collisional activation can provide an entirely instrumental method for determining double bond location in long-chain fatty alcohols. The limitation of the approach is sensitivity: 30 μg of lithiated oleyl alcohol can be identified from its CAD spectrum with the most abundant fragment ion at a S/N of 4. (This contrasts with a 10-ng detection limit for analogous cationized oleic acid.[16]) Cis and trans isomers cannot be distinguished, and this is also true for the CAD of fatty acid carboxylates.[2a] Although the location of double bonds in polyunsaturated homoconjugated fatty alcohols is complicated by competitive fragmentation and cationization of the double bond(s), the structurally informative remote decompositions are expected to predominate even with increasing unsaturation.

The combination of FAB to produce lithiated alcohols and MS–MS to give CAD is also expected to be useful for determining other structural features of long-chain fatty alcohols such as branch points and other functional groups. This is under investigation.

Acknowledgment. We are grateful to Kenneth B. Tomer for helpful suggestions. This work was supported by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE-8211164), and by the National Science Foundation (Grant No. CHE-8320388).

Registry No. Na^+, 17341-25-2; K^+, 24203-36-9; Rb^+, 22537-38-8; Li^+, 17341-24-1; $H_3C(CH_2)_7(CD_2)_2(CH_2)_6OH$, 104373-47-9; $H_3C(CH_2)_7(CD_2)_2(CH_2)_5CO_2H$, 75736-49-1; (*Z*)-$H_3C(CH_2)_7CH{=}CH(CH_2)_7CD_2OH$, 104373-46-8; (*Z*)-$H_3C(CH_2)_7CH{=}CH(CH_2)_7CO_2H$, 112-80-1; (*E*,*E*)-$H_3C(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_8OH$, 20063-91-6; (*Z*)-$H_3C(CH_2)_7CH{=}CH(CH_2)_8OH$, 143-28-2; (*Z*,*Z*)-$H_3C(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_8OH$, 506-43-4; (*Z*,*Z*,*Z*)-$H_3C(CH_2CH{=}CH)_3(CH_2)_8OH$, 506-44-5.

Isolation and Structural Characterization of the Solvated Lithium Salts of the Main Group 5 Anions $[EPh_2]^-$ (E = N, P, As, or Sb) and $[Sb_3Ph_4]^-$

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Abstract: The X-ray crystal structures of five novel complexes of the general formula $Li(solvate)_nEPh_2$ (E = N, As, or Sb and solvate = Et_2O, THF, 1,4-dioxane, or 12-crown-4) are described and discussed in conjunction with their previously published phosphorus analogues. The five new complexes are $[Li(12\text{-crown-}4)NPh_2]$ (**1**), $[Li(1,4\text{-dioxane})_3AsPh_2]$ (**2**), $[\{Li(Et_2O)_2AsPh_2\}_2]$ (**3**), the ion pairs $[Li(12\text{-crown-}4)_2][SbPh_2]\cdot{}^1/_3THF$ (**4**), and $[Li(12\text{-crown-}4)_2][Sb_3Ph_4]\cdot THF$ (**5**). The structures are indicative of, inter alia, the anomalous characteristics of As relative to P or Sb and the unique planar nature of the nitrogen derivative relative to the heavier pyramidal analogues. The complexes **2–5** are also the first reports of structurally characterized lithium diorganoarsenides and -stibinides. The complexes **4** and **5** are the first examples of a structurally characterized two-coordinate antimony species. Crystal data at 130 K with Mo Kα (λ = 0.71069 Å) for **1**, **3**, **4**, and **5** and Cu Kα (λ = 1.54178 Å) for **2** radiation are as follows: **1**, $C_{20}H_{26}LiNO_4$, M = 351.38, monoclinic, $C2/c$, a = 23.271 (9) Å, b = 13.641 (3) Å, c = 21.375 (7) Å, β = 124.77 (2)°, R = 0.043, 353 parameters, 3264 unique observed data; **2**, $C_{24}H_{34}AsLiO_6$, M = 500.4, monoclinic, $P2_1/c$, a = 15.570 (1) Å, b = 9.354 (1) Å, c = 17.334 (1) Å, β = 102.14 (1)°, R = 0.063, 280 parameters, 3336 unique observed data; **3**, $C_{40}H_{60}As_2Li_2O_4$, M = 768.6, monoclinic, $C2/c$, a = 13.804 (4) Å, b = 15.777 (5) Å, c = 19.967 (4) Å, β = 95.62 (2)°, R = 0.056, 218 parameters, 2202 unique observed data; **4**, $C_{28}H_{42}LiO_8Sb$, M = 659.37, triclinic, $P\bar{1}$, a = 12.660 (6) Å, b = 17.349 (11) Å, c = 23.761 (19) Å, α = 75.79 (6)°, β = 89.27 (5)°, γ = 68.37 (4)°, R = 0.092, 558 parameters, 8419 unique observed data; **5**, $C_{44}H_{60}O_9LiSb_3$, M = 1105.1, monoclinic, $C2/c$, a = 16.240 (4) Å; b = 19.162 (4) Å, c = 16.863 (4) Å, β = 118.38 (2)°, R = 0.056, 158 parameters, 2448 unique observed data.

