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Hydridoaluminates and hydridoborates of lithium stabilized by a Cyclen-derived NNNN-Type macrocyclic ligand

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ABSTRACT

Lithium amide $[(Me_3TACD)Li]_2$ derived from the NNNN macrocycle $(Me_3TACD)H$ ($(Me_3TACD)H$ = 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane) reacted with DIBAL(H) to give the lithium hydridoaluminate $[(Me_3TACD{\cdot}AlH^iBu_2)Li(THF)]$ (**1-THF**). With HBPin, the lithium hydridoborate $[(Me_3TACD{\cdot}HBPin)Li]$ (**2**) was obtained. Both compounds have been characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction. The monomeric structure contains a five-coordinate lithium and does not show any interaction between the lithium center and the hydride.

1. Introduction

Lithium aluminumhydride and lithium borohydride are reducing agents well established in organic chemistry [1]. In the solid state, the lithium center is coordinated by anionic, tetrahedrally coordinated hydridoaluminate in $LiAlH_4$ or by hydridoborate in $LiBH_4$ [2]. Raston et al. reported $LiAlH_4$ with chelating nitrogen donors like *N,N′*-di-*tert*-butyl-2-*tert*-butyl-ethylenediamine, *N,N′*-di-*tert*-butyl-3-*tert*-butyl-1,4-diazabutene and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) as dimeric lithium tetrahydridoaluminates that contain an eight membered $Li_2Al_2H_4$ ring [3]. Stabilization with 1,4-di-*tert*-butyl-1,4-diazabutadiene gave $[Li\{N(^tBu)CHCH_2N(^tBu)\}_2AlH_2]$ where the lithium center does not coordinate to the hydrides [4]. An excess of TMEDA led to the monomeric ion pair $[(TMEDA)_2Li][AlH_4]$ [3c], whereas the polyamine ligand tris{2-(dimethylamino)ethyl}amine (Me_6TREN) produced the contact ion pair $[(Me_6TREN)Li(\mu\text{-}H)AlH_3]$ with a monodentate AlH_4 unit [5]. Arnold et al. converted $LiAlH_4$ with the macrocyclic ligand $(^iPr_2TACN)H$ into the lithium hydridoaluminate $[(^iPr_2TACN{\cdot}AlH_3)Li]_2$ [6]; its dimeric structure is based on an $Al_2N_2Li_2H_2$ eight-membered ring that involves two Li—H—Al bridges. Mixed lithium organo hydridoaluminates that involve $Li_2Al_2H_4$ eight-membered rings were synthesized by reacting $LiAlH_4$ or $AlH_3(NMe_3)$ with alkyllithium or aryllithium reagents LiR (R = $C(SiMe_3)_3$; $C(SiMe_2Ph)_3$; $C_6H_2Me_3$; $C_6H_2Ph_3$) [7]. Lithium amido hydrido dialkylaluminates were prepared by treating ^{n}BuLi and 2,2,6,6-tetramethylpiperidine ((H)TMP) with diisobutylaluminum hydride (DIBAL(H)) in the presence of suitable donor ligands [8]. Mixed lithium amido hydridoaluminates were obtained by converting $LiAlH_4$ with diethylamine [9] or hexamethyldisilazane (HMDS) [10] in the presence of stabilizing nitrogen based ligands. Veith et al. obtained a unique lithium amido hydridoaluminate by treating Li(HMDS) with an aluminum hydride reagent [11].

$LiBH_4$ can be stabilized by ethers, amines, *N*-heterocycles and (pyrazolyl)methanes as monomeric and dimeric species; chain structures and three-dimensional networks have also been observed in the solid state [5,12]. This broad structural variety includes monodentate, bidentate and tridentate BH_4 groups coordinated to the lithium center, as well as ion pairs where the lithium center does not show an interaction with the hydrides of the BH_4 units. Mulvey and Robertson et al. found the monomeric $[\{(^tBu)N(BH_3)(CH_2)_2N(H)(^tBu)\}Li(L)]$ (L = THF, pyridine) and the dimeric $[\{(Me)N(BH_3)(CH_2)_2N(Me)_2\}Li{\cdot}(L)]_2$ (L = THF, pyridine) lithium hydridoborates as intermediates in the cyclisation of diamine boranes with 1-lithio-2-*tert*-butyl-1,2-dihydropyridine [13]. In both compounds, the boron atom coordinates to a nitrogen atom of the ligand and both are connected by one or by two hydrides. Knizek and Nöth reported monomeric and dimeric lithium oxahydridoborates with lithium centers coordinated by the oxygen atoms of the oxahydridoborates [14]. Whereas the hydrides in the

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monomeric structure do not coordinate to lithium, the hydrides at the boron atom in this dimeric structure are bridged to the lithium atom. A mixed lithium alkyl hydridoborate with one Li–H–B bridge was isolated in the compound $[(THF)_3Li\{HB(^tBu)_3\}]$ [15].

