Synthesis and solid state structures of a Ga-substituted distibene and the first Sb-analogue bicyclo[1,1,0]butane.

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Dedicated to Prof. M. Scheer on the occasion of his 60th birthday.

Abstract: RGa {R = HC[C(Me)N(2,6-*i*-Pr₂C₆H₃)]₂} reacts with Sb(NMe₂)₃ with insertion into the Sb-N bond and elimination of RGa(NMe₂)₂ **2**, yielding the Ga-substituted distibene R(Me₂N)GaSb=SbGa(NMe₂)R **1**. Thermolysis of **1** proceeded with elimination of RGa and **2** and subsequent formation of the bicyclo[1,1,0]butane analogue [R(Me₂N)Ga]₂Sb₄ **3**.

Mono-valent group 13 compounds [RM]_x (M = Al, Ga, In, Tl) and metalloid clusters [R_xM_y] (x < y) have been intensely studied over the last decades.^[1] Early studies focused on the structural characterization of these fascinating compounds including giant Al₇₇ and Ga₈₄ clusters or an unusual In₆ chain,^[2] while their chemical reactivity has been investigated in recent years.^[3] Cp^{*}M^[4] and RM (R = HC[C(Me)N(2,6-*i*-Pr₂C₆H₃)]₂,^[5] M = Al, Ga, In) were found to react with unsaturated organic functional groups such as olefins and azides, small molecules such as O₂, S₈, P₄ and others as well as with Lewis acidic main group metal and late transition metal complexes.^[6–8] The redox activity of mono-valent group 13 diyls RM plays a crucial role in small molecule activation and in reactions with main group metal compounds. Insertion reactions were observed with GaX₃ (X = Cl, Me),^[9] Me₃PbCl, Pb(OSO₂CF₃)₂ and Hg(SC₆F₅)₂,^[10] while intermetallic clusters [Sn₇{Ga(Cl)(R)}₂] and [Sn₁₇{Ga(Cl)(R)}₄] were formed in reactions with SnCl₂.^[11] Reactions of RGa with Bi(OR)₃ occurred with reduction of the Bi atoms and formation of dibismuthenes [RGa(OR')Bi]₂ (R' = C₆F₅, SO₂CF₃),^[12] and reactions of base-stabilized GeCl₂ with RGa and RGa/KC₈ yielded Ge₂(GaR)₂ and Ge₄(GaR)₂, respectively.^[13] These reactions illustrate the promising potential of RGa to serve as selective reducing agent for the synthesis of intermetallic compounds, but the reaction mechanism and the factors, which determine if simple insertion or more complex reduction reactions occur, are not fully understood.

Due to our general interest in the chemistry of group 13 diyls RM (M = Al, Ga, In) we studied reactions of RGa with Et₃Bi,^[14a] Et₄E₂ (E = Sb, Bi),^[14b] *i*-Pr₂Te and Ph₂Te₂,^[15] which proceeded with insertion of RM into the Bi-C, E-E, Te-C and Te-Te bond, respectively. We now report on reactions of RGa with EX₃ [E = Sb, Bi; X = Et, NMe₂] and solid state structures of R(Me₂N)GaSb=SbGa(NMe₂)R **1**, a Ga-stabilized distibene with a Sb=Sb double bond, and the first Sb analogue of bicyclo[1,1,0]butane, [R(Me₂N)Ga]₂Sb₄ **3**, with a butterfly-type Sb₄ unit.

RGa was reacted in different molar ratios (1:1, 2:1) at different temperatures (25 °C - 110 °C) with Et₃Sb, but in contrast to the insertion reaction with BiEt₃, which proceeded at 80 °C with formation of R(Et)GaBiEt₂, and with Et₄E₂, yielding RGa(EEt₂)₂ at ambient temperature,^[14] no reaction was observed. SbEt₃ is less reactive than Et₃Bi due to the somewhat stronger Sb-C bond and the reduction potential of RGa is too low. It should be noted, that the reaction of Sb(*n*-Bu)₃ with the stronger reducing agent Cp^{*}₂Sm gave the [Cp^{*}₂Sm]₃(μ-η²:η²:η¹-Sb₃) containing a Zintl-type Sb₃³⁻ anion.^[16] We therefore reacted RGa with Sb(NMe₂)₃ containing weaker Sb-N bonds in a 2:1 molar ratio at 75 °C, yielding R(Me₂N)GaSb=SbGa(NMe₂)R **1** and RGa(NMe₂)₂ **2** in good yields (Scheme 1). The insertion into the Sb-N bond occurred even at room temperature, but a month is needed for the formation of reasonable amounts of **1** and **2**.

