## Neutral and Anionic Antimony(III) Species Supported by a Bicyclic Guanidinate

Benjamin M. Day,<sup>[a]</sup> Martyn P. Coles,<sup>\*[b]</sup> and Peter B. Hitchcock<sup>[a]</sup>

Keywords: N ligands / Main group elements / Group 15 elements / Antimony / Stereochemically active lone pairs

Bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) was investigated as a source of anionic or neutral ligand at antimony. Reaction of the in situ generated lithium guanidinate with SbCl<sub>3</sub> in a 1:1 or 2:1 ratio forms the expected metathesis products Sb(hpp)<sub>n</sub>Cl<sub>3-n</sub> (**1**, n = 1; **2**, n = 2). The molecular structures of **1** and **2** were determined by X-ray diffraction, which shows chelating guanidinates and suggests the presence of a stereochemically active lone

## Introduction

We have a long-standing interest in the application of bicyclic guanidines as neutral<sup>[1]</sup> and anionic<sup>[2]</sup> ligands at main group and transition metal centres. Much of our work has focussed on the {6:6}-fused system, hppH (1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine), during which time we have noted a diverse range of coordination modes (Figure 1). In addition to the bidentate coordination **A**, typical for acyclic guanidinate derivatives,<sup>[3]</sup> constraining the nitrogen substituents of the amidine component into the six-membered heterocycles promotes a number of bridging modes **B**–**G** incorporating two,<sup>[4]</sup> three<sup>[4h,4i,5]</sup> or four<sup>[4h,4i,6]</sup>



Figure 1. Reported bonding modes for the bicyclic guanidinate derived from 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH).

[a] Department of Chemistry, University of Sussex, Falmer, Brighton BN1 9QJ, UK

 [b] School of Chemical and Physical Sciences, Victoria University of Wellington,
 P. O. Box 600, Wellington, New Zealand

Fax: +64-4-4635237 E-mail: martyn.coles@vuw.ac.nz pair of electrons. The reaction of two equivalents of the neutral guanidine hppH with SbCl<sub>3</sub> proceeds via proton transfer between the hpp fragments, affording the ion pair [hppH<sub>2</sub>][Sb(hpp)Cl<sub>3</sub>] (**3**), where [Sb(hpp)Cl<sub>3</sub>]<sup>-</sup> is an unusual example of a monometallic antimonate(III) anion. The molecular structure of **3** shows hydrogen bonding between two of the chlorides and the NH functionalities of the guanid-inium cation.

metals. The propensity for bridging has been explained in terms of a wide (parallel) projection of the nitrogen donor orbitals in [hpp]<sup>-</sup>. This contrasts with the situation in acyclic anions in which steric interactions between the nitrogen substituents force these orbitals to point towards the "mouth" of the ligand (Figure 2).



Figure 2. Schematic representation of the orbital projection in  $[hpp]^-$  and a generic acyclic guanidinate anion,  $[R_2NC\{NR'\}_2]^-$ .

Within groups 13 and 14, the chemistry of the [hpp]<sup>-</sup> anion has focussed mainly on the lighter elements boron<sup>[7]</sup> and silicon.<sup>[8]</sup> The corresponding coordination chemistry of aluminium,<sup>[4a]</sup> gallium<sup>[4k]</sup> and tin<sup>[4d]</sup> has shown a tendency for the ligand to adopt a bridging **B**-type coordination (Figure 1), although both **A** and **B** coordination have been noted for Sn<sup>II.[4d]</sup> We were curious to see whether coordinating the [hpp]<sup>-</sup> anion to a larger metal ion would favour chelation (**A**-type bonding) and targeted antimony(III) compounds to determine whether this would be the case [effective ionic radii: Al<sup>3+</sup> 0.535 Å, Ga<sup>3+</sup> 0.62 Å, Sb<sup>3+</sup> 0.76 Å].<sup>[9]</sup>

Earlier publications describing amidinate complexes of antimony in the  $+3^{[10]}$  and +5 oxidation states<sup>[11]</sup> were mainly restricted to structural reports. More recently attention has focussed on the coordination chemistry of antimony(III) (Figure 3),<sup>[12]</sup> with interest primarily derived from the ability of such ligands to support low-oxidation-state metals.<sup>[12b]</sup> We report herein our preliminary studies

# FULL PAPER

into the application of [hpp]<sup>-</sup> as a ligand at Sb<sup>III</sup>, including the crystal structure of an unanticipated ionic species consisting of a guanidinium cation and an antimonate(III) anion.



Figure 3. Examples of structurally characterized Sb<sup>III</sup>–amidinate and –guanidinate compounds (Ar =  $2,6-iPr_2C_6H_3$ ).