Lithium diorganoamides[3] and phosphides[4] have been widely used as reagents in organic chemistry and as ligand-transfer agents in inorganic and organometallic chemistry. The corresponding arsenic and antimony complexes have received much less attention probably because of a more restricted interest, decreased stability, and less ready availability of starting materials.[5] Also it has often been thought that the physical and chemical properties of heavier main group elements vary in a consistent manner going down a group. However, there is now a fairly large body of data which shows that there are significant periodic anomalies in the heavier main group elements. The unexpected behavior has been partly rationalized[6] on the basis of an increased effective nuclear charge as a consequence of the filling of the first d (i.e., 3d) sublevel. Thus, elements such as Ge, As, Se, and Br display interesting differences from their other group members which are not expected on the basis of interpolation. The simplest example of this lies

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in the electronegativity values of Ge, As, and Te which are, on the average, greater than the values for Si, P, and S. Many structural parameters of the title compounds (see later in Table II) also support these views.

Recently others[7,8] and this group[8-10] have been involved in the determination of the structures of a number of different lithium diorganophosphido complexes. These studies show that such complexes can adopt a variety of structures depending on the size of the organic substituent and the type of ether solvent. In this paper we report the extension of these studies to other main group 5 elements and show that there are considerable and important differences in their structures.

We have examined a total of five new complexes. Some of their salient features are (i) the first X-ray structural characterization of two-coordinate antimony, (ii) the first structural report of lithium diorganoarsenides[7,11] including the demonstration of a pyramidal arsenic in a metal derivative, (iii) the disproportionation product, $[Sb_3Ph_4]^-$, from the reaction of lithium with triphenylstibine, and (iv) structural confirmation that a simple monomeric lithium diorganoamide is planar at nitrogen, whereas the lithium phosphides and arsenides are pyramidal.

Prior work in this area has involved the publication of the structures $[\{Li_2(\mu_3\text{-}P(t\text{-}Bu)_2)(\mu_2\text{-}P(t\text{-}Bu)_2)THF\}_2]$,[7] $[\{LiP(CH(SiMe_3)_2)_2\}_2]$,[8] $[Li(12\text{-crown-}4)_2][EPh_2]$ (E = P or As),[9] $[\{Li(Et_2O)\text{-}\mu\text{-}PPh_2\}_\infty]$,[10] $[\{Li(THF)_2\text{-}\mu\text{-}PPh_2\}_\infty]$,[10] and $[\{Li(THF)\text{-}\mu\text{-}P(C_6H_{11})_2\}_\infty]$.[10] The structure of THF-solvated $LiP(SiMe_3)_2$ has also been determined. Depending on the quantity of THF, it can adopt either the dimeric $[\{Li(THF)_2P(SiMe_3)_2\}_2]$ or tetranuclear $[\{Li_2(\mu_3\text{-}P(SiMe_3)_2)(\mu_2\text{-}P(SiMe_3)_2)THF\}_2]$ structures.[11] For arsenic the only reported structures involve $[\{Na(1,4\text{-dioxane})AsPh_2\}_\infty]$ (a three-dimensional polymer)[12] and the dimeric silylated species $[\{Li(THF)_2\text{-}\mu\text{-}As(SiMe_3)_2\}_2]$.[13] See also ref 7 and 11 for unpublished work concerning relevant lithium arsenides $[(Li\text{-}\mu\text{-}As\{CH(SiMe_3)_2\}_2)_3]$[11] and $[\{Li(THF)As(t\text{-}Bu)As(t\text{-}Bu)_2\}_2]$.[7] The latter has Li–As and As–C distances very similar to those found in **2** and **3**. For antimony, the silylated complex $[\{Li(DME)\text{-}\mu\text{-}Sb(SiMe_3)_2\}_\infty]$, having a polymer chain structure, has been characterized[14] as has its bismuth analogue.[15] Somewhat more work has been published for alkali-metal diorganoamides (about 12 structures, see ref 16 for recent examples). However, compound **1**, $[Li(12\text{-crown-}4)NPh_2]$, and $[Li(12\text{-crown-}4)N(SiMe_3)_2]$,[17] **6**, are the only reports of simple mononuclear lithium diorganoamides.[11]

Experimental Section

General Procedures. All reactions were performed by using either modified Schlenk techniques (under N_2) or a Vacuum Atmospheres HE43-2 drybox (under argon). Solvents were freshly distilled from Na/K alloy–benzophenone ketyl and degassed twice immediately before use. 12-Crown-4 (Aldrich) was purified by distillation off molten sodium under partial vacuum. Solutions of the solvate complexes are extremely air sensitive (and temperature sensitive in the case of the antimony derivatives) and immediately decompose on exposure to moisture or O_2. Solutions of $LiEPh_2$ (E = P, As, or Sb) were prepared by a modification (*n*-BuLi instead of PhLi) of a procedure described by Issleib.[18] $SbPh_3$ (Alfa) was used as purchased. $SbClPh_2$[19] and $SbHPh_2$[20] were prepared by literature procedures.

$[Li(12\text{-crown-}4)NPh_2]$ (1). Diphenylamine ($NHPh_2$, 0.85 g, 5 mmol) in Et_2O (25 mL) was treated dropwise with *n*-BuLi (3 mL of a 1.6 M solution) in hexane. The pale-amber solution became slightly darker. After stirring for 1 h, 12-crown-4 (1.8 g, 10 mmol) in THF (5 mL) was added dropwise, producing a slightly lighter color and faint cloudiness. The volume was reduced in vacuo to ca. 15 mL and filtered, giving a pale-amber solution. Slow cooling to −20 °C gave colorless crystals of the product **1**. The yield (not optimized) was 0.62 g, 35%, mp 112–114 °C.

