Synthesis and Structure of the Heterobimetallic Ladder Complex $[\{(MesNH)Sn(\mu\text{-}Nma)\}_2(Li\cdot 2THF)_2]$ $(Mes = 2,4,6\text{-}Me_3C_6H_2,\ ma = 2\text{-}MeOC_6H_4)$

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Introduction

Recently, much of our research has focused on the syntheses of anionic group 13,[1] 14,[2] and 15[3] metal imido (RN^{2-}) and phosphinidene (RP^{2-}) complexes and their applications as novel ligands to a range of metals.[4] We found that the deprotonation reactions of primary amido and phosphido lithium complexes ([REHLi]; E = N, P) with the cubane $[SnN^tBu]_4$ give heterometallic complexes containing Sn(II) imido and phosphinidene anions, e.g., $[\{Sn(\mu\text{-}PCy)\}_2\{\mu\text{-}PCy\}]_2(Li\cdot THF)_4$ containing a metallacyclic $[\{Sn(\mu\text{-}PCy)\}_2\{\mu\text{-}PCy\}]_2{}^{4-}$ tetraanion.[2] However, the 1:2 reactions of $[Sn(NMe_2)_2]$ with [RNHLi] only result in the formation of the thermodynamically stable cubanes $[SnNR]_4$[5] rather than the desired $[Sn(NR)_2]^{2-}$ dianions. We report here that the use of polynuclear dimethylamido $[\{Sn(NMes)_2\}\{Sn(\mu\text{-}NMe_2)\}_2]$[6] as reagents in reactions with [RNHLi] allows the formation of imido Sn(II) anions.

Results and Discussion

The reaction of the polynuclear dimethylamido Sn(II) reagent $[\{Sn(NMes)_2\}\{Sn(\mu\text{-}NMe_2)\}_2]$ [Mes = $2,4,6\text{-}Me_3C_6H_2$][6] with [LiN(H)ma] [ma = $(2\text{-}MeO)C_6H_4$] (1:2 equiv) follows an unexpected pathway in which elimination of $[Sn(NMe_2)_2]$, rather than facile deprotonation, gives rise to the novel heterobimetallic ladder complex $[[MesNHSn(\mu\text{-}Nma)]_2(Li\cdot THF)_2]$ (**1**), containing the first example of a dinuclear Sn(II) imido dianion, $[(MesNH)Sn(\mu\text{-}Nma)]_2{}^{2-}$ (see Experimental Section). Although various alkali metal alkoxides, amides, and phosphides adopt ladder structures[7] and a few imido Si(IV) ligands form ladders with various main group metals,[8] to our knowledge, the only other bimetallic main group ladder complex is the mixed alkali metal derivative $[LiNa\{N(CH_2Ph)_2\}_2\cdot OEt_2\}_2$.[9] The selection of a dinuclear Sn(II) anion unit in **1**, stemming directly from reaction sequence involved in its formation, contrasts with the outcome of reactions of [REHLi] (E = N, P) with imido Sn(II) cubanes $[SnNR]_4$ which generate anions in which three or four of the Sn centers of the precursor survive (Scheme 1).[2]