## **Results and Discussion**

The 1:1 reaction of in situ generated Li[hpp]<sup>[4h]</sup> with one equivalent of SbCl<sub>3</sub> gave colourless crystals of Sb(hpp)Cl<sub>2</sub> (1) upon work-up (Scheme 1). The analogous procedure with 0.5 equiv. of anitimony(III) chloride afforded the bis(guanidinate) complex Sb(hpp)<sub>2</sub>Cl (2). Three resonances for the annular methylene groups in the <sup>1</sup>H and <sup>13</sup>C NMR



Scheme 1. Synthesis of  $Sb(hpp)_nCl_{3-n}$  (1, n = 1; 2 n = 2) and  $[hppH_2][Sb(hpp)Cl_3]$  (3).

spectra are consistent with a symmetrical environment for the guanidinate ligand in each compound.

The X-ray crystal structure of compound 1 (Tables 1 and 2) confirmed the formulation as the monomeric dichloride  $Sb(hpp)Cl_2$  (Figure 4a). The geometry at the metal may be described as highly distorted trigonal bipyramidal, the axial positions defined by Cl1 and N2 and a stereochemically

Table 2. Selected bond lengths [Å] and angles [°] for 1.

Sb-N1	2.060(6)	Sb-N2	2.244(7)	_
Sb-Cl1	2.587(2)	Sb-Cl2	2.414(2)	
C1-N1	1.332(9)	C1-N2	1.341(9)	
C1-N3	1.345(10)			
N1-Sb-N2	61.3(2)	N1-Sb-Cl1	85.79(17)	
N1-Sb-Cl2	96.3(2)	N2-Sb-Cl1	146.90(16)	
N2-Sb-Cl2	89.77(19)	Cl1-Sb-Cl2	90.57(7)	

Table 1. Crystal structure and refinement data for Sb(hpp)Cl<sub>2</sub> (1), Sb(hpp)<sub>2</sub>Cl (2) and [hppH<sub>2</sub>][Sb(hpp)Cl<sub>3</sub>] (3).

	1	2	3
Empirical formula	C <sub>7</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>3</sub> Sb	C <sub>14</sub> H <sub>24</sub> ClN <sub>6</sub> Sb	C <sub>14</sub> H <sub>26</sub> Cl <sub>3</sub> N <sub>6</sub> Sb
M <sub>r</sub>	330.85	433.59	506.51
T[K]	173(2)	173(2)	173(2)
Crystal size [mm]	$0.10 \times 0.05 \times 0.01$	$0.24 \times 0.14 \times 0.08$	$0.15 \times 0.10 \times 0.10$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$ (alternative No.14)	$P2_1/c$ (No. 14)	<i>P</i> 1 (No. 2)
a [Å]	9.3783(8)	12.0687(5)	7.8127(2)
b [Å]	8.1401(8)	8.3115(3)	8.5487(2)
<i>c</i> [Å]	13.8748(10)	16.9864(8)	14.8964(4)
a [°]	90	90	100.132(2)
β [°]	99.636(5)	100.511(2)	91.754(1)
γ [°]	90	90	97.835(2)
V [Å <sup>3</sup> ]	1044.26(16)	1675.30(12)	968.73(4)
Ζ	4	4	2
$d_{\rm calcd.}  [{\rm Mg}{\rm m}^{-3}]$	2.10	1.72	1.74
Absorption coefficient [mm <sup>-1</sup> ]	3.11	1.81	1.85
$\theta$ range [°]	3.50 to 26.02	1.72 to 27.48	3.49 to 25.99
Reflections collected	8878	10016	13137
Independent reflections	2049 [ $R_{\rm int} = 0.101$ ]	$3797 [R_{int} = 0.049]$	$3797 [R_{int} = 0.030]$
Reflections with $I > 2\sigma(I)$	1617	3176	3513
Data/restraints/parameters	2049/0/118	3797/0/199	3797/0/225
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.060, wR_2 = 0.146$	$R_1 = 0.030, wR_2 = 0.083$	$R_1 = 0.021, wR_2 = 0.047$
Final <i>R</i> indices (all data)	$R_1 = 0.077, wR_2 = 0.158$	$R_1 = 0.044, wR_2 = 0.112$	$R_1 = 0.024, wR_2 = 0.048$
GooF on $F^2$	1.098	1.195	1.090
Largest diff. peak/hole [eÅ <sup>-3</sup> ]	2.43 and -1.72 <sup>[a]</sup>	1.34 and -1.84	0.40 and -0.46

[a] Near Sb.



