Synthesis and solid-state structures of Ph₃E–Ga(*t*-Bu)₃ Lewis acid-base adducts

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Abstract. Three Lewis acid-base adducts Ph₃E–Ga(*t*-Bu)₃ (E = P **1**, As **2**, Sb **3**) were synthesized by reactions of Ph₃E and *t*-Bu₃Ga and characterized by heteronuclear NMR (¹H, ¹³C, ³¹P) and IR spectroscopy, elemental analysis and single crystal X-ray diffraction. Their structural parameters are discussed and compared to similar *t*-Bu₃Ga adducts. The strength of the donor-acceptor interactions within **1** - **3** was investigated in solution by temperature-dependent ¹H NMR spectroscopy and by quantum chemical calculations.

Keywords. Main group element; Lewis acid; Lewis Base, Adduct, Structure

Introduction

Lewis acid-base reactions between group 13 (R₃M) and group 15 compounds (R₃E) are of general interest in main group chemistry and have been studied for more than two centuries. Several amine–borane and phosphine–borane adducts have been structurally characterized since the earliest synthesis of F₃B–NH₃ by Gay-Lussac.^[1] The interest in such compounds in recent years increased due to their promising potential as hydrogen storage materials or molecular precursors for a large variety of polymers.^[2] The strength of the donor-acceptor interaction in adducts of the general type R₃M–ER'₃ (M = B, Al, Ga; E = N, P; R, R' = H, alkyl, aryl) was investigated in solution and in the gas phase as well as by quantum chemical calculations, clearly proving the crucial influence of the group 13 and 15 elements. In addition, the organic substituents strongly influence the strength of the donor-acceptor interaction and allow a fine-tuning of the electronic and steric properties of the Lewis acids and bases and hence the dissociation energies of the adducts.^[3] In contrast, stibines (R₃Sb) and bismuthines (R₃Bi), which are well established ligands in transition metal coordination chemistry,^[4] show much weaker tendencies to form Lewis acid-base adduct with group 13 compounds and only limited data on their solid state structures and thermodynamic stabilities are available.^[5,6] These findings correlate with the decreasing Lewis basicity (σ-donor character) of ER₃ (E = N - Bi)

with increasing atomic number of the central group 15 element, which can be attributed to the increasing reluctance of the heavier elements for isovalent hybridization due to the increasing difference in spatial extension of the orbitals.[7] This leads to an increasing p character of the E-C bonds and an increasing s-character of the *electron lone pair* of the heavier group 15 elements, which is reflected by the steadily decreasing C–E–C bond angles of Ph₃E (Ph₃P 103°, Ph₃As 100°, Ph₃Sb 96°, Ph₃Bi 94°).

In recent years, we reported on the crystal structures of several trialkylalane and -gallane adducts of trialkylstibines R₃Sb,^[8] and -bismuthines R₃Bi,^[9] as well as tetraalkyldistibines R₄Sb₂^[10] and -dibismuthines R₄Bi₂,^[11] respectively. Structural comparison of analogously substituted adducts proved that the *strength of the donor-acceptor interaction* within the adducts can be qualitatively estimated following a model initially described by Haaland and Frenking, according to which the adduct formation leads to an *increase of the M–C bond lengths* and a *decrease of the C–M–C bond angles* compared to the pure MR₃ molecule.^[12,13] In contrast, the C–E–C bond angle of the ER₃ Lewis base is expected to increase upon adduct formation.

We herein report on the synthesis and characterization of three adducts *t*-Bu₃Ga–EPh₃ (E = P **1**, As **2**, Sb **3**) including the solid-state structures, while attempts to prepare the bismuth-analogous adduct *t*-Bu₃Ga–EPh₃ **4** failed. The thermodynamic stability of **1** - **3** was investigated in solution by temperature dependent ¹H NMR spectroscopy, while quantum chemical calculations of **1** - **4** using density functional theory (DFT) methods were performed in comparison and to understand the electronic structure of these adducts in more detail.

Results and Discussion

Equimolar amounts of *t*-Bu₃Ga and Ph₃E (E = P, As, Sb) were dissolved in 5 mL of benzene or CH₂Cl₂ and stored at low temperature, yielding the corresponding adducts **1** - **3** as colorless, crystalline solids in almost quantitative yields. In contrast, the analogous reaction of *t*-Bu₃Ga with Ph₃Bi did not result in the formation of *t*-Bu₃Ga–BiPh₃, in accordance with the weak Lewis basicity of BiPh₃. While triphenylarsine and -stibine have been widely applied in transition metal complexes,^[14] whose stability clearly results from the back-bonding contribution of the transition metal, the number of main group metal adducts is rather limited. Only six adducts of the type Ph₃As–MX₃ (M = B, Al, Ga, In, Tl) and two stibine adducts, Cl₃Ga–SbPh₃ and PhGaI₂–SbPh₃,^[15] were found in the Cambridge Structural Database.