A low-temperature X-ray crystallographic study of **1** was undertaken. Details of the structural refinement are given in the Experimental Section. The structure of **1** is that of a heterobimetallic complex formed from the association of the imido Sn(II) dianion $[MesNHSn(\mu\text{-}Nma)]_2{}^{2-}$ with two THF-solvated Li^+ cations (Figure 1). This association results in an $[Li_2N_4Sn_2]$ ladder arrangement in the core. The reaction of $[\{Sn(NMes)_2\}\{Sn(\mu\text{-}NMe_2)\}_2]$ with [LiN(H)ma] has resulted in formal redistribution of the Mes and ma groups, with maN groups forming the central Sn_2N_2 ring in **1** and with the MesNH groups being terminal. The planar Sn_2N_2 core of the $[MesNHSn(\mu\text{-}Nma)]_2{}^{2-}$ dianion is rhombic shaped, with the very narrow N−Sn−N angle [78.8(2)°] and the Sn−N−Sn angle [101.2(2)°] being reminiscent of imido Sn(II) cubanes[5] [e.g., in $[SnNCy]_4$ (Cy = C_6H_{11})[5e], the average N−Sn−N angle is 80.8° and the average Sn−N−Sn angle is 98.5°]. The elongation of the internal Sn(1)−N(1a) bonds [2.191(4) Å; cf. Sn(1)−N(1), 2.154(4) Å] appears to result from the chelation of the Li^+ cations by the bridging maN and terminal MesNH groups. The pseudo-pyramidal geometry of the Sn(II) centers of **1** is symptomatic of the presence of a stereochemically active metal lone pair and stresses the formulation of the imido Sn(II) fragment as the $[MesNHSn(\mu\text{-}Nma)]_2{}^{2-}$ dianion. The geometry of the Sn(II) centers [particularly the characteristic N(1)−Sn(1)−N(2) angle of 90.4(2)°, which is typical of Sn(II) systems] is largely responsible for the highly compressed ("Z-shaped") ladder arrangement in the $[Li_2N_4Sn_2]$ core. Although the weak interactions of the MeO groups of the maN ligands with the Sn(II) centers [O(1)−Sn(1), 2.732(4) Å] are well within the sum of the van der Waals radii of O and Sn (ca. 3.7 Å), these have no discernible effect on the geometry of the metal atoms. The Z-shaped architecture of the core of **1** contrasts with the far more open arrangements found in noncyclic amido lithium ladder complexes[10] [such as in $[\{pyrrolideLi\}_2\cdot TMEDA]_2$

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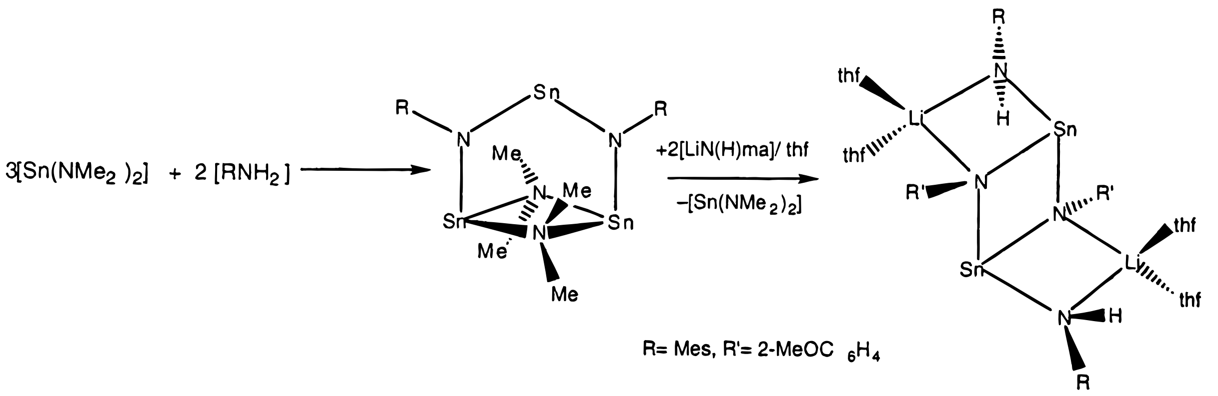
Scheme 1



