# Stable, Monomeric Imides of Aluminum and Gallium: Synthesis and Characterization of [{HC(MeCDippN)$_2$}MN-2,6-Trip$_2$C$_6$H$_3$] (M = Al or Ga; Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$; Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$)**

Ned J. Hardman, Chunming Cui, Herbert W. Roesky, William H. Fink, and Philip P. Power*

Imides of the Group 13 elements display a strong tendency to oligomerize, especially in the case of the heavier group members.[1–3] This is attributable to the larger size of the heavier elements and the polar character of their metal–nitrogen bonding. Monomeric imides have been reported only for the lightest element boron,[4] for which several examples have been spectroscopically and structurally characterized. The data show that boron and nitrogen have linear or almost linear coordination as well as B–N bond lengths in the range 1.23–1.26 Å. Furthermore, calculations[5] on the hypothetical species HBNH indicate a B–N distance of 1.23 Å and a B–N bond strength of 88 kcal mol$^{-1}$ (cf. a C–C bond length of 1.18 Å and a bond strength of ca. 94 kcal mol$^{-1}$ for isoelectronic acetylene),[6] which are consistent with B–N triple bonding. In contrast, the lowest degree of association known for congeneric aluminum or gallium imides occurs in the dimers of the general formula (RMNR′)$_2$ (M = Al[7–9] or Ga[10]) which have planar M$_2$N$_2$ (M = Al or Ga) core structures. We now show that the reaction [Eq. (1)]

$$[\{HC(CMeDippN)_2\}M] + N_3\text{-}2,6\text{-}Trip_2C_6H_3 \xrightarrow{-N_2} [\{HC(MeCDippN)_2\}MN\text{-}2,6\text{-}Trip_2C_6H_3] \quad (1)$$
$$M = Al,\ \mathbf{1};\ Ga,\ \mathbf{2}$$

of the metal(I) $\beta$-ketiminate monomers [{HC(CMeDippN)$_2$}M:] (Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$; M = Al[11] or Ga[12]) with the sterically encumbered azide N$_3$-2,6-Trip$_2$C$_6$H$_3$ (Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$)[13] yields the compounds [{HC(MeCDippN)$_2$}MN-2,6-Trip$_2$C$_6$H$_3$] (M = Al, **1**; Ga, **2**), which are the first stable monomeric imides of the heavier Group 13 elements.

The reaction shown in Equation 1 occurs near room temperature in toluene, and it affords the products **1** and **2** as pale yellow (**1**) or red (**2**) crystals in moderate yield. The mildness of the reaction conditions and the large size of the ligands are notable features of the synthetic route. Previous approaches to the synthesis of Group 13 imides have usually involved the elimination of alkanes, alkenes, or hydrogen from metal amides which generally proceeds only at elevated temperatures.[1–3, 8, 9] This has frequently led to the activation of ligand C–H bonds rather than an imide product.[10] Another disadvantage of this route is that the elimination of substituents from both the metal and nitrogen lowers their coordination number so that the imide is, in effect, less crowded than the amide precursor. This increases the likelihood of association. On the other hand, the reaction between a univalent metal species and an organoazide[7, 11] (e.g., [Eq. (1)]) increases the metal coordination number, and leaves that of nitrogen unchanged, with the result that steric crowding becomes greater. Nonetheless, previous reactions of this type involving [Cp*M] (Cp* = $\eta^5$-C$_5$Me$_5$, M = Al or Ga) with the azides RN$_3$ (R = Si(*i*Pr$_3$)$_3$, Si(*t*Bu)$_3$, SiPh$_3$, or 2,6-Me$_2$C$_6$H$_3$) have generally led to dimers [(Cp*MNR)$_2$],[7, 11] which suggested that the substituents were insufficiently large to prevent association. In contrast, the recently synthesized metal(I) species [{HC(CMeDippN)$_2$}M:][12, 13] and the bulky azide N$_3$-2,6-Trip$_2$C$_6$H$_3$[14] provide the exceptional degree of crowding required to stabilize monomeric species, thereby enabling the isolation of the imides **1** and **2**.

