, N{Si(CH₃)₃}), 2.58 (s, 12H, CH₃-Me₄TACD), 2.65 - 2.72 (m, 8H, CH₂-Me₄TACD), 2.75 - 2.82 (m, 8H, CH₂-Me₄TACD) ppm. ²D NMR (THF; 400.1 MHz): δ 3.65 (MgD) ppm. ¹³C{¹H} NMR (THF-d₈; 100.6 MHz): δ 7.67 (N{Si(CH₃)₃}₂), 47.1 (CH₃-Me₄TACD), 56.4 (CH₂-Me₄TACD) ppm. ²⁹Si{¹H} NMR (THF-d₈; 79.5 MHz): δ -11.32 ppm.

¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra of [(Me₄TACD)Mg(μ-D)₂Mg(HMDS)₂] (1-d₂)

![NMR spectra of 1-d₂](image)

Figure S 4. ¹H NMR spectrum of 1-d₂ in THF-d₈ (*) at 25 °C.
Figure S5. $^2$D NMR spectrum of 1-$d_2$ in THF with benzene-$d_6$ as internal standard (*) at 25 °C.

Figure S6. $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of 1-$d_2$ in THF-$d_8$ (*) at 25 °C ($TMS$).
Figure S7. $^{29}$Si$\{^1$H$\}$ NMR spectrum of 1-$d_2$ in THF-$d_8$ at 25 °C.

[$\text{(Me}_4\text{TACD)}_2\text{Mg}_2(\mu$-H)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$\_2$ (2). Solid [NEt$_3$H][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (213 mg, 0.4 mmol) was added in small portions to a solution of [($\text{Me}_4\text{TACD}$)Mg(μ-H)$_2$Mg(HMDS)$_2$] (1) (240 mg, 0.4 mmol) in THF (6 mL) at room temperature. Gas evolution was observed. The reaction mixture was stirred for 30 min at room temperature and the solvent was removed under reduced pressure. The colorless solid was washed with toluene (5 x 3 mL) to remove the byproduct Mg(HMDS)$_2$. The solid residue was dried under vacuum to give [($\text{Me}_4\text{TACD}$)$_2$Mg$_2$(μ-H)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$\_2$ (2) (232 mg, 0.17 mmol) in 43% yield. Single crystals suitable for X-ray analysis were obtained from a THF/n-hexane mixture at 25 °C over a period of 3 days. $^1$H NMR (THF-$d_8$; 400.1 MHz): $\delta$ 2.10 (s, 48H, CH$_3$-B(3,5-Me$_2$-C$_6$H$_3$)$_4$), 2.24 - 2.33 (m, 16H, CH$_2$-Me$_4$TACD), 2.29 (s, 24H, CH$_3$-Me$_4$TACD), 2.37 - 2.45 (m, 16H, CH$_2$-Me$_4$TACD), 3.38 (s, 2H, MgH), 6.37 (m, 8H, $^{para}$-CH-B(3,5-Me$_2$-C$_6$H$_3$)$_4$), 6.99 (m, 16H, $^{ortho}$-CH-B(3,5-Me$_2$-C$_6$H$_3$)$_4$) ppm. $^{13}$C$\{^1$H$\}$ NMR (THF-$d_8$; 100.6 MHz): $\delta$ 22.5 (CH$_3$-B(3,5-Me$_2$-C$_6$H$_3$)$_4$), 44.0 (CH$_3$-Me$_4$TACD), 53.7 (CH$_2$-Me$_4$TACD), 123.8 ($^{para}$-CH-B(3,5-Me$_2$-C$_6$H$_3$)$_4$), 133.1 (q, $^3$J$_{BC}$ = 2.9 Hz, $^{meta}$-C-B(3,5-Me$_2$-C$_6$H$_3$)$_4$), 135.7 ($^{ortho}$-CH-B(3,5-Me$_2$-C$_6$H$_3$)$_4$), 165.9 (q, $^1$J$_{BC}$ = 49.2 Hz, $^{ipso}$-C-B(3,5-Me$_2$-C$_6$H$_3$)$_4$) ppm. $^{11}$B$\{^1$H$\}$ NMR (THF-$d_8$; 128.4 MHz): $\delta$ -8.88 ppm. Anal. calc. for C$_{88}$H$_{130}$N$_8$B$_2$Mg$_2$
(1370.29 g·mol⁻¹): C, 77.13; H, 9.56; N, 8.18; Mg, 3.55. Found: C, 76.89; H, 9.08; N, 7.65; Mg, 3.20%.

^1H, ^13C{^1H} and ^11B{^1H} NMR spectra of [(Me₄TACD)₂Mg₂(μ-H)₂][B(3,5-Me₂-C₆H₃)₄]₂ (2)

Figure S8. ^1H NMR spectrum of 2 in THF-­d₈ (*) at 25 °C.
Figure S9. $^{13}\text{C}^\{1\text{H}\}$ NMR spectrum of 2 in THF-$d_8$ (*) at 25 °C (# toluene).

Figure S10. $^{11}\text{B}^\{1\text{H}\}$ NMR spectrum of 2 in THF-$d_8$ (*) at 25 °C.
[(Me₄TACD)₂Mg₂(µ-D)₂][B(3,5-Me₂-C₆H₃)₄]₂ (2-₁₂). A suspension of [NEt₃H][B(3,5-Me₂-
C₆H₃)₄] (47 mg, 0.09 mmol) in THF (2mL) was added slowly to a solution of [(Me₄TACD)Mg(µ-
D)₂Mg(HMDS)] (1-₁₂) (55 mg, 0.09 mmol) at room temperature. Gas evolution was observed.
The reaction mixture was stirred for 30 min at room temperature and the solvent was removed
under reduced pressure. The colorless solid was washed with toluene (5 x 3 mL) to remove the
byproduct Mg(HMDS). The solid residue was dried under vacuum to give [(Me₄TACD)₂Mg₂(µ-
H)₂][B(3,5-Me₂-C₆H₃)₄]₂ (2-₁₂) (49 mg, 0.04 mmol) in 79% yield. ¹H NMR (THF-₁₂8; 400.1 MHz):
δ 2.10 (s, 24H, CH₃-B(3,5-Me₂-C₆H₃)₄), 2.24 - 2.30 (m, 8H, CH₂-Me₄TACD), 2.27 (s, 12H, CH₃-
Me₄TACD), 2.36 - 2.43 (m, 8H, CH₂-Me₄TACD), 6.38 (m, 4H, para-CH-B(3,5-Me₂-C₆H₃)₄), 7.00
(m, 8H, ortho-CH-B(3,5-Me₂-C₆H₃)₄) ppm. ²D NMR (THF; 400.1 MHz): δ 3.44 (MgD)
ppm. ¹³C{¹H} NMR (THF-₁₂8; 100.6 MHz): δ 22.5 (CH₃-B(3,5-Me₂-C₆H₃)₄), 44.1 (CH₃-
Me₄TACD), 53.8 (CH₂-Me₄TACD), 123.8 (para-CH-B(3,5-Me₂-C₆H₃)₄), 133.2 (q, ³JBC = 2.9 Hz,
meta-C-B(3,5-Me₂-C₆H₃)₄), 135.7 (ortho-CH-B(3,5-Me₂-C₆H₃)₄), 165.9 (q, ¹JBC = 49.2 Hz, ipso-
C-B(3,5-Me₂-C₆H₃)₄) ppm. ¹¹B{¹H} NMR (THF-₁₂8; 128.4 MHz): δ −7.00 ppm.

