# Lewis base properties of tris(trimethylstannyl)amine: unusually short M–N bonds of the adduct compounds [X₃M·N(SnMe₃)₃] (X = Cl, Br; M = Al, Ga, In) and [Cl₂(CH₃)M·N(SnMe₃)₃] (M = Al, Ga)

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The Lewis acid/base adducts [X₃M·N(SnMe₃)₃] (**1a**: M = Al, X = Cl; **2a**: M = Ga, X = Cl; **2b**: M = Ga, X = Br; **3a**: M = In, X = Cl; **3b**: M = In, X = Br) and [Cl₂MeM·N(SnMe₃)₃] (**1b**: M = Al, **2c**: M = Ga) were prepared by the 1 : 1 mole reaction of MX₃ and MCl₂Me with N(SnMe₃)₃ at room temperature in diethyl ether and crystallised from dichloromethane at −20 °C. The new compounds were fully characterised by elemental analysis, NMR spectroscopy and single crystal X-ray diffraction. Unusually short M–N bond lengths of 1.87(1) Å for Al–N (**1a**), 1.950(7) Å for Ga–N (**2a**) and 2.148(6) Å for In–N (**3a**) were found indicating very strong donor–acceptor bonds.

## Introduction

Trimethylstannyl substituted amine, amido and imido derivatives such as (Me₃Sn)₃ ₋ ₐNRₐ (a = 0, 1, 2; R = alkyl, aryl) and Me₃Sn–N=C=NR have been recognised as versatile nitrogen transfer reagents[1] for the synthesis of metal amido, imido and nitrido compounds as well as for metal nitride clusters. Some examples may illustrate this: The treatment of [Cp*TaCl₄] with N(SnMe₃)₃ yields the cyclic nitrido derivative [Cp*TaNCl]₃[2] and more recently the synthesis of carbodiimidotitanium complexes [Cp₂Ti(N=C=NR)₂] by the reaction of trimethylstannyl-carbodiimides Me₃Sn–N=C=NR with Cp₂TiCl₂ were described[3] as well as the synthesis of substituted aminogallanes, e.g. [Me₂GaN(i-Pr)SnMe₃)]₂ by alkyltrimethyltin elimination using (Me₃Sn)₂N(i-Pr).[4] In addition, some interesting amido copper compounds, e.g. [{CuN(SnMe₃)₂}₄], were obtained by Fenske and Reiss using (Me₃Sn)₃N and CuX (X = halide).[5] In such latter cases of employing (Me₃Sn)₃N as the nitrogen transfer reagent, Lewis acid/base adducts of the general type [Lₙ(X)M·N(SnMe₃)₃] (M = metal, X = halide ligand, L = other ancillary ligands) are quite likely intermediates. However, the chemistry of tris(trimethylstannyl)amine with particular respect to its Lewis base properties towards Lewis acidic metal centres has not been studied thoroughly. To our knowledge, only Dehnicke *et al.* has reported (some years ago in 1995) on the formation of the adducts [Me₃M·N(SnMe₃)₃] by the reaction of MMe₃ with N(SnMe₃)₃ as well as on the subsequent formation of dimeric compounds [{RClInN(SnMe₃)₂}₂] with an In₂N₂ skeleton from the reaction of R₂ClIn and N(SnMe₃)₃ at room temperature in ether solution (M = Al, Ga, In; R = Me, Et).[6] However, structural data on the primary Lewis acid/base adducts have only been reported for the indium compound [Me₃In·N(SnMe₃)₃]. We were interested to use these kind of adducts as molecular precursors for the low temperature growth of metal nitride materials, especially Group 13 nitrides, as fine powders or colloids composed of nanoscale particles, and thus set out to study the thermal properties and the solid state pyrolysis of such adducts on which subject we report in some detail in a parallel publication.[7] Here we wish to give an account on the synthesis and analytical characterisation as well as on the structural properties of the Lewis acid/base adducts [X₃M·N(SnMe₃)₃] (**1a**: M = Al, X = Cl; **2a**: M = Ga, X = Cl; **2b**:

M = Ga, X = Br; **3a**: M = In, X = Cl; **3b**: M = In, X = Br) and [Cl₂MeM·N(SnMe₃)₃] (**1b**: M = Al, **2c**: M = Ga) with particular respect to the M–N donor–acceptor bonds.

