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On the Reduction of NC[‡] Chelated Organoantimony(III) Chlorides[‡‡]

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The conversion of organolithium compound **L**Li, for which **L** = [*o*-C_6H_4(CH=NC_6H_3*i*Pr_2-2,6)]$^-$, with antimony chloride gave the molecular chlorides **L**$SbCl_2$ (**1**) and $\mathbf{L}_2$SbCl (**2**) depending on the molar ratio used (either 1:1 or 2:1). Both compounds were characterized by using ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction. The reaction of **1** with two molar equivalents of K[B(*s*Bu)$_3$H] led to smooth formation of compound $\mathbf{L}_4Sb_4$ (**3**) as a result of hydrogen elimination from the unstable hydrido compound. On the contrary, a similar reaction between **2** and K[B(*s*Bu)$_3$H] (1:1) did not result in hydrogen elimination and the formation of expected distibine $\mathbf{L}_2$SbSb$\mathbf{L}_2$, but an addition of an in situ generated $\mathbf{L}_2$Sb–H bond across the C=N functionality in the pendant arm of one of the ligands was observed. The reduction of compound **2** with an excess amount of magnesium was strongly dependent on the reaction time. The distibine $\mathbf{L}_2$SbSb$\mathbf{L}_2$ (**5**) could be isolated after 4–5 h from this reaction mixture. Elongation of the reaction time to 1 d (and more) gave a more complicated reaction mixture, in which three products, distibine **5**, compound **3** and organomagnesium compound $\mathbf{L}_2$Mg(THF) (**6**), were characterized by single-crystal X-ray diffraction in addition to other unidentified products. These results can be rationalized by a migration of the ligand **L** from the antimony atom to the magnesium, thus explaining formation of both $\mathbf{L}_4Sb_4$ (**3**) compound and $\mathbf{L}_2$Mg(THF) (**6**).

Introduction

In 1965, Issleib et al. reported on the synthesis of *t*Bu_4Sb_4 as the first example of well-defined molecular organometallic compounds with central antimony atoms in, up to that moment, an unusually low oxidation state.[1] This pioneering work was followed by many other works that dealt with the preparation of analogous compounds with low-valent antimony or bismuth centres.[2] This led to the description of monocyclic derivatives of Sb and Bi R_nM_n (*n* = 3–6),[3] and several exciting polycyclic systems[2a,3h,4] as well as a significant number of distibines and dibismuthines[4a,5] R_2MMR_2 were isolated (M = Sb or Bi). Another landmark in the research in this field was the preparation of the dibismuthene RBi=BiR as an analogue of alkenes with a double bond between bismuth atoms by Okazaki and Tokitoh,[6] which was shortly followed by the isolation of antimony analogue RSb=SbR.[7] Power et al. reported on dibismuthenes and distibenes, stabilized by terphenyl ligands, that were prepared by the reduction of chlorido precursors by alkali metals as well.[8] The common feature of the majority of reported compounds is the shielding of the metallic core by ligands that are sterically very demanding, which gives sufficient kinetic stability to the compounds. Another approach toward the stabilization of such compounds is the coordination of the central antimony (or bismuth) atom to a transition-metal fragment,[9] which electronically influences and stabilizes the low-valent antimony or bismuth atom. Quite recently, Breunig et al. proved,[10] as a reminder of the electronic stabilization of low-valent antimony and bismuth atoms by transition metals, the ability of an NC chelating ligand, [*o*-$C_6H_4(CH_2NMe_2)$]$^-$ (Figure 1, A, denoted as $\mathbf{L}^{\#}$) to stabilize both low-valent anti-

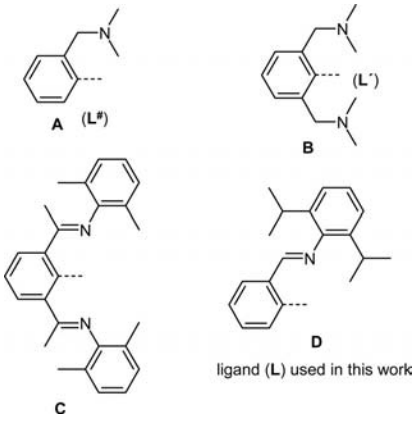

Figure 1. Structures of selected NC and NCN chelating ligands.

[‡] NC designates [*o*-C_6H_4(CH=NC_6H_3*i*Pr_2-2,6)]$^-$

[‡‡] The same ligand system for the stabilization of antimony bromides and sulfides was recently reported by M. Mehring et al. at the Third EuCheMS Chemistry Congress, Nürnberg, Germany, poster no. VIIb.097.