¹H, ¹³C{¹H} and ¹¹B{¹H} NMR spectra of [(Me₄TACD)₂Mg₂(µ-D)₂][B(3,5-Me₂-C₆H₃)₄]₂ (2-₁₂)

Figure S11. ¹H NMR spectrum of 2-₁₂ in THF-₁₂8 (*) at 25 °C (# toluene, $ Mg(HMDS)₂).
Figure S12. $^2$D NMR spectrum of $2$-$d_2$ in THF with benzene-$d_6$ (*) as internal standard at 25 °C.

Figure S13. $^{13}$C{$^1$H} NMR spectrum of $2$-$d_2$ in THF-$d_8$ (*) at 25 °C (# unidentified species).
Figure S14. $^{11}$B$^{1H}$ NMR spectrum of 2-$d_2$ in THF-$d_8$ at 25 °C.

$\text{[(Me}_{4}\text{TACD})\text{Mg(\text{H})}_3\text{BH}][\text{B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]}$ (3). A solution of BH$_3$·THF (1 M in THF, 0.1 mL, 0.1 mmol) was added to a solution of $\text{[(Me}_{4}\text{TACD})_2\text{Mg(\text{H})}_2][\text{B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]}$ (68 mg, 0.05 mmol) in THF (2mL) at room temperature and the reaction mixture was stirred for 30 min. The solvent was removed under reduced pressure and the colorless solid was washed with n-pentane (3 mL). The solid residue was dried under vacuum to give $\text{[(Me}_{4}\text{TACD})\text{Mg(\text{H})}_3\text{BH}][\text{B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]}$ (3) (59 mg, 0.08 mmol) in 84% yield. Single crystals suitable for X-ray analysis were obtained from a THP/cyclohexane mixture at 25 °C over a period of 16 h. $^1$H NMR (THF-$d_8$; 400.1 MHz): $\delta$ −0.46 (quart, $^1J_{\text{BH}} = 82.0$ Hz, 4H, BH$_4$), 2.10 (s, 24H, CH$_3$-B(3,5-Me$_2$-C$_6$H$_3)_4$), 2.29 - 3.35 (m, 8H, CH$_2$-Me$_4$TACD), 2.31 (s, 12H, CH$_3$-Me$_4$TACD), 2.39 - 2.45 (m, 8H, CH$_2$-Me$_4$TACD), 6.38 (m, 4H, para-CH-B(3,5-Me$_2$-C$_6$H$_3)_4$), 7.00 (m, 8H, ortho-CH-B(3,5-Me$_2$-C$_6$H$_3)_4$) ppm. $^{13}$C$^{1H}$ NMR (THF-$d_8$; 100.6 MHz): $\delta$ 22.5 (CH$_3$-B(3,5-Me$_2$-C$_6$H$_3)_4$), 44.7 (CH$_2$-Me$_4$TACD), 53.5 (CH$_2$-Me$_4$TACD), 123.9 (para-CH-B(3,5-Me$_2$-C$_6$H$_3)_4$), 133.3 (q, $^2J_{\text{BC}} = 2.9$ Hz, meta-C-B(3,5-Me$_2$-C$_6$H$_3)_4$), 135.7 (ortho-CH-B(3,5-Me$_2$-C$_6$H$_3)_4$), 165.9 (q, $^1J_{\text{BC}} = 49.2$ Hz, ipso-C-B(3,5-Me$_2$-C$_6$H$_3)_4$) ppm. $^{11}$B NMR (THF-$d_8$; 128.4 MHz): $\delta$ −7.00 (B(3,5-Me$_2$-C$_6$H$_3)_4), −44.9, (quint, $^1J_{\text{BH}} = 82.0$ Hz, BH$_4$) ppm. IR (KBr): $\nu =$ 3024 (w), 3004 (s), 2972 (m), 2913 (s), 2871 (s), 2842 (s), 1654 (s), 1618 (w), 1467 (s), 1385 (s), 1360 (w), 1284 (m), 1167 (m), 1081 (s), 1032 (w), 958 (s), 884 (s), 804 (s), 776 (s), 703 (m), 674 (w), 605 (w), 547 (w), 490 (w) cm$^{-1}$.
2871 (m), 2444 (w), 2291 (w), 1575 (m), 1470 (s), 1358 (w), 1298 (m), 1268 (w), 1249 (w), 1148 (m), 1108 (w), 1078 (m), 1050 (w), 1022 (m), 967 (m), 906 (w), 842 (m), 800 (w), 756 (w), 734 (m), 584 (w), 505 (w), 473 (w) cm⁻¹. Anal. calc. for C₄₄H₆₈N₄B₂Mg (698.98 g·mol⁻¹): C, 75.61; H, 9.81; N, 8.02; Mg, 3.48. Found: C, 73.40; H, 9.33; N, 7.77; Mg, 3.47%.

¹H, ¹³C{¹H} and ¹¹B NMR spectra of [(Me₄TACD)Mg(μ-H)₃BH][B(3,5-Me₂-C₆H₃)₄] (3)

Figure S15. ¹H NMR spectrum of 3 in THF-d₈ (*) at 25 °C.
Figure S16. $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of 3 in THF-$d_8$ (*) at 25 °C.

