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Synthesis and characterization of β-diketiminato complexes of antimony (III) halides

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Abstract

Treatment of SbX_3 (X = Br, Cl) with DippnacnacLi (Dippnacnac = $[\{N(C_6H_3{}^iPr_2 2,6)C(Me)\}_2CH]^-$) or Mesnacnac (Mesnacnac = $[\{N(Mes)C(Me)\}_2CH]^-$, Mes = 2,4,6, trimethyl benzene) affords different products that are dependent on the stoichiometry of the reaction and the halide precursor. When DippnacnacLi is reacted with $SbBr_3$, C–H activation of the ligand backbone is observed and an asymmetric, bridged bromide dimer is isolated. In comparison, the reaction of $SbCl_3$ with MesnacnacLi affords monomeric MesnacnacSbCl$_2$. The solid-state structures were determined using X-ray crystallography.

Keywords: β-Diketiminato (nacnac); Antimony (III) complex; C–H activation; Crystal structure

1. Introduction

In recent years use of β-diketiminato ligands (nacnac), (Dippnacnac = $[\{N(C_6H_3{}^iPr_2 2,6)C(Me)\}_2CH]^-$) or (Mesnacnac = $[\{N(Mes)C(Me)\}_2CH]^-$, Mes = 2,4,6, trimethyl benzene), have become increasingly common [1]. Complexes of transition metals, main group elements and lanthanides are all well documented [2]. These ligands are particularly useful as they can be prepared in high yields, crystallize easily and offer various coordination modes, thus have the ability to stabilize low oxidation state compounds [3]. Furthermore, steric and electronic properties of the ligands can be varied through manipulation of the R groups [4]. Complexes of the group 15 elements have been reported by Burford [5] and Lappert [6] (Fig. 1).[1]

To date, group 15 compounds of the type nanacEX$_2$ (E = P, As, Sb, Bi, X = halide) remain structurally uncharacterized.[1] From the work of Burford and Lappert it would appear that phosphorus preferentially coordinates at the γ-C rather than the more commonly observed nitrogen chelation [5,6].[1] To date, the preferred coordination of the heavier group 15 elements is unknown. The syntheses of compounds featuring group 15 elements were desirable for a variety of reasons. Firstly, examples of low valent antimony complexes are less common than their phosphorus counterparts [7], therefore structural comparisons to related main group structures were of interest and secondly for the potential applications of group 15 heterocyclic compounds [8]. Moreover, we wished to explore the further reactivity and chemistry of these compounds as precursors for organometallic syntheses.

2. Experimental

Solvents used were dried over sodium or potassium and degassed before use. All manipulations were performed under anaerobic conditions using standard Schlenk techniques. DippnacnacH, MesnacnacH and their corresponding lithium salts were prepared according to published procedures [9]. All other reagents were purchased from Aldrich and used as received.

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[1] During the review process, a manuscript reporting the synthesis and characterization of the first Phosphorus β-diketiminato was reported; D. Vidovic, Z. Lu, G. Reeske, J.A. Moore, A.H. Cowley, Chem. Commun. (2006) advance article, June 22, 2006.

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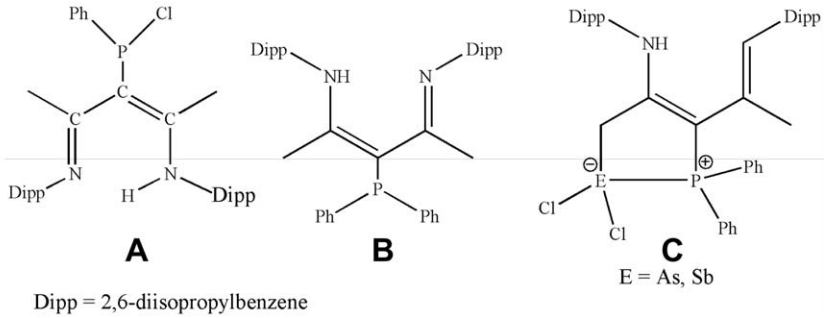


Fig. 1. β-Diketiminato compounds of the group 15 elements.

