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## Antimony(III) and bismuth(III) amides containing pendant N-donor groups – a combined experimental and theoretical study†

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*N,N*- and *N,N,N*-chelated antimony(III) and bismuth(III) chlorides  $L^{1-3}MCl_2$  **1–4** [for  $L^1$ : M = Sb (**1**), for  $L^2$ : M = Sb (**2**) and for  $L^3$ : M = Sb (**3**) and Bi (**4**)], containing ligands  $L^{1-3}$  derived from the pyrrole ring (where  $L^1 = C_4H_3N-2-(CH=N-2',6'-iPr_2C_6H_3)$ ,  $L^2 = C_4H_2N-2,5-(CH_2NMe_2)_2$ ,  $L^3 = C_4H_2N-2,5-(CH_2NC_4H_8)_2$ ), were prepared by the treatment of lithium precursors with  $SbCl_3$  or  $BiCl_3$ . Molecular structures of **1–4** were described both in solution (NMR spectroscopy) and in the solid state (single-crystal X-ray diffraction analysis). Structures of **1–4** were also subjected to a density functional theory study.

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### Introduction

Since the first reports dealing with monoanionic pincer-type ligands by Moulton *et al.*<sup>1</sup> and van Koten *et al.*<sup>2</sup> in 1976 and 1978, respectively, the chemistry of these ligands has been unambiguously developed to be one of the most exciting and studied fields of organometallic chemistry.<sup>3</sup> Although the initial interest was devoted mainly to transition metals, a significant breakthrough in the pincer main group chemistry was achieved during the last few years including several landmark discoveries.<sup>4</sup> We have been interested for some time in the utilization of pincer-type ligands in the field of heavier group 15 elements (Sb and Bi). The majority of these compounds contains classical monoanionic (carbanionic) *N,C,N*<sup>5</sup> or *O,C,O*<sup>6</sup> ligands and only a few examples of compounds containing the *N,C,O*<sup>7</sup> type are known. Noteworthy, there also exists rather a rich chemistry of antimony and bismuth complexes containing neutral donating ligands and significant progress has been achieved in this field.<sup>8</sup>

There exists a significant amount of structurally characterized antimony and bismuth amides<sup>9</sup> including interesting examples of related amidinates and  $\beta$ -diketiminates.<sup>10</sup> Nevertheless, there are, to the best of our knowledge, no examples of antimony or bismuth compounds supported by a monoanionic *N,N,N* pincer-type ligand bonded to the central metal

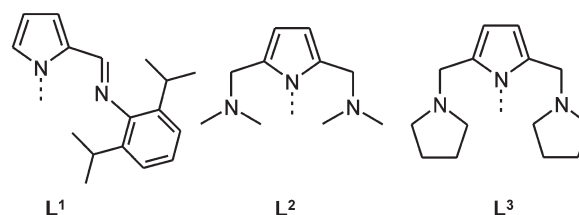


Fig. 1 Ligands used in this study.

*via* a nitrogen–metal bond.<sup>11</sup> We herein report the synthesis and structure of *N,N*- and *N,N,N*-chelated antimony(III) and bismuth(III) chlorides containing ligands  $L^{1-3}$  derived from the pyrrole ring (Fig. 1). Noteworthy, analogous ligands were used for stabilization of group 13 elements<sup>12</sup> and only recently Stalke *et al.* have reported their first utilization in the field of heavier tetrelens.<sup>13</sup> In this study, the structure of compounds **1–4** (Scheme 1) is described both in solution and in the solid state and is subjected to the theoretical investigation with particular emphasis on the description of present metal–nitrogen bonds.

