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Electronic Supporting Information

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

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Table of Contents

General remarks.....P1
Synthetic procedures and spectroscopic data for **1-9**.....P1-P26
Crystal structure analysis.....P26-P27
References.....P27

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 ^{1}H and ^{13}C{^{1}H NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane.[S1] 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). Me_3TACDH,[S2] Li-Me_3TACD,[S3] $InMe_3$,[S4] $B(C_6F_5)_3$,[S5] and $[In(CH_2SiMe_3)_2(thf)_3][B(C_6F_5)_4]$[S6] were synthesized according to literature procedures. $AlMe_3$ and $AlMe_2Cl$ were purchased from Sigma-Aldrich. $[PhNHMe_2][B(C_6F_5)_4]$ 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.

Me_3TACDH.

^{1}H NMR (400 MHz, THF-d_8): δ 2.18 (s, 3 H, *Me*$_3$-TACD), 2.24 (s, 6 H, *Me*$_3$-TACD), 2.34-2.42 (m, 11 H, C*H*$_2$), 2.50-2.57 (m, 5 H, C*H*$_2$), 2.82 (br, s, 1 H, N*H*).

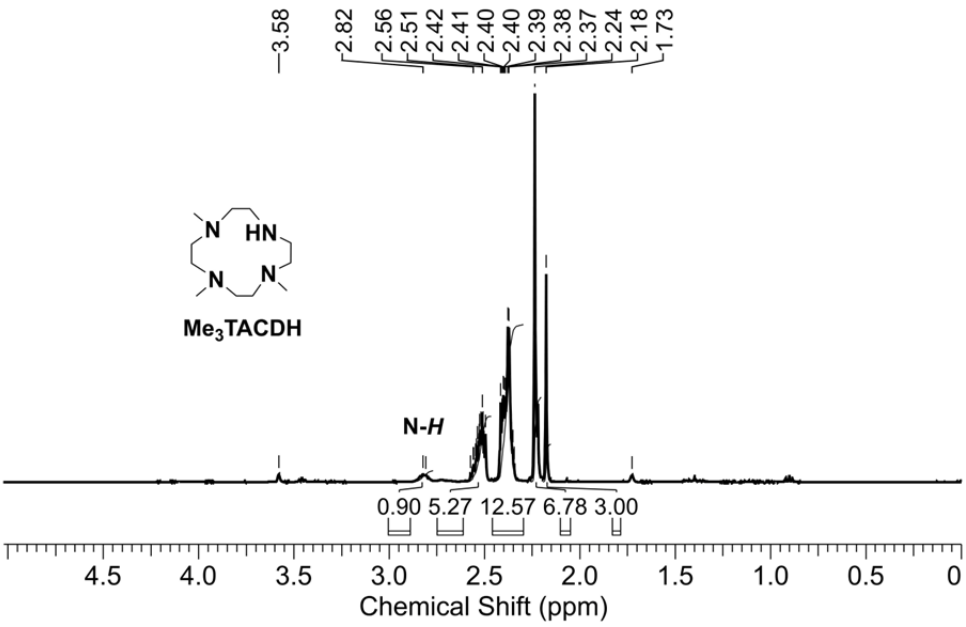

Figure S1. ^{1}H NMR spectrum of Me_3TACDH in THF-d_8.

(Me_3TACDH)AlMe_3 (1).

AlMe_3 (0.036 g, 0.500 mmol) and Me_3TACDH (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_3TACDH)AlMe_3 (0471 mmol, 95%) as a colorless oily substance. ^{1}H NMR (400 MHz, THF-d_8): δ −1.00 (s, 9 H, Al*Me*$_3$), 2.23 (s, 3 H, *Me*$_3$-TACD), 2.25 (s, 6 H, *Me*$_3$-TACD), 2.46 (br, s, 8 H, C*H*$_2$), 2.49-2.52 (m, 4 H, C*H*$_2$), 2.71 (br, s, 4 H, C*H*$_2$), 4.88 (br, s, 1 H, N*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −8.2 (Al*Me*), 43.4 (*Me*$_3$-TACD), 43.4 (*Me*$_3$-TACD), 50.0 (*C*H$_2$), 52.4 (*C*H$_2$), 54.3 (*C*H$_2$), 54.5 (*C*H$_2$). IR (KBr, cm^{-1}): 3453 (w, br, ν_{NH}), 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 $C_{14}H_{35}N_4Al$: C, 58.70; H, 12.32; N, 19.56. Found: C, 58.61; H, 12.55; N, 19.64.

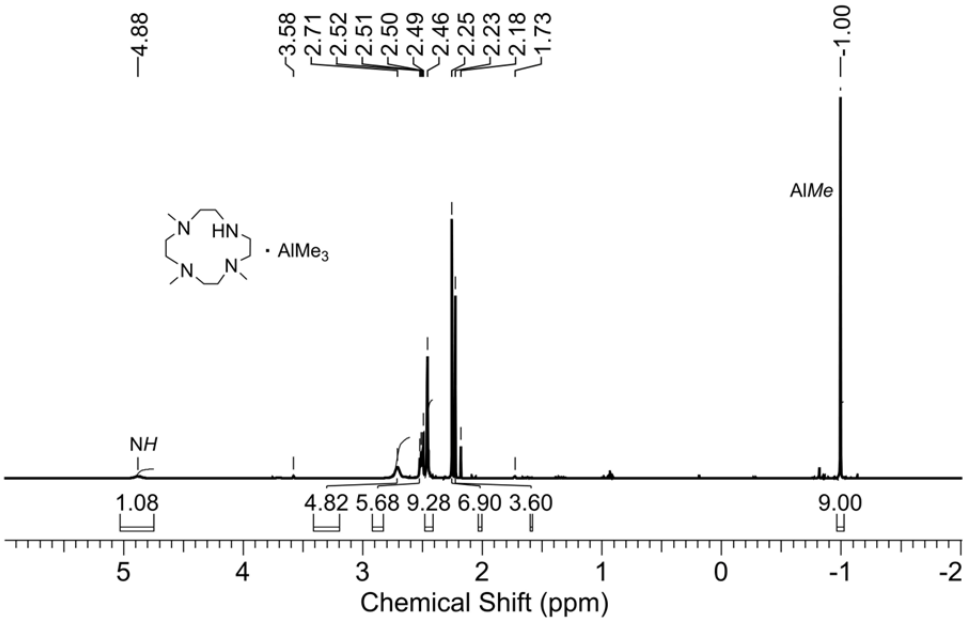

Figure S2. ^{1}H NMR spectrum of $(Me_3TACDH)AlMe_3$ in THF-d_8.

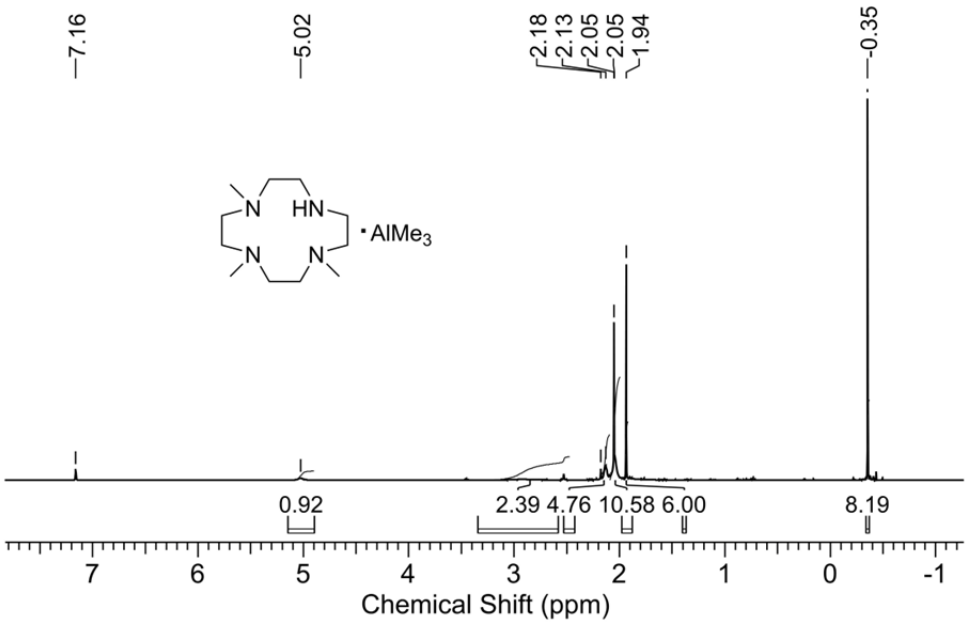

Figure S3. ^{1}H NMR spectrum of $(Me_3TACDH)AlMe_3$ in C_6D_6.

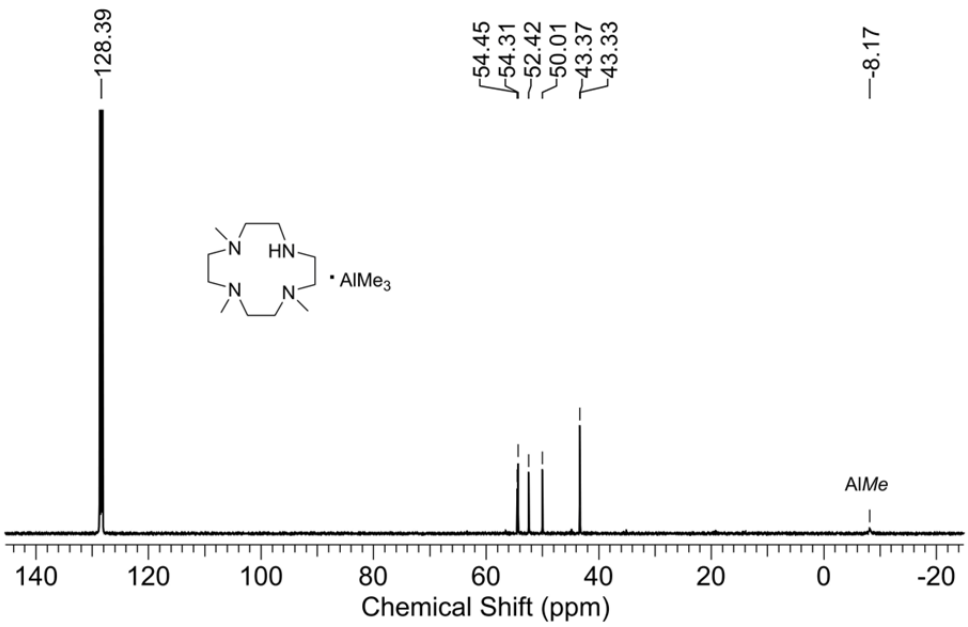

Figure S4. ^{13}C NMR spectrum of $(Me_3TACDH)AlMe_3$ in C_6D_6.

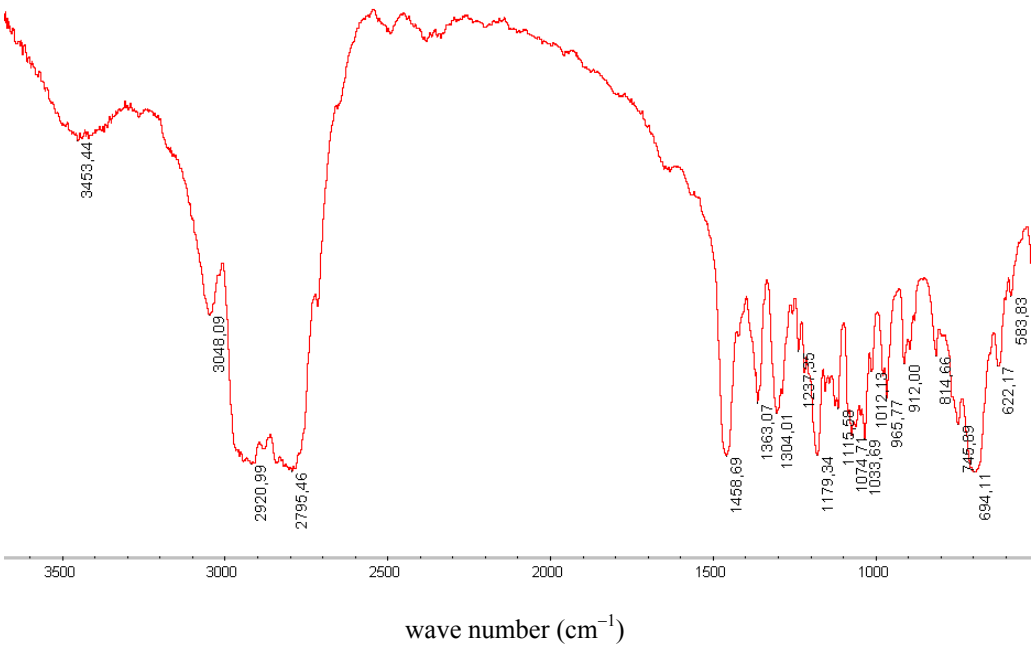

Figure S5. Solid-state IR (KBr pellet) spectrum of $(Me_3TACDH)AlMe_3$.

$(Me_3TACDH)InMe_3$ (2).

$InMe_3$ (0.090 g, 0.560 mmol) and Me_3TACDH (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 $(Me_3TACDH)InMe_3$ (0.540 mmol, 96%) as a colorless oily substance. ^{1}H NMR (400 MHz, THF-d_8): δ –0.55 (s, 9 H, In*Me*$_3$), 2.23 (s, 3 H, *Me*$_3$-TACD), 2.25 (s, 6 H, *Me*$_3$-TACD), 2.37-2.40 (m, 4 H, C*H*$_2$), 2.42-2.45 (m, 4 H, C*H*$_2$), 2.43-2.50 (m, 4 H, C*H*$_2$), 2.62-2.66 (m, 4 H, C*H*$_2$), 4.11 (br, s, 1 H, N*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): *δ* –7.3 (In*Me*), 43.6 (*Me*$_3$-TACD), 43.9 (*Me*$_3$-TACD), 48.4 (*C*H$_2$), 54.3 (*C*H$_2$), 54.7 (*C*H$_2$), 56.6

(CH_2). IR (KBr, cm^{-1}): 3167-3097 (w, br, ν_{NH}), 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 $C_{14}H_{35}N_4In$: C, 44.93; H, 9.43; N, 14.97. Found: C, 44.71; H, 9.25; N, 14.82.

