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Lithiation of a Cyclen-Derived (NNNN) Macrocycle and Its Reaction with *n*-Butyllithium

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Cyclic polyamine 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane, (Me_3TACD)H (**1**), was metalated with *n*-butyllithium in pentane to give [Li_2(Me_3TACD)$_2$] (**2**). The structure of this compound is dimeric in the solid state as shown by single-crystal X-ray diffraction. With an excess of *n*BuLi, *n*BuLi is incorporated into the product. Depending on the stoichiometry, the compounds [Li_3(*n*Bu)(Me_3TACD)$_2$] (**3**) or [Li_4(*n*Bu)$_2$(Me_3TACD)$_2$] (**4**) are formed. As shown by single-crystal X-ray diffraction, both molecular structures show a ladder motif. (Me_3TACD)H reacted with NaI/Na_2CO_3 in acetonitrile to give benzene-soluble [NaI(Me_3TACD)H] (**5**).

Introduction

Cyclic polyamines are versatile ligands for metal complexes. Current applications are found in gadolinium complexes as contrast agents for magnetic resonance imaging (MRI).[1]

More than 600 crystal structures based on the macrocyclic amine fragment "$(CH_2CH_2N)_4$" are published in the Cambridge Structural Database (CSD), but all of the experimentally determined structures of alkali metal salts of (NNNN) macrocyclic polyamines contain further donor groups that are attached to this ring system. The so-called DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetato) macrocycle offers four additional coordination sites (Figure 1).[2]

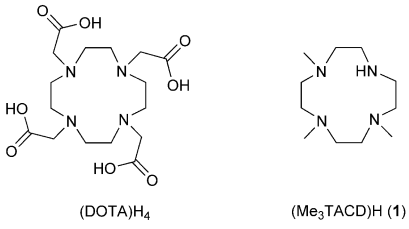

Figure 1. Derivatives of (TACD)H_4.

Recently, we introduced 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane, (Me_3TACD)H (**1**), as a precursor for a 10-electron-donor ligand and reported on the hydrosilylation activity of the yttrium hydride complex of Me_3TACD.[3] The metal complexes are obtained from an alkyl lanthanide precursor and the polyamine under metalation of the secondary amine group. A common route to metal complexes is salt metathesis starting from the metalated macrocyclic ligand (usually lithium is used).

Gas-phase structures of lithiated cyclen and its derivatives were established by computer simulation and geometry optimization.[4] The structure of Me_4TACD and its interaction with lithium ions in coordinating solvents was studied by multi-dimensional heteronuclear NMR spectroscopy techniques.[5] In the solid state, lithiated amines were found with fused $(NLi)_2$ rings in ladder structures.[6]

Results and Discussion

The macrocycle (Me_3TACD)H (**1**) is readily metalated by alkyllithium reagents (*n*BuLi or *t*BuLi) at the position of the secondary amine to give [Li_2(Me_3TACD)$_2$] (**2**) as colorless crystals by precipitation from the reaction mixture in pentane. X-ray diffraction on a single crystal proves that the composition is that of a dimeric species. The structure is based on a nearly planar Li_2N_2 ring that contains amido nitrogen atoms from both TACD ring ligands (N1 and N5). The metal atoms show relatively short bonds to both of these nitrogen atoms (within the Li_2N_2 unit) in the range 1.987(3)–2.038(3) Å. Additional close contacts to the amine units of the TACD ligands range from 2.160(3) to 2.328(3) Å (Figure 2), rendering Li1 and Li2 four-coordinate with pseudo-tetrahedral geometry [N–Li1–N 83.59(11)–130.97(15)°; N–Li2–N 80.80(11)–128.32(15)°]. This structure is related to the lithiated 1,4-diisopropyl-1,4,7-triazacyclononane, which is also dimeric in the solid state based on an Li_2N_2 fragment and contains pseudo-tetrahedrally coordinated metal atoms.[7] Compound **2** is soluble in benzene and is characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR as well as ^{7}Li NMR spectroscopy. The spectra reflect the lower symmetry of the coordinated ligand Me_3TACD as compared to the free (Me_3TACD)H (**1**). As in [Y(Me_3-

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TACD)(CH_2SiMe_3)$_2$], four signals are found in the ^{13}C NMR spectrum for the CH_2 units. The ^1H NMR spectrum shows the methylene groups as multiplets. We assigned the high-field signal of δ = 1.9 ppm to one of the two diastereotopic protons of both CH_2 groups that are adjacent to the deprotonated amido nitrogen atoms (N1 and N5) as expressed by the integration of 2 H. The ^7Li NMR spectrum shows one single resonance at δ = 1.56 ppm.

