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Synthesis and Characterization of Ge(II), Sn(II), and Pb(II) Monoamides with $-NH_2$ Ligands

Corneliu Stanciu, Shirley S. Hino, Matthias Stender, Anne F. Richards, Marilyn M. Olmstead, and Philip P. Power*

Department of Chemistry, University of California, Davis, One Shields Avenue,
Davis, California 95616

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The synthesis and characterization of the first divalent germanium, tin, and lead monoamide derivatives of the parent amide group $-NH_2$ are presented. They have the general formula $(ArMNH_2)_2$ (M = Ge, Ar = Ar′ (C_6H_3-2,6-Pr^i_2) or Ar* (C_6H_3-2,6(C_6H_2-2,4,6-Pr^i_3)); M = Sn, Ar = Ar*; M = Pb, Ar = Ar*). For germanium and tin, they were obtained by reacting the corresponding terphenyl halides of the group 14 elements with liquid ammonia in diethyl ether. The lead amide derivative $(Ar^*PbNH_2)_2$ was synthesized by reaction of $LiNH_2$ with Ar*PbBr in diethyl ether. The compounds were characterized by IR and multinuclear NMR spectroscopies and by X-ray crystallography in the case of the $(Ar'GeNH_2)_2$ or $(Ar^*SnNH_2)_2$ derivatives. They possess dimeric structures with two $-NH_2$ groups bridging the germanium and tin centers. For lead, the reaction with ammonia led to isolation of a stable ammine complex of formula $Ar^*PbBr(NH_3)$ which was characterized by IR and NMR spectroscopies and by X-ray crystallography. It is the first structural characterization of a divalent lead ammine complex.

Introduction

Stable low-valent amide derivatives of the heavier group 14 elements have been known for almost 3 decades.[1] They have the general formula $M(NR_2)_2$, (M = Ge, Sn, and Pb) where the nitrogen substituents can be a variety of bulky silyl, aryl, or alkyl groups.[1-3] To date, however, no examples of stable divalent group 14 element amides featuring the parent $-NH_2$ group have been reported. A number of stable $-NH_2$ derivatives of silicon(IV) are known,[4-8] and there are also a few stable $-NH_2$ derivatives of germanium(IV).[5,9,10] These M(IV) compounds were obtained with the use of bulky coligands which prevent self-association by elimination of NH_3. These results have not been expanded to divalent derivatives however. There has been considerable recent interest in the synthesis of stable $-NH_2$ derivatives of the neighboring group 13 elements,[11] as well as stable divalent group 14 element derivatives of the isoelectronic $-OH$ group, which were stabilized by bulky bidentate β-diketiminate ligands.[12] Like tetravalent species, the scarcity of divalent $-NH_2$ derivatives is mainly due to their tendency to condense with elimination of ammonia. This process is especially feasible in divalent compounds where the group 14 element can carry only one other substituent which renders steric protection more difficult. We now report that the use of very crowding terphenyl ligands[13] enables the synthesis and stabilization of stable Ge(II), Sn(II), and Pb(II) amides of

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* To whom correspondence should be addressed. Fax, (international) +1-530/752-8995; e-mail, pppower@ucdavis.edu.

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formula $(Ar^{*}MNH_2)_2$ (M = Ge, Sn, or Pb) or $(Ar'GeNH_2)_2$, where $Ar^{*} = C_6H_3\text{-}2,6(C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3)_2$ and $Ar' = C_6H_3\text{-}2,6(C_6H_3\text{-}2,6\text{-}Pr^i{}_2)_2$. In addition, the isolation and structural characterization of the lead(II) ammine complex $Ar^{*}PbBr(NH_3)$ are described. This is the first structural determination of an ammine complex of divalent lead and only the second example of a structurally characterized ammine complex of a divalent group 14 element.[14]

Experimental Section

General Procedures. All manipulations were carried out with use of modified Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na/K alloy and degassed twice before use. $\{Pb(\mu\text{-}Br)Ar^{*}\}_2$ was prepared according to literature procedures.[15] ^1H and ^{13}C NMR data were recorded on a Varian 300 MHz or Varian 400 MHz instrument and referenced to the deuterated solvent. The ^{119}Sn NMR spectrum was referenced to a $Sn(CH_3)_4$ standard. The ^{207}Pb NMR spectrum was referenced to $Pb(NO_3)_2$ corrected to $PbMe_4$. Melting points were recorded in glass capillaries under N_2 and are uncorrected. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer-1430 spectrometer.