active lone pair of electrons occupying an equatorial position (Figure 5a). The Sb–N and Sb–Cl distances support this with shorter bonds to the proposed equatorial atoms and longer bonds to the corresponding axial atoms [Sb–N1<sub>(eq)</sub> 2.060(6) Å vs. Sb–N2<sub>(ax)</sub> 2.244(7) Å; Sb–Cl2<sub>(eq)</sub> 2.414(2) Å vs. Sb–Cl1<sub>(ax)</sub> 2.587(2) Å]. The repulsive influence of the lone pair and acute bite angle of the guanidinate [N1–Sb–N2 61.3(2)°] cause a large reduction of the N2–Sb–Cl1 angle from its ideal linear arrangement to 146.90(16)°. Within the CN<sub>3</sub> core of the guanidinate, the C–N distances



Figure 4. (a) Thermal ellipsoid plot (30% probability) of 1; (b) schematic diagram showing the association of 1 into edge-shared dimers.



Figure 5. Top: geometries at antimony for (a) compound 1 and (b, c) alternatives for compound 2. Bottom: localized and delocalization descriptions of bonding in the Sb(hpp) fragment.

are identical (within experimental uncertainty), suggesting efficient delocalization.

The degree of aggregation of antimony compounds incorporating amidinate and guanidinate anions varies considerably with the steric profile of the ligand and the solvent from which the compound is crystallized (i.e., whether solvate molecules are included in the crystal lattice). For example, the bulky amidinate and guanidinate compounds  $Sb(RC{NR'}_2)Cl_2$  (R' = Ar; R = tBu,<sup>[12c]</sup> Cy<sub>2</sub>N<sup>[12b]</sup>), the former of which crystallizes as the bis(chloroform) solvate, are monomeric in the solid state. In contrast, when R = tBuand R' = iPr or  $Cy_{12c}$  or R = Ph and  $R' = SiMe_{3}^{10a}$ the molecules are linked by a single intermolecular Sb...Cl contact to generate corner-bridged polymeric structures. Compound 1 has two symmetry-related Sb--Cl contacts [Sb····Cl 3.240 Å] that generate an edge-shared dimer (Figure 4b), as noted in Sb(*n*BuC{N*i*Pr}<sub>2</sub>)Cl<sub>2</sub>.<sup>[12c]</sup> These intermolecular contacts may contribute to the elongation in the Sb-Cl1 bond length described above.

The crystal structure of **2** (Figure 6, Tables 1 and 3) shows a monomeric, five-coordinate antimony centre with chelating [hpp]<sup>–</sup> ligands and a terminal chloride ligand. The angles at the metal range from the small bite of the guanidinates [ $57.32(10)^\circ$  and  $60.47(11)^\circ$  for C1 and C8 ligands, respectively] to 141.64(8)° for Cl–Sb–N5. The latter value is close to that proposed for the *trans*-equatorial substituents distorted by lone-pair repulsions and chelation in **1**. A similar metal geometry was observed for the bis(amidinate) compound Sb(PhC{NSiMe<sub>3</sub>}<sub>2</sub>)<sub>2</sub>Cl,<sup>[10b]</sup> in which the metal



Figure 6. Thermal ellipsoid plot (30% probability) for 2.

Table 3. Selected bond lengths [Å] and angles [°] for 2.

	-		-
Sb-N1	2.057(3)	Sb–N2	2.526(3)
Sb-N4	2.151(3)	Sb-N5	2.209(3)
Sb-Cl	2.6831(9)	C1-N1	1.353(5)
C1-N2	1.322(5)	C1-N3	1.355(5)
C8-N4	1.340(4)	C8-N5	1.328(4)
C8-N6	1.345(4)		
N1-Sb-N2	57.32(10)	N1-Sb-N4	95.33(11)
N1-Sb-N5	91.01(11)	N1-Sb-Cl	83.38(9)
N2-Sb-N4	131.44(11)	N2-Sb-N5	79.17(10)
N2-Sb-Cl	126.39(7)	N4-Sb-N5	60.47(11)
N4-Sb-Cl	82.20(8)	N5-Sb-Cl	141.61(8)

was described as having distorted octahedral geometry with a "stereochemically strongly effective lone electron pair"; this description may be applied to the geometry of **2** (**2**-Oh, Figure 5b).