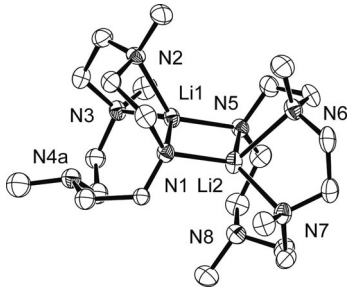
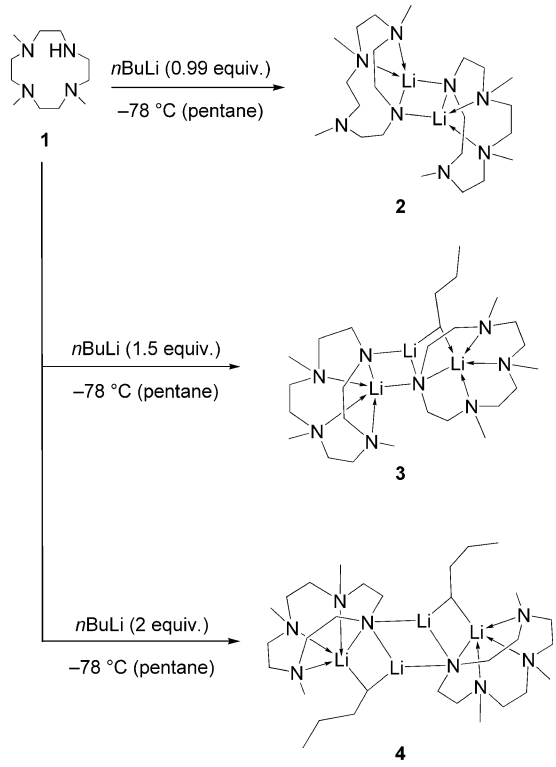


Figure 2. ORTEP view of [Li_2(Me_3TACD)$_2$] (**2**). Displacement ellipsoids are drawn at the 50% probability level. Atoms N4, C5, C6, C7, C8, and C11 were refined with split positions, and only one position is shown. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Li1–N1 2.031(3), Li1–N2 2.179(3), Li1–N3 2.160(3), Li1–N4a 3.298(4), Li1–N4b 3.254(7), Li1–N5 1.997(3), Li2–N1 1.987(3), Li2–N5 2.038(3), Li2–N6 2.328(3), Li2–N7 2.176(3), Li2–N8 2.695(3), Li1···Li2 2.450(4); N1–Li1–N5 104.99(14), N1–Li2–N5 105.08(14), Li1–N1–Li2 75.16(12), Li1–N5–Li2 74.78(12), Li1–N1–C1 103.13(13).

It is still impossible to predict the composition or the structure of a metalated polyamine. Reaction of the related 1,4-dimethyl-1,4,7-triazacyclononane with *n*-butyllithium leads to a cyclic trimer of composition [Li_3($C_8H_{18}N_3$)$_3$].[8] The nature of the reaction product may also depend on the alkyllithium reagent. Whereas 1,4,7-trimethyl-1,4,7-triazacyclononane reacts with *n*BuLi to give a dimer by deprotonation, reaction with *t*BuLi leads to an unusual μ-*t*Bu complex.[9] This compound contains one lithium atom in the rare trigonal-planar coordination geometry, is highly reactive, and decomposes in non-aliphatic solvents. We have also obtained a similar product by treating **1** with 1.5 equiv. of *n*BuLi (see Scheme 1). The resulting [Li_3(*n*Bu)(Me_3-TACD)$_2$] (**3**) contains one μ-*n*Bu fragment. It precipitates as colorless needles from the reaction mixture in pentane. By slow crystallization we have obtained a single crystal suitable for X-ray diffraction. The crystallographic data enable the molecular structure to be established, but because of the small crystal size and the resulting low intensity of the X-ray data the result of the refinement is not discussed in detail.[10] The trinuclear compound **3** is based on an Li_3N_3 framework: compounds with this motif were described before as a three-rung ladder.[6,11] Li3 is coordinated by both amido nitrogen atoms as well as the α-carbon atom of the *n*-butyl group in a trigonal geometry. Although this structure is unsymmetric, both atoms Li1 and Li2 are five-coordinate. Li1 is coordinated by five nitrogen atoms and Li2 by four nitrogen atoms and the μ-carbon atom C23 of the *n*Bu fragment. Compound **3** was characterized by NMR spectroscopy in C_6D_6 at room temperature. The ^1H NMR spectrum confirms the ratio of Me_3TACD ligand/*n*Bu fragment of 2:1. The α-CH_2 unit of the *n*-butyl fragment displays a signal at δ = –0.50 ppm in the ^1H NMR spectrum and at δ = 12.5 ppm in the ^{13}C NMR spectrum. These values are comparable to those found in related amines that contain an excess of *n*-butyllithium, indicating that this structural fragment is stable in solution.[12,13] As in **2**, the methylene groups in the Me_3TACD ring lead to four distinct signals. The ^7Li NMR spectrum shows two signals at δ = 1.42 and 3.06 ppm from the different coordination geometries.



