

Synthesis and structural characterization of the first completely alkyl-substituted Ga–Sb Lewis acid–base adducts†

Stephan Schulz* and Martin Nieger

Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Str. 1,
D-53121 Bonn, Germany. E-mail: stephan@ac4010se.chemie.uni-bonn.de

Received 11th November 1999, Accepted 21st January 2000

The simple Lewis acid–base adducts (*n*-Bu)₃Ga(SbR₃) (R = Et **1**, *n*-Pr **2**, *i*-Pr **3**, *t*-Bu **4**) and (*t*-Bu)₃Ga(SbR₃) (R = Et **5**, *n*-Pr **6**, *i*-Pr **7**, *t*-Bu **8**) were prepared by combination of *n*-Bu₃Ga or *t*-Bu₃Ga, respectively, with the corresponding trialkylstibanes in a 1 : 1 molar ratio. **1–8** were fully characterized by multinuclear NMR (¹H and ¹³C) and mass spectroscopy. In addition, the solid state structures of **5** and **7** were determined by single crystal X-ray diffraction studies.

Introduction

The bulk of our recent research has focused on the preparation and structural characterization of compounds containing Group 13–Group 15 elements, which are of current interest due to their potential to serve as single source precursors for the preparation of the corresponding semiconducting materials by MOCVD technology. Primarily, we were interested in the synthesis of Group 13 antimonides. Our investigations have led to a simple synthetic route for the preparation of nanocrystalline GaSb material,¹ as well as to several metallo-organic AlSb² and GaSb³ compounds, which were obtained as simple Lewis acid–base adducts or heterocycles containing σ-bonds between Al/Ga and Sb. The potential of [R₂AlSb(SiMe₃)₂] (R = Et, *i*-Bu) to produce AlSb thin films by HV-MOCVD (high vacuum metal-organic chemical vapor deposition) at temperatures between 325–550 °C has previously been demonstrated.⁴ However, films so-prepared showed a temperature-dependent incorporation of Si, obviously resulting from the silyl groups. Therefore, we became interested in the synthesis of precursor compounds containing only alkyl substituents.

We focused on the preparation of simple Lewis acid–base adducts of the type R₃Ga(SbR')₃ (R, R' = alkyl). While adducts of Al, Ga and In compounds with amines and phosphines are well known, investigations concerning the synthesis of Group 13–Sb adducts are rare and only a few examples have been structurally characterized: X₃B[Sb(SiMe₃)₃],⁵ R₃Al[Sb(SiMe₃)₃],^{2b} R₂AlCl[Sb(SiMe₃)₃],^{2b} R₃Ga[Sb(SiMe₃)₃],⁶ and R₃In[Sb(SiMe₃)₃].^{6a} Almost fifty years ago, Coates investigated the synthesis of Me₃Ga(EMe₃) adducts (E = N, P, As, Sb, Bi) and found their stability to decrease from NMe₃ to SbMe₃, while BiMe₃ did not react.⁷ To the best of our knowledge, no investigations concerning the structural characterization of all-alkyl-substituted Ga–Sb adducts were performed. Wells *et al.* have reported two structurally characterized Ga–Sb adducts, both containing silyl substituents bound to the Sb center.⁶ The only example of completely alkyl-substituted Ga–Sb compound was described by Cowley *et al.* They prepared [Me₂-GaSb(*t*-Bu)]₃, a six-membered heterocycle, and demonstrated its potential to give GaSb films under MOCVD conditions.⁸

Herein, we report the synthesis and solid state structures of several Lewis acid–base adducts.

Results and discussion

The simple Lewis acid–base adducts (*n*-Bu)₃Ga(SbR₃) (R = Et **1**, *n*-Pr **2**, *i*-Pr **3**, *t*-Bu **4**) and (*t*-Bu)₃Ga(SbR₃) (R = Et **5**, *n*-Pr **6**, *i*-Pr **7**, *t*-Bu **8**) were prepared by reaction of *n*-Bu₃Ga and *t*-Bu₃Ga and the corresponding trialkylstibanes in a 1 : 1 molar ratio.