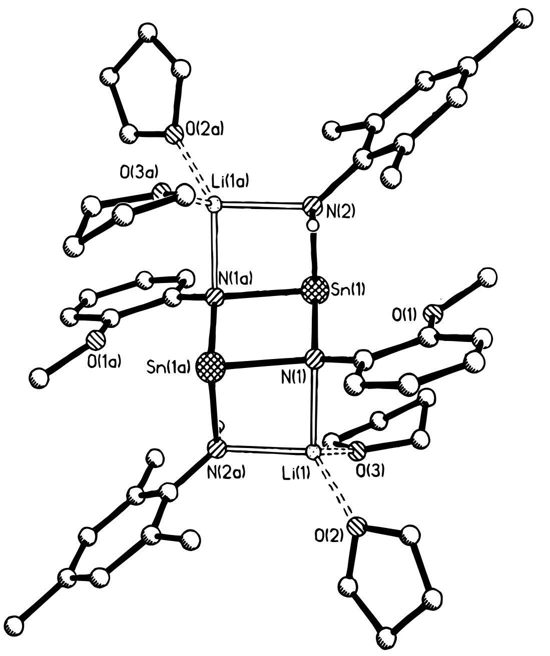


Figure 1. Molecular structure of **1**. H atoms, except those attached to N, have been omitted for clarity. Selected bond lengths (Å) and angles (°); Sn(1)−N(2), 2.154(4); Sn(1)−N(2), 2.257(4); Sn(1)−N(1a), 2.191(4); Li−O, av 1.98, Li(1a)−N(1a), 2.09(1); Li(1a)−N(2), 2.07(1); N(2)−H(N2), 0.898; N(1)−Sn(1)−N(1a), 78.8(2); N(1a)−Sn(1)−N(2), 84.4(2), N(1)−Sn(1)−N(2), 90.4(2); Sn(1)−N(1a)−Sn(1a), 101.2(2); Sn(1)−N(1a)−Li(1a), 90.2(3); Sn(1)−N(2)−Li(1a), 88.9(3); N(1)−Li(1)−N(2a), 91.7(4); O−Li(1)−N, av 116.7; O(2)−Li(1)−O(3), 99.4(4). Symmetry transformations used to generate equivalent atoms (a) −*x* + 1, −*y* + 1, −*z*.

(TMEDA = $(Me_2NCH_2)_2$)[11] and $[LiNa\{N(CH_2Ph)_2\}_2\cdot OEt_2]_2$[8] and emphasizes that the Sn−N bonding dominates the largely ionic Li−N interactions in **1**. The chelation of the Li^+ cations by the bridging maN and pendant MesNH groups (Li−N, average 2.08 Å; N−Li−N, 91.7°) gives puckered terminal LiN_2Sn rings (Li 0.58 Å out of the plane formed by the other atoms). The bond lengths involved and the pseudo-tetrahedral geometries of these ions are typical of amido lithium complexes.[10]

Table 1. PM3 Optimized Energies of Models of **1**[a]

compound	$\Delta H_{formation}$ (kcal mol^{-1})	$\Delta H_{solvation}$ (kcal mol^{-1}, per mole of H_2O)
$[(LiNH_2)\cdot\{Sn(\mu\text{-}NH)\}_2(LiNH_2)]$ (ladder, **A**)	1.4	–
$[(SnNH)_2(LiNH_2)_2]$ (cubane, **B**)	2.4	–
$[(SnNH_2)\cdot\{Li(\mu\text{-}NH)\}_2\cdot(SnNH_2)]$ (ladder, **C**)	4.5	–
$[(SnNH_2)_2(LiNH)_2]$ (cubane, **D**)	35.8	–
A·$2H_2O$	−136.6	−15.6
B·$2H_2O$[b]	−126.0	−10.8
C·$2H_2O$	−114.6	−6.2
A·$4H_2O$	−261.9	−9.2
C·$4H_2O$	−221.4	0.0

[a] $\Delta H_{formation}(H_2O)$ = −53.4 kcal mol^{-1}. [b] Further solvation of **B**·$2H_2O$ leads to **A**·$4H_2O$ with $\Delta H_{solvation}$ per mole of H_2O of 14.6 kcal mol^{-1}.

