Electronic Supporting Information

**Unexpected alkane elimination from cationic group 13 dialkyls in reaction with a macrocyclic polyamine.**

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**General remarks.**

All manipulations were performed under argon atmosphere using standard Schlenk or glove box techniques. Prior to use, glasswares were dried overnight at 130 °C and solvents were dried, distilled and degassed using standard methods. NMR measurements were performed on a Bruker DRX 400 at ambient temperature unless otherwise mentioned. The chemical shifts (δ ppm) in the 1H and 13C{1H NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane. Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), sep (septet), br. (broad), IR spectra were measured on KBr pellets using an AVATAR 360 FT-IR spectrometer. Abbreviations for IR spectra: w (weak), m (medium), s (strong), br. (broad). Me₃TACDH, Li-Me₃TACD, InMe₃, B(C₆F₅)₃, and [In(CH₂SiMe₃)₂(thf)]₂[B(C₆F₅)₄] were synthesized according to literature procedures. AlMe₃ and AlMe₂Cl were purchased from Sigma-Aldrich. [PhNHMe₂][B(C₆F₅)₄] was purchased from Boulder Scientific. Elemental analyses were performed on an **elementar vario EL** machine. X-ray diffraction data were collected on a Bruker APEX II diffractometer. Single crystal diffraction data is reported in crystallographic information files (cif) accompanying this document.

**Me₃TACDH.**

1H NMR (400 MHz, THF-d₈): δ 2.18 (s, 3 H, Me₃-TACD), 2.24 (s, 6 H, Me₃-TACD), 2.34-2.42 (m, 11 H, CH₂), 2.50-2.57 (m, 5 H, CH₂), 2.82 (br, s, 1 H, NH).
Figure S1. $^1$H NMR spectrum of Me$_3$TACDH in THF-$d_8$.

(Me$_3$TACDH)AlMe$_3$ (1).

AlMe$_3$ (0.036 g, 0.500 mmol) and Me$_3$TACDH (0.107 g, 0.500 mmol) were dissolved together in 1 mL of pentane. After 10 min, volatiles were removed under reduced pressure to obtain 0.135 g of analytically pure (Me$_3$TACDH)AlMe$_3$ (0471 mmol, 95%) as a colorless oily substance. $^1$H NMR (400 MHz, THF-$d_8$): δ −1.00 (s, 9 H, AlMe$_3$), 2.23 (s, 3 H, Me$_3$-TACD), 2.25 (s, 6 H, Me$_3$-TACD), 2.46 (br, s, 8 H, CH$_2$), 2.49-2.52 (m, 4 H, CH$_2$), 2.71 (br, s, 4 H, CH$_2$), 4.88 (br, s, 1 H, NH). $^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$): δ −8.2 (AlMe), 43.4 (Me$_3$-TACD), 50.0 (CH$_2$), 52.4 (CH$_2$), 54.3 (CH$_2$), 54.5 (CH$_2$). IR (KBr, cm$^{-1}$): 3453 (w, br, νNH), 3048 (m), 2921 (s, br), 2795 (s, br), 1459 (s), 1363 (m), 1304 (m), 1237 (w), 1179 (m), 1116 (m), 1075 (m), 1034 (m), 1012 (w), 966 (w), 912 (w), 815 (w), 745 (m), 694 (m), 622 (m), 584 (w). Anal. Calcd. for C$_{14}$H$_{35}$N$_4$Al: C, 58.70; H, 12.32; N, 19.56. Found: C, 58.61; H, 12.55; N, 19.64.
Figure S2. $^1$H NMR spectrum of (Me$_3$TACDH)AlMe$_3$ in THF-$d_8$.

Figure S3. $^1$H NMR spectrum of (Me$_3$TACDH)AlMe$_3$ in C$_6$D$_6$. 
Figure S4. $^{13}$C NMR spectrum of (Me$_3$TACDH)AlMe$_3$ in C$_6$D$_6$.

Figure S5. Solid-state IR (KBr pellet) spectrum of (Me$_3$TACDH)AlMe$_3$.