$(Ar'GeNH_2)_2$ (1). $Ar'GeCl$ (0.506 g, 1 mmol) was dissolved in ca. 20 mL of diethyl ether, and the solution was cooled in a dry ice/acetone bath. An excess of dry ammonia was added via cannula at low temperature with rapid stirring. The reaction was allowed to warm to room temperature overnight, whereupon the ether was removed under reduced pressure. The residue was extracted with hexane, filtered through Celite, concentrated to about half the initial volume of solvent, and placed in a ca. −20 °C freezer for 3 days. The product **1** was obtained as small, colorless crystals, and crystals suitable for X-ray crystallography could be grown by gradual cooling of a toluene solution. Yield: 0.38 g (0.8 mmol, 81%). Mp = 87−88 °C (dec to yellow solid). Anal. Calcd for $C_{30}H_{39}GeN$: C, 74.10; H, 8.09; N, 2.88. Found: C, 74.83; H, 8.18; N, 2.76. ^1H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 0.87$ (s, 2H, NH_2), 0.98 (d, $^3J_{H-H} = 6.8$ Hz, 12H, $o\text{-}CH(CH_3)_2$), 1.10 (d, $^3J_{H-H} = 7.2$ Hz, 12H, $o\text{-}CH(CH_3)_2$), 2.94 (sept, $^3J_{H-H} = 6.8$ Hz, 4H, $CH(CH_3)_2$), 6.94 (d, $^3J_{H-H} = 7.6$ Hz, 4H, $m\text{-}C_6H_3\text{-}2,Pr^i{}_2$), 7.00 (d, $^3J_{H-H} = 7.2$ Hz, 2H, $m\text{-}C_6H_3$), 7.09−7.13 (m, 3H, $p\text{-}C_6H_3\text{-}2,Pr^i{}_2$ and $p\text{-}C_6H_3$) ppm. $^{13}C\{^1H\}$ NMR (100.59 MHz, C_6D_6, 25 °C): $\delta = 23.37$ ($o\text{-}CH(CH_3)_2$), 26.63 ($o\text{-}CH(CH_3)_2$), 31.05 ($o\text{-}CH(CH_3)_2$), 123.76 (m-Dipp), 126.19 ($p\text{-}C_6H_3$), 128.90 ($m\text{-}C_6H_3$), 129.78 ($p\text{-}C_6H_3\text{-}2,6\text{-}Pr^i{}_2$), 139.87 ($i\text{-}C_6H_3\text{-}2,6\text{-}Pr^i{}_2$), 144.50 ($o\text{-}C_6H_3\text{-}2,6\text{-}Pr^i{}_2$), 146.36 ($o\text{-}C_6H_3$), 156.53 ($i\text{-}C_6H_3$) ppm. IR (Nujol): $\nu = 3380$ and 3308 cm^{-1} (νNH_2, weak).

$(Ar^{*}GeNH_2)_2$ (2). The same procedure and the same scale as that employed for **1** afforded 0.43 g (0.75 mmol, 75%) of **2** as small, colorless crystals which could not be grown large enough for X-ray diffraction studies. Mp = 101−102 °C (dec to yellow solid which turns black above 210 °C). Anal. Calcd for $C_{36}H_{51}GeN$: C, 75.80; H, 9.01; N, 2.46. Found: C, 76.1; H, 9.02; N, 2.36. ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 1.06$ (d, $^3J_{H-H} = 6.3$ Hz, 12H, $o\text{-}CH(CH_3)_2$), 1.13 (d, $^3J_{H-H} = 6.6$ Hz, 12H, $o\text{-}CH(CH_3)_2$), 1.38 (d, $^3J_{H-H} = 6.9$ Hz, 12H, $p\text{-}CH(CH_3)_2$), 1.62 (s, 2H, NH_2), 2.96 (sept, $^3J_{H-H} = 6.9$ Hz, 2H, $p\text{-}CH(CH_3)_2$), 3.12 (sept, $^3J_{H-H} = 6.3$ Hz, 4H, $o\text{-}CH(CH_3)_2$), 6.94 (d, $^3J_{H-H} = 6.9$ Hz, 2H, $m\text{-}C_6H_3$), 7.01 (s, 4H, $m\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 7.15 (m, 1H, $p\text{-}C_6H_3$ and solvent) ppm. $^{13}C\{^1H\}$ NMR (75.44 MHz, C_6D_6, 25 °C): $\delta = 23.67$ ($o\text{-}CH(CH_3)_2$), 24.64 ($o\text{-}CH(CH_3)_2$), 26.45 ($p\text{-}CH(CH_3)_2$), 31.35 ($o\text{-}CH(CH_3)_2$), 34.37 ($p\text{-}CH(CH_3)_2$), 121.64 ($m\text{-}C_6H_3$), 124.62 ($o\text{-}C_6H_3$), 130.85 ($p\text{-}C_6H_3$), 138.36 ($i\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 144.69 ($p\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 146.52 ($m\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 147.99 ($o\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 154.22 ($i\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$) ppm. IR (Nujol): $\nu = 3370$ and 3300 cm^{-1} (νNH_2, weak).

$(Ar^{*}SnNH_2)_2$ (3). By following the same general reaction protocol as that of **1** and **2**, we obtained 0.51 g (0.82 mmol, 83%) of large colorless crystals of **3** from cooling a hexane solution. The crystals were of X-ray quality and were analyzed by this technique. Mp = 88 °C (dec to yellow, became black above 190 °C). Anal. Calcd for $C_{30}H_{39}NSn$: C, 67.69, H, 7.88, N, 2.63. Found: C, 67.98; H, 7.45; N, 2.60. ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 0.38$ (s, 2H, NH_2), 1.11 (d, $^3J_{H-H} = 6.9$ Hz, 12H, $o\text{-}CH(CH_3)_2$), 1.29 (d, $^3J_{H-H} = 6.6$ Hz, 12H, $o\text{-}CH(CH_3)_2$), 1.36 (d, $^3J_{H-H} = 6.9$ Hz, 12H, $p\text{-}CH(CH_3)_2$), 2.92 (sept, $^3J_{H-H} = 6.9$ Hz, 2H, $p\text{-}CH(CH_3)_2$), 3.15 (sept, $^3J_{H-H} = 6.9$ Hz, 4H, $o\text{-}CH(CH_3)_2$), 7.16 (s, 4H, $m\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 7.18−7.22 (m, 3H, (m and p) C_6H_3) ppm. ^{13}C NMR (75.44 MHz, C_6D_6, 25 °C): $\delta = 23.65$ ($o\text{-}CH(CH_3)_2$), 24.71 ($o\text{-}CH(CH_3)_2$), 26.57 ($p\text{-}CH(CH_3)_2$), 31.13 ($o\text{-}CH(CH_3)_2$), 34.90 ($p\text{-}CH(CH_3)_2$), 121.30 ($m\text{-}C_6H_3$), 126.20 ($o\text{-}C_6H_3$), 130.13 ($p\text{-}C_6H_3$), 139.20 ($i\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 146.64 ($m\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 146.96 ($o\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 148.22 ($p\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 167.65 ($i\text{-}C_6H_3$) ppm. $^{119}Sn\{^1H\}$ NMR (111.8 MHz, C_6D_6, 25 °C): $\delta = 286.04$ ppm. IR (Nujol): $\nu = 3370$ and 3290 cm^{-1} (νNH_2, weak).