## Experimental

### General considerations

All manipulations were undertaken using standard Schlenk and glove-box techniques under inert gas atmospheres (purified N₂ or Argon). Solvents (including solvent for NMR measurements) were dried under Ar by standard methods and stored over molecular sieves (4 Å, Merck; residual water < 3 ppm, Karl Fischer). The precursors were synthesised from N(SnMe₃)₃,[8] MX₃ (purchased from Aldrich, dried and purified by sublimation) and MX₂Me[9] as described below. ¹H-, ¹³C- and ¹¹⁹Sn-NMR spectra were recorded in CD₂Cl₂ solution on Bruker DPX 250, DPX 200 and DRX 400 spectrometers (¹H- and ¹³C-NMR were referenced to internal solvent and corrected to TMS. The ¹¹⁹Sn-NMR data were referenced to the external standard tetramethyltin). Elemental analyses were provided by the Microanalytical Laboratory of the Ruhr University of Bochum.

### Synthesis of [X₃M·N(SnMe₃)₃] (1a: M = Al, X = Cl; 2a: M = Ga, X = Cl; 2b: M = Ga, X = Br; 3a: M = In, X = Cl; 3b: M = In, X = Br) and [Cl₂MeM·N(SnMe₃)₃] (1b: M = Al, 2c: M = Ga)

The compounds **1**–**5** were prepared according to the method outlined below using the synthesis of [Cl₃Ga·N(SnMe₃)₃] (**2a**) as a representative example: A sample of 0.246 g (1.4 mmol) GaCl₃ was dissolved in 50 mL of dry diethyl ether in a Schlenk flask (150 mL) and a solution of N(SnMe₃)₃ (0.708 g, 1.4 mmol) in 30 ml of diethyl ether was slowly added with vigorous stirring at 25 °C. An instantaneous formation of a white precipitate was observed. After overnight stirring, the volatile components were removed *in vacuo* to yield **2a** as a white powder, 0.887 g (yield: 93%). Compound **2a** is soluble in toluene, CH₂Cl₂ and THF. X-Ray quality crystals were grown from a saturated solution of **2a** in CH₂Cl₂ at −30 °C. The compound starts to decompose above 50–60 °C and no distinct and reversible

melting point could be observed. Anal. (%) Calc. (Found) for $C_9H_{27}NSn_3Cl_3Ga$: C 15.85 (15.69); H 3.96 (3.86); N 2.05 (2.19); Ga 10.23 (10.30). $^1H$-NMR ($CD_2Cl_2$): $\delta$ 0.74 (s, $J_{H-Sn}$ = 55 Hz). $^{13}C\{^1H\}$-NMR: $\delta$ 2.2 (s). $^{119}Sn\{^1H\}$-NMR: $\delta$ 147.

**[Cl₃Al·N(SnMe₃)₃] (1a).** Yield: 80%. Anal. (%) Calc. (Found) for $C_9H_{27}NSn_3Cl_3Al$: C 16.91 (16.79); H 4.23 (4.30); N 2.19 (2.08); Al 4.23 (4.50). $^1H$-NMR ($CD_2Cl_2$): $\delta$ 0.73 (s, $J_{H-Sn}$ = 53.8 Hz). $^{13}C\{^1H\}$-NMR ($CD_2Cl_2$): $\delta$ 2.55 (s). $^{119}Sn\{^1H\}$-NMR ($CD_2Cl_2$): $\delta$ 136.

**[Cl₂(CH₃)Al·N(SnMe₃)₃] (1b).** Yield: 85%. Anal. (%) Calc. (Found) for $C_{10}H_{30}AlCl_2NSn_3$: C 19.41 (19.53); H 4.85 (4.92); N 2.26 (2.35); Al 4.37 (5.03). $^1H$-NMR ($CD_2Cl_2$): $\delta$ 0.66 [s, $J_{H-Sn}$ = 58 Hz, $-N(SnMe_3)_3$], 0.38 (s, $-AlCl_2Me$). $^{13}C\{^1H\}$-NMR: $\delta$ 1.56 [s, $-N(SnMe_3)_3$], $-1.05$ (s, $-AlCl_2Me$). $^{119}Sn\{^1H\}$-NMR: $\delta$ 135.7.