Although crystals of **1** have not yet proved suitable for X-ray crystallographic studies, crystals of **2** yielded a good data set which, upon refinement, gave the structure presented in Figure 1.[15] The gallium atom is bound to two $\beta$-ketiminate nitrogens N1 and N2 (Ga1–N1, N2 1.920(3), 1.929(3) Å) and the imide nitrogen N3 (Ga1–N3 1.742(3) Å). The former pair of distances are slightly longer than what is normally observed for bonding between three-coordinate nitrogen and a three-coordinate gallium center substituted by three nitrogen ligands[16] (cf. 1.868(1) Å in [Ga{N(SiMe$_3$)$_2$}$_3$]).[17] However, this is consistent with the equal components of normal and dative character in these bonds.[18] In contrast, the Ga–N3 imide distance is shorter than that of currently known Ga–N bonds in a stable compound,[19] and represents a shortening of 6.75% relative to the Ga–N bond in [Ga{N(SiMe$_3$)$_2$}$_3$].[17] Other aspects of the structure of **2** are in harmony with the

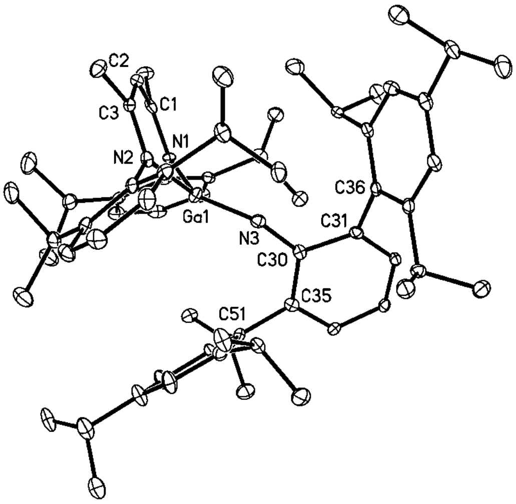

Figure 1. Structure of **2** (thermal ellipsoid (30%)). Selected bond lengths [Å] and angles [°]: Ga1-N3 1.742(3), Ga1-N1 1.920(3), Ga1-N2 1.929(3); Ga1-N3-C30 134.6(3), N1-Ga1-N2 97.47(14), N1-Ga1-N3 140.22(15), N2-Ga1-N2 114.00(15).

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[*] Prof. P. P. Power, N. J. Hardman, Prof. W. H. Fink
Department of Chemistry
University of California, Davis
One Shields Avenue, Davis, CA 95616 (USA)
Fax: (+1) 530-752-8995
E-mail: pppower@ucdavis.edu

Dr. C. Cui, Prof. H. W. Roesky
Institut für Anorganische Chemie der Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)

[**] We are grateful to the National Science Foundation, the Alexander von Humboldt Stiftung for a fellowship award to P.P.P., and the Deutsche Forschungsgemeinschaft for financial support.

multiple character of the Ga–N3 bond. For example, the imide nitrogen has a bent coordination geometry (Ga1-N3-C30 134.6(3)°), which is consistent with the presence of a stereochemically active lone pair of electrons. Thus, there is a total of two electron pairs available for the formation of the Ga1–N3 multiple bond. Although the classical model for such a bond would involve exact alignment of the Ga1 and N3 coordination planes to generate the highest overlap, the substituent sizes do not permit this configuration for steric reasons. The observed torsion angle of 26.4° thus represents a compromise between steric conflict and efficient orbital overlap. The high degree of crowding is also reflected in the N1-Ga1-N3 and N2-Ga1-N3 angles which differ by 26.22°, with the wider Ga1 angle being found in the *z* orientation with respect to the 2,6-$Trip_2C_6H_3$ group. Steric effects are probably also responsible for the slightly nonplanar coordination observed for gallium (Σ° Ga1 351.69°; Figure 2). As with most structures involving the $HC(MeCDippN)_2^-$ ligand, the $C_3N_2M$ ring is folded along the N–N vector.[20] This angle is 28.6° in **2**, and is comparable to the fold angles of 23.8, 26.3, and 33.2° observed in the gallium compounds $[\{HC(MeCDippN)_2\}GaX_2]$ (X = Cl, I, or Me, respectively).[21] The existence of Ga1–N3 multiple bonding in **2** is also supported by $^1H$ and $^{13}C$ NMR spectroscopic data. At 25 °C two sets of resonance signals are visible for the Dipp and methyl substituents of the *β*-diketiminate ring which is consistent with restricted rotation around the Ga–N bond and the presence of a Ga–N π bond involving overlap of gallium and nitrogen p orbitals.

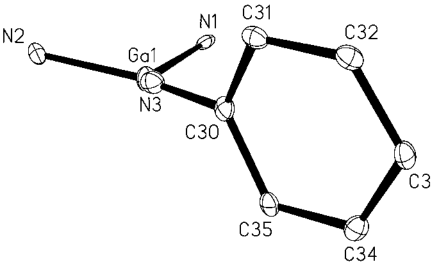
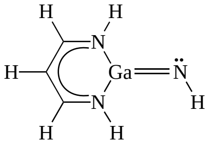


Figure 2. View of **2** along the Ga–N (imide) bond showing the slightly nonplanar geometry at gallium and the relatively low torsion angle between the gallium and nitrogen coordination planes.



