Articles

Assembly of Mixed-Metal Cages Using Polyimido Antimony(III) Anions. Syntheses and Structures of $[Sb_3(NCy)_4(HNCy)_2]K{\cdot}2$(toluene), $[Sb_2(NCy)_4]_2M_4$ (M = Cu, Ag), and $[Sb(NCy)_3]_2Pb_3$ (Cy = Cyclohexyl, C_6H_{11})

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Transmetalation reactions of the polyimido Sb(III) anions $[Sb_3(NCy)_4(HNCy)_2]^-$, $[Sb_2(NCy)_4]^{2-}$, and $[Sb(NCy)_3]^{3-}$ with metal sources allows the logical assembly of cage compounds containing various mixed-metal stoichiometries. The breadth of this approach is illustrated by the syntheses of $[Sb(NCy)_4(HNCy)_2]K{\cdot}2$(toluene) (**1**), containing an early main group metal, $[Sb_2(NCy)_4]_2M_4$ (M = Cu (**2**), Ag (**3**)), containing transition metals, and $[Sb(NCy)_3Pb_3]$ (**4**), containing a p-block metal. The low-temperature X-ray structures of complexes **1**−**4** have been determined. Crystal data: **1**, monoclinic, space group *C*2/*c*, $a = 18.418(3)$ Å, $b = 11.457(2)$ Å, $c = 24.798(6)$ Å, $\beta = 90.24(2)°$, $Z = 4$; **3**, triclinic, space group $P\bar{1}$, $a = 11.501(2)$ Å, $b = 13.752(3)$ Å, $c = 22.868(5)$ Å, $\alpha = 103.50(3)°$, $\beta = 95.89(3)°$, $\gamma = 96.71(3)°$, $Z = 2$; **4**, triclinic, space group $P\bar{1}$, $a = 11.071(2)$ Å, $b = 14.892(2)$ Å, $c = 17.262(2)$ Å, $\alpha = 65.36(3)°$, $\beta = 74.21(3)°$, $\gamma = 70.70(3)°$, $Z = 2$. The structure of **2** has been reported in preliminary form. The K^+ ion of **1** is coordinated by four of the N centers of the $[Sb_3(NCy)_4(HNCy)_2]^-$ ligand. In addition, β-C(−H)···K interactions involving four of the Cy groups and MeC(−H)···K interactions involving two toluene molecules give the K^+ ion a 10-coordinate geometry. In **2** and **3**, the N centers of two $[Sb_2(NCy)_4]^{2-}$ dianions symmetrically coordinate a central M_4 square-planar core. The symmetrical complexation of three Pb(II) centers by two $[Sb(NCy)_3]^{3-}$ trianions produces an 11-membered polyhedral cage structure in **4**.

Introduction

We recently showed that highly reactive dimethylamido Sb(III) complexes[1−3] can be employed in the syntheses of a family of polyimido Sb(III) anions.[4] The general synthetic strategy (so called "mixed-metalation") involves the stepwise deprotonation of primary amines (RNH_2), using the Sb reagents to effect the removal of the second proton. Thus, the reaction of the $[Sb(HNCy)_4]^-$ (Cy = C_6H_{11}) anion with $[Sb(NMe_2)_3]$ (1:2 equiv) gives $[Sb_3(NCy)_4(NMe_2)_2]Li$ (containing the monoanion **I**),[4b] the deprotonation of [CyNHLi] with the dimer $[(Me_2N)Sb_2(\mu\text{-}NCy)]_2$ (2:1 equiv) produces $[Sb_2(NCy)_4]_2Li_4$ (containing the dianion **II**),[4a] and the reaction of [CyNHLi] with $[Sb(NMe_2)_3]$ (3:1 equiv) gives $[Sb(LiNCy)_3]_2Li_6$ (containing the trianion **III**).[4b]

The synthesis of $[Sb_2(NCy)_4]_2Cu_4$ (**2**), from the metal exchange reaction of $[Sb_2(NCy)_4]_2Li_4$ with CuCl, illustrated that such polyimido Sb(III) anions can function as robust ligands (not undergoing reduction and/or rearrangement upon ligand transfer) and provided an enticing preliminary indication of the potential coordination chemistry of this new class of ligands.[5] We report here the further investigation of the transmetalation reactions of polyimido anions with a range of metal salts. The rigidity of these ligand systems and their application to the preparation of mixed-metal cages is illustrated by the syntheses and structures of the new cage complexes $[Sb(NCy)_4(HNCy)_2]K{\cdot}2$(toluene) (**1**), containing an early main group metal, $[Sb_2(NCy)_4]_2M_4$ (M = Cu (**2**),[5] Ag (**3**)), containing transition metals, and $[Sb(NCy)_3]_2Pb_3$ (**4**), containing a p-block metal.