We have earlier described the metalation of $(Me_3TACD)H$ ($(Me_3TACD)H = 1,4,7$-trimethyl-1,4,7,10-tetraazacyclododecane) [16] with *n*-butyllithium to the dimeric lithium complex $[(Me_3TACD)Li]_2$ [17]. Recently, we observed the formation of monomeric heterobimetallic lithium aluminum and indium adducts $[(Me_3TACD{\cdot}AlMe_2Cl)Li]$ and $[(Me_3TACD{\cdot}InMe_2Cl)Li]$ by treating $[(Me_3TACD)Li]_2$ with dimethylaluminum or dimethylindium chloride [18]. We wondered whether a hydride would coordinate to the lithium center in such systems. Here we report the formation of monomeric hydridoaluminates and hydridoborates of lithium by treating $[(Me_3TACD)Li]_2$ with DIBAL(H) and pinacolborane (HBPin).

2. Results and discussion

Lithium amide $[(Me_3TACD)Li]_2$ was previously found to be formed in the metalation of $(Me_3TACD)H$ with *n*-butyl lithium [16] as reported in the literature [17]. We have now obtained this compound from the reaction of $[LiCH_2SiMe_3]$ [20] with $(Me_3TACD)H$ in 46% yield based on $[LiCH_2SiMe_3]$ (Scheme 1). The reaction of $[(Me_3TACD)Li]_2$ with diisobutylaluminum hydride (DIBAL(H)) in toluene or THF at 25 °C gave $[(Me_3TACD{\cdot}AlH^iBu_2)Li]$ (**1**) or $[(Me_3TACD{\cdot}AlH^iBu_2)Li(THF)]$ (**1-THF**) in yields of 60% and 68%, respectively, based on DIBAL(H) (Scheme 1).

$[(Me_3TACD{\cdot}AlH^iBu_2)Li]$ (**1**) and $[(Me_3TACD{\cdot}AlH^iBu_2)Li(THF)]$ (**1-THF**) are soluble in THF, aromatic hydrocarbons (benzene, toluene) and in aliphatic hydrocarbons like *n*-pentane and *n*-hexane. The ^1H NMR spectrum of **1** in benzene-d_6 shows only signals for the Me_3TACD ligand and for the isobutyl groups of HAl^iBu_2, but no signal for the hydride. The ^7Li NMR spectrum of **1** reveals a singlet at δ 1.00 ppm and the ^{27}Al NMR spectrum a broad resonance at δ 149.2 ppm. Single crystals suitable for X-ray diffraction were obtained for $[(Me_3TACD{\cdot}AlH^iBu_2)Li(THF)]$ (**1-THF**). Fig. 1 shows the molecular structure of **1-THF** in the crystal.

$[(Me_3TACD{\cdot}AlH^iBu_2)Li(THF)]$ (**1-THF**) has a monomeric structure. The lithium center is coordinated by an oxygen atom of a THF ligand and by four nitrogen atoms of the monoanionic Me_3TACD ligand with distorted square pyramidal coordination geometry ($\tau = 0.02$) [21]. The distance between the lithium center and the amido nitrogen atom Li1–N1 of the Me_3TACD ligand of 2.146(4) Å is significantly shorter than those between the lithium center and the amine nitrogen atoms (Li1–N2: 2.224(4) Å, Li1–N3: 2.326(4) Å, Li1–N4 2.254(5) Å). A slightly shortened $Li–N_{amido}$ bond length was also found for $[(Me_3TACD{\cdot}InMe_2Cl)Li]$ [18]. The Al1–N1 distance of 1.914(2) Å is slightly longer than the Al–N distances in $[(^iPr_2TACN{\cdot}AlH_3)Li]_2$ [6] (1.877(2) Å) and $[Li\{N(^tBu)CHCH_2N(^tBu)\}_2AlH_2]$ [4] (1.888(6) Å), but comparable to the $Al–N_{amido}$ bond lengths in $[(Me_3TACD{\cdot}AlEt_3)Mg(SiHPh_2)]$ [22] and $[(Me_3TACD{\cdot}Al^iBu_3)Mg(SiH_2Ph)]$ [23], the aluminum center is also coordinated to the Me_3TACD ligand. The Li1···H1 distance of 3.52(2) Å is significantly longer than the Li–H distances in other lithium amido hydrido aluminates (1.91(3) – 2.14(5) Å) [3a,6,9,24]. This excludes an interaction between the lithium center and the hydride.