((Scheme 1 here))

1 - **3** were characterized by multinuclear NMR (¹H, ¹³C (³¹P)) spectroscopy. The ¹H NMR spectra of **1** - **3** each show a singlet for the *t*-Bu groups (1.25 **1**, 1.20 **2**, 1.27 **3**), which are shifted

to lower field compared to pure *t*-Bu₃Ga (1.15 ppm). In contrast, the resonances of the Ph groups are slightly shifted to higher field as was previously observed for comparable alane^[8e,12b] and gallane adducts^[8d,12a] of the desired type. In contrast, the ¹H NMR spectrum of a mixture of *t*-Bu₃Ga and Ph₃Bi only showed resonances at the same chemical shift of pure starting reagents (1.15 *t*-Bu; 7.03-7.19 and 7.63-7.68 Ph), even at low temperature (-60 °C).

((Table 1 here)):

((Figure 1 here))

The dissociation enthalpies of **1** to **3** were determined by temperature-dependent ¹H NMR spectroscopy (Table 1, Figure 1).^[12b] The dissociation enthalpy of *t*-Bu₃Ga–EPh₃ can be derived from the temperature dependence of the equilibrium constant *K*_{eq}, with

and

$$\ln K_{\text{eq}} = \frac{-\Delta H_{\text{D}}}{R} \cdot \frac{1}{T} + \frac{\Delta S_{\text{D}}}{R}$$

The equilibrium constant is expressed in terms of the mole fraction of the gallane present as free *t*-Bu₃Ga and the total initial concentration, [total]:

$$K_{\text{eq}} = \frac{[\text{total}] \cdot (\chi_{\text{free}})^2}{(1 - \chi_{\text{free}})}$$

The time-dependent ¹H NMR spectra over the whole temperature range only show one single resonance of the *t*-Bu group. If the ¹H NMR shift of the *t*-Bu group is directly proportional to the mole fraction of the total species present as free *t*-Bu₃Ga, χ_{free} is calculated from the ¹H NMR chemical shift of the *t*-Bu group at a given temperature.

$$\chi_{\text{free}} = \frac{\delta_{\text{sample}} - \delta_{\text{coord}}}{\delta_{\text{free}} - \delta_{\text{coord}}}$$

δ_{free} is the chemical shift of the *t*-Bu₃Ga, δ_{sample} is obtained from the adduct and δ_{coord} displays the "real" chemical shift of the adduct, which was estimated by addition of a fivefold excess of Ph₃E to *t*-Bu₃Ga, which was then measured at -70 °C. Under these conditions, it is assumed that *t*-Bu₃Ga is fully converted to *t*-Bu₃Ga–EPh₃ **1** - **3**.

According to the NMR studies, Ph₃P forms a less stable adduct in solution (10.3 kcal/mol **1**) compared to Ph₃As (13.2 kcal/ mol **2**) and Ph₃Sb (13.8 kcal/ mol **3**). Even if the absolute values are erroneous due to systematic sources of errors, i.e. the "real" chemical shift of the adducts, the trend observed within this adduct group rather surprises. The interaction between *t*-Bu₃Ga and Ph₃P in solution is slightly weaker compared to that with Ph₃As and Ph₃Sb, which are

almost identical with respect to the error of the method. These findings may result from repulsive steric interactions between the bulky organic groups, which become less important with increasing atomic radii of the central group 15 atom, and obviously overcompensate the decreasing Lewis basicity of Ph_3E with increasing atomic number ($\text{E} = \text{P}, \text{As}, \text{Sb}$).

Quantum chemical calculations were performed to further prove this trend. However, the dissociation enthalpies of the adducts $t\text{-Bu}_3\text{Ga-EPh}_3$ ($\text{E} = \text{P}$ **1'**, As **2'**, Sb **3'**, Bi **4'**) were found to steadily decrease with increasing atomic number of the group 15 element from 5.17 kcal/mol (Ph_3P), 4.29 kcal/mol (Ph_3As), 2.58 kcal/mol (Ph_3Sb) and finally to -0.80 kcal/mol (Ph_3Bi). Comparable results were previously obtained for analogous alane adducts of the general type $\text{R}_3\text{Al-ER}'_3$ ($\text{E} = \text{P} - \text{Bi}$; $\text{R} = \text{H}, \text{Me}$; $\text{R}' = \text{H}, \text{Et}, i\text{-Pr}$), whereas the dissociation enthalpies within the sterically most hindered adducts $t\text{-Bu}_3\text{Al-E}(i\text{-Pr})_3$ increased from $\text{E} = \text{P}$ to $\text{E} = \text{Sb}$ and then decreased to $\text{E} = \text{Bi}$. This trend was mainly attributed to repulsive interactions between the sterically demanding organic substituents ($i\text{-Pr}$, $t\text{-Bu}$), which are expected to show a maximum in the phosphine adduct due to the smallest atomic radius of the group 15 element.^[12b] The negative dissociation enthalpy of $t\text{-Bu}_3\text{Ga-BiPh}_3$ **4'** is in accordance with the observed lack of formation of this adduct under the conditions described above. The deviation from the dissociation enthalpies as determined by temperature-dependent ^1H NMR spectroscopy probably originates both from the inaccuracy of that method. Solvent effects, which have been included in the DFT calculations, did not change the general trend.