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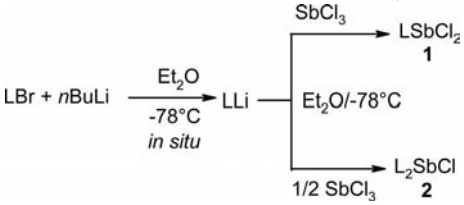
mony and bismuth atoms. The same group also proved that a related NCN pincer-type ligand, $[o,o\text{-}C_6H_4(CH_2NMe_2)_2]^-$ (Figure 1, B, denoted as **L′**) can stabilize organobismuthine $\mathbf{L'}_2BiBi\mathbf{L'}_2$.[11,12]

We have used the same ligand (**L′**) for the preparation of monocyclic stibine $\mathbf{L'}_4Sb_4$ by the reduction of the parent chlorido compound. More importantly, a unique byproduct was isolated from the reaction mixture, namely, $\mathbf{L'}_3Sb_5$ cluster compound with a propellane-like structure.[13] Recently we demonstrated that the use of the more sterically demanding NCN ligand (Figure 1, C), which contains two ketimino donor arms, allowed us to obtain unprecedented monomeric stibinidene and bismuthinidene.[14]

To shed more light on the possibility of stabilization of low-valent heavier main-group centres by similar chelating ligands, we decided to start systematic research into a similar NCN pincer as well as analogous sterically demanding NC ligands. As a part of our effort, we report here on the use of ligand **L**, $[o\text{-}C_6H_4(CH{=}NC_6H_3i\text{Pr}_2\text{-}2,6)]^-$ (Figure 1, D), which contains only one ketimino pendant arm but is armed with a bulky aryl substituent. Synthesis of starting chlorido compounds $\mathbf{L}SbCl_2$ and $\mathbf{L}_2SbCl$ and attempts toward their reduction either by means of a dehydro–coupling synthetic protocol[15] through unstable hydrido precursors or by conventional reduction with magnesium are discussed.

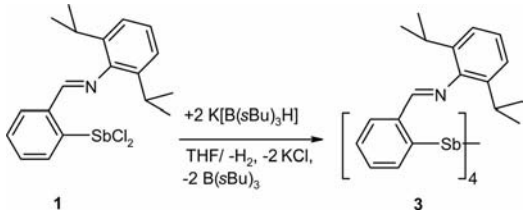
Results and Discussion

Treatment of in situ prepared organolithium compound **L**Li in diethyl ether, recently isolated by Mu et al. from hexane,[16] with antimony chloride gave either $\mathbf{L}SbCl_2$ (**1**) or $\mathbf{L}_2SbCl$ (**2**) according to the molar ratio used (Scheme 1). Both compounds were isolated as air stable white (**1**) or yellow (**2**) solids in reasonable yield (46% and 67%). The identity of **1** and **2** was established by elemental analysis, ^1H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction techniques. The ^1H NMR spectrum of **1** revealed one set of sharp signals, in which two doublets are present for the methyl groups of *i*Pr groups, thus suggesting the presence of rigid N→Sb interactions in solution. Two sets of signals were obtained in the ^1H NMR spectrum of **2**, thus pointing to the fact that both ligands are nonequivalent in the structure of **2** (probably due to different strengths of the N→Sb interactions), which is consistent with the solid state of **2** (vide infra). Interestingly, an analogous compound that contained two NC ligands, $\mathbf{L}^{\#}_2SbCl$ (Figure 1, A), displayed one set of broad signals at ambient temperature as a result of the fluxional behaviour of this compound, but at –60 °C two sets of signals were resolved, which was ascribed only to the nonequivalent degrees of N→Sb coordination.[17] This comparison points to the conclusion that the N→Sb interactions in the case of **2**, which contains ligand **L**, are more rigid than in the analogue with classical $\mathbf{L}^{\#}$ ligand (Figure 1, A).



Scheme 1. Preparation of compounds **1** and **2**.

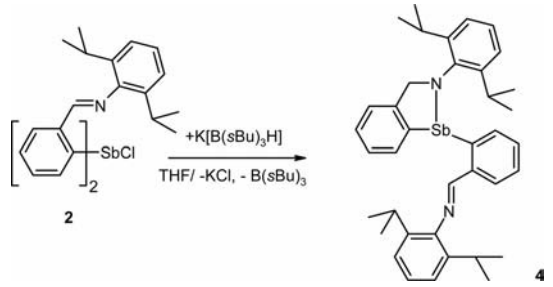
Analogously to the synthetic protocol used by us recently for preparation of low-valent antimony compounds, we treated compounds **1** and **2** with one or two equivalents of $K[B(s\text{Bu})_3H]$ with the aim of preparing unstable hydrido complexes that should eliminate hydrogen gas and form low-valent metal centres.[13,14] In the case of precursor **1**, the reaction proceeded smoothly in an expected manner through visible hydrogen-gas evolution. Organoantimony(I) compound $\mathbf{L}_4Sb_4$ (**3**) could be isolated after extraction (toluene) as an air-sensitive reddish solid in 45% yield (Scheme 2). This compound was characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy, which revealed only one set of relatively sharp signals, thereby ruling out any ring–ring equilibrium that would give rise to anything other than the four-membered ring and also proving the equivalency of all ligands in the structure. Similar findings were reported for four-membered ring systems $\mathbf{L}^{\#}_4Sb_4$[10b] or $\mathbf{L'}_4Sb_4$.[13] Compound **3** is stable for a long time both in solution and in the solid state under an argon atmosphere.



Scheme 2. Reaction of **1** with $K[B(s\text{Bu})_3H]$.