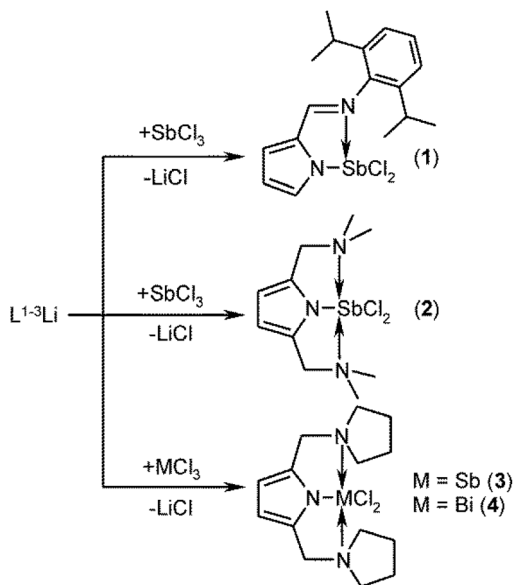
### Results and discussion

The ligand-precursors  $L^{1-3}H$  were prepared according to published procedures.<sup>13,14</sup> Parent pyrroles were first lithiated by *n*BuLi at low temperature ( $-78$  °C) and the observed lithium precursors were *in situ* treated with one molar equivalent of  $SbCl_3$  (or  $BiCl_3$ ) giving **1–4** (Scheme 1). **1–4** were obtained as colourless (**2** and **3**) or yellow crystals (**1** and **4**) in reasonable yields (53–64%). **1** is well soluble in toluene, while the pincer

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Scheme 1 Preparation of 1–4.

compounds 2–4 have only limited solubility in aromatic solvents, but are soluble in chlorinated solvents. Noteworthy, the reaction between  $L^1Li$  and  $BiCl_3$  afforded only a complicated mixture of highly sensitive products. In the case of  $L^2Li$ , the treatment with  $BiCl_3$  resulted in the formation of totally insoluble yellow powder only. The ligand  $L^3$  had to be utilized to improve the solubility of the bismuth compounds, thus leading to 4. The  $^1H$  and  $^{13}C$  NMR spectra of 1–4 revealed expected sets of signals consistent with the proposed structures (Scheme 1; see the Experimental section). Thus, one set of signals was observed for  $L^1$  in  $^1H$  and  $^{13}C$  NMR spectra of 1, where one septet for  $CH$  and two doublets for  $CH_3$  groups were detected in the corresponding  $^1H$  NMR spectrum for the flanking *iPr* groups. The  $^1H$  and  $^{13}C$  NMR spectra of pincer compounds 2–4 revealed only one signal for the methylene  $CH_2N$  group in the whole studied temperature range (295–220 K in  $CDCl_3$  for  $^1H$  NMR spectra), thereby suggesting symmetrical and rigid coordination of the ligand arms as observed in the solid state (*vide infra*). This solution behaviour of 2–4 resembles that established for their *N,C,N* analogues.<sup>5,15</sup>

Molecular structures of 1–4 were determined using a single-crystal X-ray diffraction analysis and are depicted together with related structural parameters in Fig. 2 and 3. The crystallographic data are given in the Experimental section.

The  $N(1)–Sb(1)$  bond lengths amount to 2.0810(15) (1), 2.033(3) [2.031(3) for the second independent molecule of 2] and 2.026(3) Å (3) and these values are only slightly shorter than the sum of the covalent radii of the corresponding atoms  $\sum_{rcov}(Sb, N) = 2.11$  Å.<sup>16</sup> The  $Bi(1)–N(1)$  bond length of 2.129(5) Å also coincides with  $\sum_{rcov}(Bi, N) = 2.22$  Å.<sup>16</sup> Pendant nitrogen functionalities are coordinated to the central atoms in 1–4. The  $Sb(1)–N(2)$  bond distance 2.3234(17) Å in 1 is significantly shorter than the value observed in the *C,N*-chelated analogue [2- $C_6H_4(CH=N-2',6'-iPr_2C_6H_3)$ ]SbCl<sub>2</sub> [2.416(2) Å]<sup>17</sup> and the geo-