Solid state structures. **1** (Figure 2) crystallizes in the monoclinic space group $C2/c$ with one molecule in the asymmetric unit, whereas **2** and **3** (Figures 3 and 4) are isostructural and crystallize in the trigonal space group $R\bar{3}$ with the molecule placed on a threefold axis. The asymmetric units of **2**· CHCl_3 and **3**· CHCl_3 each comprise a CHCl_3 molecule disordered by threefold rotoinversion. The organic groups are oriented in a synclinal way (C-E-Ga-C : $-24.12(7)$ to $-24.55(7)^\circ$ (**1**); $-33.06(4)^\circ$ (**2**); $-36.43(4)^\circ$ (**3**)). The deviation from the ideally staggered alignment ($\pm 60^\circ$) may be explained by either weak intramolecular $\text{CH}\cdots\pi$ interactions or steric hindrance. Although the $\bar{3}$ symmetry provides ideal circumstances for the formation of a 6PE interaction motif in the crystal packing,^[16] the Ph_3E groups are separated by the solvent molecules and can thus not form any kind of $\text{CH}\cdots\pi$ interactions. In **1** no solvent molecule is present to prevent the 6PE motif and consequently it is observed as expected. Weak $\text{Ga}\cdots\text{H}$ interactions as was observed in $t\text{-Bu}_3\text{Ga}$ have not been observed.^[12a,c]

((Figure 2 here))

((Figure 3 here))

((Figure 4 here))

((Table 2 here))

The Ga–E bond lengths (2.7126(5) Å **1**; 2.8513(3) Å **2**; 2.9337(2) Å **3**) increase with increasing atomic number of the group 15 element, reflecting the increasing covalent radii (P 1.11 Å; As 1.21 Å; Sb 1.40 Å).^[17] The Ga–P bond in **1** (Table 2) is significantly elongated compared to those observed in phosphine adducts of the type R₃P–GaR₃ containing alkyl or aryl substituents, which typically range from 2.438 to 2.719 Å (14 hits for intra- and intermolecular adducts, mean value 2.531(66) Å), and in adducts of the type R₃P–GaX₃ containing more Lewis-acidic gallium trihalides (2.348 to 2.500 Å; 14 hits, mean value 2.391(22) Å). In fact, the Ga–P bonds observed in **1** and *t*-Bu₂(*i*-Bu)Ga–P(*i*-Pr)₃ (2.720(1) Å)^[12a] represent the longest Ga–P bonds ever reported. The Ga–As bond in **2** (2.8513(3) Å) is shorter than the Ga–Sb bond (2.9337(2) Å). Both values agree with Ga–E bond lengths reported for arsine and stibine adducts of the general type X₃Ga–EX₃ (E = As, Sb, X = halogen, H, C, Si) in the Cambridge structural database. These range for arsine adducts from 2.423 to 2.905 Å (mean 2.527 Å, mean deviation 0.077 Å) and for R₃Sb adducts from 2.612 to 3.030 Å (mean 2.826 Å, mean deviation 0.105 Å).^[18] As was observed for **1**, the Ga–As bond in **2** belongs to the longest Ga–As bond reported, to date. Only the sterically hindered *t*-Bu₃Ga–As(*i*-Pr)₃ adduct shows a longer Ga–As bond (2.905(1) Å).

The E–C bond lengths in **1** (1.8233(14) - 1.8285(14) Å), **2** (1.9554(9) Å) and **3** 2.1410(9), Å) are almost identical compared to those of Ph₃E (P 1.828–1.834 Å,^[19] As 1.957 Å,^[20a] Sb 2.156 Å^[21a]), whereas the average C–E–C bond angles in **1** (103.04(6)°) and **3** (99.78(3)°) are larger than those of Ph₃E (P: 101.8–102.4,^[19] Sb: 96.1^[21a]). In contrast, **2** (98.10(3)°) shows slightly smaller C–As–C bond angles than Ph₃As (As: 100.1°;^[20a]). In accordance to these findings, the C–Ga–C angles also show no steady trend. Those of **1** (114.25(7) - 116.05(7)°) are smaller compared to those of **3** (116.266(17)°), whereas the largest values were observed for **2** (116.968(15)°). Therefore, the sum of the C–Ga–C bond angles (346.0° **1**, 350.9° **2**, 348.7° **3**), which in all adducts is below the value of trigonal-planar, sp²-hybridized *t*-Bu₃Ga (360°), doesn't show a steadily increasing trend with increasing atomic number of the group 15 element as was expected. The observed structural trends are in contrast to those previously reported for Et₃Ga–E(SiMe₃)₃ adducts (E = P - Bi),^[12a] in which the *t*-Bu₃Ga unit increasingly deviates from planarity with decreasing atomic number of the group 15 element.

The distinguished role of the Lewis acid on the Ga–E bond lengths becomes obvious when **1** - **3** are compared to adducts containing stronger Lewis acids. For instance, adducts of the type Ph₃P–GaX₃ (X = Cl 2.3717(16) Å,^[22] Br 2.3848(13)/2.3879(13) Å,^[22] I 2.416(5)/2.413(4) Å^[23]) exhibits significantly shorter Ga–P bonds, which were also found to steadily increase with decreasing Lewis acidity of GaX₃.^[22] The same findings are observed when **2** and **3** are