Scheme 1. Synthesis of **1** and **2**.

1 readily decomposes under aerobic conditions but is stable in solution and in the solid state at ambient temperature under argon atmosphere. **1** is slightly soluble in benzene and toluene at ambient temperature, but dissolves well upon heating. The ¹H NMR spectrum of **1** shows two singlets (3.09, 2.67 ppm) for the NMe₂ group and two septets (3.62, 2.90 ppm) and four doublets (1.35, 1.29, 1.02, 1.00 ppm) for the magnetically inequivalent *i*-Pr groups of the β-diketimate ligand, while the γ-CH and two methyl groups of the C₃N₂M ring are in the non-crystallographic mirror plane and exhibit only single resonances (4.75, 1.61 ppm).

The reaction of RGa with Bi(NMe₂)₃ differs significantly from those of Sb(NMe₂)₃ and BiEt₃. While the reaction with BiEt₃ gave the insertion product R(Et)GaBiEt₂ at 80 °C, the reaction with Bi(NMe₂)₃ gave Bi metal and **2** already at ambient temperature. At low temperatures (-80 °C), the reaction progress is visible by a gradual color change of the solution from orange to dark red. Monitoring the reaction by *in situ* ¹H NMR spectroscopy gave a few peaks at -80 °C, which could not be assigned to any known species. These peaks diminished with increasing temperature and only the peaks for **2** and Bi(NMe₂)₃ were observed above -30 °C (Figure S9). Even though no reaction intermediate could be isolated, we speculate that the reaction mechanism is identical to that observed with BiEt₃. However, the initially formed insertion product R(NMe₂)GaBi(NMe₂)₂ is less stable toward disproportionation into RGa(NMe₂)₂ **2**, Bi(NMe₂)₃ (Figure S10) and Bi metal than its counterpart R(Et)GaBiEt₂. The

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formation of **2** was independently verified in both reactions of RGa with E(NMe₂)₃ [E = Sb, Bi] and **2** was fully characterized by ¹H, ¹³C NMR, IR spectroscopy and single crystal X-ray diffraction.

Single crystals of **1** and **2** were obtained from a saturated toluene solution at ambient temperature (**1**) and at -30 °C (**2**) after storage for 24h. **1** crystallizes in the triclinic space group *P*-1 and **2** in the monoclinic space group *P*2₁/*n*.^[17]

Figure 1. Molecular structure of [R(Me₂N)GaSb=SbGa(NMe₂)R] **1**. H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level. Non-labeled part was generated by inversion. Selected bond lengths and angles in Å and °: Sb1-Sb2 2.6477(4), Ga1-Sb1 2.6200(4), Ga1-N1 1.9894(13), Ga1-N2 1.9826(13), Ga1-N3 1.8558(13), Ga1-Sb1-Sb2 94.71(1), N1-Ga1-N2 93.16(5), N1-Ga1-N3 107.79(6), N2-Ga1-N3 106.27(6), N1-Ga1-Sb1 112.66(4), N2-Ga1-Sb1 117.88(4), N3-Ga1-Sb1 116.37(4).