Crystal data were collected with a Bruker SMART diffractometer in using graphite monochromated molybdenum radiation ($\lambda = 0.7107$ Å). The data were corrected for absorption. Structures were solved by direct methods [10] and refined [10] via full-matrix least squares.

2.1. Preparation of **1**

A THF solution of DippnacnacLi (0.5 g, 1.2 mmol) was added rapidly by cannula to a stirred THF solution of $SbBr_3$ (0.29 g, 1.2 mmol) at −78 °C. The resultant yellow colored reaction mix was immediately removed from the dry-ice bath and allowed to reach ambient temperature. Stirring was maintained for a further 12 h, after which time the THF was removed *in vacuo* and the yellow solid extracted into toluene. Concentration of the toluene solution and storage at −5 °C for 1 day afforded **1** as crystalline yellow plates in 48% yield. M.p. 103–108 °C melts, ^{1}H NMR (d^8 PhMe, 25 °C): δ (ppm) 1.08, 1.11, 1.13, 1.14 (4 doublets, $^1J_{H-H} = 6.6$ Hz, ^{i}Pr–Me), 1.38 (s, 3H, CH_3, backbone), 1.99 (s, CH_2), 2.36, 3.02 (^{i}Pr C–*H* Dipp, multiplet, $^1J_{H-H} = 6.9$ Hz), 4.59 (br, s), 4.86 (s, N–H), 6.75 (*ortho*, H, aromatic, $^1J_{H-H} = 6.2$ Hz), 6.92 (triplet, meta H Dipp, $^1J_{H-H} = 6.2$ Hz); ^{13}C NMR ($C_6H_5CH_3$, 25 °C): δ (ppm) 24.7, 23.3 (C–^{i}Pr), 27.9 (Me-nacnac backbone) 121.7, 122.2, 123.9, 124.5, 124.7, 127.2 (aromatic ^{13}C), 141.4 (C-backbone N–*C*CN), 160.1 (Sb–C).

2.2. Preparation of **2**

A −78 °C THF solution of DippnacnacH (0.5 g, 1.22 mmol) had 1 equiv. of *n*-BuLi (0.76 mL of a 1.6 M solution) added dropwise. The solution was slowly warmed to room temperature and stirred for 4 h, after which time it was rapidly added to a stirred THF solution of $SbCl_3$ (0.33 g, 1.44 mmol) at −78 °C. An immediate color change was observed and the resultant amber colored reaction mixture was removed from the dry-ice bath and allowed to warm to ambient temperature. Stirring was maintained for a further 12 h, after which time the reaction mixture was filtered from the LiCl precipitate. Repeated filtration and concentration over a period of weeks afforded **2** in low yield. M.p. 122–125 °C, due to low yield no spectroscopic data were obtained.

2.3. Preparation of MesnacnacSbCl$_2$ (**3**)

A 100 mL Schlenk flask was charged with 0.3361 g of $SbCl_3$ (1.47 mmol) and 20 mL of THF. MesnacnacLi (0.5 g, 1.46 mmol) was dissolved in 30 mL of THF and added dropwise to a stirred THF solution of $SbCl_3$ at −78 °C. The clear yellow solution was stirred overnight. Following removal of the THF under vacuum, 20 mL of toluene was added and stirred. The clear dark yellow solution was filtered, concentrated under reduced pressure, and placed in a −30 °C freezer to obtain crystals (34.25%). M.p. 149–151 °C. ^{1}H NMR (d^8 PhMe, 25 °C): δ 1.45 (s, 6H, Me), 1.85 (s, 18H, Me_{aryl}), 3.87 (d, J_{H-H} 5.2 Hz, CH), 6.45 (s, 4H, H_{aryl}); ^{13}C NMR ($C_6H_5CH_3$, 25 °C): δ 17.1 (C_o–*Me*), 22.3 (α-Me), 25.9 (C_p–*Me*), 39.2 (C_β), 39.5 (C_α), 126.3–127.9 (br, C_o, C_m, C_p), 140.5 (*C*–N).

