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FULL PAPER

Geminal arsa(III)amide and trisubstituted antimony and bismuth amides from the sterically hindered, *N*-functionalised amido ligand $[\{2\text{-}(6\text{-Me})C_5H_3N\}NSiMe_3]^-$

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The reaction of the dimeric diethyl ether solvated lithium amide, bis[{2-(6-methyl)pyridyl}trimethylsilylamidolithium dietherate], with two equivalents of arsenic(III) trichloride in diethyl ether affords the amido arsenic dichloride compound $[\{2\text{-}(6\text{-Me})C_5H_3N\}NSiMe_3(AsCl_2)]$ (**1**), while four equivalents of arsenic(III) trichloride in diethyl ether gives the complex $[\{2\text{-}(6\text{-Me})C_5H_3N\}N(AsCl_2)_2]$ (**3**) through the cleavage of the N–Si bond. This compound is also isolated from the redistribution reaction of the previously reported compound $[\{2\text{-}(6\text{-Me})C_5H_3N\}NAsCl]_2$ (**2**) with two equivalents of $AsCl_3$ in toluene. The crystal structure of (**3**) shows it to be monomeric with two geminal $AsCl_2$ groups. One arsenic centre has pyramidal geometry with the other four-coordinate arsenic centre having distorted trigonal bipyramidal geometry with the putative lone pair of electrons occupying an equatorial position. Homoleptic triamido–antimony and –bismuth complexes are prepared from the 2:3 stoichiometric reaction of MCl_3 (M = Sb, Bi) and dimeric lithium amide. The amide nitrogen centres are coordinated *fac* to the metal centre with each ligand chelating the metal giving it six-fold coordination. The M–N(amide) bonds are much shorter than the M–N(pyridyl) bonds, suggestive of a putative lone pair of electrons intersecting the $[N(pyr)]_3$ plane. This gives the molecule a distorted octahedral shape with a non-crystallographic C_3 axis.

Introduction

Compounds containing heavier Group 15 elements (As, Sb, Bi) have attracted interest over the last decade because of their applications in heterogeneous catalysis[1–3] and as precursors for superconducting materials in MOCVD processes.[4,5] An array of structural types for Group 15 metal/metalloid complexes has been established ranging from monomeric complexes[6,7] to structures with infinite polymeric chains.[8–10] However, relatively few Group 15 metal/metalloid amide complexes have been structurally characterised, and even fewer that contain chelating amide ligands. The use of Lewis base functionalised ligands can be effective in increasing the coordination number of the Group 15 centre at the expense of bridging intermolecular coordination as well as leading to greater stability of the compounds. As an extension to developing the main group chemistry of the bulky alkyl ligands $(2\text{-pyridyl})(Me_3Si)_2C^-$, R_{py},[11] and $(2\text{-}(6\text{-Me})pyridyl)(Me_3Si)_2C^-$, MeR_{py},[12,13] we reported the synthesis and structural features of $L_{py}MCl$ (M = Sb, Bi) where L_{py} is the bulky amide ligand $(2\text{-}(6\text{-Me})\text{-pyridyl})(Me_3Si)N^-$.[14] These compounds exhibit a considerable difference in thermal and kinetic stability compared to the analogous alkyl compounds, $(MeR_{py})_2MCl$, most probably partly attributable to the stronger M–N bond compared to the M–C bond. We have also shown recently that the presence of the $SiMe_3$ group within the ligand can result in α-elimination of Me_3SiCl from substituted metal(loid) chloride complexes through the synthesis of the chloro-bridged polymeric C-centred geminal stibine, $[(2\text{-pyridyl})(Me_3Si)CSbCl]_\infty$ and the dimeric N-centred amidoarsine, $[\{2\text{-}(6\text{-Me})pyridyl\}NAsCl]_2$, derived from the intermediate $[(2\text{-pyridyl})Me_3Si)\text{-}C{=}SbCl]$ and $[\{2\text{-}(6\text{-Me})pyridyl\}N{=}AsCl]$, respectively.[15]

Herein we report an extension of our studies on the reaction of $(L_{py}Li)_2$ with Group 15 metal(loid) trichlorides. We show that stable trisubstituted antimony and bismuth amides can be prepared as monomeric compounds. We also report in full the preparation of $L_{py}AsCl_2$ and $[\{2\text{-}(6\text{-Me})pyridyl\}NAsCl]_2$ and examine the further reactions that these complexes undergo to form another interesting geminal amidoarsine, $[\{2\text{-}(6\text{-Me})\text{-pyridyl}\}N(AsCl_2)_2]$, through a synthetic route which may lead to mixed geminal metal amides.

Results and discussion

Arsenic amide complexes

The synthesis of the amido–arsenic complexes is outlined in Scheme 1. The amido–arsenic dichloride complex $L_{py}AsCl_2$ (**1**) was prepared *via* the metathesis reaction between two equivalents of $AsCl_3$ and an equivalent of the dimeric lithiated amide ligand $(L_{py}Li)_2$. This complex was also isolated from the analogous reaction in which the dimeric lithium amide to $AsCl_3$ ratio was 1:1, indicating the dichloride complex to be formed in preference to further amide substitution. This contrasts with similar reactions of the lithiated amide and MCl_3 (M = Sb, Bi), wherein further substitution can occur to form the bisamido compounds $(L_{py})_2SbCl$ and $[(L_{py})_2BiCl]_2$,[14] and triamido compounds $(L_{py})_3M$ (M = Sb (**4**), Bi (**5**)). The difference in the variety of substitution achieved is most probably a consequence of the increased size of the Group 15 metal(loid) centre as well as the presence of the bulky $SiMe_3$ group on the ligand. This is further evident from the report that a tri-substituted *N*-functionalised arsenic–thiolate complex has been described in which the three smaller thiolate ligands chelate by way of the nitrogen centre of the pyridyl ring as well as the sulfur.[6] Heating (**1**) at 80 °C for 4 hours in toluene results in the elimination of Me_3SiCl to afford the dimeric arsenic amide complex $[\{2\text{-}(6\text{-Me})pyridyl\}NAsCl]_2$ (**2**). The bis(arsenic dichloride) complex

