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Gallium(III)/Antimony(III) C-Centered *Geminal* Organodimetallic Complexes

Philip C. Andrews* and Peter J. Nichols

Department of Chemistry, Monash University, Clayton, Melbourne, Victoria 3800, Australia

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The 1,2-addition of Me_3Ga in thf to the stiba-alkene species [2-Pyr$(SiMe_3)_2$CSb═C$(SiMe_3)$2-Pyr] results in the mixed Sb/Ga *geminal* C-centered organodimetallic complex {[2-Pyr$(SiMe_3)_2$]CSb(Me)C[2-Pyr$(SiMe_3)$]Ga$(Me)_2$} (Pyr = C_5H_4N), **2**, which on heating eliminates CH_4 to form a new Sb/Ga *geminal* organodimetallic complex adopting a structure with a distorted bicyclo[2.2.2]-type core, **3**. Both complexes have been structurally authenticated by single-crystal X-ray diffraction; **2** is isostructural with its Al analogue in forming a bimetallic six-membered heterocycle, while CH_4 elimination between the −$GaMe_2$ and Me_3Si− groups in **2** results in the heterocycle being bridged by a −Ga−CH_2−Si− unit and the formation of the new complex, **3**. Both complexes are chiral, with **2** being present as both diastereoisomers, *R*,*S* and *S*,*R* (space group $P2_1/n$), while **3** is found exclusively in the *R*,*R* configuration, space group $P2_12_12_1$. ^1H and ^{13}C NMR spectra confirmed the composition of the complexes and revealed that **2** could not be quantitatively converted into **3** without significant decomposition. They also reveal that the structure of **3** is rigid in solution.

Introduction

Geminal organodimetallic complexes with differing metals at the C center are of interest due to the potential they have to react either simultaneously or sequentially with selected electrophiles.[1] Being able to conduct two transformations at a single carbon center in a one-pot process is a highly desirable outcome if we wish to reduce the complexity, reagents, and wastes in any chemical process. Their development, therefore, has the potential to be a qualitative advance over traditional monofunctional organometallic reagents and processes. One of the main factors that determines both selectivity and reactivity is the nature of the metals and the M−C bonds; *geminal* organodilithium and diGrignard complexes, while highly reactive, offer no selectivity in their reaction with electrophiles. Therefore, it is mixed p-block and mixed s- and p-block complexes that will offer the broadest application. Kauffmann[1c] has previously demonstrated the facile synthesis of mixed Li/p-block complexes and their potential as reactive intermediates in synthetic applications, though they are restricted to the simple bis-metalated methane derivatives. Subsequently, Sato[2] extended the use of mixed Li/Sn complexes, while Knochel[1b] has reported a wide range of transformations utilizing mixed *geminal* Zn/Mg complexes. However, while these investigations[1] have established their usefulness in synthesis, there is very little solid-state structural information on mixed metal *geminal* organodimetallic complexes. Solid- and solution-state structural information is an important guide to understanding both selectivity and reactivity.

Our recent investigations into the carbometalation reactions of the stiba-alkene species [2-Pyr$(SiMe_3)_2$CSb═C$(SiMe_3)$2-Pyr] (Pyr = C_5H_4N) with metal alkyls has highlighted a degree of variability in both the solid-state products, C-centered *geminal* organodimetallic complexes, and the structures they adopt. The addition of both Me_3Al[3] and Et_3In[4] result in the expected 1,2-addition products. However, while the Sb/Al complex, **1a** (Figure 1), forms a dimetallic six-membered heterocycle, the In/Sb complex, **1b**, adopts a much more open structure, with In foregoing ring closure with N_{pyr} of the bis-trimethylsilylated ligand and forming instead a planar four-membered ring, via an In···N dative bond with the monosilylated pyridyl ligand to which it is directly bound. In the case of Et_2Zn, carbometalation does not occur and a tetrameric *geminal* dizinc complex, [2-Pyr$(SiMe_3)$CZn$]_4$, is formed via transmetalation.[5]

In continuing our investigations into the formation and solid-state analysis of mixed group 13/15 *geminal* complexes we now report the formation and structural characterization by single-crystal X-ray diffraction of the first two Ga(III)/Sb(III) C-centered organodimetallics: {[2-Pyr$(SiMe_3)_2$]CSb(Me)C[2-Pyr$(SiMe_3)$]Ga$(Me)_2$}, **2**, and the product formed on heating and subsequent intramolecular CH_4 elimination, {[2-Pyr$(SiMe_3)_2$]CSb(Me)C[2-Pyr$(SiMe_2)CH_2$]Ga(Me)}, **3**.

