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Structures and Dynamics of the Tripodamide Ligand Transfer Reagents $[H_3CC\{CH_2N(Li)Si(CH_3)_3\}_3\{L\}_3]$ (L = thf, hmpta)

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Introduction

The role that alkali metal amides play as organic deprotonation reagents and amide transfer reagents[1] has fueled the extensive structural investigations of an ever increasing number of these species along with their donor solvent adducts.[2] More recently, multifunctional alkali metal amides which have gained considerable importance in the synthesis of high valent early transition metal complexes[3,4] have been the focus of such investigations and were found to display structural patterns which deviate from the conventional systematics.[5−7]

The solvates of monofunctional alkalimetal amides are known to display characteristic solvation patterns which are dominated by dimeric (cyclic) structures of the general type $[(LiNR_2)_2(L)_2]$ (R = alkyl, aryl, silyl, L = monodentate donor solvent or co-ligand) or more or less extended ladder-type structures in which the Li-atoms at the ends are co-ordinated by a co-ligand while those of the inner rungs remain unsolvated and thus three-coordinate.[2]

We have recently shown that restricting the configurational flexibility of the amido functions by their incorporation into a hydrocarbon or carbosilyl framework may lead to novel structural types in unsolvated lithium amides such as the stacked adamantoid cage of $[H_3CC\{CH_2N(Li)Si(CH_3)_3\}_3]_2$ (**1**) which contains a central $(LiN)_6$ unit[6] or the monomeric adamantoid structure of $HC\{(CH_3)_2SiN(Li)t\text{Bu}\}_3$ (**2**).[7] The latter (containing a puckered $(LiN)_3$ ring) was converted to the trimeric ladder structure $[(LiNR_2)_3(L)_2]$ upon solvation with a donor solvent (L) and has resisted all attempts to isolate and characterize the (atypical!) tris-solvate. Both the solvated and unsolvated lithium amides have proved to be the reagents of choice in the synthesis of a whole series of tripodal transition metal amido complexes. Their efficiency is, however, dictated by the presence or absence as well as the nature of a coligand, in most cases a donor solvent such as diethyl ether or THF. It was therefore of interest to investigate the hitherto unknown solvate structures derived from **1**.

Experimental Section

All manipulations were performed under an inert gas atmosphere of dried argon in standard (Schlenk) glassware which was flame dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze−pump−thaw" cycles and dried over 4-Å molecular sieves.

The ^1H-, ^{13}C-, ^{29}Si-, ^{31}P-, and ^7Li-NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable temperature unit (at 200.13, 50.32, 39.76, 81.03, and 77.78 MHz, respectively) with tetramethylsilane, LiI (1M, ext.) and H_3PO_4 (85%, external) as references.

Elemental analyses were carried out in the microanalytical laboratory of the Chemistry Department at Würzburg. $[H_3CC\{CH_2N(Li)Si(CH_3)_3\}_3]_2$ (**1**) was prepared as reported previously by us.[6] All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of Compounds. $\mathbf{H_3CC[CH_2N(Li)SiMe_3]_3(OC_4H_8)_3}$ **(3a).** To a stirred solution of 527 mg (0.75 mmol) $\{H_3CC[CH_2N(Li)SiMe_3]_3\}_2$ in 30 mL of pentane which was cooled at −30°C were added 0.365 mL (4.50 mmol) of THF. After warming to ambient temperature and concentration of the solution the reaction product **3a** precipitated as a highly crystalline colorless solid which was isolated by filtration. Yield: 0.58 g (83%). Anal. Calcd for $C_{26}H_{60}Li_3N_3O_3Si_3$: C, 55.00; H, 10.65; N, 14.80. Found: C, 54.71; H, 10.37; N, 14.66. ^1H-NMR (toluene-d_8, 295 K) δ = 0.18 (s, $Si\{CH_3\}_3$), 0.83 (s, CH_3−C), 1.47 (m, $\{CH_2$−$CH_2\}_2O$), 3.51 (CH_2−N), 3.61 ($\{CH_2$−$CH_2\}_2O$). ^{13}C-NMR (toluene-d_8, 295 K): δ = 2.7 ($Si\{CH_3\}_3$), 26.3 ($\{CH_2$-$CH_2\}_2O$), 30.5 (CH_3−C), 44.3 (CH_3−C), 63.5 (CH_2−N), 69.3 ($\{CH_2$−$CH_2\}_2O$. ^{29}Si-NMR (toluene-d_8, 295 K): δ = −3.6. ^7Li-NMR (toluene-d_8, 295 K): δ = 5.12.