Scheme 1. Metalation of (Me_3TACD)H (**1**).

After isolating the precipitate of **3**, we observed that some colorless plates were slowly growing from the supernatant liquid. A structure determination revealed that they belong to an *n*BuLi adduct of lithiated Me_3TACD with composition [Li_4(*n*Bu)$_2$(Me_3TACD)$_2$] (**4**). This compound was also obtained by treating **1** with 2 equiv. of *n*BuLi in 23% yield. The molecular structure is based on an $Li_4N_2C_2$ framework, which can be considered as an extension of the ladder structure in **3**. Two of the lithium atoms (Li1 and Li2) are coordinated by all four nitrogen atoms of a TACD ring in addition to one μ-carbon atom of an *n*Bu unit resulting in square-pyramidal geometry with Li–N distances of 2.190(3)–2.282(3) Å as well as Li–C distances of 2.211(4) and 2.210(4) Å. As in **2** (see Figure 2) and **3**, both amido nitrogen atoms are coordinated to a further lithium atom. In **4**, both lithium atoms within the central Li_2N_2 fragment are coordinated by two nitrogen atoms as well as by one μ-carbon atom from the *n*Bu fragment (Figure 3). The trigonal-planar geometry is shown by the sum of the angles

around Li3 (359°) and Li4 (360°). Each α-carbon atom of the *n*Bu fragment (C23 and C27) bridges two lithium atoms: one that is coordinated to the TACD moiety (Li1 and Li2) and one that belongs to the central Li_2N_2 fragment of the ladder structure (Li3 and Li4). The *n*-butyl αC–Li bond lengths average 2.16 Å, similar to those in $(n\text{BuLi})_6$ (average Li–C 2.16 and 2.27 Å).[13] This compound is soluble in benzene, and the ^{1}H NMR spectrum shows that this structure is also present in solution. The spectra are similar to those of **3**. The main difference is the Me_3TACD ring/*n*Bu fragment ratio of 1:1 in the ^{1}H NMR spectrum. The signal of the αCH_2 group is found at δ = –0.57 ppm in the ^{1}H NMR spectrum and at δ = 11.2 ppm in the ^{13}C NMR spectrum.

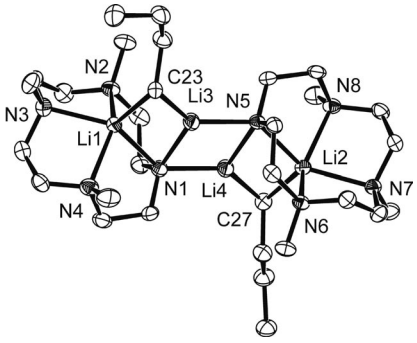
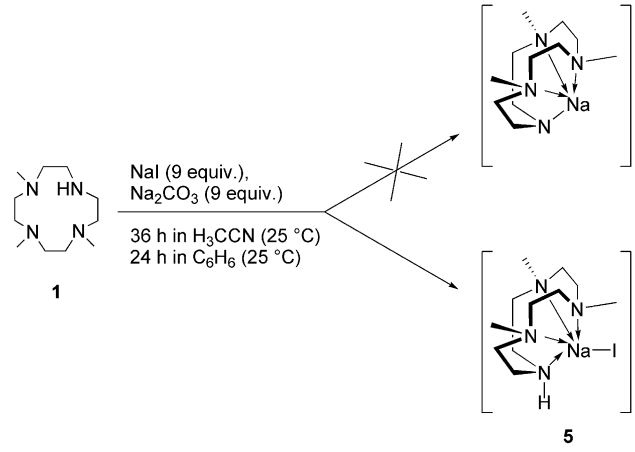