The ¹H NMR spectra show resonances due to the substituents bound to the Ga center shifted to lower field. Comparable results were observed in analogous adducts, *e.g.* R₃Al(SbR')₃,⁹ Me₃Al(PR₃)₃,¹⁰ R₃Ga(PR')₃ (R = Me, Et),¹¹ and Me₃In(NR₃)₃.¹² α-H and α-C shifts, as well as Δ(H), Δ(C), Δ_{H-H} and Δ_{C-C} values, for *n*-Bu₃Ga, *t*-Bu₃Ga and the adducts **1–8** are summarized in Table 1.

The shifts to lower field of the α-H–Ga and α-C–Ga resonances observed for the adducts do not show a uniform development between the two adduct groups. While the resonances due to the *n*-Bu₃Ga adducts (**1–4**) show the biggest lowfield shift (and therefore the biggest Δ(H) and Δ(C) values) with the electronically *strongest* base, *t*-Bu₃Sb, those due to the *t*-Bu₃Ga adducts (**5–8**) show the biggest lowfield shift with the electronically *weakest* base, Et₃Sb. The spectra of **8** show resonances at exactly the same shift as was found for the starting materials, indicating this sterically overcrowded adduct to be fully dissociated in solution. Obviously, the absolute degree of shift extension of α-H–Ga or α-C–Ga related to the pure trialkyl is not useful for determination of the dative Ga–Sb bond strength. Comparable results were found for Al–P adducts.¹⁰ In the case of the *t*-Bu₃Ga adducts **5–8**, a comparison of the internal ¹³C shift [Δ_{C-C} = δ(β-C)_{trialkylgallium} – δ(α-C)_{trialkylgallium}] of the adduct and the pure trialkylgallium compound seems to be more useful for a qualitative determination of bond strength within Ga–Sb adducts. The largest value is observed for **5**, while **8** shows exactly the same value as *t*-Bu₃Ga. Electronically, **5** should be the weakest adduct due to the low basicity of the trialkylstibane (Et₃Sb) in this compound. However, with sterically hindered Lewis acids like *t*-Bu₃Ga, *steric repulsion* between the ligands becomes the dominating factor influencing the adduct strength. The melting points, which generally decrease within this group (**5**: 106; **6**: 56; **7**: 64; **8**: 37 °C), also agree with this expectation. The Δ_{C-C} values of **1–4** are higher than the Δ_{C-C} value of pure *n*-Bu₃Ga, but they are almost within the same range and are independent from the steric size of the antimony substituents.

Due to the extreme sensitivity of **1–8** in solution towards air and moisture, cryoscopic molecular weight measurements did

† Electronic supplementary information (ESI) available: experimental data for adducts **2–4** and **6–8**. See <http://www.rsc.org/suppdata/dt/a9/a908969a/>

Table 1 Selected ^1H and ^{13}C NMR shifts, $\Delta(\text{H})$, $\Delta(\text{C})$ values and internal shifts $\Delta_{\text{H-H}}$ and $\Delta_{\text{C-C}}$ of the pure trialkylgallium precursors and the Ga component within the adducts **1–8** in C_6D_6

Compound	$\delta^1\text{H}^a$	$\delta^{13}\text{C}^b$	$\Delta(\text{H})^c$	$\Delta(\text{C})^d$	$\Delta_{\text{H-H}}^e$	$\Delta_{\text{C-C}}^f$
<i>n</i> -Bu ₃ Ga	0.61	19.3	—	—	0.71	9.2
(<i>n</i> -Bu) ₃ Ga[SbEt ₃] 1	0.73	16.1	0.12	−3.2	0.77	12.7
(<i>n</i> -Bu) ₃ Ga[Sb(<i>n</i> -Pr) ₃] 2	0.66	16.9	0.05	−2.4	—	11.9
(<i>n</i> -Bu) ₃ Ga[Sb(<i>i</i> -Pr) ₃] 3	0.74	16.6	0.13	−2.7	0.76	12.3
(<i>n</i> -Bu) ₃ Ga[Sb(<i>t</i> -Bu) ₃] 4	0.80	16.4	0.19	−2.9	0.71	12.7
<i>t</i> -Bu ₃ Ga	1.16	31.5	—	—	—	0.4
(<i>t</i> -Bu) ₃ Ga[SbEt ₃] 5	1.32	26.9	0.16	−4.6	—	6.7
(<i>t</i> -Bu) ₃ Ga[Sb(<i>n</i> -Pr) ₃] 6	1.32	27.3	0.16	−4.2	—	6.3
(<i>t</i> -Bu) ₃ Ga[Sb(<i>i</i> -Pr) ₃] 7	1.23	30.0	0.07	−1.5	—	2.1
(<i>t</i> -Bu) ₃ Ga[Sb(<i>t</i> -Bu) ₃] 8	1.16	31.5	0	0	—	0.4