$[Ar^{*}PbBr(NH_3)]$ (**4**). Orange crystals of $\{Pb(\mu\text{-}Br)Ar^{*}\}_2$[15] (0.684 g, 0.448 mmol) were dissolved in toluene (25 mL) and cooled to ca. −78 °C with rapid stirring. An excess of ammonia was condensed into this solution, whereupon the solution became pale yellow. Stirring was continued for 1 h, and the reaction mixture was allowed to warm to room temperature overnight. The toluene was removed under reduced pressure, and the residue was extracted with hexanes (60 mL) and filtered through Celite. The filtrate was placed in a ca. −20 °C freezer, whereupon yellow crystals of **4** were obtained upon storage for 2 d. Yield: 0.388 g, 56%. Mp = 94−96 °C (became colorless; at 118−121 °C, the solid melts with decomposition to a dark orange solid). ^1H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 1.10$ (d, $^3J_{HH} = 6.8$ Hz, 6H, $p\text{-}CH(CH_3)_2$), 1.18 (d, $^3J_{HH} = 6.8$ Hz, 6H, $o\text{-}CH(CH_3)_2$), 1.26 (s, 3H, NH_3), 1.30 (d, $^3J_{HH} = 6.8$ Hz, 6H, $o\text{-}CH(CH_3)_2$), 1.39 (d, $^3J_{HH} = 6.8$ Hz, 6H, $p\text{-}CH(CH_3)_2$), 2.88 (sept, $^3J_{HH} = 6.8$ Hz, 1H, $p\text{-}CH(CH_3)_2$), 2.98 (sept, $^3J_{HH} = 6.8$ Hz, 4H, $o\text{-}CH(CH_3)_2$), 3.17 (sept, $^3J_{HH} = 6.8$ Hz, 1H, $p\text{-}CH(CH_3)_2$), 7.13 (s, 4H, $m\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 7.31 (t, $^3J_{HH} = 7.6$ Hz, 1H, $p\text{-}C_6H_3$), 7.94 (d, $^3J_{HH} = 7.6$ Hz, 2H, $m\text{-}C_6H_3$) ppm. $^{13}C\{^1H\}$ NMR (100.59 MHz, C_6D_6, 25 °C): $\delta = 23.59$ ($o\text{-}CH(CH_3)_2$), 24.29 ($o\text{-}CH(CH_3)_2$), 26.29 ($p\text{-}CH(CH_3)_2$), 30.64 ($o\text{-}CH(CH_3)_2$), 34.73 ($p\text{-}CH(CH_3)_3$, 120.60 ($m\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 121.16 ($o\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 127.63 ($p\text{-}C_6H_3$), 131.82 ($i\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$), 137.44 ($m\text{-}C_6H_3$), 141.11 ($o\text{-}C_6H_3$), 148.26 ($p\text{-}C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$). UV−vis (hexane): $\lambda_{max} = 416.0$ nm, $\epsilon = 460$ M^{-1} cm^{-1}.

$(Ar^{*}PbNH_2)_2$ (5). $\{Pb(\mu\text{-}Br)Ar^{*}\}_2$ (0.723 g, 0.5 mmol) in diethyl ether (30 mL) was added dropwise to a suspension of $LiNH_2$ (1 mmol, generated from ammonia and 0.625 mL of a 1.6 M hexane solution of *n*-BuLi) in hexane (20 mL) with rapid stirring and cooling in an ice bath. The resulting off-white mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the residue was extracted with hexane (35 mL) and filtered through Celite. Reduction of the solution volume to incipient cloudiness and storage in a freezer for 2 d afforded the product **5** as colorless crystals. Despite efforts to grow crystallographic quality crystals, the compound was always obtained as a microcrystalline powder. In a typical experiment, 0.58 g (0.41

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Table 1. Selected Crystallographic Data for Compounds **1**, **3**, and **4**

	compound		
	1·1.5 toluene	**3·hexane**	**4**
formula	$C_{70.5}H_{90}Ge_2N_2$	$C_{78}H_{116}N_2Sn_2$	$C_{36}H_{51.25}Br_{0.75}N_{0.75}Pb_{0.75}$
formula weight	1110.63	1319.11	709.85
color, habit	colorless, plate	colorless, rod	yellow, block
cryst syst	monoclinic	triclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/c$
a, Å	43.490(5)	9.7531(4)	12.9533(10)
b, Å	16.840(2)	13.2513(5)	17.0324(14)
c, Å	18.469(2)	13.7548(5)	16.5380(13)
α, deg	90	92.978(1)	90
β, deg	114.265(2)	93.222(1)	107.029(3)
γ, deg	90	94.684(1)	90
V, Å^3	12331(2)	1766.1(1)	3488.7(5)
Z	8	1	4
T, K	90(3)	90(2)	90(2)
cryst dimens, mm^3	0.21 × 0.18 × 0.14	0.48 × 0.23 × 0.18	0.23 × 0.15 × 0.12
d calcd, g cm^{-3}	1.196	1.240	1.351
μ, mm^{-1}	1.016	0.749	4.516
no. of reflns	11141	6269	11081
no. of obsd reflns	7896	5841	9105
R, obsd reflns	0.0434	0.0226	0.0397
wR2, all reflns	0.1270	0.0587	0.1096

