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Unique structural isomerism involving tetrazole and amide/azide derivatives of gallium

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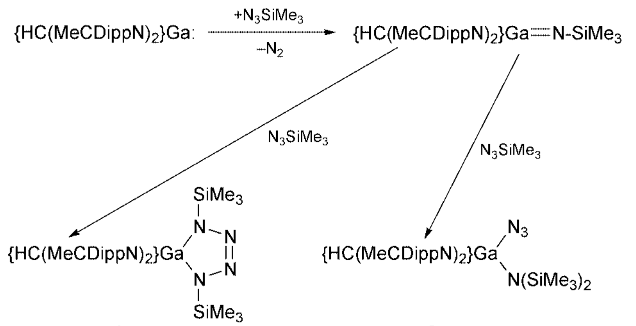
The reaction between $\{HC(MeCDippN)_2\}Ga$: (Dipp = $C_6H_3Pr^i_2$-2,6) and N_3SiMe_3 afforded the tetrazole $\{HC(MeCDippN)_2\}\overline{GaN(SiMe_3)NNN}(SiMe_3)$ 1 and its amide/azide isomer $\{HC(MeCDippN)_2\}Ga(N_3)N(SiMe_3)_2$ 2 whose stabilities are due to the unique steric properties of the $[HC(MeCDippN)_2]^-$ ligand.

Recent investigations of derivatives of the sterically encumbered β-diketiminate ligand $[HC(MeCDippN)_2]^-$ (Dipp = $C_6H_3Pr^i_2$-2,6) have shown that it can stabilize a wide variety of species with unusual coordination numbers and bonding throughout the Periodic Table.[1] In particular, its use in connection with low-valent heavier group 13 elements has resulted in the isolation of the monomeric, two-coordinate M(I) species $\{HC(MeCDippN)_2\}M$: (M = Al[2] or Ga[3]) which contain a stereochemically active lone pair of electrons at the metals. Previous work on less hindered, weakly associated M(I) species such as Cp*M (Cp* = C_5Me_5; M = Al[4] or Ga[5]) has shown that they can react with azides to give dimeric imides such as $Cp^*\overline{AlN(AlCp^*_2)Al\{N(SiMe_3)_2\}N}\{Al(Cp^*)N(SiMe_3)_2\}$[6] or $\{Cp^*GaN(C_6H_3Me_2\text{-}2,6)\}_2$[7] under elimination of N_2. We reasoned that the more crowded Ga(I) species $\{HC(MeCDippN)_2\}Ga$: might react with the simple azide N_3SiMe_3 to afford a monomeric imide $\{HC(MeCDippN)_2\}Ga{=}NSiMe_3$ which could have a GaN multiple bond. We now report that, although unassociated products were obtained from this reaction, neither of these involved a terminal gallium imide moiety. Instead, the isomers **1** and **2**, involving the reaction of 2 equivalents of N_3SiMe_3 with $\{HC(MeCDippN)_2\}Ga$:, were isolated and characterized.

The reaction of $\{HC(MeCDippN)_2\}Ga$: with N_3SiMe_3 afforded the products **1** and **2** in accordance with Scheme 1.† It is probable that the species $\{HC(MeCDippN)_2\}GaNSiMe_3$ is generated initally, and this is prevented from dimerizing to give $[\{HC(MeCDippN)_2\}GaNSiMe_3]_2$ for steric reasons. Instead, $\{HC(MeCDippN)_2\}GaNSiMe_3$ reacts with a further equivalent of N_3SiMe_3 to give the tetrazole **1**‡ and the amide/azide product **2**. Solution ^1H NMR spectroscopy of the reaction mixture shows that both **1** and **2** as well as unreacted $\{HC(MeCDippN)_2\}Ga$: and N_3SiMe_3 are detectable after stirring for 30 min at *ca.* 25 °C. Heating at *ca.* 75 °C results in a *ca.* 1 : 3 ratio of **1** and **2** which can be isolated in 73% overall yield. Both **1** and **2** were obtained as colorless crystals. However, the solubility of the tetrazole **1** is considerably less than that of **2**, so that the products can be separated quite easily by crystallization. The compound **1** is thermally robust having a melting point > 200 °C. It decomposes at *ca.* 235 °C to a red solid with N_2 elimination. Compound **2** melts at a lower temperature (161–163 °C) and also decomposes at *ca.* 230 °C to give a red solid and N_2 evolution.§



Scheme 1 Reactions of $\{HC(MeCDippN)_2\}Ga$: (Dipp = $C_6H_3Pr^i_2$-2,6) with N_3SiMe_3 to give **1** or **2**.

