The Dramatic Influence of Diamidoamine Ligands on the Structure and Reactivity of Low-Valent Tin and Bismuth Derivatives

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Keywords: Lewis acids / Bismuth / Aluminum / Phosphorus / Tin

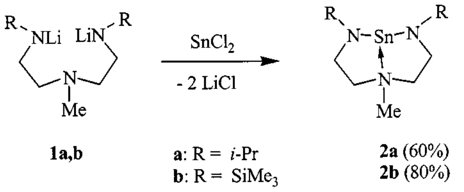
The dilithium salts of *N*-methyl-*N'*,*N''*-bis(diisopropyl)- and -(trimethylsilyl)-diethylenetriamine **1a**,**b** react with $SnCl_2$ affording the corresponding stannylenes **2a,b** in 60 and 80% yield, respectively. Compound **1b** also reacts with $BiCl_3$ to give the bismuth chloride **5** (90% yield). Derivatives **2b** and **5** have a symmetrical bicyclic structure and are monomeric both in solution and in the solid state. When **2b** is treated with $BiCl_3$ or PCl_3, an oxidation reaction leads to the hypercoordinated tin(IV) dichloride **3** (58% yield), or a transmetallation gives rise to the oniophosphane **4** (95% yield), respectively. Transmetalation reactions also occurred when **5** was treated with $AlCl_3$, $GaCl_3$ or $SnCl_2$ affording the corresponding aluminum chloride **6** (81% yield), gallium chloride **7** (38% yield) or tin dichloride **3** (38% yield). The observed reactivity for **2** and **5** is compared to that reported for Veith's stannylene or bismuth chloride.

Introduction

Compounds containing low-valent group 14 and 15 elements have attracted interest in recent times not only because of their inherently high reactivity,[1] but also because of their importance as heterogeneous catalysts[2] and as precursors for superconducting materials in MOCVD processes.[3] One of the main problems has been with the ligand design, balancing the duality between stability and reactivity.[4] We have recently shown that diamidoamino ligands $[(RNCH_2CH_2)_2NR']^{2-}$, initially developed by Cloke,[5] are powerful tools for stabilizing a large variety of group 13 Lewis acids.[6] Here we report the synthesis and reactivity of diamidoamino-stannylene and -bismuth(III)chloride derivatives, which are monomeric even in the solid state. The reactivity of these derivatives appears to be totally different from that observed with diamido-stannylenes (**I**) and -bismuth chloride derivatives (**II**) as reported by Veith et al.

Results and Discussion

The dilithium salts **1a,b**[6a] react in ether at −78 °C with $SnCl_2$ to give the corresponding stannylenes **2a,b**, which were isolated in 60 and 80% yields, respectively (Scheme 1). The ^{13}C NMR spectra show the presence of only two types of CH_2 groups, which is consistent with monomeric structures. The high field ^{119}Sn NMR chemical shifts [(C_6D_6, 298 K): **2a**, +129; **2b**, +158] strongly suggest the coordination of the amino nitrogen to the tin center, leading to a bicyclic structure.[7] This is confirmed by the presence of tin satellites for the N−Me signals in the ^1H and ^{13}C NMR spectra [**2a**: $\delta(^{13}C) = 49.0$, $^2J(^{119}SnC) = 50.2$ Hz; $\delta(^1H) = 2.11$, $^3J(^{119}SnH) = 20.0$ Hz]. Both the monomeric nature and the intramolecular coordination are retained in the solid state as shown by the molecular structure of **2b** (Figure 1). The geometric parameters around the tin center approach those of a trigonal monopyramidal geometry, indicating significant s-character for the lone pair.