mmol, 82%) of white powder was obtained which was further characterized by IR and NMR spectroscopies. Mp = 135−136 °C (dec to brown). Anal. Calcd for $C_{36}H_{51}NPb$: C, 61.33; H, 7.30; N, 1.99. Found: C, 62.05; H, 7.99; N, 1.70. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): $\delta = -0.50$ (s, 2H, NH_2), 1.10 (d, $^3J_{H-H} = 6.8$ Hz, 12H, o-CH(CH_3)$_2$), 1.24 (d, $^3J_{H-H} = 6.8$ Hz, 12H, o-CH(CH_3)$_2$), 1.31 (d, $^3J_{H-H} = 6.8$ Hz, 12H, p-CH(CH_3)$_2$), 2.87 (sept, $^3J_{H-H} = 6.8$ Hz, 2H, p-CH(CH$_3$)$_2$), 3.13 (sept, $^3J_{H-H} = 6.8$ Hz, 4H, o-CH(CH$_3$)$_2$), 7.13 (s, 4H, m-C_6H_2-2,4,6-Pr$^i_3$), 7.26 (t, $^3J_{H-H} = 7.2$ Hz, 1H, p-C_6H_3), 7.44 (d, $^3J_{H-H} = 7.6$ Hz, 2H, m-C_6H_3) ppm. ^{13}C{^{1}H} NMR (100.59 MHz, C_6D_6, 25 °C): $\delta = 23.40$ (o-CH(CH$_3$)$_2$), 24.60 (o-CH(CH$_3$)$_2$), 26.36 (p-CH(CH$_3$)$_2$), 30.81 (o-CH(CH$_3$)$_2$), 34.83 (p-CH(CH$_3$)$_2$), 120.90 (m-C_6H_3), 125.29 (o-C_6H_3), 132.59 (p-C_6H_3), 139.82 (i-C_6H_2-2,4,6-Pr$^i_3$), 146.71 (m-C_6H_2-2,4,6-Pr$^i_3$), 148.05 (o-C_6H_2-2,4,6-Pr$^i_3$), 148.22 (p-C_6H_2-2,4,6-Pr$^i_3$), 224.96 (i-C_6H_3) ppm. ^{207}Pb NMR (62.77 MHz, C_6D_6, 25 °C): $\delta = 3209.6$ ppm. IR (Nujol): $\nu = 3364$ and 3280 cm^{-1}, (νNH_2, weak).

X-ray Crystallographic Studies. Crystals of **1**, **3**, or **4** were covered with a hydrocarbon oil under a rapid flow of argon, mounted on a glass fiber attached to a copper pin, and placed in the N_2 cold stream on the diffractometer. X-ray data were collected on a Bruker SMART 1000 diffractometer at 90(2) K with use of Mo Kα ($\lambda = 0.710\,73$ Å) radiation. Absorption corrections were applied using SADABS.[16] The structures were solved with use of direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedure in SHELXL.[17] All non-hydrogen atoms were refined anisotropically, while hydrogens were placed at calculated positions and included in the refinement by using a riding model. In all cases, ammine and amide H atoms were located in a difference Fourier map. In the case of **1**, H atoms were fully refined. In **3** and **4**, they were kept as riding. The structure of Ar*PbBr(NH_3), **4**, suffers from occupational disorder in the atoms Pb, Br, and NH_3. These three moieties were refined with variable occupacy to 0.768(2) and subsequently fixed at 0.75 occupancy. The final difference map shows residual density in this region that could not be modeled. The structure also shows disorder in one of the isopropyl groups that was refined in two sets of atoms with occupancy 0.75:0.25.

Some details of the data collection and refinement are given in Tables 1 and 2. Further details are in the Supporting Information.

Results and Discussion

Synthesis and Spectroscopy. Two different reaction routes were employed to obtain the amide products. In the case of the germanium and tin derivatives, it was sufficient to treat the terphenylmetal(II) halide with excess ammonia below room temperature to obtain the amides **1**−**3**, as shown in eq 1:

$$2\mathrm{ArM(II)Cl} + \text{excess } \mathrm{NH_3(l)} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} (\mathrm{ArM(II)NH_2})_2 + 2\mathrm{NH_4Cl} \quad (1)$$

$$\begin{gathered}\mathbf{1},\ \mathrm{M} = \mathrm{Ge},\ \mathrm{Ar} = \mathrm{Ar}' \\ \mathbf{2},\ \mathrm{M} = \mathrm{Ge},\ \mathrm{Ar} = \mathrm{Ar}^* \\ \mathbf{3},\ \mathrm{M} = \mathrm{Sn},\ \mathrm{Ar} = \mathrm{Ar}^*\end{gathered}$$

For the lead derivative, however, the reaction with ammonia afforded only the ammine adduct Ar*PbBr(NH_3) (**4**), as shown in eq 2:

$$\mathrm{Ar^*PbBr} + \text{excess } \mathrm{NH_3(l)} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} \underset{\mathbf{4}}{\mathrm{Ar^*PbBr(NH_3)}} \quad (2)$$

Lewis base adducts of monomeric divalent group 14 species are usually confined to derivatives of chelating ligands, although in recent years isonitrile, ylide, and Arduengo carbene adducts have been isolated.[18] Compound **4** is the first well-characterized ammine adduct of a Pb(II) species.