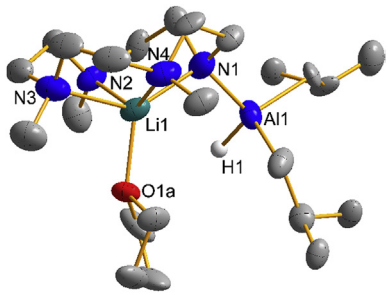
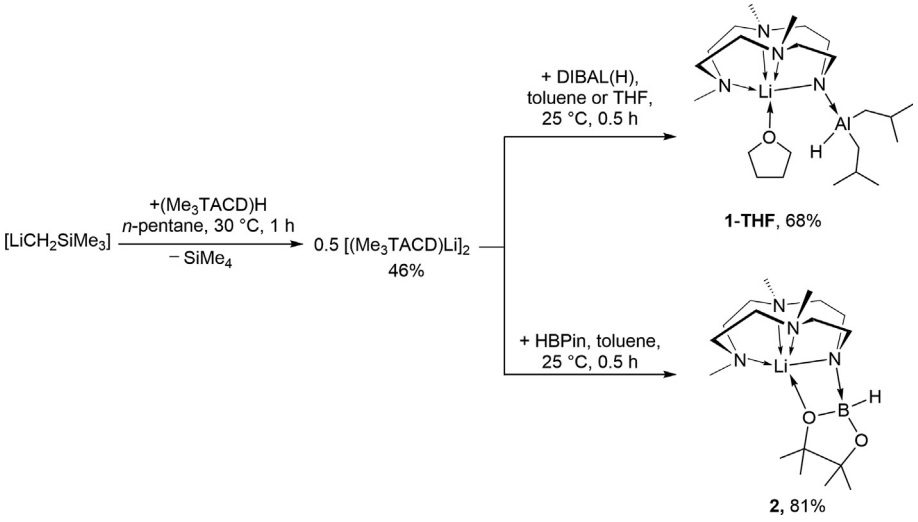


Fig. 1. Molecular structure of $[(Me_3TACD{\cdot}AlH^iBu_2)Li(THF)]$ (**1-THF**). Displacement parameters are shown at the 50% probability level. Hydrogen atoms, except for the hydride H1, are omitted for clarity. Disordered atoms are only shown with one split position. Selected interatomic distances [Å] and angles [°]: Li1–N1 2.146(4), Li1–N2 2.224(4), Li1–N3 2.326(4), Li1–N4 2.254(5), Al1–N1 1.914(2), Al1–H1 1.54(2), Li1···H1 3.52(2), N1–Li1–N3 136.48(19), N2–Li1–N4 135.37 (19).

Reaction of $[(Me_3TACD)Li]_2$ with two equivalents of pinacolborane (HBPin) in toluene at 25 °C gave $[(Me_3TACD{\cdot}HBPin)Li]$ (**2**) in 81% yield based on HBPin (Scheme 1). This compound is soluble in benzene, toluene and THF, but insoluble in aliphatic hydrocarbons *n*-pentane und *n*-hexane. The ^1H NMR spectrum shows the signals for the Me_3TACD ligand, two singlets for the methyl groups of HBPin at δ 1.36 and 1.62 ppm and a 1:1:1:1 quartet for the boron bounded hydride at δ 3.82 ppm ($^1J_{BH} = 114$ Hz). The ^7Li NMR spectrum shows a resonance at δ 0.79 ppm, the ^{11}B NMR spectrum a doublet at δ 6.71. Single crystals suitable for X-ray diffraction were obtained from a THF/*n*-



Scheme 1. Synthesis of $[(Me_3TACD{\cdot}AlH^iBu_2)Li(THF)]$ (**1-THF**) and $[(Me_3TACD{\cdot}HBPin)Li]$ (**2**).