Scheme 1. Synthesis of stannylenes **2**

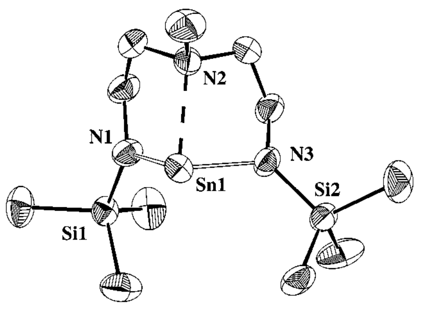


Figure 1. Molecular structure of **2b**; selected bond lengths [Å] and angles [°]: N1−Sn1 2.117(6), N2−Sn1 2.323(6), N3−Sn1 2.082(5), N1−Si1 1.712(6), N3−Si2 1.706(3); N1−Sn1−N2 77.4(2), N2−Sn1−N3 79.0(2), N1−Sn1−N3 98.1(2).

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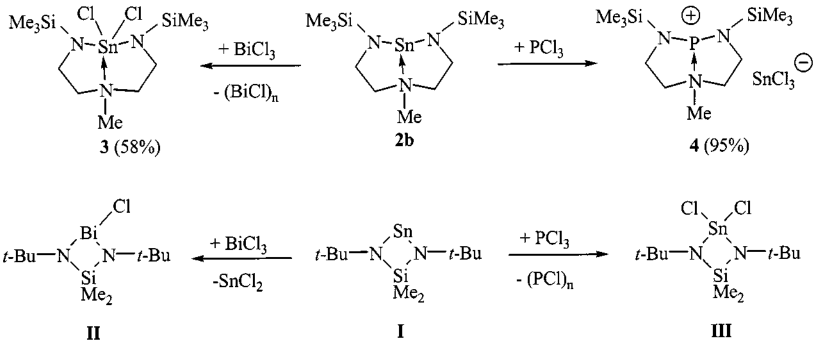


Scheme 2. Compared reactivity of **2b** and **I**

The reactivity of **2b** is “opposite” to that observed for Veith′s stannylene **I**[8] (Scheme 2). An oxidation reaction occurs upon addition of an equimolar amount of BiCl$_3$ to a thf solution of **2b** leading to the hypercoordinate tin(IV)dichloride **3** (58% yield), whereas with **I** a transmetalation reaction was observed[8c] giving rise to the bismuth chloride **II**. In contrast, an exchange reaction occurs on treatment of **2b** with one equivalent of PCl$_3$ leading to **4** (95% yield), while Veith[8d] noticed the oxidation of the stannylene **I** into **III**.

Interestingly, the ^{1}H and ^{13}C NMR spectra suggest the coordination of the amino nitrogen to the phosphorus center [CH$_3$N: $\delta(^1H) = 2.74$, $^3J_{PH} = 13.5$ Hz; $\delta(^{13}C) = 51.7$, $^2J_{PC} = 5.9$ Hz]. A single crystal X-ray diffraction study not only confirmed the bicyclic structure but also showed the ionic nature of **4** (Figure 2).

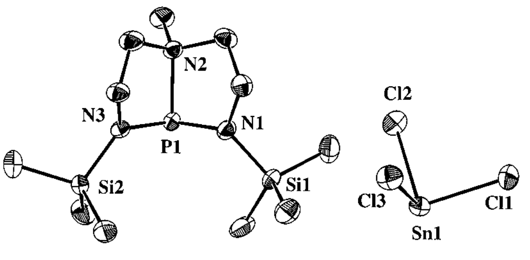
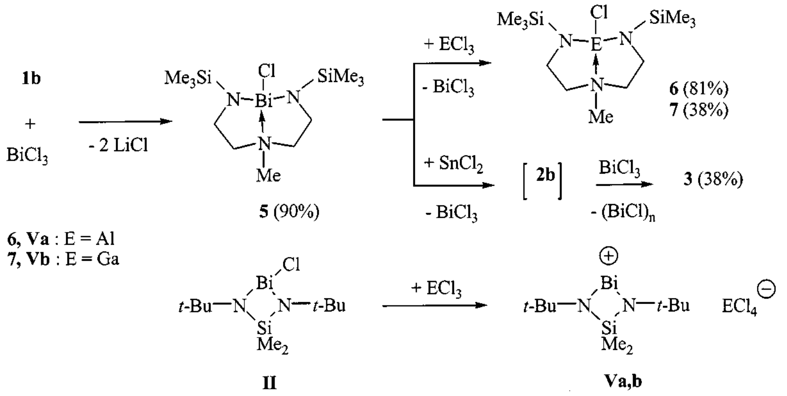


Figure 2. Molecular structure of **4**; selected bond lengths [Å] and angles [°]: N1−P1 1.684(3), N2−P1 1.897(3), N3−P1 1.664(3), N1−Si1 1.755(3), N3−Si2 1.765(3); N1−P1−N2 89.86(13), N2−P1−N3 90.05(13), N1−P1−N3 111.17(13).