The lead amide (Ar*PbNH_2)$_2$ analogue of **1**−**3** was only obtained upon reaction of Ar*PbBr with LiNH_2, as shown in eq 3:

$$2\mathrm{Ar^*PbBr} + 2\mathrm{LiNH_2} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} \underset{\mathbf{5}}{(\mathrm{Ar^*PbNH_2})_2} + 2\mathrm{LiBr} \quad (3)$$

The reaction of ammonia with the organometal halide to afford **1**−**3** was quite rapid. The initial orange-colored solutions of the precursors became a pale-yellow color at low temperature. Upon the addition of an excess of dry ammonia, the aryl germanium and tin halide solutions immediately became colorless, and a white precipitate of ammonium chloride was formed. For the lead compound **4**, there was little change in color, and the solution remained clear and yellow even at room temperature. After workup, X-ray quality crystals of **1, 3**, and **4** were obtained from hexane or toluene. Changes in the reaction conditions or changes of solvent always led to the formation of the same ammine adduct for lead, and there was no evidence in the IR (lack of the characteristic split band in the range 3200−3400 cm^{-1}) or in the ^{1}H NMR spectrum for the formation of a lead amide by this route. However, the reaction of Ar*PbBr with LiNH_2, according to eq 3, afforded the amide (Ar*PbNH_2)$_2$ (**5**) in good yield, which was character-

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(16) *SADABS: Area Detection Absorption Corrections*; Bruker AXS Inc.: Madison, WI, 1996.

(17) *SHELXS PC*, version 5.03; Bruker AXS Inc.: Madison, WI, 1994.

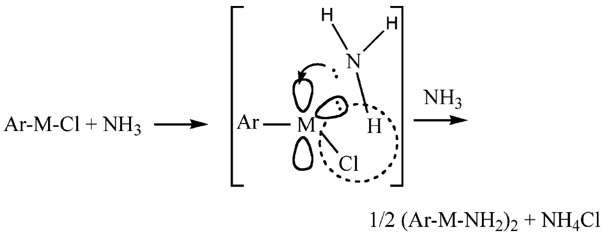
(18) Kinkhammer, K. W. *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: New York, 2002; Vol. 2, Part 1, Chapter 4.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**, **3**, and **4**

1 $(Ar'GeNH_2)_2$[a]		**3** $(Ar^*SnNH_2)_2$[b]			**4** $Ar^*PbBr(NH_3)$	
Ge(1)−N(2)	2.005(3)	Sn(1)−N(1)	2.2142(16)	2.214(2)	Pb(1)−C(1)	2.368(3)
Ge(1)−N(1)	2.009(3)	Sn(1)−N(1)#1	2.2228(17)	2.223(2)	Pb(1)−N(1)	2.490(4)
Ge(1)−C(1)	2.033(3)	Sn(1)−C(1)	2.2375(17)	2.238(2)	Pb(1)−Br(1)	2.8037(5)
Ge(2)−N(3)#1	2.021(3)	N(1)−Sn(1)#1	2.2228(17)	2.223(2)	N(1)−H(1C)	0.91
Ge(2)−N(3)	2.031(3)	C(1)−C(2)qq	1.411(2)		C(1)−C(6)	1.402(4)
Ge(2)−C(31)	2.047(3)	C(1)−C(6)	1.418(3)		C(1)−C(2)	1.406(4)
N(1)−Ge(1)#2	2.009(3)	C(2)−C(3)	1.400(3)		C(1)−Pb(1)−N(1)	99.81(13)
N(2)−Ge(1)#2	2.005(3)	C(5)−C(6)	1.399(3)		C(1)−Pb(1)−Br(1)	97.70(8)
C(1)−C(2)	1.411(4)	N(1)−Sn(1)−N(1)#1	77.98(7)		N(1)−Pb(1)−Br(1)	82.21(12)
C(1)−C(6)	1.415(4)	N(1)−Sn(1)−C(1)	90.67(6)			
N(2)−Ge(1)−N(1)	79.92(13)	N(1)#1−Sn(1)−C(1)	97.04(6)			
N(2)−Ge(1)−C(1)	97.86(9)	Sn(1)−N(1)−Sn(1)#1	102.02(7)			
N(1)−Ge(1)−C(1)	98.02(9)					
Ge(1)#1−N(1)−Ge(1)	99.95(17)					
N(3)−Ge(2)−N(3)#2	80.01(12)					
N(3)−Ge(2)−C(31)	101.99(12)					
N(3)#2−Ge(2)−C(3)	99.75(12)					
Ge(2)−N(3)−Ge(2)#2	99.99(12)					

[a] Symmetry code: #1 = −*x*, *y*, 0.5 − *z*; #2 = 0.5 − *x*, 1.5 − *y*, 1 − *z*. [b] Symmetry code: #1 = 1 − *x*, 2 − *y*, 1 − *z*.

ized by IR and ^{1}H, ^{13}C, and ^{207}Pb NMR spectroscopies. The isolation of the ammine adduct $Ar^*PbBr(NH_3)$ (**4**) strongly suggests that the initial step in the preparation of the germanium and tin amides **1**−**3** also involves the formation of an ammonia complex in which NH_3 behaves as a lone pair donor to the empty p orbital of the metal in accordance with eq 4.