Chart 1

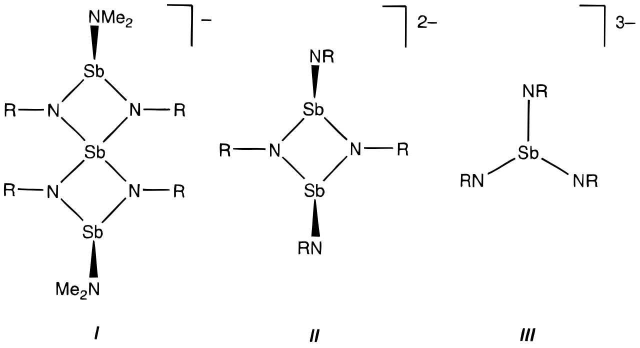

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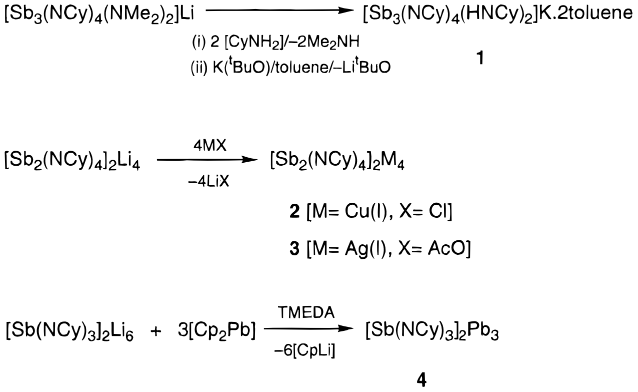
Table 1. Crystal Data for **1**, **3**, and **4**

empirical fomula	$C_{50}H_{84}KN_6Sb_3$ **1**	$C_{52}H_{96}N_8OSb_4Ag_4$ **3**	$C_{43}H_{74}N_6Pb_3Sb_2$ **4**
fw	1173.58	1767.85	1540.15
crystal system	monoclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	18.418(3)	11.501(2)	11.071(2)
b (Å)	11.457(2)	95.89(3)	14.892(3)
c (Å)	24.798(6)	22.868(5)	17.262(3)
α (deg)		103.50(3)	65.36(3)
β (deg)	90.24(2)	95.89(3)	74.21(3)
γ (deg)		96.71(3)	70.70(3)
V (Å^3)	5233(2)	3461.1(1)	2411.3(8)
Z	4	2	2
ρ_{calc} (g cm^{-3})	1.490	2.679	2.121
μ (mm^{-1})	1.655	2.679	11.578
T (°C)	−120(2)	−120(2)	−120(2)
λ (Å)	0.71073	0.71073	0.71073
R indices for $F > 4\sigma(F)^a$	$R_1 = 0.026$, w$R_2 = 0.063$	$R_1 = 0.051$, w$R_2 = 0.174$	$R_1 = 0.091$, w$R_2 = 0.237$
R indices for all data	$R_1 = 0.030$, w$R_2 = 0.066$	$R_1 = 0.079$, w$R_2 = 0.283$	$R_1 = 0.134$, w$R_2 = 0.296$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; w$R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.

Scheme 1



$$[Sb_3(NCy)_4(NMe_2)_2]Li \xrightarrow[\substack{\text{(i) 2 [CyNH}_2\text{]/–2Me}_2\text{NH} \\ \text{(ii) K(}^t\text{BuO)/toluene/–Li}^t\text{BuO}}]{} [Sb_3(NCy)_4(HNCy)_2]K.2toluene \quad \mathbf{1}$$

$$[Sb_2(NCy)_4]_2Li_4 \xrightarrow[-4LiX]{4MX} [Sb_2(NCy)_4]_2M_4$$

2 [M= Cu(I), X= Cl]

3 [M= Ag(I), X= AcO]

$$[Sb(NCy)_3]_2Li_6 + 3[Cp_2Pb] \xrightarrow[-6[CpLi]]{TMEDA} [Sb(NCy)_3]_2Pb_3 \quad \mathbf{4}$$

Table 2. Selected Bond Lengths and Angles for $[(CyNH)_2Sb_3(NCy)_4]K{\cdot}2(toluene)$ (**1**)