(Me$_3$TACDH)InMe$_3$ (2).
InMe$_3$ (0.090 g, 0.560 mmol) and Me$_3$TACDH (0.120 g, 0.560 mmol) were dissolved together in 1 mL of pentane. After 10 min, volatiles were removed under reduced pressure to obtain 0.202 g of analytically pure (Me$_3$TACDH)InMe$_3$ (0.540 mmol, 96%) as a colorless oily substance. $^1$H NMR (400 MHz, THF-$d_8$): $\delta$ –0.55 (s, 9 H, InMe$_3$), 2.23 (s, 3 H, Me$_3$-TACD), 2.25 (s, 6 H, Me$_3$-TACD), 2.37-2.40 (m, 4 H, CH$_2$), 2.42-2.45 (m, 4 H, CH$_2$), 2.43-2.50 (m, 4 H, CH$_2$), 2.62-2.66 (m, 4 H, CH$_2$), 4.11 (br, s, 1 H, NH). $^{13}$C {$^1$H} NMR (100 MHz, C$_6$D$_6$): $\delta$ –7.3 (InMe), 43.6 (Me$_3$-TACD), 43.9 (Me$_3$-TACD), 48.4 (CH$_2$), 54.3 (CH$_2$), 54.7 (CH$_2$), 56.6
(CH₂). IR (KBr, cm⁻¹): 3167-3097 (w, br, νNH), 2950 (s), 2903 (s), 2839 (s), 2792 (s), 1456 (s), 1361 (m), 1304 (m), 1236 (w), 1215 (w), 1126 (m), 1073 (m), 1034 (m), 1003 (w), 973 (w), 903 (w), 818 (w), 745 (m), 684 (s). Anal. Calcd. for C₁₄H₃₅N₄In: C, 44.93; H, 9.43; N, 14.97. Found: C, 44.71; H, 9.25; N, 14.82.

Figure S6. ¹H NMR spectrum of (Me₃TACDH)InMe₃ in THF-d₈.

Figure S7. ¹H NMR spectrum of (Me₃TACDH)InMe₃ in C₆D₆.
Figure S8. $^{13}$C NMR spectrum of (Me$_3$TACDH)InMe$_3$ in C$_6$D$_6$.

Figure S9. Solid-state IR (KBr pellet) spectrum of (Me$_3$TACDH)InMe$_3$.

[(Me$_3$TACD)AlMe][MeB(C$_6$F$_5$)$_3$] (3).

B(C$_6$F$_5$)$_3$ (0.114 g, 0.222 mmol) and AlMe$_3$ (0.016 g, 0.222 mmol) were dissolved in 1 mL of THF to produce [AlMe$_2$(thf)$_x$][MeB(C$_6$F$_5$)$_3$] in situ. After 5 min, this solution was added to another 1 mL THF solution of Me$_3$TACDH (0.048 g, 0.222 mmol). The resulting mixture was stirred for 1 h at room temperature. Subsequently, all the volatiles were removed under reduced pressure to obtain a white solid. Washing the solid with pentane (3 × 5 mL) and further drying under vacuum afforded analytically pure [(Me$_3$TACD)AlMe][MeB(C$_6$F$_5$)$_3$] (0.145 g, 0.185 mmol, 83% yield) as a white powder. Performing the same reaction in NMR-
scale in a J. Young tube confirmed the generation of \( \text{CH}_4 \) as evident by the \( ^1\text{H} \) NMR spectrum.

\( ^1\text{H} \) NMR (400 MHz, THF-\( d_8 \)): \( \delta \) -0.75 (s, 3 H, AlMe), 0.51 (br, s, 3 H, BMe), 2.54 (s, 6 H, \( \text{Me}_3\text{TACD} \)), 2.66 (s, 3 H, \( \text{Me}_3\text{TACD} \)), 2.76-3.03 (m, 14 H, \( \text{CH}_2 \)), 3.12-3.19 (m, 2 H, \( \text{CH}_2 \)).

\( ^{13}\text{C}\{^1\text{H}\} \) NMR (100 MHz, THF-\( d_8 \)): \( \delta \) -14.3 (AlMe), 10.9 (BMe) 44.0 (\( \text{Me}_3\text{TACD} \)), 46.2 (\( \text{Me}_3\text{TACD} \)), 46.4 (\( \text{CH}_2 \)), 52.0 (\( \text{CH}_2 \)), 56.2 (\( \text{CH}_2 \)), 60.9 (\( \text{CH}_2 \)), 136.2 (\( \text{C}_6\text{F}_5 \)), 137.3 (\( \text{C}_6\text{F}_5 \)), 138.5 (\( \text{C}_6\text{F}_5 \)), 148.3 (\( \text{C}_6\text{F}_5 \)), 150.7 (\( \text{C}_6\text{F}_5 \)).

\( ^{11}\text{B} \) NMR (128 MHz, THF-\( d_8 \)): \( \delta \) -14.9.