$[Li(1,4\text{-dioxane})_3AsPh_2]$ (2) and $[\{Li(Et_2O)_2AsPh_2\}_2]$ (3). An ether solution (20 mL) of $AsHPh_2$ (1.15 g, 5 mmol) was treated dropwise with *n*-BuLi (3.1 mL of 1.6 M hexane solution). The yellow solution was reduced in vacuo to dryness, giving a yellow solid in quantitative yield. This was redissolved in dioxane (2 mL) to give an orange–yellow solution, followed by slow addition of a 1:1 Et_2O/*n*-hexane mixture until a faint cloudiness was produced. Filtration and slow cooling gave yellow crystals of **2**. Similar reduction of the volume of the initial $LiAsPh_2$ ether solution to incipient crystallization followed by slow cooling gave orange–yellow crystals of **3**.

$[Li(12\text{-crown-}4)_2][SbPh_2]\cdot{}^1/_3THF$ (4). The synthesis of this compound was similar to that described for its phosphorus and arsenic analogues in a preliminary communication.[9] A solution of $SbHPh_2$ (2.14 g, 7.7 mmol) in Et_2O (50 mL), cooled in a dry ice/acetone bath, was treated dropwise with *n*-BuLi (4.9 mL of a 1.6 M solution in hexane). The orange–red solution was allowed to warm to 0 °C, and 12-crown-4 (2.5 mL) was added by syringe. The resulting orange precipitate (>90% yield) was dissolved in a minimum of THF at room temperature and filtered. Slow cooling to −20 °C gave the product **4** as dark-red crystals (2.9 g, 59%). These crystals soften around 90 °C and completely melt at 110–113 °C, giving a red liquid.

$[Li(12\text{-crown-}4)_2][Sb_3Ph_4]\cdot THF$ (5). $SbPh_3$ (1.6 g, 4.5 mmol) and Li powder (0.064 g, 9 mmol) were placed in a flask and THF (75 mL) added at 0 °C. The mixture was stirred at room temperature for 15 h, giving a dark-red solution together with a dark-grey, almost black, precipitate. Filtration and the addition of 12-crown-4 (2 mL) followed by reduction of the volume to ca. 15 mL and cooling to −20 °C gave product **5** as orange–red crystals, yields 0.14 g, 9%.

X-ray Data Collection, Solutions, and Refinement of the Structures 1–5. The general procedure for X-ray data collection was the same for all structures. The diffractometer used was a Syntex $P2_1$ equipped with a modified LT-1 apparatus for low-temperature work. Crystallographic programs used were those of SHELXTL, version 4, installed on a Data General Eclipse computer. Scattering factors were from Vol. IV of ref 21. An absorption correction[22] was applied except for compound **1**. Since all these crystals tend to decompose upon handling in the air, they were coated with a hydrocarbon oil immediately after they were removed from the Schlenk tube and mounted on a glass fiber using silicone grease. Subsequent cooling to 130 K prevented further decomposition. In the case of compound **3**, cooling below 215 K resulted in cracking; thus, this data set was collected at 235 K. Table I summarizes the experimental details for each compound. Additional details are given below.

$[Li(12\text{-crown-}4)NPh_2]$, 1. The structure was solved by direct methods. All non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms were included by using a riding model with C–H of 0.96 Å and $U_{iso}(H) = 1.2U^*_{iso}(C)$, where U^*_{iso} is the equivalent isotropic thermal parameter. There was no evidence for disorder in the crown ether in this structure.

$[Li(1,4\text{-dioxane})_3AsPh_2]$, 2. The structure was solved by a combination of direct and Patterson methods. One of the dioxane molecules was disordered, with refined weights for O(5), O(6), and C(21)–C(24) of 58% (1) and for O(7), O(6), and C(25)–C(28) of 42% (1). The largest peaks

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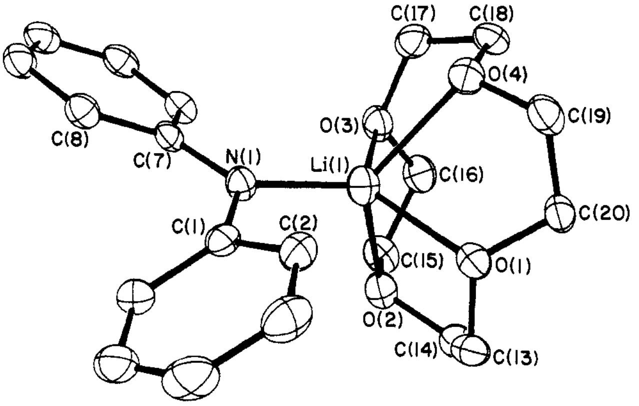

Figure 1. Computer-generated thermal ellipsoid plot of [Li(12-crown-4)NPh_2] (**1**).

on the final difference map were two ca. 1 Å from As, followed by several that were clearly due to H of the disordered dioxane. All of these were less than 0.85 e $Å^{-3}$. Refinement was carried out by using anisotropic thermal parameters for non-hydrogen atoms, except for the disordered dioxane. Hydrogen atoms were included using the riding model described for **1** except for those of the disordered dioxane.