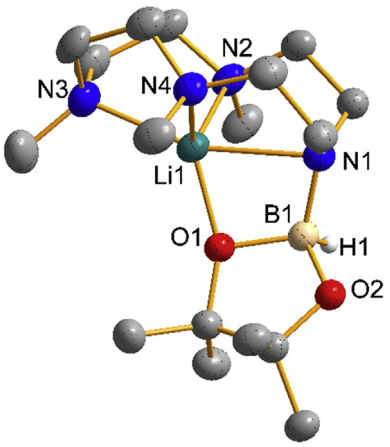


Fig. 2. Molecular structure of [(Me_3TACD·HBPin)Li] (**2**). Displacement parameters are shown at the 50% probability level. Hydrogen atoms, except for the hydride H1, are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Li1–O1 1.867(4), Li1–N1 2.298(4), Li1–N2 2.107(4), Li1–N3 2.159(4), Li1–N4 2.087(4), B1–N1 1.524(3), B1–O1 1.517(3), B1–O2 1.482(3), N1–Li1–N3 160.48(18), N2–Li1–N4 112.25(16).

pentane mixture at −30 °C within 24 h. Fig. 2 shows the molecular structure of **2**.

[(Me_3TACD·HBPin)Li] (**2**) has a monomeric structure with a lithium center coordinated by an oxygen atom of the pinacolborane unit and by four nitrogen atoms of the Me_3TACD ligand. The structure parameter τ [21] of 0.53 is between the values for square pyramidal (τ = 0) and for trigonal bipyramidal (τ = 1) coordination geometry. The Li–O bond length is with 1.867(4) Å significantly longer than the Li–O distance in the monomeric lithium oxadihydroborate described by Knizek and Nöth (1.535(4) Å) [14]. In contrast to the Me_3TACD stabilized lithium compounds **1** and [(Me_3TACD·$InMe_2Cl$)Li] [18], which show especially short distances between the lithium center and the amido nitrogen atom of the Me_3TACD ligand, **2** reveals a long distance between the lithium center and the amido nitrogen atom with 2.298(4) Å. This is caused by the four membered Li–O–B–N1 ring. The B1–O1 distance of 1.517(3) Å is significantly longer than the B1–O2 distance of 1.482(3) Å. The B1–N1 distance of 1.524(3) Å is in the range of the B–N distances of [(^{t}Bu)N(BH_3)$(CH_2)_2$N(H)(^{t}Bu)Li·(L)] (L = THF: 1.568(2) Å, L = py: 1.581(9) Å) [13]. The hydride at the boron atom points away from the lithium center which is part of the four membered Li–O–B–N1 ring.

3. Conclusion

Lithium amide [(Me_3TACD)Li]$_2$ [17] reacted with DIBAL(H) to give the lithium hydridoaluminates [(Me_3TACD·AlH^iBu_2)Li] (**1**) and [(Me_3TACD·AlH^iBu_2)Li(THF)] (**1-THF**), depending on the solvent. With HBPin, the lithium hydridoborate [(Me_3TACD·HBPin)Li] (**2**) was obtained. [(Me_3TACD·AlH^iBu_2)Li(THF)] (**1-THF**) shows a monomeric structure in the solid state without any interaction between the lithium center and the hydrides. An interaction between the lithium center and the hydride is also absent in [(Me_3TACD·HBPin)Li] (**2**), where the structure reveals a four membered Li–O–B–N ring.

4. Experimental section

General Considerations. All operations were performed under an inert atmosphere of dry argon using standard Schlenk techniques or glovebox techniques. Solvents (THF, *n*-pentane, *n*-hexane, toluene) were purified using a *MB SPS-800* solvent purification system or distilled under argon from sodium/benzophenone ketyl prior to use. Deuterated solvents (thf-d_8, benzene-d_6) were distilled under argon from sodium/benzophenone ketyl prior to use. The starting materials Me_3TACDH [19] and [$LiCH_2SiMe_3$] [20] were prepared according to literature procedures. NMR spectra were recorded on a *Bruker Avance II 400* or a *Bruker Avance III 400* spectrometer at 23 °C in J. Young-type NMR tubes. Chemical shifts (δ ppm) in ^{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. For the ^{7}Li, ^{11}B and ^{27}Al NMR spectra, the deuterium signal of the solvent was used as internal reference. 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*.

[(Me_3TACD)Li]$_2$. A solution of (Me_3TACD)H (429 mg, 2.0 mmol) in *n*-pentane (5 mL) was added dropwise to a solution of [$LiCH_2SiMe_3$] [20] (188 mg, 2.0 mmol) in *n*-pentane (5 mL) at −30 °C and the reaction mixture was stirred for 1 h at −30 °C. The solution was warmed to room temperature and the solvent was removed under reduced pressure. The crystalline solid was dried under vacuum and [(Me_3TACD)Li]$_2$ (407 mg, 0.92 mmol) was obtained in 46% yield. The NMR spectroscopic data correspond to those in the literature for [(Me_3TACD)Li]$_2$ [17].

