Synthesis and X-ray Structures of the Polycyclic Dimers {[PhB(µ-NtBu)₂AsN(tBu)H]LiI}₂ and [PhB(µ-NtBu)₂AsN(tBu)Li]₂

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Abstract. The metathesis of $[PhB(\mu-NtBu)_2]AsCl$ and tBuN(H)Liin 1:1 molar ratio in diethyl ether produced the amido derivative $[PhB(\mu-NtBu)_2AsN(tBu)H]$ (1) in good yield. The lithiation of 1 with one equivalent of *n*BuLi afforded the lithium salt $[PhB(\mu-NtBu)_2AsN(tBu)Li]$ (2a). Both 1 and 2a were characterized by multinuclear NMR spectroscopy. The crystal structure of 2a is comprised of a U-shaped, centrosymmetric dimer in which the monomeric $[PhB(\mu-NtBu)_2AsN(tBu)]^-Li^+$ units are linked by

Introduction

The dianionic boraamidinate (*bam*) ligand, $[RB(NR')_2]^{2-}$, is formally isoelectronic with the extensively studied monoanionic amidinate (am) ligand $[RC(NR')_2]^-$. Recent work on early main group and transition-metal complexes has established that the 2- charge on the bam ligand results in some interesting fundamental differences compared to the behavior of the monoanionic *am* ligand [1-5]. We have also reported the first examples of heavy Group 15 boraamidinates in which the versatile coordinating ability of the bam ligand was highlighted [6]. In addition to the monobams $[PhB(\mu-NtBu)_2]MCl$ (M = As, Sb, Bi) with a potentially useful M-Cl reactive site, the unusual 2:3 bam complexes, $M_2[PhB(\mu-NtBu)_2]_3$ (M = Sb, Bi), displayed a unique bonding arrangement in which two metal centers are each N,N'-chelated by one *bam* ligand and the two $[M(bam)]^+$ units are bridged by the third $[bam]^{2-}$ ligand. For the 1:2 Group 15 bam systems, both solvated complexes $(Et_2O)LiM[PhB(\mu-NtBu)_2]_2$ (M = As, Bi) and unsolvated ladder structures $LiM[PhB(\mu-NtBu)_2]_2$ (M = As, Sb) were observed; these complexes showed interesting fluxional behavior in solution (Berry pseudorotation) in the case of M = Sb, Bi [6].

The availability of the monofunctional reagent $[PhB(\mu-NtBu)_2]AsCl$ [6] provided an opportunity to investigate the chemistry of the arsenic atom in *bam* complexes and, in

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Li-N interactions to give a six-rung ladder. Oxidation of **2a** with one-half equivalent of I_2 in diethyl ether resulted in hydrogen abstraction from the solvent to give the dimeric lithium iodide adduct {[PhB(μ -NtBu)₂AsN(tBu)H]LiI}₂ (1 · LiI) with a central Li₂I₂ ring.

Keywords: Arsenic; Boraamidinate; Lithium; Polycyclic compounds; Crystal structures

particular, to make a direct comparison of the arsenic systems with the known phosphorus derivatives [PhB(μ -NtBu)₂PN(tBu)X] (X = H, Li) [7]. In this context we report herein (a) the synthesis and multinuclear NMR spectroscopic characterization of the arsenic boraamidinateamide [PhB(μ -NtBu)₂AsN(tBu)H] (1) and the lithium derivative [PhB(μ -NtBu)₂AsN(tBu)Li] (2a) and (b) the solid state structures of the polycyclic dimers, {[PhB(μ -NtBu)₂AsN(tBu)H]LiI}₂ (1·LiI) and [PhB(μ -NtBu)₂AsN(tBu)H]LiI}₂ (2a).

Experimental Section

General procedures

All reactions and the manipulations of products were performed under an argon atmosphere by using standard Schlenk techniques or an inert atmosphere glove box. The compounds PhBCl₂ (Aldrich, 97%), AsCl₃ (Alfa, 99%), *t*BuNH₂ (Aldrich, 99%), iodine (Aldrich, 99.8%) and *n*BuLi (Aldrich, 2.5 M solution in hexanes) were used as received. LiN(H)*t*Bu was prepared by the addition of *n*BuLi to a solution of *t*BuNH₂ in *n*-hexane at -10 °C and its purity was checked by ¹H NMR spectroscopy. The compound [PhB(μ -N*t*Bu)₂]AsCl [6] was prepared as described earlier. The solvents *n*-hexane, toluene and Et₂O were dried by distillation over Na/benzophenone under an argon atmosphere prior to use. Elemental analyses were performed by Analytical Services, Department of Chemistry, University of Calgary.