[{Li(Et_2O)$_2$$AsPh_2$}$_2$], 3. The structure was solved by direct methods. Both molecules of diethyl ether have very large thermal parameters (equivalent isotropic *U*'s average 0.21 $Å^2$ for the carbon atoms and 0.089 $Å^2$ for the oxygen atoms; the average for the remaining atoms is 0.074 $Å^2$). There is a possibility that this is due to less than full occupancy for the ether groups. The crystals melt near room temperature and crack below 215 K. Therefore, the diffraction data were collected at 235 K, and although the crystals were handled while cold, some loss of ether could have occurred. Alternatively, the large thermal motion could be real. Refinement was carried out with anisotropic thermal parameters for the non-hydrogen atoms and hydrogen atoms riding on the bonded phenyl carbon atoms as in structure **1**.

[Li(12-crown-4)$_2$][$SbPh_2$]·$^1/_3$THF, 4. A suitable crystal of this material was obtained with great difficulty, as they tend to grow as thin plates, are frequently twinned, and readily crack. The data were collected by using the "no background" method,[23] in which the intensity and background measurements are made at separate times. The structure was solved by locating the three Sb atoms from examination of the Patterson map. The three dissimilar $SbPh_2$ groups are in general positions and suffer no disorder. Li(1) and Li(3) are at general positions, and their Li(12-crown-4)$_2$ groups are well-behaved. However, Li(2) and Li(4) are on centers of inversion, and their corresponding crown ethers suffer a statistical disorder in the positions of most of the atoms. This is described in more detail in the supplementary material. The fairly large final *R* value (0.084) and number of rejected reflections (42% of the unique set had $I < 3\sigma(I)$) in this determination stem primarily from the disordered crown ethers. In addition, the final difference map shows four residuals of ca. 2–2.5 e $Å^{-3}$ in close proximity to the Sb atoms. We believe these are due to a failure to fully correct for absorption of these very thin plates. However, the determination of the geometry of the $SbPh_2^-$ is not adversely affected by these problems. Hydrogen atoms were not included in the refinement or in the structure factor calculation. Only the antimony atoms were assigned anisotropic thermal parameters. Four low angle reflections which appeared to be affected by extinction were omitted from the final cycles of refinement.

[Li(12-crown-4)$_2$][Sb_3Ph_4]·THF, 5. The structure was solved by Patterson methods. The central antimony is on a 2-fold axis and the lithium on a center of inversion. The crown ether is disordered between two sets of oxygen positions. Three of the eight carbons are common to both rings; the rest are disordered. The $Sb_3Ph_4^-$ species is well-behaved, and since most of the hydrogens appeared on a difference map, the phenyl hydrogens were included at calculated positions using the riding model. The antimony atoms were refined by using anisotropic thermal parameters.

Results and Discussion

The structures of compounds **1–5** are illustrated in Figures 1–5. Important bond lengths and angles are given in Table II. Full tables of bond distances and angles are given in the supplementary material. For comparison selected data on [Li(12-crown-4)N-

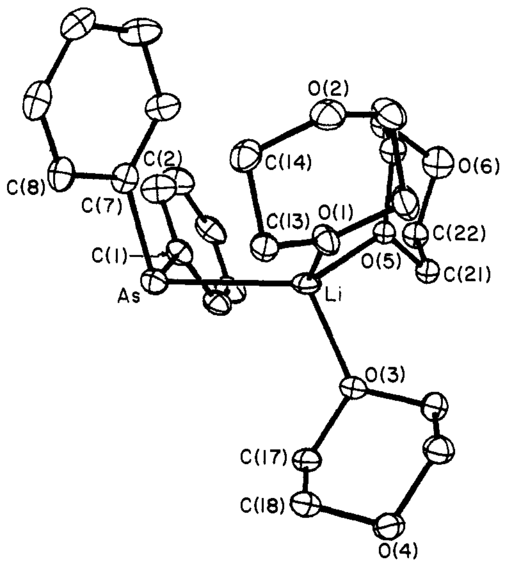

Figure 2. Computer-generated drawing of [Li(1,4-dioxane)$_3$$AsPh_2$] (**2**), illustrating pyramidal nature of arsenic.

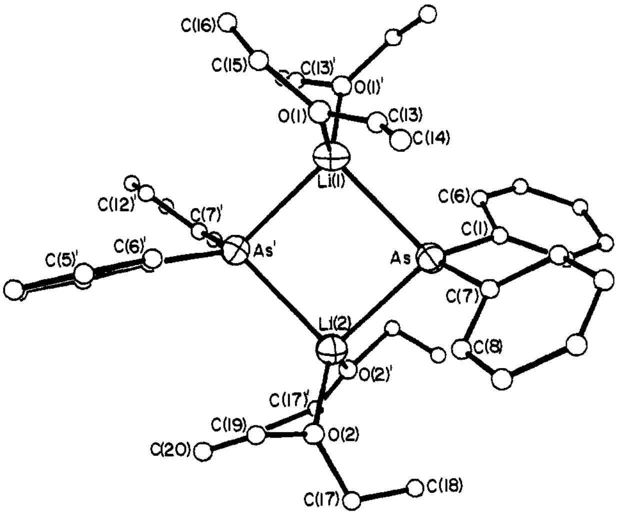

Figure 3. Computer-generated drawing of [{Li(Et_2O)$_2$$AsPh_2$}$_2$] (**3**).