n-Bu₃Ga: ^a $\delta^1\text{H}(\alpha\text{-H})$; ^b $\delta^{13}\text{C}(\alpha\text{-C})$; ^c $\Delta(\text{H}) = \delta(\alpha\text{-H})_{\text{adduct}} - \delta(\alpha\text{-H})_{\text{trialkylgallium}}$; ^d $\Delta(\text{C}) = \delta(\alpha\text{-C})_{\text{adduct}} - \delta(\alpha\text{-C})_{\text{trialkylgallium}}$; ^e $\Delta_{\text{H-H}} = \delta(\beta\text{-H})_{\text{trialkylgallium}} - \delta(\alpha\text{-H})_{\text{trialkylgallium}}$; ^f $\Delta_{\text{C-C}} = \delta(\beta\text{-C})_{\text{trialkylgallium}} - \delta(\alpha\text{-C})_{\text{trialkylgallium}}$. *t*-Bu₃Ga: ^a $\delta^1\text{H}(\beta\text{-H})$; ^b $\delta^{13}\text{C}(\alpha\text{-C})$; ^c $\Delta(\text{H}) = \delta(\beta\text{-H})_{\text{adduct}} - \delta(\beta\text{-H})_{\text{trialkylgallium}}$; ^d $\Delta(\text{C}) = \delta(\alpha\text{-C})_{\text{adduct}} - \delta(\alpha\text{-C})_{\text{trialkylgallium}}$; ^e $\Delta_{\text{H-H}} = \delta(\beta\text{-H})_{\text{trialkylgallium}} - \delta(\beta\text{-H})_{\text{trialkylgallium}}$; ^f $\Delta_{\text{C-C}} = \delta(\beta\text{-C})_{\text{trialkylgallium}} - \delta(\alpha\text{-C})_{\text{trialkylgallium}}$.

not give reliable values. Therefore, we were not able to determine in detail the degree of dissociation in solution, but we believe all the adducts to be extensively dissociated in solution. Beachley and Maloney investigated the adduct formation of several trialkylgallium compounds with phosphanes and found most of them to be extensively dissociated in solution.¹³ Due to the weaker basicity of stibanes compared to phosphanes,¹⁴ **1–8** should also dissociate in solution. However, in the absence of solvent, we believe **1–8** to be “real” adducts for the following reasons:

- (1) The combination of the weak acid *t*-Bu₃Ga with the stibanes yields solids in each case, indicating adduct formation. The solid state structures of two such compounds were determined.
- (2) *n*-Bu₃Ga is the stronger Lewis acid compared to the more sterically demanding *t*-Bu₃Ga and should give stronger adducts.
- (3) *n*-Bu₃Ga forms a solid adduct with the most sterically demanding stibane *t*-Bu₃Sb.

Mass spectra of **1–8** show only the respective starting Ga and Sb trialkyls, indicating dissociation of the adducts in the gas phase. However, the solid adducts can be sublimed without decomposition at 60–80 °C at 10^{−2} mbar.

