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# A Gallium-Substituted Distibene and an Antimony-Analogue Bicyclo[1.1.0]butane: Synthesis and Solid-State Structures

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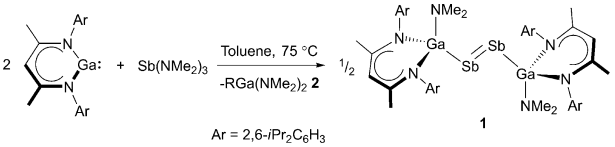
*Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday*

***Abstract:*** *RGa {R = HC[C(Me)N(2,6-iPr$_2$C$_6$H$_3$)]$_2$} reacts with Sb(NMe$_2$)$_3$ with insertion into the Sb–N bond and elimination of RGa(NMe$_2$)$_2$ (**2**), yielding the Ga-substituted distibene R(Me$_2$N)GaSb=SbGa(NMe$_2$)R (**1**). Thermolysis of **1** proceeded with elimination of RGa and **2** and subsequent formation of the bicyclo[1.1.0]butane analogue [R(Me$_2$N)Ga]$_2$Sb$_4$ (**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 $Al_{77}$ and $Ga_{84}$ clusters or an unusual $In_6$ 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*Pr$_2$C$_6$H$_3$)]$_2$;[5] M = Al, Ga, In) were found to react with unsaturated organic functional groups, such as olefins and azides, small molecules, such as $O_2$, $S_8$, $P_4$, 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 $GaX_3$ (X = Cl, Me),[9] $Me_3PbCl$, $Pb(OSO_2CF_3)_2$, and $Hg(SC_6F_5)_2$,[10] while intermetallic clusters $[Sn_7\{Ga(Cl)(R)\}_2]$ and $[Sn_{17}\{Ga(Cl)(R)\}_4]$ were formed in reactions with $SnCl_2$.[11] Reactions of RGa with Bi(OR″)$_3$ occurred with reduction of the Bi atoms and formation of dibismuthenes [RGa(OR″)Bi]$_2$ (R″ = C$_6$F$_5$, SO$_2$CF$_3$),[12] and reactions of base-stabilized $GeCl_2$ with RGa and RGa/$KC_8$ yielded $Ge_2(GaR)_2$ and $Ge_4(GaR)_2$, respectively.[13] These reactions illustrate the promising potential of RGa to serve as selective reducing agents 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.

Owing to our interest in the chemistry of Group 13 diyls RM (M = Al, Ga, In) we studied reactions of RGa with $Et_3Bi$,[14a] $Et_4E_2$ (E = Sb, Bi),[14b] *i*Pr$_2$Te, and $Ph_2Te_2$,[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 $EX_3$ (E = Sb, Bi; X = Et, NMe$_2$) and solid-state structures of R(Me$_2$N)GaSb=SbGa(NMe$_2$)R (**1**), a Ga-stabilized distibene with a Sb=Sb double bond, and the first Sb analogue of bicyclo[1.1.0]butane, [R(Me$_2$N)Ga]$_2$Sb$_4$ (**3**), with a butterfly-type $Sb_4$ unit.

RGa was treated in different molar ratios (1:1, 2:1) at different temperatures (25–110 °C) with $Et_3Sb$, but in contrast to the insertion reaction with $BiEt_3$, which proceeded at 80 °C with formation of R(Et)GaBiEt$_2$, and with $Et_4E_2$, yielding RGa(EEt$_2$)$_2$ at ambient temperature,[14] no reaction was observed. $SbEt_3$ is less reactive than $Et_3Bi$ owing 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*$_2$Sm gave the $[Cp^*_2Sm]_3(\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-}Sb_3)$ containing a Zintl-type $Sb_3^{3-}$ anion.[16] We therefore reacted RGa with Sb(NMe$_2$)$_3$ containing weaker Sb–N bonds in a 2:1 molar ratio at 75 °C, yielding R(Me$_2$N)GaSb=SbGa(NMe$_2$)R (**1**) and RGa(NMe$_2$)$_2$ (**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**.

Compound **1** readily decomposes under aerobic conditions but is stable in solution and in the solid state at ambient temperature under argon atmosphere. It is slightly soluble in benzene and toluene at ambient temperature, but dissolves well upon heating. The $^1$H NMR spectrum of **1** shows two singlets (δ = 3.09, 2.67 ppm) for the NMe$_2$ group and two septets (δ = 3.62, 2.90 ppm) and four doublets (δ = 1.35, 1.29, 1.02, 1.00 ppm) for the magnetically inequivalent *i*Pr groups of the β-diketiminate ligand, while the γ-CH and two methyl groups of the $C_3N_2M$ ring are in the non-crystallographic mirror plane and exhibit only singlets (δ = 4.75, 1.61 ppm).

