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Synthesis and Molecular Structure of the Lithiated Triamidoamine [Li$_3${N(CH$_2$CH$_2$SiBu^{t}Me$_2$)$_3$}(THF)$_n$]

Paul Roussel, Nathaniel W. Alcock, and Peter Scott*

Department of Chemistry, University of Warwick,
Coventry, CV4 7AL, UK

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Introduction

Most complexes of the triamidoamines [N(CH$_2$CH$_2$NR)$_3$]$^{3-}$ with transition elements incorporate the substituents R = Me$_3$Si and C$_6$F$_5$, these ligands being the most readily prepared.[1] The complexes have unique properties as a result, for example, of the formation of a single sterically protected apical coordination site. In contrast, the actinide complexes [U{N(CH$_2$CH$_2$NSiMe$_3$)$_3$}X] tend to have dimeric or distorted structures unless strong π-donor ligands X are used,[2] even though the closely related compounds [U{N(SiMe$_3$)$_2$}$_3$X] are monomeric and 3-fold symmetric.[3] We have found[4] that the ligand N(CH$_2$CH$_2$NSiBu^{t}Me$_2$)$_3$ (henceforth NN′$_3$) forms complexes with the f-elements which have very favorable steric properties; the three *tert*-butyl groups are oriented such that they encircle the equatorial plane in 3-fold symmetric (trigonal pyramidal) structures and thus stabilize this geometry while allowing reactivity at the remaining axial site. Unfortunately, the use of the trilithium salt [Li$_3$(NN′$_3$)] prepared by literature methods[5,6] gives low yields (0−30%) of compounds [M(NN′$_3$)Cl] on reaction with MCl$_4$ (M = U, Th, and also Mo[7]), despite that fact that the analogous titanium complex is obtained quantitatively.[5] In this note we describe the convenient large scale synthesis of crystalline [Li$_3$(NN′$_3$)(THF)$_3$], the determination of its molecular structure, and its efficient conversion to the solvent free compound [Li$_3$(NN′$_3$)].

Experimental Section

[Li$_3$(NN′$_3$)(THF)$_3$]. Lithium butyl (98.5 cm^3, 2.50 M in hexanes, 3 equiv) was added dropwise at −50 °C to a solution of distilled tris(2-aminoethyl)amine (TREN) (12 g, 0.082 mol) in dry tetrahydrofuran (200 cm^3). The mixture was stirred for 30 min during which time it was allowed to warm to 0 °C. The solution was then cooled to −50 °C, and a solution of sublimed *tert*-butylchlorodimethylsilane (37.1 g, 0.246 mol, 3 equiv) in tetrahydrofuran (40 cm^3) was added over a period of 5 min. The mixture was stirred for 30 min with slow warming to 0 °C. After evaporation of volatiles under reduced pressure at ambient temperature, a liquid nitrogen cooled probe was inserted into the flask in order to facilitate removal of the last traces of solvent in vacuo. The oily residue was extracted into pentane (3 × 50 cm^3) and filtered. If required, this solution may be evaporated to give virtually pure H$_3$(NN′$_3$). Lithium butyl (98 cm^3, 2.5 M in hexanes) was added dropwise to the combined extracts at −80 °C. The mixture was allowed to warm slowly to −30 °C and was stirred for a further 15 min. The solution was then cooled to −50 °C, and tetrahydrofuran (18 cm^3, 3 equiv) was added. The white microcrystalline solid which precipitated was isolated by cannula filtration and dried in vacuo (46 g, 78%).

^{1}H NMR (293 K, toluene-d_8): δ 3.52 (m, 12H, THF), 3.15 (t, 6H, CH$_2$), 2.35 (t, 6H, CH$_2$), 1.37 (m, 12H, THF), 1.01 (s, 27H, Bu^t), 0.05 (s, 18H, SiMe$_2$). ^{13}C{^{1}H} NMR (293 K, toluene-d_8): δ 68.69 (s, THF), 56.56 (s, CH$_2$), 45.28 (s, CH$_2$), 28.55 (s, *Me*$_3$C), 25.44 (s, THF), 20.72 (s, Me$_3$*C*), −2.46 (s, Me$_2$Si). MS (EI): *m/z* 486 [24, M$^+$ − Li$_3$(THF)$_3$], 473 [100, M$^+$ − Li$_3$(THF)$_3$ − Me].