2.4. Preparation of $[MesnacnacH_2]_2^+[SbCl_4^-][I^-]$ (**4**)

To a flask charged with 0.0737 g (0.375 mmol) of 'GaI' in 20 mL of toluene a solution of 0.1897 g (0.359 mmol) of **3** in 20 mL of Toluene were added dropwise at room temperature. The resulting dark green solution was stirred overnight, filtered and the reaction mixture concentrated under reduced pressure. Storage of the solution at room temperature for 5 days afforded green crystals of **4**. Yield = 42.3%, m.p. 124–126 °C. ^{1}H NMR (C_6D_6, 25 °C): δ 1.13 (s, 6H, Me, backbone), 2.06 (s, 18H, Me_{aryl}), 3.72 (s, 2H, NH), 4.48 (br, s), 6.13 (s, 2H, H_{aryl}), 6.50 (s, 2H, H_{aryl}); ^{13}C NMR (C_6D_6, 25 °C): δ 17.8, 22.0 (2 × *Me*, Mes), 24.2 (Me, backbone), 93.8 (C–H, backbone), 127.4 (C_o), 127.8 (C_p), 129.7 (C_m), 139.0 (*C*N); IR (ν cm^{-1}, Nujol mull), 3172.29 (*m*-N–H), 2853 (w), 1608, 1550, 1205 (m), 874.2 (m).

2.5. Preparation of $2[MesnacnacH_2]^+ \cdot [AsCl_4^-][AsCl_3][Cl^-]$ (**5**)

To a stirred toluene suspension of 'GaI' (0.28 g, 14.3 mmol) was added a toluene solution of MesnacnacAsCl_2

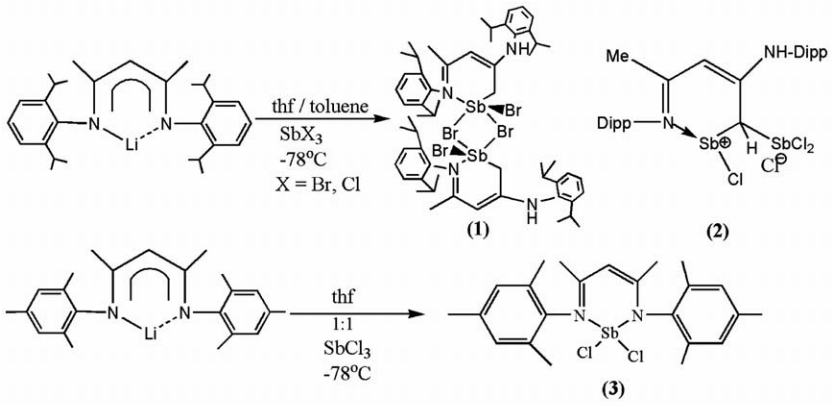
(0.4 g, 7.0 mmol) at room temperature. No immediate color change was observed. After stirring for 16 h, a metallic precipitate was observed and a brown solution. The solution was decanted and placed at −30 °C for 2 days to yield compound **5**. Yield = 35.89%, m.p. 145–146 °C. ^{1}H NMR (C_6D_6, 25 °C): δ 1.18 (s, 6H, Me, backbone), 2.10 (s, 18H, Me_{aryl}), 3.75 (s, 2H, NH), 4.52 (br, s), 6.21 (s, 2H, H_{aryl}), 6.55 (s, 2H, H_{aryl}); ^{13}C NMR (C_6D_6, 25 °C): δ 18.2, 22.5 (2 × *Me*, Mes), 24.6 (Me, backbone), 94.4(C–H, backbone), 127.9 (C_o), 128.2 (C_p), 130.1 (C_m), 139.0 (*C*N); IR (ν cm^{-1}, Nujol mull), 3152.29 (*m*-N–H), 2853 (w), 1608 (m), 1560 (m) 1215 (m).