Single crystals of **5** and **7** suitable for X-ray crystallographic study were obtained from solutions in pentane at −30 °C. In **5** and **7**, the Ga and Sb centers reside in distorted tetrahedral environments with their ligands adopting a staggered conformation relative to one another. The mean Ga–C (**5**: 2.044; **7**: 2.042 Å) and Sb–C bond lengths (**5**: 2.151; **7**: 2.184 Å), as well as the mean C–Ga–C (**5**: 116.4; **7**: 115.9°) and C–Sb–C bond angles (**5**: 97.6; **7**: 100.2°), are within the expected range. The C–Ga–Sb angles range from 100.57(12) to 101.64(12)° in **5** and from 99.07(5) to 104.48(5)° in **7**. The C–Sb–Ga angles in **5** vary from 118.95(13) to 120.84(14)°, while **7** shows a much greater variation, from 111.26(4) to 122.51(4)°. Smaller ranges were observed in Et₃Ga[Sb(SiMe₃)₃] [Si–Sb–Ga 114.50(22)–116.10(24)°] and (*t*-Bu)₃Ga[Sb(SiMe₃)₃] [Si–Sb–Ga 114.68(7)–118.53(6)°]. However, the analogous Al–Sb adduct (*t*-Bu)₃Al[Sb(*i*-Pr)₃] shows comparable C–Sb–Al bond angles [112.20(4)–121.98(4)°].⁹ The Ga–Sb distances [**5**: 2.8479(5); **7**: 2.9618(2) Å] clearly display the influence of steric bulk on the bond lengths. *i*-Pr₃Sb is more sterically demanding than Et₃Sb, leading to an elongated Ga–Sb bond distance due to an increased steric repulsion between the ligands. The Ga–Sb bond distances determined in Et₃Ga[Sb(SiMe₃)₃] [2.846(5) Å] and (*t*-Bu)₃Ga[Sb(SiMe₃)₃] [3.027(2) Å] span a wide range of almost 18 pm. **5** and **7** fit into this “bond distance window” very well. Compared to Et₃Ga[Sb(SiMe₃)₃], the steric pressure within **5** is almost the same. The basicity of Et₃Sb should be greater than that of Sb(SiMe₃)₃ for the following reasons:

- (1) The SiMe₃ group is a π -acceptor, which leads to reduced electron density at the Sb atom.

- (2) Steric repulsion between the ligands, which should yield weaker adducts, is greater in Sb(SiMe₃)₃ compared to Et₃Sb.

Therefore, the Ga–Sb bond length in **5** should be shorter than that in Et₃Ga[Sb(SiMe₃)₃]. On the other hand, *t*-Bu₃Ga is less acidic than Et₃Ga, which should lead to an elongated Ga–Sb distance. Obviously, both effects compensate for each other, resulting in very similar bond lengths. Compared to (*t*-Bu)₃Ga[Sb(SiMe₃)₃], **5** and **7** are stronger adducts, due to less steric repulsion between the ligands, hence the shorter Ga–Sb bond lengths. On steric grounds **8** should show the longest Ga–Sb bond distance, but we were not able to obtain suitable crystals for a single crystal X-ray structure determination.

MOCVD studies are currently underway in our laboratories, using the *t*-Bu₃Ga adducts in an attempt to demonstrate their potential for producing GaSb thin films.¹⁵

Experimental

General considerations

All manipulations were performed in a glovebox under a N₂ atmosphere or by standard Schlenk techniques. Pentane was carefully dried over sodium–potassium alloy under dry N₂. *n*-Bu₃Ga and *t*-Bu₃Ga,¹⁶ as well as Et₃Sb, *n*-Pr₃Sb and *i*-Pr₃Sb,¹⁷ were prepared according to literature methods. *t*-Bu₃Sb was isolated from a standard salt elimination reaction between *t*-BuLi and SbCl₃ at −100 °C. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra were referenced to internal C₆D₅H ($\delta^1\text{H}$ 7.154, $\delta^{13}\text{C}$ 128.0). Mass spectra were recorded on a VG Masslab 12-250 spectrometer in electron ionization mode at 20 eV. Melting points were observed in sealed capillaries and were not corrected.