To further probe the relative influences of Sn−N and Li−N bonding and solvation on the structure of **1**, model semiempirical (PM3)[12] calculations were performed. Details of the calculational models investigated are given in Table 1. Only small energy differences exist between the open ladder $[(LiNH_2)\{Sn(\mu\text{-}NH)\}_2(LiNH_2)]$ (**A**), the cubane $[(SnNH)_2(LiNH_2)_2]$ (**B**), and the ladder $[(SnNH_2)\{Li(\mu\text{-}NH)\}_2(SnNH_2)]$ (**C**) models. However, monosolvation of the Li^+ cations in these species leads to the preference of the $[Sn(\mu\text{-}NH)]_2$ bridged species **A**·$2H_2O$, which is 10.6 kcal mol^{-1} more stable than the cubane **B**·$2H_2O$ and 22.0 kcal mol^{-1} more stable than the $[Li(\mu\text{-}NH)]_2$ bridged open ladder **C**·$2H_2O$ (Figure 2). The preference for **A**·$2H_2O$ over **B**·$2H_2O$ is probably due to unfavorable bond angles at Sn in the cubane. Further solvation accentuates the preference for the $[Sn(\mu\text{-}NH)]_2$ ladder arrangement of **A**·$4H_2O$, the same structural pattern found in **1**. Solvation of the Li^+ cations of **B**·$2H_2O$ opens up the cubane and gives **A**·$4H_2O$ (the total $\Delta H_{solvation}$ of **B**·$2H_2O$ to **A**·$4H_2O$ being 29.1 kcal mol^{-1}). There is no gain in energy for further solvation of the Sn centers of **C**·$2H_2O$, and the alternative solvation of Li^+ in **A**·$4H_2O$ is preferred by 40.5 kcal mol^{-1}.

The calculations reveal that solvation has a marked effect on the structure adopted by this system. The importance of Lewis base solvation in **1** is that it depletes the influence of the more electropositive Li^+ cations by diminishing their competition for ligand electron density, in so doing solvation enhances the dominance of the Sn−N bonding over the structure.

We are exploring the transmetalation of **1** with transition and main group metal salts as a means to structured assembly of other heterometallic cage compounds.

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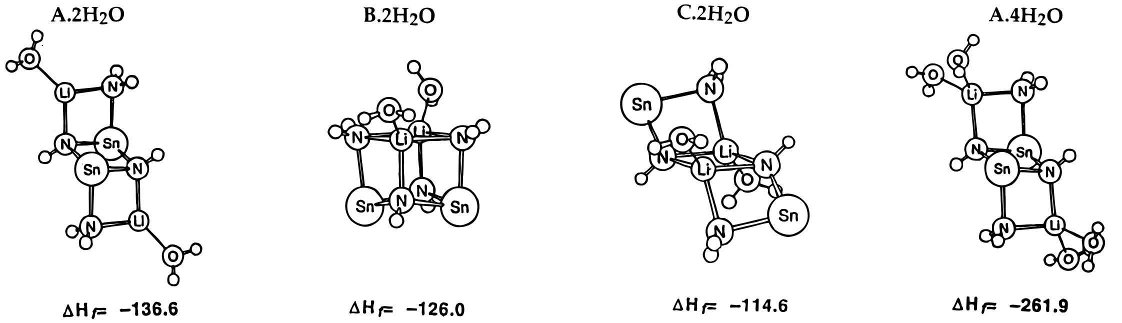

Figure 2. PM3 heats of formation ($\Delta H_{\text{formation}}$) for models of **1**.

Experimental Section

All procedures were carried out under dry, O_2-free argon using standard inert atmosphere techniques.[13] [$Sn(NMe_2)_2$] was prepared in the manner described in the literature from the 2:1 reaction of [$LiNMe_2$] with $SnCl_2$ in Et_2O in ca. 80% yield.[14] The precursor [$\{Sn(NMes)_2\}\{Sn(\mu\text{-}NMe_2)\}_2$] was prepared by the reaction of [$Sn(NMe_2)_2$] with mesNH$_2$ in THF in ca. 60% yield.[6] THF and Et_2O used in reactions were dried over Na/benzophenone, and the *o*-anisole was freshly distilled and stored over molecular sieve (13X). Complex **1** was isolated and characterized with the aid of an argon-filled glovebox (Miller-Howe, fitted with a Belle internal circulator). Melting point analysis was made using a standard apparatus and sealing a sample in airtight capillaries under argon. IR spectra were obtained using a Paragon 4000 FT/IR spectrometer. Elemental analyses (C, H, N) were performed by first sealing samples in airtight aluminum boats (1−2 mg) under argon prior to analysis using a Perkin-Elmer 240 Elemental Analyzer. ^1H NMR spectra of **1** were recorded on a Bruker WH 250 MHz spectrometer, using the solvent (benzene-d_6) resonances as the internal standard. ^{119}Sn NMR spectra were obtained using a Bruker WH 400 MHz spectrometer, using $SnCl_2/D_2O$ as an external standard.