\( ^{19}\text{F} \) NMR (THF-\( d_8 \), 377 MHz): \( \delta \) -168.9, -166.7, -132.7. IR (KBr, cm\(^{-1}\)): 2958 (s, br), 2831 (s, br), 1641 (s), 1513 (s), 1456 (s), 1356 (m), 1270 (s), 1198 (m), 1125 (m), 1087 (s), 1039 (m), 976 (s), 954 (s), 928 (s), 876 (w), 837 (m), 803 (w), 760 (m), 695 (s), 658 (s), 601 (m), 568 (m). Anal. Calcd. for \( \text{C}_{31}\text{H}_{31}\text{BF}_{15}\text{N}_4\text{Al} \): C, 47.59; H, 3.99; N, 7.16. Found: C, 47.71; H, 3.85; N, 7.32.

**Figure S10.** \( ^1\text{H} \) NMR spectrum of \([\text{Me}_3\text{TACD}]\text{AlMe}[\text{MeB(C}_6\text{F}_5)_3] \) in THF-\( d_8 \) recorded from the NMR-scale reaction. Singlet resonance at \( \delta \) 0.18 ppm confirmed the generation of \( \text{CH}_4 \).
Figure S11. $^{13}$C NMR spectrum of [(Me$_3$TACD)AlMe][MeB(C$_6$F$_5$)$_3$] in THF-$d_8$.

Figure S12. $^{11}$B{${^1}$H} NMR spectrum of [(Me$_3$TACD)AlMe][MeB(C$_6$F$_5$)$_3$] in THF-$d_8$. 
**Figure S13.** $\text{^{19}F-}^{1}H$ NMR spectrum of [(Me$_3$TACD)AlMe][MeB(C$_6$F$_5$)$_3$] in THF-$d_8$.

**Figure S14.** Solid-state IR (KBr pellet) spectrum of [(Me$_3$TACD)AlMe][MeB(C$_6$F$_5$)$_3$].

[(Me$_3$TACD)InMe][MeB(C$_6$F$_5$)$_3$] (4).

B(C$_6$F$_5$)$_3$ (0.096 g, 0.187 mmol) and InMe$_3$ (0.030 g, 0.187 mmol) were dissolved in 1 mL of THF to produce [InMe$_2$(thf)$_3$][MeB(C$_6$F$_5$)$_3$] in situ. After 5 min, this solution was added to another 1 mL THF solution of Me$_3$TACDH (0.040 g, 0.187 mmol). The resulting mixture was stirred for 6 h at room temperature. Subsequently, all the volatiles were removed under reduced pressure to obtain a white solid. Washing the solid with pentane (3 × 5 mL) and
further drying under vacuum afforded analytically pure \([(\text{Me}_{3}\text{TACD})\text{InMe}]\text{[MeB(C}_6\text{F}_5)_3]\) (0.138 g, 0.159 mmol, 85% yield) as a white powder. Performing the same reaction in NMR-scale in a J. Young tube confirmed the generation of CH\(_4\) as evident by the \(^1\)H NMR spectrum.

\(^1\)H NMR (400 MHz, THF-d\(_8\)): \(\delta\) 0.15 (br, s, 3 H, InMe), 0.51 (br, s, 3 H, BMe), 2.59 (s, 6 H, Me\(_3\)-TACD), 2.64 (s, 3 H, Me\(_3\)-TACD), 2.74-2.85 (m, 8 H, CH\(_2\)), 2.97-3.03 (m, 6 H, CH\(_2\)), 3.14-3.19 (m, 2 H, CH\(_2\)). \(^{13}\)C\(^{\text{\(^1\)H}}\) NMR (100 MHz, THF-d\(_8\)): \(\delta\) –9.4 (InMe), 10.8 (BMe) 44.2 (Me\(_3\)-TACD), 44.6 (Me\(_3\)-TACD), 49.4 (CH\(_2\)), 52.8 (CH\(_2\)), 54.6 (CH\(_2\)), 59.7 (CH\(_2\)), 136.2 (C\(_6\)F\(_5\)), 137.3 (C\(_6\)F\(_5\)), 138.6 (C\(_6\)F\(_5\)), 139.7 (C\(_6\)F\(_5\)), 148.2 (C\(_6\)F\(_5\)), 150.7 (C\(_6\)F\(_5\)). \(^{11}\)B NMR (128 MHz, THF-d\(_8\)): \(\delta\) –14.9. \(^{19}\)F NMR (THF-d\(_8\), 377 MHz): \(\delta\) –168.9, –166.7, –132.7. IR (KBr, cm\(^{-1}\)): 2925 (s, br), 1642 (s), 1521 (s), 1460 (s), 1383 (m), 1358 (m), 1302 (m), 1269 (s), 1086 (s), 1044 (m), 1026 (m), 965 (s, br), 935 (s, br), 837 (m), 803 (m), 757 (m), 737 (m), 689 (m), 661 (m), 571 (m). Anal. Calcd. for C\(_{31}\)H\(_{31}\)BF\(_{15}\)N\(_4\)In: C, 42.79; H, 3.59; N, 6.44. Found: C, 42.73; H, 3.51; N, 6.29.