To investigate the Ga–N bonding further, restricted Hartree–Fock calculations on the hypothetical molecule were performed with the Gaussian 98 program[22] using a 6-311G(d) basis set. A complete report of the calculations for **2**, and its aluminum congener **1**, will be discussed elsewhere, but some of the salient results are mentioned here. The fully planar geometry with the imido hydrogen atom coplanar with the $GaN_2C_3$ ring was found to be a minimum of the potential energy surface. The geometry, in which the imido hydrogen atom lies perpendicular to the plane of the remainder of the molecule, was optimized to a transition state for Ga–N rotation, and it showed one imaginary frequency. The energy difference between the planar form and the transition state is 48.6 $kJ\,mol^{-1}$, which may be compared with 53.8 for $H_2GaNH_2$, 18.8 for $H_2GaOH$, or 35.3 $kJ\,mol^{-1}$ for $H_2GaSH$, from similar calculations obtained previously.[23, 24] The calculated optimum Ga–N bond lengths were 1.940 and 1.726 Å for the ring nitrogen atoms and the imido nitrogen atom, respectively. These compare very favorably with the corresponding, experimental distances of the substituted compound whose synthesis is reported here (1.920(3), 1.929(3) and 1.742(3) Å). The shortened Ga–N(imide) bond and the energy difference (48.6 $kJ\,mol^{-1}$) between the planar and perpendicular Ga-N-H orientations indicate that π-bond character is present, but relatively weak. The present calculations lend some support to the view that the Ga–N imide bond consists of strong σ donation by the gallium to nitrogen, with weaker π back donation from nitrogen to gallium. Other factors affecting the nature of this bonding (e.g. possible M–N(ring) delocalization) will be discussed in a full account of this work.

In summary, metal(I) species $[\{HC(MeCDippN)_2\}M\colon]$ (M = Al or Ga) are useful precursors for the synthesis of compounds with multiple M–N bonds. Experiments to extend this approach to compounds with multiple bonds between low-coordinate heavier Group 13 metals and other elements are in progress.

## *Experimental Section*

All reactions were performed under anaerobic and anhydrous conditions.

**1**: Toluene (15 mL) was added to a mixture of $[\{HC(MeCDippN)_2\}Al\colon]$ (0.22 g, 0.5 mmol) and $N_3$-2,6-$Trip_2C_6H_3$ (0.265 g, 0.5 mmol) at – 60 °C. The mixture was allowed to warm to room temperature and a slow color change from orange-red to yellow was observed in 1 h. The solution was stirred at room temperature for an additional 3 h, concentrated (ca. 5 mL) and stored at room temperature for 2 days to afford a yellow microcrystalline solid (0.26 g, 52 %) (attempts to grow single crystals of this compound in toluene, benzene, THF, $CH_2Cl_2$ were unsuccessful). M.p. 342 °C. EI-MS: *m/z* (%): 939 (10) [$M^+$], 443 (90) [$M^+$ – HN-2,6-$Trip_2C_6H_3$]. $^1H$ NMR ($C_6D_6$, 500 MHz): $\delta = 7.21$ (m, 1 H; Ph), 7.13 (m, 1 H; Ph), 7.08 (m, 6 H; Ph), 6.97 (m, 3 H; Ph), 6.95 (m, 1 H; Ph), 6.61 (t, 1 H; Ph), 4.82 (s; *γ*-CH), 3.51, 3.41, 3.10 (sept, 3 H; $C\mathit{H}(CH_3)_2$), 2.96–2.83 (m, 3 H; $C\mathit{H}(CH_3)_2$), 2.46, 2.32 (sept, 2 H; $C\mathit{H}(CH_3)_2$), 1.51, 1.45 (s, 6 H; *β*-$CH_3$), 1.38–1.14 (m, 36 H; $CH(CH_3)_2$), 0.95 (q, 8 H; $CH\mathit{Me}_2$), 0.87 (d, 4 H; $CH\mathit{Me}_2$), 0.50 (d, 4 H; $CH(CH_3)_2$), 0.42 (q, 8 H; $CH(CH_3)_2$); $^{13}C$ NMR ($CDCl_3$, 125.73 MHz): $\delta = 169.1$ (CN), 168.9 (CN), 150.8, 149.9, 147.9, 147.6, 147.5, 146.7, 146.6, 146.1, 145.3, 143.7, 143.4, 142.3, 140.0, 138.4, 135.4, 133.4, 130.8, 127.5, 126.3, 125.9, 125.3, 125.2, 124.3, 122.9, 122.6, 122.1, 121.7, 120.7, 119.6, 113.7 (Ph), 98.8 (*γ*-C), 34.4, 33.9, 33.6, 31.4, 30.9, 29.6, 29.4, 28.3, 28.2, 27.4, ($\mathit{C}HMe_2$), 24.3, 24.2 (*β*-Me), 23.9, 23.7, 23.4, 23.3, 22.8, 22.7, 22.3, 22.0, 21.8, 21.1 ($CH\mathit{Me}_2$); $^{27}Al$ NMR ($C_6D_6$): no signal observed. Correct C,H,N analysis.