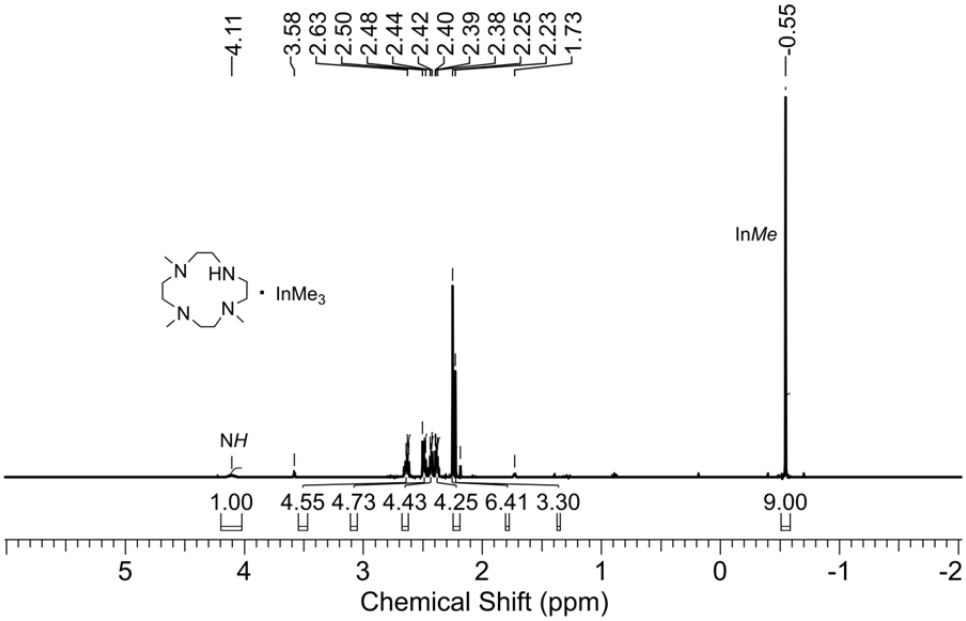

Figure S6. ^{1}H NMR spectrum of $(Me_3TACDH)InMe_3$ in THF-d_8.

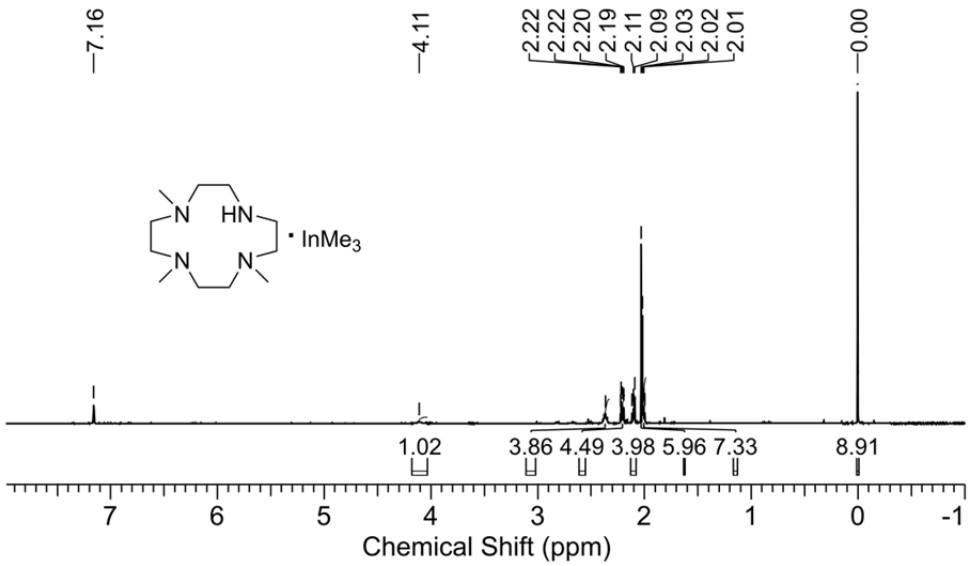

Figure S7. ^{1}H NMR spectrum of $(Me_3TACDH)InMe_3$ in C_6D_6.

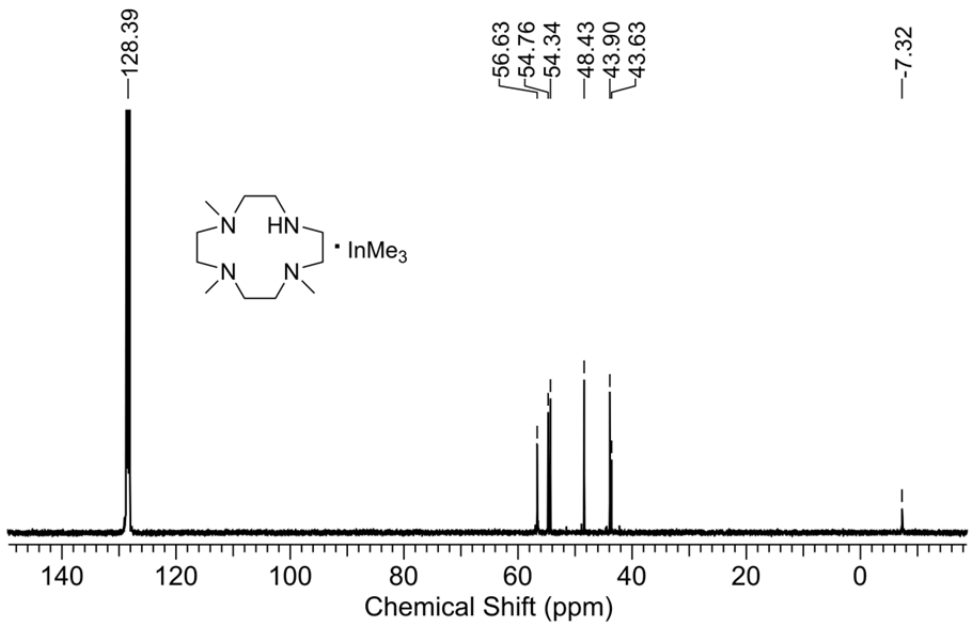

Figure S8. ^{13}C NMR spectrum of $(Me_3TACDH)InMe_3$ in C_6D_6.

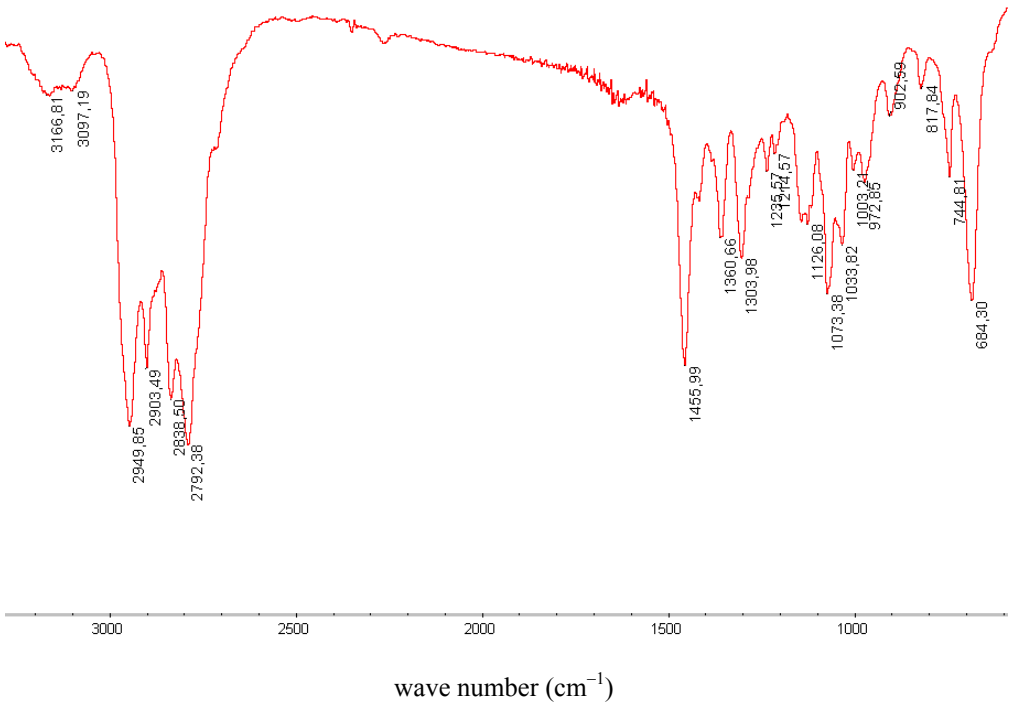

Figure S9. Solid-state IR (KBr pellet) spectrum of $(Me_3TACDH)InMe_3$.

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

$B(C_6F_5)_3$ (0.114 g, 0.222 mmol) and $AlMe_3$ (0.016 g, 0.222 mmol) were dissolved in 1 mL of THF to produce $[AlMe_2(thf)_x][MeB(C_6F_5)_3]$ in situ. After 5 min, this solution was added to another 1 mL THF solution of Me_3TACDH (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 $[(Me_3TACD)AlMe][MeB(C_6F_5)_3]$ (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 CH_4 as evident by the ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, THF-d_8): δ –0.75 (s, 3 H, Al*Me*), 0.51 (br, s, 3 H, B*Me*), 2.54 (s, 6 H, Me_3-TACD), 2.66 (s, 3 H, Me_3-TACD), 2.76-3.03 (m, 14 H, CH_2), 3.12-3.19 (m, 2 H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ –14.3 (Al*Me*), 10.9 (B*Me*) 44.0 (Me_3-TACD), 46.2 (Me_3-TACD), 46.4 (CH_2), 52.0 (CH_2), 56.2 (CH_2), 60.9 (CH_2), 136.2 (C_6F_5), 137.3 (C_6F_5), 138.5 (C_6F_5), 139.7 (C_6F_5), 148.3 (C_6F_5), 150.7 (C_6F_5). ^{11}B NMR (128 MHz, THF-d_8): δ −14.9. ^{19}F NMR (THF-d_8, 377 MHz): δ −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 $C_{31}H_{31}BF_{15}N_4Al$: C, 47.59; H, 3.99; N, 7.16. Found: C, 47.71; H, 3.85; N, 7.32.

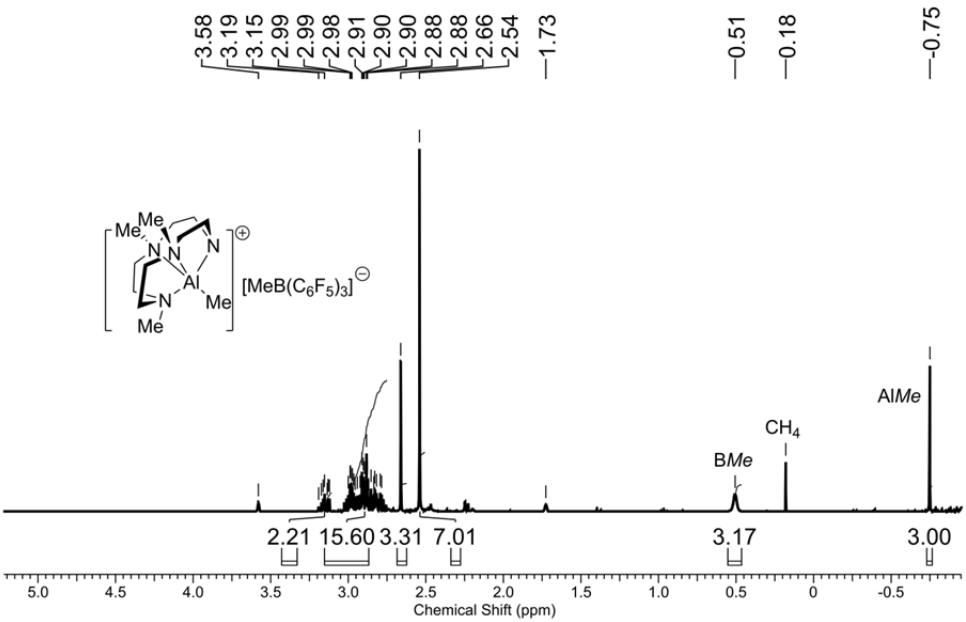

Figure S10. ^{1}H NMR spectrum of [(Me_3TACD)AlMe][MeB(C_6F_5)$_3$] in THF-d_8 recorded from the NMR-scale reaction. Singlet resonance at δ 0.18 ppm confirmed the generation of CH_4.