Compounds **1** and **2** were characterized by ^1H and ^{13}C NMR spectroscopy, by C,H,N analysis and by X-ray crystallography.¶ The structure of the tetrazole **1** (Fig. 1) features GaN_4 and GaN_2C_3 rings that are fused at gallium. The metal has distorted tetrahedral geometry and the Ga–N bonds [av. 1.947(2) Å] to the β-diketiminate nitrogens N(1) and N(2) are significantly longer than the average distance of 1.875(16) Å to the tetrazole nitrogens. The longer pair of Ga–N distances is consistent with equal components of normal and dative character in these bonds.[8] These Ga–N bond lengths also resemble those observed in other Ga(III) β-ketiminate species.[9] The shorter Ga–N distances involving the tetrazole nitrogens are in agreement with known values for bonding between four-coordinate gallium and terminal amide groups.[10] The gallium tetrazole ring is essentially planar, and the N(4)–N(5) distance of 1.265(3) Å is consistent with NN double bonding. In contrast, the gallium β-diketiminate ring is folded along the N(1)···N(2) axis such that Ga(I) lies *ca.* 0.34 Å from the averaged N_2C_3 plane. This structural feature is common to many bulky β-diketiminate derivatives.[1] The folding of the ring results in different magnetic environments for the two $SiMe_3$ groups (as well as slightly different bond lengths for Ga–N(3) and Ga–N(6)) which is manifested in different ^1H NMR chemical shifts for the $SiMe_3$ resonances.

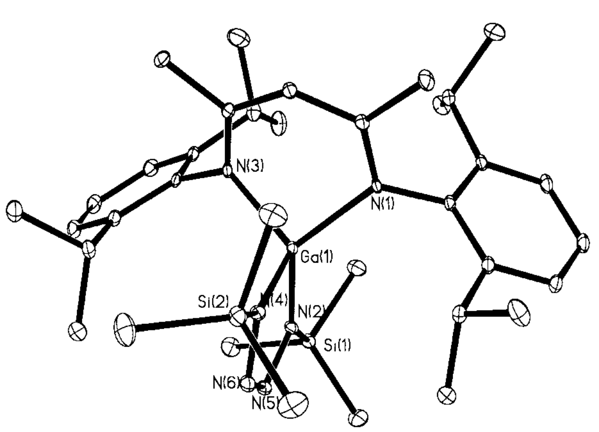


Fig. 1 Thermal ellipsoid (30%) plot of **1** with H atoms not shown. Selected bond distances (Å) and angles (°): Ga(1)–N(1) 1.945(2), Ga(1)–N(2) 1.949(2), Ga(1)–N(3) 1.858(2), Ga(1)–N(6) 1.891(2), N(3)–N(4) 1.402(3), N(4)–N(5) 1.265(3), N(5)–N(6) 1.406(2), Si(1)–N(3) 1.737(2), Si(2)–N(6) 1.750(2); N(1)–Ga(1)–N(2) 95.40(8), N(3)–Ga(1)–N(6) 85.74(7), N(1)–Ga(1)–N(6) 117.49(8), N(2)–Ga(1)–N(6) 115.64(8), N(1)–Ga(1)–N(3) 126.41(8), N(2)–Ga(1)–N(3) 118.11(8).

