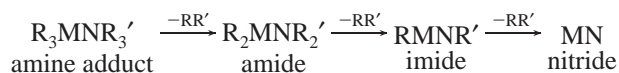# Synthesis and Characterization of the Monomeric Imides Ar′MNAr′′ (M = Ga or In; Ar′ or Ar′′ = Terphenyl Ligands) with Two-Coordinate Gallium and Indium

Robert J. Wright, Andrew D. Phillips, Thomas L. Allen, William H. Fink, and Philip P. Power*

Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, California 95616

Received November 20, 2002 ; E-mail: pppower@ucdavis.edu

There is an extensive chemistry of species with bonding between heavier group 13 elements and nitrogen.[1] Such compounds are of interest because they are isoelectronic to the corresponding carbon group 14 element derivatives, which permits interesting comparisons of properties. Also, some group 13 element nitrogen compounds, for example, gallium nitride, have important electronic applications. They can be synthesized by decomposition of molecular species in which hydrogen or organic substituents are eliminated as in[2]

$$\underset{\text{amine adduct}}{R_3MNR_3'} \xrightarrow{-RR'} \underset{\text{amide}}{R_2MNR_2'} \xrightarrow{-RR'} \underset{\text{imide}}{RMNR'} \xrightarrow{-RR'} \underset{\text{nitride}}{MN}$$

where M is Al−Tl and R and R′ are hydrogen or organic substituents.

The amine adducts[3] and amides[4] have been widely studied. The imides have also received much attention. They are usually found as strongly associated species $(RMNR')_n$ ($n \geq 4$) that have cage structures.[5] There are a few lower aggregate rings, $(RMNR')_2$[6] or $(RMNR')_3$,[7] that have three coordinate metals where M−N multiple bonding is possible. Although monomeric species, RMNR′, in which both M and N are two coordinate, and where a unique triple M−N interaction may be observed, are known for boron,[8] they are unknown for Al−Tl. Here, we describe two monomeric heavier group 13 element imides, whose structures and bonding differ considerably from those of their boron congeners.

The gallium and indium imides **1** and **2** were obtained by the reaction of the recently reported dimers Ar′MMAr′ (Ar′ = C$_6$H$_3$-2,6-Dipp$_2$; Dipp = C$_6$H$_3$-2,6-Pr$^i_2$; M = Ga or In)[9] with 2 equiv of the azide N$_3$Ar′′ (Ar′′ = C$_6$H$_3$-2,6(Xyl-4-Bu^t)$_2$) as shown by[10]

$$Ar'MMAr' + 2N_3Ar'' \xrightarrow[\text{hexane}]{0\,^\circ\text{C}} 2Ar'MNAr'' + 2N_2$$
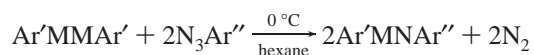
where M is Ga (**1**) or In (**2**), Ar′ = C$_6$H$_3$-2,6-Dipp$_2$ (Dipp = C$_6$H$_3$-2,6-Pr$^i_2$), and Ar′′ = C$_6$H$_3$-2,6(Xyl-4-Bu^t)$_2$.

The reaction proceeded readily in hexane at ca. 0 °C with N$_2$ evolution. The products were isolated as red (**1**) or green (**2**) crystals, which were characterized by spectroscopy and by X-ray crystallography.[11] Structural details are given in Table 1.

The monomers **1** (Figure 1) and **2** have a trans-bent, almost planar, CMNC core. The terphenyl ligands are arranged so that the central (i.e., C(1)) aryl ring at M(1) lies almost perpendicularly to the C(1)−M(1)−N(1) plane. In contrast, the aryl ring attached to the N(1) atom is almost coplanar with the C(31)−N(1)−M(1) array. Both M−N bonds are the shortest recorded between these elements in a stable compound. The Ga−N distance of 1.701(3) Å is shorter than the 1.82−1.94 Å range in monomeric Ga amides[4] and the 1.742(3) Å in the β-diketiminate imide species {H(CMe-CDippN)$_2$}GaNC$_6$H$_3$-2,6-Trip$_2$ (Trip = C$_6$H$_2$-2,4,6-Pr$^i_3$).[12] Similarly, the In−N bond in **2**, 1.928(3) Å, is significantly shorter than the 2.05−2.09 Å range in unassociated In amides.[4]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Imides Ar′MNAr′′, **1** (M = Ga) and **2** (M = In)