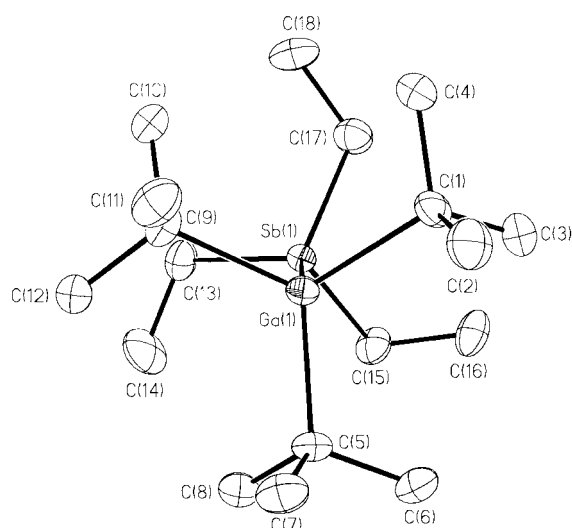
General synthesis of R₃Ga(SbR₃) adducts

Pure R₃Ga (2 mmol) and R₃Sb (2 mmol) were combined in the glovebox. **5–8** were obtained as white solids, the other adducts stayed liquid. At −30 °C **3** and **4** also solidified. **5–8** were crystallized in almost quantitative yield from pentane (5–10 mL) at −30 °C. Experimental data are given for one *n*-Bu₃Ga and one *t*-Bu₃Ga adduct only. Data for the other six adducts have been deposited as electronic supplementary information (ESI).

(*n*-Bu)₃Ga(SbEt₃) (1). Elemental analysis (C₁₈H₄₂GaSb, *M* = 450.0 g mol^{−1}), found (calc.): C, 47.82 (48.04); H, 9.32 (9.41). ^1H NMR (300 MHz, C₆D₅H, 25 °C): δ = 0.73 (m, 2H, GaCH₂CH₂CH₂CH₃), 1.02 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 3H, GaCH₂CH₂CH₂CH₃), 1.10 (m, 3H, SbCH₂CH₃), 1.23 (m, 2H, SbCH₂CH₃), 1.50 (m, $^3J_{\text{HH}}$ = 7.1 Hz, 2H, GaCH₂CH₂CH₂CH₃), 1.67 (m, 2H, GaCH₂CH₂CH₂CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (80 MHz, C₆D₅H, 25 °C): δ = 5.4 (SbCH₂CH₃), 11.4 (SbCH₂CH₃), 14.5 (GaCH₂CH₂CH₂CH₃).

Table 2 Crystallographic data for (*t*-Bu)₃Ga(SbEt₃) (**5**) and (*t*-Bu)₃Ga[Sb(*i*-Pr)₃] (**7**)

	5	7
Chemical formula	C ₁₈ H ₄₂ GaSb	C ₂₁ H ₄₈ GaSb
Formula weight	449.99	492.06
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
Crystal dimensions/mm	0.35 × 0.25 × 0.20	0.60 × 0.55 × 0.50
<i>a</i> /Å	14.1615(3)	13.6128(2)
<i>b</i> /Å	9.5735(2)	9.0089(2)
<i>c</i> /Å	16.0291(4)	20.0307(2)
β /°	90.905(2)	91.750(1)
<i>V</i> /Å ³	2172.88(8)	2455.35(7)
<i>Z</i>	4	4
μ /mm ⁻¹	2.477	2.198
Temperature/K	123(2)	123(2)
<i>D</i> _{calc} /g cm ⁻³	1.376	1.331
Reflections collected	40096	31295
Non-equivalent reflections	5368	5802
<i>R</i> _{int}	0.052	0.039
<i>R</i> 1, ^a <i>wR</i> 2 ^b	0.041, 0.114	0.020, 0.049