On the contrary, the analogous treatment of **2** with one equivalent of $K[B(s\text{Bu})_3H]$ most probably led to the formation of a hydrido compound, which may be postulated as $\mathbf{L}_2SbH$, but instead of the expected hydrogen elimination and the formation of the target compound $\mathbf{L}_2SbSb\mathbf{L}_2$, an addition of an in situ generated Sb–H bond across the C=N double bond in one of the ligand arms was observed. This reaction pathway led to isolation of compound **4** in 48% yield (Scheme 3); it contained a new Sb–N covalent bond within an aza-stiba ring. All our attempts to identify the intermediate $\mathbf{L}_2SbH$ failed. The ^1H NMR spectroscopic experiment of addition of $K[B(s\text{Bu})_3H]$ to **2** in C_6D_6 smoothly gave compound **4** after less than 1 min. (see the Supporting Information). Similarly, mixing $K[B(s\text{Bu})_3H]$ and **2** at –80 °C followed by the addition of an excess amount of *t*BuNC or *t*BuCN (10 equiv.) did not lead to addition across the Sb–H bond, but compound **4** was isolated as the major product. The identity of compound **4** and the unambiguous evidence for addition across the C=N double bond

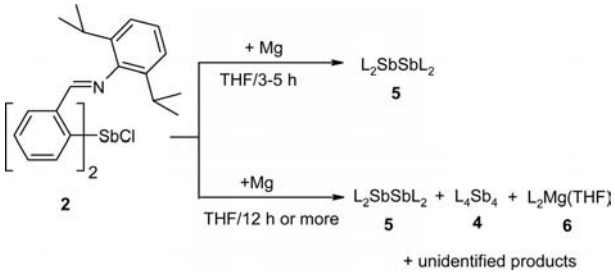
stems mainly from ^{1}H and ^{13}C NMR spectroscopic data (Figure S1). The ^{1}H NMR spectrum of **4** revealed an AX pattern at δ = 5.18 ppm, which is indicative of the formation of a methylene group CH_2N in the ligand arm. This resonance pattern is typical for classical CN- or NCN-chelated organoantimony compounds with CH_2NR_2 pendant arms. The observation of only one singlet resonance for C*H*=N (at δ = 8.05 ppm) in the ^{1}H NMR spectrum of **4**, which has an integral intensity of 1:2 compared to the AX pattern for the new CH_2N group, is further proof for the proposed structure of **4**. Finally, the signal at δ = 70.0 ppm in the ^{13}C NMR spectrum of **4** also established the formation of a *C*H_2N linkage, and only one signal with a typical chemical shift at δ = 167.8 ppm for *C*H=N was detected, thereby further supporting the proposed structure of **4**. Unfortunately, all of our numerous attempts to obtain suitable single crystals of **4** for X-ray diffraction techniques failed.



Scheme 3. Reaction of **2** with K[B(*s*Bu)$_3$H].

These findings reveal interesting differences in the reaction between either **1** or **2** and K[B(*s*Bu)$_3$H]. The reduction of the central atom and formation of compound **3** is obtained when **1** is used as starting material, whereas addition of the Sb–H bond across the C=N double bond of the ligand backbone is preferred in the second case, thereby giving compound **4**.

To overcome the problems with the preparation of compound **L**$_2$SbSb**L**$_2$, the reduction of precursor **2** with magnesium (Scheme 4), which was proven to be very convenient for the preparation of similar NC-chelated (**L**$^{\#}$) organoantimony compounds,[10] was applied. Although this method allowed us to isolate the desired compound **L**$_2$SbSb**L**$_2$ (**5**), the reaction was not as straightforward as expected. The reaction mixture started to turn orange-red immediately, and if the reaction mixture was evaporated after, typically, 3–5 h and extracted by hexane, compound **5** could by crystallized in moderate yield as an orange-red crystalline material. However, in most cases, the crude mixture contained a significant amount of starting material **2** and unfortunately this compound was also soluble in hexane. Consequently, isolation of pure **5** requires several recrystallization steps, which cause a significant decrease in the reaction yield (39%). Compound **5** was characterized by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy, which revealed only one set of signals for all four ligands in the structure of **5**, thereby suggesting the highly fluxional structure of **5** in solution at ambient temperature.



Scheme 4. Reduction of **2** by magnesium.

Prolonging the reaction time to 12 or 24 h[10] as a logical attempt to increase the reaction yield of **5** resulted in an even more complicated mixture of products, which we were not able to describe and understand completely. Besides the expected and desired compound **5**, the compound **L**$_4$Sb$_4$ **3** was identified, the presence of which was proven based on the analysis of the ^{1}H and ^{13}C NMR spectra of these mixtures. By chance, we were able to obtain from this mixture single crystals of an organomagnesium derivative **L**$_2$Mg(THF) (**6**) for X-ray diffraction measurements (see the Supporting Information). This result may be rationalized by migration of the ligand **L** from the antimony atom to magnesium, which is also supported by the identification of compound **L**$_4$Sb$_4$ (**3**), which may be formed in this reaction mixture only by a loss (migration) of one ligand. Unfortunately, all of our numerous attempts to isolate compound **6** in larger quantities by a controlled procedure from the treatment of **2** with Mg or, for example, by reduction of **1** with Mg failed. Similarly, the possibility of the formation of **6** by treating **1** or **2** with $MgCl_2$ was ruled out and only starting materials were isolated after reaction even when an excess amount of $MgCl_2$ and long reaction times (more than 1 week) were applied.