**[Br₃Ga·N(SnMe₃)₃] (2b).** Yield: 1.067 g, 87.3%. Anal. (%) Calc. (Found) for $C_9H_{27}NBr_3Sn_3Ga$: C 13.25 (13.17); H 3.31 (3.55); N 1.72 (1.90); Ga 8.56 (8.97). $^1H$-NMR ($CD_2Cl_2$): $\delta$ 0.80 (s, $J_{H-Sn}$ = 54 Hz). $^{13}C\{^1H\}$-NMR: $\delta$ 3.1 (s). $^{119}Sn\{^1H\}$-NMR: $\delta$ 147.

**[Cl₂MeGa·N(SnMe₃)₃] (2c).** Yield: 79%. Anal. (%) Calc. (Found) for $C_{10}H_{30}GaCl_2NSn_3$: C 18.15 (18.47); H 4.54 (4.67); N 2.12 (1.99); Ga 10.44 (10.68). $^1H$-NMR ($CD_2Cl_2$): $\delta$ 0.67 [s, $J_{H-Sn}$ = 53 Hz, $-N(SnMe_3)_3$], 0.16 (s, $-GaMeCl_2$). $^{13}C\{^1H\}$-NMR: $\delta$ 1.9 [s, $-N(SnMe_3)_3$], 1.47 (s, $-GaCl_2Me$). $^{119}Sn\{^1H\}$-NMR: $\delta$ 131.

**[Cl₃In·N(SnMe₃)₃] (3a).** Yield: 88%. Anal. (%) Calc. (Found) for $C_9H_{27}NSn_3Cl_3In$: C 14.86 (14.92); H 3.72 (3.86); N 1.93 (1.87); In 15.80 (16.45). $^1H$-NMR ($CD_2Cl_2$): $\delta$ 0.74 (s, $J_{H-Sn}$ = 54 Hz). $^{13}C\{^1H\}$-NMR: $\delta$ 2.2 (s). $^{119}Sn\{^1H\}$-NMR: $\delta$ 136.

**[Br₃In·N(SnMe₃)₃] (3b).** Yield: 86%. Anal. (%) Calc. (Found) for $C_9H_{27}NBr_3Sn_3In$: C 12.56 (12.64); H 3.14 (3.35); N 1.63 (1.40); In 13.35 (13.15). $^1H$-NMR ($CD_2Cl_2$): $\delta$ 0.79 (s, $J_{H-Sn}$ = 56 Hz). $^{13}C\{^1H\}$-NMR: $\delta$ 1.16 (s). $^{119}Sn\{^1H\}$-NMR: $\delta$ 139.1.

