Inorg. Chem. **1998,** *37,* 2177−2182 **2177**

Heterobimetallic (Imido)antimony/Lithium Cages Containing $[Sb(NR)_3]^{3-}$ Trianions

Michael A. Beswick,[†] Nick Choi,[‡] Christopher N. Harmer,[†] Alexander D. Hopkins,[†]
Mary McPartlin,[‡] Michael A. Paver,[†] Paul R. Raithby,[†] Alexander Steiner,[†]
Mustafa Tombul,[†] and Dominic S. Wright*,[†]

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K., and
School of Applied Chemistry, University of North London, Holloway Road, London N7 8DB, U.K.

Received August 26, 1997

The reactions of $[Sb(NMe_2)_3]$ with the primary (amido)lithiums $[PhCH_2CH_2N(H)Li]_n$, $[CyN(H)Li]_n$ ($Cy = C_6H_{11}$), $[2,4\text{-dmpN(H)Li}]_n$ [2,4-dmp = 2,4-$(MeO)_2C_6H_3$], and $[{}^tBuN(H)HLi]_n$ give the heterobimetallic cage complexes $[\{Sb(NCH_2CH_2Ph)_3\}_2Li_6\cdot 2THF]$ (**1**), $[\{Sb(NCy)_3\}_2Li_6\cdot 2HNMe_2]\cdot 2C_6H_5CH_3$ (**2**), $[Sb\{N(2,4\text{-dmp})\}_3]_2Li_6\cdot 2THF\cdot 2C_6H_5CH_3$ (**3**), and $[\{Sb(NBu^t)_3\}_2Li_6]$ (**4**), respectively. The low-temperature X-ray structures of **1**−**4** show that they are composed of 14-membered polyhedral cages constructed from the association of two $[Sb(NR)_3]^{3-}$ trianions with six Li^+ cations. Crystal data; **2**, triclinic, $P\bar{1}$, $a = 12.775(6)$ Å, $b = 13.191(9)$ Å, $c = 11.015(5)$ Å, $\alpha = 111.55(4)°$, $\beta = 95.39(4)°$, $\gamma = 115.26(4)°$; **3**, triclinic $P\bar{1}$, $a = 10.435(4)$ Å, $b = 12.654(5)$ Å, $c = 14.278(6)$ Å, $\alpha = 75.31(4)°$, $\beta = 79.33(4)°$, $\gamma = 84.33(4)°$; **4**, monoclinic $P2_1/c$, $a = 9.994(1)$ Å, $b = 17.421(2)$ Å, $c = 10.680(2)$ Å, $\beta = 111.33(1)°$ (the structure of **1** being reported previously). Lewis base solvation of the N_6Li_6 substructures of **1**−**3** results in distortion and deformation of the Li frameworks. The structural variations in the cores of **1**−**4** indicate that the bonding in these species is dominated by the valence and bonding demands of the p block metal centers.

Introduction

We have recently reported that the stepwise metalation of primary amines and phosphines $[REH_2]$ (E = N, P), utilizing $[Sb(NMe_2)_3]$ as a potent base,[1] can be used in the preparation of heterobimetallic Sb(III)/alkali metal cage complexes containing a range of imido−Sb(III) anions.[2] The simplest of these reactions involves the metalation of primary (amido)- or (phosphido)lithium complexes, $[REHLi]_n$ (E = N, P), with $[Sb(NMe_2)_3]$ giving heterobimetallic cages containing $[Sb(ER)_3]^{3-}$ trianions. For example, the reaction of $[PhCH_2CH_2N(H)Li]_n$ with $[Sb(NMe_2)_3]$ (3:1 monomer equiv) in THF gives $[\{Sb(NCH_2CH_2Ph)_3\}_2Li_6\cdot 2THF]$ (**1**), containing the $[Sb(NCH_2CH_2Ph)_3]^{3-}$ trianion.[2b] The various imido−Sb(III) anions which can be prepared by this approach (i.e., $[Sb(ER)_3]^{3-}$,[2b] $[Sb_2(NR)_4]^{2-}$[2,2a] and $[(Me_2N)Sb(NR)\}_2Sb]^{-}$ [2b]) have interesting coordination chemistries. Their transmetalation[3a,c] and cocomplexation[3b] reactions with transition metal and main group metal salts provides a strategy for the assembly of heterometallic complexes containing a variety of mixed-metal stoichiometries, e.g., transfer of the *intact* $[Sb_2(NCy)_4]^{2-}$ (Cy = cyclohexyl, C_6H_{11}) dianions of $[\{Sb_2(NCy)_4\}_2Li_4]$[2a] occurs with CuCl, giving the bimetallic cage complex $[\{Sb_2(NCy)_4\}_2Cu_4]$.[3b] This simple approach therefore furnishes a family of new ligand systems with broad synthetic applications.

We present here a full account of our investigations of the syntheses and structures of heterobimetallic complexes containing a variety of new $[Sb(NR)_3]^{3-}$ ligands. This study illustrates the generality of the preparation of these species for a range of organic groups (R). In addition to the preparation and structure of $[\{Sb(NCH_2CH_2Ph)_3\}_2Li_6\cdot 2THF]$ (**1**), which we have communicated previously,[2b] the syntheses and structures of the new complexes $[\{Sb(NCy)_3\}_2Li_6\cdot 2HNMe_2]\cdot 2C_6H_5CH_3$ (**2**), $[(Sb\{N(2,4\text{-dmp})\}_3)_2Li_6\cdot 2THF]\cdot 2C_6H_5CH_3$ (**3**) [2,4-dmp = 2,4-$(MeO)_2C_6H_3$], and $[\{Sb(NBu^t)_3\}_2Li_6$ (**4**) are described. The formation of these complexes and the analysis of the geometries and distortions within their $[Sb_2N_6Li_6]$ cores clarifies the synthetic and structural factors governing the formation of heterobimetallic p block metal/alkali metal cage compounds of this type. Underlying the formation and structures of all of these species is the dominance of the bonding requirements and valence of the Sb(III) centers involved.