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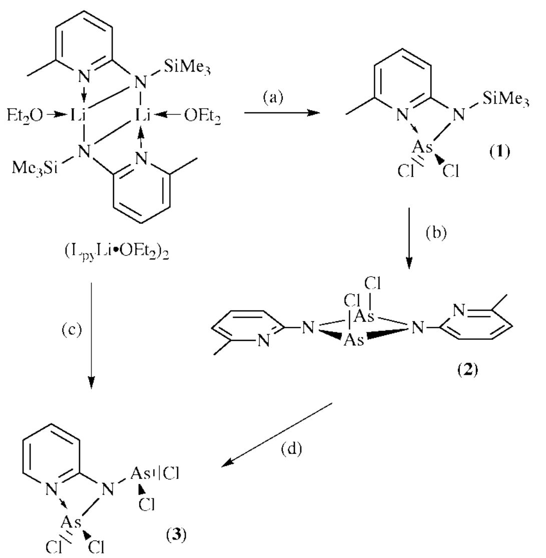
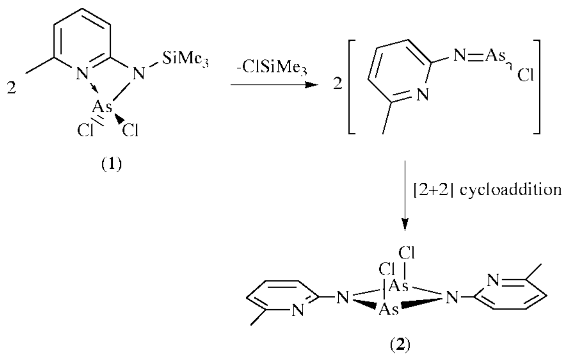


Scheme 1 Preparation of amido–arsenic complexes (**1**), (**2**) and (**3**). (a) 2 $AsCl_3$, −2 LiCl, −78 °C, Et_2O; (b) 80 °C, $-ClSiMe_3$, toluene; (c) 4 $AsCl_3$, −2 LiCl, −2 $ClSiMe_3$, −78 °C, Et_2O; (d) 2 $AsCl_3$, toluene, 25 °C.

[{2-(6-Me)pyridyl}N($AsCl_2$)$_2$] (**3**) can be prepared by two methods: (a) the reaction of four equivalents of $AsCl_3$ with ($L_{py}Li$)$_2$ *via* the elimination of LiCl and Me_3SiCl. (b) The redistribution reaction between (**2**) and two equivalents of $AsCl_3$ at room temperature. All complexes are thermally stable, albeit air and moisture sensitive and have been characterised by ^{1}H and ^{13}C NMR spectroscopy and elemental microanalysis. X-Ray crystal structure determination was used for the structural elucidation of complexes (**2**) and (**3**).

Complex (**1**) is stable at room temperature as a solid. Effervescence due to loss of Me_3SiCl is not observed on melting at 147 °C, despite this temperature being well above the decomposition temperature of the complex in toluene. The thermal stability of (**1**) is significantly different to that of the related complex $R_{py}AsCl_2$ which decomposes over several hours at room temperature with suspected elimination of Me_3SiCl to give an intractable brown tar.[11] Similar studies of 6-MeR_{py}-$AsCl_2$ show it to be thermally stable to 145 °C in the solid state with no apparent decomposition.[16] The difference in thermal stability of these complexes can be attributed to the extra bulk of the ligand with the presence of the 6-Me group on the pyridyl ring. The presence of the weak N–Si bond in (**1**) accounts for the formation of (**2**) *via* the elimination of Me_3-SiCl. In contrast, the strong C–Si bond in the similar bulky alkyl complexes does not undergo C–Si bond cleavage to form analogous arsenic alkene complexes. Complex (**1**) is assumed to be monomeric with the ligand chelating the arsenic centre through the pyridyl nitrogen centre, based on the crystal structure determination of 6-Me$R_{py}AsCl_2$.[13] The ^{1}H and ^{13}C NMR spectra of (**1**) are unexceptional. The aromatic protons of the pyridyl ring have typical chemical shifts, as do those of the Me and $SiMe_3$ groups, and are similar to $L_{py}H$. Similarly, all carbon resonances are typical, and are similar to those of the parent amine.

Complex (**2**) is the first compound to be isolated from an elimination (of Me_3SiCl) reaction for the series of related compounds $R_{py}AsCl_2$ and 6-Me$R_{py}AsCl_2$. The structure of this complex has been confirmed by X-ray diffraction studies to be dimeric in the solid state. The proposed mechanism for the formation of (**2**) is shown in Scheme 2. Loss of Me_3SiCl results from the heating of (**1**) subsequently forming an unstable imido-arsenic ylid intermediate. An intermolecular [2 + 2] cycloaddition between two of these ylids then occurs thus forming (**2**). The cycloaddition reaction of an arsenium cation involving an As=N bond has been reported.[17] The reaction of a weakly associated dimeric arsenium complex with 2,3-dimethylbutadiene results in quantitative yield of a cycloaddition product, presumably through a concerted reaction involving a Diels–Alder type cycloaddition, wherein the As=N bond in either the monomer or dimer acts as a dienophile. A similar mechanism has recently been proposed for the decomposition of $R_{py}SbCl_2$ where a polymeric product has been structurally elucidated.[15]



Scheme 2 Mechanism for [2 + 2] cycloaddition to form (**2**).

At room temperature the ^{1}H NMR spectrum of (**2**) suggests the presence of one dominant species in solution. Another set of minor signals are observed, suggesting other possible oligomeric species. All protons have characteristic chemical shifts and the resonance due to the $SiMe_3$ observed in (**1**) is absent. At low temperature, the two species integrate almost equally. No coalescence was found between −80 °C and 60 °C, showing that the two species observed cannot be accounted for by a simple restricted rotation around the C–N bond. Varying the solvent did not vary the room temperature proton spectrum. It is likely that the two species present in solution are two oligomers, such as monomers and dimers, and that crystal packing forces may dictate that the dimeric *syn*-complex crystallises preferentially in the solid state. The ^{13}C NMR spectrum also shows the existence of more than one species in solution.