Figure 3. ORTEP view of $[Li_4(n\text{Bu})_2(Me_3\text{TACD})_2]$ (**4**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Li1–N1 2.213(3), Li1–N2 2.260(4), Li1–N3 2.190(3), Li1–N4 2.199(4), Li1–C23 2.211(4), Li2–N5 2.207(3), Li2–N6 2.282(3), Li2–N7 2.193(3), Li2–N8 2.214(3), Li2–C27 2.210(4), Li3–N1 2.035(4), Li3–C23 2.111(4), Li3–N5 2.047(4), Li4–N1 2.058(4), Li4–N5 2.038(4), Li4–C27 2.108(4); N1–Li1–C23 106.60(14), Li1–N1–Li3 66.38(13), Li1–N1–Li4 136.37(14), Li1–C23–Li3 65.21(13), N1–Li3–C23 117.63(17), N1–Li3–N5 109.12(16), C23–Li3–N5 132.59(18), N1–Li4–N5 108.55(16), N1–Li4–C27 134.38(18), N5–Li4–C27 116.94(17), Li2–C27–Li4 65.67(13), N5–Li2–C27 106.31(14), Li2–N5–Li4 66.87(13).

Compound **1** reacts with a mixture of NaI and Na_2CO_3 (see Scheme 2) in analogy to a reaction between armed aza crown ether complexes and $[NaI(Me_3\text{TACD})H]$ (**5**) as described in ref.[14] The reaction proceeds slowly, and, after 48 h, ca. 55% of **5** can be isolated. The yield is increased to ca. 75% if the reaction is carried out for 70 h. The sodium atom reaches a coordination number of five by interaction with the iodine atom. The four nitrogen atoms of the Me_3-TACD ligand form the base of a square pyramid (Figure 4). All four N atoms are located in a plane with the metal atom located 1.2803(11) Å out of this plane. The distance between the metal center and N1 (NR_2H group) of 2.5108(19) Å is slightly longer than the other Na–N distances of 2.4589(18), 2.4652(18), and 2.4861(19) Å. The crystal packing reveals hydrogen bonds to the iodine atom with a closest intermolecular distance of 3.70 Å to a methyl hydrogen atom of a neighboring molecule (H9B). The covalent bonding character within this sodium compound is expressed by its solubility in benzene. The ^{1}H NMR spectrum of **5** shows partly overlapping signals for the methyl as well as for the methylene groups of $(Me_3\text{TACD})H$. The coordination to the sodium atom is reflected in the high-field shift of the signals of several CH_2 groups from δ = 2.21–2.43 to 1.74–2.13 ppm. These methylene groups lead to four signals in the $^{13}C\{^1H\}$ NMR spectrum. Because of the coordination to the metal atom, all signals are found at a higher field compared to those of $(Me_3\text{TACD})H$ (**1**), especially the signal at δ = 43.7 ppm. The ^{23}Na NMR spectrum shows one signal at δ = 17.63 ppm (sodium iodide is insoluble in benzene).



Scheme 2. Reaction of $(Me_3\text{TACD})H$ with NaI.