compared with $\text{Ph}_3\text{E}-\text{GaCl}_3$ ($\text{E} = \text{As},^{[24]} \text{Sb}^{[15]}$). The Ga–E bond lengths (As: 2.540(2) Å; Sb: 2.654(2) Å) are significantly shorter than those of **2** and **3**, whereas the sums of the C–E–C bond angles (As: 315.9°; Sb: 311.04°) are remarkably larger compared to **2** (299.3°) and **3** (294.3°) as well as uncomplexed Ph_3As (300.3°)^[20a] and Ph_3Sb (288.3°),^[21a] respectively. Surprisingly, the sum of the C–As–C bond angles in **2** (299.3°) is almost identical compared to that of Ph_3As (300.3°),^[20a] whereas $\text{Ph}_3\text{As}-\text{GaCl}_3$ (315.9°) containing the stronger Lewis acid GaCl_3 shows a significantly larger value.^[24] In contrast, the sums of the C–E–C bond angles in **1** (309.6°) and **3** (294.3°) increase upon adduct formation (Ph_3P 305.5–307.3°;^[19] Ph_3Sb 288.3°)^[21a] as was expected, even though the increase of the C–P–C bond angles (approximately 2–4°) is less pronounced compared to the increase of the sum of C–Sb–C bond angles observed for $\text{Ph}_3\text{Sb}-\text{GaCl}_3$ (311.04°).

The structural parameters observed in the solid-state structures of **1**, **2**· CHCl_3 and **3**· CHCl_3 are somewhat unexpected since they point to a slightly weaker acid-base interaction in **2** compared to **1** and **3**. We therefore performed quantum chemical calculations to investigate the electronic structure of the adduct **1'** - **3'** in more detail.

Quantum chemical calculations. The structural parameters of the QM-optimized (B3LYP/def2-TZVPP) structures of **1'** - **3'** as well as of *t*-Bu₃Ga, Ph_3As and Ph_3Sb are in good agreement with the experimentally observed values. The deviations are within 1% for bond-lengths and 3 % for angles. Only the dihedral C1–E–Ga–C7 angles deviate substantially, due to the weakness of the Ga–E bond, which opens the rotation around this axis into different energetic minima. Figure 5 displays the orbital interaction in **1'** - **3'**.

((Figure 5 here))

NBO analyses of **1'** - **4'** showed that the charge at the group 15 element in Ph_3E (0.82 P, 0.90 As, 1.06 Sb, 1.05 Bi) upon adduct formation increases (0.96 **1'**, 1.02 **2'**, 1.31 **3'**, 1.26 **4'**). At the same time, the positive charge at the Ga atom in *t*-Bu₃Ga (1.73) decreases upon adduct formation (1.46 **1'**, 1.47 **2'**, 1.41 **3'**, 1.47 **4'**). According to these results, the Ga atom in adduct **3'** receives a maximum of electron density from the group 15 element.

In agreement with the calculated dissociation enthalpies, the Mayer bond orders between gallium and the group 15 element decrease with from PPh_3 (0.352) over AsPh_3 (0.215) to BiPh_3 (0.197) with a slightly elevated value for SbPh_3 (0.291). This depicts the declining Ga–E interaction with higher atomic number of E.

Conclusion. *t*-Bu₃Ga reacts with Ph_3E with formation of *t*-Bu₃Ga–E Ph_3 ($\text{E} = \text{P}$ **1**, As **2**, Sb **3**), whereas Ph_3Bi failed to form a stable Lewis acid-base adduct. **1** to **3** were structurally characterized by single crystal X-ray diffraction. Comparison of the Ga–C bond lengths and C–

Ga-C bond angles with those of uncomplexed *t*-Bu₃Ga showed that the donor-acceptor interaction in **1** and **3** is slightly stronger than in **2**. These findings are only partially consistent with those of temperature-dependent ¹H NMR spectroscopy studies, according to which **1** exhibits the weakest donor-acceptor interaction, whereas those of **2** and **3** are comparable. In contrast, quantum chemical calculations revealed that the strength of the donor-acceptor interaction in the gas phase within the adducts *t*-Bu₃Ga–EPh₃ (E = P - Bi) steadily decreases. In accordance with the experimental findings, Ph₃Bi doesn't form a stable Lewis acid-base adduct with *t*-Bu₃Ga.

Experimental Section

General Considerations. The reactions were performed using standard Schlenk and glove-box techniques under purified argon atmosphere. Solvents were carefully dried and degassed prior to use. Deuterated solvents were stored over activated molecular sieves (4 Å). Ph₃E (E = P, As, Sb, Bi) were commercially available and used as received, while *t*-Bu₃Ga was prepared according to literature methods.^[25] ¹H (300 MHz) and ¹³C{¹H} (75.5 MHz) NMR (δ in ppm) spectra were recorded using a Bruker Avance DPX-300 spectrometer and the spectra were referenced to internal C₆D₅H (¹H: δ = 7.154; ¹³C: δ = 128.39). Microanalyses were performed at the elemental analysis laboratory of the University of Duisburg-Essen. IR spectra were measured in an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The FT-IR spectrometer was placed in an argon-filled glovebox to avoid any oxidation or hydrolysis of the samples during measurement.