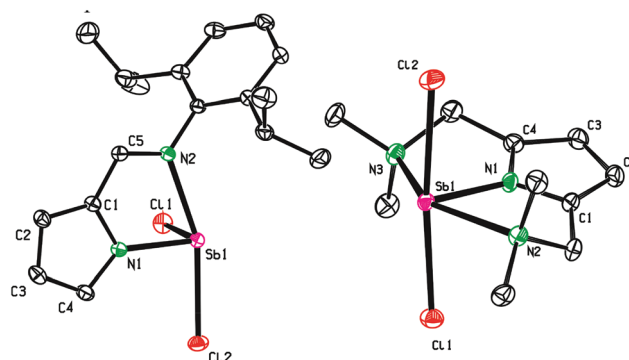


Fig. 2 ORTEP plot of molecules of 1 (left) and 2 (right, one the of two independent molecules is shown and dichloromethane solvate molecules were omitted for clarity). Anisotropic displacement parameters are depicted at the 40% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): 1:  $Sb(1)–N(1)$  2.0810(15),  $Sb(1)–N(2)$  2.3234(17),  $Sb(1)–Cl(1)$  2.3691(6),  $Sb(1)–Cl(2)$  2.5616(6),  $N(1)–Sb(1)–N(2)$  73.90(6),  $Cl(1)–Sb(1)–Cl(2)$  92.21(2),  $N(2)–Sb(1)–Cl(2)$  161.35(4). 2: (structural data for the second independent molecule are given in brackets)  $Sb(1)–N(1)$  2.033(3) [2.032(3)],  $Sb(1)–N(2)$  2.446(3) [2.458(3)],  $Sb(1)–N(3)$  2.462(3) [2.421(3)],  $Sb(1)–Cl(1)$  2.5573(10) [2.5583(10)],  $Sb(1)–Cl(2)$  2.6181(10) [2.6061(11)],  $N(2)–Sb(1)–N(3)$  144.32(9) [144.38(10)],  $Cl(1)–Sb(1)–Cl(2)$  173.54(3) [172.89(3)].

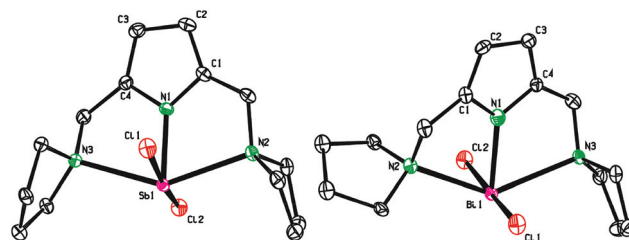


Fig. 3 ORTEP plot of molecules of 3 (left) and 4 (right). Anisotropic displacement parameters are depicted at the 40% probability level. Hydrogen atoms and the dichloromethane solvate molecule (in 3) were omitted for clarity. Selected bond lengths (Å) and angles (°): 3:  $Sb(1)–N(1)$  2.026(3),  $Sb(1)–N(2)$  2.452(2),  $Sb(1)–N(3)$  2.454(2),  $Sb(1)–Cl(1)$  2.5905(7),  $Sb(1)–Cl(2)$  2.5609(6),  $N(2)–Sb(1)–N(3)$  145.06(10),  $Cl(1)–Sb(1)–Cl(2)$  171.85(3). 4:  $Bi(1)–N(1)$  2.129(5),  $Bi(1)–N(2)$  2.505(7),  $Bi(1)–N(3)$  2.584(6),  $Bi(1)–Cl(1)$  2.644(3),  $Bi(1)–Cl(2)$  2.703(3),  $N(2)–Bi(1)–N(3)$  139.51(17),  $Cl(1)–Bi(1)–Cl(2)$  178.98(5).