3. Results and discussion

The crystalline compounds **1**–**3**, Scheme 1, were prepared from the reaction of nacnacLi (Dipp, compounds **1** and **2** or Mes, compound **3**) with $SbBr_3$ or $SbCl_3$ in a 1:1, 1:1.2 and 1:1 ratio respectively.

The structures (**1**–**3**, Scheme 1) were unequivocally established using X-ray crystallography. Table 1 displays the crystallographic data.

The crystallographic study revealed that the backbone of the Dippnacnac ligand in compounds **1** and **2** had undergone intramolecular C–H activation. This is not a



Scheme 1. Synthesis of compounds **1**–**3**.

Table 1
Crystallographic data for compounds **1**–**5**

Compound name	**1**	**2**	**3**	**4**	**5**
Chemical formula	$C_{129}H_{177}Br_4N_8Sb_4$	$C_{33}H_{48}Cl_4N_2OSb_2$	$C_{30}H_{37}Cl_2N_2Sb$	$C_{46}H_{62}Cl_4IN_4Sb$	$C_{23}H_{31}As_2Cl_8N_4$
Formula weight	2646.43	874.03	618.28	1057.41	1105.44
Crystal system	Triclinic	Triclinic	Triclinic	Tetragonal	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*P*42/*nmc*	*Pca*2(1)
T (K)	91(2)	91(2)	91(2)	91(2)	91(2)
a (Å)	14.8326(9)	12.123(7)	8.6608(14)	11.5310(5)	17.8963(15)
b (Å)	15.9125(10)	12.137(7)	12.453(2)	11.5310(5)	10.6789(9)
c (Å)	17.6414(11)	13.495(7)	16.148(3)	22.9540(14)	28.319(2)
α (°)	96.8930(10)	91.783(9)	103.161(2)	90	90
β (°)	114.6680(10)	90.617(9)	103.096(3)	90	90
γ (°)	112.8090(10)	97.652(9)	100.270(3)	90	90
V (Å^3)	3284.6(4)	1966.8(19)	1602.5(5)	3052.1(3)	5412.1(8)
Z	1	2	2	2	8
Reflections collected	28 094	10 146	13 615	24 739	44 415
Independent reflections	11 804	6886	5759	1527	9644
Data/restraints/parameter ratio	11 804/6/630	6886/0/378	5759/0/324	1527/0/83	9644/1/534
Unique data (R_{int})	0.0800	0.1123	0.1012	0.0464	0.0951
D_{calc} (Mg m^{-3})	1.338	1.476	1.281	1.151	1.355
Absorption coefficient (mm^{-1})	2.077	1.671	1.046	1.160	1.664
F(000)	1351	876	632	1068	2272
Crystal size (mm)	0.29 × 0.26 × 0.23	0.13 × 0.11 × 0.09	0.14 × 0.14 × 0.13	0.07 × 0.035 × 0.012	0.15 × 0.13 × 0.12
θ Range for collection (°)	1.56–25.25	1.51–25.25	1.35–28.24	1.77–24.40	1.44–25.25
R indices (all data)	$R_1 = 0.0882$, $wR_2 = 0.1110$	$R_1 = 0.1094$, $wR_2 = 0.2674$	$R_1 = 0.03653$, $wR_2 = 0.0999$	$R_1 = 0.0983$, $wR_2 = 0.2852$	$R_1 = 0.1325$, $wR_2 = 0.2244$
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0504$, $wR_2 = 0.0994$	$R_1 = 0.0812$, $wR_2 = 0.2403$	$R_1 = 0.0346$, $wR_2 = 0.0981$	$R_1 = 0.0910$, $wR_2 = 0.2759$	$R_1 = 0.0732$, $wR_2 = 0.1860$
Largest difference in peak and hole (*e* Å^{-3})	1.201 and −0.718	1.765 and −1.417	1.051 and −1.334	1.387 and −4.324	2.063 and −1.583