Molecular structures of **1**–**3**, **5** and **6** were determined by X-ray diffraction techniques and are depicted in Figures 2, 3, 4, 5 and Figure S3 (for the latter, see the Supporting In-

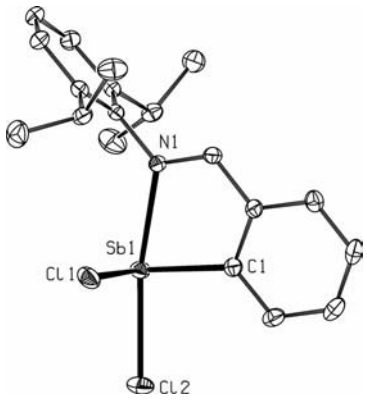


Figure 2. ORTEP diagram of compound **1** with thermal displacement parameters at 30% probability. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Sb1–C1 2.149(3), Sb1–N1 2.416(2), Sb1–Cl1 2.3704(8), Sb1–Cl2 2.4856(7); C1–Sb1–N1 74.15(8), C1–Sb1–Cl1 95.93(7), C1–Sb1–Cl2 92.62(9), N1–Sb1–Cl2 163.96(5).

formation). Relevant structural parameters are given in the figure captions.

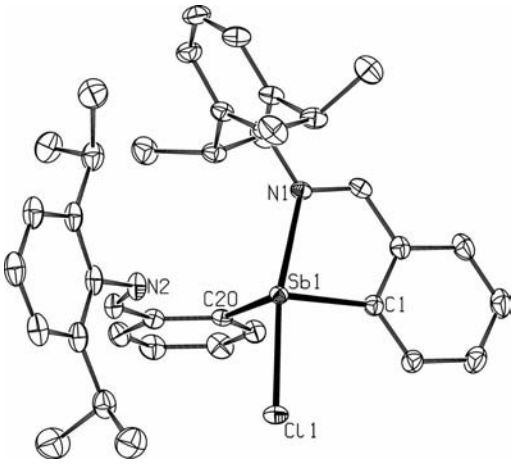


Figure 3. ORTEP diagram of compound **2** with thermal displacement parameters at 30% probability. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Sb1–C1 2.168(3), Sb1–C20 2.161(2), Sb1–N1 2.416(2), Sb1–N2 2.952(3), Sb1–Cl1 2.5149(7); C1–Sb1–N1 73.81(9), C1–Sb1–N2 163.81(8), C1–Sb1–C20 95.51(10), C1–Sb1–Cl1 91.86(7), N1–Sb1–Cl1 163.76(6), N2–Sb1–C1 163.81(8), C20–Sb1–N1 85.43(8), C20–Sb1–N2 68.38(9), C20–Sb1–Cl1 88.49(7).

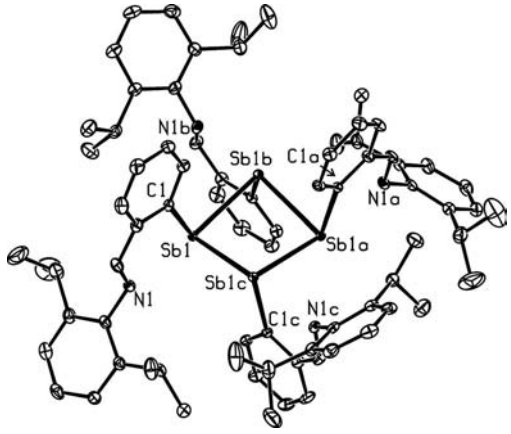


Figure 4. ORTEP diagram of the compound **3** with thermal displacement parameters at 30% probability. Hydrogen atoms were omitted for clarity. Symmetry operators: $a = {}^{3}/_{2} - x, ½ - y, z$; $b = ½ + y, 1 - x, 1 - z$; $c = 1 - y, -½ + x, 1 - z$. Selected distances [Å] and angles [°]: Sb1–C1 2.168(4), Sb1–N1 2.761(4), Sb1–Sb1b 2.8869(4); Sb1b–Sb1–Sb1c 88.12(1).

The nitrogen atom N1 is strongly coordinated to the central atom Sb1 in the structure of compound **1** [Sb1–N1 2.416(2) Å, Figure 2]. The coordination polyhedron of the central atom is, as a result of this N→Sb dative connection, best described as a pseudo-trigonal bipyramid in which the apical positions are occupied by the atoms N1 and Cl2 [the bonding angle of N1–Sb1–Cl2 is 163.96(5)°]; the chlorine atom Cl1 and the *ipso*-carbon atom C1 remain in the equatorial positions. The bonding angle of C1–Sb1–Cl1 [95.93(7)°] is more acute than the ideal value 120° as a consequence of repulsion from the lone pair of the antimony atom, which is most probably directed toward the third

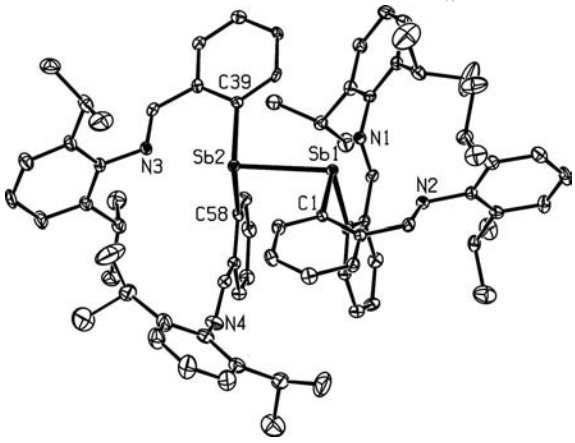


Figure 5. ORTEP diagram of compound **5** with thermal displacement parameters at 30% probability. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Sb1–Sb2 2.9194(6), Sb1–C1 2.169(5), Sb1–C20 2.198(5), Sb2–C39 2.168(5), Sb2–C58 2.166(4), Sb1–N1 3.018(4), Sb1–N2 2.979(4), Sb2–N3 2.877(4), Sb2–N4 4.559(5); C1–Sb1–C20 93.16(18), C39–Sb2–C58 98.59(19), Sb1–Sb2–C39 96.27(14), Sb1–Sb2–C58 94.59(12), Sb2–Sb1–C1 96.09(12), Sb2–Sb1–C20 93.75(13).