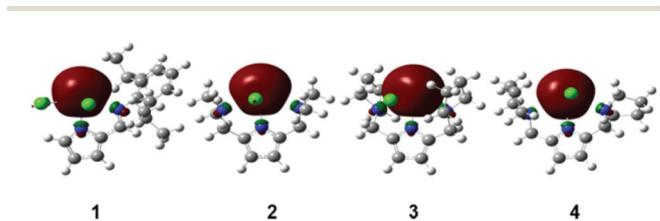
metry around the central antimony atom in 1 is best described as a see-saw type.  $N \rightarrow Sb$  interactions in 2 and 3 [in the range 2.421(3)–2.461(3) Å] are close to the values observed in a classical *N,C,N* pincer compound [C<sub>6</sub>H<sub>3</sub>-2,6-(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]SbCl<sub>2</sub><sup>18</sup> [2.491(9) and 2.422(8) Å]. Analogously, the  $N \rightarrow Bi$  intramolecular interactions in 4 [2.505(7) and 2.584(6) Å] are similar to the *N,C,N* chelated analogues: [C<sub>6</sub>H<sub>3</sub>-2,6-(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]BiCl<sub>2</sub><sup>15</sup> [2.561(3) and 2.570(4) Å] and {C<sub>6</sub>H<sub>3</sub>-2,6-[CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>]}BiCl<sub>2</sub><sup>19</sup> [2.583(5) and 2.563(4) Å]. The coordination polyhedron around the central atoms in 2–4 may be described as a distorted pseudo-octahedron with the nitrogen (pyrrole) atom placed in the apical position, while the remaining nitrogen and chlorine atoms form the basal plane. The stereochemically active lone pair (*vide further discussion*) of the central atoms is then located in the *trans* position to the

**Table 1** Bond lengths [Å] in 1–4 (Gaussian09, def2-TZVP)

	BP86	M06-L	M06-2X	Expr.
<b>1 (M = Sb)</b>				
M–N(1)	2.126	2.116	2.081	2.0810(15)
M–N(2)	2.522	2.493	2.323	2.3234(17)
M–Cl(1)	2.389	2.370	2.369	2.3691(6)
M–Cl(2)	2.464	2.441	2.561	2.5616(6)
<b>2 (M = Sb)</b>				
M–N(1)	2.072	2.059	2.033	2.033(3)
M–N(2)	2.552	2.521	2.446	2.446(3)
M–N(3)	2.552	2.521	2.461	2.462(3)
M–Cl(1)	2.593	2.580	2.557	2.5573(10)
M–Cl(2)	2.593	2.580	2.618	2.6181(10)
<b>3 (M = Sb)</b>				
M–N(1)	2.070	2.059	2.026	2.026(3)
M–N(2)	2.553	2.518	2.452	2.452(2)
M–N(3)	2.554	2.518	2.454	2.454(2)
M–Cl(1)	2.600	2.588	2.561	2.5609(6)
M–Cl(2)	2.600	2.588	2.591	2.5905(7)
<b>4 (M = Bi)</b>				
M–N(1)	2.169	2.161	2.129	2.129(5)
M–N(2)	2.589	2.551	2.505	2.505(7)
M–N(3)	2.643	2.603	2.584	2.584(6)
M–Cl(1)	2.673	2.671	2.703	2.644(3)
M–Cl(2)	2.663	2.653	2.644	2.703(3)

**Table 3** Wiberg bond indices in 1–4 (M06-2X/def2-TZVP)

	1 (M = Sb)	2 (M = Sb)	3 (M = Sb)	4 (M = Bi)
M–N(1)	0.53	0.49	0.47	0.46
M–N(2)	0.23	0.25	0.24	0.21
M–N(3)	—	0.25	0.24	0.21
M–Cl(1)	0.65	0.49	0.48	0.45
M–Cl(2)	0.75	0.49	0.48	0.43

**Fig. 4** Presentation of lone pairs of central atoms in 1–4.

pyrrole nitrogen atom. This spatial arrangement closely resembles that usually found in the *N,C,N* chelated counterparts.<sup>17–19</sup>

As 1–4 represent, to the best of our knowledge, rare examples of *N,N*- and *N,N,N*-chelated antimony and bismuth compounds, they were subjected to the theoretical study with the aim to describe in detail the bonding situation in these compounds. For organometallic compounds, we have found that BP86/def2-TZVP yield very reasonable results.<sup>20</sup> For the compounds presented here, this is not the case. Table 1 summarizes the most important bond lengths for all four compounds and a comparison with the experimental values.