[Li$_3$(NN′$_3$)]. Distillation of [Li$_3$(NN′$_3$)(THF)$_3$] at 160 °C and 10^{-6} mbar through a constriction in a horizontal glass tube gave a pure colorless oil in 91% yield on a scale of up to 5 g. ^{1}H NMR (293 K, benzene-d_6): δ 3.01 (t, 6H, CH$_2$), 2.12 (t, 6H, CH$_2$), 0.99 (s, 27H, Bu^t), 0.07 (s, 18H, SiMe$_2$). ^{13}C{^{1}H} NMR (293K, benzene-d_6): δ 56.38 (s, CH$_2$), 43.71 (s, CH$_2$), 28.18 (s, *Me*$_3$C), 20.05 (s, Me$_3$*C*), −2.87 (s, Me$_2$Si). MS (EI): *m/z* 486 (29%, M$^+$ − Li$_3$), 473 (100%, M$^+$ − Li$_3$ − Me).

Molecular structure of [Li$_3$(NN′$_3$)(THF)$_2$]. Crystals were coated with inert oil and transferred to the cold (180 K) N$_2$ gas stream on the diffractometer (Siemens SMART three-circle system with CCD area detector). The structure was solved by direct methods using SHELXS[8] with additional light atoms found by Fourier methods. Two CH$_2$ groups in one THF group are disordered between two positions [occupancy 0.60(2) and 0.40]. Si(3) and its attached alkyl groups have a major and a minor position differing by a small rotation about N(3) [occupancy 0.682(3) and 0.318]. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H atom is attached. Refinement was performed using SHELXL 96.[9] Table 1 lists full experimental data.

Results and Discussion

Synthesis of [Li$_3$(NN′$_3$)(THF)$_3$] and [Li$_3$(NN′$_3$)]. Since distillation of (NN′$_3$)H$_3$ leads to significant decomposition,[10] we decided to attempt a one-pot synthesis at low temperature. A solution of TREN in THF was treated sequentially at low temperature with 3 equiv of lithium butyl and with 3 equiv of *tert*-butylchlorodimethylsilane. Evaporation of the solvent, extraction into pentane and thorough drying in vacuo gave virtually pure H$_3$(NN′$_3$). A solution of this amine in pentane was treated at low temperature with 3 equiv of lithium butyl to give, presumably, [Li$_3$(NN′$_3$)]. While we have been unable to crystallize this material from pure pentane, addition of 3 molar equiv of THF gave a white crystalline precipitate of [Li$_3$(NN′$_3$)(THF)$_3$] in 78% yield. This reaction has been performed on a scale of up to 46 g of product.

Heating crystalline [Li$_3$(NN′$_3$)(THF)$_3$] to 140 °C at 10^{-6} mbar affords a pure distillate of colorless oil [Li$_3$(NN′$_3$)]. This

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* Corresponding author. E-mail peter.scott@warwick.ac.uk.

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Table 1. Experimental Data for the X-ray Diffraction Study of $[Li_3(NN'_3)(THF)_2]$

empirical formula	$C_{32}H_{73}Li_3N_4O_2Si_3$
fw	651.03
crystal system	triclinic
space group	$P\bar{1}$
a/Å	11.494(2)
b/Å	12.763(3)
c/Å	15.499(3)
α/deg	80.42(3)
β/deg	92.44(2)
γ/deg	81.79(3)
cell volume/Å^3	2157.2(8)
Z	2
density (calculated) g/cm^3	1.002
F(000)	720
λ(Mo K_α)/Å	0.71073
μ/cm^{-1}	1.38
temperature/°C	−93(2)
crystal size/mm	0.36 × 0.26 × 0.21
θ_{max}/deg	25
no. of unique reflcns	7297 [$R_{int} = 0.0314$]
no. of measd reflcns	10581
no. of parameters	450
T_{max}, T_{min}	0.93, 0.79 (from ψ scans)
goodness of fit on F^2	0.916
(Δp) max, min (e Å^{-3})	+0.285, −2.93 (near U)
R_1 [$I > 2\sigma(I)$], wR_2(all data)^a	0.0572, 0.1594
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0800P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

material will be useful in the synthesis of metal complexes where "base-free" systems are required.