Synthesis of Ph₃P–Ga(*t*-Bu)₃ 1. A solution of 0.26 g (1.0 mmol) Ph₃P and 0.24 g (1.0 mmol) *t*-Bu₃Ga were dissolved in 5 mL of benzene and stored at 10 °C for 48 h, yielding colorless crystals of **1**. Yield 0.36 g (98%). M.p. 71 °C. Anal. Calcd. for C₃₀H₄₂PGa (503.35 g/mol): C 71.58; H 8.41 %. Found: C 72.26; H 8.52 %. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ = 1.17 (*s*, 9H, CCH₃), 7.02-7.06, 7.36-7.38 (*m*, 18H, PPh₃). ¹³C-NMR (300 MHz, C₆D₆, 25 °C): δ = 30.37, 31.05, 128.68, 128.78, 128.90, 134.01, 134.27, 137.70, 137.57. IR: U[cm⁻¹] 2909, 2891, 2839, 1579, 1521, 1460, 1406, 1341, 1278, 1237, 1177, 1092, 1027, 954, 939, 867, 790, 750, 719, 680, 654, 620, 583, 542, 469.

Synthesis of Ph₃As–Ga(*t*-Bu)₃ 2. A solution of 0.30 g (1.0 mmol) Ph₃As and 0.24 g (1.0 mmol) *t*-Bu₃Ga were dissolved in 5 mL of CH₂Cl₂ and stored at -30 °C for 4 days, yielding colorless crystals of **2**. Yield 0.35 g (98%). M.p. 125 °C. Anal. Calcd. for C₃₀H₄₂AsGa (547.30 g/mol): C 65.84; H 7.73 %. Found: C 65.51; H 7.83 %. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ = 1.32 (*s*, 9H, CCH₃), 6.97-7.04, 7.36-7.38 (*m*, 18H, PPh₃). ¹³C-NMR (300 MHz, C₆D₆, 25 °C): δ = 29.85,

30.90, 128.64, 128.92, 134.09, 140.15. IR: U[cm⁻¹] 3055, 2972, 2942, 2922, 2835, 2703, 1979, 1579, 1460, 1432, 1361, 1305, 1243, 1174, 1086, 1073, 1023, 1008, 985, 895, 808, 755, 733, 691, 590, 540, 466, 396.

Synthesis of Ph₃Sb–Ga(*t*-Bu)₃ 3. A solution of 0.35 g (1.0 mmol) Ph₃Sb and 0.24 g (1.0 mmol) *t*-Bu₃Ga were dissolved in 5 mL of CH₂Cl₂ and stored at -30 °C for 5 days, yielding colorless crystals of **3**. Yield 0.38 g (100%). M.p. 81 °C. Anal. Calcd. for C₃₀H₄₂SbGa (594.14 g/mol): C 65.65; H 7.13 %. Found: C 65.72; H 7.25 %. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ = 1.18 (*s*, 9H, CCH₃), 7.14–7.18, 7.56–7.51 (*m*, 18H, PPh₃). ¹³C-NMR (75 MHz, C₆D₆, 25 °C): δ = 29.86, 31.14, 123.87, 129.18, 136.54, 138.49. IR: U[cm⁻¹] 3051, 2955, 2912, 2860, 2819, 2697, 2689, 1955, 1879, 1811, 1577, 1464, 1424, 1356, 1259, 1186, 1069, 997, 928, 804, 735, 687, 521, 454, 393.

X-ray Structure Solution and Refinement. Crystals of **1**, **2**·CHCl₃ and **3**·CHCl₃ were mounted on nylon loops in inert oil. Figures 2 - 4 show the solid-state structures of **1** - **3** and selected bond lengths and angles are summarized in Table 2. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated MoK_α radiation, λ = 0.71073 Å) at 100(1) K and the structures were solved by Direct Methods (SHELXS-97)^[26] and refined anisotropically by full-matrix least-squares on F² (SHELXL-2014).^[27] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Baker AXS APEX2,). Non-hydrogen atoms were refined anisotropically where possible and hydrogen atoms were refined using a riding model or rigid methyl groups. H11 was refined freely with its bond length restrained to 0.98 Å in both structures.

Crystallographic data of **1**, **2**·CHCl₃ and **3**·CHCl₃ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1830921 (**1**), CCDC-1538627 (**2**) and 1538628 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internal) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Methods. Theoretical calculations were carried out using the Orca 4.0 program^[28] at the B3LYP/def2-TZVPP level of theory,^[29] including DFT-D3 dispersion correction^[30] and the resolution-of-the-identity (RIJCOSX)^[31] technique. For the Sb and Bi atom the def2-ECP effective core potentials were employed.^[32] The natural bond orbital (NBO) analysis was performed using the NBO 6.0 program.^[33] The results from the structure optimizations and frequency calculations were used to calculate the free enthalpies of adduct dissociation, including the Boys-Bernardi counterpoise correction in order to account for the basis set superposition error.