Results and Discussion

The syntheses of complexes **1**−**4** were performed under inert atmosphere by the reactions of the lithiated primary amines $[PhCH_2CH_2N(H)Li]_n$,[2b] $[CyN(H)Li]_n$, $[2,4\text{-}(MeO)_2C_6H_3N(H)\text{-}$

[†] University of Cambridge.

[‡] University of North London.

(1) (a) Moedritzer, K. *Inorg. Chem.* **1964**, *3*, 609. (b) Kiennemann, K.; Levy, G.; Schue, F.; Tanielian. *J. Organomet. Chem.* **1972**, *35*, 143.

(2) (a) Alton, R. A.; Barr, D.; Edwards, A. J.; Paver, M. A.; Rennie, M.-A.; Russell, C. A.; Raithby P. R.; Wright D. S. *J. Chem. Soc., Chem. Commun.* **1994**, 1481. (b) Edwards, A. J.; Paver, M. A.; Rennie, M.-A.; Russell, C. A.; Raithby, P. R.; Wright, D. S. *Angew. Chem.* **1994**, *106*, 1334; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1277. (c) Barr, D.; Beswick, M. A.; Edwards, A. J.; Galsworthy, J. R.; Paver, M. A.; Rennie, M.-A.; Russell, C. A.; Raithby, P. R.; Verhorevoort, K. L.; Wright, D. S. *Inorg. Chim. Acta* **1996**, *248*, 9. (d) Paver, M. A.; Russell, C. A.; Wright, D. S. *Angew. Chem.* **1995**, *107*, 1077; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1545. (e) Beswick, M. A.; Harmer, C. N.; Hopkins, A. D.; Paver, M. A.; Raithby, P. R.; Wheatley, A. E. H.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1997**, 1879.

(3) (a) Beswick, M. A.; Harmer, C. N.; Paver, M. A.; Raithby, P. R.; Steiner, A.; Wright, D. S. *Inorg. Chem.* **1997**, *36*, 1740. (b) Barr, D.; Edwards, A. J.; Pullen, S.; Paver, M. A.; Raithby, P. R.; Rennie, M.-A.; Russell, C. A.; Wright, D. S. *Angew. Chem.* **1994**, *106*, 1960; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1875. (c) Edwards, A. J.; Paver, M. A.; Rennie, M.-A.; Russell, C. A.; Raithby, P. R.; Wright, D. S. *Angew. Chem.* **1995**, *107*, 1088; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1012.

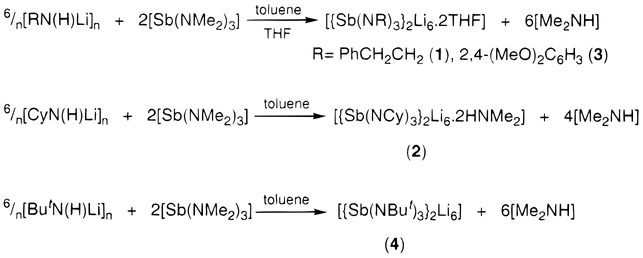
S0020-1669(97)01090-2 CCC: $15.00

Table 1. Crystal Data for [{Sb(NCy)$_3$}$_2$Li$_6$•2HNMe$_2$]•2C$_6$H$_5$CH$_3$ (**2**), [(Sb{N(2,4-dmp)}$_3$)$_2$Li$_6$•2THF]•2C$_6$H$_5$CH$_3$ (**3**) (2,4-dmp = 2,4-(MeO)$_2$C$_6$H$_3$), and [{Sb(NBu^t)$_3$}$_2$Li$_6$] (**4**)

	2	**3**	**4**
formula	$C_{54}H_{94}Li_6N_8Sb_2$	$C_{70}H_{86}Li_6N_6O_{14}Sb_2$	$C_{24}H_{54}Li_6N_6Sb_2$
fw	1140.51	1520.59	711.88
cryst system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	12.775(6)	10.435(4)	9.994(1)
b (Å)	13.191(9)	12.654(5)	17.421(2)
c (Å)	11.015(5)	14.278(6)	10.680(2)
α (deg)	111.55(4)	75.31(4)	
β (deg)	95.39(4)	79.02(3)	111.33(1)
γ (deg)	115.26(4)	84.33(4)	
V (Å$^{3)}$	1490(1)	1788(1)	1732.1(4)
Z	1	1	4
ρ_{calc} (Mg m^{-3})	1.271	1.412	1.365
μ (cm^{-1})	0.0945	0.0821	0.1580
T (°C)	−120(2)	−120(2)	−80(2)
λ (Å)	0.710 69	0.710 69	0.710 69
R indices [$F > 4\sigma(F)$]^a	$R1 = 0.041$, w$R2 = 0.102$	$R1 = 0.029$, 0.073	$R1 = 0.049$, w$R2 = 0.106$
R indices (all data)	$R1 = 0.065$, w$R2 = 0.122$	$R1 = 0.031$, $WR2 = 0.077$	$R1 = 0.098$, w$R2 = 0.149$

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = \{[\sum w(F_o{}^2 - F_c{}^2)^2]/\sum wF_o{}^4\}^{0.5}$, $w = 1/[\sigma^2(F_o{}^2) + (xP)^2 + yP]$, $P = (F_o{}^2 + 2F_c{}^2)/3$.[18]

Scheme 1



$$^6/_n[RN(H)Li]_n + 2[Sb(NMe_2)_3] \xrightarrow[THF]{toluene} [\{Sb(NR)_3\}_2Li_6.2THF] + 6[Me_2NH]$$

$R = PhCH_2CH_2$ (**1**), 2,4-(MeO)$_2$C$_6$H$_3$ (**3**)

$$^6/_n[CyN(H)Li]_n + 2[Sb(NMe_2)_3] \xrightarrow{toluene} [\{Sb(NCy)_3\}_2Li_6.2HNMe_2] + 4[Me_2NH]$$

(**2**)

$$^6/_n[Bu^tN(H)Li]_n + 2[Sb(NMe_2)_3] \xrightarrow{toluene} [\{Sb(NBu^t)_3\}_2Li_6] + 6[Me_2NH]$$

(**4**)

In **2** and **3** two toluenes are present in the lattice per molecule.