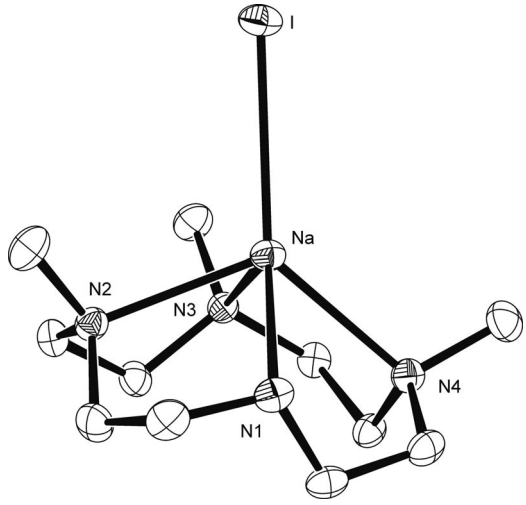


Figure 4. ORTEP view of $[NaI(Me_3\text{TACD})H]$ (**5**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Na–N1 2.5108(19), Na–N2 2.4589(18), Na–N3 2.4652(18), Na–N4 2.4861(19), Na–I 3.0441(8); N1–Na–I 136.44(5), N2–Na–I 109.37(5), N3–Na–I 105.02(5), N4–Na–I 130.33(5), Na–N1–C1 108.23(13), Na–N1–C8 105.06(12), C1–N1–C8 112.62(16).

Conclusions

The cyclic polyamine $(Me_3\text{TACD})H$ (**1**) is readily metalated with *n*BuLi to give $[Li_2(Me_3\text{TACD})_2]$ (**2**) that has a dimeric structure in the solid state. We are currently using

this compound to synthesize transition metal and lanthanide complexes by salt metathesis. The formation of the *n*BuLi adducts **3** and **4** shows that an exact amount of alkyllithium reagent must be used. Similar to other related compounds, a molecular structure with a ladder motif is found.

Experimental Section

General: All reactions and manipulations were performed under dry, oxygen-free argon. The solvents were purified according to standard procedures. All ^{1}H, ^{13}C and ^{23}Na NMR spectra were obtained with a Bruker Avance-II 400 MHz spectrometer, the ^{7}Li NMR spectra were performed with a Varian 500 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane as the external reference and were calibrated against the residual solvent resonance. The ^{7}Li NMR chemical shifts are relative to external LiCl. The ^{23}Na NMR chemical shifts are relative to external NaCl. Downfield values are reported as positive and coupling constants are given in Hz. Microanalyses were carried out at the Microanalytical Laboratory of the Department of Organic Chemistry. $(Me_3TACD)H$ (**1**) was prepared according to a literature procedure.[15] NaI and Na_2CO_3 were dried at 140 °C for 48 h. The concentration of the *n*BuLi and *t*BuLi solutions were determined by direct titration with *N*-pivaloyl-*ortho*-toluidine.[16]

$[Li_2(Me_3TACD)_2]$ (2). (a) An *n*BuLi solution in cyclohexane (0.62 mL, 2.25 M, corresponding to 1.404 mmol of *n*BuLi or 0.99 equiv.) was slowly added to a solution of $(Me_3TACD)H$ (0.304 g, 1.418 mmol) in pentane (15 mL) at –78 °C over a period of 10 min. Stirring was continued at this temperature for 25 min and at room temperature for further 30 min. After filtration, evaporation of the solvent in vacuo gave the lithium salt as a colorless solid in a yield of 0.305 g (0.692 mmol, 98%). Crystals suitable for an X-ray structure determination were obtained from pentane at –40 °C. $C_{22}H_{50}Li_2N_8$ (440.58): calcd. C 59.98, H 11.44, N 25.43; found C 59.75, H 11.40, N 25.65. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.88–1.97 (m, 2 H, CH_2), 2.14 (s, 3 H, NCH_3), 2.26–2.39 (m, 12 H, CH_2, NCH_3), 2.44–2.55 (m, 2 H, CH_2), 2.82–2.92 (m, 2 H, CH_2), 3.18–3.26 (m, 2 H, CH_2), 3.53–3.62 (m, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 43.7 (NCH_3), 44.6 (NCH_3), 54.1 (CH_2), 55.2 (CH_2), 56.5 (CH_2), 59.4 (CH_2) ppm. ^{7}Li NMR (194 MHz, C_6D_6, 25 °C): δ = 1.56 (s, LiN) ppm. **(b)** A *t*BuLi solution in hexane (0.72 mL, 1.83 M, corresponding to 1.318 mmol of *t*BuLi or 0.94 equiv.) was slowly added to a solution of $(Me_3TACD)H$ (0.301 g, 1.404 mmol) in pentane (15 mL) at –78 °C over a period of 10 min. Stirring was continued at this temperature for 25 min and at room temperature for further 30 min. After filtration, evaporation of the solvent in vacuo gave the lithium salt as a colorless solid in a yield of 0.280 g (0.636 mmol, 96%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.88–1.97 (m, 2 H, CH_2), 2.14 (s, 3 H, NCH_3), 2.27–2.38 (m, 12 H, CH_2, NCH_3), 2.45–2.53 (m, 2 H, CH_2), 2.81–2.91 (m, 2 H, CH_2), 3.17–3.25 (m, 2 H, CH_2), 3.52–3.61 (m, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 43.7 (NCH_3), 44.6 (NCH_3), 54.1 (CH_2), 55.2 (CH_2), 56.5 (CH_2), 59.5 (CH_2) ppm. ^{7}Li NMR (194 MHz; C_6D_6; 25 °C): δ = 1.56 (s, LiN) ppm.