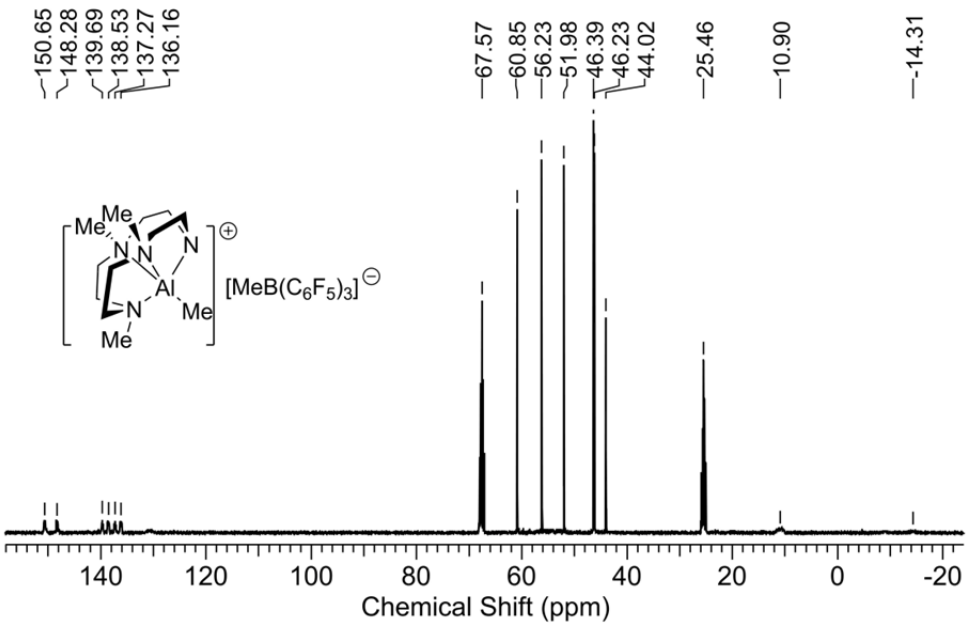

Figure S11. ^{13}C NMR spectrum of [(Me$_3$TACD)AlMe][MeB(C$_6$F$_5$)$_3$] in THF-d_8.

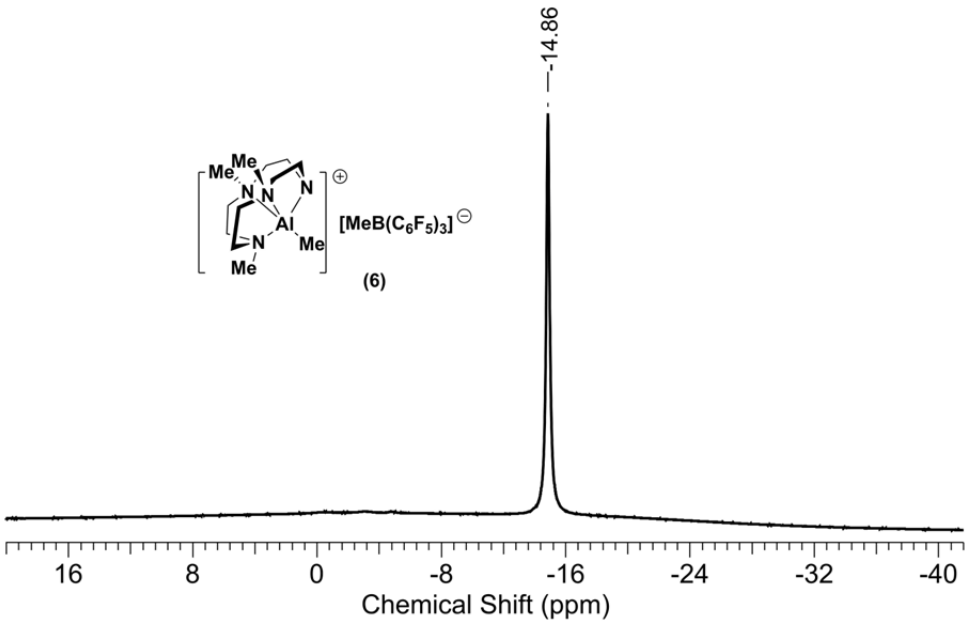

Figure S12. ^{11}B{^{1}H} NMR spectrum of [(Me$_3$TACD)AlMe][MeB(C$_6$F$_5$)$_3$] in THF-d_8.

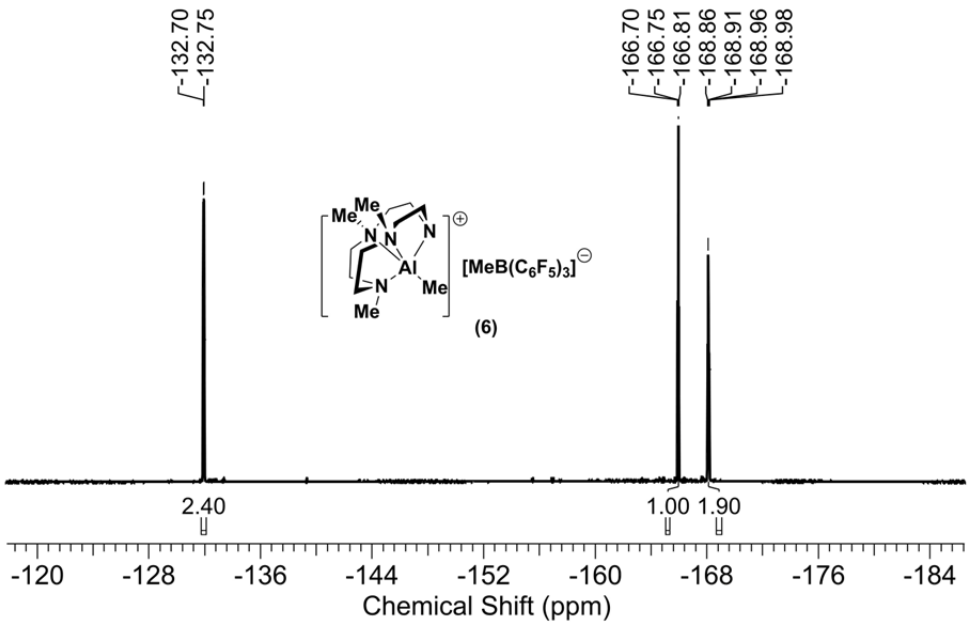

Figure S13. $^{19}F\{^{1}H\}$ NMR spectrum of $[(Me_3TACD)AlMe][MeB(C_6F_5)_3]$ in THF-d_8.

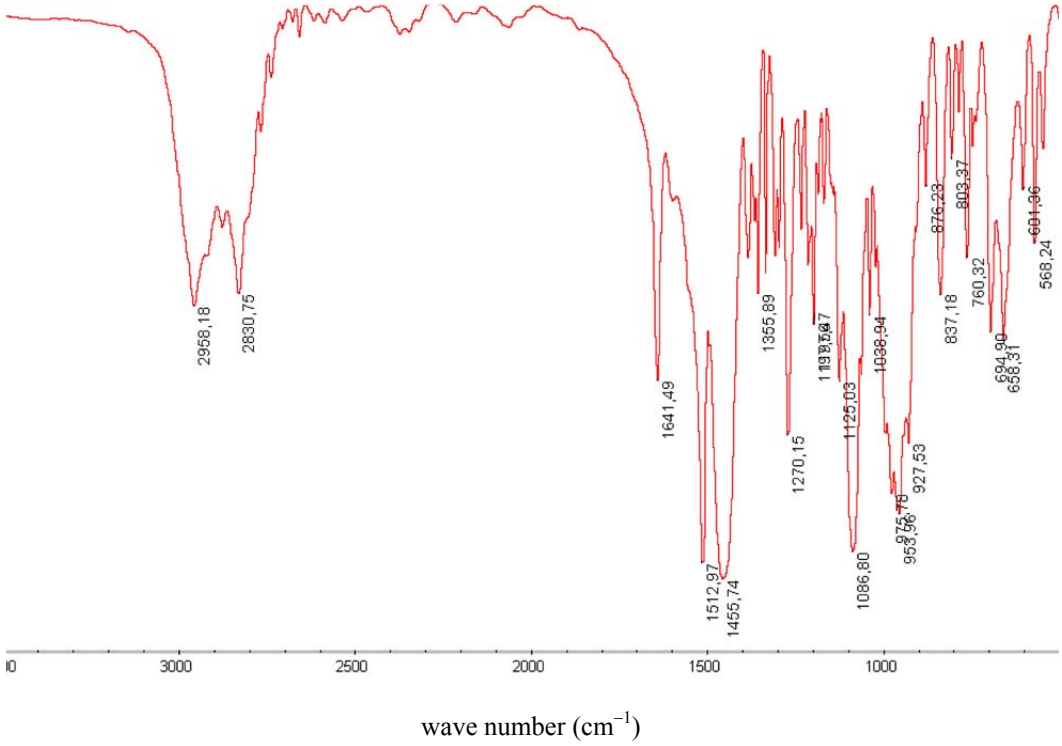

Figure S14. Solid-state IR (KBr pellet) spectrum of $[(Me_3TACD)AlMe][MeB(C_6F_5)_3]$.

$[(Me_3TACD)InMe][MeB(C_6F_5)_3]$ (4).

$B(C_6F_5)_3$ (0.096 g, 0.187 mmol) and $InMe_3$ (0.030 g, 0.187 mmol) were dissolved in 1 mL of THF to produce $[InMe_2(thf)_x][MeB(C_6F_5)_3]$ in situ. After 5 min, this solution was added to another 1 mL THF solution of Me_3TACDH (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 [(Me_3TACD)InMe][MeB(C_6F_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): δ 0.15 (br, s, 3 H, In*Me*), 0.51 (br, s, 3 H, B*Me*), 2.59 (s, 6 H, *Me*$_3$-TACD), 2.64 (s, 3 H, *Me*$_3$-TACD), 2.74-2.85 (m, 8 H, C*H*$_2$), 2.97-3.03 (m, 6 H, C*H*$_2$), 3.14-3.19 (m, 2 H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ −9.4 (In*Me*), 10.8 (B*Me*) 44.2 (*Me*$_3$-TACD), 44.6 (*Me*$_3$-TACD), 49.4 (*C*H$_2$), 52.8 (*C*H$_2$), 54.6 (*C*H$_2$), 59.7 (*C*H$_2$), 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): δ −14.9. ^{19}F NMR (THF-d_8, 377 MHz): δ −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 $C_{31}H_{31}BF_{15}N_4In$: C, 42.79; H, 3.59; N, 6.44. Found: C, 42.73; H, 3.51; N, 6.29.

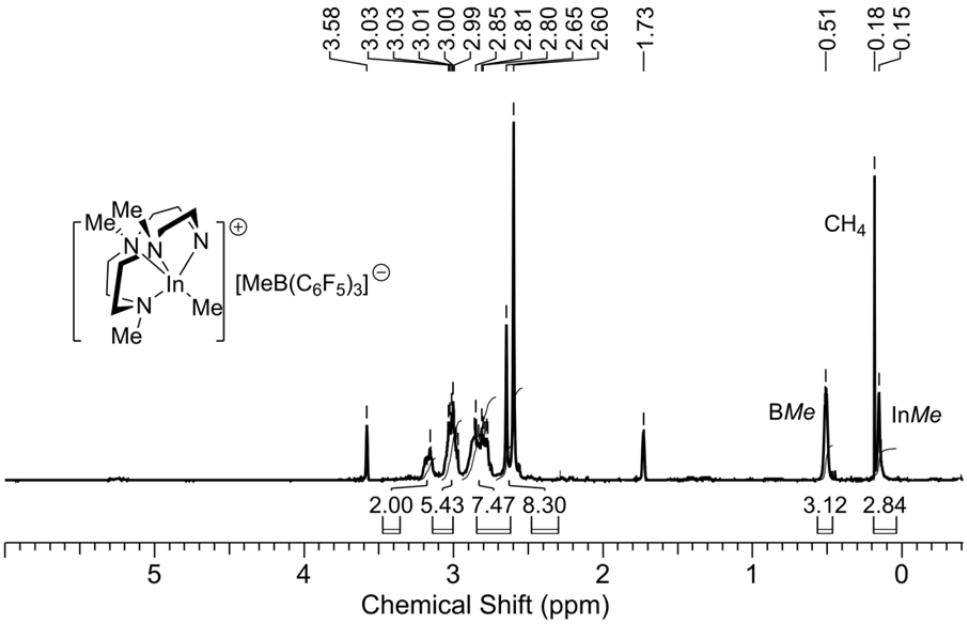

Figure S15. ^{1}H NMR spectrum of [(Me_3TACD)InMe][MeB(C_6F_5)$_3$] in THF-d_8 recorded from the NMR-scale reaction. Singlet resonance at δ 0.18 ppm confirmed the generation of CH_4.

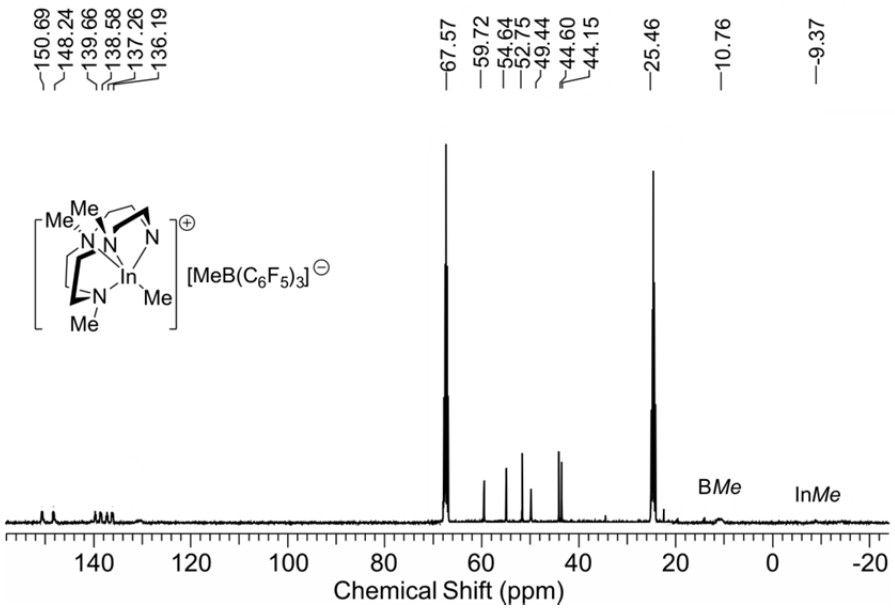

Figure S16. ^{13}C NMR spectrum of [(Me$_3$TACD)InMe][MeB(C$_6$F$_5$)$_3$] in THF-d_8.