In order to further compare diamidoamino ligands with diamido ligands we focused our attention on the corresponding bismuth(III) chloride derivative **5**. This product was obtained in 90% yield by treatment of a toluene solution of the dilithium salt **1b** with BiCl$_3$ at −78 °C (Scheme 3). Both the monomeric and bicyclic structure of **5** were supported by the ^{1}H and ^{13}C NMR spectroscopic data in solution. In the solid state, the closest intermolecular Bi···Cl contact is of 3.725 Å. This value is not appreciably larger than those observed in the polymeric (3.047 Å) and dimeric (3.554 Å) bismuth chlorides **II** and **IV**, prepared by Veith[8b] and Raston,[9] respectively. However, since in **5** the intermolecular Bi···Bi distance is short (3.731 Å) and the value of the Bi−Cl−Bi angle is small (69.13°), this compound is best regarded as a monomeric species. The coordination geometry around the bismuth center approaches a trigonal bipyramid (Figure 3). The equatorial N1−Bi−N3 angle is small (101.8°) indicating that the lone pair has a strong s-character and the N2−Bi−Cl1 angle is large (159.6°) which indicates that the amino group interacts with a vacant Bi d-type orbital.[10]

It has been reported that treatment of **II** with Lewis acids such as aluminum and gallium trichloride yielded the corresponding bismuth salt **Va,b** by abstraction of chloride.[8h] In marked contrast, **5** reacted at −78 °C in thf with AlCl$_3$ to give the corresponding aluminum chloride derivative **6** (81% yield). This transmetallation reaction even occurred



Scheme 3. Synthesis and reactivity of **5**

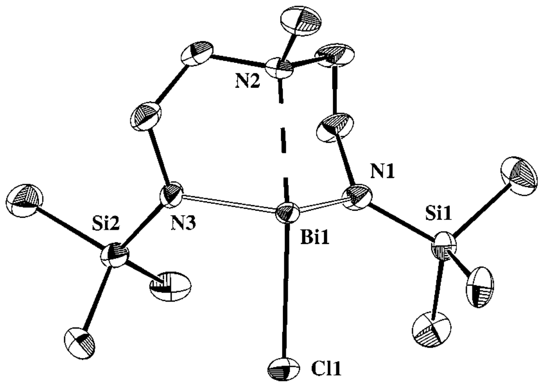


Figure 3. Molecular structure of **5**; selected bond lengths [Å] and angles [°]: N1−Bi1 2.123(5), N2−Bi1 2.496(6), N3−Bi1 2.138(6), Cl1−Bi1 2.6727(17), N1−Si1 1.714(6), N3−Si2 1.719(6); N1−Bi1−N2 75.6(2), N2−Bi1−N3 74.8(2), N1−Bi1−N3 101.8(2), N1−Bi1−Cl1 90.78(16), N2−Bi1−Cl1 159.60(14), N3−Bi1−Cl1 93.71(16).

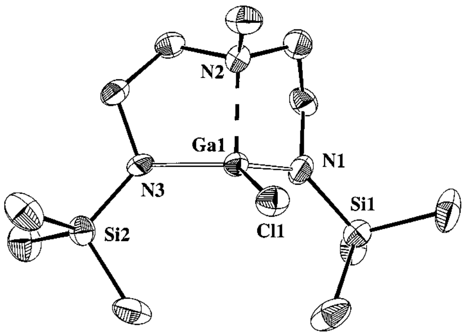


Figure 4. Molecular structure of **7**; selected bond lengths [Å] and angles [°]: N1−Ga1 1.839(16), N2−Ga1 2.043(3), N3−Ga1 1.870(15), Cl1−Ga1 2.1935(13), N1−Si1 1.711(9), N3−Si2 1.712(9); N1−Ga1−N2 90.2(4), N2−Ga1−N3 91.1(4), N1−Ga1−N3 126.08(17), N1−Ga1−Cl1 113.8(6), N2−Ga1−Cl1 111.62(10), N3−Ga1−Cl1 115.5(6).