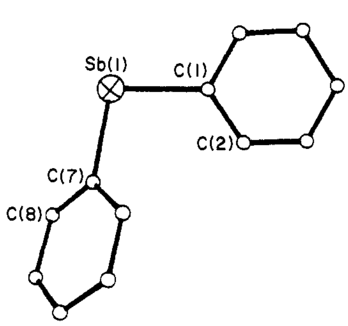

Figure 4. Computer-generated drawing of an anion [$SbPh_2$]$^-$ of **4**.

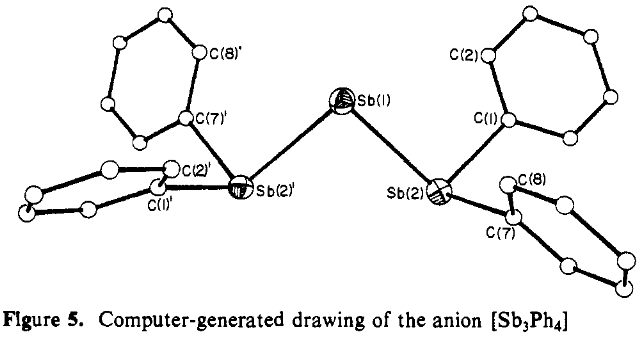

Figure 5. Computer-generated drawing of the anion [Sb_3Ph_4]

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Table I. Crystal Data and Summary of Data Collection and Refinement

	1	2	3	4	5
formula	$C_{20}H_{26}LiNO_4$	$C_{24}H_{34}O_6AsLi$	$C_{40}H_{60}O_4As_2Li_2$	$C_{28}H_{42}LiO_8Sb.{}^1/{}_3C_4H_8O$	$C_{44}H_{60}O_9LiSb_3$
fw	351.38	500.40	768.6	659.37	1105.1
crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$C2/c$	$P2_1/c$	$C2/c$	$P\bar{1}$	$C2/c$
conditions	hkl, $h + k = 2n$; $h0l$, $l = 2n$	$0k0$, $k = 2n$; $h0l$, $l = 2n$	hkl, $h + k = 2n$; $h0l$, $l = 2n$	none	hkl, $h + k = 2n$; $h0l$, $l = 2n$
crystal dims, mm	0.15 × 0.12 × 0.05	0.2 × 0.15 × 0.08	0.25 × 0.2 × 0.15	0.3 × 0.65 × 0.08	0.13 × 0.32 × 1.35
crystal color and habit	colorless plates	orange–yellow parallelepipeds	yellow parallelepipeds	red plates	orange needles
temp, K	130	130	235	130	130
a, Å	23.271 (9)	15.570 (3)	13.804 (4)	12.660 (6)	16.240 (4)
b, Å	13.641 (3)	9.354 (2)	15.777 (5)	17.349 (11)	19.162 (4)
c, Å	21.375 (7)	17.334 (4)	19.967 (4)	23.761 (19)	16.863 (4)
α, deg				75.79 (6)	
β, deg	124.77 (2)	102.14 (1)	95.62 (2)	89.27 (5)	118.38 (2)
γ, deg				68.37 (4)	
Z	12	4	4 (dimers)	6	4
V, Å^3	5574	2468	4328	4685	4617
d_{calcd}, g/cm^3	1.26	1.35	1.18	1.40	1.59
radn	Mo Kα, λ = 0.71069 Å	Cu Kα, λ = 1.54178 Å	Mo Kα, λ = 0.71069 Å	Mo Kα, λ = 0.71069 Å	Mo Kα, λ = 0.71069 Å
linear abs coeff, cm^{-1}	0.7	21.4	15.7	9.3	18.0
scan speed, deg min^{-1}	20	15	5–60	8	30
scan width, deg	1.0	1.0	1.0	1.3	1.2
max 2θ, deg	50	139	47	48	50
type of scan	ω	ω	ω	ω	ω
w offset for bkgd, deg	±1.0	±1.0	±1.0	(no bkgd method)	±1.0
range of abs factors	1.00–1.01	1.15–1.36	1.22–1.53	1.07–1.23	1.21–1.69
octants	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$h,\pm k,\pm l$	$+h,+k,\pm l$
no. of variables	353	280	218	558	158
data/variable ratio	9.2	11.9	10.1	15.1	15.5
no. of check refl.	2 (decay 8%)	2 (no decay)	2 (no decay)	2 (no decay)	2 (no decay)
no. of refl. colled	4792	4886	3493	14628	3986
R (merge)	0.013	0.024	0.023		0.019
no. of unique data	4590	4530	3207	14628	2507
no. of data used in rfmt	3264 ($I > 3\sigma(I)$)	3336 ($I > 2.5\sigma(I)$)	2202 ($I > 3\sigma(I)$)	8419 ($I > 3\sigma(I)$)	2448 ($I > 3\sigma(I)$)
$R(F)$	0.043	0.063	0.053	0.084	0.056
$R_w(F)$	0.047	0.073	0.056	0.092	0.062
weighting scheme	$[\sigma^2(F_o) + 0.00012F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.0021F_o^2]^{-1}$	$[\sigma^2(F_o)]^{-1}$	$[\sigma^2(F_o)]^{-1}$	$[\sigma^2(F_o)]^{-1}$
largest Δ/σ	0.17 for z of C(10)	0.015 for z of C(28)	0.015 for y of As	0.094 for y of C(87)	0.025 for x of C(23)
largest feature final diff map, e Å^{-3}	0.16	0.83, 1.2 Å from As	0.70, 0.89 Å from C(19)	2.5, 0.02 Å from Sb	1.26 near Sb and ca. 1 in vicinity disordered crown