The structure of **1** consists of a centrosymmetric distibene (Sb₂) unit substituted by two R(NMe₂)Ga moieties, resulting in a *trans*-bent orientation of the almost planar Ga-Sb=Sb-Ga unit (Figure 1). The Ga atoms adopt distorted tetrahedral coordination spheres. The Sb-Sb bond length (2.6477(4) Å) is shorter compared to those reported for Sb-Sb single bonds in distibenes L₂Sb-SbL₂,^[18] but comparable to that of distibenes ArSb=SbAr (Ar = 2,4,6-[CH(SiMe₃)₂]₃C₆H₂, 2.642(1) Å;^[19a] C₆H₃-2,6-Trip₂, 2.668(2) Å;^[19b] C₆H₃-2,6-Mes₂, 2.6558(5) Å;^[19b] 1,2-bis(ferrocenyl), 2.6700(7) Å;^[19c] 2,6-[CH(SiMe₃)₂]₂-4-[C(SiMe₃)₃]-C₆H₂, 2.7037(6) Å;^[19d]). The Sb-Sb-Ga bond angle (94.71(1)°) agrees well with the Sb-Sb-H angle calculated for HSb=SbH (93.0°)^[20] and values reported for ArSb=SbAr.^[19] The Ga atom in C₃N₂Ga ring is out of plane (deviation from best plane of the ligand backbone 0.6468(17) Å) and the Ga-Sb bond distance of 2.6200(4) is comparable to the sum of the covalent radii (Ga = 1.24 Å; Sb = 1.40 Å)^[21] and values reported for Ga-Sb σ-bonded compounds such as [Me₂GaSbR'₂]₃ (R' = SiMe₃, 2.6773(5)-2.7144(5) Å;^[22a] Me, 2.666(1)-2.682(1) Å;^[22b] *i*-Pr, 2.669(1)-2.694(1) Å;^[22b]) and [(dmap)Et₂GaSb(SiMe₃)₂] (2.648(1) Å; dmap = 4-dimethylamino pyridine).^[23] The structure of **2** (Fig. S12, ESI) is similar to that of RGa(NH₂)₂.^[24] The Ga atom adopts a distorted tetrahedral geometry and the Ga(1)-N(1)/(N2) bond

lengths (1.9719(10), 1.9731(10) Å) are longer than the Ga-NMe₂ bonds (Ga(1)-N(3), 1.8531(11) Å; Ga(1)-N(4), 1.8668(11) Å).

Scheme 2. Synthesis of **3**.

1 was heated in toluene-*d*₈ for 24 hours at 120 °C to investigate its thermal stability and the reaction progress was investigated by *in situ* NMR spectroscopy. The ¹H NMR spectra showed steadily decreasing resonances of **1**, while resonances due to the formation of RGa, **2** and [R(Me₂N)Ga]₂Sb₄ **3** in 1:1:2 integral ratio appeared (Figure S11), possibly via formation of digallane R(NMe₂)Ga-Ga(NMe₂)R, which disproportionates into RGa and **2** (Scheme 2).²⁵ As was observed for **1**, the ¹H NMR spectrum of **3** shows two singlets (2.80, 2.70 ppm) for the NMe₂ group, two septets (3.35, 3.15 ppm) and four doublets (1.44, 1.33, 1.23, 1.05 ppm) for the magnetically inequivalent *i*-Pr groups as well as single resonances (4.64, 1.50 ppm) of the γ-CH and both methyl groups of the β-diketiminato ligand. The formation of insoluble (metallic) material was not observed under these harsh conditions. Storage of the solution at 0 °C for 12 h gave orange crystals of [R(Me₂N)Ga]₂Sb₄ **3**.¹⁷

Figure 2. Molecular structure of [R(Me₂N)Ga]₂Sb₄ **3**. H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 20% probability level. Non-labeled part was generated by mirror symmetry #1: x, -y+1/2, z. Selected bond lengths and angles in Å and °: Sb(1)-Ga(1) 2.5975(5), Sb(1)-Sb(3) 2.8139(4), Sb(1)-Sb(2) 2.8298(4), Sb(2)-Sb(3) 2.7920(5), Ga(1)-N(1) 1.985(3), Ga(1)-N(2) 1.989(3), Ga(1)-N(3) 1.851(3), Ga(1)-Sb(1)-Sb(3) 105.770(14), Ga(1)-Sb(1)-Sb(2) 101.704(14), Sb(3)-Sb(1)-Sb(2) 59.300(13), Sb(3)-Sb(2)-Sb(1) 60.065(11), Sb(3)-Sb(2)-Sb(1)a 60.065(11), Sb(1)-Sb(2)-Sb(1)a 75.084(14), Sb(2)-Sb(3)-Sb(1) 60.635(11), Sb(2)-Sb(3)-Sb(1)a 60.636(11), Sb(1)-Sb(3)-Sb(1)a 75.585(14), N(3)-Ga(1)-N(1) 109.95(15), N(3)-Ga(1)-N(2) 105.60(14), N(1)-Ga(1)-N(2) 93.05(13), N(3)-Ga(1)-Sb(1) 124.64(11), N(1)-Ga(1)-Sb(1) 104.49(10), N(2)-Ga(1)-Sb(1) 114.49(9).