### Single crystal X-ray diffraction analysis of the new compounds

Single crystals suitable for X-ray diffraction studies were grown by slow cooling of saturated $CH_2Cl_2$ solutions of the compounds to temperatures between 0 and $-30$ °C. The colourless crystals were selected under a microscope using a glove-box and transferred into Lindemann glass capillaries under dry Ar. Intensity data were collected at 203 K, (except for compound **2a** which was cooled to 183 K) with a Bruker AXS CCD 1000 diffractometer (Mo-K$\alpha$ radiation, $\lambda$ = 0.71073 Å, graphite monochromator, $\omega$-scan). Empirical absorption correction was applied. The structures were solved by direct methods (SHELXL-97)[16] and refined by full-matrix least-squares methods based on $F^2$ with all observed reflections. The thermal reliability index $wR_2$ is defined as $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealised locations using a standard riding model. The tin atoms of [Cl₃Ga·N(SnMe₃)₃] (**2a**) exhibit a disorder. The two positions for each tin atom were finally refined using occupation factors of 0.95 and 0.05, respectively. The calculated residual electron densities for the structures of compounds **1a** and **2c** are somewhat high (around 4 e Å$^{-3}$) which may be due to a similar low fraction of disordered $N(SnMe_3)_3$ groups which however could not be resolved. Crystallographic data and data collection parameters for the compounds are summarised in Table 1. Selected bond lengths and angles are given in Table 2. Drawings of the molecular structure in the solid state of the compounds [Cl₃Al·N(SnMe₃)₃] (**1a**), [Cl₂(CH₃)Ga·N(SnMe₃)₃] (**2c**) and [Br₃In·N(SnMe₃)₃] (**3b**) as the representative examples of the series are given in Figs. 1a–c.
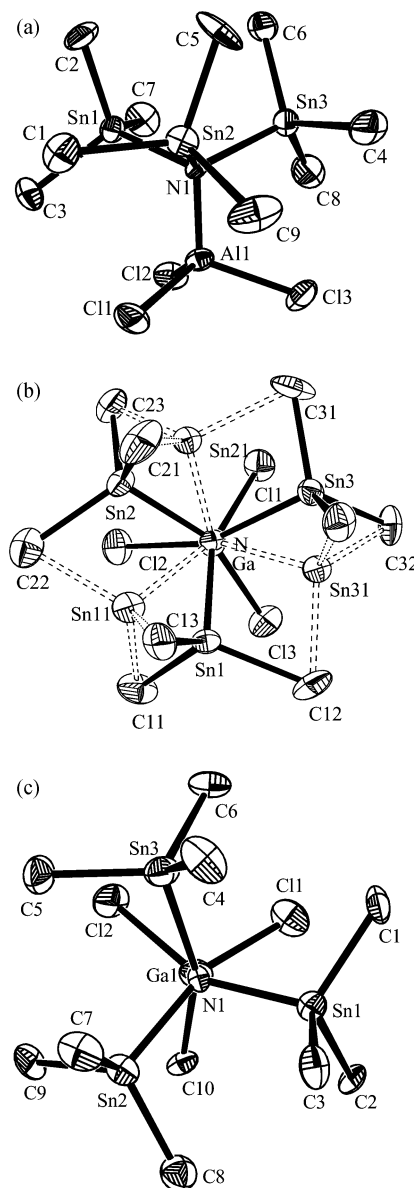
**Fig. 1** The molecular structures of representative examples of the series of new adducts [RX₂M·N(SnMe₃)₃] (**1–3**): (a) [Cl₃Al·N(SnMe₃)₃] (**1a**), (b) [Cl₃Ga·N(SnMe₃)₃] (**2a**) and (c) [Cl₂MeGa·N(SnMe₃)₃] (**2c**) including the disordering of the tin atoms. (ORTEP[17] drawings at a 50% level of probability, hydrogen atoms have been omitted for clarity.)

CCDC reference numbers 145599 (**1a**), 148508 (**1b**), 161554 (**2a**), 161555 (**2b**), 148509 (**2c**), 148507 (**3a**) and 148506 (**3b**).

See http://www.rsc.org/suppdata/dt/b2/b203489c/ for crystallographic data in CIF or other electronic format.

## Results and discussion

### Synthesis, properties and analytical characterisation

The 1 : 1 adducts of MX₃ with N(SnMe₃)₃ [X₃M·N(SnMe₃)₃] (**1–3**) (see Scheme 1) are instantaneously and quantitatively

$$MX_2R + N(SnMe_3)_3 \longrightarrow [X_2RM-N(SnMe_3)_3]$$

**1 - 3**

R = X, Me; X = Cl, Br

**Scheme 1**
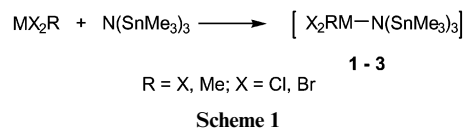
formed at room temperature in diethyl ether solution. These adducts were isolated as air and moisture sensitive colourless crystalline solids by recrystallisation from saturated dichloromethane solutions at $-20$ °C. At room temperature and above

**Table 1** Crystal data and structure refinement parameters for **1a**, **1b**, **2a**, **2b**, **2c**, **3a** and **3b**