with a strong Lewis acid such as $GaCl_3$, in toluene at −78 °C; the gallium derivative **7** being isolated in 38%. According to an X-ray diffraction study, the gallium chloride **7** is monomeric and presents a trigonal-pyramidal geometry similar to that observed for the corresponding aluminum chloride **6**[6] (Figure 4).

Since the diamidoaminobismuth chloride **5** undergoes novel transmetallation reactions with group 13 Lewis acids, it was of interest to extend this reactivity to group 14 Lewis acids. A thf solution of **5** reacted at −78 °C with an equimolar amount of $SnCl_2$, to give the tin dichloride derivative **3** in 38% yield. Since we have shown above (Scheme 2) that the stannylene **2b** reacts with $BiCl_3$ to give **3**, it is quite clear that a transmetallation reaction also occurs between **5** and $SnCl_2$ to give the stannylene **2b**, which is subsequently oxidized to **3** by the resulting $BiCl_3$. Therefore, this exchange reaction (**5**→**2b**) is the opposite of that observed by Veith (**I** →**II**).[8]

Conclusion

The dramatic difference observed in the reactivity of stannylene **2** and bismuth chloride **5** with that of **I** and **II**, respectively, can be rationalized by the electron donation from the axial nitrogen, which decreases the electrophilicity of the metal centers. The transmetalation reactions observed for bismuth chloride **5** with group 13 and 14 halides which occur under very mild conditions, suggest they could probably be generalized, especially for the synthesis of transition metal complexes.

Experimental Section

All experiments were performed under dry argon. Melting points are uncorrected ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded with Bruker AC80, AC200, WM250 or AMX400 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{119}Sn NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external Me_4Sn. Conventional glassware was used.

2a: To an ether solution (20 mL) of the lithium salt of *N*-methyl-*N′*,*N′′*-bis(diisopropyl)diethylenetriamine **1a** (4.7 mmol) was added an ether suspension (20 mL) of $SnCl_2$ (0.891 g, 4.7 mmol) at −78 °C. The solution became golden yellow, and was allowed to warm to room temperature and stirred overnight. After filtration, and removal of the solvent under vacuum, **2a** was obtained as a yellow oil (0.89 g, 60%). − ^1H NMR (C_6D_6, 250.134 MHz): δ = 1.49 (d, $^3J_{HH}$ = 6.2 Hz, 6 H, CH_3CH), 1.54 (d, $^3J_{HH}$ = 6.2 Hz, 6 H, CH_3CH), 2.11{s, $^3J(^{119}SnH)$ = 20 Hz, 3 H, CH_3N}, 2.37 (m, 4 H, CH_2), 3.11 (m, 2 H, CH_2), 3.47 (m, 2 H, CH_2), 3.67 (sept, $^3J_{HH}$ = 6.2 Hz, 2 H, CH). − $^{13}C\{^1H\}$ NMR (C_6D_6, 62.896 MHz): δ = 26.64, 26.93 (CH_3CH), 49.05 {$^2J(^{119}SnC)$ = 50.2 Hz, CH_3N}, 54.64 (CH_2NCH_3), 55.04 (CH), 63.32 (CH_2NCH). − $^{119}Sn\{^1H\}$ NMR (C_6D_6, 32.248 MHz): δ = +129. − $C_{11}H_{25}N_3Sn$: calcd. C 41.54, H 7.92, N 13.21; found C 41.10, H 7.65, N 13.42.