[(Me_3TACD·AlH^iBu_2)Li] (1). Neat DIBAL(H) (28 mg, 0.2 mmol) was added dropwise to a solution of [(Me_3TACD)Li]$_2$ [17] (44 mg, 0.1 mmol) in toluene (2 mL) and the reaction solution was stirred for 30 min at room temperature. The solvent was removed under reduced pressure and the oily residue was dissolved in *n*-pentane or *n*-hexane (1 mL). Cooling the solution to −30 °C for 24 h led to the precipitation of a colorless solid. Decanting the solution and drying the solid under vacuum gave [(Me_3TACD·AlH^iBu_2)Li] (**1**) (44 mg, 0.12 mmol) in 60% yield. ^{1}H NMR (C_6D_6; 400.1 MHz): δ 0.48 (dd, $^3J_{HH}$ = 6.8 Hz, $^1J_{HH}$ = 13.6 Hz, 2H, CH_2-Al^iBu_2), 0.55 (dd, $^3J_{HH}$ = 6.8 Hz, $^1J_{HH}$ = 13.6 Hz, 2H, CH_2-Al^iBu_2), 1.48 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CH_3-Al^iBu_2), 1.49 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH_3-Al^iBu_2), 1.53–1.62 (m, 2H, CH_2–Me_3TACD), 1.71 (s, 3H, CH_3–Me_3TACD), 1.74–1.85 (m, 4H, 2 x CH_2–Me_3TACD), 2.00–2.10 (m, 4H, 2 x CH_2–Me_3TACD), 2.14 (s, 6H, 2 x CH_3–Me_3TACD), 2.40–2.44 (m, 4H, 2 x CH_2–Me_3TACD), 2.46 (sept., $^3J_{HH}$ = 6.8 Hz, 2H, 2 x CH-Al^iBu_2), 3.54–3.61 (m, 2H, CH_2–Me_3TACD) ppm. ^{13}C{^{1}H} NMR (C_6D_6; 100.6 MHz): δ 24.0 (CH_2-Al^iBu_2), 28.6 (CH-Al^iBu_2), 29.4 (CH_3-Al^iBu_2), 29.7 (CH_3-Al^iBu_2), 42.4 (CH_3–Me_3TACD), 43.5 (CH_3–Me_3TACD), 52.1 (CH_2–Me_3TACD), 53.8 (CH_2–Me_3TACD), 55.5 (CH_2–Me_3TACD), 60.6 (CH_2–Me_3TACD) ppm. ^{7}Li NMR (C_6D_6; 155.5 MHZ): δ = 1.00 ppm. ^{27}Al NMR (C_6D_6; 104.3 MHZ): δ 149.2 ppm. Anal. calc. For $C_{19}H_{44}N_4LiAl$ (362.51 g mol^{-1}): C, 62.95; H, 12.23; N, 15.46. Found: C, 62.79; H, 12.01; N, 15.65%.

[(Me_3TACD·AlH^iBu_2)Li(THF)] (1-THF). Neat DIBAL(H) (36 mg, 0.25 mmol) was added dropwise to a solution of [(Me_3TACD)Li]$_2$ [17] (55 mg, 0.125 mmol) in THF (2 mL) and the solution was stirred for 30 min at room temperature. A few drops of *n*-pentane were added to the solution and the mixture was cooled for 24 h at −30 °C. A colorless solid precipitated; the solution was decanted off and the solid residue was dried under vacuum to obtain [(Me_3TACD·AlH^iBu_2)Li(THF)] (**1-THF**) (74 mg, 0.17 mmol) in 68% yield. Crystals suitable for X-ray diffraction were obtained from THF/*n*-pentane at −30 °C over a period of 24 h ^{1}H NMR (C_6D_6; 400.1 MHz): δ 0.49 (dd, $^3J_{HH}$ = 6.8 Hz, $^1J_{HH}$ = 13.6 Hz, 2H, CH_2-Al^iBu_2), 0.55 (dd, $^3J_{HH}$ = 6.8 Hz, $^1J_{HH}$ = 13.6 Hz, 2H, CH_2-Al^iBu_2), 1.41 (THF), 1.49 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CH_3-Al^iBu_2), 1.50 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH_3-Al^iBu_2), 1.53–1.61 (m, 2H, CH_2–Me_3TACD), 1.70 (s, 3H, CH_3–Me_3TACD), 1.72–1.78 (m, 4H, 2 x CH_2–Me_3TACD), 1.80–1.87 (m, 2H, CH_2–Me_3TACD), 2.00–2.10 (m, 4H, 2 x CH_2–Me_3TACD), 2.13 (s, 6H, 2 x CH_3–Me_3TACD), 2.40–2.45 (m, 2H, CH_2–Me_3TACD), 2.47 (sept., $^3J_{HH}$ = 6.8 Hz, 2H, 2 x CH-Al^iBu_2), 3.57 (THF), 3.53–3.60 (m,