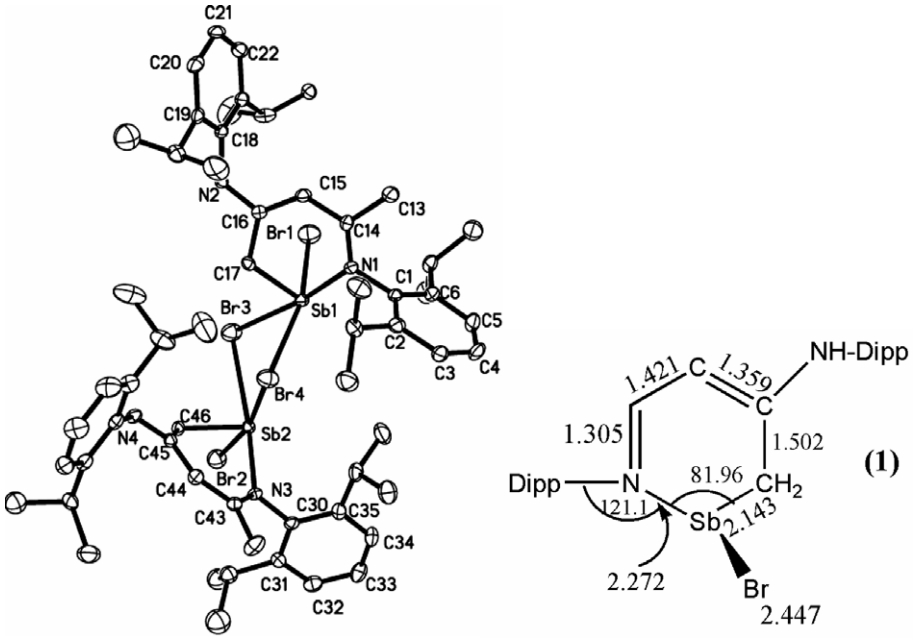


Fig. 2. ORTEP of **1** at 50% probability, hydrogen atoms are removed for clarity.

new phenomenon for these ligands, however, is usually associated with more reactive species, for example the early transition elements and the β-diketiminato compounds of the alkaline earth metals [11]. Intramolecular C–H activation is thought to be attributed to the presence of the reactive Sb–X (X = halide) [12] and the conditions which the reactions were performed. In order to observe C–H activation the addition of DippnacnacLi to the antimony halide must proceed rapidly and the reaction mixture brought to room temperature quickly. Compound **1** was isolated as a yellow crystalline solid and is a bridged Sb(III) compound. The structure and selected bond lengths are depicted in Fig. 2 (see Table 2).

The bond lengths in **1** compare well to those of the optimized C–H activated Dippnacnac^{2-} ion as predicted by ab initio calculations [11a]. Each antimony atom is attached to a nitrogen atom of the ligand, a terminal and bridged bromide (Scheme 1, Fig. 2). The Sb–Br bond lengths vary from 2.446 Å, Sb(1)–Br(1), to 2.98 Å, Sb(2)–Br(2), and highlight the lack of symmetry in the bridged Sb–Br conformation. These values are not unusual for Sb–Br bonds [13,14] and this asymmetry appears to be a common characteristic in the 32 reported Sb–Br bridged structures [14]. Each Sb center can be viewed as a distorted trigonal bipyramidal structure with a vacant coordination site presumably occupied by the Sb lone pair. A related compound **2** can be isolated if a slight excess of $SbCl_3$ is present in the reaction. Compound **2** was isolated serendipitously in low yield from the reaction when DippnacnacLi was prepared *in situ* from DippnacnacH, and the reaction mixture is kept in THF (see Fig. 3).