Figure S17. $^{11}$B NMR spectrum of 3 in THF-$d_8$ at 25 °C.
[(Me₄TACD)Mg(μ-H)BHpin)][B(3,5-Me₂-C₆H₃)₄] (4). A solution of pinacolborane (22 μL, 19 mg, 0.15 mmol) in THF (1 mL) was added to a solution of [[(Me₄TACD)₂Mg(μ-H)₂][B(3,5-Me₂-C₆H₃)₄]]; (2) (103 mg, 0.075 mmol) in THF (3 mL) and the reaction solution was stirred for 15 min at 25 °C. The solvent was removed under reduced pressure and the colorless solid was washed with n-pentane (3 mL) and dried under vacuum. [[(Me₄TACD)Mg(μ-H)BHpin)][B(3,5-Me₂-C₆H₃)₄] (4) (115 mg, 0.14 mmol) was obtained in 94% yield. ¹H NMR (THF-d₈; 400.1 MHz): δ 1.13 (s, 12H, CH₃-BPin), 2.10 (s, 24H, CH₃-[B(3,5-Me₂-C₆H₃)₄]), 2.32 - 2.43 (m, 16H, CH₂-Me₄TACD), 2.39 (s, 12H, CH₃-Me₄TACD), 6.38 (m, 4H, para-CH-[B(3,5-Me₂-C₆H₃)₄]), 7.00 (m, 8H, ortho-CH-[B(3,5-Me₂-C₆H₃)₄]) ppm, BH resonance not detected. ¹³C{¹H} NMR (THF-d₈; 100.6 MHz): δ 22.5 (CH₃-[B(3,5-Me₂-C₆H₃)₄]), 25.3 (s, 12H, CH₃-BPin, identified by HSQC NMR), 45.7 (CH₃-Me₄TACD), 54.6 (CH₂-Me₄TACD), 123.9 (para-CH-[B(3,5-Me₂-C₆H₃)₄]), 133.2 (q, 3JBC = 2.9 Hz, meta-C-[B(3,5-Me₂-C₆H₃)₄]), 135.7 (ortho-CH-[B(3,5-Me₂-C₆H₃)₄]), 165.9 (q, 1JBC = 49.2 Hz, ipso-C-[B(3,5-Me₂-C₆H₃)₄]) ppm. ¹¹B NMR (THF-d₈; 128.4 MHz): δ 1.42 (br, BPin), −8.88 (B(3,5-Me₂-C₆H₃)₄) ppm. IR (KBr): ν = 3024 (w), 3000 (s), 2973 (s), 2913 (s), 2866 (m), 2282 (w), 2197 (w), 1575 (m), 1501 (m), 1467 (s), 1384 (w), 1359 (w), 1298 (m), 1269 (w), 1249 (w), 1213 (w), 1156 (s), 1109 (w), 1080 (m), 1049 (w), 1025 (m), 967 (m), 906 (w), 840 (m), 800 (w), 756 (w), 736 (m), 691 (w), 662 (w), 581 (w), 507 (w), 448(w) cm⁻¹. Anal. calc. for C₅₀H₇₈N₄O₂Mg (813.13 g∙mol⁻¹): C, 73.86; H, 9.67; N, 6.89; Mg, 2.99. Found: C, 72.01; H, 9.25; N, 6.67; Mg, 2.58 %.
\(^1\)H, \(^{13}\)C\(^{\{1\}H}\)-APT, and \(^{11}\)B\(^{\{1\}H}\) NMR spectra of [(Me\(_4\)TACD)Mg(\(\mu\)-H)BHpin][B(3,5-Me\(_2\)-C\(_6\)H\(_3\))\(_4\)] (4).

\(\text{Figure S18.} \ \^1\)H NMR spectrum of 4 in THF-\(d_8\) (*) at 25 °C.

\(\text{Figure S19.} \ \^{13}\)C\(^{\{1\}H}\)-APT NMR spectrum of 4 in THF-\(d_8\) (*) at 25 °C.
**Figure S20.** $^{11}$B NMR spectrum of 4 in THF-$d_8$ at 25 °C.

**Solid state structure of [(Me$_4$TACD)Mg(μ-H)BHpin)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (4)**

Single crystals of [(Me$_4$TACD)Mg(μ-H)BHpin)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (4) were obtained from a THF/cyclohexane mixture at −30 °C over a period of 16 h. 4 displays a monomeric structure with a magnesium centre coordinated by four nitrogen atoms of the Me$_4$TACD ligand and by one hydride and one oxygen atom of the pinacolborate ligand (Figure S21).
Figure S21. Molecular structure of \([(\text{Me}_4\text{TACD})\text{Mg(\(\mu\)-H)BHPin})\text{][B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{]}\text{] (4). Displacement parameters are shown at the 50\% probability level. Hydrogen atoms, except for the hydrides H1 and H2, are omitted for clarity. The borate anion is not shown. Selected interatomic distances [Å] and angles [°]: Mg1ꞏꞏꞏB1 2.593(4), Mg1ꞏꞏꞏH1 2.75(5), Mg1–H2 2.56(4), Mg1–N1 2.217(3), Mg1–N2 2.287(3), Mg1–N1 2.217(3), Mg1–N2 2.287(3), Mg1–N3 2.222(3), Mg1–N4 2.280(3).