$(SiMe_3)_2]^{17}$ (6), $[\{Li(THF)_2\text{-}\mu\text{-}PPh_2\}_\infty]^{10}$ (7), $[\{Li(Et_2O)\text{-}\mu\text{-}PPh_2\}_\infty]^{10}$ (**8**), $[Li(12\text{-crown-}4)_2][PPh_2]^9$ (**9**), and $[Li(12\text{-crown-}4)_2][AsPh_2]\cdot THF^9$ (**10**) are also included. The figures illustrate several important features of interest in the structures. These are as follows: (i) Even though 12-crown-4 is effective at achieving anion–cation separation for the heavier element compounds, it is unable to do so in the two amido compounds **1** and 6. (ii) The central CEC angles (E = P, As, or Sb) in **4**, **9**, and **10** illustrate the irregularity of arsenic within the main group 5 elements. (iii) The pyramidal nature of arsenic in the monomeric complex **2** is in sharp contrast to the planar nitrogen in **1** and 6 and indeed most metal amide complexes.[3] (iv) Complexes **4** and **5** are the first structurally characterized examples of two-coordinate antimony.[24] (v) Complexes **2** and **3** are the first structural reports of lithium diorganoarsenides.[7,11] (vi) The unexpected appearance of the anion in **5** is from the treatment of $SbPh_3$ with lithium powder.

Several generalizations may also be made by inspection of the structural details given in Table II. All of the E–C distances are within the expected range of values for the respective elements. Also the Li–E values in compounds **1**–**3** are close to those expected on the basis of the sum of the atomic radii and close to those seen in the silylated complex $[\{Li(THF)_2\text{-}\mu\text{-}As(SiMe_3)_2\}_2]$.[13] There is an expected slight lengthening of the Li–As distance in **3** compared to **2** due its bridging nature. The Li–O distances are closely related to the coordination number (four, five, or eight) of the Li^+ ion and are in agreement with the extrapolated values from tables of Shannon–Prewitt radii.[25]

The structures of several of the new complexes merit specific mention. For example, the lithium amide $[Li(12\text{-crown-}4)NPh_2]$ (**1**) may be compared to the structures of 6 and also the complex $[Li(12\text{-crown-}4)_2][CHPh_2]^{26}$ due to the isoelectronic relationship of $[NPh_2]^-$ and $[CHPh_2]^-$. Our intention upon the addition of 12-crown-4 to an ether solution of $LiNPh_2$ was to crystallize a compound having the free ion $[NPh_2]^-$ in the lattice. This interesting moiety has not yet been reported. We think our failure in this regard is due to the considerable strength of the Li–N bond compared to the corresponding Li–C species. The gain in lattice energy on crystallizing a material with separate ions is presumably not sufficient to compensate for Li–N bond rupture. Both compounds **1** and 6 are in fact the only published examples (but see ref 11) of monomeric solvated lithium amides. The most important structural feature is that both **1** and 6 have planar geometry at the nitrogens, in common with other metal amides.[3] In view of the fact that lithium is five coordinate, the Li–N bond lengths,

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Table II. Summary of Important Bond Lengths (Å) and Angles (deg) in Compounds **1–10**

complex	C–E–C	Li–E–C	dihedral between Ph	E–C	E–Li	Li–O
$[Li(12\text{-crown-}4)NPh_2]^a$ (**1**)	118.3 (2) 119.6 (2)	119.5 (1) 120.2 (1)	50 55	1.384 (2) 1.394 (2) 1.387 (2)	2.007 (5) 2.047 (5)	2.227 (5) 2.242 (4) 2.169 (3) 2.169 (3) 2.160 (5)
$[Li(12\text{-crown-}4)N(SiMe_3)_2]^b$ (**6**)	123.5 (1)	117.3 (2) 119.0 (1)		1.681 (2)	1.965 (4)	2.094 (4) 2.107 (4) 2.393 (4) 2.332 (4)
$[Li(1,4\text{-dioxane})_3AsPh_2]^a$ (**2**)	102.2 (2)	92.0 (3) 97.9 (2)	45	1.959 (6) 1.962 (6)	2.660 (10)	1.953 (9) 1.931 (10) 1.937 (12) 1.968 (14)
$[\{Li(Et_2O)_2AsPh_2\}_2]^{a,c}$ (**3**)	102.4 (2)	116.12 (av)	48	1.935 (5) 1.955 (6)	2.708 (9) 2.757 (9)	1.974 (8) 1.997 (8)
$[\{Li(THF)_2PPh_2\}_\infty]^{d,e}$ (**7**)	102.8 (5)	95.9 (6) 95.4 (6) 108.2 (5) 114.6 (6)	52	1.842 (12) 1.862 (11)	2.629 (22) 2.634 (21)	1.937 (22) 1.988 (22)
$[\{Li(Et_2O)PPh_2\}_\infty]^{d,f}$ (**8**)	103.3 (3) 104.7 (2)		59.8 52.8	1.828 (5) 1.829 (5) 1.838 (6) 1.836 (5)	2.496 (10) 2.486 (10) 2.492 (10) 2.483 (10)	1.925 (10) 1.966 (11)
$[Li(12\text{-crown-}4)_2][PPh_2]^{d,g}$ (**9**)	105.2 (2)		43	1.811 (4) 1.804 (4)		2.383 (av)
$[Li(12\text{-crown-}4)_2][AsPh_2]\cdot THF^g$ (**10**)	108.6 (2)		11	1.972 (5) 1.972 (5)		2.368 (av)
$[Li(12\text{-crown-}4)_2][SbPh_2]\cdot {}^1/_3THF^a$ (**4**)	96.8 (4) 97.6 (4) 102.4 (4)		39 52 49	2.154 (9) 2.168 (13) 2.157 (10) 2.173 (12) 2.129 (12) 2.157 (13)		2.37 (av)
$[Li(12\text{-crown-}4)_2][Sb_3Ph_4]\cdot THF^{a,h}$ (**5**)	92.7 (4)		82	2.166 (11) 2.190 (12)		2.38 (av)