It appears that BP86 overestimates strongly all M–N bonds such that the description is not convincing. In the last year, the pure functional M06-L came up, which is highly useful for organometallic chemistry as well,<sup>21</sup> but this functional fails in the correct description of the structures. Hence, we tried the hybrid functional M06-2X which finally gave very good results in accordance with the experimental data. Then, we investigated all the compounds by natural bond orbital analysis using NBO6.0. Besides the natural charges in Table 2, we analysed the Wiberg bond indices (Table 3). The second order perturbation theory predicted all characteristic M–N bonds to be covalent two-electron–two centre bonds.

**Table 2** NBO charges (in  $e^-$  units) in 1–4 (M06-2X/def2-TZVP)

	1 (M = Sb)	2 (M = Sb)	3 (M = Sb)	4 (M = Bi)
M	1.57	1.70	1.74	1.85
N(1)	–0.67	–0.71	–0.73	–0.71
N(2)	–0.55	–0.46	–0.47	–0.48
N(3)	—	–0.46	–0.47	–0.46
Cl(1)	–0.56	–0.67	–0.67	–0.70
Cl(2)	–0.48	–0.67	–0.67	–0.71

The natural charges show that the pyrrole donor is more negatively charged compared to the other N donors (as expected). However, taking into consideration that pyrrole coordinates as anionic ligands, the charge difference is not so large. The Wiberg bond index displays clearly that the pyrrole donor possesses almost the double donor strength than the imine (1) or amine (2–4) donors: the pyrrole–metal bond has a WBI of 0.53–0.46 whereas the imine/amine–metal bond is estimated to a WBI of only 0.21–0.25. Finally, the stereochemically active lone pair of central atoms is then located in the *trans* position to the pyrrole nitrogen atom in all four complexes (Fig. 4). The lone pair has a mixed s and p character which gives the stereochemical preference (p-character in percent: 1: 19%, 2: 15%, 3: 14%, 4: 8%). 8% for the bismuth compound 4 appears to be not much but gives a direction to the spherical s-orbital contribution.

## Conclusions

In conclusion, *N,N*- and *N,N,N*-chelated antimony and bismuth compounds 1–4 were prepared and their structures were described both from an experimental and a theoretical point of view. It was shown that the metal–nitrogen(pyrrole) bond is a covalent two-electron–two centre bond. The strength of additional N→M (M = Sb or Bi) intramolecular interactions is well comparable with the carbanionic *N,C,N* analogues, thereby proving promising potential of  $L^{1-3}$  and related ligands for stabilization of antimony and bismuth compounds similar to classical pincer-type ligands. The reactivity of 1–4 and analogous compounds is currently under investigation.

## Experimental

### General procedures

All manipulations were carried out under an argon atmosphere using standard Schlenk tube techniques. All solvents were dried by standard procedures or using a Pure Solv–Innovative

Technology equipment.  $C_6D_6$  and  $CDCl_3$  were distilled from  $LiAlH_4$  and degassed before use. The  $^1H$ ,  $^{13}C$  NMR spectra were recorded on a Bruker 400 MHz spectrometer, using a 5 mm tunable broadband probe. Appropriate chemical shifts in  $^1H$  and  $^{13}C$  NMR spectra were related to the residual signals of the solvent [ $CDCl_3$ :  $\delta(^1H) = 7.27$  ppm and  $\delta(^{13}C) = 77.23$  ppm,  $C_6D_6$ :  $\delta(^1H) = 7.16$  ppm,  $\delta(^{13}C) = 128.39$  ppm]. Elemental analyses were performed by an LECO-CHNS-932 analyser.