Results and Discussion

Complex **2** is formed on the low-temperature addition (−78 °C) of a slight excess of a thf solution of Me_3Ga to

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* Corresponding author. E-mail: p.andrews@sci.monash.edu.au.

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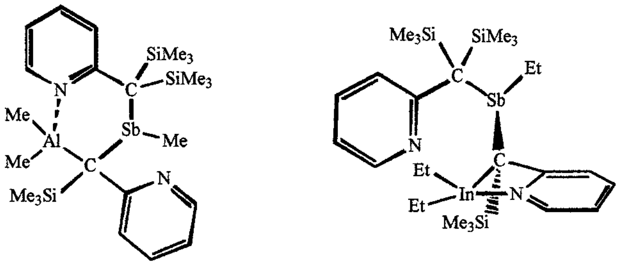

1a **1b**

Figure 1. Structures of the Al/Sb, **1a**, and the In/Sb, **1b**, *geminal* organodimetallic complexes.

the deep red hexane solution of the stiba-alkene (Scheme 1). The synthesis and confirmation of the stiba-alkene nature of the red oil, produced from the 2:1 reaction of $[2\text{-Pyr}(SiMe_3)_2CLi\cdot\text{tmeda}]$ with $SbCl_3$, has been previously reported.[4] On cooling to −25 °C a large crop of colorless rodlike crystals of **2** are obtained. The crystals are air and moisture sensitive and melt in the range 84−86 °C. The composition and structure of **2** has been determined by elemental analysis, NMR, and single-crystal X-ray diffraction. Electrospray mass spectrometry indicated only that the complex had fragmented in the spectrometer with no peaks close to, or above, the molecular weight of the complex.

A single crystal was mounted under oil, and data were collected at −150 °C. The crystal structure obtained revealed that the complex adopts a structure analogous to that previously reported for the Al/Sb complex, **1a**. The crystals are chiral at the Sb and C_{gem} centers with both distereoisomers (*R*,*S* and *S*,*R*) present in the enantiomeric mixture, as indicated by the $P2_1/n$ space group. The structure is shown in Figure 2 and, as can be seen, adopts a six-membered *geminal* dimetallic heterocycle with ring closure resulting from the dative $Ga-N_{pyr}$ bond. While this is in agreement with the structural outcome of carbometalation of the stiba-alkene Me_3Al, **1a**, it is in contrast to the four-membered heterocycle obtained in the reaction with Et_3In (Figure 1, **1b**). We are, as yet, unable to make a comparison with the solid-state structure of the complex obtained in the reaction with Me_3In since, although the reaction itself proceeds smoothly, we have been thus far unsuccessful at growing crystals that diffract sufficiently well, despite numerous attempts. This is primarily due to the crystals growing as extremely thin plates and stacking.

In the Al complex the $Al-C_{gem}$ is the longest Al−C bond; however, this is not the case for Ga in **2**. The Ga−Me distances are found to be 1.987(4) and 2.017(4) Å, for C(23) and C(24), respectively, while the $Ga-C(1)_{gem}$ distance is 2.016(4) Å.

In comparing **2** with **1a**, it is of interest to observe any changes that occur, on replacement of Al with Ga, on the bond distances and angles at the *geminal* carbon. In general, Ga(III) characteristically tends to behave in a less electropositive manner than Al(III), apparently as a result of d-block contraction, and therefore different structural outcomes can often be expected. One main feature of this is the tendency of aluminum hydrides and alkyls to associate and for Al to form five- and six-coordinate complexes.[6] The $Sb-C_{gem}$ distance in **1a**, 2.167(7) Å, is marginally shorter than that in **2**, 2.182(4) Å. It has been postulated by Bickelhaupt[7] that an increase in negative charge on the carbon center, caused by having two metals present, leads to a shortening of the M−C bonds (see below). While this has not yet been shown to be the case for the less electropositive group 13/15 *geminal* complexes herein described, and in other bis p-block complexes reported elsewhere,[8] it may account for the shortening of the Sb−C bond in the Al complex when compared with Ga. The $C_{gem}-SiMe_3$ and $C_{gem}-Pyr$ distances are exactly the same in both complexes. The M−C−M′ angle in **2**, 108.3(2)°, is slightly more obtuse than in **1a**, 106.7(3)°.