[a] This work. [b] Reference 17 (the distances and angles for carbon refer to silicon in this case). [c] LiAsLi = 88.3 (4), 90.7 (3), AsLiAs = 90.3 (4) Å. [d] Reference 10. [e] PLiP = 145.6 (3), LiPLi =119.7 (2) Å. [f] PLiP = 129.6 (4), 139.6 (4), LiPLi = 136.9 (3), 126.0 (3) Å. [g] Reference 9. [h] SbSbSb = 88.8 (1) Å, Sb–Sb = 2.761 (1)°.

2.007 (5) and 2.047 (5) Å,[3,6] may be considered to be somewhat short and therefore strong. This is also in agreement with the difficulty in removing the Li^+ ion by 12-crown-4.

It is interesting to note that the monomeric arsenic compound **2** is pyramidal at arsenic ($\sum$angles ≈ 292°). Also the unreported compound $[Li(THF)_3PH(2,4,6\text{-}Me_3C_6H_2)]$[27] has pyramidal geometry ($\sum$angles = 301°) at phosphorus. These compounds are a further illustration of the fact that terminal metal diorganophosphides and -arsenides can adopt pyramidal geometries at the pnictide throughout the periodic table.[28] In contrast most metal terminal amide complexes are planar at nitrogen.[3]

The distinctive feature of **3** is due to the fact that it is dimeric, whereas the corresponding phosphorus compounds $[\{Li(THF)_2PPh_2\}_\infty]$, **7**, and $[\{Li(Et_2O)PPh_2\}_\infty]$, **8**, are chainlike polymers. This is contrary to what is expected based on the size of the group 5 atom since **7** and **8** are more crowded than **3**. The CAsC angle of **3** in comparison with **10** is also more acute than expected since the corresponding angle in the three phosphorus compounds **7**, **8**, and **9** varies only slightly. We have previously argued[9] that the large CAsC angle in the $[AsPh_2]^-$ ion could be explained, in part, on the basis of Bent's rule.[29] The wide CAsC angle implies considerable s character in the As–C bonds and relatively more p character (compared to $[PPh_2]^-$) in the two lone-pair orbitals of arsenic. This in turn imposes a more acute LiAsLi angle than LiPLi. This is borne out by the ca. 90° LiAsLi angle in **3** and the much higher LiPLi angles (all >120°) in **7** and **8**. The smaller LiAsLi angle, in effect, increases crowding, limiting the degree of association to two rather than the chain formation seen in **7** and **8**.

The ion $[SbPh_2]^-$, like its phosphorus and arsenic analogues in **9** and **10**,[9,10] is well separated in the lattice and is the first structure of a mononuclear two-coordinate derivative of antimony. However, inspection of Table II shows no regular trend in CEC angles in these ions for E = P, As, or Sb. We regard this as another manifestation of Bent's rule as previously described.[9] The formation of the $[Sb_3Ph_4]^-$ ion in the treatment of $SbPh_3$ with Li powder was unexpected. It is unlikely that the addition of 12-crown-4 to the reaction mixture caused the appearance of $[Sb_3Ph_4]^-$ via disproportionation of $[SbPh_2]^-$ since the latter ion can readily be isolated in moderate yield in the synthesis of **4**. One possible explanation is that lithium powder may reduce $SbPh_3$ further, giving elemental Sb which may then be solubilized by $LiSbPh_2$ in ether solution. Alternatively a radical mechanism involving $SbPh_2$ may occur. Preferential precipitation of $[Sb_3Ph_4]^-$ as its $[Li(12\text{-crown-}4)_2]^+$ salt is probably a consequence of solubility factors. Experiments are presently under way to examine the solubilization of Sb in solutions of $LiEPh_2$ salts. The Sb–Sb distance in $[Sb_4Ph_4]^-$ of 2.761 (1) Å may be compared to a number of compounds having Sb–Sb bonds which have been structurally characterized. Examples are R_2SbSbR_2 (R = Me,[31] Ph,[32] or $SiMe_3$[33]) having Sb–Sb lengths of 2.862 (2), 2.837 (1), 2.867 (1)