Li]$_n$, and [Bu^{t}N(H)Li]$_n$, respectively, with [Sb(NMe$_2$)$_3$] (3:1 monomer equiv) in toluene or toluene/THF solutions (Scheme 1). ^{1}H NMR and IR spectroscopic studies of all four compounds illustrate that complete deprotonation of the primary amines had occurred during these reactions. In addition, analytical and ^{1}H NMR studies showed that there is one molecule of THF to each [Sb(NR)$_3$]$^{3-}$ trianion unit in **1** and **3**. These studies also provided an initial indication of lattice solvation by toluene in crystalline samples of **2** and **3**. Although the N−H stretching vibration is very broad and weak in the IR spectrum of **2**, the room-temperature ^{1}H NMR spectrum and elemental analysis of the complex clearly illustrate that two Me$_2$NH molecules are present to each molecular cage. The X-ray crystallographic study of **2** later showed that these molecules are coordinated to two Li$^+$ cations of the core. This ligand, which is generated during the reaction of [RN(H)Li] with [Sb(NMe$_2$)$_3$] and which is a gas above 7 °C, is suprisingly robust, and analytical and ^{1}H NMR studies illustrate that the coordinated Me$_2$NH is only removed by placing **2** under prolonged vacuum and heating (10^{-1} atm, ca. 50 °C, 15 min). Similar coordination by Me$_2$NH occurs in the formation of the P analogue of **2**, [{Sb(PCy)$_3$}$_2$Li$_6$•6HNMe$_2$],[2e] in which all six of the Li$^+$ cations of the core are coordinated. However, in the latter this ligation is considerably less stable.

Low-temperature X-ray crystallographic studies were undertaken on complexes **1**−**4**. Details of the structural refinements of the new complexes **2**−**4** are given in Table 1. Selected bond lengths and angles for these are detailed in Tables2−4. Since the structure of **1** has been communicated previously, detailed structural data on this complex are not included here and its structure is discussed by way of comparison with the new complexes reported.

Table 2. Selected Bond Lengths and Angles for [{Sb(NCy)$_3$}$_2$Li$_6$•2HNMe$_2$]•2C$_6$H$_5$CH$_3$ (**2**)

Bond Lengths (Å)^a

Sb(1)−N(1)	2.094(4)	Li(2)−N(2)	2.051(8)
Sb(1)−N(2)	2.063(4)	Li(2)−N(3a)	1.994(8)
Sb(1)−N(3)	2.067(4)	Li(3)−N(2)	2.135(8)
Li(1)−N(1)	2.019(8)	Li(3)−N(3)	2.162(9)
Li(1)−N(3)	2.048(8)	Li(3)−N(1a)	2.168(9)
Li(1)−N(2a)	2.005(8)	Li(3)−N(4)	2.118(9)
Li(2)−N(1)	2.021(8)		

Bond Angles (deg)

N(2)−Sb(1)-N(1)	93.6(2)	N(2)−Sb(1)-N(3)	93.7(2)
N(3)−Sb(1)-N(1)	92.8(2)		

^{a} Symmetry transformations used to generate equivalent atoms labeled "a": $-x + 1$, $-y + 2$, $-z$.

Table 3. Selected Bond Lengths and Angles for [(Sb{N(2,4-dmp)}$_3$)$_2$Li$_6$•2THF]•2C$_6$H$_5$CH$_3$ (**3**) (2,4-dmp = 2,4-(MeO)$_2$C$_6$H$_3$)

Bond Lengths (Å)^a

Sb(1)−N(1)	2.051(3)	Li(2)−N(1a)	2.099(6)
Sb(1)−N(2)	2.053(3)	Li(2)−N(3a)	2.012(6)
Sb(1)−N(3)	2.056(3)	Li(2)−O(21)	1.937(6)
Li(1)−N(1)	2.074(7)	Li(3)−N(3)	2.333(7)
Li(1)−N(2a)	2.159(7)	Li(3)−N(1a)	2.155(7)
Li(1)−N(3a)	2.058(7)	Li(3)−N(2a)	2.186(7)
Li(1)−O(31a)	2.432(7)	Li(3)−O(4)	1.992(6)
Li(1)−O(11)	1.978(6)	Li(3)−O(31)	2.197(7)
Li(2)−N(2)	2.043(6)		

Bond Angles (deg)

N(1)−Sb(1)-N(2)	90.3(1)	N(2)−Sb(1)-N(3)	91.8(1)
N(1)−Sb(1)-N(3)	90.3(1)		

^{a} Symmetry transformations used to generate equivalent atoms labeled "a": $-x + 2$, $-y + 2$, $-z + 2$.

The structures of **1**−**4** have similar, 14-membered [Sb$_2$N$_6$Li$_6$] cores, constructed from the association of two [Sb(NR)$_3$]$^{3-}$ trianions with six Li$^+$ cations. The cores of these molecules can be described (*conceptually*) as composed of equatorial [N$_6$Li$_6$] stacks which are capped on their open N$_3$Li$_3$ faces by Sb(III) centers.[4] Although the unsolvated cage complexes [Bu^{t}Ge(AsSiPr^i)$_3$}$_2$Li$_6$][5] and [{R′Si(NR)$_3$}$_2$Li$_6$] (R = Me$_3$Si, R′ =

---

[4] (a) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47. (b) Mulvey, R. E. *Chem. Rev.* **1991**, *20*, 167.

[5] Zsolnai, L.; Huttner, G.; Driess, M. *Angew. Chem.* **1993**, *105*, 1549; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1439.