Table 2
Selected bond lengths (Å) and bond angles (°) of **1**

Sb(1)–Br(3)	2.7911(16)
Sb(1)–Br(4)	2.9119(16)
Sb(2)–C(46)	2.141(6)
Sb(2)–N(3)	2.188(4)
Sb(2)–Br(2)	2.5315(17)
Sb(2)–Br(4)	2.7234(16)
C(17)–Sb(1)–N(1)	81.96(19)
C(17)–Sb(1)–Br(1)	90.05(15)
N(1)–Sb(1)–Br(1)	92.54(12)
Br(1)–Sb(1)–Br(3)	89.52(5)

Compound **2** is somewhat unusual in that C–H bond activation and a subsequent deprotonation has occurred. LiCl is displaced and Sb(1) sits in the C–N pocket. The geometry around this antinomy (Sb1) is T-shaped and Cl(1)–Sb(1)–N(1) lie almost at an 180° angle. The excess $SbCl_3$ in the reaction mixture is coordinated as an $SbCl_2$ fragment to the adjacent carbon atom in the nacnac backbone. The +1 charge on Sb(1) is balanced by a chloride ion that sits in close proximity to a Dipp (2,6-diisopropyl benzene) group at a distance of 2.967 Å from the $SbCl_2$ fragment. While the exact mechanism for formation is unclear, it appears that from isolation of compound **1**, this is the primary product formed. It is envisaged that the reaction proceeds in a similar manner as observed in the formation of (C, Fig. 1) [5], nucleophilic displacement of the chloride on the excess $SbCl_3$ present in the reaction and inter- or intramolecular tautomerism that gives access to the carbon for coordination.

In an attempt to isolate nacnac$SbCl_2$ the reaction of MesnacnacLi (R = Mes = 2,4,6 trimethylbenzene) with $SbCl_3$ was carried out. Compound **3** was isolated in a moderate yield. Examination of the solid-state structure revealed it as monomeric Mesnacnac$SbCl_2$, as shown in Fig. 4.

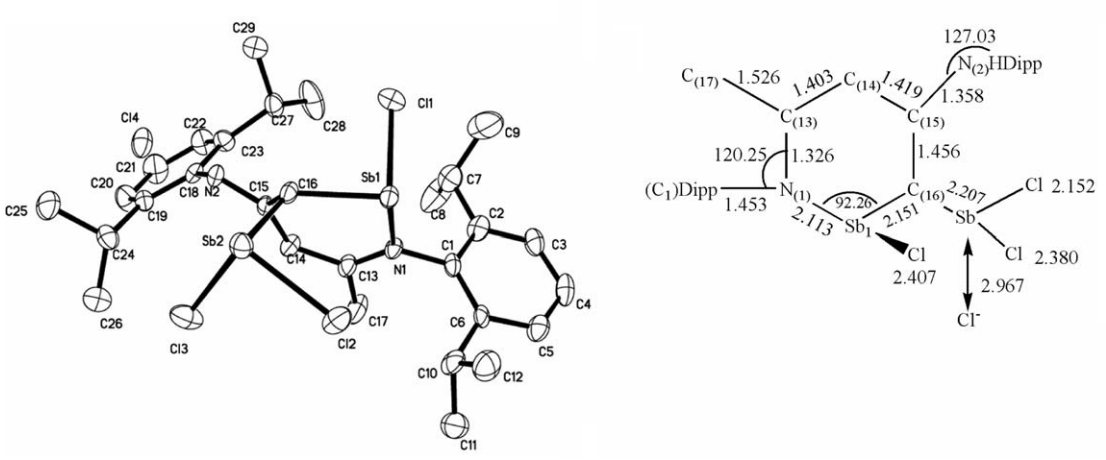


Fig. 3. Solid-state structure of **2**, thermal ellipsoids at 30% probability, selected bond lengths (Å) and bond angles (°) are depicted – hydrogen atoms are removed for clarity. A molecule of THF is omitted from the diagram.