**Figure S15.** \(^1\)H NMR spectrum of \([(\text{Me}_{3}\text{TACD})\text{InMe}]\text{[MeB(C}_6\text{F}_5)_3]\) in THF-d\(_8\) recorded from the NMR-scale reaction. Singlet resonance at \(\delta\) 0.18 ppm confirmed the generation of CH\(_4\).
Figure S16. $^{13}$C NMR spectrum of [(Me$_3$TACD)InMe][MeB( triF)$_3$] in THF-$d_8$.

Figure S17. $^{11}$B{H} NMR spectrum of [(Me$_3$TACD)InMe][MeB(triF)$_3$] in THF-$d_8$. 
Figure S18. $^{19}$F-$^1$H NMR spectrum of [(Me$_3$TACD)InMe][MeB(C$_6$F$_5$)$_3$] in THF-$d_8$.

Figure S19. Solid-state IR (KBr pellet) spectrum of [(Me$_3$TACD)InMe][MeB(C$_6$F$_5$)$_3$].

[(Me$_3$TACD)AlMe][B(C$_6$F$_5$)$_4$] (5).
A 2 mL THF solution of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (0.467 g, 0.583 mmol) was added to an 1 mL THF solution of AlMe$_3$ (0.042 g, 0.583 mmol). After 5 min, the resulting solution mixture was added to another 2 mL THF solution of Me$_3$TACDH (0.125 g, 0.583 mmol). This final mixture was then stirred for 1 h at room temperature. Subsequently, all the volatiles were removed under reduced pressure to obtain a white solid. Washing the solid with pentane (3 ×
5 mL) and further drying under vacuum afforded analytically pure [(Me3TACD)AlMe][B(C₆F₅)₄] (0.474 g, 0.507 mmol, 87% yield) as a white powder. X-ray quality single crystals were obtained from pentane diffusion into a concentrated THF solution at −35 ºC. ¹H NMR (400 MHz, THF-d₈): δ −0.74 (s, 3 H, AlMe), 2.55 (s, 6 H, Me₃-TACD), 2.67 (s, 3 H, Me₃-TACD), 2.77-3.04 (m, 14 H, CH₂), 3.13-3.20 (m, 2 H, CH₂). ¹³C{¹H} NMR (100 MHz, THF-d₈): δ −14.7 (AlMe), 44.1 (Me₃-TACD), 46.3 (Me₃-TACD), 46.4 (CH₂), 52.0 (CH₂), 56.3 (CH₂), 60.9 (CH₂), 136.1 (C₆F₅), 138.1 (C₆F₅), 138.5 (C₆F₅), 140.5 (C₆F₅), 148.2 (C₆F₅), 150.6 (C₆F₅). ¹¹B NMR (128 MHz, THF-d₈): δ −16.6. ¹⁹F NMR (THF-d₈, 377 MHz): δ −168.5, −165.0, −132.7. IR (KBr, cm⁻¹): 2952 (s, br), 2858 (s, br), 1644 (s), 1515 (s), 1464 (s), 1412 (w), 1375 (m), 1277 (s), 1086 (s), 980 (s), 928 (m), 775 (s), 756 (s), 684 (s), 661 (s), 611 (m), 573 (m). Anal. Calcd. for C₃₆H₂₈BF₂₀N₄Al: C, 46.27; H, 3.02; N, 6.00. Found: C, 45.98; H, 2.94; N, 5.84.

Figure S20. ¹H NMR spectrum of [(Me₃TACD)AlMe][B(C₆F₅)₄] in THF-d₈.
Figure S21. $^{13}$C{'H} NMR spectrum of [(Me$_3$TACD)AlMe][B(C$_6$F$_5$)$_4$] in THF-d$_8$.

Figure S22. $^{11}$B{'H} NMR spectrum of [(Me$_3$TACD)AlMe][B(C$_6$F$_5$)$_4$] in THF-d$_8$. 
Figure S23. $^{19}$F{¹H} NMR spectrum of [(Me₃TACD)AlMe][B(C₆F₅)₄] in THF-$d_8$.