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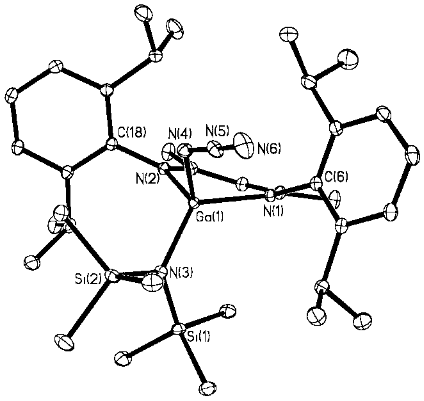

Fig. 2 Thermal ellipsoid (30%) plot of **2** with H atoms not shown. Selected bond distances (Å) and angles (°): Ga(1)–N(1) 1.946(1), Ga(1)–N(2) 1.958(1), Ga(1)–N(3) 1.884(1), Ga(1)–N(4) 1.918(1), Si(1)–N(3) 1.746(1), Si(2)–N(3) 1.751(1); N(1)–Ga(1)–N(2) 98.28(5), N(3)–Ga(1)–N(4) 111.82(6), N(1)–Ga(1)–N(3) 122.45(5), N(2)–Ga(1)–N(3) 113.23(5), Ga(1)–N(3)–Si(1) 123.39(7), Ga(1)–N(3)–Si(2) 115.32(7).

The structure of amide/azide compound **2** (Fig. 2) also features gallium bound to four nitrogens in a distorted tetrahedral fashion. The Ga–N(β-diketiminate) bonds [av. 1.952(7) Å] have very similar lengths to the corresponding bonds in **1**. The β-diketiminate ring is folded along the N(1)···N(2) axis such that Ga(I) lies *ca.* 0.21 Å from the averaged N_2C_3 plane. The Ga–N$(SiMe_3)_2$ bond length [1.884(1) Å] is close to the 1.872(2) Å reported for $\{Cp^*\{(Me_3Si)_2N\}Ga(\mu\text{-}N_3)\}_2$.[7] The Ga–N(azide) bond length, 1.918(3) Å, is essentially the same as the 1.921(4) Å observed in a bulky aryl-substituted bis(azide) of gallium.[11] Within the N_3 moiety, the N–N distances are similar to those previously observed in gallium azides.[12] Like **1**, compound **2** displays two different resonances for the $SiMe_3$ peaks—probably due to restricted rotation of the amide moiety around the Ga–N bond as a result of steric effects. Rotational barriers as high as 18.6 kcal mol^{-1} have been observed for group 13 metal–nitrogen bonds in sterically congested systems.[13] Variable temperature ^{1}H NMR studies of **1** or **2** in toluene did not result in the collapse of the $SiMe_3$ signals to a single resonance.

The isolation of tetrazole–amide/azide isomers appears to be unique.||[14] Their stability can be rationalized on the basis of the size of the $[HC(MeCDippN)_2]^-$ ligand which prevents dimerization of the intermediate $\{HC(MeCDippN)_2\}GaNSiMe_3$, but allows reaction with a further equivalent of the less hindered N_3SiMe_3. Owing to the multipolar nature of the NNNSi array, this reaction proceeds by two distinct pathways to afford **1** and **2**.