| Compound | **1a** Cl₃Al·N(SnMe₃)₃ | **1b** Cl₂MeAl·N(SnMe₃)₃ | **2a** Cl₃Ga·N(SnMe₃)₃ | **2b** Br₃Ga·N(SnMe₃)₃ | **2c** Cl₂MeGa·N(SnMe₃)₃ | **3a** Cl₃In·N(SnMe₃)₃ | **3b** Br₃In·N(SnMe₃)₃ |
|---|---|---|---|---|---|---|---|
| Formula | $C_9H_{27}Cl_3AlNSn_3$ | $C_{10}H_{30}AlCl_2NSn_3$ | $C_9H_{27}Cl_3GaNSn_3$ | $C_9H_{27}Br_3GaNSn_3$ | $C_{10}H_{30}GaCl_2NSn_3$ | $C_9H_{27}Cl_3InNSn_3$ | $C_9H_{27}Br_3InNSn_3$ |
| Formula weight | 638.72 | 618.30 | 681.46 | 814.84 | 661.04 | 726.56 | 859.94 |
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic | Cubic | Orthorhombic | Cubic | Cubic |
| Space group | $Pca2_1$ | $Pca2_1$ | $Pca2_1$ | $P2_13$ | $Pca2_1$ | $P2_13$ | $P2_13$ |
| $a$/Å | 12.651(2) | 12.703(2) | 12.657(1) | 12.947(1) | 12.719(3) | 12.902(1) | 12.989(3) |
| $b$/Å | 13.088(2) | 13.093(2) | 13.093(1) | 12.947(1) | 13.047(3) | 12.902(1) | 12.989(3) |
| $c$/Å | 12.651(2) | 12.703(1) | 12.671(1) | 12.947(1) | 12.719(3) | 12.902(1) | 12.989(3) |
| $V$/Å³ | 2094.8(4) | 2112.7(4) | 2099.9(4) | 2170.1(3) | 2110.6(7) | 2147.7(3) | 2191.4(8) |
| $Z$ | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| $\mu$/mm⁻¹ | 3.959 | 3.800 | 5.163 | 10.151 | 5.011 | 4.867 | 9.875 |
| Crystal size/mm | 0.2 × 0.1 × 0.1 | 0.2 × 0.2 × 0.1 | 0.30 × 0.25 × 0.20 | 0.3 × 0.25 × 0.20 | 0.4 × 0.35 × 0.30 | 0.4 × 0.36 × 0.25 | 0.45 × 0.35 × 0.30 |
| Reflections collected/unique | 4832/2941 | 4833/2891 | 4843/2156 | 5337/1299 | 4848/2947 | 5260/1277 | 3882/1277 |
| Reflections observed [$I > 2\sigma(I)$] | 2806 | 2846 | 2089 | 1265 | 2696 | 1244 | 1145 |
| $R$(int) | 0.0484 | 0.0309 | 0.0485 | 0.0603 | 0.0425 | 0.0477 | 0.0701 |
| $R$ [$I > 2\sigma(I)$], $wR2$ | 0.0558, 0.1597 | 0.0384, 0.1046 | 0.0412, 0.0981 | 0.0763, 0.1918 | 0.0691, 0.1869 | 0.0218, 0.0503 | 0.0275, 0.0425 |
| $R$ (all data), $wR2$ | 0.0591, 0.1687 | 0.0395, 0.1054 | 0.0427, 0.1001 | 0.0773, 0.1921 | 0.0748, 0.1909 | 0.0227, 0.0507 | 0.0350, 0.0440 |

the compounds are not stable, especially when kept in solution. Prolonged stirring (longer than 15 h) at room temperature in diethyl ether suspension during the preparation leads to decomposition, most likely into the dimeric compounds, *e.g.* $[X_2GaN(SnMe_3)_2]_2$, due to the formation of $Me_3SnCl$, which was identified by the NMR data of the reaction solution. However, these dimeric products were not isolated in a pure form. At temperatures below −20 °C compounds **1**–**3** are more stable in solution and the isolated pure crystalline compounds can be stored without noticeable decomposition for a number of weeks when kept under argon with cooling (−20 °C). According to thermogravimetric studies, the compounds start to decompose above 50–60 °C.[7] Well defined reversible melting points or sharp decomposition points were not observed. Similar properties were reported for the related compounds $[Me_3M\cdot N(SnMe_3)_3]$ by Dehnicke *et al.*[6]

The proposed formulations of **1**–**3** as Lewis acid/base adducts are consistent with the microanalytical data as well as with the NMR spectroscopic data. The ¹H- and ¹³C{¹H}-NMR data compare well with the known compound $[Me_3M\cdot N(SnMe_3)_3]$ and the respective values of the free base $N(SnMe_3)_3$ in $C_6D_6$ solution, but the ¹¹⁹Sn{¹H}-NMR signals are shifted down-field significantly to 131–136 ppm as compared with 86.3 ppm for the free tris(trimethylstannyl)amine.[10]