### Computational details

The calculations were performed with Gaussian09<sup>22</sup> by using the BP86<sup>23</sup> and M06-L<sup>24</sup> pure functional and with the hybrid functional M06-2X<sup>24</sup> with the Ahlrichs def2-TZVP basis set,<sup>25</sup> which includes effective core potentials on antimony and bismuth. Tight convergence criteria were applied. Both stationary points were characterized by frequency analysis and show the correct number of negative eigenvalues (zero for a local minimum). Based on the geometry obtained by the M06-2X/def2-TZVP method, a NBO analysis was performed by using this method with NBO 6.0.<sup>26</sup> The Wiberg indices were used as implemented in Gaussian09.<sup>22</sup>

### Syntheses

**Synthesis of  $L^1SbCl_2$  (1).** Hexane solution of  $nBuLi$  (2.6 mL, 4.2 mmol, 1.6 M solution) was added to a pre-cooled ( $-80$  °C) solution of  $L^1H$  (1.064 g, 4.2 mmol) in diethylether (30 mL) and then stirred for 1 h at r.t. The resulting white suspension of  $L^1Li$  was added to a pre-cooled solution ( $-40$  °C) of  $SbCl_3$  (0.954 g, 4.2 mmol) in diethylether (30 mL). The reaction mixture was stirred for 3 h at r.t. and evaporated *in vacuo*. The remaining insoluble solid was extracted with warm toluene (30 mL,  $60$  °C) and the yellow extract was slightly concentrated and after storage of this solution for several days at  $-30$  °C gave yellow single-crystals of **1**, which were collected by filtration and dried *in vacuo*. Yield: 1.15 g (62%). M.p.  $151$  °C. Anal. calc. for  $C_{17}H_{21}Cl_2N_2Sb$  ( $M_W$  446.03): C, 45.8; H, 4.8; Found: C, 45.5; H, 4.6%.  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  0.98 (d, 6H,  $CH(CH_3)_2$ ), 1.13 (d, 6H,  $CH(CH_3)_2$ ), 2.92 (sept, 2H,  $CH(CH_3)_2$ ), 6.23 (dd, 1H, pyrrole CH), 6.60 (dd, 1H, pyrrole CH), 7.08 (m, 3H,  $C_6H_3$ ), 7.58 (d, 1H,  $CH=N$ ), 8.11 (d, 1H, pyrrole CH).  $^{13}C$  NMR (100.61 MHz,  $C_6D_6$ ):  $\delta$  24.5 (s,  $CH(CH_3)_2$ ), 26.0 (s,  $CH(CH_3)_2$ ), 29.1 (s,  $CH(CH_3)_2$ ), 115.5 (s, pyrrole CH), 123.2 (s, pyrrole CH), 124.6 (s,  $C_6H_3$ ), 127.9 (s,  $C_6H_3$ ), 135.2 (s, pyrrole C), 136.1 (s, pyrrole CH), 141.4 (s,  $C_6H_3$ ), 142.4 (s,  $C_6H_3$ ), 157.2 (s,  $CH=N$ ).

**Synthesis of  $L^2SbCl_2$  (2).** Hexane solution of  $nBuLi$  (5.2 mL, 8.3 mmol, 1.6 M solution) was added to a pre-cooled ( $-80$  °C) solution of  $L^2H$  (1.510 g, 8.3 mmol) in diethylether (30 mL) and stirred for 1 h at r.t. The resulting yellow solution was added to a pre-cooled solution ( $-40$  °C) of  $SbCl_3$  (1.900 g, 8.3 mmol) in diethylether (30 mL). The reaction mixture was stirred for 3 h at r.t. and evaporated *in vacuo*. The remaining insoluble solid was extracted with dichloromethane (30 mL) and the rosy extract was slightly concentrated and storage of this solution for several days at  $-30$  °C gave colourless single-

crystals of **2**, which were collected by filtration and dried *in vacuo*. Yield: 1.64 g (53%). M.p.  $124$  °C. Anal. calc. for  $C_{10}H_{18}Cl_2N_3Sb$  ( $M_W$  372.94): C, 32.2; H, 4.9; Found: C, 32.4; H, 4.7%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  2.88 (s, 12H,  $N(CH_3)_2$ ), 4.03 (s, 4H,  $CH_2N$ ), 6.00 (s, 2H, pyrrole CH).  $^{13}C$  NMR (100.61 MHz,  $CDCl_3$ ):  $\delta$  47.5 (s,  $N(CH_3)_2$ ), 58.1 (s,  $CH_2N$ ), 107.3 (s, pyrrole CH), 131.2 (s, pyrrole C).