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Notes and references

† All manipulations were carried out under anaerobic and anhydrous conditions. A toluene solution (50 mL) of N_3SiMe_3 (0.38 mL, 2.9 mmol) was added dropwise to a rapidly stirred solution of $\{HC(MeCNDipp)_2\}Ga$: (0.66 g, 1.41 mmol) in toluene (20 mL), with cooling in an ice-bath. The solution was allowed to rise to room temperature and was then heated to *ca.* 75 °C for 1 h. The solution was concentrated to *ca.* 20 mL and cooled for 24 h in a *ca.* 4 °C refrigerator to afford colorless crystals of the product **1** (0.18 g, 19%). Anal. Calc. (found) for $C_{35}H_{59}N_6GaSi_2$: C, 60.94 (61.11), H, 8.62 (8.81), N, 12.25 (12.01)%. Mp 217–220 °C. ^{1}H NMR (300 MHz, C_6D_6) δ 7.06–7.04 (m, 6H, aromatic H of Ar group), 4.89 (s, 1H, methine CH), 3.30 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*Me), 3.20 (sept, $^3J_{HH}$ 6.6 Hz, 2H, C*H*Me), 1.50 (s, 6H, CMe), 1.32 (d, $^3J_{HH}$ 6.6 Hz, 6H, CH*Me*$_2$), 1.14 (d, $^3J_{HH}$ 6.6 Hz, 6H, CH*Me*$_2$), 1.08 (d, $^3J_{HH}$ 6.6 Hz, 6H, CH*Me*$_2$), 1.06 (d, $^3J_{HH}$ 6.6 Hz, 6H, CH*Me*$_2$), 0.54–0.12 [s, 9H, Si$(CH_3)_3$]: $^{13}C\{^1H\}$ (75 MHz, C_6D_6) δ 172.81 (CN), 145.48 (*C*Me) 142.76, 140.50 (*o*-C on C_6H_3), 127.54 (*p*-C on C_6H_3), 125.52, 124.26 (*m*-C on C_6H_3), 99.94 (γ-C), 29.10, (*C*HMe$_2$), 28.92 (CH*Me*$_2$), 25.30, 25.25 (CH*Me*$_2$) 24.37 (C*Me*) 1.93, 0.99 [Si(*C*H$_3$)$_3$]. The isomeric product **2** was obtained by decanting the supernatant liquid from **1** and cooling in a *ca.* −20 °C freezer for 48 h to afford colorless crystals of **2** (0.52 g, 54%). Mp 161–163 °C. ^{1}H NMR (300 MHz C_6D_6) δ 7.15 (s, 6H, aromatic H or Ar groups), 4.83 (s, 1H, methine CH), 3.60 (sept, $^3J_{HH}$ 6.6 Hz, 2H, C*H*Me), 3.29 (sept, $^3J_{HH}$ 6.6 Hz, 2H, C*H*Me), 1.48 (d, $^3J_{HH}$ 6.6 Hz, 6H, CH*Me*$_2$), 1.44 (d, $^3J_{HH}$ 6.6 Hz, 6H, CH*Me*$_2$), 1.40 (s, 6H, CMe), 1.16 (d, $^3J_{HH}$ 6.6 Hz, 6H, CH*Me*$_2$), 1.11 (d, $^3J_{HH}$ 6.6 Hz, 6H, CH*Me*$_2$), 0.23, 0.41 [s, 9H, Si$(CH_3)_3$]: $^{13}C\{^1H\}$ (75 MHz, C_6D_6) δ 171.39 (CN), 145.11 (*C*Me) 144.25, 141.01 (*o*-C on C_6H_3), 128.08 (*p*-C on C_6H_3), 125.58, 124.92 (*m*-C on C_6H_3), 100.32 (γ-C), 29.09, 28.45 (*C*HMe$_2$), 25.93, 25.58 (CH*Me*$_2$), 25.25 (C*Me*), 25.09, 24.82 (CH*Me*$_2$), 5.90, 5.78 [Si(*C*H$_3$)$_3$].

‡ Professor H. W. Roesky has informed us that a similar reaction involving $\{HC(MeCDippN)_2\}Al$: and N_3SiMe_3 affords the aluminium analog of **1**. The contrasting behavior of the gallium system, with its preference for the amide/azide over the tetrazole product, is another illustration of the differences between aluminium and gallium chemistry.

§ Attempts at thermal interconversion of **1** and **2** have so far been unsuccessful.

¶ *Crystal data* for **1** and **2** at 90 K with Mo-Kα radiation (λ = 0.71073 Å): **1**: $C_{35}H_{59}GaN_6Si_2$, M = 689.78, colorless parallelepiped, monoclinic, space group $P2_1/n$, a = 12.3462(4), b = 21.9781(7), c = 14.0957(4) Å, β = 91.064(1)°, Z = 4, D_c = 1.198 g cm^{-3}, μ = 0.813 mm^{-1}, $R1$ = 0.0454 for 4934 [$I > 2\sigma(I)$] data.

2: $C_{35}H_{59}Ga_2N_6Si_2$, M = 689.78, colorless parallelepiped, orthorhombic, space group $Pbcn$, a = 20.1655(8), b = 17.8134(7), c = 21.546(9) Å, Z = 8, D_c = 1.200 g cm^{-3}, μ = 0.815 mm^{-1}, $R1$ = 0.0354 for 9374 [$I > 2\sigma(I)$] data. CCDC 156697 and 156698. See http://www.rsc.org/suppdata/cc/b1/b100466m/ for crystallographic data in .cif or other electronic format.

|| Non-isomeric amide/azide and tetrazole derivatives of germanium have been obtained by reaction of Ge(II) species with azides that have different substituents. See ref. 14.

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