Figure S24. Solid-state IR (KBr pellet) spectrum of [(Me₃TACD)AlMe][B(C₆F₅)₄].

[(Me₃TACD)InMe][B(C₆F₅)₄] (6).

A 2 mL THF solution of [PhNMe₂H][B(C₆F₅)₄] (0.300 g, 0.374 mmol) was added to an 1 mL THF solution of InMe₃ (0.060 g, 0.375 mmol). The resulting solution mixture was then added to another 2 mL THF solution of Me₃TACDH (0.081 g, 0.378 mmol). This final mixture was then stirred for 24 h at room temperature. Subsequently, all the volatiles were removed under reduced pressure to obtain a white solid. Washing the solid with pentane (3 × 5 mL) and further drying under vacuum afforded analytically pure [(Me₃TACD)InMe][B(C₆F₅)₄] (0.310 g).
g, 0.303 mmol, 81% yield) as a white powder. $^1$H NMR (400 MHz, THF-$d_8$): $\delta$ 0.07 (s, 3 H, InMe), 2.55 (s, 6 H, $M e_3$-TACD), 2.60 (s, 3 H, $M e_3$-TACD), 2.68-2.82 (m, 8 H, $C H_2$), 2.90-3.01 (m, 6 H, $C H_2$), 3.10-3.15 (m, 2 H, $C H_2$). $^{13}$C{$^1$H} NMR (100 MHz, THF-$d_8$): $\delta$ -13.4 (InMe), 44.1 ($M e_3$-TACD), 44.7 ($M e_3$-TACD), 50.3 ($C H_2$), 52.1 ($C H_2$), 55.4 ($C H_2$), 59.9 ($C H_2$), 136.1 ($C_6F_5$), 138.1 ($C_6F_5$), 138.5 ($C_6F_5$), 140.5 ($C_6F_5$), 148.2 ($C_6F_5$), 150.6 ($C_6F_5$). $^{11}$B NMR (128 MHz, THF-$d_8$): $\delta$ -16.6. $^{19}$F NMR (THF-$d_8$, 377 MHz): $\delta$ -168.3, -164.8, -132.6. IR (KBr, cm$^{-1}$): 2993 (m), 2974 (m), 2883 (s), 2837 (m), 2809 (w), 1644 (s), 1516 (s), 1463 (s), 1412 (m), 1374 (m), 1328 (w), 1303 (m), 1279 (s), 1168 (m), 1139 (m), 1086 (s), 1042 (m), 1028 (m), 979 (s), 911 (m), 841 (m), 775 (s), 756 (s), 726 (m), 689 (s), 662 (s), 611 (m), 602 (m), 573 (m). Anal. Calcd. for $C_{36}H_{28}BF_{20}N_4In$: C, 42.30; H, 2.76; N, 5.48. Found: C, 42.67; H, 2.93; N, 5.33.

Figure S25. $^1$H NMR spectrum of [(Me$_3$TACD)InMe][B(C$_6$F$_5$)$_4$] in THF-$d_8$. 

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**Figure S26.** $^{13}$C{1H} NMR spectrum of [(Me$_3$TACD)InMe][B(C$_6$F$_5$)$_4$] in THF-$_d_8$.

**Figure S27.** $^{11}$B{1H} NMR spectrum of [(Me$_3$TACD)InMe][B(C$_6$F$_5$)$_4$] in THF-$_d_8$.

**Figure S28.** $^{19}$F{1H} NMR spectrum of [(Me$_3$TACD)InMe][B(C$_6$F$_5$)$_4$] in THF-$_d_8$. 
[(Me₃TACD)InCH₂SiMe₃][B(C₆F₅)₄] (7).