**Synthesis of  $L^3SbCl_2$  (3).** Hexane solution of  $nBuLi$  (2.7 mL, 4.4 mmol, 1.6 M solution) was added to a pre-cooled ( $-80$  °C) solution of  $L^3H$  (1.030 g, 4.4 mmol) in diethylether (30 mL) and stirred for 1 h at r.t. The resulting yellowish suspension of  $L^3Li$  was added to a pre-cooled solution ( $-40$  °C) of  $SbCl_3$  (1.006 g, 4.4 mmol) in diethylether (30 mL). The reaction mixture was stirred for 3 h at r.t. and evaporated *in vacuo*. The remaining insoluble solid was extracted with dichloromethane (30 mL) and the rosy extract was slightly concentrated and storage of this solution for several days at  $-30$  °C gave colourless single-crystals of **3**, which were collected by filtration and dried *in vacuo*. Yield: 1.21 g (64%). M.p.  $156$  °C. Anal. calc. for  $C_{14}H_{22}Cl_2N_3Sb$  ( $M_W$  425.01): C, 39.6; H, 5.2; Found: C, 39.8; H, 5.4%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  2.05 (m, 8H,  $NC_4H_8$ ), 2.83 (m, 4H,  $NC_4H_8$ ), 4.00 (m, 4H,  $NC_4H_8$ ), 4.18 (s, 4H,  $CH_2N$ ), 6.00 (s, 2H, pyrrole CH).  $^{13}C$  NMR (100.61 MHz,  $CDCl_3$ ):  $\delta$  23.2 (s,  $NC_4H_8$ ), 54.8 (s,  $CH_2N$ ), 56.3 (s,  $NC_4H_8$ ), 106.5 (s, pyrrole CH), 131.4 (s, pyrrole C).

**Synthesis of  $L^3BiCl_2$  (4).** Hexane solution of  $nBuLi$  (3.4 mL, 5.4 mmol, 1.6 M solution) was added to a pre-cooled ( $-80$  °C) solution of  $L^3H$  (1.260 g, 5.4 mmol) in diethylether (30 mL) and stirred for 1 h at r.t. The resulting yellow suspension was added to a pre-cooled solution ( $-40$  °C) of  $BiCl_3$  (1.701 g, 5.4 mmol) in diethylether (30 mL). The reaction mixture was stirred for 3 h at r.t. and evaporated *in vacuo*. The remaining insoluble solid was extracted with dichloromethane (30 mL) and the yellow extract was slightly concentrated and storage of this solution for several days at  $-30$  °C gave yellow-orange single crystals of **4**, which were collected by filtration and dried *in vacuo*. Yield: 1.62 g (59%). M.p.  $154$  °C. Anal. calc. for  $C_{14}H_{22}Cl_2N_3Bi$  ( $M_W$  512.23): C, 32.8; H, 4.3; Found: C, 32.6; H, 4.4%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  2.03 (m, 8H,  $NC_4H_8$ ), 3.17 (m, 4H,  $NC_4H_8$ ), 4.08 (m, 4H,  $NC_4H_8$ ), 4.53 (s, 4H,  $CH_2N$ ), 6.03 (s, 2H, pyrrole CH).  $^{13}C$  NMR (100.61 MHz,  $CDCl_3$ ):  $\delta$  23.5 (s,  $NC_4H_8$ ), 56.0 (s,  $NC_4H_8$ ), 56.7 (s,  $CH_2N$ ), 107.6 (s, pyrrole CH), 139.0 (s, pyrrole C).