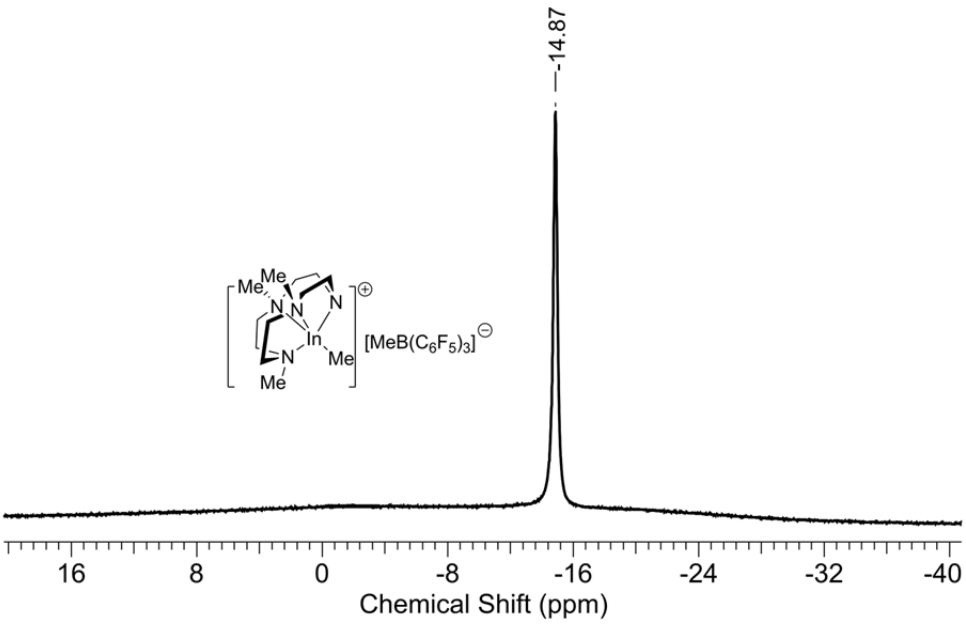

Figure S17. ^{11}B{^{1}H} NMR spectrum of [(Me$_3$TACD)InMe][MeB(C$_6$F$_5$)$_3$] in THF-d_8.

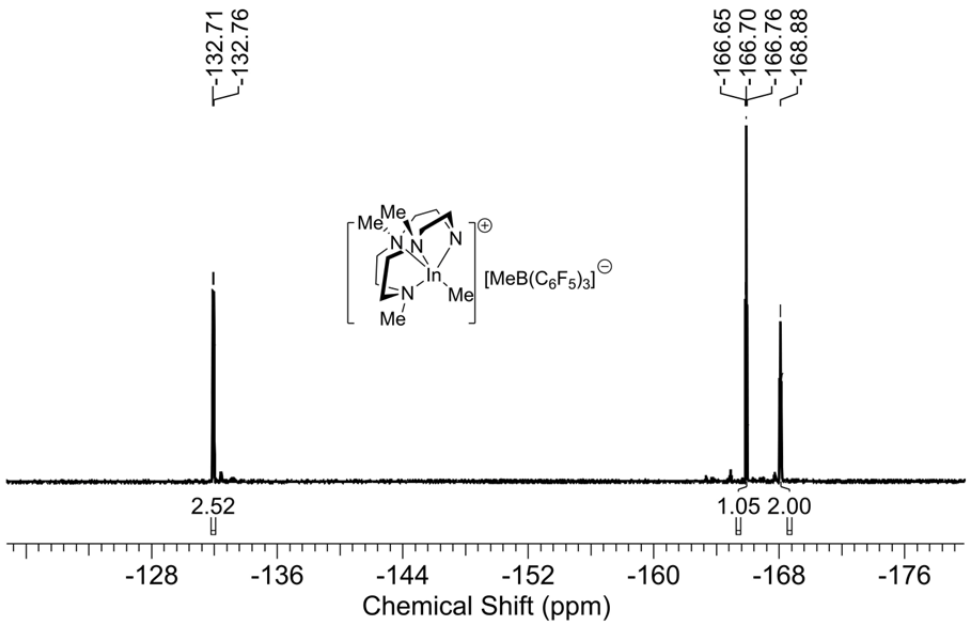

Figure S18. $^{19}F\{^{1}H\}$ NMR spectrum of $[(Me_3TACD)InMe][MeB(C_6F_5)_3]$ in THF-d_8.

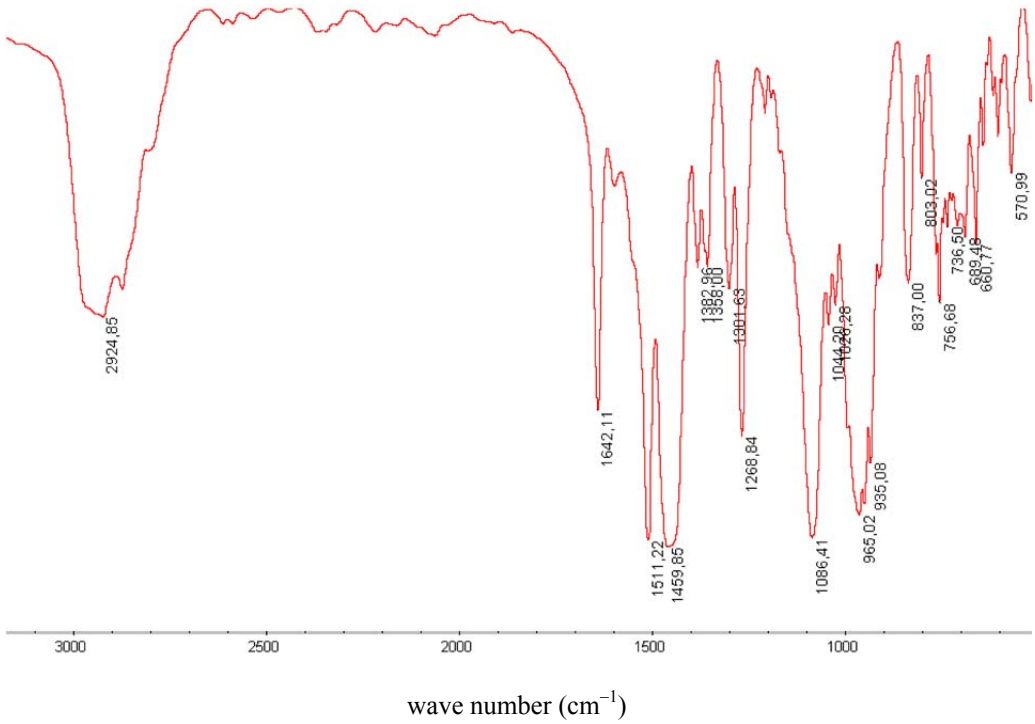

Figure S19. Solid-state IR (KBr pellet) spectrum of $[(Me_3TACD)InMe][MeB(C_6F_5)_3]$.

$[(Me_3TACD)AlMe][B(C_6F_5)_4]$ (5).

A 2 mL THF solution of $[PhNMe_2H][B(C_6F_5)_4]$ (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_3TACDH (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 [(Me_3TACD)AlMe][B(C_6F_5)$_4$] (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 ˚C. ^{1}H NMR (400 MHz, THF-d_8): δ −0.74 (s, 3 H, Al*Me*), 2.55 (s, 6 H, *Me*$_3$-TACD), 2.67 (s, 3 H, *Me*$_3$-TACD), 2.77-3.04 (m, 14 H, C*H*$_2$), 3.13-3.20 (m, 2 H, C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ −14.7 (Al*Me*), 44.1 (*Me*$_3$-TACD), 46.3 (*Me*$_3$-TACD), 46.4 (*C*H$_2$), 52.0 (*C*H$_2$), 56.3 (*C*H$_2$), 60.9 (*C*H$_2$), 136.1 (*C*$_6$F$_5$), 138.1 (*C*$_6$F$_5$), 138.5 (*C*$_6$F$_5$), 140.5 (*C*$_6$F$_5$), 148.2 (*C*$_6$F$_5$), 150.6 (*C*$_6$F$_5$). ^{11}B NMR (128 MHz, THF-d_8): δ −16.6. ^{19}F NMR (THF-d_8, 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), 1025 (m), 980 (s), 928 (m), 775 (s), 756 (s), 684 (s), 661 (s), 611 (m), 573 (m). Anal. Calcd. for $C_{36}H_{28}BF_{20}N_4Al$: C, 46.27; H, 3.02; N, 6.00. Found: C, 45.98; H, 2.94; N, 5.84.

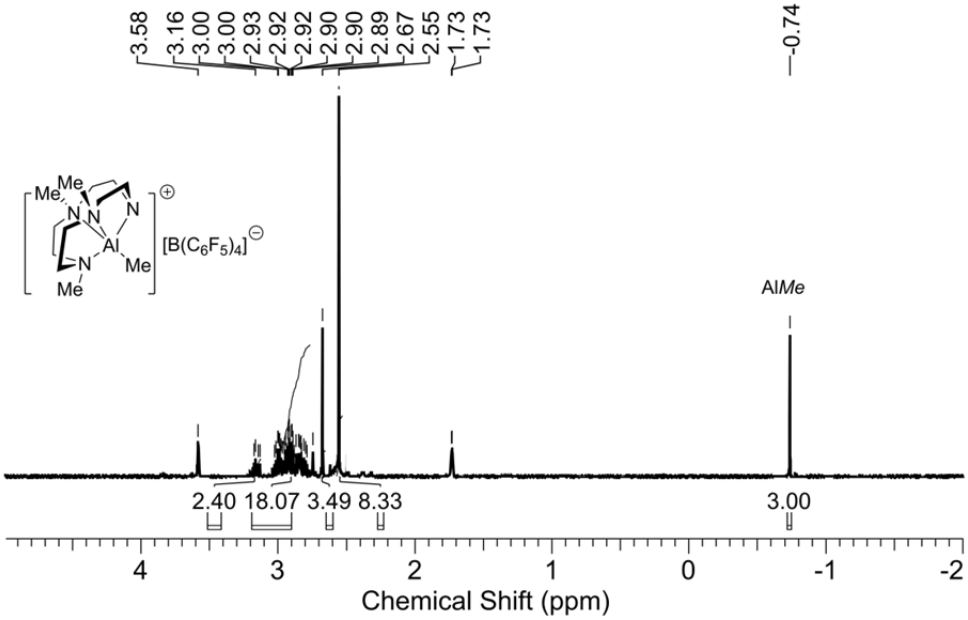

Figure S20. ^{1}H NMR spectrum of [(Me_3TACD)AlMe][B(C_6F_5)$_4$] in THF-d_8.

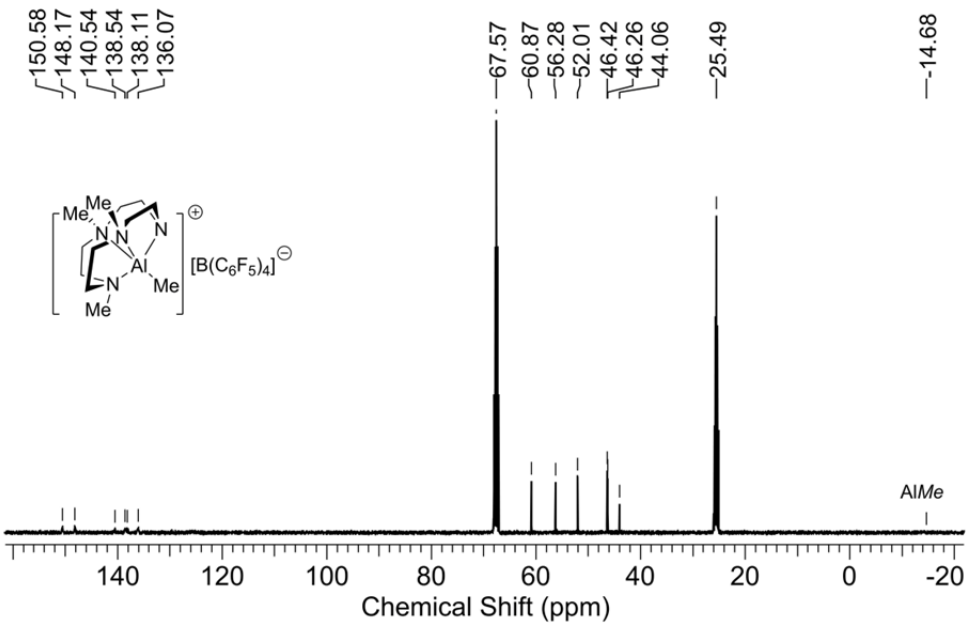

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of $[(Me_3TACD)AlMe][B(C_6F_5)_4]$ in THF-d_8.