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Supporting information for this article (experimental details including $^1$H and $^{13}$C NMR and IR spectra of **1**–**3** as well as crystallographic data for **1**–**3**. High-resolution mass spectra of **1**–**3** could not be recorded owing to the lack of suitable instrumentation) is available on the WWW under http://dx.doi.org/10.1002/anie.201502827.

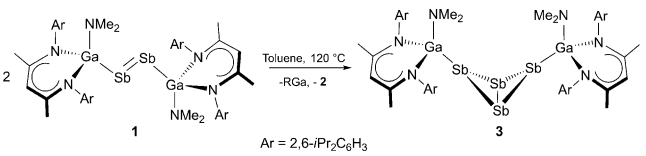
  

The reaction of RGa with $Bi(NMe_2)_3$ differs significantly from those of $Sb(NMe_2)_3$ and $BiEt_3$. While the reaction with $BiEt_3$ gave the insertion product $R(Et)GaBiEt_2$ at 80 °C, the reaction with $Bi(NMe_2)_3$ gave Bi metal and **2** even at ambient temperature. At low temperatures (−80 °C), the reaction progress is visible by a gradual color change of the solution from orange to dark red. Monitoring the reaction by in situ $^1$H NMR spectroscopy at −80 °C gave a few signals which could not be assigned to any known species. These signals diminished with increasing temperature and only the signals for **2** and $Bi(NMe_2)_3$ were observed above −30 °C (Figure S9 in the Supporting Information). Even though no reaction intermediate could be isolated, we speculate that the reaction mechanism is identical to that observed with $BiEt_3$. However, the initially formed insertion product $R(NMe_2)GaBi(NMe_2)_2$ is less stable toward disproportionation into $RGa(NMe_2)_2$ (**2**), $Bi(NMe_2)_3$ (Figure S10), and Bi metal than its counterpart $R(Et)GaBiEt_2$. The formation of **2** was independently verified in both reactions of RGa with $E(NMe_2)_3$ (E = Sb, Bi) and **2** was fully characterized by $^1$H, $^{13}$C 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 24 h. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ and **2** in the monoclinic space group $P2_1/n$.[17]

The structure of **1** consists of a centrosymmetric distibene ($Sb_2$) unit substituted by two $R(NMe_2)Ga$ moieties, resulting in a *trans*-bent orientation of the almost planar Ga-Sb=Sb-Ga unit (Figure 1). The Ga atoms have distorted tetrahedral coordination spheres. The Sb–Sb bond (2.6477(4) Å) is shorter than Sb–Sb single bonds in distibines $L_2Sb–SbL_2$,[18] but comparable to that of distibenes ArSb=SbAr (Ar = 2,4,6-$[CH(SiMe_3)_2]_3C_6H_2$, 2.642(1) Å;[19a] $C_6H_3$-2,6-$Trip_2$, 2.668(2) Å;[19b] $C_6H_3$-2,6-$Mes_2$, 2.6558(5) Å;[19b] 1,2-bis(ferrocenyl), 2.6700(7) Å;[19c] 2,6-$[CH(SiMe_3)_2]_2$-4-$[C(SiMe_3)_3]$-$C_6H_2$, 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 $C_3N_2Ga$ ring is out of plane (deviation from best plane of the ligand backbone 0.6468(17) Å) and the Ga–Sb bond length 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 $[Me_2GaSbR'_2]_3$ (R′ = $SiMe_3$, 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 $[(dmap)Et_2GaSb(SiMe_3)_2]$ (2.648(1) Å; dmap = 4-dimethylamino pyridine).[23] The structure of **2** (Figure S12) is similar to that of $RGa(NH_2)_2$.[24] The Ga atom adopts a distorted tetrahedral geometry and the Ga1–N1/N2 bonds (1.9719(10), 1.9731(10) Å) are longer than the Ga–$NMe_2$ bonds (Ga1–N3, 1.8531(11) Å; Ga1–N4, 1.8668(11) Å).

Compound **1** was heated in $[D_8]$toluene for 24 h at 120 °C to investigate its thermal stability and the reaction progress was investigated by in situ NMR spectroscopy. The $^1$H NMR spectra showed a steady decrease in the intensity of the resonances of **1**, while resonances arising from the formation of RGa, **2**, and $[R(Me_2N)Ga]_2Sb_4$ (**3**) in 1:1:2 integral ratio appeared (Figure S11), possibly via formation of digallane $R(NMe_2)Ga–Ga(NMe_2)R$, which disproportionates into RGa and **2** (Scheme 2).[25] As was observed for **1**, the $^1$H NMR spectrum of **3** shows two singlets (δ = 2.80, 2.70 ppm) for the $NMe_2$ group, two septets (δ = 3.35, 3.15 ppm), and four doublets (δ = 1.44, 1.33, 1.23, 1.05 ppm) for the magnetically inequivalent *i*Pr groups as well as singlets (δ = 4.64, 1.50 ppm) of the γ-CH and both methyl groups of the β-diketiminate 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 $[R(Me_2N)Ga]_2Sb_4$ **3**.[17]