Spectroscopic methods

The ¹H, ⁷Li, ¹¹B and ¹³C NMR spectra were obtained in d_8 -THF at 23 °C on a Bruker DRX 400 spectrometer operating at 399.59, 155.30, 128.20 and 100.49 MHz, respectively. ¹H and ¹³C spectra are referenced to the solvent signal and the chemical shifts are reported relative to (CH₃)₄Si. ⁷Li and ¹¹B NMR spectra are referenced externally and the chemical shifts are reported relative to a



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1.0 M solution of LiCl in D_2O and to a solution of $BF_3\cdot Et_2O$ in $C_6D_6,$ respectively.

Synthesis of [PhB(µ-NtBu)₂AsN(tBu)H] (1)

A mixture of $[PhB(\mu-NtBu)_2]AsCl (0.597 g, 1.75 mmol)$ and tBuN(H)Li (0.138 g, 1.75 mmol) was cooled to $-80 \,^{\circ}C$ and cold diethyl ether (50 mL, $-80 \,^{\circ}C$) was added via cannula. The reaction mixture was stirred for $1/_2$ h at $-80 \,^{\circ}C$ and *ca*. 5 h at room temperature. The precipitate of LiCl was removed by filtration and the solvent was evaporated under vacuum to give 1 as a white powder (0.514 g, 78 %). Anal. Calcd for $C_{18}H_{33}AsBN_3$: C 57.31; H 8.82; N 11.14. Found: C 56.67; H 9.22; N 10.53 %.

¹H NMR (d₈-THF, 23 °C): δ 7.20-7.37 [m, 5H, C₆H₅], 3.20 [s, 1H, NH], 1.32 [s, 9H, C(CH₃)₃], 1.09 [s, 18H, C(CH₃)₃]. ¹³C{¹H} NMR: δ 127.6-132.0 [C₆H₅], 52.6 [C(CH₃)₃], 52.2 [C(CH₃)₃], 33.8 [C(CH₃)₃], 33.7 [C(CH₃)₃]. ¹¹B NMR: δ 34.7.

Synthesis of [PhB(µ-NtBu)₂AsN(tBu)Li] (2a)

A solution of **1** (0.660 g, 1.75 mmol) in *n*-hexane (30 mL) was cooled to -80 °C and 0.70 mL of *n*BuLi (2.5 M in hexanes, 1.75 mmol) was added via syringe. The reaction mixture was stirred for $1/_2$ h at -80 °C and 15 h at room temperature. Solvent was evaporated and the resulting off-white powder was washed with cold *n*-hexane (*ca.* 5 mL) giving **2a** as a white powder (0.490 g, 73 %). Anal. Calcd for C₁₈H₃₂AsBLiN₃: C 56.43; H 8.42; N 10.97. Found: C 55.47; H 8.15; N 9.72 %. X-ray quality crystals of **2a** were obtained from *n*-hexane in 6 d at 5 °C.

¹H NMR (d₈-THF, 23 °C): δ 7.11-7.38 [m, 5H, C₆H₅], 1.29 [s, 9H, C(CH₃)₃], 1.09 [s, 18H, C(CH₃)₃]. ¹³C{¹H} NMR: δ 126.7-132.7 [C₆H₅], 54.7 [C(CH₃)₃], 52.6 [C(CH₃)₃], 37.6 [C(CH₃)₃], 33.9 [C(CH₃)₃]. ⁷Li NMR: δ 1.01. ¹¹B NMR: δ 34.2.

Oxidation of [PhB(µ-NtBu)₂AsN(tBu)Li] (2a) with I₂

A solution of **2a** (0.268 g, 0.70 mmol) in diethyl ether (30 mL) was cooled to -80 °C and a solution of I₂ (0.089 g, 0.35 mmol) in diethyl ether (30 mL) was added via cannula. The reaction mixture was stirred for ¹/₂ h at -80 °C and 2 h at room temperature. Solvent was evaporated under vacuum and the resulting off-white powder was washed with cold *n*-hexane (*ca.* 10 mL) giving a white powder (0.289 g, 81 %, calculated as a 1:1 mixture of **1** and LiI). X-ray quality crystals of **1** · LiI were obtained from toluene in 1 d at 23 °C.