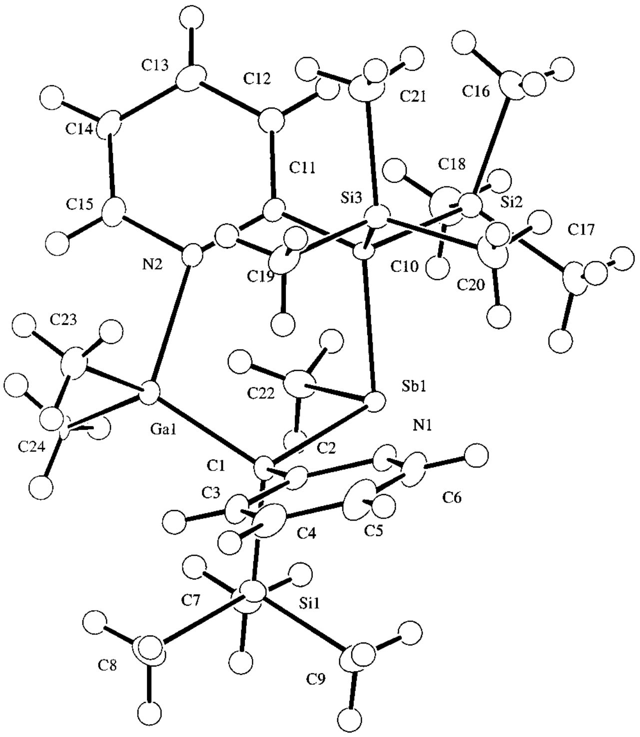

Figure 2. Molecular structure of **2**.

The ^1H and ^{13}C NMR spectra, obtained in benzene-d_6, are consistent with the solid-state structure. The protons associated with Me_2Ga- are located at δ 0.13, with those of $MeSb-$ at a slightly higher frequency, δ 0.92 (cf. δ 1.08 in **1a**). The $SiMe_3$ groups appear at δ 0.45, δ 0.21, and δ −0.16. In the ^{13}C spectrum the Me_2Ga- and $MeSb-$ signals appear at δ 1.36 and δ 0.42, respectively. Two distinct signals are present representing the metal-bound quaternary carbons, at δ 33.7 and δ 33.2, one of which is the *geminal* C. This contrasts slightly with the spectrum of **1a**, in which only one signal is apparent, at δ 34.0. Taking into consideration the chemical shifts of the analogous quaternary carbons in the In/Sb complex, at δ 33.3 and δ 34.0, it is becoming clear that despite expectations, there is almost no significant increase in nuclear charge on C_{gem} over that in the protonated ligand, δ 33.4, though one major difference is the absence of the second Me_3Si group, which may have some influence.

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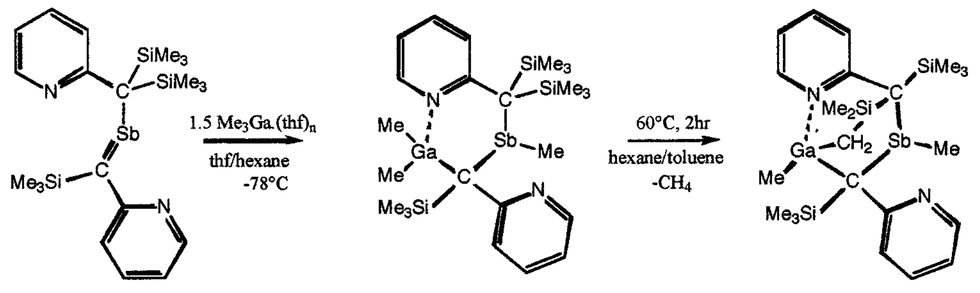
Scheme 1. Synthesis of the Ga/Sb *Geminal* Organodimetallics 2 and 3



2 **3**

Complex **3** was obtained by two methods. Warming a hexane/toluene solution of **2** to 60 °C for 4 h and allowing it to cool slowly to room temperature, followed by refrigeration at 4 °C, resulted in a crop of colorless cubelike crystals among a colorless microcrystalline material. Single-crystal X-ray diffraction studies on the larger crystals revealed that intramolecular CH_4 elimination had occurred in **2**, resulting in a new Sb/Ga *geminal* dimetallic complex with a distorted bicyclo-[2.2.2]-type core, **3**. Crystals of **3** were also obtained by the dropwise addition of a thf solution of Me_3Ga to the red oil at room temperature. This method results in partial decomposition, as evidenced by the presence of a small amount of elemental Ga. Subsequent filtration and cooling leads to a crystalline mixture of **2** and **3**.