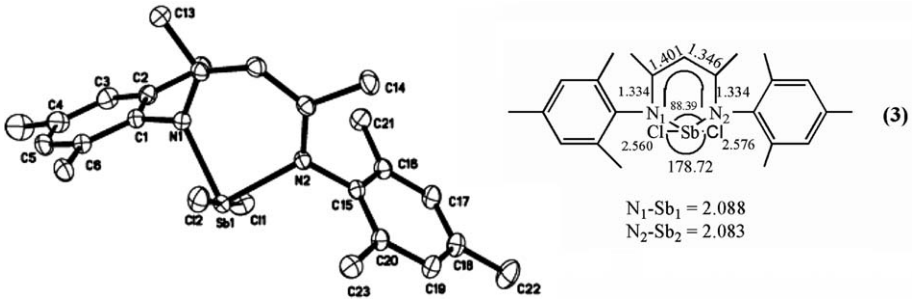


Fig. 4. X-ray structure of MesnacnacSbCl2. Thermal ellipsoids are shown at 50% probability.

The crystallographic analysis revealed 'normal' Sb–Cl (2.5662(7) Å) and Sb–N (Sb(1)–N(1) 2.088(2)) bond lengths and bond angles [7]. The coordination geometry of the Sb is as predicted by VSEPR for an AX_5E structure. Within the 'see-saw' structure the Cl(1)–Sb(1)–Cl(2) arrangement is almost linear with an angle of 178.72°. An angle of 88.38° for N(1)–Sb(1)–N(2) is also close to the 90° right angle expected. These small deviations from the predicted values are associated with the sterics of the bulky ligand and the possibility of lone pair delocalization, which is also responsible for the asymmetry of the molecule. The fact that the bond lengths from the chelating nitrogen atoms to their respective carbons and antimony within the Mesnacnac are of similar lengths reinforces the probability of delocalization within the ligand.

Attempts to reduce **1** and **3** using potassium, sodium, KC_8 or Mg with the aim of forming low valent Sb species were generally unsuccessful. Treatment of $MesnacnacSbCl_2$ with 2 equiv. of the softer reducing agent, gallium (I) iodide afforded compound **4**. From the X-ray analysis of **4** it can be seen that the Mesnacnac ligand opens up forming a highly symmetrical structure that is protonated at both nitrogen atoms. The cationic structure is balanced by the presence of an $SbCl_4^-$ anion. Within the asymmetric unit there are two Mesnacnac cations with an iodide ion from the 'GaI' as the anion for the second cation (see Fig. 5 and Table 3).

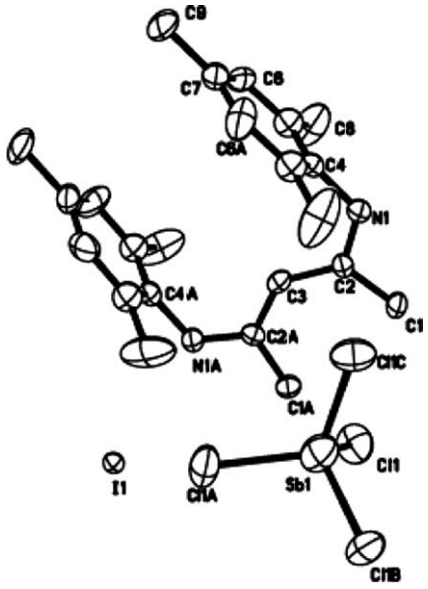


Fig. 5. Structure and selected bond lengths and angles for $2[MesnacnacH_2]^+ \cdot SbCl_4^-I^-$, compound **4**, the second $MesnacnacH_2^+$ and hydrogen atoms are omitted for clarity.