The isolation of (**3**) by either method illustrated in Scheme 1 leads to some interesting conclusions. Firstly, the isolation of (**3**) from the reaction between ($L_{py}Li$)$_2$ and $AsCl_3$ shows that the N–Si bond in this system is weak and can be easily cleaved. Secondly, the ligand redistribution of (**2**) with two equivalents of $AsCl_3$ indicates that the As_2N_2 ring of (**2**) can be disrupted, leading to interesting possibilities for the synthesis of heterobimetallic complexes. The ^{1}H and ^{13}C NMR spectra of (**3**) are unexceptional. One set of well resolved resonances are seen in the spectra which distinguishes (**3**) from (**2**).

Crystal structures of (2) and (3). Crystallographic data of (**2**) and (**3**) are listed in Table 1. Important bond distances and angles of (**2**) and (**3**) are listed in Tables 2 and 3, respectively. Compound (**2**) crystallises as pale yellow prismatic crystals from toluene in the monoclinic space group $P2_1/c$ with the asymmetric unit comprised of a dimeric moiety with a cyclic planar As_2N_2 core, Fig. 1, packed in an elegant array. The molecule possesses non-crystallographic C_2 symmetry, the rotation axis passing through the centre of the molecule and perpendicular to the plane of the As_2N_2 molecular core. The pyridyl substituents are coplanar with the As_2N_2 ring and do not exhibit internal coordination from the pyridyl nitrogen centre to the arsenic centre presumably in consequence of steric limitations imposed by the sp^2 nitrogen. The third coordination site of each arsenic centre is occupied by chloride moieties, arranged in *syn* and quasi normal fashion to the As_2N_2 ring. This unusual *syn* arrangement of the chloride ligands most likely results from the orientation requirements of the [2 + 2] cycloaddition mechanism discussed previously.

The As–N(amide) bond distances range from 1.809(3)–1.857(3) Å, comparable with typical As–N(sp^2) bond distances, which have been suggested to be approximately 1.84 Å.[18] The

Table 1 Crystal data and details of the data collection and structure refinement for [{2-(6-Me)C_5H_3N}NAsCl]$_2$, (**2**), [{2-(6-Me)C_5H_3N}N($AsCl_2$)$_2$], (**3**), and [{2-(6-Me)C_5H_3N}$NSiMe_3$]$_3$M (M = Sb (**4**), Bi (**5**))[a]

	(**2**)	(**3**)	(**4**)	(**5**)
Formula	$C_{12}H_{12}As_2Cl_2N_4$	$C_6H_6As_2Cl_4N_2$	$C_{27}H_{45}N_6SbSi_3$	$C_{27}H_{45}N_6BiSi_3$
M	433.01	397.78	659.72	746.94
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.926(4)	10.608(6)	14.865(6)	14.912(5)
b/Å	13.005(3)	8.296(3)	11.682(17)	11.812(4)
c/Å	14.224(4)	8.073(4)	11.296(10)	11.389(4)
α/°		78.75(3)	116.13(9)	116.11(2)
β/°	122.61(2)	68.12(4)	94.04(5)	94.03(3)
γ/°		68.91(4)	104.01(7)	104.73(2)
U/Å^3	1546.6(9)	613.6(5)	1673(3)	1703(1)
Crystal size/mm	0.58 × 0.24 × 0.28	0.38 × 0.55 × 0.28	0.50 × 0.65 × 0.25	0.28 × 0.28 × 0.20
D_c/g cm^{-3}	1.859	2.153	1.309	1.456
Z	4	2	2	2
μ/cm^{-1}	46.6	62.4	9.6	53.1
$A^*_{(\text{min, max})}$	2.64, 3.60 (anal)	3.44, 6.04 (anal)	1.23, 1.47 (gauss)	2.55, 3.20 (gauss)
$2\theta_{\text{max}}$/°	50	50	45	50
No. unique reflections	3540	2172	4362	5986
No. observed data	2144	1278	4017	5176
R	0.055	0.044	0.025	0.038
R'	0.051	0.051	0.032	0.038

[a] Unique data collected at *ca.* 297 K on an ENRAF-Nonius CAD 4 instrument; graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107_3$ Å); statistical weights; anisotropic thermal parameters refined for all non-hydrogen atoms for absorption corrected 'observed' data, with $I > 2\sigma(I)$ [$I > 3\sigma(I)$ for (**4**)]; hydrogen atoms were inserted at calculated position and constrained, with isotropic thermal parameters at $1.25U_{eq}$ of the attached carbon. For (**3**), a full sphere was measured, $R_{int} = 0.10$, for (**4**) a further hemisphere within $2\theta_{max} = 40°$, $R_{int} = 0.022$.

Table 2 Selected bond distances (Å) and angles (°) of (**2**); primed atoms lie in the alternate half of the molecule (n = 1, 2)

As(n)–Cl(n)	2.228(2), 2.233(2)	As(n)–N(n2)	1.857(3), 1.854(3)
N(n2)–C(n2)	1.414(7), 1.393(7)	As(n)–N(n'2)	1.821(7), 1.809(3)
Cl(2)–As(1)–N(n2)	100.2(2), 100.2(2)	Cl(1)–As(2)–N(n2)	101.4(2), 99.0(2)
As(1)–N(n2)–As(2)	103.5(2), 103.2(2)	As(n)–N(n2)–C(n2)	131.5(7), 134.4(7)
N(12)–As(n)–N(22)	76.5(3) 76.8(3)	As(n')–N(n2)–C(n2)	123.6(7), 122.4(7)

Table 3 Selected bond distances (Å) and angles (°) of (**3**)