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Å, respectively, and the polymetallates Sb_4^{2-} and Sb_7^{3-}. The distances in Sb_4^{2-} are rather short (average 2.75 Å, bond order = 1.25 from MO theory) and very close to the value obtained in **5**.[34] In Sb_7^{3-} the distances vary between 2.717 (2) and 2.906 (2) Å.[34] Interestingly the Sb–Sb distance, 2.663 Å, in $[trans\text{-}\eta^2\text{-}\{(CO)_5WSb(Ph)Sb(Ph)W(CO)_5\}W(CO)_5]$, which is thought to have a bond order of about 1.5, is also very close to the values seen in **5**.[35] The above data suggest that the Sb–Sb "single" bond in **5** is significantly shorter than expected. Shortened E–E distances have been seen in species such as $[P\{P(O)(O\text{-}i\text{-}Pr)_2\}_2]^-$[36] and $[P\{P(O)Ph_2\}_2]^-$[37] (P–P = 2.12–2.15 Å) where p–d π bonding has been cited as a factor in shortening the P–P bonds. It may be possible that a similar interaction is occurring here. The SbSbSb angle of 88.8 (1)° is acute. This is difficult to account for in terms of Bent's rule unless the $SbPh_2$ group is considered to be a more electronegative substituent than Ph, which seems unlikely. The Sb(2)Sb(2)′ distance is 3.864 (1) Å, ruling out significant bonding interactions between these atoms.

One other structural feature detailed in Table II concerns the dihedral angles between the phenyl rings. It is apparent that there is a rough correlation between this parameter and the C–E–C angle, but no correlation that would indicate a multiple bonding interaction between the π levels in the phenyl rings and the main group 5 central atom.

In conclusion, the results in this paper show that (i) 12-crown-4 is a useful reagent in abstracting lithium ions from their $[ER_2]^-$ (E = P, As, or Sb) salts, forming rare two-coordinate group 5 anions; (ii) the structures of the arsenic complexes are significantly different from their phosphorus and antimony analogues; (iii) it is probable that lithium derivatives of terminal amides are mostly planar, whereas the monomeric heavier element derivatives are pyramidal at the pnictide; (iv) it may also be possible to solubilize main group 5 elements such as As, Sb, or Bi in solutions of their $LiER_2$ derivatives in the same way that phosphorus has been solubilized with soft anionic bases.[37]

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Supplementary Material Available: Tables of atom coordinates, anisotropic thermal parameters, bond distances and angles, and hydrogen coordinates (28 pages). Ordering information is given on any current masthead page.

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Artificial Allosteric System. 4. T/R Characterization of an Artificial Allosteric System by Resonance Raman Spectroscopy and O_2 or CO Affinity

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Abstract: Selective preparation of a pentacoordinate gable porphyrin·Fe^{II}_2·α,ω-diimidazolylpropane which serves as a model for R-state Hb was achieved (ca. 97%). Its CO affinity and resonance Raman spectrum were studied in order to compare it with the corresponding pentacoordinate T complex previously prepared by use of diimidazolylmethane as a bridging ligand. Imidazolylpropionylamido-TPP·Fe^{II} was newly prepared as a T model to compare its CO affinity and resonance Raman spectrum with the corresponding R model, imidazolylvaleramido-TPP·Fe^{II}. These T/R couples combined with known T/R couples—Hb $\alpha_2\beta_2$ vs. isolated α or β; Fe^{II}·TpivPP·DMI (1,2-dimethylimidazole) vs. Fe^{II}·TpivPP·1MI (1-methylimidazole); Fe^{II}·pocket porphyrin·DMI vs. Fe^{II}·pocket porphyrin·1MI—confirm that structural differentiation of the T state from the R state is conveniently made by considerable low-frequency shift by 8–34 cm^{-1} in the resonance Raman ν_{Fe-N} stretch and remarkable decrease in CO and O_2 affinities. The observed CO and O_2 affinity changes due to T → R structure change are ranging between 33 and 420 for $K_{O_2}(R)/K_{O_2}(T)$ and between 40 and 750 for $K_{CO}(R)/K_{CO}(T)$. On the basis of these appropriate T- and R-structure models, the magnitudes of cooperativity operating in O_2 and CO binding to native (Hb, number of cooperative sites $n = 4$) and artificial (gable·Fe^{II}, $n = 2$) allosteric systems, defined by $(K_n/K_1)/(K_R/K_T)$, were estimated to be considerably smaller than unity, suggesting that the R forms of the allosteric systems are not fully relaxed compared to the "ideal" R form independently prepared.

Allosteric control of successive O_2 binding to hemoglobin (Hb) is best interpreted by remarkable conformation change from the low O_2 affinity form, T (tense), to the high O_2 affinity form, R (relaxed), on O_2 binding to the subunit protein (α or β) in the tetrameric protein $(\alpha_2\beta_2)$.[1] The conformation change in the *oxy* subunit(s) further causes induced T → R conformation change in the *deoxy* subunit.

The allosteric effect itself is well characterized by the sigmoid curve in isothermal O_2 binding (cooperativity) on one hand, while T and R structures are characterized by X-ray[2] or EXAFS[2] only in limited examples. However, selective preparation of artificial

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