¹H NMR (THF-d₈, 23 °C): δ 7.17-7.39 [m, 5H, C₆H₅], 3.21 [s, 1H, NH], 1.34 [s, 9H, C(CH₃)₃], 1.10 [s, 18H, C(CH₃)₃]. ¹³C{¹H} NMR: δ 127.6-132.0 [C₆H₅], 52.6 [C(CH₃)₃], 52.2 [C(CH₃)₃], 33.8 [C(CH₃)₃], 33.7 [C(CH₃)₃]. ⁷Li NMR: δ 0.79. ¹¹B NMR: δ 34.6.

X-ray structure determination

Crystals of {[PhB(μ -N*t*Bu)₂AsN(*t*Bu)H]LiI}₂ (**1**·LiI) and [PhB(μ -N*t*Bu)₂AsN(*t*Bu)Li]₂ (**2a**) were coated with Paratone 8277 oil and mounted on a glass fiber. Diffraction data were collected on a Nonius KappaCCD diffractometer using monochromated MoK_{α} radiation ($\lambda = 0.71073$ Å) at -100 °C. The data sets were corrected for Lorentz and polarization effects, and empirical absorption correction was applied to the net intensities. The structures were solved by direct methods using SHELXS-97 [8] and refined using SHELXL-97 [9]. In the structure of **1**·LiI, the N*H* hydrogen atom was located from the difference Fourier map and refined normally. After the full-matrix least-squares refinement of the non-hydrogen

Table 1 Crystal structure data for 1 · LiI and 2a.^{a)}

	1 · LiI	2a
Formula	C36H66A82B2I2Li2N6	C36H64As2B2Li2N6
M_r	1022.09	766.27
Crystal size, mm	0.10 imes 0.08 imes 0.02	$0.20 \times 0.16 \times 0.12$
Crystal system	triclinic	monoclinic
Space group	$P\overline{1}$	C2/c
a, Å	10.598(2)	10.404(2)
b, Å	10.758(2)	18.933(4)
<i>c</i> , Å	13.087(3)	21.030(4)
α , deg	92.74(3)	90.00
β , deg	111.28(4)	99.87(3)
y, deg	118.55(3)	90.00
V, Å ³	1175.8(8)	4081(1)
Ζ	1	4
$D_{\rm calcd}$, g cm ⁻³	1.443	1.247
$\mu(MoK_{\alpha}), cm^{-1}$	2.763	1.669
<i>F</i> (000), e	512	1616
hkl range	$\pm 12, \pm 12, \pm 15$	±12, ±22, ±25
° range, deg	2.24-25.03	2.26-25.02
Refl. measured	7956	13086
Refl. unique	4128	3603
$R_{\rm int}$	0.0323	0.0876
Param. refined	230	217
Reflns $[I \ge 2\sigma (I)]$	3235	2672
$R_1 [I > 2\sigma (I)]^{b}$	0.0326	0.0556
wR_2 (all data) ^{c)}	0.0742	0.1300
GoF on F ²	1.052	1.048
$\Delta \rho_{\rm fin}$ (max/min), e Å ⁻³	0.58 and -0.48	0.96 and -1.16

^{a)} λ (MoK α) = 0.71073 Å ^{b)} $R_1 = \Sigma ||F_o| - |F_c|| \Sigma |F_o|$

^{c)} $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{\frac{1}{12}}.$

atoms with anisotropic thermal parameters, the hydrogen atoms bonded to carbons were placed in calculated positions [C-H = 0.98 Å for C(CH₃)₃ and 0.95 Å for phenyl hydrogens]. The isotropic thermal parameters of these atoms were fixed at 1.2 times to that of the corresponding carbon for phenyl hydrogens, and 1.5 times for C(CH₃)₃. In the final refinement, the hydrogen atoms were riding on their respective carbon atoms. Crystallographic data are summarized in Table 1. CCDC-667032 and CCDC-667033 contain the supplementary crystallographic data for compounds 1 · LiI and **2a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/ data_request/cif.