equatorial position. There is no intermolecular contact of significance in the crystal structure of **1**; this is in contrast to dichloro derivative $\mathbf{L}^{\#}SbCl_2$ (Figure 1, A), in which the intermolecular Sb···Cl contacts lead to formation of an infinite chain.[17] This fact reflects the higher steric hindrance of the ligand **L**.

Both nitrogen atoms N1 and N2 are coordinated to the central atom Sb1 in **2**, but the bond lengths point to a different strength of these contacts: compare Sb1–N1 2.416(2) to Sb1–N2 2.952(3) Å, as suggested already for the structure in solution (vide supra). Nevertheless, if the weaker interaction with the N2 atom is also taken into account, the resulting coordination polyhedron of the central atom may be described as a strongly pseudo-tetragonal pyramid. The apical position is occupied by the C20 atom. The equatorial plane is formed by the second *ipso*-carbon atom C1 and nitrogen donor atoms and the chlorine atom Cl1. The N1, Cl1 and C1, N2 are placed in *trans* positions [N1–Sb1–Cl1 163.76(6) and N2–Sb1–C1 163.81(8)].

The molecular structure of compound **3** proved the tetrameric nature of the compound with the central Sb_4 ring. This ring is strongly puckered and the ligands **L** are placed in *all-trans* fashion around the Sb_4 girdle, which coincides with the structure described in solution. The Sb–Sb bond lengths within the ring are 2.8869(4) Å and the bonding Sb–Sb–Sb angles amount to 88.12(1)°. These bond lengths are a bit longer in comparison to analogous tetrameric $\mathbf{L}^{\#}{}_4Sb_4$ (Figure 1, A), and the bonding angles are also significantly wider [cf. the range of Sb–Sb contacts 2.8474(5)–2.8605(4) Å and Sb–Sb–Sb angles 78.462(11)–80.825(12)°].[10b] All nitrogen atoms are coordinated to the central antimony atoms with bond lengths of 2.761(4) Å, a value that is longer than that in parent chlorido precursor $\mathbf{L}SbCl_2$ (**1**), which reflects the lower Lewis acidity of the central antimony in **3** compared to **1**. More importantly,

these N→Sb interactions are considerably weaker than those detected in the monomeric stibinidene stabilized by NCN pincer ligand (Figure 1, C), in which the Sb–N distances are 2.352(3) and 2.346(3) Å and indicate very strong interactions.[14] These strong N→Sb interactions are crucial for the stabilization of monomeric stibinidene. But in the case of compound **3**, support of the central antimony atom by only one pendant ketimino donor arm, although more sterically demanding, is not sufficient for stabilization of the monomeric structure and so the backbone of **3** is dominated by an internal Sb_4 ring, thus rendering the N→Sb interaction less important (weaker) for stabilization of the central antimony atom.

The Sb1–Sb2 bond length of 2.9194(6) Å in the molecular structure of **5** is considerably longer than corresponding values in Ph_4Sb_2 (2.834 Å), Me_4Sb_2 (2.86 Å) or $[(Me_3Si)_2CH]_2(H)_2Sb_2$ (2.8304 Å).[4a,5c,18] The comparable distibine $\mathbf{L}^{\#}{}_2SbSb\mathbf{L}^{\#}{}_2$ has not, to the best of our knowledge, been reported. The elongation of the Sb–Sb bond may be in part ascribed to a steric repulsion of four ligands **L** as well as to N→Sb interactions. Both nitrogen atoms N1 and N2 are coordinated to the antimony atom Sb1 [Sb1–N1 3.018(4), Sb1–N2 2.979(4) Å], but in the case of the antimony atom Sb2 only the N3 atom remains orientated towards the central metal [Sb2–N3 2.877(4) Å], with the second nitrogen atom N4 being pendant [Sb2–N4 4.559(5) Å]. This situation is rather similar to the dibismuthine $\mathbf{L}^{\#}{}_2BiBi\mathbf{L}^{\#}{}_2$ (Figure 1, A), in which only three of four ligand arms are likewise coordinated to bismuth atoms.[10a] Nevertheless, all N→Sb interactions in **5** are very weak, if not negligible, which coincides with fluxional behaviour of all four ligands in the structure of **5** in solution (vide supra).

Conclusion

We have demonstrated that the use of **L**, with only one ketimino ligand arm, is not sufficient for stabilization of the monomeric stibinidene. Only cyclic tetrameric compound **3** could be isolated from the reaction of parent chloride compound **1** with K[B(*s*Bu)$_3$H]. This fact may be mainly ascribed, in our opinion, to the absence of steric protection of the second *ortho* position in the ligand structure. Therefore future research will be devoted to the preparation of NC ligands substituted in the second *ortho* position with a bulky group. Interestingly, an analogous reaction with diorganoantimony precursor $\mathbf{L}_2SbCl$ (**2**) resulted in the addition of the in situ generated Sb–H bond across the C=N double bond of one of the ligand arms, thereby yielding compound **4** with an aza-stiba ring. The reactivity of heterocyclic compound **4** is currently being extensively studied in our labs, as are the trapping reactions of the present Sb–H bond with various multiple-bond-containing substrates. Similar systems are now being studied with other central atoms as well.