FULL PAPER

An alternative description for the geometry of **2** is a distorted trigonal bipyramidal geometry (**2**-tbp, Figure 5c) in which N2 is only loosely coordinated to the antimony centre. Evidence for this comes from a very long Sb–N2 bond [2.526(3) Å] compared to the remaining Sb–N distances in **2** [2.057(3)–2.209(3) Å] and those in **1**. We also note localization of  $\pi$ -electron density in the N1–C1–N2 component of the [hpp]<sup>-</sup> ligand, indicated by long C1–N1 and short C1–N2 bonds [1.353(5) and 1.322(5) Å, respectively]. This is consistent with a large contribution from localized bonding of the **I**/**I**' type previously noted for amidinates in fivecoordinate aluminium systems.<sup>[13]</sup> The  $\pi$ -bonding in the other guanidinate ligand shows a similar, although less pronounced, trend.

In addition to using the [hpp]<sup>-</sup> anion as a ligand in coordination chemistry, the neutral guanidine, hppH, also serves as an effective N-donor ligand.<sup>[4h,5a,14]</sup> The typical bonding mode is by lone-pair donation from the imine nitrogen to an available orbital on the metal centre. For metal halide compounds, this interaction may be strengthened by intramolecular hydrogen bonding to the halide atom (Figure 7). Many bis(*N*-donor ligand) adducts of antimony(III) chloride are known, including, for example, those of 1,4-diazabutadiene,<sup>[15]</sup> bipy,<sup>[16]</sup> 1,2-bis(aryl-imino)acenaphthene,<sup>[17]</sup> 4-phenylpyridine<sup>[18]</sup> and 2,6-dimethylaniline.<sup>[19]</sup> We therefore investigated the use of hppH as a neutral N-donor ligand with antimony(III) chloride as the metal reagent.



Figure 7. Coordination of a neutral hppH guanidine at a generic metal halide fragment showing stabilization by intramolecular hydrogen bonding.

The reaction between two equivalents of hppH and SbCl<sub>3</sub> afforded colourless crystals of **3** after the appropriate work-up (Scheme 1). The crystals were insoluble in common NMR spectroscopic solvents but dissolved in [D<sub>3</sub>]-acetonitrile, enabling spectroscopic analysis. Key features include a broad resonance at 7.57 ppm with a relative integral of 2H in the <sup>1</sup>H NMR spectrum, as well as two resonances at 159.2 and 152.5 ppm (corresponding to the *C*N<sub>3</sub> carbon atom) in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. These data indicate two different ligand environments and suggest that one may be associated with a guanidinium component as the low-field resonance in the proton NMR spectrum is typical for the N*H* atoms of the [hppH<sub>2</sub>]<sup>+</sup> cation.<sup>[20]</sup>

X-ray diffraction analysis (Figure 8, Tables 1 and 4) showed that **3** consists of the hydrogen-bonded ion pair  $[hppH_2][Sb(hpp)Cl_3]$ . This salt may be considered as the net result of a proton transfer between hppH molecules to af-

ford the cation  $[hppH_2]^+$  and the anion  $[hpp]^-$ , the latter of which coordinates to SbCl<sub>3</sub>. Mechanistic details of this reaction are not known.



Figure 8. Thermal ellipsoid plot (30% probability) of 3.

Table 4. Selected bond lengths [Å] and angles [°] for 3.

Sb-N1	2.2602(17)	Sb-N2	2.0756(17)
Sb-Cl1	2.5932(6)	Sb-Cl2	2.6570(6)
Sb-Cl3	2.5906(6)	C1-N1	1.320(3)
C1-N2	1.357(3)	C1-N3	1.337(3)
C8-N4	1.337(3)	C8–N5	1.338(3)
C8-N6	1.331(3)		
N1-Sb-N2	61.00(6)	N1-Sb-Cl1	87.00(5)
N1-Sb-Cl2	96.72(5)	N1-Sb-Cl3	144.33(5)
N2-Sb-Cl1	93.50(5)	N2-Sb-Cl2	84.51(5)
N2-Sb-Cl3	84.82(5)	Cl1-Sb-Cl2	174.225(19)
C11-Sb-C13	85.108(19)	C12-Sb-C13	89.31(2)