### The molecular structures of 1–3

The molecular structures of all new compounds **1**–**3** in the solid state were determined by single crystal X-ray diffraction. Crystallographic data and data collection parameters of this homologous series of compounds are summarised in Table 1 (for further details see the Experimental section). Selected bond lengths and angles are given in Table 2. The molecular structures of **1a**, **2a** and **2c** as representative examples of the homologous series are shown in Figs. 1a–c. The structures of the new adducts **1**–**3** are largely without unexpected features as far as the M–X, M–C as well as the Sn–C bonds and the respective bond angles M–N–Sn, Sn–N–Sn and X–M–X and X–M–C are concerned. The atoms M, N and Sn form a slightly distorted tetrahedral structure, in which both M and N centres are four coordinate. Some deviation from the ideal staggered conformation is most likely due to crystal packing in the solid state. In solution the molecules expectedly exhibit higher symmetry as seen from the simple NMR spectra (fast rotation around the M–N bond).

The interesting structural features are the dative M–N bond lengths and the variations of the N–Sn bond lengths in this homologous series. The M–N bond lengths of **1**–**3** are unusually short, while the N–Sn bond lengths appear rather long. For example the Al–N bond length of **1a** at 1.872(12) Å seems to be the shortest Al–N donor–acceptor bond length to date and the Ga–N and In–N values likewise (based on a CSD search). This is seen from the following selection of related adducts $[R_3Al\cdot NR'_3]$ with a variation of the substituents at the Al centre: solid state $[Cl_3Al\cdot NMe_3]$ 1.96(1) Å,[11] gaseous monomeric $[H_3Al\cdot NMe_3]$ 2.063(8) Å,[12] gaseous monomeric $[Me_3Al\cdot NMe_3]$ 2.099(10) Å,[13] and solid state $[(Me_3Si)_3Al\cdot NMe_3]$ 2.040(6) Å.[14] Similar comparison can be drawn for the gallium congeners of **1a**, $[X_3Ga\cdot N(SnMe_3)_3]$ (**2a**: X = Cl, **2b**: X = Br) with quite short donor–acceptor bonds of 1.950(7) and 1.9539(2) Å when compared with gaseous $[Cl_3Ga\cdot NH_3]$ of 2.057(11) Å and gaseous $[Me_3Ga\cdot NMe_3]$ of 2.20(3) Å as well as for the indium compound **3a** with 2.148(6) Å and **3b** with 2.158(8) Å for the In–N bond. The structures and the bonding of the parent adducts $[H_3M\cdot NH_3]$ as well as a number of other species $[H_mMNH_n]$ ($m$, $n$ = 0, 1, 2, 3) have recently been the subject of a theoretical analysis (Gaussian 98, B3LYP method) which provided reliable values for the dative M–N bond lengths for the molecules $[H_3M\cdot NH_3]$ in the gaseous state: Al–N, 2.093; Ga–N, 2.180; In–N 2.379 Å.[15] The short dative M–N bonds of

**Table 2** Selected bond lengths (Å) and bond angles (°) for compounds **1–3**

| Compound | 1a | 1b | 2a | 2b | 2c | 3a | 3b |
|---|---|---|---|---|---|---|---|
| M–N | 1.87(1) | 1.919(8) | 1.950(7) | 1.954(1) | 2.00(2) | 2.148(6) | 2.158(8) |
| N–Sn(1) | 2.19(1) | 2.154(6) | 2.156(6) | 2.173(2) | 2.13(1) | 2.166(2) | 2.167(3) |
| N–Sn(2) | 2.16(1) | 2.156(6) | 2.161(6) | 2.173(2) | 2.16(1) | 2.166(2) | 2.167(3) |
| N–Sn(3) | 2.17(1) | 2.166(7) | 2.174(7) | 2.173(2) | 2.15(2) | 2.166(2) | 2.167(3) |
| M–C | | 2.014(9) | | | 2.02(2) | | |
| | | | | | | | |
| M–N–Sn(1) | 109.5(5) | 109.2(4) | 108.7(3) | 108.1(6) | 108.1(6) | 108.5(2) | 108.6(2) |
| M–N–Sn(2) | 110.7(5) | 108.9(3) | 109.0(3) | 106.9(6) | 106.9(6) | 108.5(2) | 108.6(2) |
| M–N–Sn(3) | 112.2(5) | 113.3(3) | 108.8(3) | 111.2(7) | 111.2(7) | 108.5(2) | 108.6(2) |
| Sn(1)–N–Sn(2) | 107.8(5) | 109.5(3) | 110.3(3) | 111.1(6) | 111.1(6) | 110.5(2) | 110.3(2) |
| Sn(1)–N–Sn(3) | 108.7(5) | 109.3(3) | 110.3(3) | 109.3(6) | 109.3(6) | 110.5(2) | 110.3(2) |
| Sn(2)–N–Sn(3) | 108.8(4) | 108.6(3) | 109.7(3) | 110.1(6) | 110.1(6) | 110.5(2) | 110.3(2) |