$\mathbf{H_3CC[CH_2N(Li)SiMe_3]_3(OP(NMe_2)_3)_3}$ **(3b).** To a stirred solution of 527 mg (0.75 mmol) $\{H_3CC[CH_2N(Li)SiMe_3]_3\}_2$ in 30 mL of toluene which was cooled at −30°C were added 0.810 mL (4.50 mmol) of HMPTA. After warming to ambient temperature the solution was concentrated to 4 mL and layer with 10 mL of pentane the reaction product **3a** precipitated as a highly crystalline colorless solid which

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Table 1. Crystal Data and Experimental Datails for **3a** and **3b**

	3a	**3b**
empirical formula	$C_{26}H_{60}N_3O_3Si_3Li_3$	$C_{32}H_{90}N_{12}O_3P_3Si_3Li_3$
fw	567.855	889.14
cryst syst	orthorhombic	monoclinic
cell params		
a (Å)	18.271(4)	12.903(3)
b (Å)	20.212(4)	23.876(4)
c (Å)	10.298	18.509(4)
β (deg)		104.37(3)
V (Å^3)	3803(2)	5523(3)
Z	4	4
D_{calc} (g cm^{-1})	0.992	1.069
space group	$P2_12_12_1$	$P2_1/c$
F(000)	1248	1944
μ(Mo Kα) (cm^{-1})[a]	1.4	2.1
θ_{max} (deg)	25	21
hkl range	+21, +23, +12	±12, ±24, +18
no. of reflcns measured[b]	3775	1946
no. of unique reflcns; merging R	3775	1856; 0.0507
no. of obsd reflcns	946 [$I \geq 2\sigma(I)$]	1665 [$I \geq 3\sigma(I)$]
no. of variables[c]	131	225
residuals: R; R_w[d]	0.0946; 0.0946	0.0991; 0.0994

[a] An empirical absorption correction, using the program DIFABS (Walker, N.; Stuart, D. *Acta Crystallogr. A* **1993**, *39*, 158) was applied for both crystals. The data were corrected for Lorentz and polarization effects. [b] The intensities of the representative reflections were measured every 5 h of X-ray exposure time. They remained constant throughout the data collection indicating in both cases crystal and electronic stability (no decay correction was applied). [c] Neutral atom scattering factors were taken from: Cromer. D. T.; Waber, J. T. *International Tables of X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. Anomalous dispersion effects were included in the final F_{calc} (Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781). [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$.

was isolated by filtration. Yield: 1.00 g (75%). Anal. Calcd for $C_{32}H_{90}Li_3N_{12}P_3O_3Si_3$: C, 43.23; H, 10.20; N, 18.90. Found: C, 43.49; H, 10.32; N, 19.12. ^{1}H-NMR (toluene-d_8, 295 K) δ = 0.42 (s, Si-{CH_3}$_3$), 0.97 (s, CH_3–C), 2.36 (d, $^3J_{PH}$ = 9.2 Hz, N{CH_3}$_2$), 3.56 (CH_2–N). ^{13}C-NMR (toluene-d_8, 295 K): δ = 2.4 (Si{CH$_3$}$_3$), 30.0 (CH$_3$–C), 37.0 (N{CH$_3$}$_2$), 43.4 (CH$_3$–C), 63.6 (CH$_2$–N). ^{29}Si-NMR (toluene-d_8, 295 K): δ = 3.4. ^{7}Li-NMR (toluene-d_8, 295 K): δ = 4.89. ^{31}P-NMR (toluene-d_8, 295 K): δ = 29.3.