Table 4. Selected Bond Lengths and Angles for $[\{Sb(NBu^t)_3\}_2Li_6]$ (**4**)

Bond Lengths (Å)[a]			
Sb(1)−N(1)	2.075(5)	Li(2)−N(1a)	2.06(1)
Sb(1)−N(2)	2.064(5)	Li(2)−N(2)	2.05(1)
Sb(1)−N(3)	2.071(5)	Li(2)−N(3)	2.05(1)
Li(1)−N(1)	2.08(1)	Li(3)−N(1)	2.04(1)
Li(1)−N(2)	2.03(1)	Li(3)−N(2a)	2.05(1)
Li(1)−N(3a)	2.05(1)	Li(3)−N(3)	2.05(1)
		av Li···C(Bu*t*)	2.65

Bond Angles (deg)			
N(1)−Sb(1)-N(2)	91.8(2)	N−Li−N (av)	110.8
N(1)−Sb(1)-N(3)	91.6(2)	Li−N−Li (av)	67.8
N(2)−Sb(1)-N(3)	91.9(2)		

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

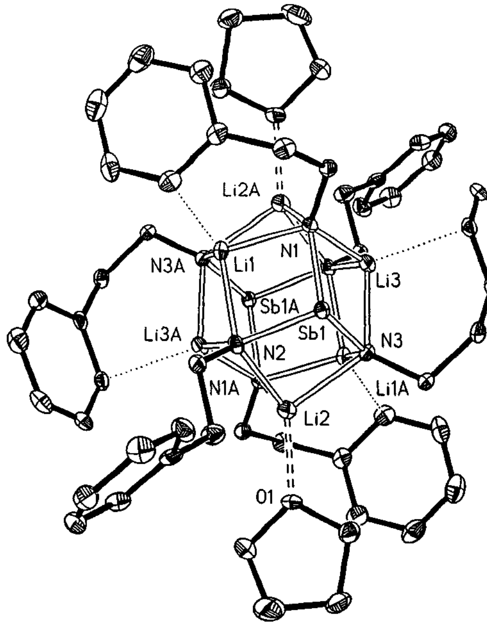


Figure 1. Molecular structure of **1** (toluene solvation in the lattice not shown). Thermal elipsoids are drawn at the 40% probability level. H atoms are omitted for clarity.

Me, Bu^t, Ph;[6] R = Bu^t, R′ = Ph;[7] R = Me, R′ = Bu^t [8]) have core structures similar to those of **1**−**4**, the latter are the only complexes containing $[Sb(NR)_3]^{3-}$ trianions to be structurally characterized.

In **1**, two of the Li^+ cations are solvated by THF ligands [Li(2)−O(1) 1.954(8) Å]. In addition, the other four Li^+ cations of the core are involved in relatively short agostic ortho C(−H)···Li interactions with the Ph rings of adjacent $PhCH_2CH_2N$ groups (Figure 1). These groups straddle the N−Li bonds within each $[Sb(NCH_2CH_2Ph)_3Li_3]$ half of **1** and form loosely linked $[C_4NLi]$ six-membered rings. The C···Li distances (2.472 Å) involved are intermediate between those observed in organolithium complexes[9] (e.g., 2.37 Å between the tetrameric units in $[MeLi]_4$[10]) and those observed in some (amido)lithium complexes (e.g., 2.70 Å for the shortest C···Li distance in $[(PhCH_2)_2NLi]_3$[11]).

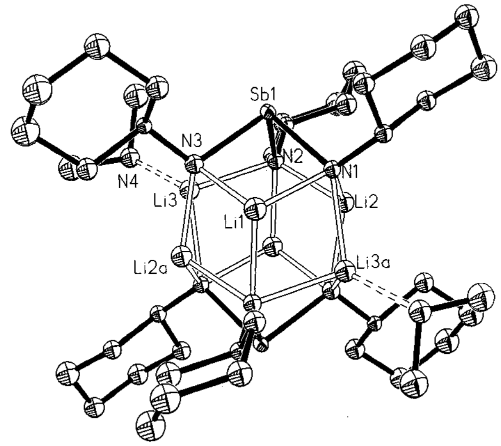


Figure 2. Molecular structure of **2** (toluene solvation in the lattice not shown). Thermal elipsoids are drawn at the 40% probability level. H atoms are omitted for clarity.

In **2**, no THF solvation of the core is present (Figure 2). Instead two Me_2NH ligands occupy equivalent positions to the thf ligands which solvate the core of **1** [Li(3)−N(4) 2.118(9) Å]. The solvation of the core of **2** by only two Me_2NH ligands contrasts with the solvation of all six of the Li^+ cations in $[\{Sb(PCy)_3\}_2Li_6 \cdot 6Me_2NH]$ [P−Li range 2.55(3)−2.66(3) Å].[2e] This restricted solvation stems from the presence of shorter N−Li bonds in **2** and the consequent increase in steric shielding of the core as compared to the P analogue. Owing principally to the similar pattern of solvation by the THF and Me_2NH ligands in **1** and **2**, the $[N_6Li_6]$ fragments of both complexes exhibit a similar pattern of distortion in their N−Li distances [range 1.998(7)−2.157(8) Å in **1** and 1.994(8)−2.168(9) Å in **2**]. The longest N−Li bonds in both complexes are made with the four-coordinate, ligand-solvated Li^+ cations (average 2.150 Å in **1** and average 2.155 Å in **2**), and the shortest are made with the unsolvated Li centers [average 2.050 Å in **1** and average 2.067 Å in **2**]. The similarity in the pattern and magnitude of the N−Li bond lengths in the cores of **1** and **2** provides a direct indication that the agostic contacts in **1** are extremely weak and therefore provide little core disruption.

Although the essential core arrangement of **3** is similar to that found in the structures of **1** and **2**, the presence of the 2-MeO substituents on the (2,4-dmp)N groups results in an elaborate pattern of intramolecular complexation of the Li^+ cations (Figure 3a). The 2-MeO groups of each of the $[Sb\{N(2,4\text{-dmp})\}_3]^{3-}$ trianions straddle the N_6Li_6 belt of the core, engaging the Li^+ cations associated with the other trianion unit (cf. **1** in which the agostic contacts occur within each half of the core). Two of the 2,4-dmp ligands of each trianion adopt similar monodentate bridging modes, and the other adopts a μ-O mode. For Li(1), the coordination of the O atom of a monodentate ligand [Li(1)−O(11) 1.978(6) Å] and the weak attachment of a μ-O bridging ligand [Li(1)−O(31a) 2.432(7) Å] give this center a pseudo-five-coordinate geometry. A similar five-coordinate arrangement is attained for Li(3), which is attached to a μ-O ligand [Li(3)−O(31) 2.197(7) Å] and additionally coordinated by a THF molecule [Li(3)−O(4) 1.992(6) Å]. Li(2) is coordinated solely by a monodentate ligand, resulting in a pseudotetrahedral geometry [Li(2)−O(21) 1.937(6) Å]. Thus, each of the Li^+ cations of the $[Sb\{N(2,4\text{-dmp})\}_3]Li_3$ halves of **3** have different coordination environments.