The  $[Sb(hpp)Cl_3]^-$  anion is an unusual example of a monometallic antimonate(III) anion. The propensity for halides to bridge in anionic antimonate systems has strong grounding in the literature. Although [SbCl<sub>4</sub>]<sup>-</sup> was structurally described as early as 1970,<sup>[21]</sup> close contacts (less than 4.0 Å, the sum of the van der Waals radii) to additional chloride ions are frequently encountered in the solid state. The most common description of this unit is an octahedrally coordinated antimony within a polymeric chain bridged by chloride ions.<sup>[22]</sup> Both the bromide and the iodide systems are known as isolated octahalodiantimonate(III) ions,  $[X_3Sb(\mu-X)_2SbX_3]^{2-}$  (X = Br,<sup>[23]</sup> I<sup>[24]</sup>). Substitution by phenyl groups in the anions form the  $[Cl_2(Ph)Sb(\mu\text{-}Cl)_2Sb(Ph)Cl_2]^{2-}$  dimer for the monophenyl anion, and the monomer is only formed for the diphenyl derivative [SbCl<sub>2</sub>Ph<sub>2</sub>]<sup>-.[25]</sup> This system is further complicated by reports of [Cl<sub>3</sub>(Ph)Sb(µ-Cl)Sb(Ph)Cl<sub>3</sub>]<sup>3-</sup> as a bimetallic trianion, which retains a single chloride bridge.<sup>[26]</sup> It appears that the formation of two strong hydrogen bonds to the  $[hppH_2]^+$  cation is sufficient to prevent the anion from dimerizing through the chlorides in 3.

Considering a lone pair lying in the plane between N1 and Cl3, the geometry of Sb is best considered as distorted octahedral, with Cl1 and Cl2 *trans* to one another [Cl1–Sb–Cl2 174.225(19)°] and a typically small bite angle for the [hpp]<sup>-</sup> anion [N1–Sb–N2 61.00(6)°]. The difference in Sb–N bond length [Sb–N1 2.2602(17) Å, Sb–N2 2.0756(17) Å]

is reflected in a shorter C1–N1 [1.320(3) Å] relative to C1–N2 [1.357(3) Å] and is consistent with a large contribution from the localized form of  $\pi$ -bonding (I/I', Figure 5).<sup>[13]</sup>

The  $[hppH_2]^+$  cation forms hydrogen bonds to Cl1 and Cl3, with intermolecular Cl···HN distances of 2.51 and 2.52 Å, respectively. The C–N bond lengths within the core are equivalent (within  $3\sigma$ ), indicating effective delocalization of the positive charge. Similar hydrogen bonding between  $[hppH_2]^+$  and metal halide anions have been recorded for  $[CuCl_4]^{2-[27]}$  and  $[TaCl_6]^{-.[28]}$ 

#### Conclusions

In summary, we have demonstrated that the large size of the  $Sb^{3+}$  ion enables the [hpp]<sup>-</sup> anion to bond through both available nitrogen atoms as a chelating ligand. The structure of both 1 and 2 indicate the presence of a stereochemically active lone pair, which, in addition to the narrow bite angle of the chelating guanidinate anion(s), generates highly distorted metal geometries. We have also shown that simple adduct formation with neutral hppH does not readily occur, the preferred mode of reactivity involving salt formation to afford a rare monometallic five-coordinate antimonate(III) anion.

## **Experimental Section**

**General Procedures:** All manipulations were carried out under dry nitrogen with standard Schlenk line and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were dried with appropriate drying agents and degassed prior to use. NMR spectra were recorded by using a Bruker Avance DPX 300 MHz spectrometer at 300.1 (<sup>1</sup>H) and 75.4 (<sup>13</sup>C{<sup>1</sup>H}) MHz or a Varian VNMRS 500 MHz spectrometer at 500.1 (<sup>1</sup>H), 125.4 (<sup>13</sup>C{<sup>1</sup>H}) MHz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances. Elemental analyses were performed by S. Boyer at London Metropolitan University. Compounds hppH and SbCl<sub>3</sub> were purchased from Sigma–Aldrich and used as received.

Sb(hpp)Cl<sub>2</sub> (1): *n*BuLi in hexanes (1.8 mmol, 0.7 mL, 2.6 M) was added dropwise to solution of hppH (0.252 g, 1.8 mmol) in THF at -78 °C. The resultant mixture was warmed to ambient temperature and stirred for 1 h, after which time full conversion to the lithium salt was assumed. The "hppLi" solution was added to SbCl<sub>3</sub> (0.413 g, 1.8 mmol) in THF (ca. 20 mL) at -78 °C to obtain a colourless solution. The solution was warmed to ambient temperature for 1 h, after which time a dark grey precipitate had formed. The volatiles were removed under vacuum, and the product was extracted with CH2Cl2. Yield 0.13 g, 22.3%. X-ray crystallographic quality crystals were obtained by slowly cooling a hot (ca. 70 °C) toluene solution to room temperature. C<sub>7</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>3</sub>Sb (330.85): calcd. C 25.41, H 3.66, N 12.70; found C 25.49, H 3.53, N 12.86. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 303 K):  $\delta$  = 3.43, 3.23, 2.03 (m, 8 H, hpp-CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = *, 46.0, 39.9, 23.6$  (hpp-CH<sub>2</sub>) ppm; \* resonance for CN<sub>3</sub> not observed.