Bond Lengths (Å)^b			
Sb(1)−N(3)	2.093(3)	K(1)−N(1)	2.803(4)
Sb(1)−N(2)	2.220(3)	K(1)−N(3)	2.813(3)
Sb(2)−N(1)	2.103(4)	β-C(Cy)−H···K	range 2.77−2.95
Sb(2)−N(2)	2.004(3)	CH_2−H···K	3.05
Sb(2)−N(3)	2.055(3)		

Bond Angles (deg)			
N(3)−Sb(1)−N(2a)	87.9(1)	Sb(2)−N(1)−K(1)	97.8(1)
N(3)−Sb(1)−N(2)	74.4(1)	Sb(2)−N(3)−K(1)	98.7(1)
N(2)−Sb(2)−N(3)	80.0(1)	N(1)−K(1)−N(3)	65.8(1)
N(1)−Sb(1)−N(2)	96.0(1)	N(3)−K(1)−N(3a)^a	69.9(1)
N(1)−Sb(1)−N(3)	94.4(1)	N(1)−K(1)−N(1a)^a	167.1(2)
Sb(1)−N(3)−K(1)	94.6(1)		

[a] Symmetry transformation used to generate equivalent atoms: (a) $-x + 1$, y, $z + {}^3/_2$.

Results and Discussion

The polyimido Sb(III) anions **I**−**III** were prepared in the manner described previously.[4] $[Sb(NCy)_4(HNCy)_2]K{\cdot}2(toluene)$ (**1**) was prepared by the two-step *in situ* reaction of $[Sb_3(NCy)_4(NMe_2)_2]Li$ with $[CyNH_2]$ (1:2 equiv, respectively), resulting in the replacement of the terminal NMe_2 groups for NHCy, followed by metal exchange with $[K^tBuO]$ in toluene as the solvent. $[Sb_2(NCy)_4]_2M_4$ [M = Cu (**2**),[5] Ag (**3**)] were synthesized in good yields (60% for **2** and 52% for **3**) by the transmetalation reactions of $[Sb_2(NCy)_4]_2Li_4$ with CuCl and Ag(AcO) (AcO = $MeCO_2^-$), respectively. These reactions occur rapidly at room temperature in toluene with little or no decomposition into the metals. However, attempts to prepare **3** using AgCl resulted in decomposition into Ag metal. The preparation of **4** was accomplished by the transmetalation reaction of $[Sb(NCy)_3]_2Li_6$ with $[Cp_2Pb]$ (1:3 equiv) in toluene. The reaction requires *ca.* 1 equiv of TMEDA $[(Me_2NCH_2)_2]$ to dissolve the insoluble product initially formed (the complex then being crystallized in 50% yield). (See Scheme 1)

Prior to their investigation by low-temperature X-ray crystallography, complexes **1**−**4** were basically characterized by obtaining their melting points and elemental analyses and by ^1H NMR spectroscopy. All the complexes are surprisingly thermally stable (up to *ca.* 200 °C for **1**). Although satisfactory elemental analyses (C, H, N) were obtained for **1**−**3**, the C content of **4** was found to be consistently slightly high. ^1H NMR studies of all the complexes were not particularly informative due to the broadness of the Cy resonances found in the region δ 0.5−2.5. ^{13}C NMR studies were similarly uninformative for complexes **3** and **4** (particularly for **3**, where its low solubility even in THF led to weak resonances). However, although the $-CH_2-$ groups for the terminal and bridging NCy groups of **1** are not distinct at room temperature, there are two resonances for the α-C(−H) groups for these ligand environments. The ^1H and ^{13}C NMR spectra of **1** also illustrate that the reaction producing **1** involves metal exchange of Li for K rather than producing a co-complex containing $[K^tBuO]$, as occurs in the reaction of $[Sb(NCy)_3]Li_6$ with $[K^tBuO]$.[6]

The low-temperature (−120 °C) X-ray structures of complexes **1**−**4** were obtained. Since the structure of **2** has already been communicated,[5] it will not be appropriate to discuss this complex at length here, except by way of comparison. Details of the structural refinements of complexes **1**, **3**, and **4** are shown in Table 1. Tables 2−4 give selected bond lengths and angles for **1**, **3**, and **4**, respectively.