**1–3** are thus clearly a consequence of *reduced* steric repulsion at both centres M and N *combined* with an optimum strength of the Lewis acid/base interaction by the halide substituents at the centre M (concentration of the acceptor LUMO) and the more polarised N–Sn bond of the base N(SnMe₃)₃ with a higher negative charge density at the N atom as compared with alkyl amines or ammonia.

The Al–N and Ga–N distances of the methyl derivatives **1b** of 1.919(8) Å and **2c** of 2.00(2) Å are expectedly slightly longer than in the trihalide adducts **1a** and **2a–b** because of the somewhat reduced Lewis-acidity of the Cl₂MeM moiety. For the indium adducts **3a** and **3b** [In–N: 2.148(6) and 2.158(8) Å, respectively] the same trend is observed when compared with the In–N bond length of [Me₃In·N(SnMe₃)₃] at 2.39(3) Å.[6] The different halide substituents (Cl *vs.* Br) have expectedly almost no influence on the M–N bonding.

Another interesting indication of the variation of the Lewis acid/base interaction in this series of compounds can be seen by very small but significant and systematic chances of the N–Sn bond lengths: the *shortest* M–N bond is reflected by the *longest* N–Sn bonds of 2.17(1) Å as the mean value for **1a**, and the mono methyl derivatives **1b** and **2c** exhibit somewhat *shorter* N–Sn bonds of 2.159(6) Å as the corresponding mean value. Consequently, the adduct [Me₃In·N(SnMe₃)₃] reveals the *shortest* N–Sn bond of 2.102(8) Å in this series. The observed N–Sn bond lengths of the adducts **1–3** are expectedly *longer* than for free, not coordinatively bound stannylamines which exhibit N–Sn bond lengths in the range of 2.02 (±0.03) Å; the parent molecule N(SnMe₃)₃ reveals a mean N–Sn distance of 2.04 Å in the solid state.[10]

### Pyrolysis studies of 1–3

A study on the thermal properties and the solid state pyrolysis of **1–3** as molecular precursors for Group III nitride materials has been performed and is reported in detail elsewhere.[7] It was shown that the precursors of the type [X₃M·N(SnMe₃)₃] (**1a**, **2a–b**; **3a–b**) decompose between 50 and 350 °C by partly releasing Me₃SnCl. Polycrystalline powders of AlN, GaN and InN were obtained after prolonged pyrolysis under inert conditions (argon, *in vacuo*) above 350 °C but were contaminated with metallic tin according to the X-ray powder diffraction patterns. However, pyrolysis of the *organometallic* precursors [Cl₂MeM·N(SnMe₃)₃] (**1b**, **2c**) yielded tin-free nitride materials at temperatures below 350 °C due to the parallel elimination of SnMe₄ and Me₃SnCl, as evidenced by X-ray powder diffraction, elemental analysis, NMR and IR spectroscopy of the products.[7]

### Conclusion

The Lewis acid/base adducts [X₃M·N(SnMe₃)₃] and [Cl₂MeM·N(SnMe₃)₃] were prepared by the 1 : 1 mole reaction of MX₃ and MCl₂(CH₃) with N(SnMe₃)₃. Unusually short M–N bond lengths of 1.87(1) Å for Al–N (**1a**), 1.950(7) Å for Ga–N (**2a**) and 2.148(6) Å for In–N (**3a**) were found indicating very strong donor–acceptor bonds. It should be noted here, that compound **2c** in particular may be suitable as a precursor for GaN materials by pyrolysis at low temperatures.[7]

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