Synthesis of 1. To a solution of [$\{Sn(NMes)_2\}\{Sn(\mu\text{-}NMe_2)\}_2$] (0.89 g, 1.5 mmol) in toluene (10 mL) was added a solution of [LiN(H)ma] at 25 °C [3.0 mmol, prepared by the in situ reaction of 0.35 mL (3.0 mmol) of maNH$_2$ with 2.0 mL of ^{n}BuLi (3.0 mmol, 1.5 mol L^{-1}, in hexanes) in 5 mL of toluene and 2 mL of THF]. The solution was stirred (5 min), changing color from orange to yellow-green, and brought to reflux (5 min). The solution was filtered (Celite, porosity 3) to remove a small amount of insoluble material, and all the solvent was removed in vacuo (producing an oil). Et_2O (10 mL) was added, and the yellow precipitate was dissolved by adding THF (ca. 5 mL). Storage of this solution (−18 °C, 24 h) gave yellow cubic crystals of **1**; yield of crystalline material 0.59 g (37%); mp 106−108 °C (decomp dark red solid >250 °C); IR (Nujol) $\nu_{\max}$ (cm^{-1}) = ca. 3040 (w) (aryl C−H str.), 1576 (m) (aryl C···C str.), 1239 (vs) (C−O str.), other bands at 1111 (m), 1046 (m), 1019 (m), 855 (m), 723 (s) (no sharp N−H str. observed); ^1H NMR (250 MHz, +25 °C, benzene-d_6), δ= 7.41 (d.d., 1H, C(3)−H, ma), 6.99 (d.t., 1H, C(4)−H, ma), 6.91 (s, br., 2H, Mes), 6.75 (d.t., 1H, C(5)−H, ma), 6.54 (d.d., 1H, C(6)−H, ma), 3.45 (m., 4H, THF) (coincident with 4-Me of Mes, 3H), 3.28 (s., 6H, 2,6-Me of Mes), 2.35 (s., 3H, OMe of ma), 1.30 (m., 4H, THF), the N−H could not be identified unequivocally; ^{119}Sn NMR (162 MHz, +25 °C, benzene-d_6, rel. to $SnCl_2/D_2O$) −961.3 (s.); elemental anal., found C, 53.9, H, 6.6, N, 5.6; calcd C, 54.8, H, 6.7, N, 5.3.

X-ray Structure of 1. $C_{48}H_{70}Li_2N_4O_6Sn_2$, M = 1050.34, monoclinic, space group $P\bar{1}$ (No. 2), a = 11.080(7) Å, b = 11.720(7) Å, c = 10.561(5) Å, α = 104.45(4)°, β = 99.70(5)°, γ = 102.01(5)°, V = 1263(1) Å^3, Z = 1, ρ_{calcd} = 1.381 M gm^{-3}, λ = 0.710 73 Å, T = 153(2) K, μ(Mo Kα) = 1.036 mm^{-1}. Data were collected on a Rigaku AFC5R diffractometer using an oil-coated rapidly cooled crystal[15] of dimensions 0.20 × 0.15 × 0.15 mm by the $\theta/2\omega$ method (3.01° ≤ θ ≤ 27.51°). Of a total of 6091 collected reflections, 5795 were independent (R_{int} = 0.035). The structure was solved (SIR92)[16] by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1(F > 4\sigma(F)) = 0.046$ and w$R2$ = 0.129 (all data) [$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (0.0567P)^2]$, $P = F_o^2 + (2F_c^2/3)$];[17] the largest peak and hole in the final difference map were 0.999 and −0.897 e Å^{-3}, respectively. The H atoms attached to the MesN groups were located in the difference map.

PM3 Calculations on Models of 1. Calculations were performed on a Silicon Graphics R4400 workstation using VAMP 5.6 (Oxford Molecular) with no geometric constraints being employed during structural optimizations.[13]

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Supporting Information Available: For the crystal structure of **1**, tables of crystal data and structural refinements, anisotropic and isotropic thermal parameters, and full tables of bond distances angles and atomic coordinates (5 pages). An X-ray crystallographic file, in CIF format, is also available. Ordering and access information is given on any current masthead page.

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