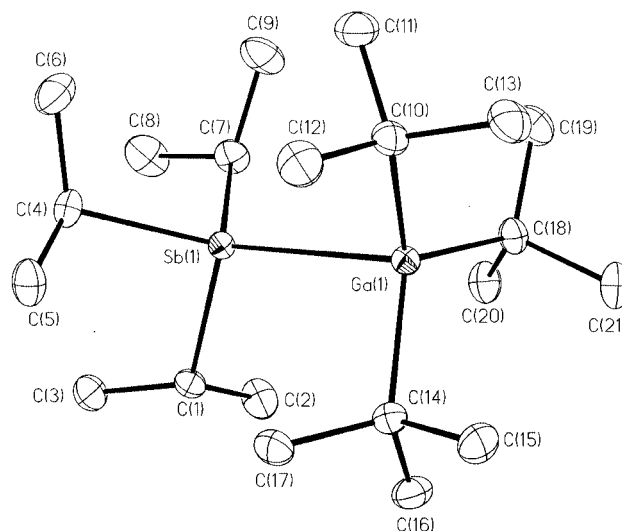
^a For *I* > 2σ(*I*). ^b For all data.**Fig. 1** ORTEP diagram (50% probability ellipsoids) showing the staggered conformation and atom-numbering scheme for **5**; selected bond lengths (Å) and angles (°): Ga(1)–Sb(1) 2.8479(5), Ga(1)–C(1) 2.058(4), Ga(1)–C(5) 2.035(4), Ga(1)–C(9) 2.039(4), Sb(1)–C(13) 2.156(4), Sb(1)–C(15) 2.150(4), Sb(1)–C(17) 2.148(5); C(1)–Ga(1)–C(5) 116.71(17), C(1)–Ga(1)–C(9) 115.88(17), C(5)–Ga(1)–C(9) 116.72(17), C(13)–Sb(1)–C(15) 97.32(18), C(13)–Sb(1)–C(17) 97.91(19), C(15)–Sb(1)–C(17) 97.55(19), C(1)–Ga(1)–Sb(1) 101.64(12), C(5)–Ga(1)–Sb(1) 100.83(12), C(9)–Ga(1)–Sb(1) 100.57(12), C(13)–Sb(1)–Ga(1) 120.84(14), C(15)–Sb(1)–Ga(1) 118.95(13), C(17)–Sb(1)–Ga(1) 119.26(13).

CH₂CH₂CH₃), 16.1 (GaCH₂CH₂CH₂CH₃), 28.8 (GaCH₂CH₂CH₂CH₃), 31.0 (GaCH₂CH₂CH₂CH₃). EI-MS (*m/z*, %): 240 (40) [*n*-Bu₃Ga⁺], 208 (35) [Et₃Sb⁺], 57 (100) [*n*-Bu⁺].

(*t*-Bu)₃Ga(SbEt₃) (**5**). Elemental analysis (C₁₈H₄₂GaSb, *M* = 450.0 g mol⁻¹), found (calc.): C, 47.91 (48.04); H, 9.34 (9.41). Mp: 106 °C. ¹H NMR (300 MHz, C₆D₆H, 25 °C): δ = 1.06 (m, 3H, SbCH₂CH₃), 1.28 (m, 2H, SbCH₂CH₃), 1.32 (s, 9H, *t*-Bu). ¹³C{¹H} NMR (80 MHz, C₆D₆H, 25 °C): δ = 5.9 (SbCH₂CH₃), 11.1 (SbCH₂CH₃), 26.9 (GaC(CH₃)₃), 33.7 (GaC(CH₃)₃). EI-MS (*m/z*, %) 240 (55) [*t*-Bu₃Ga⁺], 208 (25) [Et₃Sb⁺], 57 (100) [*t*-Bu⁺].

X-Ray structure solution and refinement

Crystallographic data are summarized in Table 2. Figs. 1 and 2 show ORTEP diagrams of the solid state structures of **5** and

**Fig. 2** ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **7**; selected bond lengths (Å) and angles (°): Ga(1)–Sb(1) 2.96178(19), Ga(1)–C(10) 2.0392(15), Ga(1)–C(14) 2.0429(16), Ga(1)–C(18) 2.0450(16), Sb(1)–C(1) 2.1866(15), Sb(1)–C(4) 2.1805(15), Sb(1)–C(7) 2.1843(17); C(10)–Ga(1)–C(14) 115.74(7), C(10)–Ga(1)–C(18) 115.70(7), C(14)–Ga(1)–C(18) 116.20(7), C(1)–Sb(1)–C(4) 98.29(6), C(1)–Sb(1)–C(7) 100.96(6), C(4)–Sb(1)–C(7) 101.33(7), C(10)–Ga(1)–Sb(1) 104.48(5), C(14)–Ga(1)–Sb(1) 99.07(5), C(18)–Ga(1)–Sb(1) 102.05(5), C(1)–Sb(1)–Ga(1) 111.26(4), C(4)–Sb(1)–Ga(1) 122.51(4), C(7)–Sb(1)–Ga(1) 118.74(5).