As is apparent from the crystal structure of **3**, Figure 3, the elimination has occurred between one of the methyl groups on the Ga and one on Me_3Si, leading to a methylene bridging $-(Me)_2-Si-CH_2-Ga(Me)-$ unit. The *geminal* dimetallic nature of **2** is retained in **3**.

Complex **3** crystallizes in the chiral space group $P2_12_12_1$ and is shown here in the *R*,*R* configuration. The crystals are still mildly air and moisture sensitive and melt with decomposition between 131 and 133 °C. The Ga center is four-coordinate, bonding datively to the N_{pyr} in the bis-silylated pyridyl moiety, as is found in **1a** and **2**, and in contrast to **1b**. The Ga1−N2 bond length of 2.143(7) Å is shorter than that in **2** (2.190(4) Å), though both are typical of four-coordinate nitrogen-bound Ga alkyls.[9] The Ga−Me and $Ga-CH_2$ distances are almost identical, being 1.984(9) and 1.980(9) Å, respectively, and are comparable with the analogous bond distances in **2**. Again, the distances are slighly shorter than the $Ga-C_{gem}$ distance of 2.037(7) Å, which, as alluded to above, contradicts the notion that a buildup of charge at the C_{gem} center would result in a significant shortening of the bonds, as has been described for $[(SiMe_3)_2C(MgBr)_2\cdot 4thf]$.[7] It is consistent, though, with the analogous bond distance in the In/Sb complex, which also shows a slight elongation, and with the ^{13}C NMR results. Interestingly, a different pattern of bond distances is evident in the bonding environment of Sb in comparison to that found in **1a**. In **3**, Sb−C(10), 2.281(7) Å, is much longer than Sb−C(1), the *geminal* carbon, 2.176(7) Å, which in turn is longer than Sb−C(22), 2.147(7) Å, while comparative bond distances in **1a** are 2.247(7), 2.167(7), and 2.178(7) Å, respectively. In **2**, while the Sb(1)−C(10) distance is 2.253(4) Å and is again the longest bond, the two other comparative bonds are this time identical: Sb−C(1) and Sb−C(22) being 2.182(4) and 2.180(4) Å, respectively. So in **3**, while the shorter $Sb-C_{gem}$ distance is maintained, it is not the shortest Sb−C distance, as it is in **1a**, emphasizing again that, in general, the $metal-C_{gem}$ bonds may not necessarily show any significant contraction. The more highly electropositive group 1 and 2 metals though may show different outcomes.

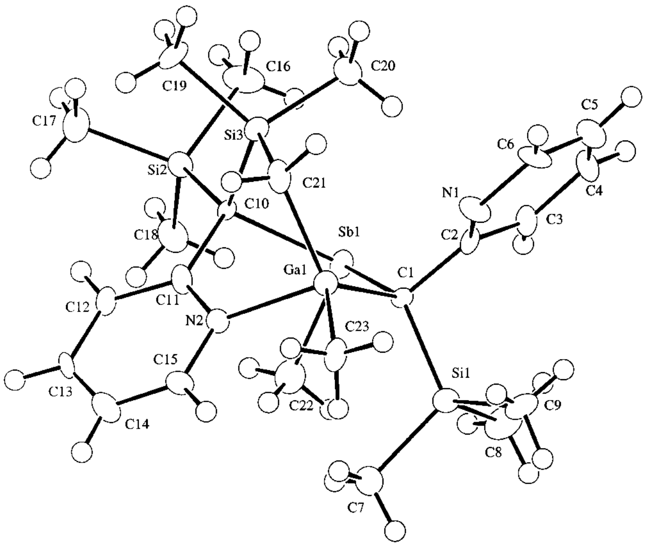


Figure 3. Molecular structure of **3**.