(4)

1-3

For germanium and tin, the eliminated HCl is immediately complexed by ammonia to give NH_4Cl. Where such an elimination pathway is unavailable, an ammine complex can be isolated. This was recently shown by the isolation of (*R*)-[Ge{$O_2C_{20}H_{10}(SiMe_2Ph)_2$-3,3′}($NH_3$)] which was formed by the desilylation of the −N($SiMe_3$) ligand when Ge{$N(SiMe_3)_2$}$_2$ was treated with a bidentate phenol. This is the only other well-characterized divalent group 14 element ammine complex.[14] The lead(II) ammine complex **4** is quite stable (mp = 94−96 °C). It seems probable that HCl elimination takes place less readily than that for the germanium and tin analogues due to the greater size of lead which decreases the steric pressure for elimination and allows the complex to be isolated. Another factor involves the more ionic nature of the lead halogen bond, as depicted by eq 5:

$$\underset{\mathbf{4}}{Ar^*PbBr(NH_3)} \rightleftharpoons [Ar^*Pb(NH_3)]^+ + [Br]^- \qquad (5)$$

The possibility of ionization is supported by a recent report[19] that described the formation and structure of the $[Ar^*Pb(py)_2]^+$ cation. The incipient $[Ar^*Pb(NH_3)]^+[Br]^-$ character of **4** makes HBr elimination much less likely than in the more covalent germanium or tin analogues. In **4**, the ^{1}H NMR signal due to complexed ammonia is observed at 1.26 ppm which is almost 2 ppm further downfield than the −0.50 ppm observed for the amide **5**. This downfield shift is consistent with the incipient ionic character of **4**. In the ^{1}H NMR spectra of $(Ar^*GeNH_2)_2$, $(Ar^*SnNH_2)_2$, and $(Ar^*PbNH_2)_2$, the $-NH_2$ signals are observed at 1.62, 0.38, and −0.50 ppm, respectively. These shifts are in agreement with the increase in electropositive character upon descending the group from Ge to Pb. The ^{119}Sn NMR spectrum of **3** afforded a signal at 286.0 ppm. This signal lies ca. 800 ppm upfield of the 1196.8 ppm signal observed for the two-coordinate aryl amide species SnAr*{$N(SiMe_3)_2$}.[15] The very large difference between the chemical shifts, which implies an increase in shielding for **3**, can be attributed to the increase in the coordination number of tin from 2 to 3. While ^{1}H and ^{13}C NMR spectra for molecule **4** were easily obtained, no ^{207}Pb NMR signal could be observed. The difficulty in detecting this signal could be associated with the large anisotropies expected for the components of the chemical shift tensor, or the presence of the quadrupolar nuclei ^{79}Br and ^{81}Br linked to the lead atom could be a factor in broadening the ^{207}Pb NMR signal. The difficulty associated with obtaining a ^{207}Pb NMR signal for this complex is consistent with the reports of Eaborn, Smith, and co-workers[20] on the organolead chlorides and [Pb(μ-Cl){$C(SiMe_3)_3$}]$_3$, {Pb(μ-Cl)$C(SiMe_3)_2(SiMe_2OMe)$}]$_2$, [Pb(μ-Cl)$C(SiMe_3Ph)_3$}$_2$], as well as our previous work[15,21] on the related organolead bromides of {Pb(μ-Br){C_6H_3-2,6(C_6H_2-2,6-Pr^i_2-4-Bu^t)}}$_2$, {Pb(μ-Br)Ar′}$_2$, {Pb(μ-Br)Ar*}$_2$, and Ar*Pb(py)Br species. In contrast to the difficulties in obtaining ^{207}Pb NMR spectrum of **4**, a C_6D_6 solution of **5** afforded a broad signal at 3209.6 ppm ($\upsilon_{1/2}$ = 260 Hz). Most organolead(II) ^{207}Pb NMR data that are currently known concern two-coordinate diorgano lead or closely related species whose signals are

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(19) Hino, S.; Brynda, M.; Phillips, A. D.; Power, P. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2655−2658.

(20) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Soezerli, S. E. *Organometallics* **1997**, *16*, 5653.

(21) Pu, L.; Twamley, B.; Power, P. P. *Organometallics* **2000**, *19*, 2874.

usually observed in the range 8000−10 000 ppm.[22] Thus, a chemical shift at a considerably higher field for **5** is consistent with a higher coordination number for lead in the dimer despite the more electronegative, electron withdrawing $-NH_2$ substituent.

A further aspect of the spectroscopic studies of these compounds concerns their IR spectra. It is notable that the four isolated amides display clear, characteristic bands between 3260 and 3400 cm^{-1}. There are two bands in each case which is consistent with the presence of an $-NH_2$ group. On the other hand, the ammonia complex of lead does not show a band in this range, but it displays a weak band at a higher frequency of 3492 cm^{-1}, along with others at 1605 and 715 cm^{-1}, which have been tentatively assigned to stretching, deformation vibrational modes, asymmetric and symmetric, respectively, of the coordinated NH_3 molecule.

Structures. The asymmetric unit of the structure of $(Ar'GeNH_2)_2$, **1**, a toluene solvate, is unusual in that two half-molecules of the dimeric species have different crystallographic symmetry elements: a 2-fold axis passes through the two N atoms in the case of Ge(1), and a center of inversion is located in the center of the Ge_2N_2 rhombus in the case of Ge(2). Nevertheless, the two distinct dimers are practically identical, and in both, the Ar′ groups are disposed trans to the Ge_2N_2 rhombus. There are no close contacts to the open coordination site of Ge nor H-bonding contacts to the amide H atoms. Figure 1a shows the structure of the dimer with 2-fold crystallographic symmetry, and Figure 1b shows a different view of the dimer with inversion symmetry. Structure **3**, $(Ar^*SnNH_2)_2$, a hexane solvate, has crystallographic inversion symmetry as well as no close contacts to either Sn or the $-NH_2$ groups. A drawing of the dimer is given in Figure 2. Structure **4**, $Ar^*PbBr(NH_3)$, has no crystallographically imposed symmetry. Figure 3 shows the molecule with 50% thermal ellipsoids. In contrast to the Ge and Sn amides, one of the ammine H atoms shows a weak intermolecular contact to an inversion-related Br at a distance of 2.87 Å.