As(1)–Cl(11)	2.202(2)	As(1)–N(1)	2.361(7)
As(1)–Cl(12)	2.260(3)	As(1)–N(2)	1.883(8)
As(2)–Cl(21)	2.190(3)	As(2)–N(2)	1.808(9)
As(2)–Cl(22)	2.188(2)	N(1)–C(2)	1.35(1)
Cl(11)–As(1)–Cl(12)	94.3(1)	Cl(12)–As(1)–N(2)	91.5(2)
Cl(21)–As(2)–Cl(22)	96.4(1)	Cl(21)–As(2)–N(2)	98.7(2)
Cl(11)–As(1)–N(1)	89.2(2)	Cl(22)–As(2)–N(2)	99.3(2)
Cl(11)–As(1)–N(2)	99.1(2)	N(1)–As(1)–N(2)	63.0(3)
Cl(12)–As(1)–N(1)	154.5(2)	As(1)–N(2)–C(2)	103.0(6)

As–N bond distances are comparable to those in the dimeric arsenic amide complexes [{Bu^{t}NAsCl}$_2$][19] and [{[2,4,6-(CF_3)$_3$-C_6H_2]NAsCl}$_2$][20] of 1.819(4) and 1.865(3) Å, respectively, with differences in bond distances attributable to differences in the bulk of the ligands. The N(amide)–C bond distances in (**2**) are 1.393(7) and 1.414(7) Å. These lie between the usual values of 1.47 and 1.30 Å for single and double N–C bonds, and are also typical of single bond distances in aryl amines. The bond distances within the pyridyl moiety are usual, and comparable with those found in related complexes such as [6-MeR$_{py}$MCl$_2$] (M = P, As),[13] [(L$_{py}$)$_2$MCl] (M = Sb, Bi)[14] and [R$_{py}$SbCl$_2$].[11] In summary, the bonds associated with the ring core of the molecule are single bonds; delocalisation over the whole molecule is not found, but is, rather, restricted to the pyridyl substituents. The As–Cl bond distances of 2.228(2) and 2.233(2) Å are comparable to those in [6-MeR$_{py}$AsCl$_2$] at 2.189(2) and 2.327(1) Å.[13]

The arsenic centre is in a distorted pyramidal coordination environment with the Cl–As–N bond angles ranging from 99.0(2)–101.4(2)° and the N–As–N bond angles within the four membered ring being 76.5(3) and 76.8(3)°. The bond angles around the amide nitrogen centre sum to a value which is consistent with a planar sp^2 nitrogen centre (Σ(As–N–As,C) = $358._6$, 360°) although there is considerable deviation from the ideal trigonal 120° value with the As–N–As and As–N–C bond angles ranging between 103.2(2) and 103.5(2)° and 122.4(7) and 134.4(7)°, respectively.

Complex (**3**) crystallises as colourless prismatic crystals from hexane in the triclinic space group $P\bar{1}$ with the asymmetric unit consisting of one monomeric molecule (Fig. 2). The ligand is both bridging and chelating with the arsenic centres having three- and four-fold coordination. The chloride moieties are directed toward the same side of the molecule giving them a *syn* arrangement with respect to the plane of the molecule, so that the molecule is devoid of symmetry.

The As–N(amide) bond distances in (**3**) are 1.808(9) and 1.883(8) Å, with the longer distance being associated with the four-coordinate arsenic centre. These distances are comparable with those of (**2**). The As–N(pyridyl) distance in (**3**) is considerably longer at 2.361(7) Å. A relatively long As–N(pyridyl) bond was also observed in [MeR$_{py}$AsCl$_2$] (2.285(2) Å), resulting in a smaller bite angle of 63.0(3)° for the ligand in this study (*cf.* 65.8(1)° in [MeR$_{py}$AsCl$_2$]).[13] The As–Cl bond distances in (**3**) range from 2.188(2)–2.260(3) Å, depending on the coordination environment of the associated arsenic centre. These are comparable to bond distances of [MeR$_{py}$AsCl$_2$] (2.189(2) and 2.327(1) Å)[13] and the μ-bridging amido-complexes [{AsCl-[NPh(CF_3)$_3$-2,4,6]}$_2$][20] and [{AsCl(NBu^t)}$_2$][19] of 2.216(1) and 2.2181(1) Å, and 2.249(3) and 2.252(9) Å.

The coordination geometry about the four-coordinate arsenic centre can be described as distorted trigonal bipyramidal where the pyridyl nitrogen and Cl(11), which is close to the plane of the pyridyl ring, occupy axial positions, and N(2), Cl(12) and the lone pair of electrons occupy the equatorial sites (N(1)–As(1)–Cl(12) 154.5(2)°, Cl(12)–As(1)–N(2) 91.5(2)°, Cl(12)–

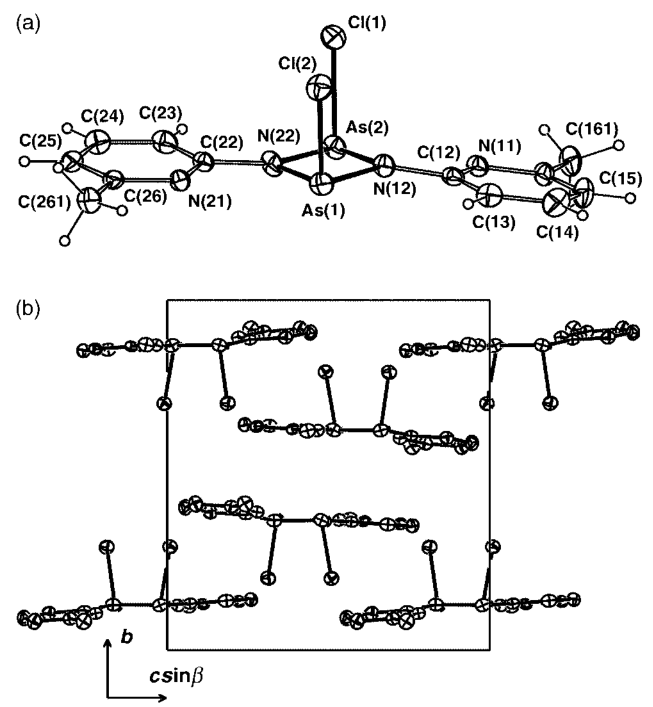


Fig. 1 (a) Molecular projection of $[\{2\text{-}(6\text{-Me})C_5H_3N\}NAsCl]_2$, (**2**), showing atom labelling scheme. Non-hydrogen thermal ellipsoids are drawn at the 20% probability level here and in subsequent figures, hydrogen atoms having arbitary radii of 0.1 Å. (b) The unit cell of (**2**) projected down *a*.