Cooling a solution of $[Li_3(NN'_3)(THF)_3]$ in pentane to −30 °C led to elimination of one THF ligand and the formation of colorless crystals of the dimer $[\{Li_3(NN'_3)(THF)_2\}_2]$. The molecular structure of this compound as determined by X-ray crystallography (Table 1) is shown in Figure 1. Selected bond distances and angles are listed in Table 2. The molecule, which has an inversion center midway between Li(2) and Li(2A), contains two triamidoamine ligands linked *via* coordination of one amido N(2) atom each to the Li(2)−Li(2A) unit. One THF molecule makes up the essentially trigonal planar coordination at each Li(2/2A). Two amido nitrogen atoms N(1) and N(3) bridge Li(1) and Li(3) forming a butterfly with hinge angle 7.9°. The nonbonded Li(1)−Li(2) and Li(2)−Li(2A) distances of 2.408(10) and 2.371(7) Å are not unusually short.[11] The amino N(4) is the third ligand at Li(1) which has pyramidal geometry; the Li atom is 1.0 Å out of the plane, and the mean N−Li−N angles are 97.6°. A disordered THF molecule completes the slightly pyramidal geometry about each Li(3/3A) which lie 0.32 Å out of the plane.

The structure of $[\{Li_3(NN'_3)(THF)_2\}_2]$ contrasts with that of the monomeric trimethylsilyl-substituted analogue $[Li_3(NN_3)(THF)_2]$ which contains a trigonal monopyramidal lithium atom in the solid state, although a fluxional process involving positional exchange of lithium atoms occurs on the NMR time scale with $\Delta G_c = 44.2$ kJ/mol.[12] For $[Li_3(NN'_3)(THF)_n]$ (n = 0, 2, 3), ^1H, ^{13}C, and ^7Li NMR spectra were essentially invariant over the temperature range −90 to 20 °C. Hence a structure similar to that shown in Figure 1 is not retained in solution.

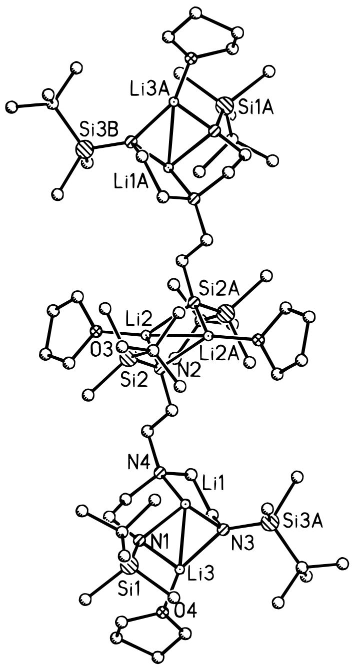

Figure 1. Molecular structure of $[Li_3(THF)_2(NN'_3)]$ (non-hydrogen atoms). Disorder in some THF molecules and in Si(3) and its associated alkyl groups not shown.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Li_3(THF)_2(NN'_3)]^a$

Li(1)−N(3)	1.979(6)	N(3)−Li(1)−N(1)	107.2(2)
Li(1)−N(1)	1.977(5)	N(3)−Li(1)−N(4)	91.6(2)
Li(1)−N(4)	2.022(6)	N(1)−Li(1)−N(4)	93.3(2)
Li(1)−Li(3)	2.371(7)	O(3)−Li(2)−N(2)#1	124.7(3)
Li(2)−O(3)	1.937(5)	O(3)−Li(2)−N(2)	129.2(3)
Li(2)−N(2)#1	1.992(5)	N(2)#1−Li(2)−N(2)	106.0(2)
Li(2)−N(2)	2.008(6)	O(3)−Li(2)−Li(2)#1	176.7(4)
Li(2)−Li(2)#1	2.408(10)	N(2)#1−Li(2)−Li(2)#1	53.3(2)
Li(3)−O(4)	1.913(6)	N(2)−Li(2)−Li(2)#1	52.7(2)
Li(3)−N(1)	1.994(6)	O(4)−Li(3)−N(1)	118.7(3)
Li(3)−N(3)	2.002(6)	O(4)−Li(3)−N(3)	127.8(3)
		N(1)−Li(3)−N(3)	105.6(3)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, -y + 1, -z + 1$.

Conclusion

The lithiated triamidoamine $[Li_3(NN'_3)(THF)_3]$ is conveniently prepared in a one-pot procedure. We have found that use of this new source of the ligand leads to greatly increased yields of subsequent complexes. For example, its reaction with UCl_4 gives $[U(NN'_3)Cl]$ in 95% isolated yield.

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Supporting Information Available: X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead change.

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