The low-temperature X-ray structure of **1** shows it to be the heterobimetallic complex $[(CyNH)_2Sb_3(NCy)_4]K{\cdot}2(toluene)$. The $[(CyNH)_2Sb(NCy)_4]^-$ anion and its mode of complexation to the alkali metal cation are similar to those occurring in the precursor $[(Me_2N)_2Sb_3(NCy)_4]Li$ (Figure 1).[4b] Similar to that of the latter, the alkali metal cation of **1** is complexed by two of the μ-NCy groups of the anion [N(3)−K(1) 2.813(3) Å] and by both of the terminal NHCy groups [N(1)−K(1) 2.803(4) Å]. The accommodation of the larger K^+ cation into this framework results in only minor distortions in the N−Sb−N angles in the Sb_3N_6 unit of **1** compared to those in $[(Me_2N)_2Sb_3(NCy)_4]Li$.[4b]

The highly distorted square-based pyramidal geometry of the K^+ ion in **1** (average N−K−N 67.2°) leaves the cation open to

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(6) 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.

Table 3. Selected Bond Lengths and Angles for $[Sb_2(NCy)_4]Ag_4 \cdot THF$ (**3**)

Bond Lengths (Å)			
Sb(1)−N(1)	2.07(1)	Sb(1)−N(4)	2.04(1)
Sb(1)−N(2)	2.07(1)	Sb(2)−N(3)	2.044(9)
Sb(2)−N(1)	2.07(1)	Sb(3)−N(5)	2.94(1)
Sb(2)−N(2)	2.08(1)	Sb(4)−N(6)	2.04(1)
Sb(3)−N(7)	2.07(1)	av Ag···Ag	2.81
Sb(3)−N(8)	2.068(9)	av N(3−6)−Ag	2.154
Sb(4)−N(7)	2.10(1)	av N(1,2,7,8)···Ag	3.158
Sb(4)−N(8)	2.089(9)		

Bond Angles (deg)			
Sb_2N_2 rings		av Ag···Ag···Ag	90.0
av N−Sb−N	77.8	av N−Ag−N	165.4
av Sb−N−Sb	99.2	av Ag−N−Ag	80.7

Table 4. Selected Bond Lengths and Angles for $[Sb(NCy)_3]_2Pb_3$ (**4**)

Bond Lengths (Å)			
Sb(1)−N(1)	2.06(3)	Pb(2)−N(3)	2.41(3)
Sb(1)−N(2)	1.98(3)	Pb(2)−N(4)	2.39(3)
Sb(1)−N(3)	2.05(3)	Pb(2)−N(6)	2.44(2)
Sb(2)−N(4)	2.00(3)	Pb(3)−N(1)	2.36(3)
Sb(2)−N(5)	2.08(3)	Pb(3)−N(2)	2.47(3)
Sb(2)−N(6)	2.06(2)	Pb(3)−N(4)	2.46(3)
Pb(1)−N(1)	2.43(3)	Pb(3)−N(5)	2.45(3)
Pb(1)−N(3)	2.43(3)	av Pb···Pb	3.69
Pb(1)−N(5)	2.36(3)	av Pb···Sb	3.46
Pb(1)−N(6)	2.39(2)		
Pb(2)−N(2)	2.40(2)		

Angles (deg)			
av N−Sb−N	85.7	Pb(μ-N)$_2$Pb rings	
Sb(μ-N)$_2$Pb rings		av Pb−N−Pb	99.6
av Sb−N−Pb	101.6	av N−Pb−N	74.6
av N−Pb−N	70.0		

further coordination. This low coordination number leads to further agostic C(−H)···K$^+$ interactions with four of the β-C−H positions of the $[(CyNH)_2Sb(NCy)_4]^-$ anion (range 2.77−2.95 Å) and with the Me groups of two lattice-bound toluene molecules (*ca.* 3.05 Å) (Figure 1b). Thus, the coordination number of the K$^+$ ion (including these loose interactions) is 10. Arene···K$^+$ π-interactions have been observed in the solid-state structures of a number of metalloorganic derivatives (with typical arene centroid···K distances of 3.18−3.59 Å),[7] and agostic aliphatic C−H···K$^+$ interactions are now a well-established feature in the structures of organopotassium complexes (typically 3.0−3.4 Å).[8] The nature of this bonding is most likely to be electrostatic, rather than covalent.

The low-temperature X-ray structures of **2**[5] and **3** show that both complexes contain central M$_4$ square planar cores (M = Cu (**2**), Ag (**3**)) which are complexed by two $[Sb_2(NCy)_4]^{2-}$ anions (the structure of **3** is shown in Figure 2). In **3**, there is one lattice-bound THF ligand per molecule in the unit cell which is disordered over two sites.