X-ray Crystallographic study of 3a and 3b. The clear, colorless crystals of of both compounds had a block shaped prismatic habit. A fragment of a crystal of **3a** with the approximate dimensions 0.48 × 0.42 × 0.42 mm was mounted under argon in a Lindemann capillary. A crystal of **3b** having the approximate dimensions 0.46 × 0.45 × 0.34 mm was mounted in a similar way. The X-ray diffraction data were collected using a Philips PW1100 four-circle diffractometer with graphite monochromated Mo Kα radiation using the θ-2θ scan technique.[8] Both crystals were very weak diffractors which resulted in a lack of high angle diffraction data. Unit cell parameters were determined by a least-squares analysis of 25 automatically centered reflections in the range 10° < θ < 15°. Full details are presented in Table 1.

The data analysis and refinement was carried out with the programs of the SHELX-76 and SHELX-86 software packages.[9] Both structures were solved by using direct methods and subsequent difference-Fourier maps. Initial refinement showed very high thermal parameters for the tetrahydrofuran groups in **3a** and the terminal carbon atoms in **3b**. For **3a** a difference Fourier map calculated with a fine grid allowed the carbon atoms to be resolved into two peaks. The site occupancies of the pairs of atoms were fixed to total 1.0 and the individual value in the range of 0.30–0.70 were obtained after two cycles of refinement with fixed thermal parameter (U = 0.08 Å^2). In the subsequent stages, the thermal parameters were refined but the positional parameters were fixed and not refined further. For **3b** a difference-Fourier map calculated without the methyl groups on the HMPTA molecules showed a region of slightly extended electron density which allowed no further resolution. The H-atoms were assigned calculated positions with a fixed thermal parameter of 0.08 Å (except for the hydrogen atoms on the disordered carbons of **3a**) and were allowed to "ride" on the relevant carbon atoms in the final cycles of full-matrix refinement in which all atoms had isotropic thermal parameters. The positional parameters of **3a** and **3b** are listed in Tables 2 and 3 respectively.

Table 2. Fractional Atomic Coordinates of **3a** Where the Second Disordered Conformation of the THF Molecule is Labeled with Primed Numbers

atom	x	y	z
Si(1)	0.3899(4)	0.8218(4)	0.1331(8)
Si(2)	0.0820(4)	0.8476(3)	0.3994(7)
Si(3)	0.1521(4)	0.5988(3)	0.1806(7)
N(1)	0.3041(6)	0.7949(7)	0.1607(16)
N(2)	0.1492(8)	0.8183(7)	0.3038(14)
N(3)	0.1886(8)	0.6750(6)	0.1686(17)
C(1)	0.2528(11)	0.8115(10)	0.0534(20)
C(2)	0.1264(12)	0.8241(11)	0.1705(23)
C(3)	0.1597(14)	0.7153(12)	0.0496(25)
C(4)	0.1752(11)	0.7900(11)	0.0582(23)
C(5)	0.1394(11)	0.8110(9)	−0.0762(20)
C(11)	0.4317(15)	0.7830(13)	−0.0210(20)
C(12)	0.4529(13)	0.8006(14)	0.2773(19)
C(13)	0.3937(16)	0.9169(6)	0.1227(30)
C(21)	0.0437(14)	0.9348(8)	0.3660(30)
C(22)	0.1186(15)	0.8500(14)	0.5749(15)
C(23)	−0.0054(10)	0.7942(12)	0.3982(28)
C(31)	0.1396(14)	0.5526(11)	0.0184(16)
C(32)	0.0568(8)	0.5977(11)	0.2606(22)
C(33)	0.2115(11)	0.5407(10)	0.2849(21)
O(1)	0.3008(9)	0.8954(9)	0.4515(17)
C(1a)	0.35910	0.88090	0.55950
C(1a′)	0.30490	0.86370	0.58900
C(2a)	0.35190	0.92600	0.65060
C(2a′)	0.29040	0.92590	0.67800
C(3a)	0.32740	0.97730	0.58170
C(3a′)	0.28040	0.97260	0.61690
C(4a)	0.28580	0.96910	0.46520
C(4a′)	0.24570	0.95640	0.49610
O(2)	0.2134(9)	0.6909(8)	0.4929(18)
C(1b)	0.27990	0.69770	0.52970
C(1b′)	0.29110	0.66730	0.50240
C(2b)	0.31010	0.64450	0.63220
C(2b′)	0.27840	0.67020	0.65870
C(3b)	0.21680	0.64260	0.69260
C(3b′)	0.22590	0.60510	0.66450
C(4b)	0.15450	0.67980	0.61000
C(4b′)	0.17050	0.65140	0.56720
O(3)	0.3716(8)	0.6314(7)	0.1532(16)
C(1c)	0.41390	0.61380	0.25500
C(1c′)	0.43410	0.59660	0.22080
C(2c)	0.47290	0.55720	0.11890
C(2c′)	0.45020	0.54340	0.19800
C(3c)	0.44570	0.56900	0.00920
C(3c′)	0.42000	0.53440	0.06800
C(4c)	0.37690	0.59750	0.01430
C(4c′)	0.36380	0.58090	0.06400
Li(1)	0.2511(20)	0.8399(18)	0.3128(37)
Li(2)	0.1765(20)	0.7273(19)	0.3172(43)
Li(3)	0.2997(20)	0.6947(17)	0.1622(38)