3 crystallizes in the monoclinic space group $P2_1/m$.^[17] Its central structural motif is the butterfly-shaped Sb_4 unit, which is substituted by two $Ga(NMe_2)R$ ligands (Figure 2). The Sb-Sb bond lengths (2.7920(5) - 2.8298(4) Å) are significantly elongated compared to that in **1** but comparable to values reported for Sb-Sb single bonds in distibines R_4Sb_2 ^[18] and cyclostibines $(RSb)_x$.^[26] Unfortunately, structural data of the Sb_4 cluster, which is the most stable species in the gas phase up to 1050 K,^[27] are not available since Sb_4 is thermodynamically unstable toward formation of amorphous Sb in the solid state. However, Sb_4 clusters were discovered by STM in vapor phase deposited Sb thin films^[28] and the Sb-Sb bond length (2.87 Å) in the Sb_4 tetrahedron was determined by high level CI calculations,^[29] which is slightly elongated compared to values observed in **3**. The Ga-Sb bond length in **3** (2.5975(5) Å) is slightly shorter than in **1** (2.6200(4) Å), while the structure parameters of the R ligand are almost identical to those observed for **1** and **2**, respectively.

Neutral group 15 analogues (P_4 , As_4) of bicyclo[1,1,0]butane are well known since the first synthesis of $[(Me_3Si)_2N]_2P_4$ and Mes_2P_4 ,^[30,31] which was formed together with diphosphene Mes_2P_2 in the reaction of $MesLi$ with P_4 , and are typically synthesized by activation reactions of elemental P_4 and As_4 with main group and transition metal complexes.^[32] In addition, complexes with intact P_4 and As_4 ligands were recently reported.^[33] In contrast, analogous Sb_4 complexes are unknown, to date, while several neutral cyclotetrasibines R_4Sb_4 ^[34] and compounds containing the planar $[Sb_4]^{2-}$ dianion were structurally characterized.^[35] Weigand et al. recently thermolyzed $[(Me_3P)_4Sb_4]^{4+}$ and speculated on the formation of a $[(Me_3P)_2Sb_4]^{2+}$ intermediate.^[36] Analogous dicationic compounds of the lighter homologues P and As such as $[(Ph_3E)_2P_4]^{2+}$ ($E = P, As$) and the bicyclic phosphinophosphonium monocationic $[Mes^*_2P_4Cl]^+$ as well as the Lewis acid-stabilized version of the RP_4 anion have also recently been structurally characterized.^[37-39] $[(Me_3P)_4Sb_4]^{4+}$ was initially formed by thermolysis reaction of $[Sb(PMe_3)_3]^{3+}$ via reductive elimination of $[Me_3PPMe_3]^{2+}$ and generation of $[Sb(PMe_3)]^+$, which stepwise dimerizes to $[(Me_3P)_2Sb_2]^{2+}$ and finally $[(Me_3P)_4Sb_4]^{4+}$.^[40] To the best of our knowledge, $Mes^*_2P_2Sb_2$ is the only structurally characterized Sb-containing bicyclo[1,1,0]butane derivative.^[41] It was formed by reaction of Cp^*SbCl_2 with $Mes^*P(SiMe_3)Li$, eventually through formation of stibaphosphene $Cp^*Sb=PMe^*$ as reaction intermediate, which undergoes Cp^*-Sb bond cleavage and formation of a radical, which further reacts under Sb-Sb bond formation. The Sb-Sb bond length of $Mes^*_2P_2Sb_2$ (2.723(1) Å), which in contrast to **3** adopts a *exo/endo* form, is shorter compared to that observed in **3** (2.7920(5) Å), while the fold angle (103.2°) is significantly larger than that in **3** (89.359(10)°). It should be mentioned that the attempted synthesis of an NHC stabilized Sb_4 complex by reduction of an NHC- $SbCl_3$ adduct failed,^[42] which clearly illustrates the high synthetic potential of the insertion-reduction method using monovalent RGa compared to the widely established coordination-reduction approach by use of NHCs.