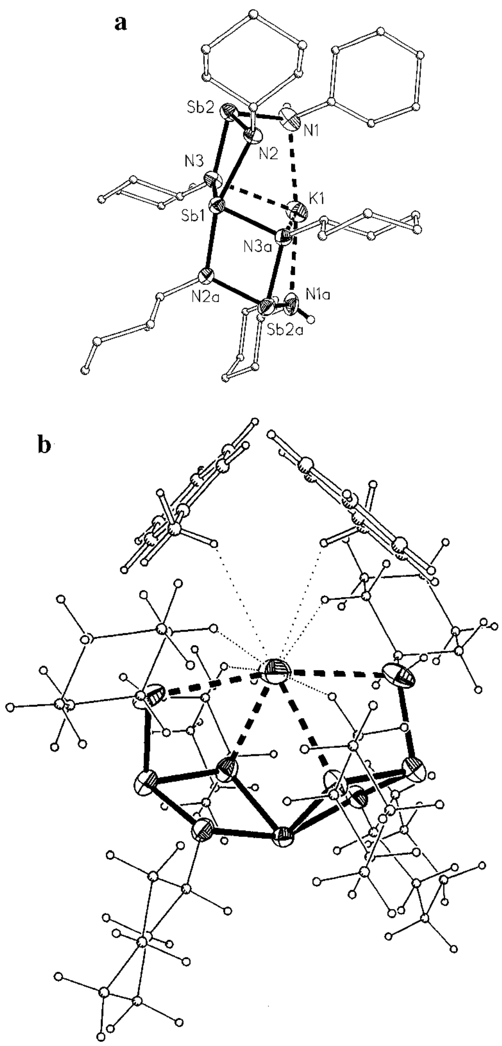

Figure 1. (a) Structure of $[(CyNH)_2Sb_3(NCy)_4]K \cdot 2(toluene)$ (**1**). Toluene molecules are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. (b) Structure of **1** showing agostic C−H···K interactions with β-C−H and toluene CH$_3$ groups. Thermal ellipsoids are drawn at the 50% probability level.

The geometries of the $[Sb_2(NCy)_4]^{2-}$ anions of **2** and **3** are very similar, with the average Sb−N distances in both complexes (2.05−2.08 Å in **2**; cf. 2.07−2.09 Å in **3**) and the angles within the Sb$_2$N$_2$ rings (average Sb−N−Sb 99.6° and average N−Sb−N 78.2° in **2**; cf. average Sb−N−Sb 99.2° and average N−Sb−N 77.8° in **3**) falling in the same range. The Sb−N distances within the $[Sb_2(NCy)_4]^{2-}$ dianions are typical of those found in other amido Sb complexes.[9] The stabilizations of the M$_4$ cores in both complexes are also similar, with the pendant CyN− arms of each of the terminal $[Sb_2(NCy)4]^{2-}$ ligands forming M−(μ-N)−M bridges at opposite edges of the M$_4$ units (average Cu−N 1.93 Å in **2**, average Ag−N 2.15 Å in **3**). Presumably, the M$_4$ fragments in **2** and **3** are largely held together by these M−(μ-N)−M bridges, which result in roughly linear geometries for the Cu or Ag centers in the cores (average N−Cu−N 168.7° in **2**, average N−Ag−N 165.4° in **3**). However, longer range M···(μ-N)···M interactions also occur with the Sb-bridging Cy centers of the $[Sb_2(NCy)_4]^{2-}$ ligands (average Cu···N 2.75 Å in **2** and average Ag···N 3.16 Å in **3**). As a result of these weak interactions, the $[Sb(\mu\text{-}NCy)]_2$ rings of the dianions in both complexes are forced into distinctly puckered conformations so as to bring the μ-N centers of each into closer contact with opposite M···M edges of the M$_4$ core (the μ-N wingtips of the butterfly-shaped Sb$_2$N$_2$ rings are inclined at *ca.* 155.2° in **2**[5] and 151.7° in **3** with respect to Sb···Sb contacts).

The possibility of M···M bonding in the M$_4$ units of **2** and **3** cannot be discounted. The Cu···Cu distances in the core of **2**

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(7) For example, see: (a) Schavevien, C. J.; van Mechelen, J. B. *Organometallics* **1991**, *10*, 1704. (b) Fuentes, G. R.; Coan, P. S.; Streih, W. E.; Caulton, K. G. *Polyhedron* **1991**, *10*, 2371. (c) Geary, M. J.; Cayton, R. H.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Polyhedron* **1992**, *11*, 1369. (d) Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1993**, 554.

(8) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169 and references therein.

(9) Björgvisson, M.; Roesky, H. W.; Pauer, F.; Sheldrick, G. M. *Chem. Ber.* **1992**, *125*, 767. Neubert, W.; Pritzkow, H.; Latscha, H. P. *Angew. Chem.* **1988**, *100*, 298; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 287.