It was melting point comparisons and ^1H and ^{13}C NMR spectra that revealed that the crystals obtained from the reactions were a mixture of **2** and **3**. The conversion of **2** to **3** is never quantitative, with the highest ratio of **2**:**3**, as determined by a comparison of peak integration in ^1H spectra, being ca. 40:60. Excessive heating, in an attempt to increase yields, has only led to decomposition. 1D and 2D ^1H and ^{13}C NMR, with correlations, has allowed for the individual signals in each compound to be determined and assigned, even though there is some overlap in the pyridyl proton signals. Surprisingly, there are almost no chemical shift differences for the signals attributable to **2** in the mixture when compared with those in the spectra of the pure crystalline compound. Assigning these peaks, and with the aid of ^1H 2D spectrum, allowed for the identification of those signals wholly relating to **3**. The

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[9] For example: (a) Jutzi, P.; Bangel, M.; Neumann, B.; Stammler, H. G. *Organometallics* **1996**, *15*, 4559. (b) Byers, J. J.; Pennington, W. T.; Robinson, G. H. *Acta Crystallogr., Sect. C* **1992**, *48*, 2023. (c) Robinson, G. H.; Pennington, W. T.; Lee, B.; Self, M. F.; Hrncir, D. D. *Inorg. Chem.* **1991**, *30*, 809. (d) Schumann, H.; Hartmann, V.; Wassermann, W.; Dietrich, A.; Gorlitz, F. H.; Pohl, L.; Hostalek, M. *Chem. Ber.* **1990**, *123*, 2083. (e) Hallock, R. B.; Hunter, W. E.; Atwood, J. L.; Beachley, O. T., Jr. *Organometallics* **1985**, *4*, 547. (f) Krause, H.; Sille, K.; Hausen, H.-D.; Weidlein, J. *J. Organomet. Chem.* **1985**, *235*, 253.

solution structure is essentially rigid, as evidenced by the two doublets representing each of the two protons in the Ga−CH$_2$−Si bridge appearing at δ −0.78 (J_{HH} 12 Hz) and δ −0.11 (J_{HH} 12 Hz). The dd signals for H^6 protons on the two pyridyl groups (centered on δ 8.48 and δ 8.31) are also now quite distinct, being separated by 0.17 ppm. In comparison with **2** the MeSb− signal is now located at δ 0.35, a significant upfield shift of 0.57 ppm, and the MeGa− signal at δ 0.57, a move downfield by 0.44 ppm. In the ^{13}C NMR, the Ga−CH$_2$−Si signal is broad and located at δ 0.8, with MeGa at δ −1.4, while MeSb is shifted upfield slightly from its position in the spectrum of **2** to δ 0.3. One other point of interest is that one of the metal-bound quaternary carbons has shifted upfield and now gives a signal at δ 28.8, while the other is located in the more expected position of δ 32.8. This could reflect the change in the Sb−C$_{gem}$ bond length seen in **3** when compared with **1a** and **2**.

We have, thus far, shown that the carbometalation of stabilized C═M bonds is a new and interesting route into *geminal* organodimetallic complexes. One intrinsic problem, though, with this route over those described elsewhere[1] is the requirement that bulky groups are needed to kinetically protect the rather unstable C═M bonds prior to any 1,2-addition. This, therefore, also has the potential to limit the application of the complexes in synthesis. Despite this, we are now hoping to undertake an analysis of the usefulness of the 13/15 complexes in some simple synthetic processes and also to gauge their potential as single-source precursors in CVD experiments. The results will be reported in due course.

Experimental Section

All compound manipulations were carried out under dry, inert atmopshere conditions (Ar gas) using standard Schlenk techniques and a glovebox. All solvents were dried by reflux over Na/K alloy and degassed prior to use. Benzene-d_6 was dried over 4 Å molecular sieves. Neat Me$_3$Ga was purchased from Strem and added to thf prior to use. SbCl$_3$ was purchased from Aldrich and was purified by sublimation. ^{n}BuLi was purchased from Merck-Schuchardt and standardized before use. 2-Pyr(Me$_3$Si)$_2$CH was synthesized according to the literature procedure.[10] Elemental analyses were conducted by CMAS, Melbourne, Australia. All ^{1}H and ^{13}C NMR were recorded on a Brucker AM400 MHz spectrometer with chemical shifts referenced internally to benzene-d_6.