Results and Discussion

The investigation of the solvation properties of [H$_3$CC{CH$_2$N(Li)Si(CH$_3$)$_3$}$_3$]$_2$ has now revealed the preferential formation of the corresponding fully solvated species [H$_3$CC{CH$_2$N(Li)Si(CH$_3$)$_3$}$_3${L}$_3$] [L = thf (**3a**), hmpta (**3b**)] which is in stark contrast to the solvation behavior of **2** which only generated the bis-solvate. This situation was thought to be a consequence

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Table 3. Fractional Atomic Coordinates of **3b**

atom	*x*	*y*	*z*
Si(1)	0.1384(5)	0.0817(2)	0.0845(3)
C(11)	0.0447(13)	0.1192(8)	0.0062(8)
C(12)	0.0615(13)	0.0306(7)	0.1274(10)
C(13)	0.2233(13)	0.0403(7)	0.0354(10)
Si(2)	0.4990(5)	0.1317(3)	0.3640(4)
C(21)	0.4671(17)	0.0691(6)	0.4153(12)
C(22)	0.6350(10)	0.1199(11)	0.3485(14)
C(23)	0.5197(18)	0.1915(7)	0.4311(11)
Si(3)	0.1612(5)	0.2781(3)	0.3033(4)
C(31)	0.0953(17)	0.3418(6)	0.2536(12)
C(32)	0.0630(15)	0.2490(10)	0.3525(12)
C(33)	0.2755(13)	0.3039(9)	0.3790(10)
N(1)	0.2095(10)	0.1243(5)	0.1522(7)
N(2)	0.4019(9)	0.1403(6)	0.2842(6)
N(3)	0.1969(11)	0.2289(5)	0.2479(7)
C(1)	0.2754(15)	0.1665(8)	0.1229(12)
C(2)	0.4274(16)	0.1857(9)	0.2365(12)
C(3)	0.2675(15)	0.2513(8)	0.2047(12)
C(4)	0.3392(15)	0.2091(8)	0.1742(12)
C(5)	0.3928(14)	0.2460(8)	0.1244(11)
P(1)	0.4452(5)	−0.0415(3)	0.2138(4)
O(1)	0.3738(9)	0.0040(5)	0.2280(8)
N(11)	0.3779(12)	−0.0984(4)	0.1887(9)
C(111)	0.2627(18)	−0.1007(10)	0.1535(14)
C(112)	0.4234(18)	−0.1543(10)	0.1883(14)
N(12)	0.5005(15)	−0.0219(10)	0.1485(9)
C(121)	0.5300(19)	0.0380(11)	0.1438(15)
C(122)	0.5358(24)	−0.0571(13)	0.1008(18)
N(13)	0.5387(11)	−0.0604(7)	0.2853(7)
C(131)	0.5106(19)	−0.0829(11)	0.3523(15)
C(132)	0.6466(23)	−0.0515(13)	0.2924(18)
P(2)	0.1235(5)	0.0672(3)	0.3719(4)
O(2)	0.1725(11)	0.1011(6)	0.3216(7)
N(21)	−0.0050(7)	0.0605(11)	0.3432(14)
C(211)	−0.0676(23)	0.0991(13)	0.3077(18)
C(212)	−0.0384(24)	0.0006(15)	0.3272(20)
N(22)	0.1661(17)	0.0032(4)	0.3808(15)
C(221)	0.2036(22)	−0.0281(13)	0.3288(17)
C(222)	0.2205(25)	−0.0156(14)	0.4571(19)
N(23)	0.1517(17)	0.0943(9)	0.4546(7)
C(231)	0.2238(21)	0.1384(12)	0.4827(16)
C(232)	0.0700(26)	0.0863(15)	0.4936(21)
P(3)	−0.1521(5)	0.2082(3)	0.1131(4)
O(3)	−0.0553(8)	0.1797(5)	0.1591(7)
N(31)	−0.1291(16)	0.2424(8)	0.0433(8)
C(311)	−0.1910(18)	0.2409(11)	−0.0307(14)
C(312)	−0.0282(22)	0.2745(12)	0.0533(17)
N(32)	−0.2031(13)	0.2524(7)	0.1609(10)
C(321)	−0.2287(21)	0.2342(11)	0.2308(17)
C(322)	−0.2325(21)	0.3074(11)	0.1423(15)
N(33)	−0.2441(10)	0.1617(5)	0.0842(9)
C(331)	−0.2210(18)	0.1041(10)	0.0737(14)
C(332)	−0.3594(18)	0.1733(10)	0.0617(14)
Li(1)	0.3218(22)	0.0786(13)	0.2242(18)
Li(2)	0.2528(23)	0.1585(13)	0.2840(18)
Li(3)	0.0965(26)	0.1730(16)	0.1846(22)