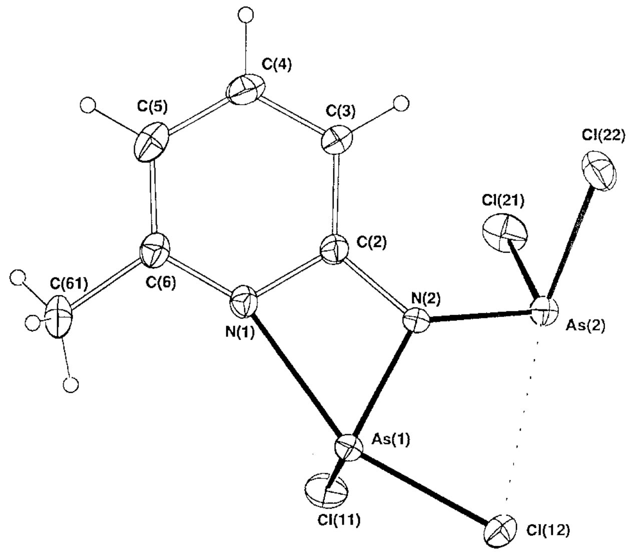
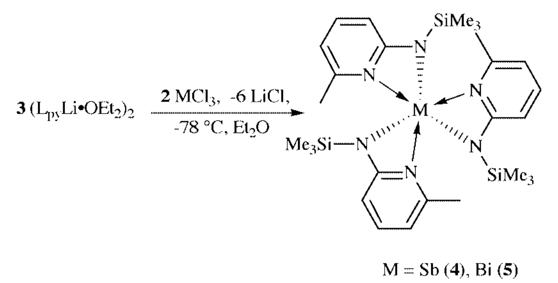


Fig 2 Molecular projection of $[\{2\text{-}(6\text{-Me})C_5H_3N\}N(AsCl_2)_2]$, (**3**), showing atom labelling scheme.

As(1)–Cl(1) 94.3(1)°, N(1)–As(1)–Cl(11) 89.2(2)°, N(2)–As(1)–Cl(11) 99.1(2)°). The three-coordinate arsenic centre has pyramidal coordination geometry where the lone pair of electrons occupy the vertex of the pyramid; the angles associated with the p-orbital bonding, lie close to 90° (Cl(21)–As(2)–Cl(22) 96.4(1)°, Cl(21)–As(2)–N(2) 98.7(2)° and N(2)–As(2)–Cl(22) 99.3(2)°). The geometry about N(2) is significantly distorted and can be attributed to the small bite angle of the ligand.

Trisubstituted antimony and bismuth amides

The trisubstituted antimony (**4**) and bismuth (**5**) amide complexes were prepared *via* metathetical exchange reactions between the metal trichloride and the lithiated parent amine $(L_{py}Li)_2$ in a 2 : 3 stoichiometric ratio, Scheme 3. The structures of the thermally stable, air and moisture sensitive complexes were confirmed using single crystal X-ray diffraction studies. Microanalysis of compound (**5**) was not possible due to the presence of an inseparable impurity. The thermal stabilities of these two compounds are markedly different to related antimony and bismuth alkyl complexes where the trialkyl complexes could not be formed. The attempted synthesis of $(R_{py})_3Bi$ from $BiCl_3$ and three equivalents of $R_{py}Li$ in THF results in the "head–to-tail" coupled dialkyl, $2\text{-}CH(SiMe_3)_2C_5H_3NR_{py}\text{-}5$, which is thought to arise from reductive coupling and/or nucleophilic attack of a coordinated R_{py} ligand followed by rearrangement.[11] The analogous diamido–metal chloride complexes have been reported.[14] These are also thermally stable complexes, unlike the analogous dialkyl complexes, $[R_{py}MCl]$. Treatment of $SbCl_3$ with two equivalents of the lithium R_{py} yields only an intractable oil accompanied with rapid loss of $ClSiMe_3$, while the analogous reaction with $BiCl_3$ results in a red crystalline solid which decomposes at 0 °C to (*E*)-$[BiR_{py}\text{-}(CH_2CH{=}C)(SiMe_3)(C_5H_4N\text{-}2)]$.[11]



Scheme 3 Preparation of triamido–Group 15 complexes (**4**) and (**5**).

Both the ^1H and ^{13}C NMR spectra of (**4**) show a second set of resonances in d_6-benzene with chemical shifts of the two species being typical for both the pyridyl protons and the Me groups. In d_8-toluene, only one species is seen in solution in the ^1H NMR spectrum at room temperature and no other species were seen in the temperature range of −63 to 67 °C. Variation of the concentration of (**4**) in deuterated benzene showed there was a concentration dependent relationship between the two species in solution. It is possible that a benzene molecule may coordinate to the metal centre through π-interactions between the aromatic ring and the lone pair of electrons of the metal, a type of interaction which has previously been structurally elucidated for both antimony and bismuth.[8,9] It is also possible that oligomers of the complex exist in solution through either the π-interactions as described above involving the aryl rings of the pyridyl substituents or by other means. This, however, was not accessible through variable temperature and variable concentration NMR studies. A similar situation was evident in the ^1H NMR spectra of (**5**).

Crystal structures of (4) and (5). Crystallographic data of (**4**) and (**5**) are listed in Table 1, and important bond distances and angles are listed in Table 4. Both compounds crystallise as colourless and yellow prismatic crystals, respectively, in the triclinic space group $P\bar{1}$ and are isostructural. The asymmetric unit for both compounds consists of one monomeric molecule with pseudo C_3 symmetry, Fig. 3. The amido-centres bind to the metal centre and the ligand chelates through the pyridyl nitrogen to give the metal a six-coordinate octahedral environment with the amido-centres *fac*, distorted, perhaps, because of a stereochemically active lone pair of electrons on the metal, together with the steric constraints of the ligand. This gives the molecules overall propeller-like structures with the lone pair of electrons pointing toward the $[N(pyr)]_3M$ face.