A 2 mL THF solution of [In(CH₂SiMe₃)₂(thf)₃][B(C₆F₅)₄] (320 g, 0.270 mmol) was added to an 1 mL THF solution of Me₃TACDH (0.058 g, 0.271 mmol). The resulting solution mixture was stirred for 24 h at room temperature. Subsequently, all the volatiles were removed under reduced pressure to obtain a white solid. Washing the solid with pentane (3 × 5 mL) and further drying under vacuum afforded analytically pure [(Me₃TACD)InCH₂SiMe₃][B(C₆F₅)₄] (0.261 g, 0.238 mmol, 88% yield) as a white powder. X-ray quality single crystals were obtained from pentane diffusion into a concentrated THF solution at –35 °C. ¹H NMR (400 MHz, THF-d₈): δ –0.10 (s, 2 H, InCH₂SiMe₃), 0.11 (s, 9 H, InCH₂SiMe₃), 2.55 (s, 6 H, Me₃TACD), 2.60 (s, 3 H, Me₃TACD), 2.68-2.82 (m, 8 H, CH₂), 2.90-3.01 (m, 6 H, CH₂) 3.10-3.15 (m, 2 H, CH₂). ¹³C{¹H} NMR (100 MHz, THF-d₈): δ −5.4 (InCH₂SiMe₃), 2.1 (InCH₂SiMe₃), 44.4 (Me₃-TACD), 44.4 (Me₃-TACD), 50.1 (CH₂), 52.2 (CH₂), 55.0 (CH₂), 59.5 (CH₂), 136.1 (C₆F₅), 138.1 (C₆F₅), 138.5 (C₆F₅), 140.6 (C₆F₅), 148.2 (C₆F₅), 150.6 (C₆F₅). ¹¹B NMR (128 MHz, THF-d₈): δ −16.6. ¹⁹F NMR (THF-d₈, 377 MHz): δ −168.5, −165.0, −132.7. IR (KBr, cm⁻¹): 2956 (m, br), 2858 (m, br), 1644 (s), 1515 (s), 1463 (s), 1411 (w), 1384 (m), 1373 (w), 1304 (w), 1275 (s), 1247 (m), 1109 (s), 1087 (s), 1030 (m), 978 (s), 908 (w), 868 (s), 836 (s), 773 (s), 756 (s), 713 (m), 690 (s), 661 (s), 608 (w), 570 (w). Anal. Calcd. for C₃₉H₄₀BF₂₀N₄SiIn: C, 42.80; H, 3.32; N, 5.12. Found: C, 43.07; H, 3.54; N, 5.39.
Figure S30. $^1$H NMR spectrum of [(Me$_3$TACD)InCH$_2$SiMe$_3$][B(C$_6$F$_5$)$_4$] in THF-$d_8$.

Figure S31. $^{13}$C\{$^1$H\} NMR spectrum of [(Me$_3$TACD)InCH$_2$SiMe$_3$][B(C$_6$F$_5$)$_4$] in THF-$d_8$. 
Figure S32. $^{11}$B$^{\text{1H}}$ NMR spectrum of [(Me$_3$TACD)InCH$_2$SiMe$_3$][B(C$_6$F$_5$)$_4$] in THF-$d_8$.

Figure S33. $^{19}$F$^{\text{1H}}$ NMR spectrum of [(Me$_3$TACD)InCH$_2$SiMe$_3$][B(C$_6$F$_5$)$_4$] in THF-$d_8$. 
Figure S34. Solid-state IR (KBr pellet) spectrum of [(Me₃TACD)InCH₂SiMe₃][B(C₆F₅)₄].

(Me₃TACD)Li(μ-Cl)AlMe₂ (8).
A 2 mL THF solution of (Li-Me₃TACD)₂ (0.064 g, 0.292 mmol) was added to another 2 mL THF solution of AlMe₂Cl (0.027 g, 0.292 mmol). The solution mixture was stirred for 2 h at room temperature. All the volatiles were then removed to obtain a white solid residue. It was then extracted with n-pentane (3 x 5 mL). Removal of n-pentane from the combined extract afforded analytically pure [(Me₃TACD)Li(μ-Cl)AlMe₂] (0.062 g, 0.198 mmol, 68%) as a colorless white powder. ¹H NMR (400 MHz, benzene-d₆): δ -0.04 (s, 6 H, AlMe₂), 1.61-1.67 (m, 2 H, CH₂), 1.76-1.90 (m, 10 H, Me₃-TACD and CH₂), 2.05-2.12 (m, 8 H, Me₃-TACD and CH₂), 2.31-2.36 (m, 2 H, CH₂), 3.56-3.63 (m, 2 H, CH₂), 3.56-3.63 (m, 2 H, CH₂). ¹³C{¹H} NMR (benzene-d₆, 100 MHz): δ 40.0 (Me₃-TACD), 43.2 (Me₃-TACD), 51.7 (CH₂), 53.3 (CH₂), 55.5 (CH₂), 60.3 (CH₂). ⁷Li{¹H} NMR (156 MHz, benzene-d₆): δ 1.1. IR (KBr, cm⁻¹): 2924 (s, br), 2853 (s, br), 1464 (s), 1361 (s), 1317 (m), 1272 (m), 1193 (s), 1171 (s), 1127 (s), 1107 (s), 1084 (m), 1065 (s), 1043 (s), 1030 (m), 1017 (m), 976 (m), 907 (s), 844 (s), 755 (w), 691 (s), 666 (s). Anal. Calcd. for C₁₃H₃₁N₄ClLiAl: C, 49.92; H, 9.99; N, 17.91. Found: C, 49.68; H, 9.64; N, 17.67.
Figure S35. $^1$H NMR spectrum of (Me$_3$TACD)Li(μ-Cl)AlMe$_2$ in benzene-$d_6$.