Results and Discussion

Synthesis and characterization of $[PhB(\mu-NtBu)_2AsN(tBu)X]$ (1, X = H; 2a, X = Li)

The reaction of $[PhB(\mu-NtBu)_2]AsCl$ with tBuN(H)Li in diethyl ether produces $[PhB(\mu-NtBu)_2AsN(tBu)H]$ (1) as an analytically pure, white powder in *ca*. 80 % yield (eq. 1). The ¹H NMR spectrum of 1 shows a singlet at 3.20 ppm for the NH hydrogen and two singlets at 1.32 and 1.09 ppm with relative intensities 1:2 for the exocyclic N(H)*t*Bu and endocyclic N*t*Bu groups, respectively. The ¹¹B NMR spectrum of 1 exhibits a single resonance at 34.7 ppm.

$$\begin{split} \label{eq:constraint} \begin{split} [PhB(\mu\text{-}NtBu)_2]AsCl &+ tBuN(H)Li \rightarrow \\ & [PhB(\mu\text{-}NtBu)_2AsN(tBu)H] + LiCl \quad (1) \\ & (1) \end{split}$$

The treatment of 1 with one equivalent of *n*BuLi is accompanied by the disappearance of the NH resonance in

the ¹H NMR spectrum, which now exhibits two singlets for N*t*Bu groups at 1.29 and 1.09 ppm in a 1:2 intensity ratio. A single resonance is observed in the ⁷Li NMR spectrum at 1.01 ppm, consistent with the formation of the lithium derivative [PhB(μ -N*t*Bu)₂AsN(*t*Bu)Li] (**2a**) (eq. (2)).

$$[PhB(\mu-NtBu)_2AsN(tBu)H] + nBuLi \rightarrow [PhB(\mu-NtBu)_2AsN(tBu)Li] + nBuH (2)$$

(1) (2a)

The crystal structure of **2a** with the atomic numbering scheme is depicted in Figure 1, and the pertinent bond parameters are summarized in Table 2. The structure is comprised of a centrosymmetric dimer in which monomeric $[PhB(\mu-NtBu)_2AsN(tBu)]^-Li^+$ units are formed by N,N'-chelation of the anion to the Li^+ cation through the amide nitrogen and one of the *bam* nitrogens. These units are linked by Li-N interactions to give a six-rung ladder with one three-coordinate and two four-coordinate nitrogens in each half of the molecule.



Figure 1 Crystal structure of $[PhB(\mu-NtBu)_2AsN(tBu)Li]_2$ (2a) with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. ^a Symmetry operation: -x, y, 1.5-z.

Table 2 Selected bond lengths/Å and angles/° in { $[PhB(\mu-NtBu)_2-AsN(tBu)H]LiI$ } (1 · LiI) and $[PhB(\mu-NtBu)_2AsN(tBu)Li]_2$ (2a)

	1.131	2a		1 · LiI	2a
	L				
Distances					
As1-N1	1.917(3)	1.958(4)	Li1-N1	2.195(7)	2.071(10)
As1-N2	1.870(3)	1.923(4)	Li1-N3	2.145(7)	2.031(9)
As1-N3	1.858(3)	1.787(4)	Li1-N3 ^{a)}	_ ``	2.056(10)
B1-N1	1.481(6)	1.481(7)	Li1-I1	2.682(7)	_
B1-N2	1.427(6)	1.403(6)	Li1-I1 ^{b)}	2.767(7)	-
Angles					
N1-As1-N2	73.5(1)	71.2(2)	N1-Li1-N3	80.7(2)	88.1(4)
N1-As1-N3	96.2(1)	99.2(2)	N1-Li1-I1	127.4(3)	_ ``
N2-As1-N3	101.9(2)	106.3(2)	N1-Li1-I1 ^{b)}	117.5(3)	_
N1-B1-N2	102.3(3)	103.0(4)	N3-Li1-I1	128.4(3)	_
B1-N1-As1	89.2(2)	89.5(3)	N3-Li1-I1 ^{b)}	87.2(3)	_
B1-N2-As1	92.8(3)	93.2(3)	I1-Li1-I1 ^{b)}	102.5(2)	_
Li1-N1-As1	89.9(2)	82.8(3)	Li1-I1-Li1 ^{b)}	77.5(2)	-
Li1-N3-As1	93.1(2)	88.3(3)			

Symmetry operations: a) -x, y, 1.5-z b) 1-x, 2-y, 1-z.

A similar structure has been reported for the phosphorus-containing analogue, $[PhB(\mu-NtBu)_2PN(tBu)Li]_2$ (2b) [7]. Significantly, the *bam* ligands in 2a adopt a *cisoid* arrangement with respect to the central Li₂N₂ ring giving a U-shaped structure, whereas a transoid conformation resulting in an S-shaped arrangement is observed for 2b (Scheme 1). This difference can be explained in the context of the laddering principle for describing the oligomeric structures of alkali metal amides [10]. In cases where laddering is limited to dimerization by bulky substituents, a transoid geometry is most often observed [11], although exceptions have been noted [12]. The pentacyclic structures of 2a and 2b may be considered as six-rung ladders formed by the dimerization of a lithium amide in which one of the substituents on nitrogen is a (bam)E (E = P. As) unit. In view of the shorter P-N compared to As-N bonds, the transoid geometry in 2b may be preferred in order to minimize interactions between tert-butyl groups attached to the first and sixth rungs of the ladder. We note, however, that the curvature of the *cisoid* arrangement in 2a is small so that these steric interactions are limited.