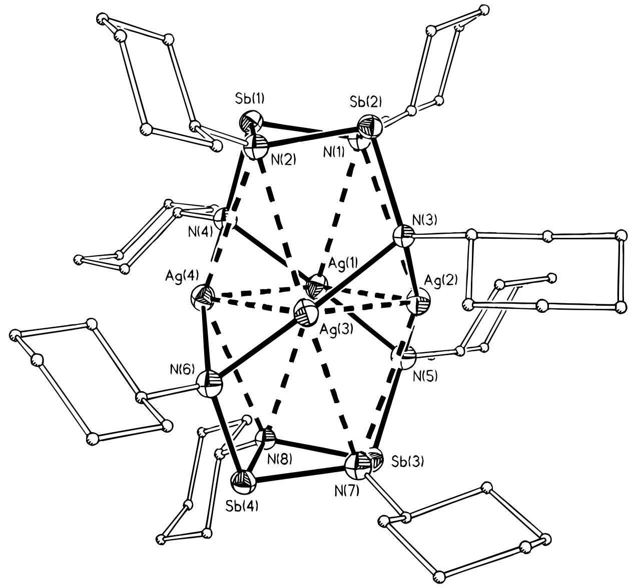

Figure 2. Structure of $[Sb_2(NCy)_4]Ag_4\cdot THF$ (**3**). THF lattice solvation is omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.

(average 2.57 Å),[5] although somewhat longer than those observed in $[CuCH_2SiMe_3]_4$ (2.42 Å),[10] are almost identical to those present in Cu metal (2.56 Å).[11] The Ag···Ag distances in **3** (average 2.81 Å) are similar both to those in Ag metal (2.88 Å)[11] and to those observed in the structures of a number of Ag_4 complexes (*ca.* 3.0−3.1 Å).[12]

A structural motif similar to that observed in **2** and **3** was observed recently in $[C_6H_4O_2(Me_2SiN^tBu)_2]_2M_4$ (M = Cu, Ag), in which two essentially organic dianions stabilize M_4 square planar cores (M = Cu, average Cu···Cu 2.67 Å; M = Ag, average Ag···Ag 3.0 Å).[13] However, whereas in both **2** and **3** the four N donor centers of each $[Sb_2(NCy)_4]^{2-}$ dianion (two pendant CyN, two μ-NCy) bridge all four sides of the M_4 cores, in $[C_6H_4O_2(Me_2SiN^tBu)_2]_2M_4$ the four donor centers of each ligand (two pendant ^tBuN, two O) bridge only two adjacent sides of the M_4 fragments.

The low-temperature X-ray structure of **4** shows that it is an 11-membered polyhedron in which two $[Sb(NCy)_3]$ units symmetrically complex three Pb(II) centers at the equator of the $[Sb_2N_6Pb_3]$ cage (Figure 3). The $[Sb(NCy)_3]$ units of **4** are similar to those found in the cage structure of $[Sb(NCH_2CH_2Ph)_3]_2Li_6\cdot 2THF$[3b] However, although the Sb−N bond lengths are similar to those found in $[Sb(NCH_2CH_2Ph)_3]_2Li_6\cdot 2THF$[3b] (average 2.04 Å in **4**; cf. 2.06 Å), there is a marked reduction in the N−Sb−N angles of **4** (average N−Sb−N 85.7°; cf. average N−Sb−N 94.5°). Each of the N centers of the $[Sb(NCy)_3]$ moieties μ_2-bridge the Pb(II) atoms of the central Pb_3 triangle of **4** (average Pb−N 2.42 Å, average Pb−(μ-N)−Pb 99.6°), resulting in similar square-based pyramidal geometries for all of the Pb centers (average N−Pb−N 74.6°). Presumably as a result of the relatively high coordination number of 4 for the Pb(II) atoms, the Pb−N bonds connecting the $[Sb(NCy)_3]$ and Pb_3 units are slightly longer than those normally found in metalloorganic Pb(II) complexes, e.g., average 2.33 Å in $[Pb(\mu\text{-}N{=}C(^tBu)Ph)_3Li\cdot THF]$,[14] where the Pb(II) atom has a more typical pyramidal, three-coordinate arrangement. This square-based pyramidal geometry is symptomatic of the stereochemical activity of the *exo* lone pairs on the Pb(II) atoms and has precedent in the structures of $[\{X(\overline{\cdot\cdot}NSiMe_3)_2\}_2Pb]$ [X = Ph_2P, $C(\{4\text{-}F_3C\}C_6H_4)$].[15]