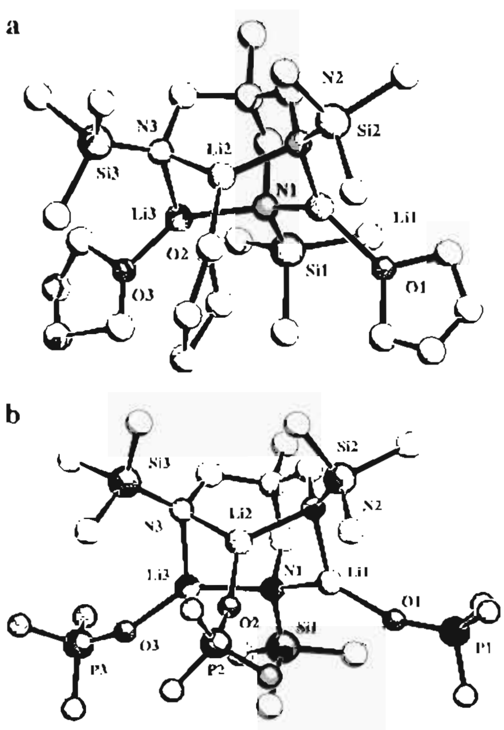

Figure 1. (a) Molecular structure of **3a**: Principal bond lengths (Å) and interbond angles (deg): N(1)−Li(1) 2.05(4), N(1)−Li(3) 2.03(4), N(2)−Li(2) 1.91(4), N(2)−Li(1) 1.91(4), N(3)−Li(2) 1.88(4), N(3)−Li(3) 2.07(4), O(1)−Li(1) 2.03(4), O(2)−Li(2) 2.07(4), O(3)−Li(3) 1.84(4); Li(3)−N(3)−Li(2) 92(2), Li(2)−N(2)−Li(1) 88(2), Li(3)−N(1)−Li(1) 115(2), N(2)−Li(1)−N(1) 109(2), N(3)−Li(3)−N(1) 103(2), N(3)−Li(1)−N(2) 121(2). (b) Molecular structure of **3b**. The methyl groups of the Me_2N units have been omitted for clarity: N(1)−Li(1) 2.03(3), N(1)−Li(3) 2.07(4), N(2)−Li(1) 1.98(3), N(3)−Li(3) 2.02(4), N(2)−Li(2) 1.97(3), N(3)−Li(2) 1.89(3), O(1)−Li(1) 1.90(3), O(2)−Li(2) 1.95(3), O(3)−Li(3) 1.90(3), N(1)−Li(3)−N(2) 99(1), N(3)−Li(3)−N(1) 98(1), N(2)−Li(2)−N(3) 119(2), Li(2)−N(2)−Li(1) 78(1), Li(3)−N(3)−Li(2) 75(1), Li(1)−O(1)−P(1) 155(1), Li(2)−O(2)−P(2) 162(1), Li(3)−O(3)−P(3) 148(1).