***Scheme 2.*** Synthesis of **3**.

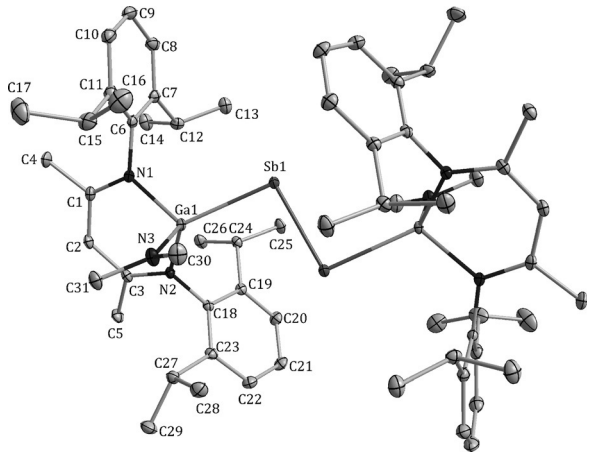



***Figure 1.*** Molecular structure of $R(Me_2N)GaSb=SbGa(NMe_2)R$ (**1**). H-atoms have been omitted for clarity and displacement ellipsoids are set at 30% probability. The non-labeled part was generated by inversion. Selected bond lengths [Å] and angles [°]: Sb1–Sb1a 2.6477(4), Ga1–Sb1 2.6200(4), Ga1–N1 1.9894(13), Ga1–N2 1.9826(13), Ga1–N3 1.8558(13); Ga1-Sb1-Sb1a 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).

Compound **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 bonds (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 because $Sb_4$ is thermodynamically unstable forming 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 in **3** (2.5975(5) Å) is

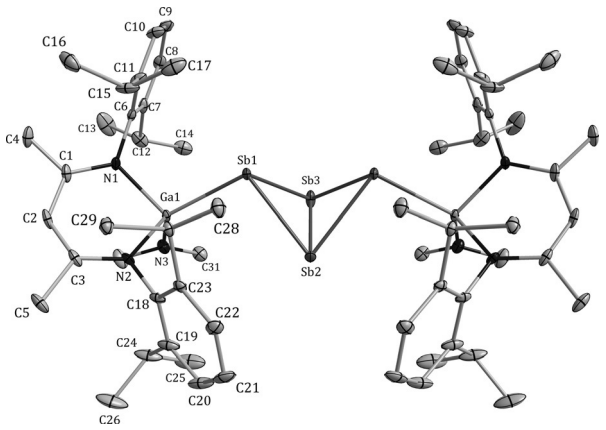



***Figure 2.*** Molecular structure of $[R(Me_2N)Ga]_2Sb_4$ (**3**). H-atoms have been omitted for clarity and displacement ellipsoids are set at 20% probability. The non-labeled part was generated by mirror symmetry #1: $x,-y+1/2,z$. Selected bond lengths [Å] and angles [°]: Sb1–Ga1 2.5975(5), Sb1–Sb3 2.8139(4), Sb1–Sb2 2.8298(4), Sb2–Sb3 2.7920(5), Ga1–N1 1.985(3), Ga1–N2 1.989(3), Ga1–N3 1.851(3); Ga1-Sb1-Sb3 105.770(14), Ga1-Sb1-Sb2 101.704(14), Sb3-Sb1-Sb2 59.300(13), Sb3-Sb2-Sb1 60.065(11), Sb3-Sb2-Sb1a 60.065(11), Sb1-Sb2-Sb1a 75.084(14), Sb2-Sb3-Sb1 60.635(11), Sb2-Sb3-Sb1a 60.636(11), Sb1-Sb3-Sb1a 75.585(14), N3-Ga1-N1 109.95(15), N3-Ga1-N2 105.60(14), N1-Ga1-N2 93.05(13), N3-Ga1-Sb1 124.64(11), N1-Ga1-Sb1 104.49(10), N2-Ga1-Sb1 114.49(9).

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**.

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 cyclotetrastibines $R_4Sb_4$[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 the 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 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 $Mes^*P(SiMe_3)Li$, through the formation of stibaphosphene Cp*Sb=PMes* as an 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 than that observed in **3** (2.7920(5) Å), while the fold angle (103.2°) is significantly larger than that in **3** (89.359(10)°). Note 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 under investigation.

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**Keywords:** Group 13 elements · main-group elements · metal–metal interactions · multiple bonding

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