### X-ray crystallography

Suitable single-crystals of **1–4** were mounted on a glass fibre with an oil and measured on a four-circle diffractometer KappaCCD with a CCD area detector by monochromatized  $MoK\alpha$  radiation ( $\lambda = 0.71073$  Å) at 150(1) K. The numerical<sup>27</sup> absorption corrections from the crystal shape were applied for all crystals. The structures were solved by the direct method (SIR92)<sup>28</sup> and refined by a full matrix least squares procedure based on F2 (SHELXL97).<sup>29</sup> Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors  $H_{iso}$  ( $H$ ) = 1.2  $U_{eq}$  (pivot atom) or of 1.5  $U_{eq}$  for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl,



methylene, and hydrogen atoms in the aromatic ring, respectively. The final difference maps displayed no peaks of chemical significance as the highest peaks and the holes are in close vicinity ( $\sim 1$  Å) of heavy atoms. Slightly disordered dichloromethane, used as a solvent in the case of **2**, was treated by standard procedures, where one of the chlorine atoms is refined into two positions with a 60/40 occupancy ratio. Crystallographic data for structural analysis are summarized below and has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1017116–1017119.

**Crystallographic data for 1.**  $C_{17}H_{21}Cl_2N_2Sb$ ,  $M = 446.01$ , monoclinic,  $P2_1/c$ ,  $a = 11.1671(7)$ ,  $b = 10.8550(5)$ ,  $c = 17.3739(7)$  Å,  $\beta = 119.731(4)^\circ$ ,  $V = 1828.81(18)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150(1)$  K, 23 704 total reflections, 5544 independent reflections ( $R_{\text{int}} = 0.027$ ,  $R_1$  (obs. data) = 0.021,  $wR_2$  (all data) 0.050),  $S = 1.139$ ,  $\Delta\rho$ , max., min. [ $e$  Å<sup>-3</sup>] 0.571,  $-0.786$ , CCDC 1017116.

**Crystallographic data for 2.**  $C_{10}H_{18}Cl_2N_3Sb \cdot CH_2Cl_2$ ,  $M = 457.85$ , monoclinic,  $P2_1/c$ ,  $a = 8.6800(7)$ ,  $b = 26.242(2)$ ,  $c = 16.6360(12)$  Å,  $\beta = 113.379(8)^\circ$ ,  $V = 3478.3(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $T = 150(1)$  K, 24 447 total reflections, 7647 independent reflections ( $R_{\text{int}} = 0.045$ ,  $R_1$  (obs. data) = 0.031,  $wR_2$  (all data) 0.071),  $S = 1.180$ ,  $\Delta\rho$ , max., min. [ $e$  Å<sup>-3</sup>] 0.949,  $-1.162$ , CCDC 1017119.

**Crystallographic data for 3.**  $2(C_{14}H_{22}Cl_2N_3Sb) \cdot CH_2Cl_2$ ,  $M = 934.92$ , monoclinic,  $C2$ ,  $a = 19.8552(4)$ ,  $b = 8.2449(3)$ ,  $c = 14.0093(6)$  Å,  $\beta = 130.412(4)^\circ$ ,  $V = 1746.19(15)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 150(1)$  K, 6524 total reflections, 3739 independent reflections ( $R_{\text{int}} = 0.026$ ,  $R_1$  (obs. data) = 0.016,  $wR_2$  (all data) 0.042),  $S = 1.146$ ,  $\Delta\rho$ , max., min. [ $e$  Å<sup>-3</sup>] 0.414,  $-0.815$ , CCDC 1017117.

**Crystallographic data for 4.**  $C_{14}H_{22}BiCl_2N_3$ ,  $M = 512.23$ , monoclinic,  $P2_1/c$ ,  $a = 8.7020(5)$ ,  $b = 20.6791(14)$ ,  $c = 12.1480(7)$  Å,  $\beta = 132.669(5)^\circ$ ,  $V = 1607.3(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150(1)$  K, 13 439 total reflections, 3650 independent reflections ( $R_{\text{int}} = 0.039$ ,  $R_1$  (obs. data) = 0.042,  $wR_2$  (all data) 0.096),  $S = 1.216$ ,  $\Delta\rho$ , max., min. [ $e$  Å<sup>-3</sup>] 3.800,  $-3.006$ , CCDC 1017118.

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