---

(6) Brauer, D. J.; Bürger, H.; Liewald, G. L.; Wilke, J. *J. Organomet. Chem.* **1985**, *287*, 305.

(7) Brauer, D. J.; Bürger, H.; Liewald, G. L. *J. Organomet. Chem.* **1986**, *308*, 119.

(8) Veith, M.; Spaniol, A.; Pöhlmann, J.; Gross, F.; Huch, V. *Chem. Ber.* **1993**, *126*, 2625.

(9) Setzer, W.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(10) (a) Weiss, E.; Lucken, E. A. C. *J. Organomet. Chem.* **1964**, *2*, 197. (b) Weiss, E.; Hencken. *J. Organomet. Chem.* **1970**, *21*, 265.

(11) (a) Armstrong, D. R.; Mulvey, R. E.; Walker, G. T.; Barr, D.; Snaith, R. *J. Chem. Soc., Dalton Trans.* **1988**, 617. (b) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 285.

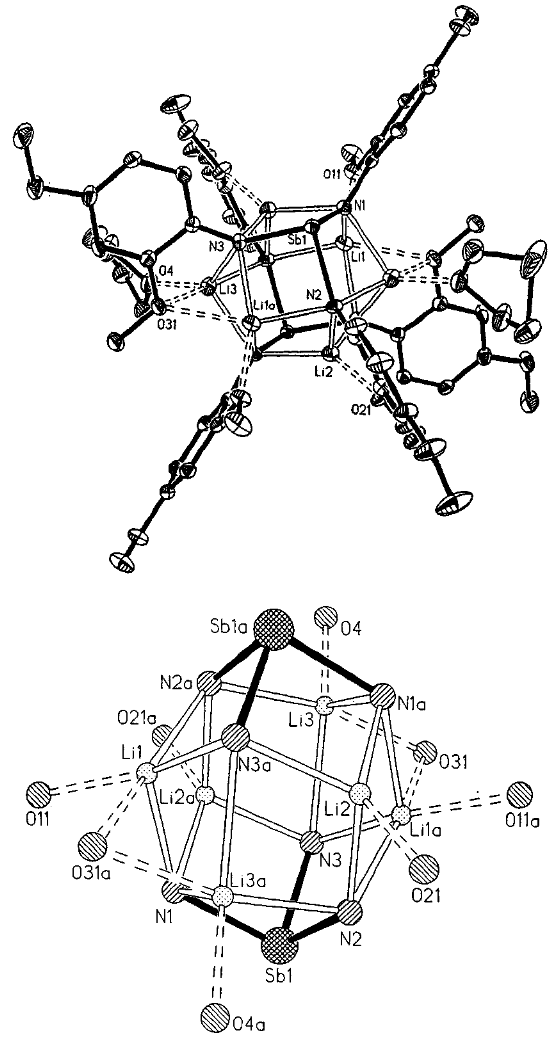


Figure 3. (a) Molecular structure of **3** (toluene solvation in the lattice not shown). Thermal elipsoids are drawn at the 40% probability level. H atoms are omitted for clarity. (b) Connectivity of surrounding ligand coordination.

The pattern of N−Li bonds in the [N_6Li_6] fragment of **3** mirrors closely the extent of solvation and the different coordination geometries of the Li centers. As a result of the extent and variety of inter- and intramolecular solvation, the [$Sb_2N_6Li_6$] core of **3** is far more distorted than in **1** and **2** [N−Li range 2.012(6)−2.333(7) Å] (Figure 3b). The shortest N−Li bonds occur for four-coordinate Li(2) (average N−Li 2.051 Å) and pseudo-five-coordinate Li(1) (average 2.059 Å). The combination of μ-O bridging of Li(3) and Li(1a) by a dmp ligand [over the Li(3)N(1a)Li(1)N(3) face of the core] and the THF solvation of Li(3) results in a very irregular geometry for this metal center and in a drastic elongation and weakening of the Li(3)−N(3) bond [2.333(7) Å; cf. average 2.099 Å for the other Li−N bonds].

The solid-state structures of **1**−**3** illustrate that the N_6Li_6 frameworks in these complexes are highly flexible and easily deformed by Lewis base solvation. This is particularly apparent in **3** in which the additional strain induced by intramolecular MeO solvation results in the onset of fragmentation of the core. However, despite the very large differences in the steric demands of the organic substituents in **1**−**3** and in the extents of solvation and disruption of their N_6Li_6 units, only small differences in the Sb−N bond lengths and N−Sb−N angles in the [$Sb(NR)_3$]$^{3-}$ trianions of these complexes occur (Sb−N average 2.063 Å, N−Sb−N average 94.5° in **1**; Sb−N average 2.075 Å, N−Sb−N average 93.4° in **2**; Sb−N average 2.053 Å, N−Sb−N average 90.8° in **3**). Overall, the [$Sb_2N_6Li_6$] core geometries of **1**−**3** are subject to the competing bonding demands of the Sb(III) and Li atoms and to solvation. However, the small variation in the configuration of the [$Sb(NR)_3$]$^{3-}$ trianions and the comparative flexibility of the [N_6Li_6] units in these complexes highlights the fact that the [$Sb(NR)_3$]$^{3-}$ units are the robust chemical entities in these species and that it is the directionality which the greater covalency of the Sb−N bonding imparts which fundamentally underlies the [$Sb_2N_6Li_6$] core structures observed (*not* the N_6Li_6 units in which essentially nondirectional ionic bonding is present[12]).