Finally, distibine **5** can be prepared in low yield by reduction of the precursor $\mathbf{L}_2SbCl$ with magnesium provided that the reaction time is 3–5 h. Prolonging the reaction time leads to a complicated reaction mixture, in which compounds **3** and **5** were characterized along with organomagnesium compound **6**. This finding may be explained by migration of the ligand **L** from the antimony atom to magnesium. We are currently studying the reduction of compound $\mathbf{L}_2SbCl$ (**2**) with alkali metals.

Experimental Section

General Procedures: All air- and moisture-sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube techniques. All solvents were dried by standard procedures and distilled prior to use. ^1H and ^{13}C spectra were recorded with a Bruker 400 spectrometer using a 5 mm tuneable 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]. The starting ligand *o*-$C_6H_4(CH{=}NC_6H_3iPr_2$-2,6)Br was prepared according to the literature procedure.[16]

[*o*-$C_6H_4(CH{=}NC_6H_3iPr_2$-2,6)]$SbCl_2$ (1): *n*BuLi (7.9 mL, 13 mmol, 1.6 M solution in hexane) was added to a solution of *o*-$C_6H_4(CH{=}NC_6H_3iPr_2$-2,6)Br (4.35 g, 13 mmol) in diethyl ether (100 mL) at –70 °C and stirred for 1 h. The resulting yellow-orange suspension of lithium compound was added to a solution of $SbCl_3$ (2.88 g, 13 mmol) in diethyl ether (100 mL) precooled to –40 °C. The resulting mixture was allowed to reach room temperature and stirred for an additional 3 h. The volume of the reaction mixture was reduced to around 30 mL. The insoluble material was filtered off and washed with hexane (15 mL). The remaining yellowish solid was extracted by dichloromethane (20 mL). Evaporation of the extract gave **1** as yellowish powder (this powder may be crystallized from dichloromethane/hexane to obtain single crystals suitable for X-ray studies). Yield 2.66 g, 46%; m.p. 217–219 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.13 [d, 6 H, $CH(CH_3)_2$], 1.25 [d, 6 H, $CH(CH_3)_2$], 2.91 [sept, 2 H, $CH(CH_3)_2$], 7.26 (m, 3 H, $C_6H_3iPr_2$-2,6), 7.69 (dd, 1 H, C_6H_4), 7.83 (m, 2 H, C_6H_4), 8.49 (s, 1 H, C*H*=N), 8.79 (d, 1 H, C_6H_4) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 25.1 [s, $CH(CH_3)_2$], 25.7 [s, $CH(CH_3)_2$], 29.0 [s, $CH(CH_3)_2$], 124.4, 127.6, 131.5, 133.0, 134.5, 136.3, 138.9, 140.7, 141.7, 153.3 (s, Ar–*C*), 169.2 (s, *C*H=N) ppm. $C_{19}H_{22}Cl_2NSb$ (457.05): calcd. C 49.9, H 4.9; found C 49.7, H 4.6.

{[*o*-$C_6H_4(CH{=}NC_6H_3iPr_2$-2,6)]}$_2SbCl$ (2): *n*BuLi (5.9 mL, 9.4 mmol, 1.6 M solution in hexane) was added to a solution of *o*-$C_6H_4(CH{=}NC_6H_3iPr_2$-2,6)Br (3.25 mg, 9.4 mmol) in diethyl ether (60 mL) at –70 °C and stirred for 1 h. The resulting yellow-orange suspension of lithium compound was added to a solution of $SbCl_3$ (1.1 g, 9.4 mmol) in diethyl ether (50 mL) precooled to –20 °C. The resulting mixture was allowed to reach room temperature and stirred for an additional 12 h. The volume of the reaction mixture was reduced to around 10 mL. The insoluble material was filtered off and washed with cold (–30 °C) hexane (5 mL). The remaining yellow solid was extracted by dichloromethane (20 mL). Evaporation of the extract gave **2** as yellow powder (this powder may be crystallized from hot hexane to obtain single crystals suitable for X-ray studies). Yield 2.2 g, 68%; m.p. 185–187 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.46 [d, 3 H, $CH(CH_3)_2$], 0.77 [d, 3 H, $CH(CH_3)_2$], 0.93 [d, 6 H, $CH(CH_3)_2$], 1.02 [d, 6 H, $CH(CH_3)_2$], 1.07 [d, 3 H, $CH(CH_3)_2$], 1.10 [d, 3 H, $CH(CH_3)_2$], 1.84 [sept, 1 H, $CH(CH_3)_2$], 2.83 [m, 3H-overlap of two signals, $CH(CH_3)_2$], 7.01 (d, 1 H, C_6H_4), 7.10–7.26 (m, 7 H, $C_6H_3iPr_2$-2,6 and C_6H_4), 7.45 (dd, 1 H, C_6H_4), 7.60 (d, 1 H, C_6H_4), 7.70 (dd, 1 H, C_6H_4), 7.80