The Sb–N(amide) bond distances of (**4**) range from 2.159(3) to 2.167(3) Å (av. 2.16_3 Å). These are longer than those of the triamido–stibine $[Sb\{N(H)(C_6H_2Bu^t_3\text{-}2,4,6)\}_3]$ of 2.041(6)–2.064(6) Å, which have been described as typical for Sb–N(amide) covalent bonds.[21] The difference in bond distances

Table 4 Selected bond distances (Å) and angles (°) of (**4**) and (**5**)

	1		2		3		Average	
Ligand	**4**	**5**	**4**	**5**	**4**	**5**	**4**	**5**
M–N(*n*1)	2.604(4)	2.632(6)	2.595(4)	2.623(8)	2.620(3)	2.641(6)	2.60_6	2.63_2
M–N(*n*2)	2.163(4)	2.298(3)	2.159(3)	2.285(6)	2.167(3)	2.284(5)	2.16_3	2.28_9
N(*n*2)–Si(*n*)	1.755(4)	1.736(6)	1.757(3)	1.750(7)	1.759(4)	1.763(6)	1.75_9	1.75
N(*n*1)–M–N(*n*2)	56.2(1)	55.3(2)	56.3(1)	55.0(2)	56.1(1)	54.4(2)	$56._2$	$54._9$
N(*n*1)–M–N(*n* + 1,1)	118.6(6)	118.4(2)	114.7(1)	114.8(2)	119.3(1)	119.9(2)	$117._5$	$117._7$
N(*n*1)–M–N(*n* + 1,2)	83.8(1)	84,6(2)	83.0(2)	83.6(2)	84.8(1)	85.5(2)	$83._9$	$84._6$
N(*n*1)–M–N(*n* − 1,2)	152.9(1)	152.8(2)	155.1(1)	154.6(2)	153.1(1)	151.9(2)	$153._7$	$153._1$
N(*n*2)–M–N(*n* + 1,2)	99.3(1)	99.8(2)	97.1(1)	97.5(2)	97.1(1)	97.8(2)	$97._8$	$98._4$
Metal deviations from planes (Å)								
δM(C$_5$N(ar))	0.564(6)	0.47(1)	0.636(6)	0.52(1)	0.612(6)	0.49(1)	0.60	0.49
Torsion angles (M-N(*n*2)–Si(*n*)–C(*n*23) (°)								
τ	−30.8(3)	−28.3(6)	−30.0(2)	−29.2(5)	−27.2(3)	−23.7(7)	−29	−27

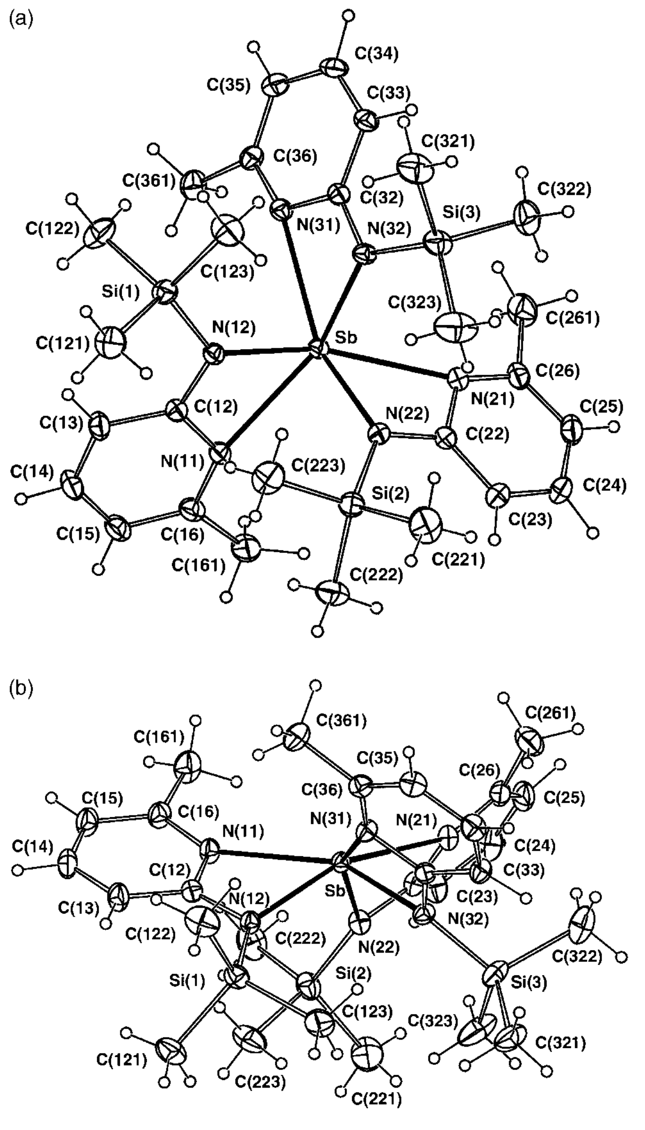


Fig. 3 Molecular projection of [{2-(6-Me)C$_5$H$_3$N}NSiMe$_3$]$_3$Sb, (**4**) ((**5**) is isostructural) projected down (a) and normal to (b) the non-crystallographic C_3 axis, showing atom labelling scheme.

can be attributed to the increased coordination number of antimony in (**4**). The Sb–N(amide) distances are also longer than those of [(L$_{py}$)$_2$SbCl] 2.095(8)–2.127(8) Å,[14] and the cyclic [Me$_2$Si(NBu^t)$_2$SbCl] 1.995(6) Å,[22] in accordance with an increase of the coordination number at the antimony centre.

The Sb–N(pyridyl) bond distances of 2.595(4)–2.620(3) Å (av. 2.60_6 Å) are substantially longer than the Sb–N(amide) bonds as expected, but are shorter than those found in the complex [Sb(2-SC$_5$H$_4$N)$_3$] of 2.837(3) Å.[6] The N–Si bond distances of 1.755(4)–1.759(4) Å (av. 1.75_9 Å) are more similar to those of [Me$_2$Si(NBu^t)$_2$SbCl] which are 1.737(6) Å,[22] and [(L$_{py}$)$_2$SbCl] of 1.735(9)–1.757(8) Å,[14] longer than the N–Si bond distances of [(L$_{py}$Li·Et$_2$O)$_2$] (1.705(5) Å),[23] consistent with the largely covalent nature of the Sb–N bond placing minimal electronic charge density on the nitrogen centre and that increasing the coordination number of the antimony centre has little effect on this covalency.