2H, CH_2–Me$_3$TACD) ppm. ^{13}C{^{1}H} NMR (C_6D_6; 100.6 MHz): δ 24.5 (CH_2-Al^{i}Bu$_2$), 26.1 (THF), 28.6 (CH-Al^{i}Bu$_2$), 29.4 (CH_3-Al^{i}Bu$_2$), 29.7 (CH_3-Al^{i}Bu$_2$), 42.4 (CH_3–Me$_3$TACD), 43.5 (CH_3–Me$_3$TACD), 52.1 (CH_2–Me$_3$TACD), 53.8 (CH_2–Me$_3$TACD), 55.4 (CH_2–Me$_3$TACD), 60.6 (CH_2–Me$_3$TACD), 68.2 (THF) ppm. ^{7}Li NMR (C_6D_6; 155.5 MHZ): δ 0.90 ppm. ^{27}Al NMR (C_6D_6; 104.3 MHZ): δ 150.5 ppm. Anal. calc. For $C_{23}H_{52}N_4OLiAl$ (434.62 g mol^{-1}): C, 63.56; H, 12.06; N, 12.89. Found: C, 61.79; H, 11.77; N, 13.52%.

[(Me$_3$TACD·HBPin)Li] (2). Neat pinacolborane (26 mg, 0.2 mmol) was added dropwise to a solution of [(Me$_3$TACD)Li]$_2$ [17] (44 mg, 0.1 mmol) in toluene (2 mL) and the solution was stirred for 30 min at room temperature. The solvent was removed and the colorless solid was washed with *n*-pentane (2 mL). The solid was dried under vacuum and [(Me$_3$TACD·HBPin)Li] (**2**) (57 mg, 0.16 mmol) was isolated in 81% yield. ^{1}H NMR (C_6D_6; 400.1 MHz): δ 1.36 (s, 6H, CH_3-HBPin), 1.62 (s, 6H, CH_3-HBPin), 1.67–1.74 (m, 2H, CH_2–Me$_3$TACD), 1.79–1.85 (m, 2H, CH_2–Me$_3$TACD), 1.84 (s, 3H, CH_3–Me$_3$TACD), 1.90–1.93 (m, 4H, 2 x CH_2–Me$_3$TACD), 1.95–2.03 (m, 2H, CH_2–Me$_3$TACD), 2.05–2.12 (m, 2H, CH_2–Me$_3$TACD), 2.18 (s, 6H, 2 x CH_3–Me$_3$TACD), 2.36–2.40 (m, 2H, CH_2–Me$_3$TACD), 3.82 (q, $^1J_{BH}$ = 114 Hz, 1H, *H*BPin), 3.77–3.85 (m, 2H, CH_2–Me$_3$TACD) ppm. ^{13}C{^{1}H} NMR (C_6D_6; 100.6 MHz): δ 27.5 (CH_3-HBPin), 29.5 (CH_3-HBPin), 42.2 (br. s, CH_3–Me$_3$TACD), 44.2 (br. s, CH_3–Me$_3$TACD), 50.9 (CH_2–Me$_3$TACD), 54.8 (CH_2–Me$_3$TACD), 56.4 (CH_2–Me$_3$TACD), 61.5 (CH_2–Me$_3$TACD), 76.8 (*C*-HBPin) ppm. ^{7}Li NMR (C_6D_6; 155.5 MHz): δ 0.79 ppm. ^{11}B NMR (C_6D_6; 128.4 MHz): δ 6.71 (d, $^1J_{BH}$ = 113.5 Hz) ppm. Anal. calc. For $C_{17}H_{38}N_4O_2BLi$ (348.27 g mol^{-1}): C, 58.63; H, 11.00; N, 16.09. Found: C, 58.77; H, 11.02; N, 16.39%.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.05.005.

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