**2**: A toluene (25 mL) solution of $[\{HC(MeCDippN)_2\}Ga\colon]$ (0.487 g, 1 mmol) was added dropwise to a stirred solution of $N_3$-2,6-$Trip_2C_6H_3$ (0.524 g, 1 mmol) in toluene (10 mL) with cooling in an ice bath. The mixture gradually assumed a red color and nitrogen gas evolution was observed. Stirring was continued for 12 h and the solvent was reduced in volume to about 15 mL. Cooling in a refrigerator (ca. 4 °C) for 20 h afforded yellow crystals of **2** · PhMe. Yield: 0.73 g (74 %); m.p. 229–230 °C; UV/Vis: $\lambda_{max} = 560$ nm (sh); $^1H$ NMR ($C_6D_6$, 300 MHz): $\delta = 7.29$–6.94 (m; ArH), 6.69 (t, $^3J = 7.8$ Hz, 1 H; *p*-$C_6H_3$), 4.71 (s, 1 H; *γ*-CH), 3.56 (sept, $^3J = 6.9$ Hz, 2 H; *p*-$C\mathit{H}(CH_3)_2$), 3.28–2.78 (overlapping septets, 8 H; *o*-$C\mathit{H}(CH_3)_2$), 1.51, 1.46 (s, 6 H; *β*-$CH_3$), 1.40–1.25 (m, 36 H; $CH(CH_3)_2$), 0.96 (q, 8 H; $CH(CH_3)_2$), 0.85 (d, 4 H; $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (75 MHz): $\delta = 170.38$ (CN), 150.91, 150.55, 148.89, 148.13, 147.61, 147.35, 146.11, 144.49, 144.37, 142.32, 140.76, 137.99, 136.01, 134.34, 131.45, 131.19, 125.54, 124.98, 124.59, 124.33, 123.47, 122.70, 120.68, 119.85 (ArC), 97.15 (*γ*-C), 35.00, 34.79, 33.32, 31.22, 30.34, 30.18, 29.33, 28.84, 28.66, 27.90, 27.47, 26.95, 26.84, 25.86, 25.57, 25.39, 25.05, 24.84, 24.58, 23.97, 23.54, 21.79 (alkyl H). Correct C,H,N analysis.

Received: December 27, 2000
Revised: March 1, 2001 [Z16335]

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## The Novel Open-Framework Vanadium Silicates $K_2(VO)(Si_4O_{10})\cdot H_2O$ (VSH-1) and $Cs_2(VO)(Si_6O_{14})\cdot 3H_2O$ (VSH-2)**

Xiqu Wang, Lumei Liu, and Allan J. Jacobson*

Porous silicates that contain transition metals in octahedral or distorted octahedral framework sites have attracted interest in part stimulated by the catalytic properties of the Ti-doped microporous silicate TS-1 for epoxidation reactions.[1, 2] A prominent example of a mixed octahedral/tetrahedral compound is the titanium silicate ETS-10 that has a 12-ring channel system. The framework of ETS-10 contains single chains of corner-shared $TiO_6$ octahedra isolated from each other by silicate tetrahedra and as a consequence has unusual optical properties in addition to its absorption and catalytic properties.[3–8]

In contrast to octahedral/tetrahedral frameworks containing titanium and zirconium, analogous open-framework systems based on niobium and vanadium as the octahedral or distorted octahedral component are relatively rare. A vanadium silicate called AM-6 with the same structure as ETS-10 has been reported.[9] The only other known open-framework silicates containing vanadium are cavansite and

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[*] Prof. A. J. Jacobson, Dr. X. Wang, L. Liu
Department of Chemistry
University of Houston
Houston, TX 77204-5641 (USA)
Fax: (+1) 713-743-2787
E-mail: ajjacob@uh.edu

[**] We thank the National Science Foundation (DMR-9805881) and the Robert A. Welch Foundation for support. This work made use of MRSEC/TCSUH Shared Experimental Facilities supported by the National Science Foundation under Award Number DMR-9632667 and the Texas Center for Superconductivity at the University of Houston.

1433-7851/01/4011-2174 $ 17.50+.50/0