The main feature of the structures **1** and **3** is that they are both dimers in which the $-NH_2$ groups bridge the germanium and tin atoms symmetrically. The Ge_2N_2 or Sn_2N_2 cores are planar with rhombohedral shapes and with acute angles near 80° at Ge or Sn and a wider angle of 100° at N. The hydrogen atoms lie in a plane perpendicular to that formed by the Ge_2N_2 or Sn_2N_2 units. The Ge and Sn centers have trigonal pyramidal coordination as shown by the sums of the angles at germanium of 275.8[281.7°] and at tin of 265.7°. The Ge−N and Sn−N bond lengths are near 2.02 and 2.21 Å. These are ca. 0.13 Å longer than terminal Ge−N and Sn−N bonds in a variety of monomeric divalent species, for example, the Ge−N bond length of 1.89(1) Å in $Ge\{N(SiMe_3)_2\}_2$ or of 2.09(1) Å in $Sn\{N(SiMe_3)_2\}_2$.[23] The observed Ge−N bridging distances in **1** are in good agreement with the reported range 2.022(7)−2.068(4) Å in the chelated derivatives $MeSi(NBu^t)_3Ge_2X$ ($X = Cl$, $N(SiMe_3)_2$, and PPh_2)[24] in which one of the nitrogen atoms bridges two germaniums. The bridging Sn−N distances in **3** are significantly shorter than the 2.265(4) Å observed for the structure of $Me_2NSn(\mu\text{-}NMe_2)_2SnNMe_2$.[25] In addition, it is much shorter than the ca. 2.39 Å observed in the structure of the weakly dimerized $\{Sn(NBu^t)_2SiMe_2\}_2$.[26] The steric effects of the larger substituents on the bridging nitrogens may lengthen the bridging bonds in these cases.

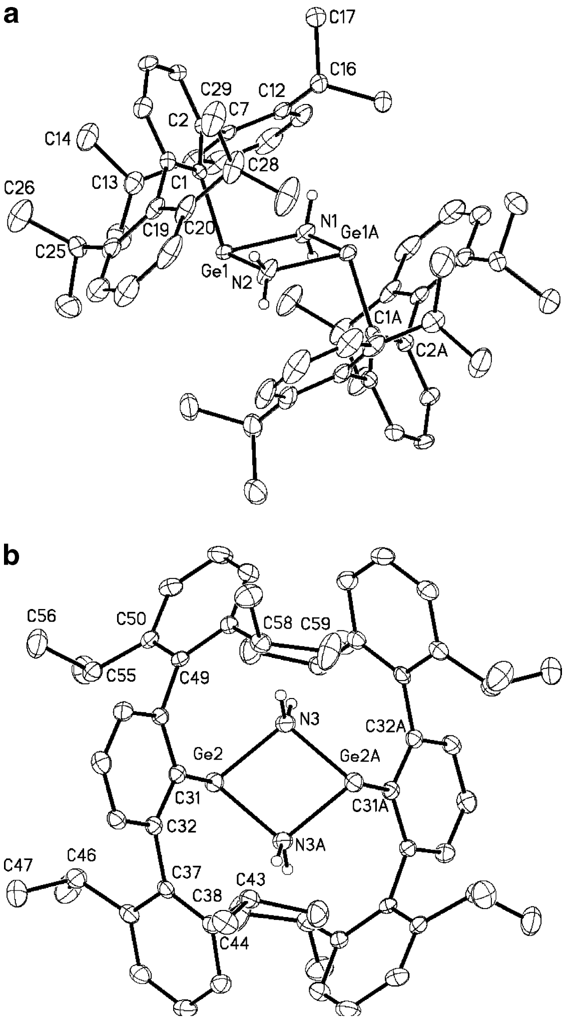

Figure 1. Thermal ellipsoid (30%) drawing of two independent molecules (a and b) of **1**. Hydrogens atoms, except those at nitrogen, are not shown for clarity.

The lead−ammonia adduct isolated from the reaction of Ar^*PbBr and $NH_3(l)$ is a unique example of a Pb(II) complex of ammonia. Ammine complexes are well-known for most transition metals. For main group elements, however, stable complexes are most numerous for group 13 and earlier groups, although a number of ammine complexes of silicon,[27] germanium,[28] and tin[29] have been structurally characterized. Nonetheless, these structures concern tetravalent species, and

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[22] Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **2002**, *47*, 1.
[23] Fjelberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *Chem. Commun.* **1983**, 639.
[24] Veith, M.; Zimmer, M. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1471.
[25] Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 413.
[26] Veith, M. *Z. Naturforsch.* **1978**, *B33*, 7.
[27] For example, $[NH_4][Si(NH_3)F_5]$ and $Si(NH_3)_2F_4$ in the following references: Plitzko, C.; Meyer, G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1646. Popov, A. I.; Valkovskii, M. D.; Sukhoverkhov, V.; Chumaevski, N. A.; Sakhorav, A. V.; Gelmboldt, V. O.; Ennam, A. A. *Zh. Neorg. Khim.* **1991**, *36*, 375.

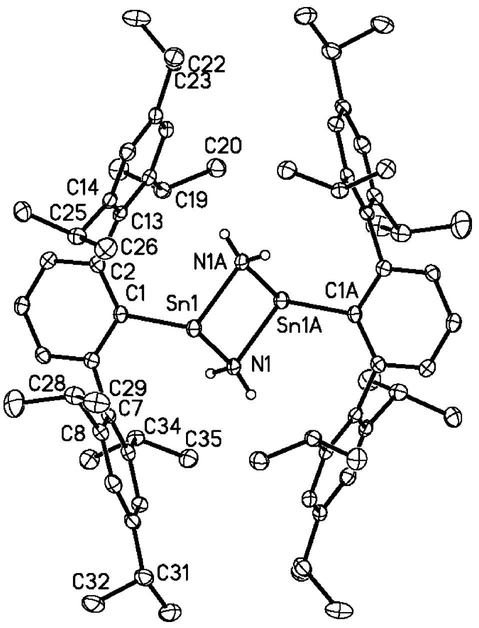

Figure 2. Thermal ellipsoid (30%) drawing of **3**. Hydrogen atoms, except those at nitrogen, are not shown for clarity.