\([(\text{Me}_4\text{TACD})\text{Mg(H}_2\text{Al}\text{tBu}_2)\text{][B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{]}\text{] (5). Neat DIBAL(H) (14 mg, 0.1 mmol) was added to a solution of \([(\text{Me}_4\text{TACD})\text{2Mg(\(\mu\)-H)\text{]}\text{][B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{]}\text{]}\text{] (68 mg, 0.05 mmol) in THF (2mL) at room temperature and the reaction mixture was stirred for 30 min. The solvent was removed under reduced pressure and the colorless solid was washed with \(n\)-pentane (3 mL). The solid residue was dried under vacuum to give \([(\text{Me}_4\text{TACD})\text{Mg(H}_2\text{Al}\text{tBu}_2)\text{][B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{]}\text{] (5) (69 mg, 0.08 mmol) in 83\% yield.}

\(^1\text{H} \text{NMR (THF-\text{d}_8; 400.1 MHz): } \delta 0.02 (d, ^3J_{HH} = 7.0 \text{ Hz, 4H, } CH_2-Al^t\text{Bu}_2), 0.95 (d, ^3J_{HH} = 6.5 \text{ Hz, 12H, } CH_3-Al^t\text{Bu}_2), 1.81 (sept, ^3J_{HH} = 6.8 \text{ Hz, 2H, } CH_2-Al^t\text{Bu}_2), 2.10 (s, 24H, } CH_3-B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{), 2.29 (s, 12H, } CH_2-\text{Me}_4\text{TACD}, 2.29 - 2.35 (m, 8H, } CH_2-\text{Me}_4\text{TACD}, 2.39 - 2.46 (m, 8H, } CH_2-\text{Me}_4\text{TACD), 3.04 (br s, 2H, Mg-H_2Al), 6.39 (m, 4H, } para-CH-B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{), 7.00 (m, 8H, } ortho-CH-B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{) ppm.}^{13}\text{C} \{^1\text{H} \text{NMR (THF-\text{d}_8; 100.6 MHz): } \delta 19.9 (CH_2-Al^t\text{Bu}_2), 22.5 (CH_3-B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{), 28.2 (CH-Al^t\text{Bu}_2), 28.6 (CH_3-Al^t\text{Bu}_2), 44.8 (CH_2-\text{Me}_4\text{TACD), 53.6 (CH_2-\text{Me}_4\text{TACD), 123.9 (para-CH-B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{), 133.3 (q, } ^3J_{BC} = 2.9 \text{ Hz, meta-C-B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{), 135.7 (ortho-CH-B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{), 165.9 (q, } ^1J_{BC} = 49.2 \text{ Hz, ipso-C-B(3,5-\text{Me}_2-\text{C}_6\text{H}_3)\text{) ppm.}^{27}\text{Al NMR (THF-\text{d}_8; 104.3 MHz): } \delta 130.8 \text{ ppm.}^{11}\text{B} \{^1\text{H} \text{NMR (THF-\text{d}_8; 128.4 MHz): } \delta -7.00 \text{ ppm.} \text{IR (KBr): } v = 3745 (w), 3025 (w), 3003 (m), 2974 (s), 2917 (s), 2857 (m), 1654 (w), 1576 (m), 1541 (m), 1465 (s), 1357 (w), 1298 (m),
1242 (s), 1149 (s), 1078 (w), 1061 (w), 1021 (w), 966 (w), 904 (w), 841 (m), 792 (m), 754 (w), 736 (m), 664 (w), 581 (w), 507 (w) cm$^{-1}$. Anal. calc. for C$_{52}$H$_{84}$N$_4$BMg (827.37 g·mol$^{-1}$): C, 75.49; H, 10.23; N, 6.77; Mg, 2.94; Al 3.26. Found: C, 74.17; H, 9.95; N, 6.96; Mg, 3.29; Al, 3.04%.

$^1$H, $^{13}$C$^{[1]}$H, $^{27}$Al and $^{11}$B$^{[1]}$H NMR spectra of [(Me$_4$TACD)Mg(H$_2$Al'Bu$_2$)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (5)

**Figure S22.** $^1$H NMR spectrum of 5 in THF-$d_8$ (*) at 25 °C.
Figure S23. $^{13}\text{C}^{1\text{H}}$ NMR spectrum of 5 in THF-$d_8$ (*) at 25 °C.

Figure S24. $^{11}\text{B}^{1\text{H}}$ NMR spectrum of 5 in THF-$d_8$ at 25 °C.
Figure S25. $^{27}$Al NMR spectrum of 5 in THF-$d_8$ at 25 °C.

$[(\text{Me}_4\text{TACD})\text{Mg(OCH}_2\text{Ph})][\text{B}(3,5-$Me$_2$-C$_6$H$_3$)$_4]$ (6). To a solution of $[(\text{Me}_4\text{TACD})_2\text{Mg}(\mu-$H)$_2][\text{B}(3,5-$Me$_2$-C$_6$H$_3$)$_4]$ (2) (68 mg, 0.05 mmol) in THF (4 mL) a solution of benzaldehyde (11 mg, 0.1 mmol) in THF (1 mL) was added and the reaction mixture was stirred for 10 min at room temperature. The solvent was removed under reduced pressure and the colorless solid residue was washed with diethyl ether (6 mL) and $n$-pentane (4.5 mL). The solid was dried under vacuum to give $[(\text{Me}_4\text{TACD})\text{Mg(OCH}_2\text{Ph})][\text{B}(3,5-$Me$_2$-C$_6$H$_3$)$_4]$ (7) (74 mg, 0.08 mmol) in 85% yield. Single crystals suitable for X-ray analysis were obtained from THF/$n$-pentane over a period of 16 h at 25 °C. $^1$H NMR (THF-$ds$; 400.1 MHz): δ 2.09 (s, 24H, C$_3$H$_3-$[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 2.30 - 2.44 (m, 16H, CH$_2$-Me$_4$TACD), 2.32 (s, 12H, CH$_3$-Me$_4$TACD), 4.92 (s, 2H, OCH$_2$Ph), 6.37 (m, 4H, para-CH-B(3,5-$Me_2$-C$_6$H$_3$)$_4$), 7.00 (m, 8H, ortho-CH-B(3,5-$Me_2$-C$_6$H$_3$)$_4$), 7.04 (m, 1H, para-CH-OCH$_2$Ph), 7.17 (m, 2H, meta-CH-OCH$_2$Ph), 7.27 (m, 2H, ortho-CH-OCH$_2$Ph) ppm. $^{13}$C($^1$H) NMR (THF-$ds$; 100.6 MHz): δ 22.5 (CH$_3$-[B(3,5-$Me_2$-C$_6$H$_3$)$_4$]), 45.7 (CH$_3$-Me$_4$TACD), 54.4 (CH$_2$-Me$_4$TACD), 68.4 (OCH$_2$Ph), 123.8 (para-CH-B(3,5-$Me_2$-C$_6$H$_3$)$_4$), 126.1 (para-CH-OCH$_2$Ph), 126.7 (meta-CH-OCH$_2$Ph), 128.4 (ortho-CH-OCH$_2$Ph), 133.2 (q, $^3$J$_{BC}$ = 2.9 Hz, meta-C-B(3,5-$Me_2$-C$_6$H$_3$)$_4$), 135.7 (ortho-CH-B(3,5-$Me_2$-C$_6$H$_3$)$_4$), 165.9 (q, $^1$J$_{BC}$ = 49.2 Hz, ipso-C-B(3,5-$Me_2$-C$_6$H$_3$)$_4$).
C₆H₅)₄) ppm. ¹¹B{¹H} NMR (THF-d₈; 128.4 MHz): δ = -7.02 ppm. Anal. calc. for C₅₁H₇₁N₄BOMg (791.27 g·mol⁻¹): C, 77.41; H, 9.04; N, 7.08; Mg, 3.07. Found: C, 76.73; H, 9.63; N, 7.25; Mg, 3.33%.