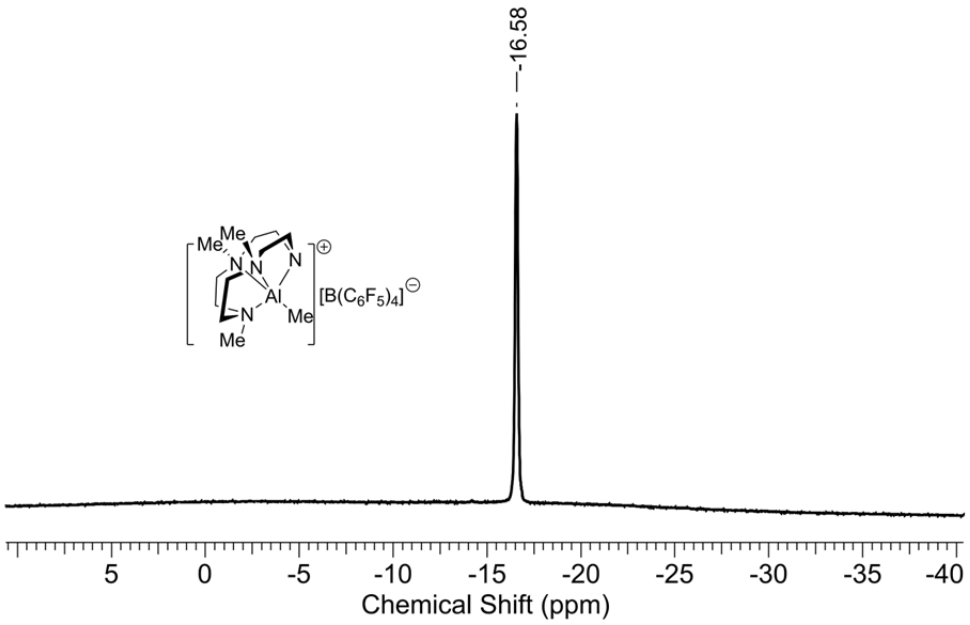

Figure S22. $^{11}B\{^{1}H\}$ NMR spectrum of $[(Me_3TACD)AlMe][B(C_6F_5)_4]$ in THF-d_8.

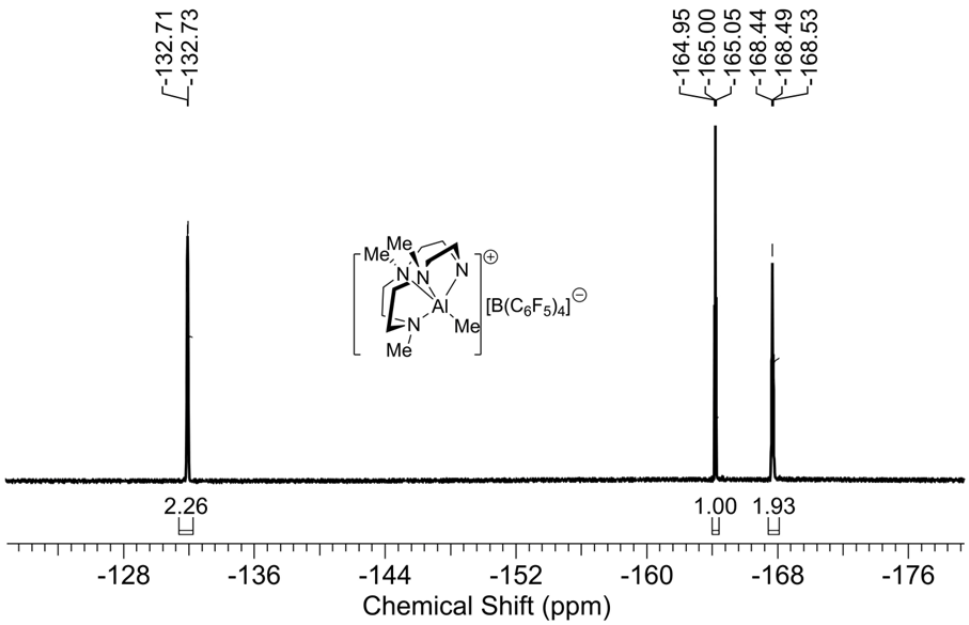

Figure S23. $^{19}F\{^{1}H\}$ NMR spectrum of $[(Me_3TACD)AlMe][B(C_6F_5)_4]$ in THF-d_8.

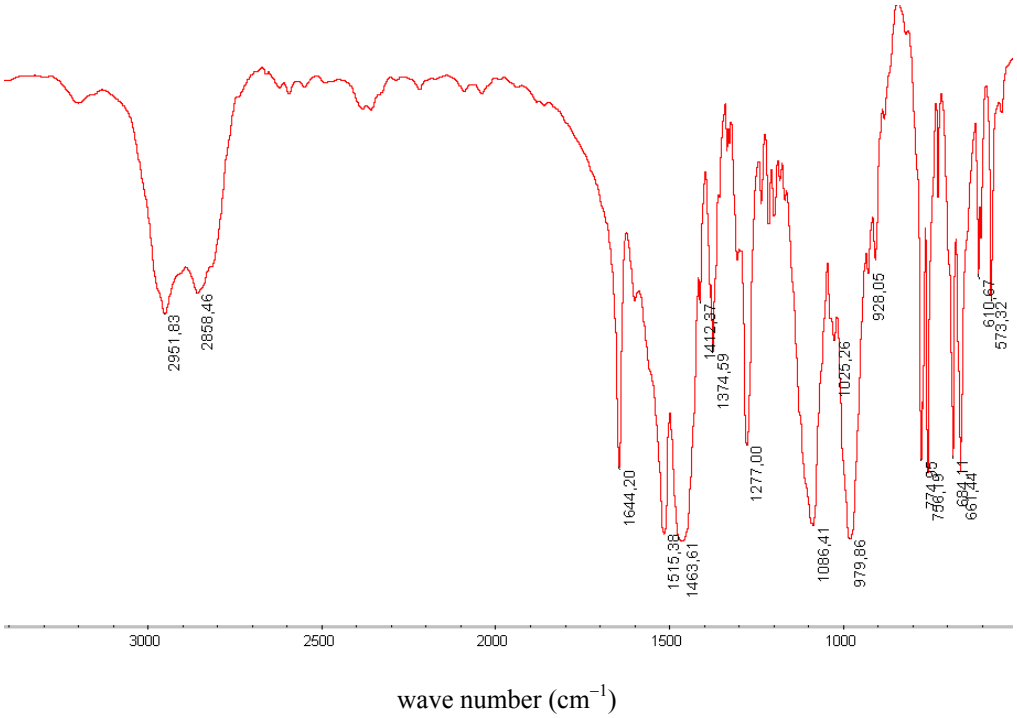

Figure S24. Solid-state IR (KBr pellet) spectrum of $[(Me_3TACD)AlMe][B(C_6F_5)_4]$.

$[(Me_3TACD)InMe][B(C_6F_5)_4]$ (6).

A 2 mL THF solution of $[PhNMe_2H][B(C_6F_5)_4]$ (0.300 g, 0.374 mmol) was added to an 1 mL THF solution of $InMe_3$ (0.060 g, 0.375 mmol). The resulting solution mixture was then added to another 2 mL THF solution of Me_3TACDH (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 $[(Me_3TACD)InMe][B(C_6F_5)_4]$ (0.310

g, 0.303 mmol, 81% yield) as a white powder. ^{1}H NMR (400 MHz, THF-d_8): δ 0.07 (s, 3 H, In*Me*), 2.55 (s, 6 H, *Me*$_3$-TACD), 2.60 (s, 3 H, *Me*$_3$-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): δ −13.4 (In*Me*), 44.1 (*Me*$_3$-TACD), 44.7 (*Me*$_3$-TACD), 50.3 (*C*H$_2$), 52.1 (*C*H$_2$), 55.4 (*C*H$_2$), 59.9 (*C*H$_2$), 136.1 (*C*$_6$F$_5$), 138.1 (*C*$_6$F$_5$), 138.5 (*C*$_6$F$_5$), 140.5 (*C*$_6$F$_5$), 148.2 (*C*$_6$F$_5$), 150.6 (*C*$_6$F$_5$). ^{11}B NMR (128 MHz, THF-d_8): δ −16.6. ^{19}F NMR (THF-d_8, 377 MHz): δ −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.

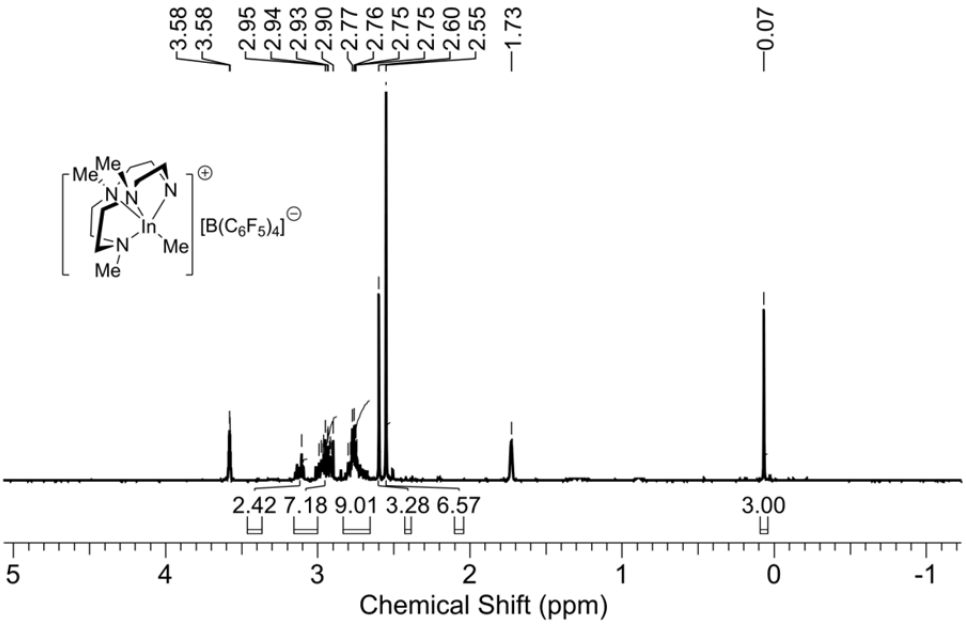

Figure S25. ^{1}H NMR spectrum of [(Me$_3$TACD)InMe][B(C$_6$F$_5$)$_4$] in THF-d_8.

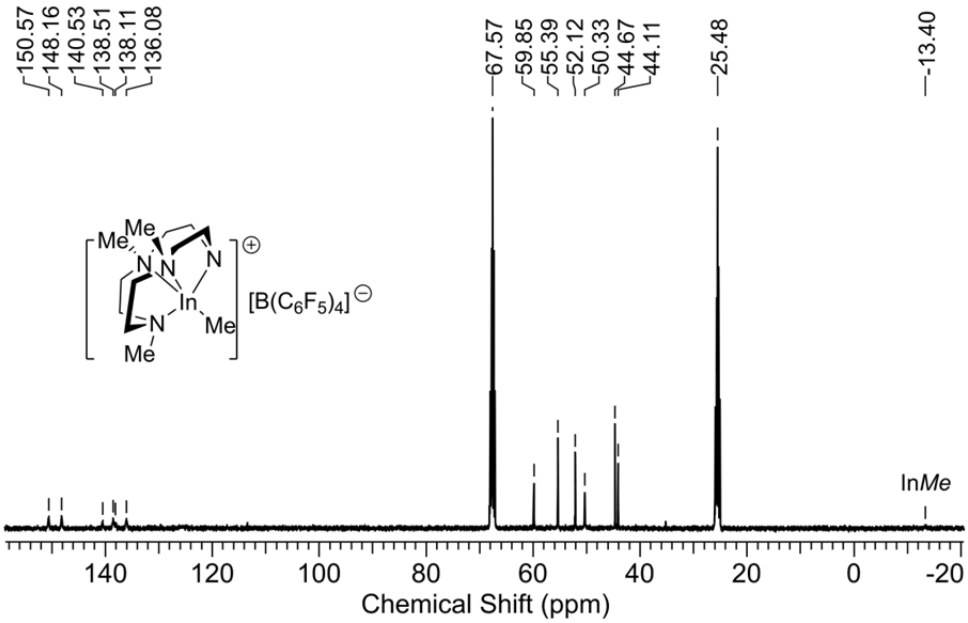

Figure S26. $^{13}C\{^1H\}$ NMR spectrum of $[(Me_3TACD)InMe][B(C_6F_5)_4]$ in THF-d_8.

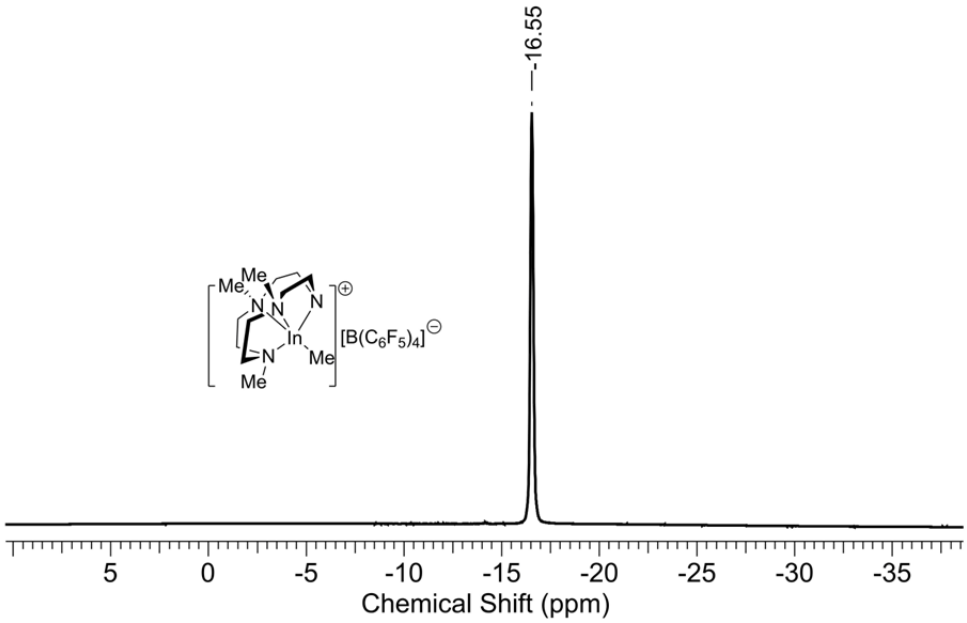

Figure S27. $^{11}B\{^1H\}$ NMR spectrum of $[(Me_3TACD)InMe][B(C_6F_5)_4]$ in THF-d_8.