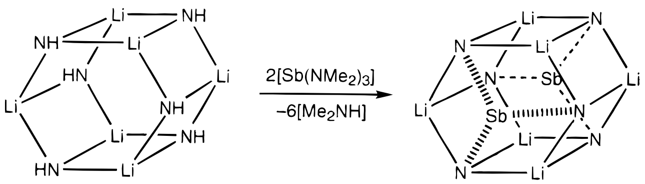


Figure 4. Proposed "structure directed" assembly of **1**.

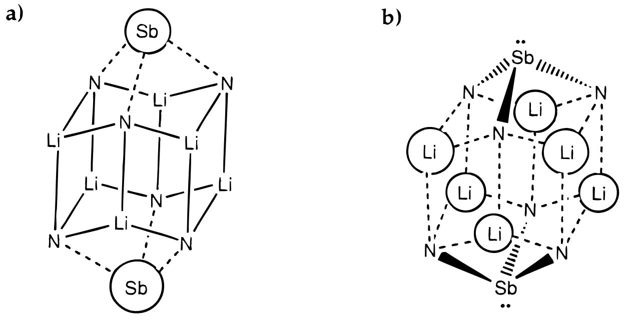


Figure 5. (a) Rigid N_6Li_6 "bed" with Sb^{3+} ions on faces. (b) Rigid [$Sb(NR)_3$]$^{3-}$ trianions with flexible, ionically bonded N_6Li_6 core.

On the basis of the apparent similarity between the cyclic octameric ladder structure of [$Bu^tN(H)Li$]$_8$ and the hexameric "ladder" core of **1**, it was recently proposed that the structure of **1** is templated by the rigid cyclic ladder structure of [$PhCH_2CH_2N(H)Li$]$_n$ (which it is postulated may have a cyclic hexameric structure, $n = 6$) (Figure 4).[12] According to this view these species are composed of rigid N_6Li_6 "ladders" in which Sb^{3+} ions are bound "to the bed of N atoms on each side of the core, ... akin to the way in which metal cations fit macrocyclic crown-ether holes" (Figure 5a).[12] However, the extensive range of structural data presented in this paper leads us to an alternative conclusion concerning these molecules. Our evidence illustrates that these structures are constructed from essentially rigid [$Sb(NR)_3$]$^{3-}$ trianions which are loosely associated with six Li^+ cations (Figure 5b). The fact that the [$Sb(NR)_3$]$^{3-}$ trianions are the robust chemical entities in these complexes is illustrated not just by the structural analyses of **1**−**3** but also by the reaction of **2** with [Cp_2Pb], resulting in the cage complex [{$Sb(NCy)_3$}$_2Pb_3$] in which the *intact* [$Sb(NCy)_3$]$^{3-}$ trianions survive.[3a] In addition, the reaction of **2** with [Bu^tOK] (1:3 equiv) results in symmetrical cage expansion of the core and in the formation of [{$Sb(NCy)_3$}$_2Li_3$]$_2$(Bu^tOK)$_3$, in which the N_6Li_6 core is broken down.[3b] The central N_6Li_6 substructures of **1**−**3** are of secondary importance. These simply maximize ionic contact in the most effective way,[4] and their occurrence has no necessary mechanistic implications.

---

(12) Barnett, N. D. R.; Clegg, W.; Horsburgh, L.; Linsay, D. M.; Liu, Q.-Y.; McKenzie, F. M.; Mulvey, R. E.; Williard, P. G. *J. Chem. Soc., Chem. Commun.* **1996**, 2321.

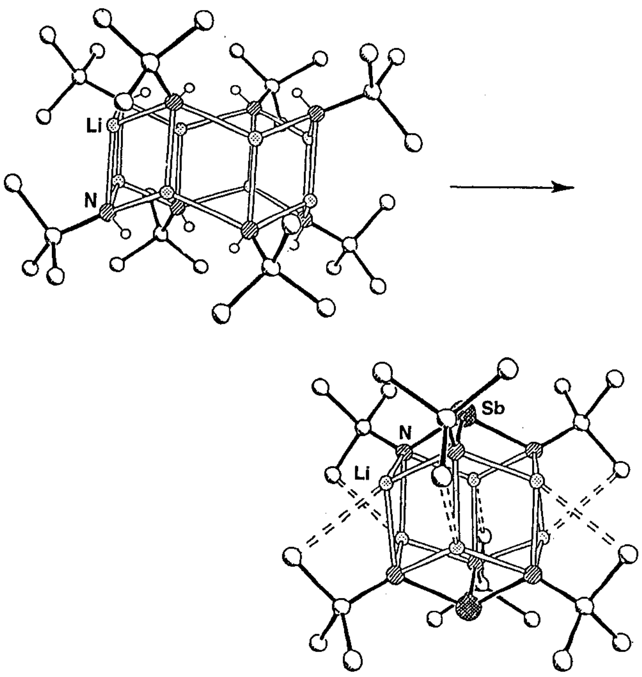


Figure 6. Conversion of octameric cyclic ladder into **4**.

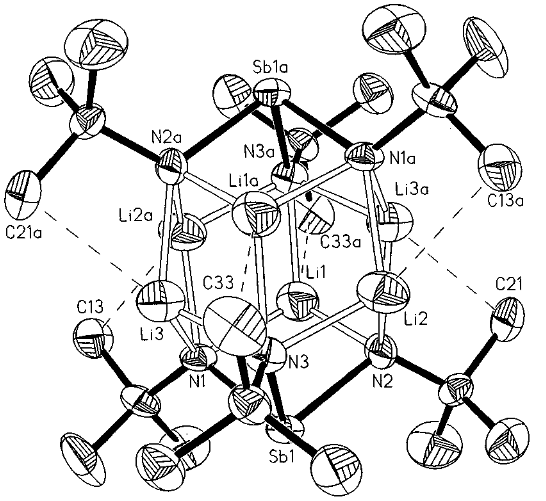


Figure 7. Molecular structure of **4**. Thermal elipsoids are drawn at the 40% probability level. H atoms are omitted for clarity.