¹¹H, ¹³C{¹H}, and ¹¹B{¹H} NMR spectra of [(Me₄TACD)Mg(OCH₂Ph)][B(3,5-Me₂-C₆H₅)₄] (6)

**Figure S26.** ¹H NMR spectrum of 6 in THF-d₈ (*) at 25 °C (n-pentane).
Figure S27. $^{13}$C{$_1^H$} NMR spectrum of 6 in THF-$d_8$ (*) at 25 °C.

Figure S28. $^{11}$B{$_1^H$} NMR spectrum of 6 in THF-$d_8$ at 25 °C.
[(Me₄TACD)Mg(OCHPh₂)][B(3,5-Me₂-C₆H₃)₄] (7). To a solution of [(Me₄TACD)₂Mg₂(μ-H)₂][B(3,5-Me₂-C₆H₃)₄] (2) (68 mg, 0.05 mmol) in THF (4 mL) was added a solution of benzophenone (18 mg, 0.1 mmol) in THF (1 mL) at room temperature and the reaction mixture was stirred for 10 min. The solvent was removed under reduced pressure and the colorless solid residue was washed with diethyl ether (6 mL) and n-pentane (4.5 mL). The solid was dried under vacuum to give [(Me₄TACD)Mg(OCHPh₂)][B(3,5-Me₂-C₆H₃)₄] (7) (74 mg, 0.08 mmol) in 85% yield. ¹H NMR (THF-d₈; 400.1 MHz): δ 2.09 (s, 24H, CH₃-B(3,5-Me₂-C₆H₃)₄), 2.21 (s, 12H, CH₃-Me₄TACD), 2.21 - 2.30 (m, 8H, CH₂-Me₄TACD), 2.33 - 2.40 (m, 8H, CH₂-Me₄TACD), 5.90 (OCHPh₂), 6.37 (m, 4H, para-CH-B(3,5-Me₂-C₆H₃)₄), 6.99 (m, 8H, ortho-CH-B(3,5-Me₂-C₆H₃)₄), 7.01 (m, 2H, para-CH-Ph), 7.13 (m, 4H, meta-CH-Ph), 7.35 (m, 4H, ortho-CH-Ph) ppm. ¹³C{¹H} NMR (THF-d₈; 100.6 MHz): δ 22.5 (CH₃-B(3,5-Me₂-C₆H₃)₄), 25.3 (s, 12H, CH₃-Bpin, identified by HSQC), 43.7 (CH₃-Me₄TACD), 53.4 (CH₂-Me₄TACD), 123.8 (para-CH-B(3,5-Me₂-C₆H₃)₄), 126.3 (para-CH-Ph), 127.3 (ortho-CH-Ph), 128.4 (meta-CH-Ph), 133.2 (q, ³JBC = 2.9 Hz, meta-CH-B(3,5-Me₂-C₆H₃)₄), 135.7 (ortho-CH-B(3,5-Me₂-C₆H₃)₄), 153.9 (ipso-C-Ph), 165.9 (q, ¹JBC = 49.2 Hz, ipso-C-B(3,5-Me₂-C₆H₃)₄) ppm. ¹¹B{¹H} NMR (THF-d₈; 128.4 MHz): δ -7.00 ppm. Anal. calc. for C₅₇H₇₅N₄BOMg (867.37 g·mol⁻¹): C, 78.93; H, 8.72; N, 6.46; Mg, 2.80. Found: C, 76.68; H, 8.51; N, 6.17; Mg, 2.86 %.
$^1$H, $^{13}$C{${}^1$H}, and $^{11}$B{${}^1$H} NMR spectra of [(Me4TACD)Mg(OCHPh2)][B(3,5-Me2-C6H3)4] (7)

Figure S29. $^1$H NMR spectrum of 7 in THF-$d_8$ (*) at 25 °C.

Figure S30. $^{13}$C{${}^1$H} NMR spectrum of 7 in THF-$d_8$ (*) at 25 °C (# n-pentane, $:$ unidentified species).
Figure S31. $^{11}$B{$^1$H} NMR spectrum of 7 in THF-d$_8$ at 25 °C.

$^{(\text{Me}_{4}\text{TACD})}\text{Mg}(1,2\text{-DHP})][\text{B}(3,5\text{-Me}_{2}\text{C}_{6}\text{H}_{3})_4]$ (8a). To a solution of $^{[(\text{Me}_{4}\text{TACD})_2\text{Mg}_2(\mu\text{-H})_2][B(3,5\text{-Me}_{2}\text{C}_{6}\text{H}_{3})_4]}$ (2) (103 mg, 0.05 mmol) in THF (4 mL) was added a solution of neat pyridine (12 μL, 12 mg, 0.1 mmol) and the reaction mixture was stirred for 2 h at 50 °C. The solvent was removed under reduced pressure and the colorless solid residue was washed with n-pentane (9 mL). The solid was dried under vacuum to give $^{[(\text{Me}_{4}\text{TACD})\text{Mg}(1,2\text{-DHP})][\text{B}(3,5\text{-Me}_{2}\text{C}_{6}\text{H}_{3})_4]}$ (8a) (100 mg, 0.13 mmol) as slightly yellow powder in 87% yield. Crystals suitable for X-ray analysis were obtained from layering a highly concentrated THF solution with benzene.