**Sb(hpp)<sub>2</sub>Cl (2):** Compound **2** was made by using the same synthetic procedure as that described for **1**, with hppH (0.648 g, 4.9 mmol), a solution of *n*BuLi in hexanes (5.0 mmol, 2.0 mL, 2.5 M) and SbCl<sub>3</sub> (0.560 g, 2.5 mmol). The product was isolated as a white powder



that was purified by crystallization from THF at -20 °C. Yield 0.40 g, 37%. C<sub>14</sub>H<sub>24</sub>ClN<sub>6</sub>Sb (433.59): calcd. C 38.78, H 5.58, N 19.38; found C 38.67, H 5.61, N 19.30. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 303 K):  $\delta$  = 3.33 (m, 8 H, hpp-CH<sub>2</sub>), 3.11 (m, 8 H, hpp-CH<sub>2</sub>), 1.91 (m, 8 H, hpp-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  = \*, 46.3, 40.6, 23.8 (hpp-CH<sub>2</sub>) ppm; \* resonance for CN<sub>3</sub> not observed.

**[hppH<sub>2</sub>][Sb(hpp)Cl<sub>3</sub>] (3):** A solution of hppH (0.50 g, 3.6 mmol) in THF (ca. 30 mL) was added dropwise to a solution of SbCl<sub>3</sub> (0.41 g, 1.8 mmol) in THF (ca. 25 mL). A cloudy white precipitate formed, which coagulated to a gummy solid over a period of 1 h. Warming this mixture to approximately 60 °C and filtering afforded a colourless filtrate that was allowed to cool slowly to room temperature, affording colourless crystals **3**. Yield 0.19 g, 21%. C<sub>14</sub>H<sub>26</sub>Cl<sub>3</sub>N<sub>6</sub>Sb (506.51): calcd. C 33.19, H 5.17, N 16.59; found C 33.25, H 5.08, N 16.48. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 300 K):  $\delta =$  7.57 (br. s, 2 H, hppH<sub>2</sub>), 3.22 (m, 16 H, hpp-CH<sub>2</sub>), 1.92 (m, 8 H, hpp-CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>CN, 300 K):  $\delta =$  159.2, 152.5 (CN<sub>3</sub>), 47.1 (br), 40.7, 38.7, 24.1, 21.3 (hpp-CH<sub>2</sub>) ppm.

**Crystallographic Data Collection and Refinement Procedures:** Details of the crystal data, intensity collection and refinement for complexes **1**, **2** and **3** are presented in Table 1. Crystals were covered in an inert oil, and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. Data was collected at 173(2) K with Mo- $K_a$  radiation at 0.71073 Å. The structures were refined with SHELXL-97.<sup>[29]</sup>

CCDC-848242 (for 1), -848243 (for 2) and -848244 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

## Acknowledgments

We wish to thank the University of Sussex for funding (B. M. D.) and Dr Nikos Tsoureas for collecting X-ray diffraction data for compound **2**.

- [1] M. P. Coles, Dalton Trans. 2006, 985-1001.
- [2] M. P. Coles, Chem. Commun. 2009, 3659-3676.
- [3] P. J. Bailey, S. Pace, Coord. Chem. Rev. 2001, 214, 91-141.
- [4] a) S. L. Aeilts, M. P. Coles, D. C. Swenson, R. F. Jordan, V. G. Young Jr., Organometallics 1998, 17, 3265-3270; b) F. A. Cotton, X. Feng, D. J. Timmons, Inorg. Chem. 1998, 37, 4066-4069; c) M. P. Coles, P. B. Hitchcock, J. Chem. Soc., Dalton Trans. 2001, 1169-1171; d) S. R. Foley, G. P. A. Yap, D. S. Richeson, Polyhedron 2002, 21, 619-627; e) M. P. Coles, P. B. Hitchcock, Organometallics 2003, 22, 5201-5211; f) M. D. Irwin, H. E. Abdou, A. A. Mohamed, J. P. Fackler Jr., Chem. Commun. 2003, 2882-2883; g) M. P. Coles, P. B. Hitchcock, Inorg. Chim. Acta 2004, 357, 4330-4334; h) M. P. Coles, P. B. Hitchcock, Chem. Commun. 2005, 3165-3167; i) C. Brinkmann, F. García, J. V. Morey, M. McPartlin, S. Singh, A. E. H. Wheatley, D. S. Wright, Dalton Trans. 2007, 1570-1572; j) A. A. Mohamed, A. P. Mayer, H. E. Abdou, M. D. Irwin, L. M. Pérez, J. P. Fackler Jr., Inorg. Chem. 2007, 46, 11165-11172; k) G. Robinson, C. Y. Tang, R. Köppe, A. R. Cowley, H.-J. Himmel, Chem. Eur. J. 2007, 13, 2648-2654; l) A. A. Mohamed, H. E. Abdou, A. Mayer, J. P. Fackler Jr., J. Cluster Sci. 2008, 19, 551-559.
- [5] a) F. A. Cotton, C. A. Murillo, D. J. Timmons, *Polyhedron* 1999, 18, 423–428; b) S. J. Birch, S. R. Boss, S. C. Cole, M. P. Coles, R. Haigh, P. B. Hitchcock, A. E. H. Wheatley, *Dalton Trans.* 2004, 3568–3574; c) M. P. Coles, P. B. Hitchcock, *Eur. J. Inorg. Chem.* 2004, 2662–2672.