Note: the numbering scheme used below for reporting the NMR chemical shifts for protons and carbons in the pyridyl ligands is standard for 2-picoline derivatives, with the exocyclic C being labeled 7. The further use of the letters a, b, c, and d simply serves to identify those protons related through belonging to individual pyridyl rings.

Synthesis of 2. Me$_3$Ga (7.5 mmol, 0.87 g) in thf (10 mL) was added dropwise to a cooled, −78 °C, hexane solution of the stiba-alkene [2-Pyr(SiMe$_3$)$_2$CSb═C(SiMe$_3$)2-Pyr] (5 mmol). The solution remains red in color. After 30 min the cool bath is removed and the solution stirred and allowed to warm slowly to ambient temperature. Approximately one-third of the solvent mixture is removed in vacuo and the solution placed in a refrigerator at 4 °C. Colorless crystals of **2** are obtained overnight. Yield: 73% (not maximized and based on overall consumption of 2-Pyr(SiMe$_3$)$_2$CH). Mp: 84−86 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 8.12 (ddd, J = 0.9, 1.8, 5.1 Hz, 2H, H^{6ab}), 7.33 (ddd, J = 1.1, 1.1, 8.2, 1H, H^{3b}) 7.13 (m, 2H, H^{3a5b}) J = 1.9, 7.2, 9.2 Hz, 1H, H^{5a}), 6.50 (ddd, J = 1.1, 6.2, 7.3 Hz, 1H, H^{4b}), 6.25 (ddd, J = 1.2, 6.0, 7.3, 1H, H^{4a}) 0.92 (s, 3H, MeSb), 0.45 (s, 9H, Me$_3$Si), 0.21 (s, 9H, Me$_3$Si), 0.13 (s, 6H, Me$_2$Ga), −0.16 (s, 9H, Me$_3$Si) ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 25 °C): δ 172.9 (C^{2a}), 168.2 (C^{2b}), 149.2 (C^{6a}), 147.2 (C^{6b}), 136.2 (C^{3a}), 135.4 (C^{3b}), 125.6 (C^{5ab}), 118.7 (C^{4a}) 117.8 (C^{4b}), 33.7 (q−C), 33.2 (q-C), 5.9 (Me$_3$Si), 2.6 (Me$_3$Si), 2.5 (Me$_3$Si), 1.36 (Me$_2$-Ga), 0.42 (MeSb). Anal. (calcd, %): C, 45.2 (45.3); H, 6.9 (7.0); N, 4.4 (4.4).

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2 and 3

	2	3
Sb−C(1)	2.182(4)	2.176(7)
Sb−C(22)	2.180(4)	2.147(9)
Sb−C(10)	2.253(4)	2.281(7)
Ga−C(1)	2.016(4)	2.037(7)
Ga−C(23)	1.987(4)	1.984(9)
Ga−C(21)		1.980(9)
Ga−C(24)	2.017(4)	
Ga−N(2)	2.190(3)	2.143(7)
Si(3)−C(21)	1.878(4)	1.845(9)
C(10)−Si(3)	1.931(4)	1.927(8)
C(1)−Sb−C(10)	105.1(1)	101.2(3)
C(10)−Sb−C(22)	92.6(3)	96.2(3)
C(1)−Sb−C(22)	97.3(1)	100.8(3)
C(1)−Ga−C(21)		118.7(3)
C(1) −Ga−C(23)	119.3(2)	119.0(4)
C(1) −Ga−C(24)	109.1(2)	
C(21)−Ga−C(23)		116.9(4)
N(2)−Ga−C1	107.1(1)	98.7(3)
N(2)−Ga−C(23)	101.9(1)	104.4(4)
Sb−C(1)−Ga	108.3(2)	109.0(3)

Synthesis of 3. (i). A thf (10 mL) solution of Me$_3$Ga (0.58 g, 5 mmol) was added dropwise to a hexane solution (10 mL) of the red oil (4 mmol) at room temperature. An exothermic reaction occurs, with the solution color becoming pale orange. After stirring for 1 h the presence of a small amount of powdery black Ga metal indicates some decomposition. Filtration, removal of approximately one-third of the solvent in vacuo, and refrigeration (4 °C) results in a crop of colorless crystals (**2** and **3**).