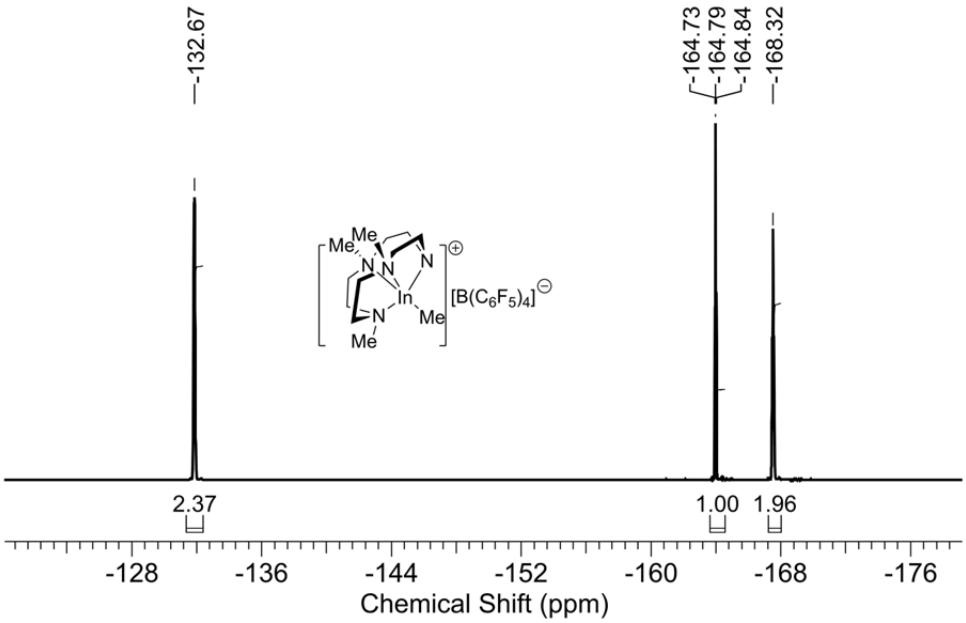

Figure S28. $^{19}F\{^1H\}$ NMR spectrum of $[(Me_3TACD)InMe][B(C_6F_5)_4]$ in THF-d_8.

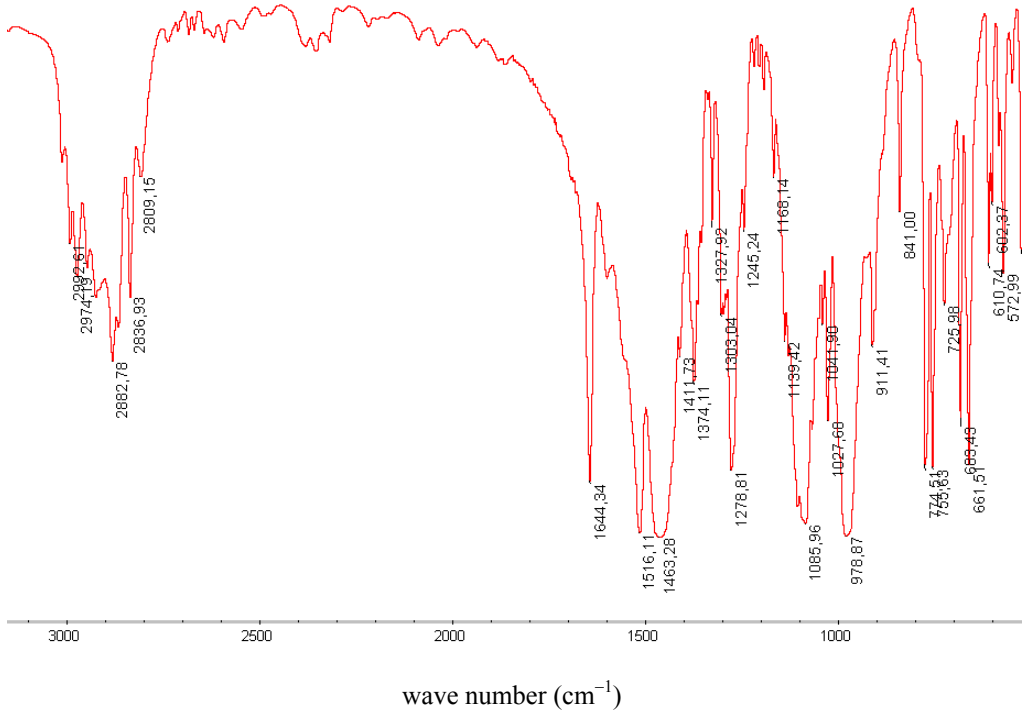

Figure S29. Solid-state IR (KBr pellet) spectrum of $[(Me_3TACD)InMe][B(C_6F_5)_4]$.

$[(Me_3TACD)InCH_2SiMe_3][B(C_6F_5)_4]$ (7).

A 2 mL THF solution of $[In(CH_2SiMe_3)_2(thf)_3][B(C_6F_5)_4]$ (320 g, 0.270 mmol) was added to an 1 mL THF solution of Me_3TACDH (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 $[(Me_3TACD)InCH_2SiMe_3][B(C_6F_5)_4]$ (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. ^{1}H NMR (400 MHz, THF-d_8): δ –0.10 (s, 2 H, InCH_2SiMe$_3$), 0.11 (s, 9 H, InCH$_2$SiMe_3), 2.55 (s, 6 H, Me_3TACD), 2.60 (s, 3 H, Me_3TACD), 2.68-2.82 (m, 8 H, CH_2), 2.90-3.01 (m, 6 H, CH_2) 3.10-3.15 (m, 2 H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ –5.4 (InCH_2SiMe$_3$), 2.1 (InCH$_2$SiMe_3), 44.4 (Me_3-TACD), 44.4 (Me_3-TACD), 50.1 (CH_2), 52.2 (CH_2), 55.0 (CH_2), 59.5 (CH_2), 136.1 (C_6F_5), 138.1 (C_6F_5), 138.5 (C_6F_5), 140.6 (C_6F_5), 148.2 (C_6F_5), 150.6 (C_6F_5). ^{11}B NMR (128 MHz, THF-d_8): δ −16.6. ^{19}F NMR (THF-d_8, 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 $C_{39}H_{36}BF_{20}N_4SiIn$: C, 42.80; H, 3.32; N, 5.12. Found: C, 43.07; H, 3.54; N, 5.39.

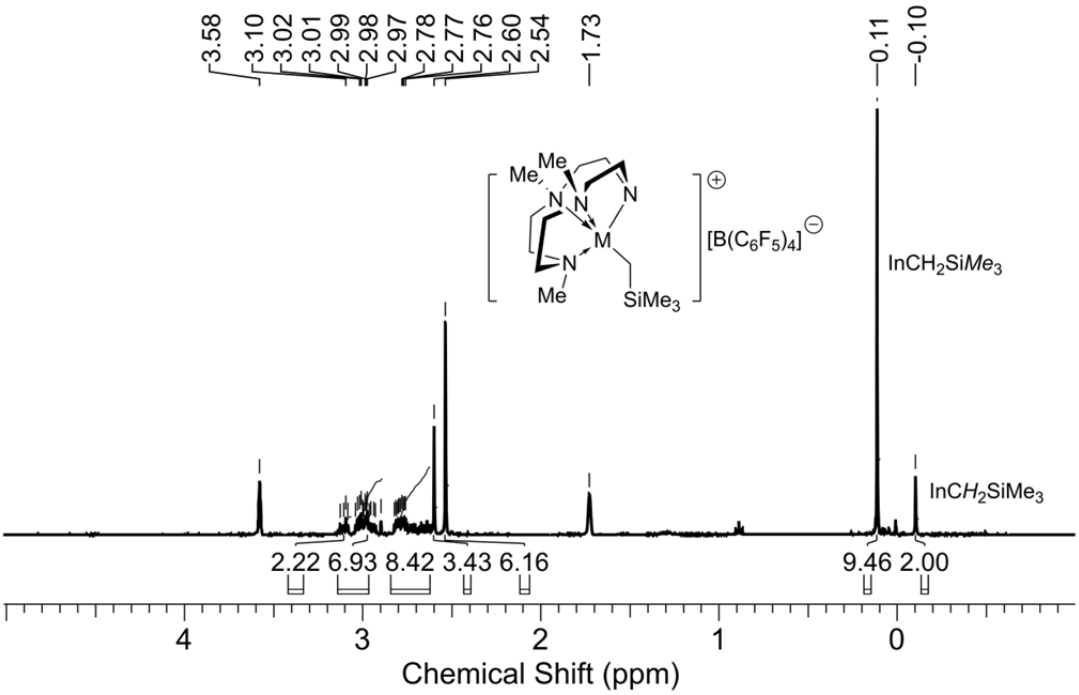

Figure S30. ^{1}H NMR spectrum of [(Me$_3$TACD)InCH$_2$SiMe$_3$][B(C$_6$F$_5$)$_4$] in THF-d_8.

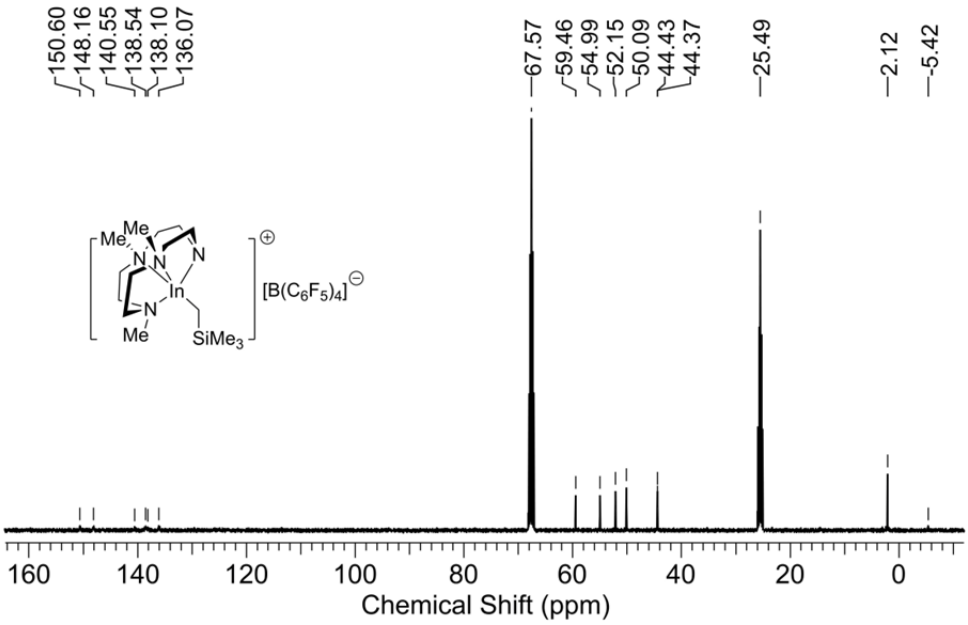

Figure S31. ^{13}C{^{1}H} NMR spectrum of [(Me$_3$TACD)InCH$_2$SiMe$_3$][B(C$_6$F$_5$)$_4$] in THF-d_8.

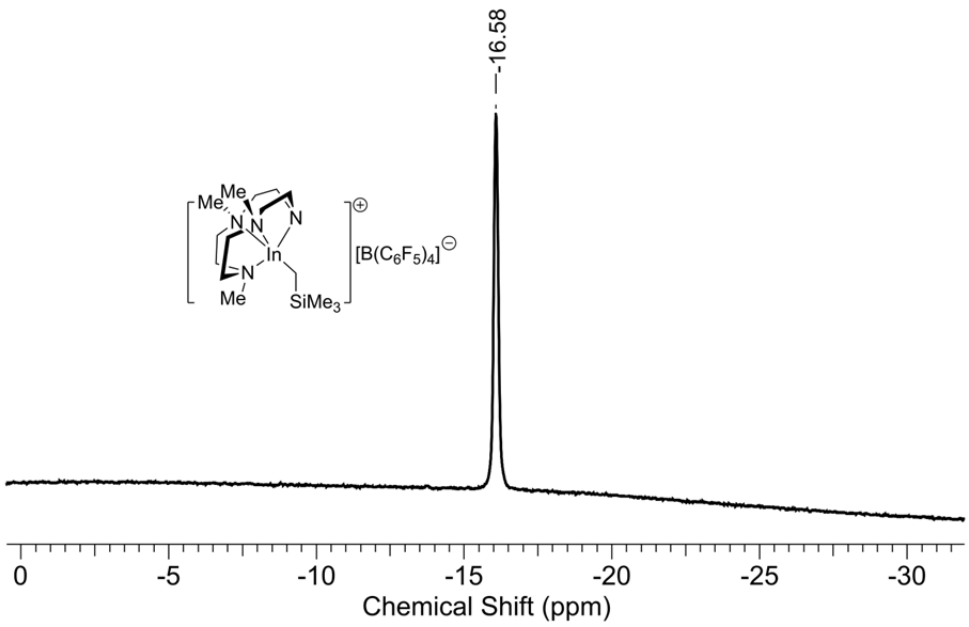

Figure S32. $^{11}B\{^{1}H\}$ NMR spectrum of $[(Me_3TACD)InCH_2SiMe_3][B(C6F_5)_4]$ in THF-d_8.