Scheme 1 The *cisoid* and *transoid* conformations observed for 2a and 2b, respectively.

The As-N bond length to the exocyclic amide nitrogen in 2a is ca. 0.15 Å shorter than the As-N bonds to the bam ligand suggesting a stronger electrostatic interaction between As1 and N3. The As-N bond to the three-coordinate nitrogen atom (N2) in the bam ligand is unusually long $(1.923(4) \text{ Å}), cf. 1.789(3) \text{ Å} in LiAs[PhB(\mu-NtBu)_2];$ 1.845(2) and 1.876(2) Å in $(Et_2O)LiAs[PhB(\mu-NtBu)_2]$ [6], and only ca. 0.03 Å shorter than the As-N bond to the fourcoordinate nitrogen (N1). The disparity of ca. 0.08 Å in the B-N bond lengths is, however, fairly typical for the *bam* ligand when three- and four-coordinate nitrogen atoms are present [1, 6]. The three Li-N interactions in 2a are almost equal in length, and those involving the amide nitrogen (Li1-N3, Li1-N3^a) are comparable to the values reported for the phosphorus analogue 2b [7]. Curiously, the difference in conformation results in a shorter Li-N interaction (by ca. 0.10 Å) to the four-coordinate nitrogen in the bam ligand (N1) in 2a than the corresponding distance in 2b (2.171(3) Å) [7]. All four-membered rings (AsBN₂, AsLiN₂, Li_2N_2) in 2a are notably non-planar with torsion angles in the range 8.7-15.3°.

Oxidation of 2a with I₂; crystal structure of {[PhB(µ-NtBu)₂AsN(tBu)H]LiI}₂ (1 · LiI)

In an attempt to produce the neutral aminyl radical [PhB(μ -N*t*Bu)₂AsN(*t*Bu)], the reaction of **2a** with one-half equivalent of I₂ was performed in diethyl ether at -80 °C (eq. (3)). After the addition of iodine a clear, colorless solution was observed; there was no indication of the intermediate formation of a colored paramagnetic species. Subsequent removal of the solvent gave a white powder.

$$\begin{split} \label{eq:asymptotic} \begin{split} & [\text{PhB}(\mu\text{-}Nt\text{Bu})_2\text{AsN}(t\text{Bu})\text{Li}] \,+\, {}^{1}\!\!/_2 \,\, \text{I}_2 \rightarrow \\ & \quad [\text{PhB}(\mu\text{-}Nt\text{Bu})_2\text{AsN}(t\text{Bu})] \,+\, \text{LiI} \quad (3) \\ & \quad (\textbf{2a}) \end{split}$$

¹H NMR spectrum of the product measured in d₈-THF revealed three singlets at 3.21, 1.34 and 1.10 ppm in a relative ratio of 1:9:18, in addition to the characteristic resonances for the phenyl group. The ${}^{13}C{}^{1}H$ NMR spectrum showed two signals at 52.6 and 52.2 ppm for the α -carbons and two resonances at 33.8 and 33.7 ppm for the methyl carbons of the NtBu-groups. Single resonances were observed at 34.6 and 0.79 ppm in the ¹¹B and ⁷Li NMR spectra, respectively. The similarity of these resonances with those observed for 1, specifically the presence of the signal at 3.21 ppm with an intensity of 1 relative to the intensities of 9 and 18 observed for the two NtBu signals in the 1 H NMR spectrum, suggests the presence of an N-H functionality, which may be explained by the formation of 1 due to hydrogen abstraction from the solvent. The single resonance in the ⁷Li NMR spectrum is attributed to the lithium iodide by-product.