$^1$H NMR (THF-d$_8$; 400.1 MHz): δ 2.10 (s, 24H, CH$_3$-[B(3,5-Me$_2$C$_6$H$_3$)$_4$]), 2.30-2.44 (m, 16H, CH$_2$-Me$_4$TACD), 2.35 (s, 12H, CH$_3$-Me$_4$TACD), 3.46 (d, 2H, 3$^J_{\text{HH}} = 4.3$ Hz, 2H-NC$_5$H$_6$), 4.21 (dtdd, 1H, 3$^J_{\text{HH}} = 8.3$ Hz, 3$^J_{\text{HH}} = 6.0$ Hz, 6$_^J_{\text{HH}} = 0.8$ Hz, 3H-NC$_5$H$_6$), 4.72 (dd, 1H, 3$^J_{\text{HH}} = 5.5$ Hz, 3$^J_{\text{HH}} = 6.0$ Hz, 6$_^J_{\text{HH}} = 0.8$ Hz, 6H-NC$_5$H$_6$), 5.76 (dd, 1H, 3$^J_{\text{HH}} = 8.3$ Hz, 3$^J_{\text{HH}} = 5.5$ Hz, 4H-NC$_5$H$_6$), 6.38 (m, 4H, para-CH-B(3,5-Me$_2$C$_6$H$_3$)$_4$), 6.45 (dd, 1H, 3$^J_{\text{HH}} = 6.0$ Hz, 5$_^J_{\text{HH}} = 0.8$ Hz, 6H-NC$_5$H$_6$), 7.00 (m, 8H, ortho-CH-B(3,5-Me$_2$C$_6$H$_3$)$_4$) ppm. $^{13}$C{$^1$H} NMR (THF-d$_8$; 100.6 MHz): δ 22.5 (CH$_3$-[B(3,5-Me$_2$C$_6$H$_3$)$_4$]), 43.8 (CH$_3$-Me$_4$TACD), 48.9 (1C-NC$_5$H$_6$), 53.7 (CH$_2$-Me$_4$TACD), 69.1 (2C-NC$_5$H$_6$), 69.4 (4C-NC$_5$H$_6$), 123.9 (para-CH-B(3,5-Me$_2$C$_6$H$_3$)$_4$), 128.1 (3C-
(NC₅H₆), 133.3 (q, Jᵦ = 2.9 Hz, meta-C-B(3,5-Me₂-C₆H₃)₄), 135.7 (ortho-CH-B(3,5-Me₂-C₆H₃)₄), 148.7 (5C-NC₅H₆), 165.9 (q, Jᵦ = 49.2 Hz, ipso-C-B(3,5-Me₂-C₆H₃)₄) ppm. ¹¹B{¹H}-NMR (THF-d₈; 128.4 MHz): δ −7.02 ppm. Anal. calc. for C₄₉H₇₀N₅BMg (764.25 g·mol⁻¹): C, 77.01; H, 9.23; N, 9.16; Mg, 3.18. Found: C, 74.77; H, 8.81; N, 8.92; Mg, 2.72 %.

¹H, ¹³C{¹H}, and ¹¹B{¹H} NMR spectra of [(Me₄TACD)Mg(1,2-DHP)][B(3,5-Me₂-C₆H₃)₄] (8a)

![NMR spectrum](image)

**Figure S32.** ¹H NMR spectrum of 8a in THF-d₈ (*) at 25 °C.
**Figure S33.** $^{13}$C{$^1$H} NMR spectrum of 8a in THF-$d_8$ (*) at 25 °C (# benzene).

**Figure S34.** $^{11}$B{$^1$H} NMR spectrum of 8a in THF-$d_8$ at 25 °C.
[(Me₄TACD)Mg(1,4-DHP)][B(3,5-Me₂-C₆H₃)₄] (8b). To a solution of [(Me₄TACD)Mg(1,2-DHP)][B(3,5-Me₂-C₆H₃)₄] (2) (76 mg, 0.1 mmol) in THF (5 mL) a solution of [Mg(THF)₆][B(3,5-Me₂-C₆H₃)₄] (9) (13 mg, 0.01 mmol; 10 mol%) was added and the reaction mixture was heated to 70 °C for 4 h. The solvent was removed under reduced pressure and the colorless solid residue was washed with n-pentane (3 x 3 mL). The solid was dried under vacuum and was crystallized from THF/cyclohexane at −30 °C over a period of 3 days to give [(Me₄TACD)Mg(1,4-DHP)][B(3,5-Me₂-C₆H₃)₄] (8b) (65 mg, 0.08 mmol) as colorless powder in 85% yield. ¹H NMR (THF-d₈; 400.1 MHz): δ 2.10 (s, 24H, CH₃-B(3,5-Me₂-C₆H₃)₄), 2.23 - 2.41 (m, 16H, CH₂-Me₄TACD), 2.33 (s, 12H, CH₃-Me₄TACD), 3.09 (m, 2H, 4H-NC₅H₆), 3.83 (m, 2H, 3H-NC₅H₆), 5.78 (m, 2H, 2H-NC₅H₆), 6.38 (m, 4H, para-CH-B(3,5-Me₂-C₆H₃)₄), 7.01 (m, 8H, ortho-CH-B(3,5-Me₂-C₆H₃)₄) ppm. ¹³C{¹H} NMR (THF-d₈; 100.6 MHz): δ 22.5 (CH₃-B(3,5-Me₂-C₆H₃)₄), 43.9 (CH₃-Me₄TACD), 25.5 (4C-NC₅H₆; overlapped by THF-d₈ signal but identified by HSQC), 53.6 (CH₂-Me₄TACD), 93.8 (3C-NC₅H₆), 123.9 (para-CH-B(3,5-Me₂-C₆H₃)₄), 133.3 (q, ᵃJBC = 2.9 Hz, meta-C-B(3,5-Me₂-C₆H₃)₄), 135.7 (ortho-CH-B(3,5-Me₂-C₆H₃)₄), 138.9 (2C-NC₅H₆), 165.9 (q, ᵃJBC = 49.2 Hz, ipso-C-B(3,5-Me₂-C₆H₃)₄) ppm. ¹¹B{¹H} NMR (THF-d₈; 128.4 MHz): δ −7.00 ppm. Anal. calc. for C₄₉H₇₀N₅BMg (764.25 g·mol⁻¹): C, 77.01; H, 9.23; N, 9.16; Mg, 3.18. Found: C, 74.09; H, 9.10; N, 8.80.