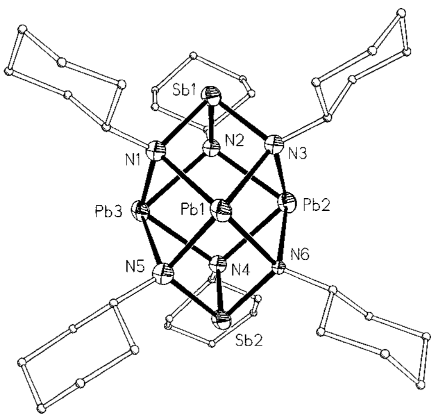

Figure 3. Structure of $[Sb(NCy)_3]_2Pb_3$ (**4**). Thermal ellipsoids are drawn at the 50% probability level.

Clearly the $[Sb_2N_6Pb_3]$ core of **4** is held together by N−Sb and N−Pb bonding, rather than any significant metal···metal interactions (average Pb···Sb 3.46 and average Pb···Pb 3.69 Å; cf. Pb−Pb 3.00−3.24 Å in the trigonal bipyramidal cage $[Pb_5]^{2-}$ [16] and the estimated Pb−Sb covalent bond length of *ca.* 2.80 Å[11]). However, it is nonetheless interesting to note that the trigonal bipyramidal $[Sb_2Pb_3]$ metal fragment of **4** is (conceptually) an $n + 1$ (Wade's rule) polyhedron. To our knowledge, the cage arrangement and (group 14/15 metal) stoichiometry of this complex are unprecedented structural features.

A number of alkali metal complexes containing group 14 imido anions (related to those present in **1**−**4**) have been structurally characterized,[17] and Veith has prepared several mixed-metal compounds using the transmetalation reactions of analogous imido silicon anions with main group metal salts.[18] However, the coordination chemistry of the Sb(III) imido anions has not been investigated until these current studies. The formation of complexes **1**−**4** illustrates the application of polyimido Sb(III) anions in the construction of heterometallic cage compounds containing a variety of mixed-metal stoichiometries. These polyimido anions are robust ligands which do not rearrange upon reaction.

Experimental Section

General Preparative Techniques. All the reactions were undertaken under dry, O_2-free argon using a vacuum line and standard inert-

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atmosphere techniques.[19] THF and toluene were dried by distillation over Na/benzophenone, and hexane was distilled over Na. TMEDA was dried using molecular sieves (13X). The syntheses of the starting materials $[Sb_3(NCy)_4(NMe_2)_2]Li$ (containing the monoanion **I**),[4a] $[Sb_2(NCy)_4]_2Li_4$ (containing the dianion **II**),[4b] and $[Sb(LiNCy)_3]_2Li_6$ (containing the trianion **III**)[4b] were carried out using literature methods. Complexes **1**−**4** were isolated and characterized with the aid of a N_2-filled glovebox (Miller-Howe; fitted with a Belle internal circulation system). Melting points were determined by using a conventional apparatus and sealing samples in capillaries under N_2. Elemental analyses (C, H, N) were performed by first sealing samples in airtight aluminum boats (1−2 mg) prior to analysis using a Perkin-Elmer 240 elemental analyzer. ^1H NMR spectra were recorded on a Bruker WH 250 MHz spectrometer, using the NMR solvents as internal reference standards.

Synthesis of 1. $CyNH_2$ (0.50 g, 5.0 mmol) was added to a solution of $[Sb_3(NCy)_4(NMe_2)_2]Li$ (1.77 g, 2.5 mmol) in toluene (10 mL). The mixture was stirred at 20 °C (0.5 h) before a solution of $K(^tBuO)$ (0.28 g, 2.5 mmol) in toluene (10 mL) was added. Further stirring at 20 °C (0.5 h) gave a cloudy, dark yellow solution. This was filtered (porosity 3, Celite) and reduced to *ca.* 5 mL under vacuum, and hexane (15 mL) was added, giving a yellow precipitate. The precipitate was heated back into solution, and storage at 20 °C (24 h) yielded light yellow crystals of **1**. The toluene solvent found in the solid-state structure of the complex was liberated on isolating the complex and placing it under vacuum (30 min, 0.1 atm). The following data were obtained for the powder produced. Yield: 1.34 g (46%). Dec: 200 °C, finally at 240 °C. ^1H NMR (+25 °C, 250 MHz, benzene-d_6): δ 2.50 (mult), 1.00−2.20 (overlapping mult) (Cy groups); the N−H could not be observed. ^{13}C NMR (+25 °C, 250 MHz, THF-d_8): δ 57.9 (d, C(α)−H, μ-NCy), 54.4 (d) [d, C(α)−H, terminal NCy], 46.0 (t), 43.3 (t), and 40.2 (t) [$-CH_2-$, NCy], 21.4 [q, $-CH_3$, toluene]. Anal. Found: C, 42.8; H, 6.8; N, 8.4. Calcd: C, 43.7; H, 7.1; N, 8.5.