Even the cyclic ladder arrangement of $[Bu^tN(H)Li]_8$ (the only unsolvated primary (amido)lithium complex to be structurally characterized)[12] is not robust enough to support or direct assembly of complexes such as **1**−**3**. The reaction of $[Bu^tN(H)Li]_8$ with $[Sb(NMe_2)_3]$ gives the trianion complex $[\{Sb(N^tBu)_3\}_2Li_6]$ (**4**) in which the octameric core of the primary (amido)lithium precursor is not retained (Figure 6). Even if the $[N_8Li_8]$ core were to be sustained throughout the course of this reaction, an $[N_2Li_2]$ dimer unit would ultimately have to be expelled to generate **4**. This is simply because the demands of Sb(III) valence, Sb−N bonding, and the associated stoichiometry provide the determining structural direction here.

Despite the lack of Lewis base or intramolecular solvation of the Li core of **4** (Figure 7), the Sb−N bonds (average 2.070 Å) and N−Sb−N angles (average 91.8°) are within the range of values observed for the $[Sb(NR)_3]^{3-}$ anions of **1**−**3**. The association of the $[Sb(NBu^t)_3]^{3-}$ trianions of **4** gives a symmetrical $[Sb_2N_6Li_6]$ core in which the N−Li bond lengths [2.03(1)−2.08(1) Å] fall in a range similar to those observed in the cyclic ladder structure of $[Bu^tN(H)Li]_8$ (2.03−2.07 Å). However, unlike this ladder structure, in which the internal N−Li "rungs" are on average shorter (2.035 Å) than the external N−Li bonds (average 2.058 Å), there is no distinctive pattern of N−Li bond lengths occurring in the $[N_6Li_6]$ substructure of **4** which could prompt its description as a ladder as opposed to a stack (the internal and "rung" N−Li bonds having the same average of 2.05 Å). As can be judged from the reaction producing **4** (Figure 6) and the flexibility of the N_6Li_6 cores in complexes of this type, the geometric similarity of the N_2Li_2 ring units of **4** [N−Li−N 110.8°, Li−N−Li 67.8°] to the Li_2N_2 units in $[Bu^tN(H)Li]_8$ (N−Li−N average 108.2°, Li−N−Li average 71.8°[12]) simply reflects the demands of optimum N−Li bonding in the N_6Li_6 belt and does not imply any form of structural direction. A further feature of **4** is the presence of agostic C(−H)···Li contacts [C···Li average 2.65 Å], which span the equatorial N_6Li_6 belt and strengthen the association of the $[Sb(NBu^t)_3]Li_3$ halves of the cage. These contacts, which are similar to those occurring in $[(PhCH_2)_2NLi]_3$ (shortest 2.70 Å)[11] but markedly longer than those present in tetrameric $[Bu^tLi]_4$ (average 2.374 Å),[13] do not occur in $[Bu^tN(H)Li]_8$.[12] The absence of Me_2NH solvation of the core of **4** is surprising bearing in mind the solvation of the core of **2** by this ligand. This is most likely to be a result of the more efficient shielding of the $[N_6Li_6]$ core of **4** by the surrounding Bu^t ligand framework.

Conclusions

The syntheses and structures of **1**−**4** illustrate that the reactions of $[Sb(NMe_2)_3]$ with primary (amido)lithiums, $[RN(H)Li]_n$, provide a general route to complexes containing $[Sb(NR)_3]^{3-}$ trianions. The variations in the $[Sb_2N_6Li_6]$ cores of these species suggest that the group 15 trianion units dominate these arrangements and that the $[N_6Li_6]$ subunits perform an associative role. There is no evidence for any form of structural direction by the primary (amido)lithium complexes in these reactions, and the structures of the products largely depend on the valence and bonding demands of the group 15 elements as well as Lewis base solvation.

The ready formation of imido group 15 trianions of type $[Sb(ER)_3]^{3-}$ [allowing the variation in the donor atom (E = N, P, etc.) and the incorporation of auxiliary functionality into the organic groups (R) (such as MeO in **3**)] provides a versatile family of multifunctional anion ligands whose affinities and number of donation sites can potentially can be tuned for the complexation of particular metal ions. The investigation of the coordination chemistry of this new family of ligands is an exciting prospect.

Experimental Section

General Preparative Techniques. All the reactions were undertaken under dry, O_2-free argon using a vacuum line and standard inert-atmosphere techniques.[14] THF and toluene were dried by distillation over Na/benzophenone. The $PhCH_2CH_2NH_2$, $CyNH_2$, and Bu^tNH_2 were dried with molecular sieve (13X) before use in the syntheses of **1**, **2**, and **4**. 2,4-dmpNH_2 was freshly distilled prior to the synthesis of **3**. $[Sb(NMe_2)_3]$ was prepared in the manner described in the literature by the 3:1 reaction of $[Me_2NLi]$ with $SbCl_3{\cdot}Et_2O$.[1] Removal of the solvent followed by distillation gave the complex as a volatile colorless liquid (ca. 80%). This can be stored conveniently as a standardized toluene solution at −35 °C. Complexes **1**−**4** were isolated and characterized with the aid of a N_2-filled glovebox (Miller-Howe, fitted with a Belle

---

(13) Kottke, T.; Stalke, D. *Angew. Chem.* **1993**, *105*, 619; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 580.

(14) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

internal circulation system). Melting points were determined using a conventional apparatus and sealing samples in capillaries under N_2. Elemental analyses (C, H, and N) were performed by first sealing samples in airtight aluminum boats (1−2 mg) prior to analysis using a Perkin-Elmer CE 440 elemental analyzer. IR spectra were obtained as Nujol mulls using NaCl windows on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker WH 250 MHz spectrometer, using the NMR solvents as internal reference standards. For the synthesis of **1**, see ref 2b.