## FULL PAPER

- [6] a) S. R. Boss, M. P. Coles, R. Haigh, P. B. Hitchcock, R. Snaith, A. E. H. Wheatley, *Angew. Chem.* 2003, 115, 5751; *Angew. Chem. Int. Ed.* 2003, 42, 5593–5596; b) S. R. Boss, M. P. Coles, V. Eyre-Brook, F. García, R. Haigh, P. B. Hitchcock, M. McPartlin, J. V. Morey, N. Hiroshi, P. R. Raithby, H. A. Sparkes, C. W. Tate, A. E. H. Wheatley, *Dalton Trans.* 2006, 5574–5582.
- [7] a) O. Ciobanu, P. Roquette, S. Leingang, H. Wadepohl, J. Mautz, H.-J. Himmel, *Eur. J. Inorg. Chem.* 2007, 4530–4534;
  b) R. Dinda, O. Ciobanu, H. Wadepohl, O. Hübner, R. Acharyya, H.-J. Himmel, *Angew. Chem.* 2007, *119*, 9270; *Angew. Chem. Int. Ed.* 2007, *46*, 9110–9113;
  c) O. Ciobanu, F. Allouti, P. Roquette, S. Leingang, M. Enders, H. Wadepohl, H.-J. Himmel, *Eur. J. Inorg. Chem.* 2008, 5482–5493;
  d) O. Ciobanu, D. Emeljanenko, E. Kaifer, J. Mautz, H.-J. Himmel, *Inorg. Chem.* 2008, *47*, 4774–4778;
  e) O. Ciobanu, E. Kaifer, M. Enders, H.-J. Himmel, *Angew. Chem.* 2009, *121*, 5646; *Angew. Chem. Int. Ed.* 2009, *48*, 5538–5541.
- [8] a) D. Kummer, S. H. A. Halim, W. Kuhs, G. Mattern, J. Organomet. Chem. 1993, 446, 51–65; b) S. H. Oakley, M. P. Coles, P. B. Hitchcock, Dalton Trans. 2004, 1113–1114; c) S. H. Oakley, M. P. Coles, P. B. Hitchcock, Inorg. Chem. 2004, 43, 5168–5172; d) J. Maaranen, O. S. Andell, T. Vanne, I. Mutikainen, J. Organomet. Chem. 2006, 691, 240–246; e) M. P. Coles, S. E. Sözerli, J. D. Smith, P. B. Hitchcock, Organometallics 2007, 26, 6691–6693; f) M. P. Coles, S. M. El-Hamruni, J. D. Smith, P. B. Hitchcock, Organometallics 2007, 26, 6691–6693; f) M. P. Coles, S. M. El-Hamruni, J. D. Smith, P. B. Hitchcock, Angew. Chem. 2008, 120, 10301; Angew. Chem. Int. Ed. 2008, 47, 10147–10150; g) M. P. Coles, S. E. Sözerli, J. D. Smith, P. B. Hitchcock, I. J. Day, Organometallics 2009, 28, 1579–1581; h) R. S. Ghadwal, K. Pröpper, B. Dittrich, P. G. Jones, H. W. Roesky, Inorg. Chem. 2011, 50, 358–364.
- [9] R. D. Shannon, Acta Crystallogr., Sect. A 1976, 32, 751-767.
- [10] a) C. Ergezinger, F. Weller, K. Dehnicke, Z. Naturforsch. Teil B 1988, 43, 1119–1124; b) U. Patt-Seibel, U. Müller, C. Ergezinger, B. Borgsen, K. Dehnicke, D. Fenske, G. Baum, Z. Anorg. Allg. Chem. 1990, 582, 30–36.
- [11] a) F. Weller, J. Pebler, K. Dehnicke, K. Hartke, H.-M. Wolff, Z. Anorg. Allg. Chem. 1982, 486, 61–69; b) W. Höneise, W. Schwarz, G. Heckmann, A. Schmidt, Z. Anorg. Allg. Chem. 1986, 533, 55–64.
- [12] a) P. J. Bailey, R. O. Gould, C. N. Harmer, S. Pace, A. Steiner, D. S. Wright, *Chem. Commun.* 1997, 1161–1162; b) S. P. Green, C. Jones, G. Jin, A. Stasch, *Inorg. Chem.* 2007, *46*, 8–10; c) B. Lyhs, S. Schulz, U. Westphal, D. Bläser, R. Boese, M. Bolte, *Eur. J. Inorg. Chem.* 2009, 2247–2253.
- [13] M. P. Coles, D. C. Swenson, R. F. Jordan, V. G. Young Jr., Organometallics 1997, 16, 5183–5194.