Figure S36. $^{13}$C{^1}H NMR spectrum of (Me$_3$TACD)Li(μ-Cl)AlMe$_2$ in benzene-$d_6$. 
Figure S37. $^7$Li$^1$H NMR spectrum of (Me$_3$TACD)Li(µ-Cl)AlMe$_2$ in benzene-$d_6$.

Figure S38. Solid-state IR spectrum of (Me$_3$TACD)Li(µ-Cl)AlMe$_2$.

**InMe$_2$Cl.**

A 2 mL THF solution of Ph$_3$CCl (0.420 g, 1.506 mmol) was added to another 2 mL THF solution of InMe$_3$ (0.241 g, 1.507 mmol). Immediately upon mixing, the solution turned from colorless to bright yellow. Volatiles were removed to obtain a yellow solid residue. Recrystallization of this material from concentrated n-pentane solution at −35 °C afforded InMe$_2$Cl (0.2440 g, 1.356 mmol, 90%) as a white crystalline solid.
\((\text{Me}3\text{TACD})\text{Li(}\mu\text{-Cl})\text{InMe}_2\) (9).

\((\text{Li-}\text{Me}_3\text{TACD})_2\) (0.081 g, 0.368 mmol) and \(\text{InMe}_2\text{Cl}\) (0.066 g, 0.366 mmol). The solution mixture was stirred for 2 h at room temperature. All the volatiles were then removed to obtain a white solid residue. It was then extracted with n-pentane (3 x 5 mL). Removal of n-pentane from the combined extract afforded analytically pure \([(\text{Me}_3\text{TACD})\text{Li(}\mu\text{-Cl})\text{InMe}_2]\) (0.113 g, 0.282 mmol, 77%) as a colorless white powder. \(\delta\) 0.22 (s, 6 H, \(\text{InMe}_2\)), 1.66-1.72 (m, 2 H, \(\text{CH}_2\)), 1.77-1.96 (m, 9 H, \(\text{Me}_3\text{-TACD}\) and \(\text{CH}_2\)), 2.02-2.08 (m, 2 H, \(\text{CH}_2\)), 2.15-2.21 (m, 8 H, \(\text{Me}_3\text{-TACD}\) and \(\text{CH}_2\)), 2.50-2.55 (m, 2 H, \(\text{CH}_2\)), 3.30-3.37 (m, 2 H, \(\text{CH}_2\)). \(^{13}\text{C}\{^1\text{H}\}\) NMR (benzene-\(d_6\), 100 MHz): \(\delta\) 43.0 (\(\text{Me}_3\text{-TACD}\)), 43.2 (\(\text{Me}_3\text{-TACD}\)), 53.2 (\(\text{CH}_2\)), 53.8 (\(\text{CH}_2\)), 54.4 (\(\text{CH}_2\)), 59.0 (\(\text{CH}_2\)). \(^{7}\text{Li}\{^1\text{H}\}\) NMR (156 MHz, benzene-\(d_6\)): \(\delta\) 1.1. IR (KBr, cm\(^{-1}\)): 2965 (s, br), 2911 (s, br), 2850 (s, br), 1464 (s), 1359 (s), 1298 (s), 1146 (m), 1120 (m), 1111 (s), 1083 (m), 1059 (m), 1032 (m), 968 (s), 910 (s), 846 (w), 804 (w), 753 (m), 681 (s, br), 579 (m, br). Anal. Calcd. for \(\text{C}_{13}\text{H}_{31}\text{N}_4\text{ClLiIn}\): C, 38.97; H, 7.80; N, 13.99. Found: C, 39.13; H, 7.64; N, 14.12.

**Figure S39.** \(^1\text{H}\) NMR spectrum of \((\text{Me}_3\text{TACD})\text{Li(}\mu\text{-Cl})\text{InMe}_2\) in benzene-\(d_6\).
Figure S40. $^{13}$C{1H} NMR spectrum of (Me$_3$TACD)Li(μ-Cl)InMe$_2$ in benzene-$d_6$.