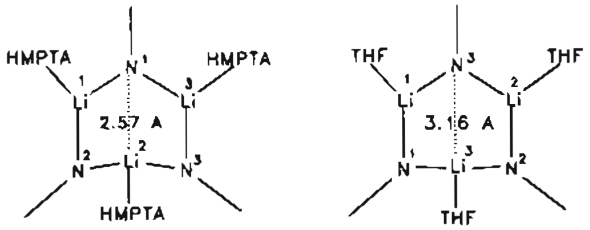

Figure 2. Comparison of the structures of the solvated $\{LiN\}_3$ units in **3a** and **3b**.

of the more open structures of the neopentane-derived tripod amids in comparison with the trisilylmethane derivatives, a notion which needed to be substatiated by a structural study of the solvates.

By monitoring the titration of **1** with THF and HMPTA by ^7Li-NMR spectroscopy, a complete consumption of the starting material and the formation of a uniform product is observed after addition of 1 equivalent of THF (HMPTA) per Li-amide unit, i.e. 6 equiv of coligand/molecule of **1** (eq 1). The

$$\underset{\mathbf{1}}{[H_3CC\{CH_2N(Li)Si(CH_3)_3\}_3]_2} + 6\ \text{ligand} \rightarrow \underset{\mathbf{3a/b}}{2\ H_3CC\{CH_2N(Li\text{-ligand})Si(CH_3)_3\}_3} \quad (1)$$

formation of the tris-solvated species in the early stages of the titration indicates a degree of cooperativity of the process reminiscient of that observed in the lithiation reaction leading to **2**. Chemical exchange between the reaction intermediates and the final product occurs slowly on the NMR time scale. Intramolecular chemical exchange in **3b** can, however, be observed at low temperatures (*vide infra*).

Single crystal X-ray structure analyses of **3a** (Figure 1a) and **3b** (Figure 1b) have revealed the complete solvation of the lithium amide as indicated by the observed stoichiometry of the reaction leading to a structural arrangement which does not follow the patterns observed previously in the structural chemistry of monofunctional alkali metal amides.

The structural centerpiece in both compounds is the distorted adamantoid cage with the solvated $(LiN)_3$-ring at its base which is bridged by the neopentane unit of the ligand. Two of the Li atoms (Li1 and Li3) and the three amido N-atoms lie at five corners of a six membered ring (**3a**: d_{av}(Li−N) = 1.97 Å, d_{av}(Li−O) = 1.98 Å; **3b**: d_{av}(Li−N) = 1.99 Å, d_{av}(Li−O) = 1.92

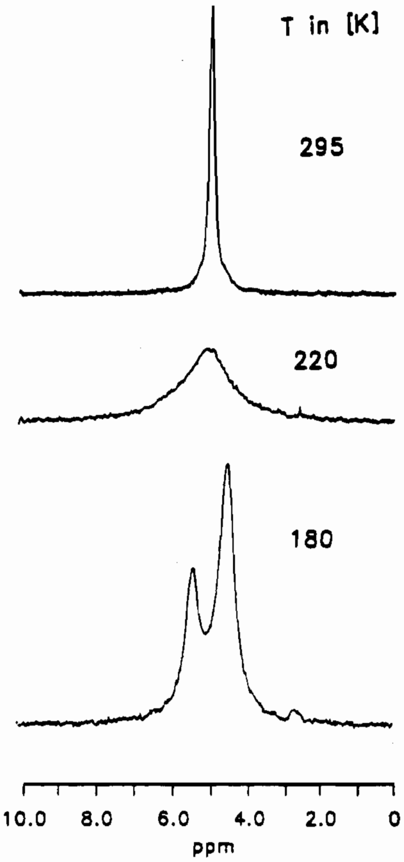

Figure 3. Variable temperature ^{7}Li-NMR study of **3b** (recorded in toluene-d_8).