2b: Using the same experimental procedure as above employing the lithium salt of *N*-methyl-*N′*,*N′′*-bis(trimethylsilyl)diethylenetriamine **1b** (3.6 mmol) and $SnCl_2$ (0.682 g, 3.6 mmol), colorless crystals (1.15 g, 80%) were obtained from a toluene solution (6 mL) at −20 °C. − m.p. < 20 °C. − ^1H NMR (C_6D_6, 400.135 MHz): δ = 0.41 (s, 18 H, $SiCH_3$), 2.02 {s, $^3J(^{119}SnH)$ = 19 Hz, 3 H, CH_3N}, 2.15 (m, 4 H, CH_2), 3.35 (m, 2 H, CH_2), 3.44 (m, 2 H, CH_2). − $^{13}C\{^1H\}$ NMR (C_6D_6, 100.624 MHz): δ = 2.25 ($SiCH_3$), 48.32 {$^2J(^{119}SnC)$ = 54.0 Hz, CH_3N}, 50.09 (CH_2NCH_3), 65.99 (CH_2NSi). − $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.495 MHz): δ = +0.03. − $^{119}Sn\{^1H\}$ NMR (C_6D_6, 149.248 MHz): δ = +158. − $C_{11}H_{29}N_3Si_2Sn$: calcd. C 34.93, H 7.73, N 11.11; found C 34.67, H 7.76, N 11.22.

3: A thf solution (5 mL) of $BiCl_3$ (0.123 g, 0.38 mmol) was added dropwise to a thf solution (5 mL) of stannylene **2b** (0.147 g, 0.38 mmol) at −78 °C. The color of the solution changed from dark brown to black after the solution was allowed to warm to room temperature. After filtration, the solvent was removed under vacuum. The residue was treated with toluene (20 mL) and, after filtration, the solvent was removed under vacuum. Colorless crystals were obtained from a pentane solution (4 mL) at −20 °C (0.101 g, 58%). − m.p. < 20 °C. − ^1H NMR (C_6D_6, 250.133 MHz): δ = 0.43 (s, 18 H, $SiCH_3$), 1.87 (ddd, J_{HH} = 9.4, 5.1 and 3.5 Hz, 2 H, CH_2), 2.02 (s, 3 H, CH_3N), 2.04 (ddd, J_{HH} = 9.4, 5.6 and 3.4 Hz, 2 H, CH_2), 2.86 (m, 4 H, CH_2). − $^{13}C\{^1H\}$ NMR (C_6D_6, 62.896 MHz):

δ = 3.10 ($SiCH_3$), 41.41 (CH_3N), 44.00 ($\mathit{C}H_2NCH_3$), 57.86 (CH_2NSi). − $^{119}Sn\{^1H\}$ NMR (C_6D_6, 29.881 MHz): δ = −228. − $C_{11}H_{29}Cl_2N_3Si_2Sn$: calcd. C 29.41, H 6.51, N 9.36; found C 29.64, H 6.22, N 9.33.

4: Neat freshly distilled PCl_3 (0.072 mL, 0.8 mmol) was added dropwise to a toluene solution (6 mL) of diamidoaminostannylene **2b** (0.315 g, 0.8 mmol) at −90 °C. The solution was allowed to warm to room temperature and became yellow after 30 min. The solvent was removed under vacuum and the yellow-orange oil obtained was washed with pentane (5 mL) and ether (5 mL). Colorless crystals were obtained from a C_6D_6 solution (1 mL) at room temperature (0.315 g, 95%). − m.p. 110 °C. − ^1H NMR (C_6D_6, 250.134 MHz): δ = −0.02 (s, 18 H, $SiCH_3$), 2.61 (m, 2 H, CH_2), 2.74 {d, J_{PH} = 13.5 Hz, 3 H, CH_3N}, 3.03 (m, 2 H, CH_2), 3.43 (m, 2 H, CH_2), 4.70 (m, 2 H, CH_2). − $^{13}C\{^1H\}$ NMR (C_6D_6, 62.896 MHz): δ = 1.01 ($SiCH_3$), 51.70 {d, J_{PC} = 5.9 Hz, CH_3N}, 53.39 ($\mathit{C}H_2NCH_3$), 64.67 (CH_2NSi). − $^{31}P\{^1H\}$ NMR (C_6D_6, 81.02 MHz): δ = +169. − $C_{11}H_{29}Cl_3N_3PSi_2Sn$: calcd. C 25.63, H 5.67, N 8.15; found C 25.30, H 5.58, N 8.22.