Figure S41. $^7$Li{1H} NMR spectrum of (Me$_3$TACD)Li(μ-Cl)InMe$_2$ in benzene-$d_6$. 
Crystal Structure Analysis.

Data were collected on a Bruker CCD area-detector diffractometer with Mo Kα radiation (monolayer optics, $\lambda = 0.71073$ Å) using $\omega$ scans. The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed using SAINT; absorption corrections were applied with SADABS. All non-hydrogen atoms were refined anisotropically using all reflections with the program SHELXL-2013 as implemented in the program system WinGX. All hydrogen atoms were placed in calculated positions and treated as riding. The graphical representations were performed with the program DIAMOND.

Table S1. Crystallographic and Refinement Data for 5, 7 and 9.

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<tr>
<th></th>
<th>5</th>
<th>7</th>
<th>9</th>
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<tbody>
<tr>
<td></td>
<td>$C_{214}H_{28}AlBF_{20}N_4$</td>
<td>$C_{39}H_{36}BF_{20}InN_4Si$</td>
<td>$C_{13}H_{31}ClInLiN_4$</td>
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<tr>
<td>$M_w$, g.mol$^{-1}$</td>
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<td>1094.44</td>
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<td>Cryst size, mm</td>
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<td>$0.10 \times 0.13 \times 0.23$</td>
<td>$0.32 \times 0.33 \times 0.57$</td>
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<tr>
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<td>colourless block</td>
<td>colourless rod</td>
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<tr>
<td>Cryst syst.</td>
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<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
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<td>$P2_1/n$</td>
<td>$P2_1/n$</td>
</tr>
<tr>
<td>$T$, K</td>
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<td>100(2)</td>
</tr>
<tr>
<td>$a$, Å</td>
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<td>12.1268(18)</td>
<td>12.5522(19)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>13.135(7)</td>
<td>20.852(3)</td>
<td>9.3814(14)</td>
</tr>
</tbody>
</table>
\[ c, \, \text{Å} \quad 13.498(6) \quad 17.479(3) \quad 16.834(3) \]
\[ \alpha, \, \text{degree} \quad 92.447(14) \]
\[ \beta, \, \text{degree} \quad 94.364(13) \quad 107.209(3) \quad 110.434(2) \]
\[ \gamma, \, \text{degree} \quad 93.859(14) \]
\[ V, \, \text{Å}^3 \quad 1832.8(15) \quad 4222.0(11) \quad 1857.6(5) \]
\[ Z \quad 2 \quad 4 \quad 4 \]
\[ D_{\text{calc}}, \, \text{g} \cdot \text{cm}^{-3} \quad 1.693 \quad 1.722 \quad 1.433 \]
\[ \mu(\text{Mo K} \alpha), \, \text{mm}^{-1} \quad 0.194 \quad 0.713 \quad 1.412 \]
\[ F(000) \quad 940 \quad 2184 \quad 824 \]
\[ \theta \, \text{range, deg} \quad 2.12-25.50 \quad 1.56-25.19 \quad 2.50-26.63 \]
\[ \text{Reflns collected} \quad 15773 \quad 44898 \quad 11109 \]
\[ \text{Indep reflns (Rint)} \quad 6755 (0.196) \quad 7565 (0.0768) \quad 3807 (0.0344) \]
\[ \text{Reflns obsd}[|F| > 2\sigma(F)] \quad 3101 \quad 5513 \quad 3369 \]
\[ \text{Data/restraints/params} \quad 6755 / 0 / 563 \quad 7565 / 0 / 601 \quad 3807 / 0 / 186 \]
\[ R_1, \, wR_2 \, [|F| > 2\sigma(F)] \quad 0.0742, 0.1514 \quad 0.0407, 0.0751 \quad 0.0265, 0.0612 \]
\[ R_1, \, wR_2 \, \text{(all data)} \quad 0.1786, 0.1990 \quad 0.0681, 0.0848 \quad 0.0311, 0.0630 \]
\[ \text{Goodness-of-fit on } F^2 \quad 0.963 \quad 1.008 \quad 1.064 \]
\[ \Delta \rho_{\text{max}, \text{min}}, \, \text{e} \cdot \text{Å}^{-3} \quad 0.403, -0.404 \quad 0.574, -0.447 \quad 0.607, -0.544 \]

\[ a) R_1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|) \quad b) wR_2 = [\{\Sigma w(Fo^2 - Fc^2)^2\}/\{\Sigma w(Fo^2)\}]^{1/2} \]

References.