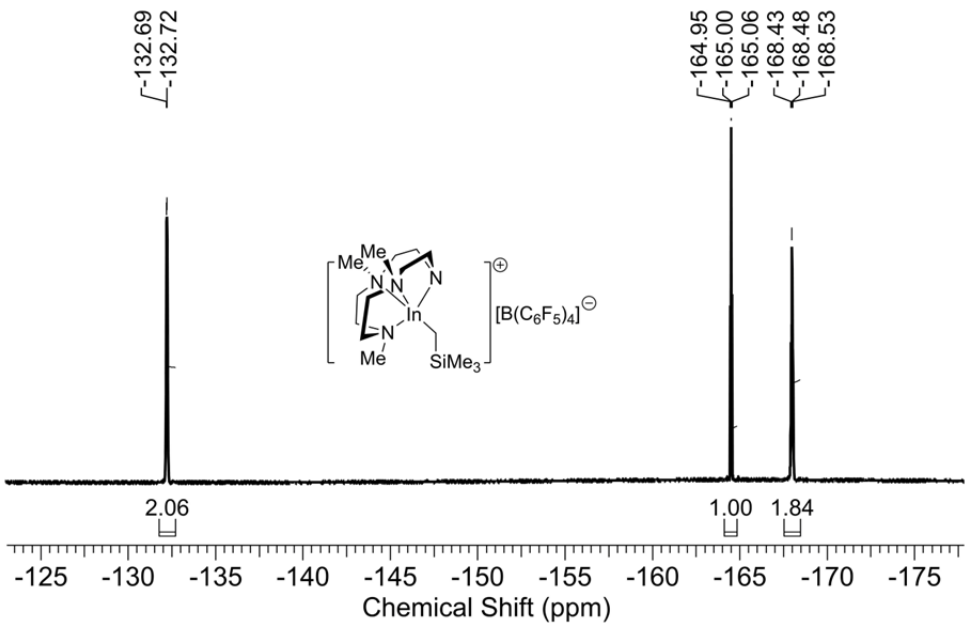

Figure S33. $^{19}F\{^{1}H\}$ NMR spectrum of $[(Me_3TACD)InCH_2SiMe_3][B(C_6F_5)_4]$ in THF-d_8.

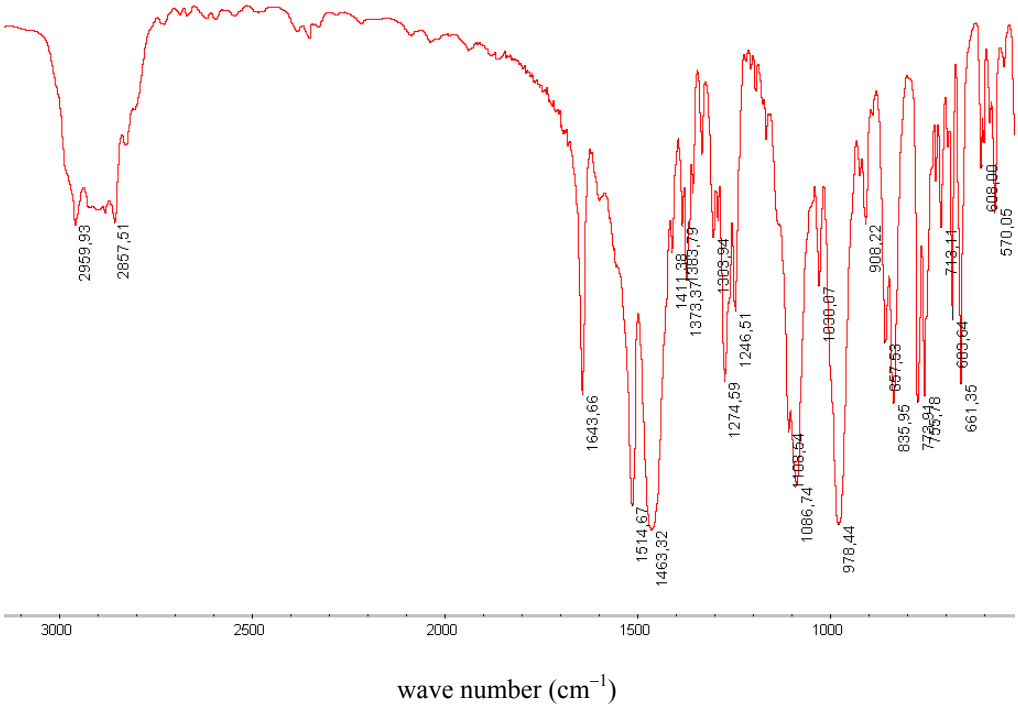

Figure S34. Solid-state IR (KBr pellet) spectrum of $[(Me_3TACD)InCH_2SiMe_3][B(C_6F_5)_4]$.

$(Me_3TACD)Li(\mu\text{-}Cl)AlMe_2$ (8).

A 2 mL THF solution of $(Li\text{-}Me_3TACD)_2$ (0.064 g, 0.292 mmol) was added to another 2 mL THF solution of $AlMe_2Cl$ (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 $[(Me_3TACD)Li(\mu\text{-}Cl)AlMe_2]$ (0.062 g, 0.198 mmol, 68%) as a colorless white powder. ^{1}H NMR (400 MHz, benzene-d_6): δ –0.04 (s, 6 H, AlMe_2), 1.61-1.67 (m, 2 H, CH_2), 1.76-1.90 (m, 10 H, Me_3-TACD and CH_2), 2.05-2.12 (m, 8 H, Me_3-TACD and CH_2), 2.31-2.36 (m, 2 H, CH_2), 3.56-3.63 (m, 2 H, CH_2). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz): δ 40.0 (Me_3-TACD), 43.2 (Me_3-TACD), 51.7 (CH_2), 53.3 (CH_2), 55.5 (CH_2), 60.3 (CH_2). ^{7}Li{^{1}H} NMR (156 MHz, benzene-d_6): δ 1.1. IR (KBr, cm^{-1}): 2924 (s, br), 2853 (s, br), 1464 (s), 1361 (s), 1317 (m), 1300 (s), 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 $C_{13}H_{31}N_4ClLiAl$: C, 49.92; H, 9.99; N, 17.91. Found: C, 49.68; H, 9.64; N, 17.67.

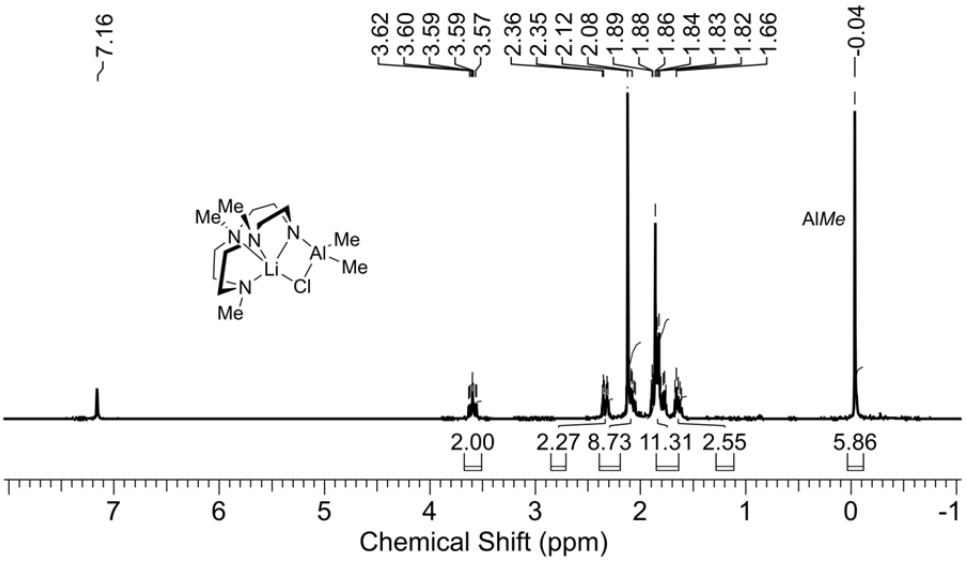

Figure S35. ^{1}H NMR spectrum of $(Me_3TACD)Li(\mu\text{-}Cl)AlMe_2$ in benzene-d_6.

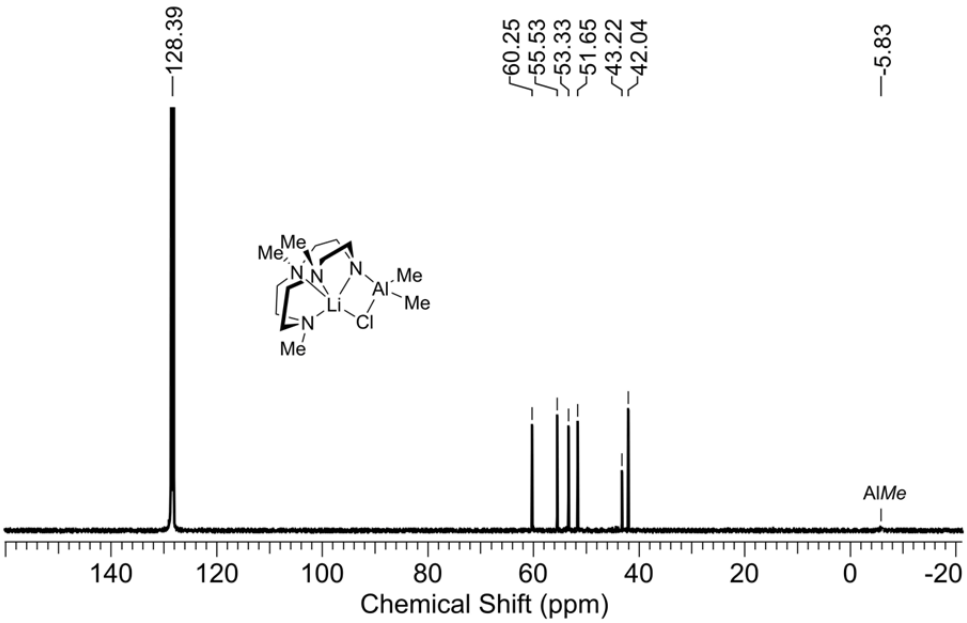

Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of $(Me_3TACD)Li(\mu\text{-}Cl)AlMe_2$ in benzene-d_6.

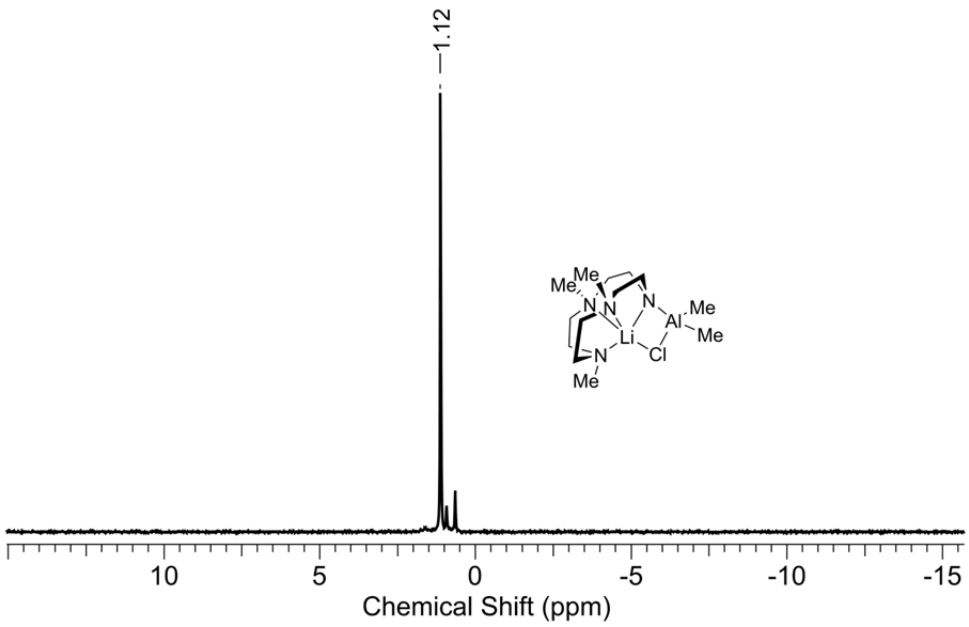

Figure S37. $^{7}Li\{^{1}H\}$ NMR spectrum of $(Me_3TACD)Li(\mu\text{-}Cl)AlMe_2$ in benzene-d_6.

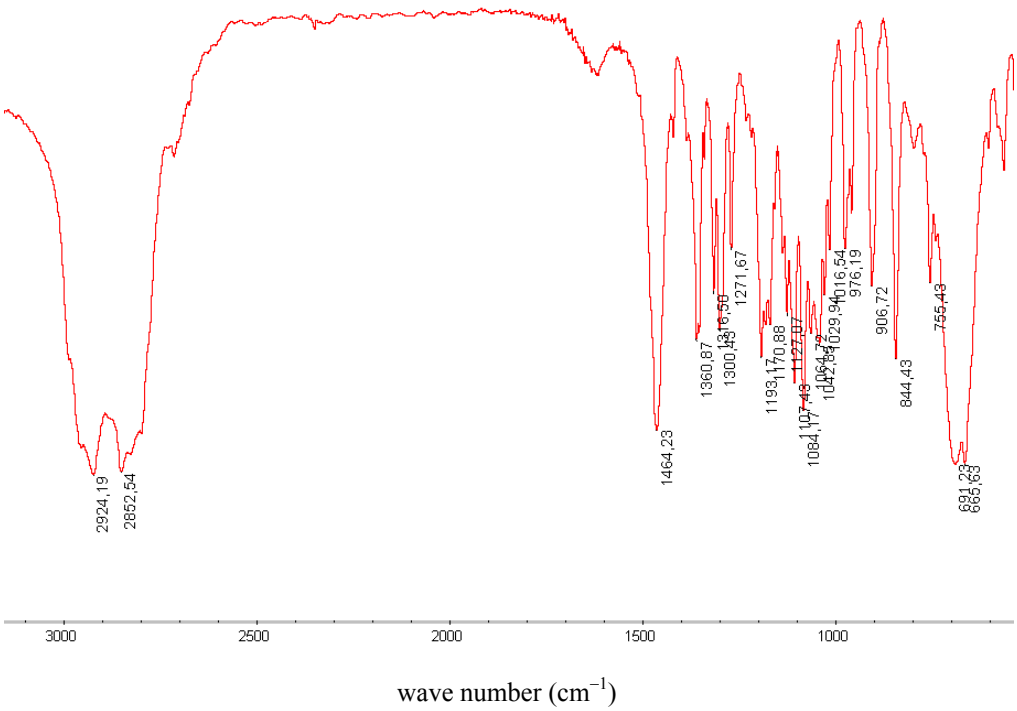

Figure S38. Solid-state IR spectrum of $(Me_3TACD)Li(\mu\text{-}Cl)AlMe_2$.