5: Using the same procedure as for **2a**, but with toluene instead of ether, and $BiCl_3$ (0.232 g, 0.73 mmol), colorless crystals were obtained from a toluene solution (2 mL) at −20 °C (0.334 g, 90%). − m.p. 133 °C (dec.). − ^1H NMR (C_6D_6, 200.132 MHz): δ = 0.46 (s, 18 H, $SiCH_3$), 1.56 (ddd, J_{HH} = 12.1, 6.6 and 3.3 Hz, 2 H, CH_2), 1.65 (s, 3 H, CH_3N), 1.91 (ddd, J_{HH} = 12.1, 6.6 Hz and 3.3 Hz, 2 H, CH_2), 3.95 (ddd, J_{HH} = 14.5, 6.6 and 3.3 Hz, 2 H, CH_2), 4.16 (ddd, J_{HH} = 14.5, 6.6 and 3.3 Hz, 2 H, CH_2). − $^{13}C\{^1H\}$ NMR (C_6D_6, 62.896 MHz): δ = 2.98 ($SiCH_3$), 44.76 (CH_3N), 47.92 ($\mathit{C}H_2NCH_3$), 65.80 (CH_2NSi). − $C_{11}H_{29}BiClN_3Si_2$: calcd. C 26.22, H 5.80, N 8.34; found C 26.34, H 5.70, N 8.39.

6[6a] was prepared following the same procedure as for **7**.

7: A toluene solution (6 mL) of $GaCl_3$ (0.201 g, 1.12 mmol) was added dropwise to a toluene solution (10 mL) of bismuth chloride **5** (0.569 g, 1.12 mmol) at −78 °C. The pale yellow solution was allowed to warm to room temperature. After filtration, the solvent was removed under vacuum, and colorless crystals (0.157 g, 38%) were obtained from a toluene solution (2 mL) at −20 °C. − m.p. 180 °C (dec.). − ^1H NMR ($CDCl_3$, 200.132 MHz): δ = 0.41 (s, 18 H, $SiCH_3$), 1.79 (ddd, J_{HH} = 11.3, 6.1 and 5.1 Hz, 2 H, CH_2), 1.91 (s, 3 H, CH_3N), 2.05 (ddd, J_{HH} = 11.3, 6.1 and 4.8 Hz, 2 H, CH_2), 2.83 (m, 4 H, CH_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.896 MHz): δ = 0.84 ($SiCH_3$), 41.77 ($\mathit{C}H_2NCH_3$), 41.99 (CH_3N), 58.40 (CH_2NSi). − $C_{11}H_{29}ClGaN_3Si_2$: calcd. C 36.22, H 8.01, N 11.52; found C 36.26, H 8.05, N 11.48.

X-ray Crystal Structure Determination of 2b, 4, 5 and 7:

2b: $C_{11}H_{29}N_3Si_2Sn$, M = 378.24, triclinic, $P\bar{1}$, a = 9.047(2) Å, b = 10.209(2) Å, c = 11.906(2) Å, α = 103.62(2)°, β = 100.02(2)°, γ = 113.71(2)°, V = 932.8(3) $Å^3$, Z = 2, ρ_c = 1.347 Mg m^{-3}, *F(000)* = 388, λ = 0.71073 Å, T = 173(2) K, μ (Mo K_α) = 1.487 mm^{-1}, crystal size 0.7 × 0.6 × 0.6 mm, 2.42° < θ < 23.25°, 9933 reflections (2523 independent, R_{int} = 0.1104) were collected at low temperatures using an oil-coated shock-cooled crystal[11] on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-97)[12] and 201 parameters using 71 restraints were refined using the least-squares method on F^2.[13] Largest electron density residue: 1.606 e $Å^{-3}$, R_1 {for F>2σ(F)} = 0.058 and wR_2 = 0.134 (all data) with $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}0.5$. The disorder of a trimethylsilyl group was refined anisotropically on two positions with the occupancy 0.64/0.36 using ADP and distance restraints.