- [14] a) M. P. Coles, P. B. Hitchcock, Polyhedron 2001, 20, 3027-3032; b) S. H. Oakley, M. P. Coles, P. B. Hitchcock, Inorg. Chem. 2003, 42, 3154-3156; c) S. H. Oakley, M. P. Coles, P. B. Hitchcock, Inorg. Chem. 2004, 43, 7564-7566; d) S. H. Oakley, D. B. Soria, M. P. Coles, P. B. Hitchcock, Dalton Trans. 2004, 537-546; e) J. F. Berry, F. A. Cotton, P. Huang, C. A. Murillo, X. Wang, Dalton Trans. 2005, 3713-3715; f) S. H. Oakley, D. B. Soria, M. P. Coles, P. B. Hitchcock, Polyhedron 2006, 25, 1247-1255; g) F. A. Cotton, J. P. Donahue, N. E. Gruhn, D. L. Lichtenberger, C. A. Murillo, D. J. Timmons, L. O. Van Dorn, D. Villagrán, X. Wang, Inorg. Chem. 2006, 45, 201-213; h) A. Peters, U. Wild, O. Hübner, E. Kaifer, H.-J. Himmel, Chem. Eur. J. 2008, 14, 7813-7821; i) U. Wild, P. Roquette, E. Kaifer, J. Mautz, O. Hübner, H. Wadepohl, H.-J. Himmel, Eur. J. Inorg. Chem. 2008, 1248-1257; j) G. M. Chiarella, D. Y. Melgarejo, A. Rozanski, P. Hempte, L. M. Perez, C. Reber, J. P. Fackler Jr., Chem. Commun. 2010, 46, 136-138.
- [15] D. Gudat, T. Gans-Eichler, M. Nieger, Chem. Commun. 2004, 2434–2435.
- [16] A. Lipka, H. Wunderlich, Z. Naturforsch. Teil B 1980, 35, 1548–1551.
- [17] N. J. Hill, G. Reeske, J. A. Moore, A. H. Cowley, *Dalton Trans.* 2006, 4838–4844.
- [18] A. Lipka, Z. Naturforsch. Teil B 1983, 38, 341-346.
- [19] N. Burford, E. Edelstein, J. C. Landry, M. J. Ferguson, R. Mc-Donald, *Chem. Commun.* 2005, 5074–5076.
- [20] M. S. Khalaf, S. H. Oakley, M. P. Coles, P. B. Hitchcock, CrystEngComm 2008, 10, 1653–1661.
- [21] S. K. Porter, R. A. Jaconson, J. Chem. Soc. A 1970, 1356-1359.
- [22] M. G. B. Drew, P. P. K. Claire, G. R. Willey, J. Chem. Soc., Dalton Trans. 1988, 215–218.
- [23] A. T. Mohammed, U. Muller, Z. Naturforsch. Teil B 1985, 40, 562–564.
- [24] S. Pohl, W. Saak, D. Haase, Angew. Chem. 1987, 99, 462; Angew. Chem. Int. Ed. Engl. 1987, 26, 467–468.
- [25] M. Hall, D. B. Sowerby, J. Organomet. Chem. 1988, 347, 59– 70.
- [26] W. S. Shedrick, C. Martin, Z. Naturforsch. Teil B 1992, 47, 919–924.
- [27] I. Díaz, V. Fernández, J. L. Martínez, L. Beyer, A. Pilz, U. Müller, Z. Naturforsch. Teil B 1998, 53, 933–938.
- [28] D. B. Soria, J. Grundy, M. P. Coles, P. B. Hitchcock, *Polyhedron* 2003, 22, 2731–2737.
- [29] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Göttingen, 1997.

Received: October 27, 2011

Published Online: January 9, 2012