$InMe_2Cl$.

A 2 mL THF solution of Ph_3CCl (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 $InMe_2Cl$ (0.2440 g, 1.356 mmol, 90%) as a white crystalline solid.

(Me3TACD)Li(μ-Cl)InMe$_2$ (9).

(Li-Me$_3$TACD)$_2$ (0.081 g, 0.368 mmol) and InMe$_2$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 [(Me$_3$TACD)Li(μ-Cl)InMe$_2$] (0.113 g, 0.282 mmol, 77%) as a colorless white powder. δ 0.22 (s, 6 H, In*Me*$_2$), 1.66-1.72 (m, 2 H, C*H*$_2$), 1.77-1.96 (m, 9 H, *Me*$_3$-TACD and C*H*$_2$), 2.02-2.08 (m, 2 H, C*H*$_2$), 2.15-2.21 (m, 8 H, *Me*$_3$-TACD and C*H*$_2$), 2.50-2.55 (m, 2 H, C*H*$_2$), 3.30-3.37 (m, 2 H, C*H*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz): δ 43.0 (*Me*$_3$-TACD), 43.2 (*Me*$_3$-TACD), 53.2 (*C*H$_2$), 53.8 (*C*H$_2$), 54.4 (*C*H$_2$), 59.0 (*C*H$_2$). ^{7}Li{^{1}H} NMR (156 MHz, benzene-d_6): δ 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 $C_{13}H_{31}N_4ClLiIn$: C, 38.97; H, 7.80; N, 13.99. Found: C, 39.13; H, 7.64; N, 14.12.

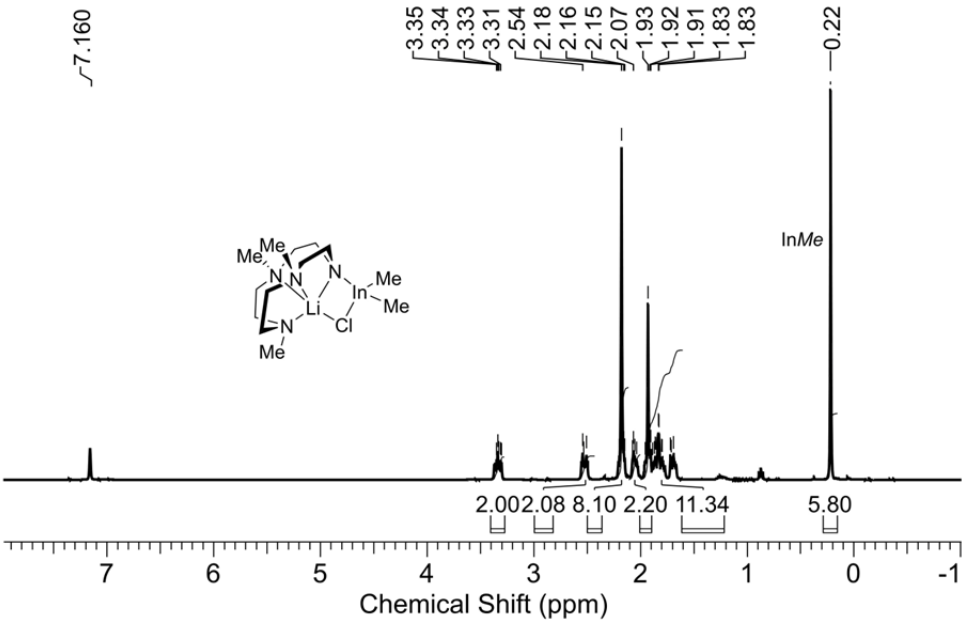

Figure S39. ^{1}H NMR spectrum of (Me$_3$TACD)Li(μ-Cl)InMe$_2$ in benzene-d_6.

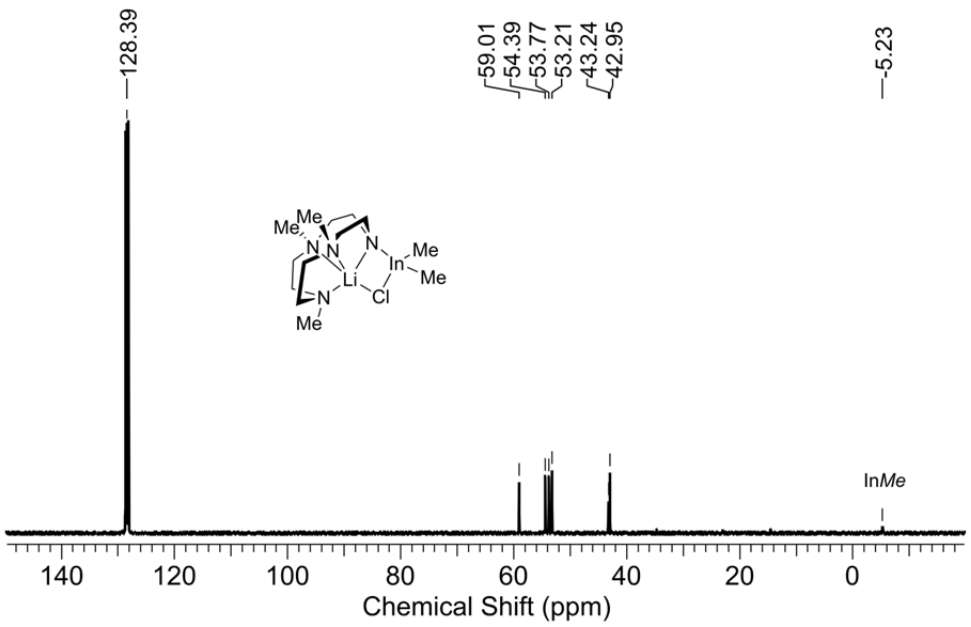

Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of $(Me_3TACD)Li(\mu\text{-}Cl)InMe_2$ in benzene-d_6.

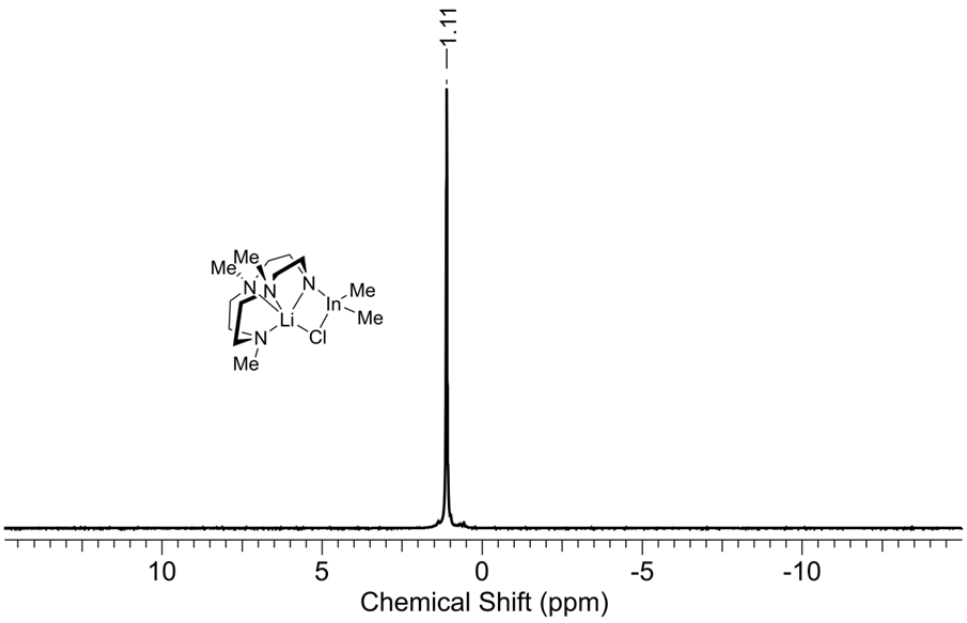

Figure S41. $^{7}Li\{^{1}H\}$ NMR spectrum of $(Me_3TACD)Li(\mu\text{-}Cl)InMe_2$ in benzene-d_6.

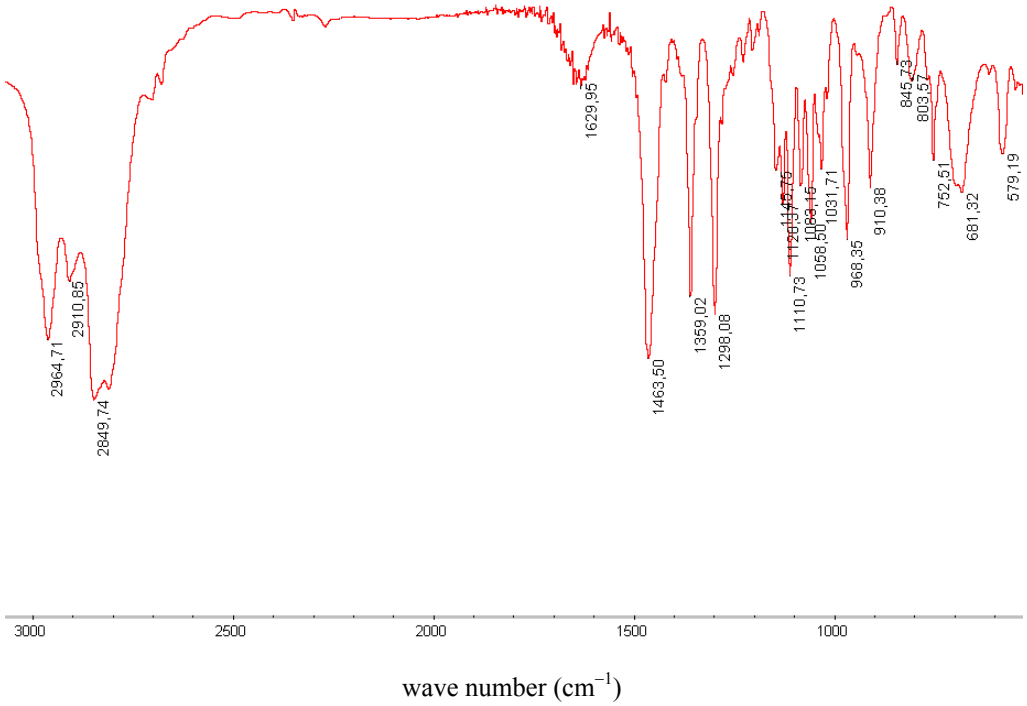

Figure S42. Solid-state IR (KBr pellet) spectrum of $(Me_3TACD)Li(\mu\text{-}Cl)InMe_2$.

Crystal Structure Analysis.

Data were collected on a Bruker CCD area-detector diffractometer with Mo Kα radiation (monolayer optics, λ = 0.71073 Å) using ω scans.[S7] 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.[S8] The structures were solved by direct methods (SIR-92).[S9] All non-hydrogen atoms were refined anisotropically using all reflections with the program SHELXL-2013 as implemented in the program system WinGX.[S10] All hydrogen atoms were placed in calculated positions and treated as riding. The graphical representations were performed with the program DIAMOND.[S11]

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

	5	**7**	**9**
Formula	$C_{214}H_{28}AlBF_{20}N_4$	$C_{39}H_{36}BF_{20}InN_4Si$	$C_{13}H_{31}ClInLiN_4$
M_w, g.mol^{-1}	934.41	1094.44	400.63
Cryst size, mm	0.11 × 0.12 × 0.33	0.10 × 0.13 × 0.23	0.32 × 0.33 × 0.57
Crystal color and habit	colourless block	colourless block	colourless rod
Cryst syst.	triclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/n$	$P2_1/n$
T, K	100(2)	100(2)	100(2)
a, Å	10.405(5)	12.1268(18)	12.5522(19)
b, Å	13.135(7)	20.852(3)	9.3814(14)

c, Å	13.498(6)	17.479(3)	16.834(3)
α, degree	92.447(14)		
β, degree	94.364(13)	107.209(3)	110.434(2)
γ, degree	93.859(14)		
V, Å^3	1832.8(15)	4222.0(11)	1857.6(5)
Z	2	4	4
D_{calcd}, g·cm^{-3}	1.693	1.722	1.433
μ(Mo K$_\alpha$), mm^{-1}	0.194	0.713	1.412
F(000)	940	2184	824
θ range, deg	2.12-25.50	1.56-25.19	2.50-26.63
Reflns collected	15773	44898	11109
Indep reflns (R_{int})	6755 (0.196)	7565 (0.0768)	3807 (0.0344)
Reflns obsd [$I > 2\sigma(I)$]	3101	5513	3369
Data/restraints/params	6755 /0 /563	7565 / 0 / 601	3807 /0 /186
R_1, wR_2 [$I > 2\sigma(I)$]	0.0742, 0.1514	0.0407, 0.0751	0.0265, 0.0612
R_1, wR_2 (all data)	0.1786, 0.1990	0.0681, 0.0848	0.0311, 0.0630
Goodness-of-fit on F^2	0.963	1.008	1.064
$\Delta\rho_{max, min}$, e·Å^{-3}	0.403, -0.404	0.574, -0.447	0.607, -0.544

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2-Fc^2)^2\}/\{\Sigma w(Fo^2)^2\}]^{1/2}$

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