(dd, 1 H, C_6H_4), 7.88 (d, 1 H, C_6H_4), 8.36 (s, 1 H, C*H*=N), 8.46 (s, 1 H, C*H*=N), 8.84 (d, 1 H, C_6H_4) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 22.3, 24.1, 24.3, 24.6, 25.1, 25.2, 28.0, 28.2, 28.6 [s, region of $CH(CH_3)_2$ and $CH(CH_3)_2$], 123.1, 123.4, 124.1, 124.5, 126.9, 129.3, 129.7, 132.1, 132.9, 133.4, 133.5, 135.7, 138.0, 138.7 (overlap of two signals), 140.0, 140.3, 140.6, 144.0, 147.1, 148.4, 155.9 (s, Ar–*C*), 164.9 (s, *C*H=N), 169.7 (s, *C*H=N) ppm. $C_{38}H_{44}ClN_2Sb$ (685.99): calcd. C 66.5, H 6.5; found C 66.8, H 6.7.

{[*o*-C_6H_4(CH=NC_6H_3*i*Pr_2-2,6)]Sb}$_4$ (3): A solution of K[B(*s*Bu)$_3$H] (3.7 mL, 1 M solution, 3.7 mmol) in THF was added to a stirred solution of **1** (0.84 g, 1.84 mmol) in THF (30 mL) at room temperature. Immediately after addition, elimination of hydrogen was observed and the reaction mixture turned red-brown. The resulting mixture was stirred for an additional 1 h at room temperature and evaporated in vacuo. The residue was washed with hexane (10 mL). The solid residue was extracted with toluene (30 mL) to give a red-orange solution. Evaporation of this solution gave **3** as a reddish powder (this powder may be crystallized from toluene/hexane mixture to obtain single crystals suitable for X-ray studies). Yield 320 mg, 45%; m.p. 162–165 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.01 [d, 12 H, $CH(CH_3)_2$], 3.31 [br., 2 H, $CH(CH_3)_2$], 6.32 (dd, 1 H, C_6H_4), 6.76 (dd, 1 H, C_6H_4), 6.99 (m, 3 H, C_6H_3*i*Pr_2-2,6), 7.04 (d, 1 H, C_6H_4), 8.36 (s, 1 H, C*H*=N), 8.48 (d, 1 H, C_6H_4) ppm. ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 24.8 [s, $CH(CH_3)_2$], 28.6 [s, $CH(CH_3)_2$], 123.5, 125.1, 127.2, 130.4, 135.1, 135.3, 139.0, 139.4, 145.5, 149.4 (s, Ar–*C*), 166.2 (s, *C*H=N) ppm. $C_{76}H_{88}N_4Sb_4$ (1544.58): calcd. C 59.1, H 5.7; found C 59.2, H 6.0.

[*o*-C_6H_4(CH=NC_6H_3*i*Pr_2-2,6)]Sb[*o*-$C_6H_4CH_2N(C_6H_3$*i*Pr_2-2,6)] (4): A solution of K[B(*s*Bu)$_3$H] (1.8 mL, 1 M solution, 1.8 mmol) in THF was added to a stirred solution of **2** (1.22 g, 1.8 mmol) in THF (40 mL) at room temperature. The resulting mixture was stirred for an additional 30 min at room temperature and evaporated in vacuo. The residue was extracted with hexane (30 mL). The yellow extract was concentrated to around 10 mL (until the first yellow precipitate started to emerge) and crystallization for 12 h at room temperature gave a bright yellow powder of **4**. Yield 0.57 g, 48%; m.p. 192–194 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.06 [d, 3 H, $CH(CH_3)_2$], 1.10 [d, 6 H, $CH(CH_3)_2$], 1.13 [d, 6 H, $CH(CH_3)_2$], 1.21 [d, 3 H, $CH(CH_3)_2$], 1.27 [d, 3 H, $CH(CH_3)_2$], 1.55 [d, 3 H, $CH(CH_3)_2$], 3.01 [sept, 1 H, $CH(CH_3)_2$], 3.23 [br., 2 H, $CH(CH_3)_2$], 4.44 [sept, 1 H, $CH(CH_3)_2$], 5.18 (AX pattern, 2 H, NCH_2), 6.94 (dd, 1 H, C_6H_4), 7.02–7.19 (m, 10 H, C_6H_4 and C_6H_3*i*Pr_2-2,6), 7.28 (dd, 1 H, C_6H_4), 7.63 (d, 1 H, C_6H_4), 8.05 (s, 1 H, C*H*=N), 8.73 (d, 1 H, C_6H_4) ppm. ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 24.3, 25.3 (overlap of two signals), 25.5, 26.0, 28.9, 29.0, 29.6 [s, region of $CH(CH_3)_2$ and $CH(CH_3)_2$], 70.0 (s, NCH_2), 123.6, 123.9, 124.6, 125.5, 125.7, 126.4, 126.7, 128.7, 128.8, 131.9, 133.5, 134.7, 135.5, 139.9, 140.2, 146.9, 148.1, 149.0, 149.3, 151.8, 151.9, 153.6 (s, Ar–*C*), 167.8 (s, *C*H=N) ppm. $C_{38}H_{45}N_2Sb$ (651.55): calcd. C 70.1, H 7.0; found C 70.3, H 7.3.