In summary, the first Sb analogue of bicyclo[1,1,0]butane, $[R(Me_2N)Ga]_2Sb_4$ **3**, was obtained in a controlled reaction in

good yield by thermal treatment of the distibene $R(Me_2N)GaSb=SbGa(NMe_2)R$ **1**, which was synthesized by reaction of RGa with $Sb(NMe_2)_3$ containing rather weak Sb-N bonds. The general applicability of the proposed reaction mechanism for the formation of other main group metalloid clusters as well as initial studies on the chemical reactivity of both **1** and **3** are currently under investigation.

Experimental Section

¹H and ¹³C NMR and IR spectra of **1** - **3** as well as crystallographic data for **1** - **3** are given in the electronic supplement. High-resolution mass spectra of **1** - **3** could not be recorded due to the lack of suitable instrumentation.

Synthesis of $R(Me_2N)GaSb=SbGa(NMe_2)R$ (1**) and $RGa(NMe_2)_2$ (**2**).** A solution of RGa (51 mg, 0.104 mmol) and $Sb(NMe_2)_3$ (13.2 mg, 10 μ L, 0.052 mmol) in 0.5 mL of toluene was heated at 75 °C for 24 h. Analytically-pure deep red crystals of **1**, which were obtained after storage for 24 h at ambient temperature, were isolated by filtration. The mother liquid was dried and the resulting red solid was washed with warm (50 °C) hexane to remove **2**, yielding an additional amount of pure **1** (**1** is insoluble in hexane). The hexane solution was concentrated and stored at -30 °C, yielding colorless crystals of **2** after 24 h.

1: M.p. 240 °C (dec.). Yield: 22 mg (64 %). Anal. Calcd. for $C_{62}H_{94}N_6Ga_2Sb_2$: C, 57.00; H, 7.25; N, 6.43. Found: C, 56.63; H, 7.32; N, 6.35 %. IR (neat): ν 2958, 2864, 2752, 1522, 1436, 1392, 1314, 1254, 1179, 1098, 1017, 969, 936, 857, 792, 756, 637, 542, 438 cm^{-1} . ¹H NMR (toluene- d_8 , 300 MHz, 25 °C): δ 7.07-6.86 (m, 6 H, $C_6H_5(Pr)_2$), 4.75 (s, 1 H, γ -CH), 3.62 (sept, $^3J_{HH} = 6.9$ Hz, 2 H, $CH(CH_3)_2$), 3.09 (s, 3 H, NMe_2), 2.90 (sept, $^3J_{HH} = 6.9$ Hz, 2 H, $CH(CH_3)_2$), 2.67 (s, 3 H, NMe_2), 1.61 (s, 6 H, $ArNCCH_3$), 1.35 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $CH(CH_3)_2$), 1.29 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $CH(CH_3)_2$), 1.02 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $CH(CH_3)_2$), 1.00 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $CH(CH_3)_2$). The low solubility of **1** prohibits its ¹³C NMR characterization.