The white powder was recrystallized from toluene. An X-ray crystal structure determination confirmed the formation of 1 and revealed that LiI is incorporated in the structure to give an adduct in which 1 is N,N'-chelated to the Li^+ cation through the exocyclic N(H)*t*Bu group and one of the bam nitrogens; iodide counterions bridge two monomeric units to give a centrosymmetric dimer (Figure 2a). The overall structure is pentacyclic with a central Li₂I₂ ring which is tilted by ca. 76° with respect to the neighboring LiAsN₂ rings. The *bam* ligands in $1 \cdot$ LiI adopt a *trans* arrangement with respect to the planar Li₂I₂ ring (Figure 2b). A number of complexes in which LiI is entrapped in ladder [13] or cubic [14] structures have been reported. The most relevant examples for comparison with the structure of $1 \cdot \text{LiI}$ are the dimeric adducts [(2,6-dimethylpyridine)LiI]₂ [15] and [(2-pyridyl-CH₂N(H)SitBuMe₂)LiI]₂ [16], both of which contain central Li₂I₂ rings with four-coordinate Li⁺ ions.

In order to provide a context for a comparison of metrical parameters, the structure of $1 \cdot \text{LiI}$ can be related to that of **2a** by the formal addition of HI to each of the monomer units. The protonation of N3/N3^a in **2a** results in cleavage of the Li1-N3/N3^a bonds. The As-N bonds in the *bam* ligand in $1 \cdot \text{LiI}$ are *ca*. 0.05 Å shorter than in the lithium derivative **2a**, whereas no significant difference can be observed in the B-N bond lengths between the two com-



Figure 2 (a) Crystal structure of $\{[PhB(\mu-NtBu)_2AsN(tBu)H]LiI\}_2$ (1·LiI), and (b) the pentacyclic (NBNAsNHLiI)_core in 1·LiI with the atomic numbering scheme. Hydrogen atoms bonded to carbons have been omitted for clarity. ^a Symmetry operation: 1-x, 2-y, 1-z.

pounds (Table 2). The As-N bond to the exocyclic amide nitrogen in $1 \cdot \text{LiI}$ is equal in length with the As-N bond to the three-coordinate nitrogen in the *bam* ligand in $1 \cdot \text{LiI}$. The As1-N3 bond length is, however, considerably longer (by 0.07 Å) than the corresponding bond in **2a**. The analogous disparity in the P-N bond lengths is less pronounced in the phosphorus derivatives, [PhB(μ -NtBu)₂PN(tBu)X] (X = H, Li) [7], in which the hydrogen-containing compound is monomeric. The difference in As-N bond lengths between $1 \cdot \text{LiI}$ and **2a** is, however, an indication of weakening of the electrostatic interaction between As1 and N3 as a result of the N-H bond formation in $1 \cdot \text{LiI}$.

The Li···N interactions in $1 \cdot \text{LiI}$ are expectedly weaker (by *ca.* 0.12 Å) than the corresponding contacts in **2a** due to the strong Li⁺···I⁻ connections in $1 \cdot \text{LiI}$. Consistently with **2a**, the Li···N contact to the *bam* nitrogen is *ca.* 0.05 Å longer than the analogous interaction to the amide nitrogen in $1 \cdot \text{LiI}$. The difference in Li···N interactions is also reflected in the inequality of 0.08 Å in the Li···I contacts [2.682(7) vs. 2.767(7) Å], *cf.* 2.754(5) and 2.783(5) Å in [(2-pyridyl-CH₂N(H)SitBuMe₂)LiI]₂ [16].

Shortening of the As-N bonds in $1 \cdot \text{Lil}$ compared to 2a expectedly results in *ca.* 2.3° wider N-As-N angle, whereas

the remaining bond angles within the *bam* ligands are equal within estimated standard deviation. Similarly, lengthening of the As1-N3 bond and Li…N interactions in 1 · LiI affords narrower N-As1-N3 and N1-Li1-N3 angles compared to **2a**. The four-coordinate Li⁺ cation shows significant distortion from tetrahedral geometry with the angles in the wide range of $80.7(2)-128.4(3)^\circ$. The planar Li₂I₂ four-membered ring exhibits considerable deviation from ideal square with the bond angles of 77.5(2) and $102.5(2)^\circ$ for Li-I-Li and I-Li-I, respectively, *cf*. 76.2(2) and $103.8(2)^\circ$ for [(2-pyridyl-CH₂N(H)SitBuMe₂)LiI]₂ [16].

In an attempt to prevent the formation of 1 in the oneelectron oxidation of 2a (eq. 3), the reaction was repeated in the hydrogen-free solvent CS₂ at -80 °C. At room temperature, a red solution was obtained, but no EPR signal could be detected. Recrystallization attempts from CS₂ failed and the product decomposed in organic solvents, e.g. benzene, to give 1 and a number of unidentified compounds.

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