$[Li_3(nBu)(Me_3TACD)_2]$ (3): An *n*BuLi solution in cyclohexane (0.80 mL, 1.65 M, corresponding to 1.320 mmol of *n*BuLi or 1.51 equiv.) was slowly added to a solution of $(Me_3TACD)H$ (0.187 g, 0.872 mmol) in pentane (10 mL) at –78 °C over a period of 10 min. Stirring was continued at this temperature for 30 min and at room temperature for further 30 min. After filtration, evaporation of the solvent in vacuo gave the lithium salt as a colorless solid in a yield of 0.202 g (0.400 mmol, 92%). Crystals suitable for an X-ray structure determination were obtained from pentane at –40 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = –0.49 (t, $^{3}J_{H,H}$ = 8.28 Hz, 2 H, CH_2), 1.42 (t, $^{3}J_{H,H}$ = 7.28 Hz, 3 H, $(CH_2)_3CH_3$), 1.74–1.96 (m, 10 H, CH_2), 2.07 (s, 6 H, NCH_3), 2.08–2.13 (m, 4 H, CH_2), 2.22–2.24 (m, 2 H, CH_2), 2.26–2.36 (m, 20 H, CH_2, NCH_3), 2.62–2.69 (m, 4 H, CH_2), 2.94–3.03 (m, 4 H, CH_2), 3.37–3.45 (m, 4 H, CH_2) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 12.5 (CH_2), 15.0 [$(CH_2)_3CH_3$], 34.2 (CH_2), 36.4 (CH_2), 44.0 (NCH_3), 44.9 (NCH_3), 53.7 (CH_2), 54.0 (CH_2), 54.7 (CH_2), 59.5 (CH_2) ppm. ^{7}Li NMR (194 MHz, C_6D_6, 25 °C): δ = 1.42 (s, LiN), 3.06 (s, LiC) ppm.

$[Li_4(nBu)_2(Me_3TACD)_2]$ (4): An *n*BuLi solution in cyclohexane (0.84 mL, 1.65 M, corresponding to 1.386 mmol of *n*BuLi or 2.01 equiv.) was slowly added to a solution of $(Me_3TACD)H$ (0.148 g, 0.690 mmol) in pentane (8 mL) at –78 °C over a period of 30 min. Stirring was continued at this temperature for 30 min and at room temperature for further 30 min. After filtration, evaporation of the solvent in vacuo gave the lithium salt as a colorless solid in a yield of 0.045 g (0.079 mmol, 23%). Crystals suitable for an X-ray structure determination were obtained from pentane at –40 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = –0.57 (t, $^{3}J_{H,H}$ = 8.28 Hz, 4 H, CH_2), 1.41 [t, $^{3}J_{H,H}$ = 7.27 Hz, 6 H, $(CH_2)_3CH_3$], 1.69–1.77 (m, 4 H, CH_2), 1.82–1.93 (m, 8 H, CH_2), 1.95–2.00 (m, 4 H, CH_2), 2.01–2.04 (m, 2 H, CH_2), 2.04–2.17 (m, 14 H, CH_2, NCH_3), 2.23 (s, 9 H, NCH_3), 2.28 (s, 3 H, NCH_3), 2.29–2.36 (m, 2 H, CH_2), 2.61–2.69 (m, 4 H, CH_2), 2.94–3.04 (m, 4 H, CH_2), 3.29–3.46 (m, 4 H, CH_2) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 11.4 (CH_2), 14.8 [$(CH_2)_3CH_3$], 34.8 (CH_2), 36.5 (CH_2), 43.3 (NCH_3), 43.9 (NCH_3), 44.9 (NCH_3), 51.2 (CH_2), 53.7 (CH_2), 54.0 (CH_2), 59.3 (CH_2) ppm. ^{7}Li NMR (194 MHz, C_6D_6, 25 °C): δ = 1.42 (s, LiN), 1.65 (s, LiN), 3.00 (s, LiC) ppm.