2: M.p. 196 - 200 °C. Yield 20 mg (67 %). Anal. Calcd. for $C_{33}H_{53}N_4Ga$: C, 68.87; H, 9.28; N, 9.73. Found: C, 68.35; H, 9.22; N, 9.79 %. IR (neat): ν 2962, 2866, 2800, 2753, 1525, 1462, 1437, 1383, 1318, 1295, 1190, 1108, 978, 953, 864, 797, 760, 638, 558, 444 cm^{-1} . ¹H NMR (C_6D_6 , 300 MHz, 25 °C): δ 7.16 (s, 6 H, $C_6H_5(Pr)_2$), 4.71 (s, 1 H, γ -CH), 3.52 (sept, $^3J_{HH} = 6.9$ Hz, 2 H, $CH(CH_3)_2$), 3.47 (sept, $^3J_{HH} = 6.9$ Hz, 2 H, $CH(CH_3)_2$), 2.92 (s, 3 H, NMe_2), 2.79 (s, 3 H, NMe_2), 2.22 (s, 6 H, NMe_2), 1.55 (s, 6 H, $ArNCCH_3$), 1.42 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $CH(CH_3)_2$), 1.41 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $CH(CH_3)_2$), 1.30 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $CH(CH_3)_2$), 1.15 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $CH(CH_3)_2$). ¹³C NMR (C_6D_6 , 75.5 MHz, 25 °C): δ 169.3 ($ArNCCH_3$), 144.8 ($Ar-C$), 144.1 ($Ar-C$), 142.8 ($Ar-C$), 127.2 ($Ar-C$), 124.7 ($Ar-C$), 124.2 ($Ar-C$), 96.2 (γ -CH), 43.9 ($N(CH_3)_2$), 43.6 ($N(CH_3)_2$), 43.2 ($N(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 25.5 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 24.8 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$), 23.5 ($ArNCCH_3$).

Synthesis of $R(Me_2N)Ga]_2Sb_4$ (3**).** A solution of **1** (25 mg, 0.0191 mmol) in 0.5 mL of toluene- d_8 was heated for 24 hours at 120 °C. After cooling to room temperature, the solvents were removed and the residue was redissolved in 0.5 mL of hexane. **3** was obtained as orange crystals after storage for 24 h at ambient temperature. M.p. 200 - 208 °C (dec.). Yield 12.4 mg (84 %). Anal. Calcd. for $C_{62}H_{94}N_6Ga_2Sb_4$: C, 48.05; H, 6.11; N, 5.42. Found: C, 47.85; H, 6.17; N, 5.63 %. IR (neat): ν 2961, 2925, 2865, 2751, 1547, 1520, 1460, 1436, 1394, 1316, 1259, 1167, 1089, 1014, 965, 937, 856, 791, 758, 706, 544 cm^{-1} . ¹H NMR (toluene- d_8 , 300 MHz, 25 °C): δ 7.26-7.12 (m, 6 H, $C_6H_5(Pr)_2$), 4.64 (s, 1 H, γ -CH), 3.35 (sept,

$^3J_{HH} = 6.9$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$, 3.15 (sept, $^3J_{HH} = 6.9$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$, 2.80 (s, 3 H, NMe_2), 2.70 (s, 3 H, NMe_2), 1.50 (s, 6 H, ArNCCH_3), 1.44 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.34 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.23 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.06 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (toluene- d_6 , 75.5 MHz, 25 °C): δ 168.1 (ArNCCH_3), 145.3 (Ar-C), 143.3 (Ar-C), 143.1 (Ar-C), 127.5 (Ar-C), 125.8 (Ar-C), 124.7 (Ar-C), 97.0 (γ -CH), 46.9 ($\text{N}(\text{CH}_3)_2$), 44.7 ($\text{N}(\text{CH}_3)_2$), 44.6 ($\text{N}(\text{CH}_3)_2$), 29.5 ($\text{CH}(\text{CH}_3)_2$), 28.0 ($\text{CH}(\text{CH}_3)_2$), 26.2 ($\text{CH}(\text{CH}_3)_2$), 25.6 ($\text{CH}(\text{CH}_3)_2$), 25.2 ($\text{CH}(\text{CH}_3)_2$), 24.8 ($\text{CH}(\text{CH}_3)_2$), 23.9 (ArNCCH_3).

