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Use of the 2,6-bis[(dimethylamino)methyl]phenyl ligand to form some pentacoordinate derivatives of P(III), As(III), Sb(III) and Bi(III)

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Abstract

Reaction of Li[2,6-$(Me_2NCH_2)_2C_6H_3$] with ECl_3 results in the chelated dichlorides, [2,6-$(Me_2NCH_2)_2C_6H_3$]ECl_2 (E = P (**1**), As (**2**), Sb (**3**), Bi (**4**)). Compounds **1** and **2** are converted into the corresponding EH_2 derivatives, [2,6-$(Me_2NCH_2)_2C_6H_3$]EH_2 (E = P (**5**), As (**6**)) by reduction with $LiAlH_4$. The structure of **3** has been determined by X-ray crystallography. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.135(1)$, $b = 8.620(1)$, $c = 16.245(2)$ Å, $\beta = 95.87(1)°$, $V = 1551(2)$ Å^3 and $Z = 4$. The geometry at Sb is distorted square pyramidal.

Introduction

Considerable recent emphasis has been placed on the stabilization of main-group fragments in unusual environments. In particular, much progress has been made by the attachment of bulky groups to the main-group element or to a neighboring site [1]. However, in many cases the requisite steric blockade substantially modifies or even inhibits reactivity at the main-group center. Chelation represents an alternative approach to the generation of novel main-group element bonding modes. In the context of transition metal chemistry, van Koten and co-workers have discovered that the potentially tridentate ligand [2,6-$(Me_2NCH_2)_2C_6H_3$]$^-$ is very useful for the stabilization of unusual oxidation states and for the isolation of reactive intermediates [2]. However, very little use has been made of this ligand in main-group chemistry, examples being confined to Li [3], Sn [3, 4], Ga [5, 6] and In [6, 7]. We report the first examples of Group 15 complexes that feature this ligand. The structure of the antimony derivative, [2,6-$(Me_2NCH_2)_2C_6H_3$]$SbCl_2$, was determined by X-ray crystallography.

Experimental

General procedure

All experiments were performed under a dry, oxygen-free dinitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. The Group 15 trichlorides and $LiAlH_4$ were procured commercially and used as supplied. The lithium reagent Li[2,6-$(Me_2NCH_2)_2C_6H_3$] was prepared according to the literature method [3]. All solvents were freshly distilled over appropriate drying agents immediately prior to use. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a General Electric QE 300 instrument operating at 300, 75.5 and 121.5 MHz, respectively. ^{1}H and ^{13}C NMR spectra were referenced to Me_4Si (0.0 ppm) and ^{31}P spectra to external 85% H_3PO_4, positive values to high field in each case. Mass spectra were recorded on Du Pont Consolidated 21-491 and 21-100 spectrometers. The latter was used for high-resolution mass spectra (HRMS).

2,6-Bis[(dimethylamino)methyl]phenyldichlorophosphine, [2,6-$(Me_2NCH_2)_2C_6H_3$]PCl_2 (1)

A freshly prepared Et_2O solution of Li[2,6-$(Me_2NCH_2)_2C_6H_3$] (7.5 mmol) was added dropwise via cannula to a cooled (−78 °C) solution of 1.01 g (7.38 mmol) of PCl_3 in 50 ml of Et_2O. The reaction mixture was allowed to warm to 25 °C and was stirred for a further 12 h at this temperature. Following filtration of the reaction mixture, the resulting white, solid residue was recrystallized from CH_2Cl_2. Colorless, microcrystalline **1** (m.p. 156 °C, decomp.) was isolated in 55.4% yield (1.2 g, 4.09 mmol). HRMS: Calc. for $C_{12}H_{19}Cl_2N_2P$, *m/z* 292.06627. Found, 292.06639. ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 7.55 (1H, t, C_6H_3), 7.36 (2H, d, C_6H_3), 4.37 (4H, s, CH_2N) 2.83 (6H, s, NCH_3) 2.82 (6H, s, NCH_3). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ: 141.80, 134.20, 125.02

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(aryl), 130.7 (d, ^1J(PC) 33.0 Hz, C1), 63.41 (s, CH_2N), 63.36 (s, CH_2N), 46.30 (s, NCH_3), 46.10 (s, NCH_3). ^{31}P NMR (121.5 MHz, CD_2Cl_2) δ: 131.95 (s).