The N(amide)–Sb–N(amide) bond angles of 97.1(1)–99.3(1)° (av. $97._8$°) are greater than 90° for ideal octahedral coordination which can be attributed to the acute bite angles of the ligands of 56.1(1)–56.3(1)° (av. $56._2$°) as well as to the effect that any lone pair of electrons on the antimony centre would have on the orientation of the pyridyl rings which chelate *cis* to that site, resulting in larger N(pyridyl)–Sb–N(pyridyl) bond angles of 114.7(1)–119.3(1)°.

The packing diagram of (**4**) shows that there are no intermolecular associations within the crystal due to π-interactions between the pyridyl groups of the molecules and the lone pair of electrons of another molecule which has been observed for [Sb(SC$_6$H$_3$Me$_2$-2,6)$_3$] where the Sb–ring centroid distance is 3.28_5 Å.[24]

The Bi–N(amide) bond distances in (**5**) range from 2.284(5)–2.298(3) Å (av. 2.28_9 Å), and may be compared to the Bi–N bond distances of [Bi(NMe$_2$)$_3$] (2.180(21)–2.189(18) Å),[7] and the more bulky complex [Bi{NH(C$_6$H$_2$Bu^t-2,4,6)}$_3$] (2.14(2)–2.21(13) Å).[21] The longer distances of (**5**) correlate with the steric demands of the ligand and the coordination number at the bismuth centres which increases from three to six. The Bi–N(pyridyl) bond distances of 2.623(8)–2.641(6) Å (av. 2.63_2 Å) are considerably longer than the Bi–N(amide) bond distances, consistent with the Bi–N(pyridyl) dative bond, and are comparable to those of [(L$_{py}$)$_2$BiCl]$_2$ of 2.49(1) and 2.60(1) Å where the differences in lengths can be attributed to increased steric hindrance around the bismuth centre.[14] The average difference in the amido– and dative pyridyl Bi–N bond lengths of 0.34 Å are considerably smaller than the average difference in the same Sb–N bond distances of 0.44 Å due to the more Lewis acidic bismuth centre having a stronger interaction with the Lewis basic pyridyl nitrogen centres, a trend which has also been found in the diamido complexes.[14] Again, the N–Si bond distances in (**5**) of 1.736(6)–1.763(6) Å (av. 1.75 Å) are consistent with the covalent nature of the Bi–N(amide) bond.

The distortions from octahedral geometry of the bismuth centre for (**5**) have the same consequences as for (**4**). In (**5**) the bite angles of the ligands are 54.4(2)–55.3(2)°. These acute bond angles and the presence of the stereochemically active lone pair of electrons results in larger N(amide)–Bi–N(amide) bond angles of 97.5(2)–99.8(2)° and N(pyridyl)–Bi–N(pyridyl) bond angles of 114.8(2)–119.9(2)°.

Conclusions

We have been able to prepare and characterise an amido–arsenic dichloride compound from the reaction of $(L_{py}Li)_2$ and $AsCl_3$, which can undergo further reaction *via* the elimination of Me_3SiCl to form a dimeric geminal amido–arsine, (**2**). An arsine rich geminal amido–arsine, (**3**), can be prepared from the reaction of $(L_{py}Li)_2$ and four equivalents of $AsCl_3$ *via* the elimination of LiCl and Me_3SiCl. This compound can also be prepared through the redistribution reaction of (**2**) with two equivalents of $AsCl_3$ indicating that the As_2N_2 ring can easily be disrupted, which is of interest for the possible synthesis of bimetallic complexes that may have potential as single source precursors for thin films prepared from MOCVD processes. These complexes have increased thermal and kinetic stability compared to their alkyl analogues featuring the (R_{py}) and (MeR_{py}) ligands, with (**2**) and (**3**) being the first isolated and characterised decomposition products of this series through the loss of Me_3SiCl by N–Si bond cleavage. Structural studies of (**2**) and (**3**) indicate that all As–N(amide) bonds are single bonds and that any delocalisation within the molecules is restricted to the pyridyl ring. The *syn* structure of (**2**) is consistent the proposed [2 + 2] cycloaddition mechanism for this reaction.

Triamido–antimony, (**4**), and –bismuth, (**5**), complexes have also been prepared and structurally characterised from the reaction of three equivalents of $(L_{py}Li)_2$ with two equivalents of MCl_3 (M = Sb, Bi). Again, this is in contrast to the analogous alkyl complexes where no trialkyl–metal complexes have been isolated and fully characterised due to rapid decomposition, most probably through the loss of Me_3SiCl again. The analogous triamido–arsenic complex has not been isolated probably due to the smaller covalent radii of arsenic compared to antimony and bismuth and the steric bulk of the ligand.

Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. Solvents were dried over NaK alloy under nitrogen before use. The aryl amide $\{2\text{-}(6\text{-}Me)C_5H_3N\}NHSiMe_3$, $(L_{py}Li\cdot OEt_2)_2$,[23] and the arsenic amide, $[\{2\text{-}(6\text{-}Me)C_5H_3N\}NAsCl]_2$, (**2**),[15] were prepared according to literature procedures, Bu^{n}Li was obtained from Metallgesellschaft AG, Germany, as a 1.60 M solution in hexane, being standardised prior to use. All other reagents were obtained from Aldrich. $AsCl_3$ was purified by distillation while $SbCl_3$ and $BiCl_3$ were purified by sublimation before use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC200 or AM300 spectrometer operating at 200 MHz and 300 MHz (^1H) and 50.3 MHz and 75.5 MHz ($^{13}C\{^1H\}$), respectively, using broad band proton decoupling, in deuterated benzene and referenced to the residual resonances of the solvent (δ 7.15 and 128.0, respectively). The Chemical and Micro Analytical Services Pty. Ltd., Melbourne, performed the elemental microanalyses. Melting points were determined in sealed glass capillaries under vacuum and are uncorrected.