{[*o*-C_6H_4(CH=NC_6H_3*i*Pr_2-2,6)]$_2$Sb}$_2$ (5): A solution (20 mL) of **2** (1.37 g, 2 mmol) in THF was added to Mg (73 mg, 3 mmol) in THF (10 mL) activated by $BrCH_2CH_2Br$ (150 μL) at room temperature. The resulting mixture was stirred until the yellow colour changed to red-orange, typically after 3–5 h (the reaction was stopped if the reaction mixture started to turn back to yellow-orange and an opalescence formed) and then evaporated in vacuo. The residue was extracted with hexane (25 mL). The red-orange extract was concentrated to around 10 mL and crystallization for 5 h at room temperature gave orange-red crystals of **5** [in many cases the product was contaminated (around 5–10% according to NMR spectroscopy) by starting compound **2** and additional recrystallization from hexane was necessary, which lowered the yield]. Yield 0.51 g, 39%; m.p. 224 °C, melt starts to decompose. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.96 [d, 6 H, $CH(CH_3)_2$], 1.02 [d, 6 H, $CH(CH_3)_2$], 2.89 [sept, 2 H, $CH(CH_3)_2$], 6.72 (dd, 1 H, C_6H_4), 6.96 (dd, 1 H, C_6H_4), 7.06 (m, 3 H, C_6H_3*i*Pr_2-2,6), 7.57 (d, 1 H, C_6H_4), 7.91 (d, 1 H, C_6H_4), 8.39 (s, 1 H, C*H*=N), ppm. ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 24.3 [s, $CH(CH_3)_2$], 24.7 [s, $CH(CH_3)_2$], 28.6 [s, $CH(CH_3)_2$], 123.6, 125.1, 128.4, 131.1, 132.4, 138.7, 141.2, 141.6, 142.3, 149.7 (s, Ar–*C*), 165.6 (s, *C*H=N) ppm. $C_{76}H_{88}N_4Sb_2$ (1301.08): calcd. C 70.2, H 6.8; found C 70.5, H 5.7.

X-ray Crystallography: Suitable single crystals of the compounds were mounted on a glass fibre with oil and measured with a KappaCCD four-circle diffractometer with a CCD area detector by monochromatized Mo-K_α radiation (λ = 0.71073 Å) at 150(1) K. The numerical[19] absorption corrections from the crystal shape were applied for all crystals. The structures were solved by direct methods (SIR92)[20] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97).[21] 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, respectively, in the aromatic ring. There is a disordered isopropyl group in the structure of **5**; this disorder was solved by splitting the methyl groups into two positions. The final difference maps displayed no peaks of chemical significance as the highest peaks and holes are in close vicinity (ca. 1 Å) of heavy atoms.

CCDC-804248 (for **1**), -804249 (for **2**), -804250 (for **3**), -804251 (for **5**) and -804252 (for **6·THF**) 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.

Crystallographic Data for 1: $C_{19}H_{22}Cl_2NSb$, M_r = 457.03, monoclinic, $P2_1/c$, a = 9.6010(4) Å, b = 13.8080(8) Å, c = 16.8582(11) Å, β = 120.854(6)°, V = 1918.6(2) Å^3, Z = 4, T = 150(1) K, 19556 total reflections, 4373 independent [R_{int} = 0.031, $R1$ (obsd. data) = 0.027, wR_2 (all data) 0.048].

Crystallographic Data for 2: $C_{37}H_{44}ClN_2Sb·0.75(CH_2Cl_2)$, M_r = 749.65, monoclinic, $C2/c$, a = 33.2431(12) Å, b = 12.9942(9) Å, c = 20.0118(7) Å, β = 118.771(9)°, V = 7581.4(3) Å^3, Z = 8, T = 150(1) K, 37617 total reflections, 8555 independent [R_{int} = 0.036, $R1$ (obsd. data) = 0.034, wR_2 (all data) 0.070].

Crystallographic Data for 3: $C_{76}H_{88}N_4Sb_4$, M_r = 1544.50, tetragonal, $P4/n$, a = 21.0521(12) Å, b = 21.0520(15) Å, c = 8.7760(5) Å, V = 3889.4(4) Å^3, Z = 2, T = 150(2) K, 20526 total reflections, 4453 independent [R_{int} = 0.040, $R1$ (obsd. data) = 0.035, wR_2 (all data) 0.078].

Crystallographic Data for 5: $C_{76}H_{88}N_4Sb_2$, M_r = 1301.00, orthorhombic, $Pna2_1$, a = 15.0210(12) Å, b = 17.6420(19) Å, c = 25.424(12) Å, V = 6737.4(13) Å^3, Z = 4, T = 293(2) K, 43363 total reflections, 12370 independent [R_{int} = 0.059, $R1$ (obsd. data) = 0.041, wR_2 (all data) 0.068], Flack parameter 0.028(17).

Crystallographic Data for 6·THF: $C_{42}H_{52}MgN_2O$, M_r = 625.17, monoclinic, Cc, a = 14.3911(12) Å, b = 12.3382(9) Å, c = 20.4189(11) Å, β = 93.642(7)°, V = 3618.2(4) Å^3, Z = 4, T = 150(1) K, 11439 total reflections, 5750 independent [R_{int} = 0.041, $R1$ (obsd. data) = 0.058, wR_2 (all data) 0.133]; Flack parameter for **6** is not reliable.[22]

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra of compound **4**, that is, from treatment of **2** with K[B(*s*Bu)$_3$H]. Molecular structure of compound **6** with relevant structural parameters.

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