Acknowledgements

S. Schulz gratefully acknowledges financial support by the University of Duisburg-Essen.

Keywords: Main group elements • Metal-metal interactions • Multiple Bonding • Group 13 elements

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- final difference Fourier synthesis $0.989 \text{ e} \cdot \text{\AA}^{-3} / -0.504 \text{ e} \cdot \text{\AA}^{-3}$; max./min. transmission 0.63/0.75; $R_1 = 0.0267$ ($I > 2\sigma(I)$), $wR_2 = 0.0659$ (all data).
- 2:** $[\text{C}_{33}\text{H}_{53}\text{GaNa}]$, $M = 575.51$, colourless crystal, $(0.420 \times 0.370 \times 0.330 \text{ mm})$; monoclinic, space group $P2_1/n$; $a = 8.9066(3) \text{ \AA}$, $b = 21.1155(7) \text{ \AA}$, $c = 17.7985(6) \text{ \AA}$; $\alpha = 90^\circ$, $\beta = 104.4130(10)^\circ$, $\gamma = 90^\circ$, $V = 3241.96(19) \text{ \AA}^3$; $Z = 4$; $\mu = 0.875 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.179 \text{ g} \cdot \text{cm}^{-3}$; 79665 reflexes ($\theta_{\text{max}} = 28.812^\circ$), 8407 unique ($R_{\text{int}} = 0.0261$); 357 parameters; largest max./min in the final difference Fourier synthesis $0.680 \text{ e} \cdot \text{\AA}^{-3} / -0.445 \text{ e} \cdot \text{\AA}^{-3}$; max./min. transmission 0.64/0.75; $R_1 = 0.0278$ ($I > 2\sigma(I)$), $wR_2 = 0.0735$ (all data).
- 3:** $[\text{C}_{68}\text{H}_{108}\text{Ga}_2\text{N}_6\text{Sb}_4]$, $M = 1636.04$, pale orange crystal, $(0.135 \times 0.102 \times 0.068 \text{ mm})$; monoclinic, space group $P2_1/m$; $a = 10.6160(5) \text{ \AA}$, $b = 30.1197(14) \text{ \AA}$, $c = 11.9994(6) \text{ \AA}$; $\alpha = 90^\circ$, $\beta = 108.513(2)^\circ$, $\gamma = 90^\circ$, $V = 3638.3(3) \text{ \AA}^3$; $Z = 2$; $\mu = 2.234 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.493 \text{ g} \cdot \text{cm}^{-3}$; 37799 reflexes ($\theta_{\text{max}} = 30.543^\circ$), 10874 unique ($R_{\text{int}} = 0.0242$); 405 parameters; largest max./min in the final difference Fourier synthesis $3.766 \text{ e} \cdot \text{\AA}^{-3} / -1.422 \text{ e} \cdot \text{\AA}^{-3}$; max./min. transmission 0.62/0.75; $R_1 = 0.0464$ ($I > 2\sigma(I)$), $wR_2 = 0.1093$ (all data). The ADPs of the hexane molecule suggest disorder which could not be modeled satisfactorily. RIGU and SADI restraints were applied to improve the model. The crystallographic data (without structure factors) were deposited as „supplementary publication no. CCDC-1054882 (1), CCDC-1054883 (2) and CCDC-1054884 (3)“ at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).
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Entry for the Table of Contents

COMMUNICATION

Comparative studies on the reaction of RGa with EX_3 [$\text{E} = \text{Sb, Bi}$; $\text{X} = \text{Et, NMe}_2$] show the subtle influence of the organic substituents on the reactivity of the group 15 compound and on the stability of the initially formed insertion product R(X)GaEX_2 . The use of $\text{Sb(NMe}_2)_3$ containing rather weak Sb-N bonds resulted in the formation of a distibene **1**, which was thermally converted into **3**, the first Sb-analogue of bicyclo[1,1,0]butane.

*L. Tuscher, C. Ganesamoorthy, D. Bläser, C. Wölper and S. Schulz**

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Synthesis and solid state structures of a Ga-substituted distibene and the first Sb-analogue bicyclo[1,1,0]butane.

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DOI: 10.1002/anie.201502827

URN: urn:nbn:de:hbz:464-20201125-132736-0

This is the **peer reviewed version** of the following article: *Angew. Chem. Int. Ed.* 2015, 54,10657-10661, which has been published in final form at:
<https://doi.org/10.1002/anie.201502827>

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