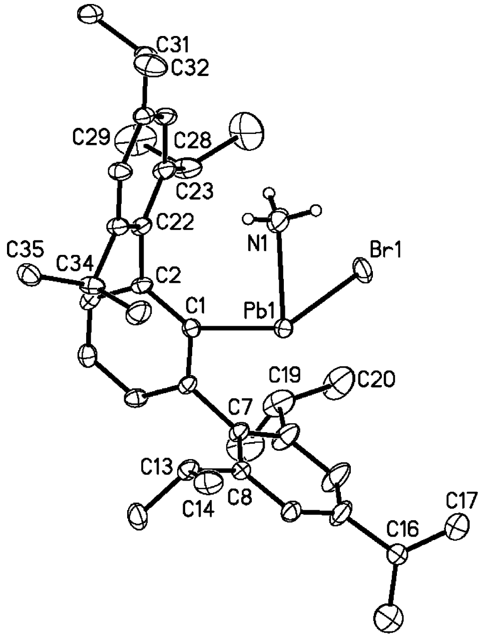

Figure 3. Thermal ellipsoid (30%) drawing of **4**. Hydrogen atoms, except those at nitrogen, are not shown for clarity.

only one divalent ammine derivative of these elements, the species (R)-[Ge{$O_2C_{20}H_{10}(SiMe_2Ph)_2$-3,3′}($NH_3$)], has been characterized.[14] Lead ammine complexes of any kind are much rarer. An early report[30] described the addition of ammonia to lead(II) nitrate and sulfate and the formation of monoammonate, triammonate, and hexammonates of $Pb(NO_3)_2$ as well as di- and tetrammonates of $Pb(SO_4)_2$ although no structural details could be given. In addition, the formation of lead(II) thionitrosyl complex of ammonia has been described.[31] It was examined by X-ray diffraction, but the position of the ammonia nitrogen could not be determined with certainty. An X-ray crystallographic analysis of the structure of **4** clearly shows that the complex is monomeric with a Pb−N bond distance of 2.490(4) Å, which is about 0.23 Å longer than that expected for a Pb−N single bond in a Pb(II) amide such as that in Pb{$N(SiMe_3)_2$}$_2$ (Pb−N = 2.26(2) Å).[23] The lead is pyramidally coordinated ($\Sigma° = 279.82°$) by the C(1) of the aryl, the ammonia nitrogen, and a bromine. The ammonia nitrogen lone pair is coordinated through the "empty" 6p orbital on lead. This results in a wider C(2)−C(1)−Pb(1) angle on the side at which NH_3 is coordinated. The Pb(1)−C(1) (2.368(3) Å) bond distance is slightly longer than those seen for {Pb(μ-Br)Ar*}$_2$ (2.329(11) Å)[21] and Ar*Pb(py)Br (2.322(4) Å),[21] while the Pb(1)−Br(1) (2.8037(5) Å) distance is ca. 0.1 Å longer than the 2.7063(6) Å in Ar*Pb(py)Br. The longer bond lengths and greater pyramidalization of the geometry of the lead center in **4** (cf. $\Sigma° =$ Pb 286.65° in Ar*Pb(py)Br) can be attributed to the greater Lewis basicity of ammonia. The Pb(1)−N(1) distance of 2.490(4) Å is marginally (only 3σ) shorter than the Pb−N distance (2.502(4) Å) found in Ar*Pb(py)Br consistent with its greater Lewis base character. But this has to be viewed in light of the higher coordination number at nitrogen in **4** which predicts a longer Pb−N bond and not the shortening experimentally observed.

A final comment concerns the isoelectronic relationship between **1**−**3** and **5** and the corresponding methyl derivatives which display three different structures for their Ge,[32a] Sn,[32b] and Pb[21] derivatives, respectively. The preservation of the bridged structure in the amides is due undoubtedly to the superior bridging properties of $-NH_2$ in comparison to $-CH_3$.

Conclusions

The reactions of bulky low-valent organo group 14 halides of germanium and tin with liquid ammonia have proven to be an effective pathway for the synthesis of the first low-valent group 14 element derivatives of the parent amide group $-NH_2$. These allowed the first crystal structures of $-NH_2$ derivatives of germanium(II) and tin(II) to be determined. An unique ammonia adduct of lead(II) was also characterized. A simple mechanism has been proposed for the ammonolysis reaction which accounts for the isolation of the ammine adduct rather than the amide in the case of lead. The lead $-NH_2$ derivative could only be obtained by use of the more reactive lithium amide.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

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(28) For example, [NH_4]($Ge(NH_3)F_5$] in the following reference: Weber, W.; Schweda, E. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1529.

(29) For example, $Sn(ND_3)_2F_4$ in the following reference: Woodward, P.; Vogt, T.; Weber, W.; Schweda, E. *J. Solid State Chem.* **1998**, *138*, 350.

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(32) (a) Eichler, B. E.; Power, P. P. *Inorg. Chem.* **2000**, *39*, 5444−5449. (b) Stender, M.; Pu, L.; Power, P. P. *Organometallics* **2001**, *20*, 1820−1824.

Note Added after ASAP: As a result of a production error, this manuscript was released ASAP on March 22, 2005, with a minor text error in the last paragraph of Results and Discussion. The correct version was published on March 24, 2005.

Supporting Information Available: CIF files for **1**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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