2,6-Bis[(dimethylamino)methyl]phenyldichloroarsine, [2,6-($Me_2NCH_2)_2C_6H_3]AsCl_2$ (2)

The reaction of 7.5 mmol of Li[2,6-$(Me_2NCH_2)_2C_6H_3$] with 1.34 g (7.38 mmol) of $AsCl_3$ in Et_2O solution was carried out as described above for **1**. After completion of the reaction, the solvent and volatiles were removed by evacuation and the resulting residue was recrystallized from toluene to afford a 52% yield (1.30 g, 3.86 mmol) of colorless microcrystalline **2** (m.p. 203 °C, decomp.) HRMS: Calc. for $C_{12}H_{19}AsCl_2N_2$, *m/z* 337.021950. Found, 337.018216. ^1H NMR (300 MHz, CD_2Cl_2) δ: 7.02 (1H, t, C_6H_3), 6.73 (2H, d, C_6H_3), 3.65 (4H, s, CH_2N), 2.44 (12H, s, NCH_3). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ: 149.92, 141.77, 129.36, 123.98 (aryl), 62.76 (br s, CH_2N), 47.08 (s, NCH_3), 47.01 (s, NCH_3).

2,6-Bis[(dimethylamino)methyl]phenyldichlorostibine, [2,6-($Me_2NCH_2)_2C_6H_3]SbCl_2$ (3)

The reaction of 7.5 mmol of Li[2,6-$(Me_2NCH_2)_2C_6H_3$] with 1.68 g (7.38 mmol) of $SbCl_3$ in Et_2O solution was carried out as described above for **1**. After completion of the reaction, the solvent and volatiles were removed by evacuation and the resulting residue was recrystallized from toluene to afford a 56% yield (1.60 g, 4.1 mmol) of colorless, crystalline **3** (m.p. 210 °C, decomp.) HRMS: Calc. for $C_{12}H_{19}Cl_2N_2Sb$, *m/z* 381.996. Found, 381.994. ^1H NMR (300 MHz, C_6D_6) δ: 7.10 (1H, t, C_6H_3), 6.81 (2H, d, C_6H_3), 3.63 (4H, s, CH_2N), 2.31 (12H, s, NCH_3). ^{13}C NMR (75.5 MHz, C_6D_6) δ: 143.17, 129.05, 124.62 (aryl), 63.68 (s, CH_2N), 46.26 (s, NCH_3).

2,6-Bis[(dimethylamino)methyl]phenyldichlorobismuthine, [2,6-($Me_2NCH_2)_2C_6H_3]BiCl_2$ (4)

The reaction of 7.5 mmol of Li[2,6-$(Me_2NCH_2)_2C_6H_3$] with 2.33 g (7.38 mmol) of $BiCl_3$ in Et_2O solution was carried out as described above for **1**. After completion of the reaction, the solvent and volatiles were removed by evacuation and the resulting residue was extracted with C_6H_6 for 24 h in a Soxhlet apparatus. Removal of the C_6H_6 left a 39% yield (1.35 g, 2.89 mmol) of colorless, microcrystalline **4** (m.p. 250 °C, decomp.). HRMS: Calc. for $C_{12}H_{19}BiCl_2N_2$, *m/z* 470.07292. Found, 470.07290. ^1H NMR (300 MHz, CD_2Cl_2) δ: 7.58 (3H, m. C_6H_3), 4.46 (4H, s, CH_2N), 2.91 (12H, s, NCH_3). ^{13}C NMR (75.5 MHz, CD_2Cl_2) 152.13, 129.71, 128.68 (aryl), 68.24 (s, CH_2N), 47.08 (s, NCH_3).