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References

- [1] J. L. Gay-Lussac, J. L. Thenard, *Mem. Phys. Chim. Soc. d'Arcueil* **1809**, 2, 210; as cited in V. Jonas, G. Frenking, *J. Chem. Soc., Chem. Commun.* **1994**, 1489.
- [2] A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, 110, 4023.
- [3] a) M. Becerra, M. Real-Enriquez, C. Espinosa-Gavilanes, C. H. Zambrano, R. Almeida, F. J. Torres, L. Rincón, *Theo. Chem. Acc.* **2016**, 135, 77; b) N. A. Young, *Coord. Chem. Rev.* **2013**, 257, 956; c) A. Y. Timoshkin, M. Bodensteiner, T. N. Sevastianova, A. S. Lisovenko, E. I. Davydova, M. Scheer, C. Graßl, A. V. Butlak *Inorg. Chem.* **2012**, 51, 11602; d) A. Y. Timoshkin, G. Frenking *Organometallics* **2008**, 27, 371; e) A. F. Jalbout, A. Boutalib, *J. Phys. Chem. A* **2006**, 110, 12524; f) F. Bessac, G. Frenking, *Inorg. Chem.* **2006**, 45, 6956; g) S. S. Mallajosyula, A. Datta, S. K. Pati, *J. Phys. Chem. A* **2006**, 110, 5156; h) K. R. S. Chandrakumar, Sourav Pal, *J. Phys. Chem. A* **2002**, 106, 11775; i) A. Jarid, A. Boutalib, *J. Phys. Chem. A* **2000**, 104, 9220; j) A. Y. Timoshkin, A. V. Suvorov, H. F. Bettinger, H. F. Schaefer III, *J. Am. Chem. Soc.* **1999**, 121, 5687; k) H. Anane, A. Jarid, A. Boutalib, *J. Phys. Chem. A* **1999**, 103, 9847; l) J. M. Brunel, B. Faure, M. Maffei, *Coord. Chem. Rev.* **1998**, 178-180, 665.
- [4] a) J. Burt, W. Levason, G. Reid, *Coord. Chem. Rev.* **2014**, 260, 65; b) S. Schulz, *Adv. Organomet. Chem.* **2003**, 49, 225; c) S. Schulz in *Structure and Bonding*, Vol. 103: Group 13 Chemistry I: Fundamental New Developments, Ed. H. W. Roesky, D. A. Atwood, **2002**, 117ff.
- [5] a) M. S. Lube, R. L. Wells, P. S. White, *J. Chem. Soc., Dalton Trans.* **1997**, 285; b) R. L. Wells, E. E. Foos, P. S. White, A. L. Rheingold, L. M. Liable-Sands, *Organometallics* **1997**, 16, 4771; c) R. A. Baldwin, E. E. Foos, R. L. Wells, P. S. White, A. L. Rheingold, G. P. A. Yap, *Organometallics* **1996**, 15, 5035.
- [6] G. E. Coates, *J. Chem. Soc.* **1951**, 2003.
- [7] W. Kutzelnigg, *Angew. Chem.* **1984**, 96, 262; *Angew. Chem. Int. Ed.* **1984**, 23, 272.
- [8] a) S. Schulz, A. Kuczkowski, M. Nieger, H. Saxell, *J. Organomet. Chem.* **2010**, 695, 2281; b) S. Schulz, A. Kuczkowski, M. Nieger, *J. Chem. Crystallogr.* **2010**, 40, 1163; c) D. Schuchmann, S. Schulz, U. Flörke, *Acta Cryst.* **2007**, E63, m1606; d) S. Schulz, M. Nieger, *J. Chem. Soc., Dalton Trans.* **2000**, 639; e) S. Schulz, A. Kuczkowski, M. Nieger, *J. Organomet. Chem.* **2000**, 604, 202; f) S. Schulz, M. Nieger, *Organometallics* **1999**, 18, 315; g) S. Schulz, M. Nieger, *J. Organomet. Chem.* **1998**, 570, 275.