¹H, ¹³C{¹H}, and ¹¹B{¹H} NMR spectra of [(Me₄TACD)Mg(1,4-DHP)][B(3,5-Me₂-C₆H₃)₄] (8b)
Figure S35. $^1$H NMR spectrum of 8b in THF-$d_8$ (*) at 25 °C.

Figure S36. $^{13}$C{$^1$H} NMR spectrum of 8b in THF-$d_8$ (*) at 25 °C (# unidentified species).
[Mg(THF)₆][B(3,5-Me₂-C₆H₃)₄]₂ (9). To a solution of [Mg(²-Bu)₂] (14 mg; 0.1 mmol) in THF (2 mL) a suspension of [NEt₃H][B(3,5-Me₂-C₆H₃)₄] (107 mg, 0.2 mmol) was added and the reaction mixture was stirred for 16 h at room temperature. The solvent was removed under vacuum and the colorless residue was washed with n-pentane (3 mL). The solvent was dried under vacuum and [Mg(THF)₆][B(3,5-Me₂-C₆H₃)₄]₂ (9) (98 mg, 0.07 mmol) was obtained in 74% yield. ¹H NMR (THF-d₈; 400.1 MHz): δ = 2.08 (s, 48H, C₃H₃-B(3,5-Me₂-C₆H₃)₄), 6.35 (m, 8H, para-CH-B(3,5-Me₂-C₆H₃)₄), 6.96 (m, 16H, ortho-CH-B(3,5-Me₂-C₆H₃)₄) ppm. ¹³C{¹H} NMR (THF-d₈; 100.6 MHz): δ = 22.5 (CH₃-[B(3,5-Me₂-C₆H₃)₄]), 123.6 (para-CH-B(3,5-Me₂-C₆H₃)₄), 133.0 (q, J_B-C = 2.9 Hz, meta-C-B(3,5-Me₂-C₆H₃)₄), 135.6 (ortho-CH-B(3,5-Me₂-C₆H₃)₄), 165.8 (q, J_B-C = 49.2 Hz, ipso-C-B(3,5-Me₂-C₆H₃)₄) ppm. ¹¹B{¹H} NMR (THF-d₈; 128.4 MHz): δ = −6.93 ppm. Anal. calcd. for C₈₈H₁₂₀B₂O₆Mg (1319.85 g·mol⁻¹): C, 80.08; H, 9.16; Mg, 1.84. Found: C, 78.76; H, 9.24.

Figure S37. ¹¹B{¹H} NMR spectrum of 8b in THF-d₈ at 25 °C.
$^1$H, $^{13}$C$^1{^1}$H, and $^{11}$B$^1{^1}$H NMR spectra of [Mg(THF)$_6$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$\cdot$2 (9)

![NMR spectra](image)

Figure S38. $^1$H NMR spectrum of 9 in THF-$d_8$ (*) at 25 °C.

![NMR spectra](image)

Figure S39. $^{13}$C$^1{^1}$H NMR spectrum of 9 in THF-$d_8$ (*) at 25 °C.
Solid state structure of $[\text{Mg(THF)}_6][(\text{B}(3,5-\text{Me}_2-\text{C}_6\text{H}_3)_4)]_2$ (9).

Single crystals of $[\text{Mg(THF)}_6][\text{B}(3,5-\text{Me}_2-\text{C}_6\text{H}_3)_4]_2$ (9) were obtained from a THF/n-hexane mixture at $-30 \, ^\circ\text{C}$ over a period of 16 h. 9 displays a solvent separated ion pair containing a cationic magnesium centre coordinated by six oxygen atoms and two $[\text{B}(3,5-\text{Me}_2-\text{C}_6\text{H}_3)_4]$ anions. The structure of $[\text{Mg(THF)}_6][\text{B}(3,5-\text{Me}_2-\text{C}_6\text{H}_3)_4]_2$ (9) is similar to that of $[\text{Mg(THF)}_6][\text{BPh}_4]_2$. The only difference is that herein each solvated cation is surrounded by a framework of four instead of eight borate anions due to the higher steric demand of the $[\text{B}(3,5-\text{Me}_2-\text{C}_6\text{H}_3)_4]$ anion compared to the $[\text{BPh}_4]$ anion (Figure S41).
Isomerization of \([(\text{Me}_4\text{TACD})\text{Mg}(1,2\text{-DHP})][\text{B}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\text{d}_4]\) (8a) into \([(\text{Me}_4\text{TACD})\text{Mg}(1,4\text{-DHP})][\text{B}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\text{d}_4]\) (8b) in the presents of \([\text{Mg(THF)}\text{_6}][\text{B}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\text{d}_4]\) (9) in THF-\text{d}_8 at 70 °C.

To investigate the reaction of 8a into 8b in the presents of \([\text{Mg(THF)}\text{_6}][\text{B}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\text{d}_4]\) (9) in THF-\text{d}_8 samples with \([(\text{Me}_4\text{TACD})\text{Mg}(1,2\text{-DHP})][\text{B}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\text{d}_4]\) (8a) (7.6 mg; 0.01 mmol), \([\text{Mg(THF)}\text{_6}][\text{B}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\text{d}_4]\) (9) (1.3 mg; 0.001 mmol; 10 mol%) and hexamethylbenzene (internal standard: 1.6 mg; 0.01 mmol) in THF-\text{d}_8 (0.5 mL) were prepared. The samples were heated up to 70 °C and the conversion of 8a into 8b was monitored by \textsuperscript{1}H NMR spectroscopy. The plot of the concentration of 8a versus time is shown in Figure S42. The reaction follows a zero order kinetics and a reaction rate of \(k = (1.64\pm0.06)\times10^{-6} \text{ mol\cdot L}^{-1}\cdot\text{s}^{-1}\) is determined.
Exchange reactions of [(Me₄TACD)Mg(1,2-DHP)][B(3,5-Me₂-C₆H₃)₄] (8a) and [(Me₄TACD)Mg(1,4-DHP)][B(3,5-Me₂-C₆H₃)₄] (8b) in pyridine-d₅