2,6-Bis[(dimethylamino)methyl]phenylphosphine, [2,6-($Me_2NCH_2)_2C_6H_3]PH_2$ (5)

A solution of 2.93 g (10.0 mmol) of **1** in 30 ml of Et_2O was added dropwise via cannula to a suspension of 0.948 g (25.0 mmol) of $LiAlH_4$ in 40 ml of Et_2O at 0 °C. After the reaction mixture had been stirred for 12 h, the excess $LiAlH_4$ was destroyed by the slow addition of 40 ml of cold distilled water. The organic layer was separated and dried over anhydrous $MgSO_4$. After filtration and evacuation of the solvent, the resulting liquid was vacuum distilled (b.p. 100 °C/76 torr) to afford colorless liquid **5** in 58% yield (1.3 g, 5.8 mmol). HRMS: Calc. for $C_{12}H_{21}N_2P$, *m/z* 224.1442. Found, 224.1443. ^1H NMR (300 MHz, CD_2Cl_2) δ: 7.18 (3H, m, C_6H_3), 3.76 (2H, d, ^1J(PH) 206 Hz), 3.47 (4H, s, CH_2N), 2.21 (12H, s, NCH_3). ^{13}C NMR (75.5 MHz, CD_2Cl_2), 142.03, 128.03, 125.90 (aryl), 64.39 (s, CH_2N), 44.17 (s, NCH_3). ^{31}P NMR (121.5 MHz, CD_2Cl_2) δ: −146 (t, ^1J(PH) 206 Hz).

2,6-Bis[(dimethylamino)methyl]phenylarsine, [2,6-($Me_2NCH_2)_2C_6H_3]AsH_2$ (6)

The reaction of 3.37 g (10.0 mmol) of **2** with 0.948 g (25.0 mmol) of $LiAlH_4$ in Et_2O solution was carried out as described above for **5**. Colorless liquid **6** (b.p. 110 °C/10^{-3} torr) (m.p. 30 °C) was obtained in 68% yield (1.82 g, 6.8 mmol). HRMS: Calc. for $C_{12}H_{21}AsN_2$, *m/z* 268.09206. Found, 268.09209. ^1H NMR (300 MHz,

TABLE 1. Crystallographic data for [2,6-$(Me_2NCH_2)_2C_6H_3]SbCl_2$ (3)

Formula	$C_{12}H_{19}Cl_2N_2Sb$
Molecular weight	383.77
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	11.135(1)
b (Å)	8.620(1)
c (Å)	16.245(2)
α (°)	90
β (°)	95.87(1)
γ (°)	90
V (Å^3)	1551(2)
Z	4
F(000)	832
Crystal size (mm)	0.4×0.4×0.4
Monochromator	graphite
Radiation	Mo Kα (0.71069 Å)
D_{calc} (g cm^{-3})	1.647
Temperature (K)	298
2θ Range (°)	2–40 (h, k, $\pm l$)
No. reflections measured	2619
No. reflections with $I > 6.0\sigma(I)$	2599
Linear absorption coefficient (cm^{-1})	21.28
Transmission factors (%)	
max.	98.15
min.	76.07
Crystal decay (%)	<2
Absorption correction	empirical
R	0.0609
R_w	0.0683
Goodness of fit	3.91
No. parameters	154

TABLE 2. Positional parameters for $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]SbCl_2$ (**3**) with e.s.d.s in parentheses

Atom	x/a	y/b	z/c	U_{eq}
Sb	0.21947(6)	0.43379(8)	0.09473(4)	0.032(4)
Cl(1)	0.3765(3)	0.2111(4)	0.1066(2)	0.060(9)
Cl(2)	0.0670(3)	0.6613(4)	0.0994(2)	0.058(7)
N(1)	0.3773(9)	0.634(1)	0.1317(6)	0.048(3)
N(2)	0.0835(8)	0.243(1)	0.1430(5)	0.039(6)
C(1)	0.2441(8)	0.243(1)	0.1430(5)	0.039(6)
C(1)	0.2441(8)	0.449(1)	0.2244(5)	0.031(2)
C(2)	0.2019(9)	0.328(1)	0.2717(6)	0.036(5)
C(3)	0.221(1)	0.334(1)	0.3580(6)	0.046(10)
C(4)	0.283(1)	0.457(2)	0.3949(7)	0.056(24)
C(5)	0.3262(9)	0.577(2)	0.3480(6)	0.048(12)
C(6)	0.3070(9)	0.574(1)	0.2624(6)	0.037(1)
C(7)	0.347(1)	0.703(1)	0.2106(7)	0.051(17)
C(8)	0.500(1)	0.564(2)	0.1408(8)	0.068(31)
C(9)	0.370(1)	0.765(1)	0.0626(8)	0.075(30)
C(10)	0.142(1)	0.187(1)	0.2270(6)	0.048(15)
C(11)	−0.037(1)	0.314(1)	0.1502(8)	0.057(24)
C(12)	0.072(1)	0.100(1)	0.0829(8)	0.059(25)