- [9] a) A. Kuczkowski, S. Schulz, M. Nieger, *Eur. J. Inorg. Chem.* **2001**, 2605. (b) A. Kuczkowski, F. Thomas, S. Schulz, M. Nieger, *Organometallics* **2000**, *19*, 5758.
- [10] (a) D. Schuchmann, A. Kuczkowski, S. Fahrenholz, S. Schulz, U. Flörke, *Eur. J. Inorg. Chem.* **2007**, 931; (b) A. Kuczkowski, S. Fahrenholz, S. Schulz, M. Nieger, *Organometallics* **2004**, *23*, 3615; (c) A. Kuczkowski, S. Schulz, M. Nieger, P. Saarenketo, *Organometallics* **2001**, *20*, 2000.
- [11] A. Kuczkowski, S. Schulz, M. Nieger, *Angew. Chem.* **2001**, *113*, 4351; *Angew. Chem. Int. Ed.* **2001**, *40*, 4222.
- [12] a) A. Kuczkowski, S. Schulz, M. Nieger, *Appl. Organomet. Chem.* **2004**, *18*, 244; (b) A. Kuczkowski, S. Schulz, M. Nieger, P. R. Schreiner, *Organometallics* **2002**, *21*, 1408; (c) A. R. Cowley, A. J. Downs, S. Marchant, V. A. Macrae, R. A. Taylor, S. Parsons, *Organometallics* **2005**, *24*, 5702
- [13] a) A. Haaland, *Angew. Chem.* **1989**, *101*, 1017; *Angew. Chem. Int. Ed.* **1989**, *28*, 992; (b) A. Haaland, in *Coordination Chemistry of Aluminum*, Ed. G.H. Robinson, VCH Verlagsgesellschaft, Weinheim **1993**; (c) V. Jonas, G. Frenking, M. T. Reetz, *J. Am. Chem. Soc.* **1994**, *116*, 8741; (d) A. Y. Timoshkin, G. Frenking, *Organometallics* **2008**, *27*, 371.
- [14] Cambridge Structural Database V5.38 (update May 2017); see also: F. H. Allen, *Acta Crystallogr. B* **2002**, *58*, 380. 422 hits on Ph₃As-TM adducts and 201 hits on Ph₃Sb-TM adducts, coordination number of As/Sb restricted to 4, any transition metal (TM) atom, TM-As/Sb bond defined as type "single bond".
- [15] a) M. J. Heeg, M. Kudrat, C. H. Winter, CCDC 781778: Experimental Crystal Structure Determination, **2010**, DOI: 10.5517/ccv7hn6; (b) C. Jones, C. Schulten, A. Stasch, *Main Group Metal Chem.* **2005**, *28*, 89.
- [16] Dance, I. & Scudder, M. *J. Chem. Soc., Chem. Commun.*, **1995**, -, 1039-1040
- [17] P. Pykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186.
- [18] Cambridge Structural Database V5.38 (update May 2017); see also: F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *B58*, 380. 15 hits on X₃As-GaX₃ adducts (X = H, C, Si, halogen) and 201 hits on Ph₃Sb-TM adducts, coordination number of Ga/As/Sb restricted to 4 and Ga-As/Sb bond defined as type "single bond".
- [19] B. Ziemer, A. Rabis, H.-U. Steinberger, *Acta Cryst.* **2000**, *C56*, e58–e59.
- [20] a) A. N. Sobolev, V. K. Belsky, N. Yu. Chernikova, F. Yu. Akhmadulina, *J. Organomet. Chem.* **1983**, *244*, 129; (b) M.-U.-Haque, H. A. Tayim, J. Ahmed, W. Horne, *J. Crystallogr. Spectrosc. Res.* **1985**, *15*, 561.

- [21] a) V. Sharutin, N. Somov, CCDC 1026101: *Experimental Crystal Structure Determination* **2017**, DOI: 10.5517/ccdc.csd.cc13fr1b; b) E. A. Adams, J. W. Kolis, W. T. Pennington, *Acta Crystallogr. C* **1990**, *46*, 917.
- [22] F. Cheng, H. L. Codgbrook, A. L. Hector, W. Levason, G. Reid, M. Webster, W. Zhang, *Polyhedron* **2007**, *26*, 4147.
- [23] a) L.-J. Baker, L.A. Kloo, C.E.F. Rickard, M.J. Taylor, *J. Organometal. Chem.* **1997**, *545–546*, 249; b) M.A. Brown, J.A. Castro, D.G. Tuck, *Can. J. Chem.* **1997**, *75*, 333.
- [24] E. Conrad, J. Pickup, N. R. Burford, R. McDonald, M. J. Ferguson, *Can. J. Chem.* **2010**, *88*, 797.
- [25] H.-U. Schwering, E. Jungk, J. Weidlein, *J. Organomet. Chem.* **1975**, *91*, C4.
- [26] G. M. Sheldrick, *Acta Crystallogr. A* **1990**, *46*, 467.
- [27] a) G. M. Sheldrick, SHELXL-2014, Program for the Refinement of Crystal Structures University of Göttingen, Göttingen (Germany) 2014. See also: b) G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112; c) shelXle, *A Qt GUI for SHELXL*, C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281.
- [28] F. Neese, Wiley Interdisc. Rev. Comp. Mol. Sci. **2012**, *2*, 73.
- [29] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- [30] a) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456; b) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [31] F. Neese, K. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2009**, *356*, 98.
- [32] B. Metz, H. Stoll, M. Dolg, *J. Chem. Phys.* **2000**, *113*, 2563.
- [33] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013); <http://nbo6.chem.wisc.edu>.

Scheme and Figure Captions

Scheme 1. Synthesis of **1** - **3**.

Figure 1. Temperature dependence of the equilibrium constant (P = black, As = red, Sb = blue).

Figure 2. Solid state structure of **1** (thermal ellipsoids are shown at 50% probability levels); H atoms and solvent molecule are omitted for clarity. The asymmetric unit is labeled and displayed in dark colors.

Figure 3. Solid state structure of **2** (thermal ellipsoids are shown at 50% probability levels); H atoms and solvent molecule are omitted for clarity. The asymmetric unit is labeled and displayed in dark colors.

Figure 4. Solid state structure of **3** (thermal ellipsoids are shown at 50% probability levels); H atoms and solvent molecule are omitted for clarity. The asymmetric unit is labeled and displayed in dark colors.

Figure 5. Highest occupied (HOMO-2, HOMO) and lowest unoccupied orbitals (LUMO) in **1** (top), **2** (middle) and **3** (bottom).

Table 1: Temperature-Dependent ^1H -NMR Chemical Shift and Thermodynamic Data of the *t*-Bu₃Ga–EPh₃ Adducts (E = P **1**, As **2**, Sb **3**) in Toluene-*d*₈.