7, including selected bond lengths and angles. Data were collected on a Nonius Kappa-CCD diffractometer. Absorption corrections were applied. The structures were solved by direct methods (SHELXS-86)¹⁸ and refined by full-matrix least-squares on *F*². All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).¹⁹

CCDC reference number 186/1817.

See <http://www.rsc.org/suppdata/dt/a9/a908969a/> for crystallographic files in .cif format.

Acknowledgements

Stephan Schulz gratefully thanks the DFG for a Fellowship award. Financial support was given by the Fonds der Chemischen Industrie, DFG and Professor E. Niecke, Universität Bonn.

References

- S. Schulz, L. Martinez and J. L. Ross, *Adv. Mater. Opt. Electron.*, 1996, **6**, 185; S. Schulz and W. Assenmacher, *Mater. Res. Bull.*, 2000, in the press.
- (a) S. Schulz and M. Nieger, *Organometallics*, 1998, **17**, 3398; (b) S. Schulz and M. Nieger, *Organometallics*, 1999, **18**, 315; (c) S. Schulz, A. Kuczkowski and M. Nieger, *Organometallics*, 2000, in the press.
- S. Schulz and M. Nieger, *J. Organomet. Chem.*, 1998, **570**, 275.
- H. S. Park, S. Schulz, H. Wessel and H. W. Roesky, *Chem. Vap. Deposit.*, 1999, **5**, 179.
- M. S. Lube, R. L. Wells and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1997, 285.
- (a) R. A. Baldwin, E. E. Foos, R. L. Wells, P. S. White, A. L. Rheingold and G. P. A. Yap, *Organometallics*, 1996, **15**, 5035; (b) R. L. Wells, E. E. Foos, P. S. White, A. L. Rheingold and L. M. Liable-Sands, *Organometallics*, 1997, **16**, 4771.
- G. E. Coates, *J. Chem. Soc.*, 1951, 2003.
- A. H. Cowley, R. A. Jones, C. M. Nunn and D. L. Westmoreland, *Chem. Mater.*, 1990, **2**, 221.
- S. Schulz, A. Kuczkowski and M. Nieger, unpublished work.
- A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 1988, 3047.
- A. Leib, M. T. Emerson and J. P. Oliver, *Inorg. Chem.*, 1965, **4**, 1825.
- D. C. Bradley, H. Dawes, D. M. Frigo, M. B. Hursthouse and B. Hussain, *J. Organomet. Chem.*, 1987, **325**, 55.

- 13 O. T. Beachley and J. D. Maloney, *Organometallics*, 1997, **16**, 4016.
- 14 K. C. H. Lange and T. M. Klapötke, in *The Chemistry of Functional Groups, The chemistry of organic arsenic, antimony and bismuth compounds*, J. Wiley and Sons, New York, 1994, ch. 8.
- 15 Adducts **1–8** may be sublimed at 10^{-3} mbar between 60–80 °C without decomposition. NMR spectra prepared from freshly sublimed compounds show resonances due to the organic ligands. Integration gives the expected 1 : 1 complex. Initial pyrolysis studies using **4** and **8** were performed in sealed capillaries at 350 °C. In both cases, black powders were obtained. Elemental analyses indicated the presence of Ga and an excess of Sb. The crystallinity of the particles so-formed was poor.
- 16 R. A. Kovar, G. Loaris, H. Derr and J. O. Callaway, *Inorg. Chem.*, 1974, **13**, 1476.
- 17 M. Wieber, in *Gmelin Handbook of Inorganic Chemistry*, 8th edn., *Sb Organoantimony Compounds Part 1*, ed. H. Bitterer, Springer Verlag, Berlin, 1981.
- 18 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 19 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, 1997.

Paper a908969a