Synthesis of 3. Ag(AcO) (4.0 g, 5.48 mmol) was added to a solution of $[Sb_2(NCy)_4]_2Li_2$ (1.77 g, 1.37 mmol) in THF (20 mL). The mixture was stirred at 20 °C (24 h). Filtration (porosity 3, Celite) removed the decomposition products (principally Ag metal), giving a red-brown solution. Reduction of the filtrate to *ca*. 5 mL under vacuum and addition of hexane (15 mL) gave a precipitate of **3**. Yield: 1.25 g (52%). Dec: 115 °C. ^1H NMR (+25 °C, 250 MHz, benzene-d_6): δ 2.5−1.2 (br overlapping mult, Cy groups), 3.71 (mult), 1.38 (mult) (THF); accurate integration could not be obtained due to the presence of overlapping multiplets in the Cy region. ^{13}C NMR (+25 °C, 250 MHz, THF-d_8): δ 51.9 (d, C(α)−H, NCy), 47.0 (t), 42.2 (t) and 37.0 (t) [$-CH_2-$, NCy]. Anal. Found: C, 35.4; H, 5.6; N, 6.0. Calcd: C, 35.3; H, 5.4; N, 6.3. The elemental analysis confirms that the THF lattice solvation is retained upon isolation of **3**. Crystals suitable for X-ray diffraction were grown from THF solution

Synthesis of 4. $[Sb(NCy)_3]_2Li_6$ (0.712 g, 2.0 mmol) and $[Cp_2Pb]$[20] (1.01 g, 3.0 mmol) were dissolved in toluene (20 mL), giving a yellow precipitate. The mixture was heated to reflux, and TMEDA ($\{Me_2NCH_2\}_2$) was added dropwise until almost all of the solid had dissolved (*ca.* 1 mL). The solution was filtered while hot (porosity 3, Celite) and the filtrate reduced under vacuum to *ca.* 10 mL, producing a yellow powder. The solid was heated into solution, and storage at 20 °C (2 days) gave large yellow cubic crystals of **4**. Yield: 0.72 g (50%). Dec: 195−200 °C. ^1H NMR (+25 °C, 250 MHz, benzene-d_6): δ 1.5−2.5 (br overlapping mult, Cy groups). ^{13}C NMR (+25 °C, 250 MHz, benzene-d_6): δ 51.4 (s) [C(α)−H, NCy], 46.2 (t), 42.1 (t), and 38.0 (t) [$-CH_2-$, NCy]. Anal. Found: C, 31.7; H, 4.5; N, 5.6. Calcd: C, 30.0; H, 4.2; N, 5.8.

X-ray Structure Determinations. Crystals were mounted directly from solution under argon using a perfluorocarbon oil, which protected them from atmospheric O_2 and moisture.[21] The oil froze at reduced temperatures and held the crystal static in the X-ray beam. Data were collected on a Stoe-Siemens AED four-circle diffractometer, and semiempirical absorption corrections based on ψ scans were employed for all complexes.[22] For **1**, distance and isotropic thermal parameter restraints were employed for the disordered toluene molecules. All the C atoms of the toluene were refined isotropically, with all other non-hydrogen atoms being refined anistropically. For **3**, distance restraints were employed for the disordered lattice-bound THF molecule (disordered over two sites with 50% occupancy in each), with only the Ag and Sb atoms being refined anisotropically. For **4**, all non-hydrogen atoms were refined anisotropically. For all complexes, the H atoms were fixed geometrically. All structures were solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares calculations on F^2 (SHELXL-93[23]). Details of the structure refinements for all complexes are shown in Table 1. Atom coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallography Data Centre.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **1**, **3**, and **4** are available on the Internet only. Access information is given on any current masthead page.

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(20) *Health and safety warning*: Great care should be exercised in the disposal of the black residue formed after sublimation of $[Cp_2Pb]$ for a prolonged period. Sudden exposure can lead to a *very* violent exothermic reaction followed by explosion (do not attempt to fight initial fire). Never add concentrated acids.

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