(ii). A hexane/toluene (5 mL/10 mL) solution of **2** (1.2 g, 1.9 mmol) is warmed in an oil bath for 4 h at 60 °C. The solution is allowed to cool and placed in a refrigerator at 4 °C. Colorless crystals are obtained overnight. These are shown to be a mixture of **2** and **3**.

Yield of **3**: 34% (best obtained and calculated by NMR). Mp: 131−133 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 8.47 (dd, J = 1.8, 5.5 Hz, 1H, H^{6c}), 8.30 (ddd, J = 0.8, 1.8, 4.9 Hz, 1H, H^{6d}), 7.41 (dd, J = 0.8, 8.0 Hz, 1H, H^{3c}), 7.7 (m, 2H, H^{3c5d}), 6.89 (ddd, J = 2.0, 7.4, 9.3 Hz, 1H, H^{5c}), 6.51 (m, 1H, H^{4d}), 6.24 (m, 1H, H^{4c}), 0.57 (s, 3H, MeGa), 0.35 (s, 3H, MeSb), 0.34 (s, 9H, Me$_3$Si), 0.99 (s, 12H, Me$_3$Si, MeSi), −0.78 (d, J = 12 Hz, 1H, CH$_2$), −0.25 (s, 3H, MeSi), −0.11 (d, J = 12 Hz, 1H, CH$_2$), ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 25 °C): δ 171.3 (C^{2c}), 168.3 (C^{2d}), 148.6 (C^{6c}), 147.7 (C^{6d}), 136.9 (C^{3c}), 135.7 (C^{3d}), 126.2 (C^{5c}), 125.9 (C^{5d}), 118.2 (C^{4c}) 118.1 (C^{4d}), 32.8 (q−C), 28.8 (q−C), 6.8 (MeSi), 3.6 (Me$_3$Si), 2.8 (MeSi), 2.6 (Me$_3$Si), 0.28 (MeSb), −1.4 (MeGa). Anal. (calcd, %): C, 45.0 (44.5); H, 6.7 (6.5); N, 4.3 (4.5). Crystals separated manually.

X-ray Crystallography. Structure determinations were carried out on an Enraf-Nonius Kappa CCD diffractometer. Crystals were mounted under oil in a stream of argon gas and data collected at T = 123 K.

Crystallographic data for 2: C$_{24}$H$_{44}$N$_2$Si$_3$GaSb, M = 636.35, crystal dimens 0.20 × 0.18 × 0.15 mm, monoclinic, $P2_1/n$ (No. 14), a = 11.4393(2) Å, b = 14.4835(3) Å, c = 17.9492(3) Å, b = 101.602(1)°, V = 2913.09(9) Å^3, D_c (Z = 4) = 1.451 g cm^{-3}; $F(000)$ = 1304 $\mu_{\mathrm{MoK\alpha}}$ = 19.88 cm^{-1} (no correction), $2\theta_{\max}$

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[10] Papasergio, R. I.; Raston, C. L.; Skelton, B. W.; Twiss, P.; White, A. H. *Dalton Trans.* **1990**, 1161.

= 55.7°, Mo Kα radiation, final R, R_w = 0.033, 0.041, GoF 2.24, N_o = 5218 observed ($I > 2\sigma(I)$) reflections out of N = 6550 unique; solved by direct methods. All hydrogen atoms were placed in calculated positions.

Crystallographic data for 3: $C_{23}H_{40}N_2Si_3GaSb$, M = 620.31. crystal dimens 0.2 × 0.2 × 0.15 mm, orthorhombic, $P2_12_12_1$ (No. 19), a = 10.1603(3) Å, b = 12.6934(5) Å, c = 21.2318(8) Å, V = 2738.2(1) Å^3, D_c (Z = 4) = 1.505 gcm^{-3}; $F(000)$ = 1264 $\mu_{\mathrm{MoK}\alpha}$ = 21.13 cm^{-1} (no correction), $2\theta_{max}$ = 60.04°, Mo Kα radiation, final R, R_w = 0.053, 0.043, GoF 2.43, N_o = 3086 observed ($I > 3\sigma(I)$) reflections out of N = 4228 unique; solved by direct methods. All hydrogen atoms were placed in calculated positions.

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Supporting Information Available: Crystallographic data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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