Ph₃P–Ga'Bu₃ 1					
T [K]	1/T [10 ⁻³ K ⁻¹]	δ _{sample} [ppm]	χ _{free}	K _{eq}	ln K
273	3.66	1.25	0.74	0.085	-2.47
243	4.12	1.42	0.29	4.46·10 ⁻³	-5.41
213	4.69	1.53	0.10	4.44·10 ⁻⁴	-7.71
δ _{coord}	δ _{free}	conc.	ΔH [kcal/mol]	ΔS [cal/(K·mol)]	
1.53	1.15	0.04	10.3	32.9	

Ph₃As–Ga'Bu₃ 2					
T [K]	1/T [10 ⁻³ K ⁻¹]	δ _{sample} [ppm]	χ _{free}	K _{eq}	ln K
273	3.66	1.20	0.85	0.198	-1.62
243	4.12	1.35	0.47	0.016	-4.12
213	4.69	1.49	0.08	2.64·10 ⁻⁴	-8.24
δ _{coord}	δ _{free}	conc.	ΔH [kcal/mol]	ΔS [cal/(K*mol)]	
1.52	1.15	0.04	13.2	45.7	

Ph₃Sb–Ga'Bu₃ 3					
T [K]	1/T [10 ⁻³ K ⁻¹]	δ _{sample} [ppm]	χ _{free}	K _{eq}	ln K
273	3.66	1.27	0.66	0.052	-2.95
243	4.12	1.41	0.28	4.25·10 ⁻³	-5.46
213	4.69	1.50	0.036	5.26·10 ⁻⁴	-9.85
δ _{coord}	δ _{free}	conc.	ΔH [kcal/mol]	ΔS [cal/(K*mol)]	
1.51	1.15	0.04	13.8	35.5	

Table 2: Bond distances [Å] and angles [°] of *t*-Bu₃Ga–EPh₃ (**1** - **3**), *t*-Bu₃Ga^[11a,c] and Ph₃E (E = As, Sb). Theoretical (average) values (B3LYP/def2-TZVPP) are given in square brackets.

	1	2	3	<i>t</i>-Bu₃Ga*	Ph₃P^{[19]#}	Ph₃As^{[15]#}	Ph₃Sb^{[16]§}
Ga–E	2.7126(5), [2.687]	2.8513(3), [2.826]	2.9337(2), [2.957]	—	—	—	—
av. Ga–C	2.0451(17), 2.0489(16), 2.0633(16), [2.070]	2.0351(9), [2.059]	2.0333(10), [2.055]	2.018, ^[11a] 2.008, ^[11c] [2.044]	—	—	—
av. E–C	1.8233(14), 1.8249(14), 1.8285(14), [1.830]	1.9554(9), [1.956]	2.1410(9), [2.148]	—	1.828-1.834, [1.841]	1.957, ^[15a] 1.943-1.957, ^[15b] [1.968]	2.156, ^[16a] 2.155, ^[16b] [2.163]
C–Ga–C	116.05(7), 114.53(7), 114.25(7), [115.03]	116.266(17), [116.22]	116.968(15), [117.13]	119.9, ^{[11a]*} 120.0, ^[11c] [119.95]	—	—	—
C–E–C	102.62(6), 103.14(6), 103.37(6), [103.36]	99.78(3), [101.01]	98.10(3), [98.44]	—	101.8-102.4, [101.05]	100.1, ^[15a] 99.6(4)- 100.5(5) ^[15b] , [98.94]	96.1, ^[16a] 96.2, ^[16b] [96.11]
E–Ga–C	102.30(5), 103.76(5), 103.57(5), [103.08]	101.29(3), [101.37]	100.14(3), [99.85]	—	—	—	—
C–E–Ga	115.09(4), 115.88(4), 114.99(5), [115.05]	117.98(3), [116.99]	119.29(2), [119.00]	—	—	—	—
ΣC–Ga–C	346.0, [346.00]	348.7, [348.6]	350.9, [351.4]	359.5, ^{[11a]*} 360.0, ^[11c] [359.8]	—	—	—

$\Sigma C-E-C$	309.6, [310.07]	299.3, [303.0]	294.3, [295.3]	—	305.5-307.3, [303.15]	300.3, ^[15a] 298.0-301.4 ^[15b] , [296.8]	288.3, ^[16a] 288.7, ^[16b] [288.3]
$C-E-Ga-C$	-24.12(7), - 24.47(7), - 24.55(7), [- 24.47]	-33.06(4), [- 24.26]	-36.43(4), [- 22.70]	—	—	—	—

*Contains six independent molecules in the asymmetric unit with weak intermolecular $Ga \cdots H$ interactions between *t*-Bu₃Ga molecules. The gas phase structure of *t*-Bu₃Ga shows an ideal trigonal-planar coordinated Ga atom (Ga–C 2.034(2) Å; C–Ga–C 120°; D. W. H. Rankin, personal communication). #Contains four independent molecules in the asymmetric unit. §Contains two independent molecules in the asymmetric unit.

For Table of Contents Entry

Lewis acid-base adducts $\text{Ph}_3\text{E}-\text{Ga}(t\text{-Bu})_3$ (E = P **1**, As **2**, Sb **3**) were synthesized and the structural parameters of **1** - **3** are discussed and compared to similar $t\text{-Bu}_3\text{Ga}$ adducts of the desired type. The strength of the donor-acceptor interactions was investigated in solution by temperature-dependent ^1H NMR spectroscopy and by quantum chemical calculations.

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