$[NaI(Me_3TACD)H]$ (5): A solution of $(Me_3TACD)H$ (0.433 g, 2.0 mmol) in acetonitrile (5 mL) was added dropwise to a suspension of NaI (1.901 g, 18 mmol) and Na_2CO_3 (2.710 g, 18 mmol) in acetonitrile (40 mL) at room temperature. After stirring at room temperature for 70 h, the solution was filtered, and the solvent was evaporated in vacuo. Crude **5** (0.543 g, 1.5 mmol, 75%) was obtained as a colorless powder after filtration of the solution and evaporation of the solvent. For purification the product was recrystallized from benzene at room temperature. Single crystals were obtained by slow crystallization from benzene at room temperature. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.74–2.00 (m, 12 H, CH_2), 2.01–2.12 (m, 2 H, CH_2), 2.34 (s, 6 H, NCH_3), 2.38 (s, 3 H, NCH_3), 2.52–2.63 (m, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 43.7 (CH_2), 44.5 (NCH_3), 46.2 (NCH_3), 53.0 (CH_2), 53.7 (CH_2), 55.1 (CH_2) ppm. ^{23}Na NMR (105.5 MHz, C_6D_6, 25 °C): δ = 17.63 (s, NaN) ppm.

X-ray Diffraction Data: The crystallographic data for **2**, **4**, and **5** are reported in Table 1. X-ray diffraction intensity data for **2** and **5** were collected with a Bruker CCD area detector with graphite-monochromated Mo-K_α radiation by using ω-scans. For **4**, an Incoatec microsource with multilayer optics was used. Cell refinement, data reduction, and empirical absorption corrections were carried out with the program systems SMART, SADABS, and Platon, respectively.[17,18] All structures were solved with the program SIR-92[19] as incorporated in the WINGX package.[20] Final refinements based on F^2 were carried out with the program SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms, which were included by using a riding model with isotropic *U* val-

Table 1. Crystallographic data for **2**, **4**, and **5**.

	2	**4**	**5**
Empirical formula	$C_{22}H_{50}Li_2N_8$	$C_{30}H_{68}Li_4N_8$	$C_{11}H_{26}IN_4Na$
M_r [g mol^{-1}]	440.58	568.68	364.25
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a [Å]	8.771(2)	15.4509(11)	9.3405(7)
b [Å]	27.387(7)	9.1904(6)	9.1214(7)
c [Å]	11.858(3)	25.5757(18)	19.3229(14)
β [°]	110.826(4)	91.591(2)	100.8280(10)
V [Å^3]	2662.3(11)	3630.3(4)	1617.0(2)
Z	4	4	4
F(000)	976	1264	736
μ (Mo-K_α) [mm^{-1}]	0.067	0.061	1.996
T [K]	100(2)	100(2)	130(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Measured reflections	31046	31571	23676
Unique reflections	5427	7431	4798
$R_{int.}$	0.0629	0.0665	0.0960
Data/restraints/parameters	5427/0/283	7431/0/403	4798/0/160
Final R indices [$I > 2\sigma(I)$], $R1$, $wR2$	0.0536, 0.1223	0.0628, 0.1637	0.0318, 0.0631
Final R indices all data, $R1$, $wR2$	0.0702, 0.1323	0.0814, 0.1775	0.0378, 0.0657
GoF on F^2	1.029	1.053	0.968
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$ [e Å^{-3}]	0.328, –0.282	0.462, –0.224	1.889, –0.941

ues depending on the U_{eq} of the adjacent carbon atoms.[21] In the Me_3TACD ring ligand of **2**, the position of the atoms N4, C6, C7, C8, C9, and C11 were refined with split positions and isotropic displacement parameters. In **5**, the hydrogen atoms of the α-carbon atom of the butyl fragment C23 and C27 were located in a Fourier difference map and refined in their position. Graphical representations were obtained with the program ORTEP-3.[22] CCDC-766057 (for **2**), -766058 (for **3**), -766059 (for **4**), and -766060 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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