Numerous attempts to crystallize $DippnacnacAsCl_2$ and the Bi analogue using a variety of solvents and R substituents on the ligand all failed. $MesnacnacAsCl_2$ was confirmed spectroscopically and in order to try to form a

Table 3
Selected bond lengths (Å) and bond angles (°) of **4**

Sb(1)–Cl(1)	2.165(2)
N(1)–C(2)	1.314(10)
N(1)–C(4)	1.437(9)
C(1)–C(2)	1.504(9)
Cl(1)#1–Sb(1)–Cl(1)	107.53(8)
C(2)–N(1)–C(4)	122.9(6)
N(1)–C(2)–C(3)	119.1(7)

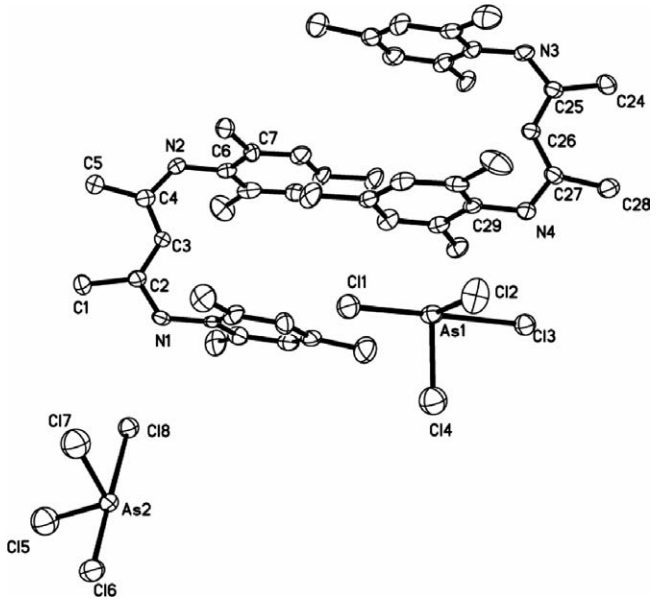


Fig. 6. ORTEP of $[MesnacnacH_2]^+ \cdot AsCl_4^-$ (thermal ellipsoids at 50% probability) and selected bond lengths (Å) and bond angles (°): As(1)–Cl(1) 2.308(3); As(1)–Cl(2) 2.184(4); N(1)–C(2) 1.337(14); N(1)–C(15) 1.414(14); C(1)–C(6) 1.382(8); C(1)–C(2); 1.414(8) and C(4)–N(2)–C(6) 125.7(10).

derivative for structural characterization the reaction with 'GaI' was performed. The reaction outcome shows similarity with that of the Sb reaction, compound **4**. The arsenic atom is displaced from the ligand and forms the anion $AsCl_4^-$, which is the counter ion for the $MesnacnacH_2^+$ cation (Fig. 6).

4. Conclusions

Compounds **1**–**5** are novel β-diketiminato antimony complexes and show that through manipulation of the halide precursor, reaction stoichiometry and the R substituent on the nacnac different reaction outcomes can be achieved. Reactions using DippnacnacLi with $SbBr_3$ and $SbCl_3$ proceed rapidly with C–H activation observed. Using $SbCl_3$ and MesnacnacLi, monomeric Mesnacnac antimony (III) chloride is isolated. Further work will focus on exploring the chemistry of **1**–**3** as synthons for organometallic syntheses and the preparation of the heavier congeners of the group 15 elements.

Acknowledgements

A.F.R. thanks Professor Cameron Jones, Cardiff University, for helpful discussions.

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Appendix A. Supplementary information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 611223 for compound **1**, CCDC No. 611229 for compound **2**, CCDC No. 611225 for compound **3**, CCDC No. 611226 for compound **4** and CCDC No. 611224 for compound **5**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: (int code) +44 1223 336 033 or email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.036.

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