TABLE 3. Selected bond distances (Å) and bond angles (°) for $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]SbCl_2$ (**3**) with e.s.d.s in parentheses

Distances	
Sb–Cl(1)	2.591(3)
Sb–N(1)	2.491(9)
Sb–C(1)	2.100(9)
Sb–Cl(2)	2.600(3)
Sb–N(2)	2.422(8)
Angles	
Cl(1)–Sb–Cl(1)	174.0(1)
Cl(2)–Sb–N(1)	85.3(2)
Cl(2)–Sb–N(2)	94.1(2)
Cl(1)–Sb–C(1)	87.4(3)
N(1)–Sb–C(1)	72.4(3)
Sb–N(1)–C(7)	105.7(6)
Cl(1)–Sb–N(1)	92.3(2)
Cl(1)–Sb–N(2)	84.9(2)
N(1)–Sb–N(2)	147.3(3)
C(2)–Sb–C(1)	86.6(3)
N(2)–Sb–C(1)	74.9(3)

C_6D_6) δ: 7.14 (3H, br, C_6H_3), 3.64 (2H, s, AsH_2), 3.44 (4H, s CH_2N), 2.10 (12H, s, CH_3N). ^{13}C NMR (75.5 MHz, C_6D_6), 143.47, 136.92, 127.72, 125.94 (aryl), 65.52 (s, CH_2N), 43.53 (s, NCH_3).

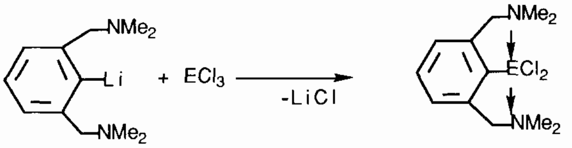
X-ray analysis of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]SbCl_2$ (3)

A colorless, cubic crystal of **3** was sealed in a Lindemann capillary and mounted on an Enraf-Nonius CAD4 diffractometer. Initial lattice parameters were determined from a least-squares fit to 25 accurately centered reflections $15 \leqslant 2\theta \leqslant 25°$ and subsequently refined using higher angle data. These indicated a monoclinic lattice. The data were collected over the following ranges: *h*, 0 to +12; *k*, 0 to +9; *l*, −17 to +17. The final scan speed for each reflection was determined from the net intensity gathered in an initial prescan and ranged from 2 to 7° min^{-1}. The ω-scan angle and aperture settings were determined as described previously [8]. Crystal stability and orientation were monitored periodically throughout data collection by means of two check reflections. The data were corrected for the effects of Lorentz, polarization and absorption (empirical). Pertinent data collection and structure refinement details are summarized in Table 1.

The position of the Sb atom was determined from a Patterson map and subsequent difference Fourier maps revealed the locations of all non-hydrogen atoms. The hydrogen atoms were place in calculated positions and were not refined. The final refinement converged smoothly to give the residuals shown in Table 1. The weighting scheme employed was $w = ((\sigma F)^2 + 0.000625F^2)^{-1}$. The positional parameters for **3** are listed in Table 2 and a selection of bond distances and angles appears in Table 3.

Results and discussion

The dichlorides $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]ECl_2$ (E = P (**1**), As (**2**). Sb (**3**), Bi (**4**)) represent the first Group 15 complexes of the 2,6-bis[(dialkylamino)methyl]phenyl ligand system. Colorless solids **1**–**4** were prepared in 39–56% yields via the metathetical reaction of $Li[2,6\text{-}(Me_2NCH_2)_2C_6H_3]$ with the appropriate element trihalide in Et_2O solution at −78 °C (eqn.(1)).



(1)

E=P (**1**), As (**2**), Sb (**3**), Bi (**4**).