To investigate the reactions of 8a and 8b with pyridine-d₅ samples with [(Me₄TACD)Mg(1,2-DHP)][B(3,5-Me₂-C₆H₃)₄] (8a) or [(Me₄TACD)Mg(1,4-DHP)][B(3,5-Me₂-C₆H₃)₄] (8b) (7.6 mg; 0.01 mmol) and hexamethylbenzene (internal standard: 1.6 mg; 0.01 mmol) in pyridine-d₅ (0.5 mL) were prepared. 8a and 8b show slow exchange in pyridine-d₅ at 70 °C under the formation of a mixed deuterohydropyridyl species (8a-4H-d₅ and 8b-4H-d₅). Further reaction to the completely deuterated species (8a-d₆ and 8b-d₆) proceeded over time. The products 8b-4H-d₅ and 8b-d₆ are identified by ¹H and ²D NMR spectroscopy (Figure S43).
Figure S43. $^1$H NMR spectrum of [(Me$_4$TACD)Mg(1,4-DHP)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (8b) in pyridine-$d_5$ (*) after 17 h at 70 °C (top) and 2D NMR spectrum of the reaction of [(Me$_4$TACD)Mg(1,4-DHP)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (8b) in pyridine-$d_5$ after 5 days at 70 °C, dried and diluted in pyridine with benzene-$d_6$ (S) as internal standard (bottom).

The amount of 8a and 8b in the reaction mixture was determined by $^1$H NMR spectroscopy. The plot of ln(c/c$_0$) versus time is shown in Figure S44.
Crystal Structure Determinations

X-ray diffraction data were collected at –173 °C on a Bruker D8 goniometer with APEX CCD area-detector (1, 6, 8a) or on an Eulerian 4-circle diffractometer STOE STADIVARI (2, 3, 4, 9) in ω-scan mode. All structures were solved by direct methods using SIR-97.[9] The crystal lattice of 2 contains co-crystallized THF, the crystal of 4 contains THF as well as cyclohexane, the crystal of 8a contains co-crystallized benzene. The structure of 9 reveals crystallographically imposed inversion symmetry for the cationic fragment $[\text{Mg(C}_4\text{H}_8\text{O)}_6]^{2+}$ fragment with the atom Mg1 located on Wyckoff position 2a.

All refinements were carried out against $F^2$ with SHELXL[10] with anisotropic displacement parameters for the non-hydrogen atoms, as implemented in the program system WinGX.[11] Hydrogen atoms were included in calculated positions and were treated as riding during the refinement. The hydride atoms of the central Mg$_2$H$_2$ fragment in 1 were located in a Fourier difference map and refined in their position. In 2, related positions for the Mg$_2$H$_2$ hydrides were located in a single Fourier difference map with 0.64 and 0.71 e Å$^{-3}$, but their position could not be reliably refined due to the disorder in this data set. Using these positions for hydrogen atoms H1 and H2, refinement of their isotropic displacement parameters gave values that agree well with the other atoms of this structure. The hydrogen atoms of the BH$_4$ fragment in 3 (H1, H2, H3 and H4),
of the BH$_2$ unit in 4 (H1A and H1B), as well as of the C$_{5}$H$_6$B ring in 8a (H13, H14, H15, H16, H17A, H17B) were refined in their position.

Disorder was revealed in the structure of 2, where it was taken into account by split positions for the atoms C13 – C20 (methylene units) and C23, C24 (methyl units) of a Me$_4$TACD ligand, as well as for both co-crystallized THF ligands (C90, as well as O2, C93 – C96). The split positions within the THF molecules were refined with isotropic displacement parameters. Attempted refinement with anisotropic parameters did not lead to physically meaningful values. Due to the pronounced disorder within one of these THF molecules, same distance restraints (SAME instruction within the program SHELXL) were used in the refinement. The crystal structure of 9 shows a small disorder within a THF ligand coordinated to the metal centre that could be resolved by split positions for the positions of C10 and C11.

In the refinement of the crystal structure of 2, twinning was taken into account by a twin rotation matrix (-1 0 0, 0 1 0, 0 0 -1) relating two components with a batch scale factor (BASF) of 0.48766. Figure S45 shows the staggered conformation of the magnesium compound 2 in comparison to the previously described calcium complex [(Me$_4$TACD)$_2$Ca$_2$(µ-H)$_2$]$^{2+}$ and the lutetium complex [(Me$_4$TACD)$_2$Lu$_2$(µ-H)$_4$]$^{2+}$.[12, 13]

Graphical representations were obtained with the program DIAMOND.[14] CCDC-1891829 (1), CCDC-1891830 (2), CCDC-1891831 (3), CCDC-1891832 (4) and CCDC-1891833 (6), CCDC-1891834 (8a) and CCDC-189182935 (9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table S1. Crystallographic data of 1, 2, 3 and 4.

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Table S2. Crystallographic data of 6, 8a and 9.

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S39
**DFT Calculations**

**Computational details**

Quantum-chemical calculations were performed with the Gaussian09 suite of programs (revision D.02)\(^{14}\) using the Becke’s 3-parameter hybrid functional\(^{15}\) combined with the non-local correlation functional provided by Perdew/Wang\(^{16}\). The 6-311+G(d) all-electron basis set was used for the magnesium atom, and the 6-31G(d) for the remaining atoms\(^{17}\).

We have also considered in the present study the dispersion effects. In particular the third generation of Grimme’s dispersion corrections with Becke-Johnson damping\(^{18}\) model on the B3PW91 geometries (single point calculations). All stationary points have been identified for minimum (Nimag = 0) Natural population analysis (NPA) was performed using Weinhold’s methodology\(^{19}\).
Figure S46. HOMO of the molecular dication \([(\text{Me}_4\text{TACD})_2\text{Mg}_2(\mu-\text{H})_2]^2^+\) (2).

The HOMO of the molecular dication in the complex \([(\text{Me}_4\text{TACD})_2\text{Mg}_2(\mu-\text{H})_2][\text{B}(3,5-\text{Me}_2\text{C}_6\text{H}_3)_4]\) clearly shows the bonding of the hydrides within the central \(\text{Mg}_2\text{H}_2\) fragment. The disruption of the dimer by THF to give the associated monomers was computed to be favorable by 35.9 kcal/mol. In the absence of THF, the corresponding disruption is favored by 34.0 kcal/mol what indicates that the THF only has a minor stabilizing effect on the monomer.

Table S3. Cartesian coordinates of optimized structures

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