4: $C_{11}H_{29}Cl_3N_3PSi_2Sn$, M = 515.56, triclinic, $P\bar{1}$, a = 6.374(1) Å, b = 12.868(2) Å, c = 13.913(2) Å, α = 100.39(2)°, β = 98.47(2)°, γ = 93.07(2)°, V = 1106.4(3) $Å^3$, Z = 2, ρ_c = 1.548 Mg m^{-3}, *F(000)* = 520, λ = 0.71073 Å, T = 173(2) K, μ (Mo K_α) = 1.695 mm^{-1}, crystal size 0.4 × 0.3 × 0.1 mm, 1.99° < θ < 23.53°, 8463 reflections (3113 independent, R_{int} = 0.0375) were collected at low temperatures using an oil-coated shock-cooled crystal[11] on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-97)[12] and 197 parameters were refined using the least-squares method on F^2.[13] Largest electron density residue: 0.475 e $Å^{-3}$, R_1 {for F>2σ(F)} = 0.025 and wR_2 = 0.065 (all data) with $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}0.5$.

5: $C_{11}H_{29}BiClN_3Si_2$, M = 503.98, monoclinic, $P2_1/n$, a = 10.063(1) Å, b = 13.280(2) Å, c = 15.006(2) Å, β = 109.16(1)°, V = 1894.3(4) $Å^3$, Z = 4, ρ_c = 1.767 Mg m^{-3}, *F(000)* = 976, λ = 0.71073 Å, T = 173(2) K, μ (Mo K_α) = 9.566 mm^{-1}, crystal size 0.6 × 0.5 × 0.5 mm, 2.10° < θ < 23.25°, 15301 reflections (2718 independent, R_{int} = 0.0883) were collected at low temperatures using an oil-coated shock-cooled crystal[11] on a STOE-IPDS diffractometer. A numerical absorption correction was employed and the min./max. transmissions are 0.0857 and 0.2607. The structure was solved by direct methods (SHELXS-97)[12] and 171 parameters were refined using the least-squares method on F^2.[13] Largest electron density residue: 1.022 e $Å^{-3}$, R_1 {for F>2σ(F)} = 0.029 and wR_2 = 0.074 (all data) with $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}0.5$.

7: $C_{11}H_{29}ClGaN_3Si_2$, M = 364.72, monoclinic, $P2_1/m$, a = 6.472(2) Å, b = 18.624(5) Å, c = 7.688(3) Å, β = 96.64(4)°, V = 920.5(5) $Å^3$, Z = 2, ρ_c = 1.316 Mg m^{-3}, *F(000)* = 384, λ = 0.71073 Å, T = 153(2) K, μ (Mo K_α) = 1.760 mm^{-1}, crystal size 0.5 × 0.4 × 0.1 mm, 2.67° < θ < 24.21°, 6014 reflections (1514 independent, R_{int} = 0.0445) were collected at low temperatures using an oil-coated shock-cooled crystal[11] on a STOE-IPDS diffractometer. A numerical absorption correction was employed and the min./max. transmissions are 0.5865 and 0.7727. The structure was solved by direct methods (SHELXS-97)[12] and 164 parameters using 71 restraints were refined using the least-squares method on F^2.[13] Largest electron density residue: 0.273 e $Å^{-3}$, R_1 {for F>2σ(F)} = 0.024 and wR_2 = 0.055 (all data) with $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}0.5$. The mirror leads to a disorder of the whole molecule, which was refined anisotropically by ignoring the symmetry (PART-1) using ADP and distance restraints. A refinement in $P2_1$ gives the same disorder.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Data Centre as supplementary publication no. CCDC-112754 (**2b**), CCDC-112755 (**4**), CCDC-112756 (**5**) and CCDC-112757 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Thanks are due to the CNRS and Beaufour-Ipsen for financial support of this work.

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Received June 14, 1999
[I99212]