The overall compositions of **1**–**4** were established on the basis of high-resolution mass spectral data. The NMR data for these dichlorides (see 'Experimental') are suggestive of a structure in which the $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]$ ligand is bonded in a tridentate fashion. However, only the Sb derivative **3** proved to be suitable for X-ray analysis. The solid state of **3** consists of individual molecules and there are no short intermolecular contacts. The geometry at Sb is best described as distorted square pyramidal (Fig. 1). Although the Cl(1)–Sb–Cl(2) angle (174.0(1)°) is close to the ideal angle of 180°, the N(1)–Sb–N(2) angle is significantly more acute (147.3(3)°), doubtless due to the incorporation of N(1) and N(2) into five-membered rings (Fig. 2). The closest structural analogue of **3** is the anion $[PhSbCl_4]^{2-}$ (**6**) [9]. Like the Bi(III) halide complexes $[Ph_2Bi_2I_6]^{2-}$ and $[PhBiBr_2(THF)]_x$ [10], **6**

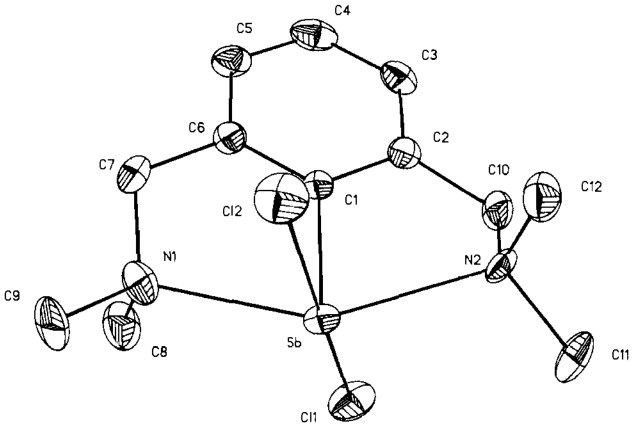


Fig. 1. View (ORTEP) of 3 showing the atom numbering scheme.

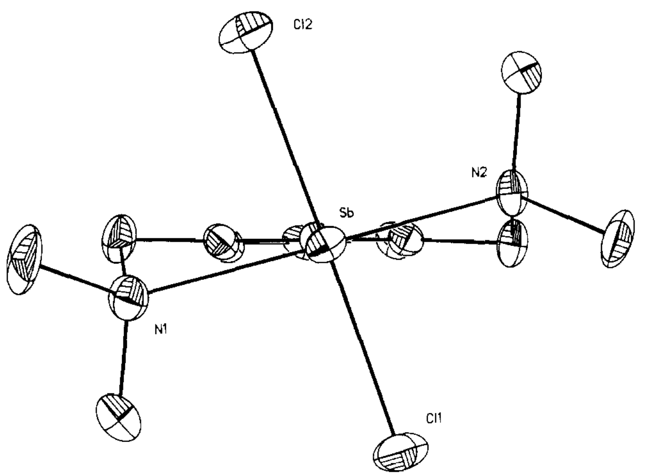


Fig. 2. View of 3 down the Sb–C(1) axis.

possesses a square pyramidal structure. The structure of **6** is slightly complicated by the hydrogen bonding of two of the chlorides to the gegenion; however, the Sb–Cl bond distances for the two non-hydrogen-bonded chlorides in **6** (2.537(3) and 2.591(3) Å) [9] are quite similar to those in **3** (2.591(3) and 2.600(3) Å). There are rather few Sb–N bond distances cited in the literature. In $Ph_3Sb(NCO)_2$ the Sb–N bond distance of 2.123(4) Å is close to the sum of single bond covalent radii [11] while in the Sb(III) amine complex $Cl_3Sb \cdot NH_2Ph$ this bond distance is unusually long (2.525(44) Å) [12]. The Sb–N bond distances in **3** are also long (2.491(9) and 2.422(8) Å) and thus consistent with the idea of internal solvation by the amine groups. Note that if the amines are omitted from the coordination sphere, the residual $(aryl)SbCl_2$ moiety possesses a T-shaped geometry. Finally, since the stereochemical activity of Sb lone pairs is often not obvious [9] it is of interest to compare the Cl–E–Cl angle in **3** with that in $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaCl_2$ (111.01(8)°) [5]. In the case of **3**, therefore, the Sb lone pair appears to play an important stereochemical role.

The reaction of **1** and **2** with $LiAlH_4$ in Et_2O at 0 °C, followed by hydrolysis affords $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PH_2$ (**5**) and $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]AsH_2$ (**6**) in 58 and 68% yields, respectively. Both compounds are colorless, distillable liquids, above 30 °C.

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