Synthesis

$[\{2\text{-}(6\text{-}Me)C_5H_3N\}NSiMe_3(AsCl_2)]$. A colourless solution of $[\{2\text{-}(6\text{-}Me)C_5H_3N\}NSiMe_3Li]_2$ (0.51 g, 1.37 mmol) in Et_2O (*ca.* 20 ml) was slowly added to a colourless solution of $AsCl_3$ (0.25 ml, 2.97 mmol) in Et_2O (*ca.* 20 ml) at −78 °C. The solution was allowed to warm to ambient temperature and a white precipitate formed. The mixture was allowed to stir for 17 hours whereupon the Et_2O was removed *in vacuo* and hexane was added and the mixture filtered. Recrystallisation from hexane (*ca.* 10 ml) at −30 °C afforded prismatic crystals (0.51 g, 73%). mp 146–149 °C; ^1H NMR (200 MHz, C_6D_6) δ 7.02 (1H, dd, $^3J_{H\text{-}H}$ 8.40 Hz, 7.21 Hz, *p*-C*H*), 6.56 (1H, d, $^3J_{H\text{-}H}$ 8.45 Hz, *o*-C*H*), 6.15 (1H, d, $^3J_{H\text{-}H}$ 7.19 Hz, *o*-C*H*), 2.03 (3H, s, CH_3), 0.42 (9H, s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6) δ 169.0, 154.7, 137.7, 111.6, 111.3 (C_5H_3N), 23.1 (CH_3), 3.0 ($SiCH_3$); found C 33.45, H 4.62, N 9.01%, calc for $C_9H_{15}N_2SiAsCl_2$ C 33.25, H 4.65, N 8.62%.

$[\{2\text{-}(6\text{-}Me)C_5H_3N\}N(AsCl_2)_2]$. *Method 1.* Bu^{n}Li (2.05 ml of a 1.30 M hexane solution) was added dropwise to a colourless solution of $\{2\text{-}(6\text{-}Me)C_5H_3N\}NHSiMe_3$ (0.52 g, 2.88 mmol) in Et_2O (*ca.* 30 ml) at −78 °C. The solution was allowed to warm to ambient temperature and allowed to stir for 2 hours. The resulting yellow solution was added dropwise to a colourless solution of $AsCl_3$ (0.48 ml, 5.72 mmol) in Et_2O (*ca.* 20 ml) at −78 °C. The solution was allowed to warm to ambient temperature and a white precipitate formed. The mixture was allowed to stir for 13 hours whereupon the Et_2O was removed *in vacuo* and hexane added and the mixture filtered. Recrystallisation in hexane (*ca.* 10 ml) by slow cooling from 50 °C afforded colourless prismatic crystals (0.46 g, 34%). Mp 94–95 °C; ^1H NMR (300 MHz, C_6D_6) δ 7.30 (1H, dd, $^3J_{H\text{-}H}$ 7.5 Hz, *p*-C*H*), 6.80 (1H, m, *o*-C*H*), 6.02 (1H, d, $^3J_{H\text{-}H}$ 7.8 Hz, *o*-C*H*), 1.79 (3H, s, CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ 155.9, 139.7, 138.7, 117.5, 111.3 (C_5H_3N), 16.4 (CH_3); found C 18.52, H 1.43, N 7.04%, calc for $C_6H_6N_2As_2Cl_4$ C 18.12, H 1.52. N 7.75%.

Method 2. $AsCl_3$ (0.14 ml, 1.66 mmol) was gradually added to a colourless solution of (**2**) (0.48 g, 0.83 mmol) in toluene (*ca.* 40 ml) at ambient temperature. The mixture was allowed to stir for 2 days whereupon it was filtered and the volume reduced *in vacuo*. Recrystallisation from toluene (*ca.* 20 ml) at 25 °C afforded colourless prismatic crystals (0.48 g, 89%).

$[\{2\text{-}(6\text{-}Me)C_5H_3N\}NSiMe_3]_3Sb$. Bu^{n}Li (3.00 ml of a 1.60 M hexane solution) was added dropwise to a colourless solution of $\{2\text{-}(6\text{-}Me)C_5H_3N\}NHSiMe_3$ (0.86 g, 4.77 mmol) in Et_2O (*ca.* 30 ml) at −78 °C. The solution was allowed to warm to ambient temperature and allowed to stir for 2 hours. The resulting yellow solution was added dropwise to a colourless solution of $SbCl_3$ (0.37 ml, 1.62 mmol) in Et_2O (*ca.* 20 ml) at −78 °C. The solution was allowed to warm to ambient temperature and a white pecipitate formed. The mixture was allowed to stir for 16 hours whereupon the Et_2O was removed *in vacuo* and hexane added and the mixture filtered. Recrystallisation in hexane (*ca.* 10 ml) at −30 °C afforded colourless prismatic crystals (0.53 g, 51%). ^1H NMR (major component) (200 MHz, C_6D_6) δ 7.04–5.84 (3H, m, C_5H_3N), 1.74 (3H, s, CH_3), 0.22 (9H, s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (major component) (50.3 MHz, C_6D_6) δ 159.7, 156.9, 137.5, 112.2, 106.7 (C_5H_3N), 24.3 (CH_3), 0.17 ($SiCH_3$); found C 43.88, H 6.79, N 12.74%, calc for $C_{27}H_{45}N_6SbSi_3$ C 49.16, H 6.88. N 11.15%.

$[\{2\text{-}(6\text{-}Me)C_5H_3N\}NSiMe_3]_3Bi$. As above procedure using $BiCl_3$ (yield 48%). ^1H NMR (major component) (200 MHz, C_6D_6) δ 7.14–6.04 (3H, m, C_5H_3N), 1.82 (3H, s, CH_3), 0.21 (9H, s, $Si(CH_3)_3$).

Crystallography

Crystallographic data for (**2**), (**3**), (**4**) and (**5**) are listed in Table 1.

CCDC reference number 186/1858.

See http://www.rsc.org/suppdata/dt/a9/a909338i/ for crystallographic files in .cif format.

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