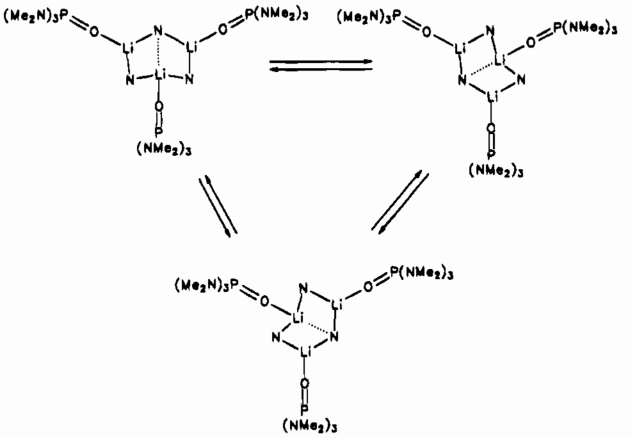

Figure 4. Proposed mechanism for the chemical exchange observed in the ^{7}Li-NMR spectra of **3b** recorded in toluene-d_8 between 180 and 220 K.

Å), with the third solvated Li atom (Li(2)) leaning away from an idealized chair conformation (in **3a** slightly, in **3b** markedly!) toward N(1). However, this Li••N distance of 3.15(4) Å in **3a** and 2.50(3) Å in **3b**, which lies well outside the range of Li–N(amide) contacts normally found, precludes an interpretation along the lines of a conventional ring-ladder interconversion (Figure 2).[2] It may though be viewed as an arrangement which represents a hitherto unobserved intermediate regime between a (puckered) ring and a ladder structure, the formation of the latter being inhibited by the solvation of the inner rung by a thf or an hmpta molecule which draws the Li atom away from the respective opposite nitrogen atom.

Whereas **3a** is closer to an ideal ring geometry, **3b** is to be seen as a distorted amide ladder. The detailed geometry is probably dictated by the steric requirements of the coordinated "solvent".

While the ^{1}H-, ^{7}Li-, ^{31}P- and ^{13}C-NMR spectra of both **3a** and **3b** recorded in d$_8$-toluene at room temperature indicate an effective molecular threefold symmetry, cooling of the solution of **3b** leads to exchange broadening in the ^{1}H- and ^{7}Li-NMR spectra while no appreciable effect is observed in **3a**. At 180 K the broad ^{7}Li resonance in **3b** (δ = 4.89 at 295 K, 4.75 at 220 K, LiI/H$_2$O ext.) splits into two separate signals (δ = 5.37, 4.48) which have an approximate intensity ratio of 1:2 (Figure 3). This may represent the freezing of the dynamic process in which the position of the Li atom in the "collapsed" part of the ring (Li(2) in Figure 1) is exchanged (Figure 4). It should be noted that $^2J(^{31}\mathrm{P}-^7\mathrm{Li})$ coupling, reported by other researchers for Li–HMPTA adducts, could not be resolved even at 180 K.[10]

Probably due to the more "ring-like" structure of **3a** a similar dynamic behavior is not observed on the NMR timescale. The ^{7}Li and ^{29}Si chemical shifts are also consistent with a slightly different overall solvate structure of **3a** in comparison to **3b**. It therefore appears that the structural differences observed in the solid state structures of the compounds may at least in part pertain in solution.

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Supplementary Material Available: Text detailing the structure determination, a figure showing the whole complex with labels, and tables of the positional and thermal parameters, interatomic distances, angles, and torsion angles for **3a** and **3b** (21 pages). Ordering information is given on any masthead page.

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