Synthesis of 2. [Bu^{n}Li] (50 mL, 1.5 mol L^{-1} in hexanes, 75 mmol) was added dropwise to a solution of [CyNH$_2$] (8.58 mL, 75 mmol) in toluene (20 mL) at 0 °C. To the white precipitate formed was added [Sb(NMe$_2$)$_3$] (25 mmol in toluene, 10 mL) at −78 °C. Warming to room temperature and bringing to reflux (1 h) gave a yellow solution with some decomposition. The black decomposition product was removed by filtration (Celite, porosity 3) and the solution reduced under vacuum until **2** precipitated as a white powder (13.2 g, 55%). Isolation of this powder under vacuum and heating to 50 °C (10^{-1} atm, 15 min) removes the lattice-bound toluene solvation and Me$_2$NH, producing material which is suitable for transmetalation reactions (see ref 3a). If this material is isolated without heating, the lattice and Me$_2$NH solvation remain. The following analytical and spectroscopic data refer to this material: decomp > 200 °C; IR (Nujol) $\nu_{\max}$/cm^{-1} = ca. 3100 (w, br, N−H str), 1040 (s), 960 (ms); ^{1}H NMR (250 MHz, benzene-d_6, +25 °C) δ = 7.0 (mult, 10H, C−H toluene), 3.38 (mult, 6H, C(α)−H Cy), 2.17 (s, 12H, Me$_2$NH), 2.11 (s, 6H, Me of toluene), 1.79−1.0 (overlapping mult, 60H, Cy). Anal. Found: C, 50.8; H, 5.7; N, 5.6. Calcd for **2**: C, 50.3; H, 5.3; N, 6.3.

Synthesis of 3. [Bu^{n}Li] (8.75 mL, 1.5 mol L^{-1} in hexanes, 13.2 mmol) was added dropwise to a solution of 2,4-dmpNH$_2$ in THF (20 mL), giving an orange solution. [Sb(NMe$_2$)$_3$] was added (4.4 mmol in 5 mL of toluene). An orange suspension was produced after bringing the mixture to reflux (5 min). Addition of THF (30 mL) gave an orange solution with some decomposition. After filtration (Celite, porosity 3) and reduction of the filtrate under vacuum, a yellow precipitate was formed which was heated back into solution. Storage of this solution at room temperature (24 h) produced large yellow cubic crystals of **3** (2.58 g, 44.2%): decomp > 240 °C; IR (Nujol) $\nu_{\max}$/cm^{-1} = 1235(vs) (C−O str), other bands at 1130 (s), 1125 (s), 1035 (s), 822 (s); ^{1}H NMR (250 MHz, C$_6$D$_6$, +25 °C) δ = 7.0 (mult, 10H, aryl C−H toluene), 6.35 (mult, 18H, aryl C−H of 2,4-dmp), ca. 3.50 (mult, 8H, THF), 3.41 (s, 18H, 2-MeO of dmp), 3.24 (s, 18H, 4-MeO of dmp). Anal. Found: C, 56.9; H, 8.6; N, 10.1. Calcd for **3**: C, 56.8; H, 8.4; N, 9.8.

Synthesis of 4. [Bu^{n}Li] (2.6 mL, 1.5 mol L^{-1} in hexanes, 39.0 mmol) was added dropwise to a solution of Bu^{t}NH$_2$ (4.0 mL, 38.0 mmol) in hexane (15 mL), and after brief reflux a suspension of [Bu^{t}N(H)Li]$_8$ formed. To the chilled suspension was added [Sb(NMe$_2$)$_3$] (12.58 mmol in 3.7 mL of toluene). The solution was brought to reflux and the solvent reduced under vacuum to ca. 10 mL, producing a precipitate which was gently warmed back into solution. Storage of this solution at room temperature (24 h) produced white needle crystals of **4** (1.58 g, 41.0%): decomp 160 °C; ^{1}H NMR (250 MHz, C$_6$D$_6$, +25 °C) δ = 1.32 (s, Bu^t). Anal. Found: C, 40.5; H, 7.6; N, 11.9. Calcd for **4**: C, 41.0; H, 8.3; N, 11.9.

X-ray Structure Determinations. Crystals were mounted directly from solution under argon using a perfluorocarbon oil (Riedel-deHaën) which protects them from atmospheric O$_2$ and moisture.[15] The oil freezes at reduced temperatures and holds the crystal static in the X-ray beam. Data were collected on a Stoe-Siemens AED four-circle diffractometer for **2** and **3** and a Siemens P4 four-circle diffractometer for **4**. Graphite-monochromated Mo Kα radiation and semiempirical absorption corrections based on ψ-scans were employed for all complexes.[16] Details of the structural refinement of **1** are given in ref 2b. In **2** and **3**, all the non-hydrogen atoms were refined anisotropically [accept for the lattice-bound toluene molecules (two for each cage molecule) which are each disordered over two (50:50) sites about a 2-fold axis]. The coordinated THF molecule in **3** is disordered over two (50:50) sites at C(42) and C(43). All non-hydrogen atoms in **4** were refined anisotropically. The structures of all the complexes were solved by direct methods (SHELXTL PLUS[17a] for **2** and **3** and SHELTL for **4**[17b]) and refined by full-matrix least squares on F^2 (SHELXL-93[18]). Largest difference between peak and hole in the final electron density map: for **2**, 1.446, −1.050 e Å^{-3}; for **3**, 0.828, −0.617 e Å^{-3}; for **4**, 1.004 and −0.877 e Å^{-3}. Atom coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallography Data Centre.

Acknowledgment. We gratefully acknowledge the EPSRC (M.A.B., C.N.H., A.D.H., M.M.), the Royal Society (P.R.R., D.S.W.), Electron Tubes, Ruislip, U.K. [Case award for A.D.H. (industrial supervisor Dr. N. C. Stoodley)], Jesus College Cambridge (Fellowship for M.A.P.), and Kirikkale University, Turkey (M.T.), for financial support. We also thank Dr. J. Davies (Cambridge, U.K.) for structural work on complex **2**.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of complexes **2**−**4** are available on the Internet only. Access information is given on any current masthead page.

IC971090K

---

(15) Stalke, D.; Kottke, T. *J. Appl. Crystallogr*. **1993**, *26*, 615.

(16) Sheldrick, G. M. XEMP, program for structure adsorption.

(17) Sheldrick, G. M. (a) SHELXTL-PLUS, Structure solution and refinement package, **1990**. (b) SHELXL (PC version 5.03) Siemens Analytical, Inc., Madison, WI, 1994.

(18) Sheldrick, G. M. SHELXL-93, structure refinement package, University of Göttingen, 1993.