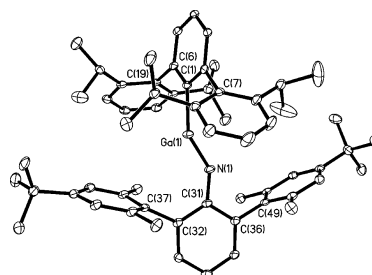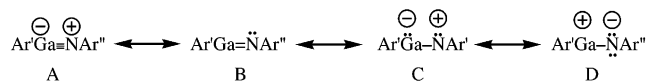| parameter	Ga (**1**)	In (**2**)
M−N	1.701(3)	1.928(3)
M−C	1.940(3)	2.127(3)
N−C	1.377(5)	1.355(4)
N−M−C	148.2(2)	142.2(1)
M−N−C	141.7(3)	134.9(2)
C−M−N−C	177.7(4)	173.5(3)

Figure 1. Thermal ellipsoid plot (without H atoms) of **1**. The structure of **2** is analogous. Bond distances and angles are given in Table 1.

Apart from the M−N bond lengths, the most notable feature of **1** and **2** is the trans-bent arrangement of the core C(1)M(1)N(1)C-(31) atoms. The trans-bending in **2** exceeds that in **1** by ca. 6° at the metal and nitrogen atoms. The bent geometry contrasts with the linearity of the boron imides RBNR, which have short B−N distances in the range ca. 1.23−1.26 Å[8] (cf., 1.18 Å in acetylene)[13] consistent with B−N triple bonding. Moreover, the B−N bond strength in HBNH has been calculated to be only slightly less than that in HCCH.[14] The M−N bonding in **1** and **2** can be regarded as an interaction of the triplet forms of the nitrene Ar′′N and the monovalent metal species Ar′M. The nitrene Ar′′N probably exists as a triplet in the ground state because photodetachment experiments on the related PhN showed it to be ca. 4 kcal mol^{-1} lower in energy than the singlet.[15] For the Ar′M moieties, calculations on the model species M−H have shown that the triplet states lie 46.7 (Ga) and 47 (In) kcal mol^{-1} above the singlet forms.[16] Thus, the sum of the singlet−triplet gaps for the Ar′′N and Ar′M fragments is probably in the range 40−45 kcal mol^{-1}. Their combination leads initially to a doubly bonded structure with an MN bond strength of at least 40−45 kcal mol^{-1}, in which the lone pair remains on nitrogen as illustrated by B. Alternatively, the structure could be described as an adduct between the singlet Ar′Ga and singlet nitrene to give D.

$$\underset{A}{\overset{\ominus\ \oplus}{Ar'Ga\!\equiv\!NAr''}} \longleftrightarrow \underset{B}{Ar'Ga\!=\!\ddot{N}Ar''} \longleftrightarrow \underset{C}{\overset{\ominus\ \oplus}{Ar'\ddot{Ga}\!-\!NAr'}} \longleftrightarrow \underset{D}{\overset{\oplus\ \ominus}{Ar'Ga\!-\!\ddot{N}Ar''}}$$

However, the structures of **1** and **2** show that there is a bent geometry at the metal, suggesting a contribution from C. Calculations[17] for trans-RGaNR (R = H or Ph) model compounds afford
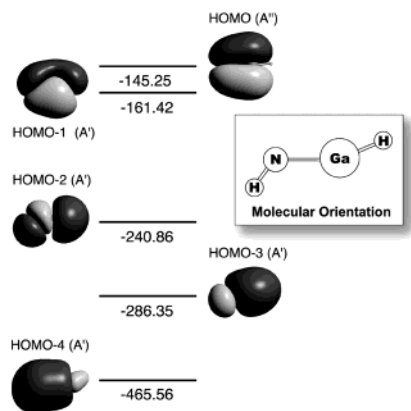
Figure 2. MO illustrations and energies (kcal mol^{-1}) for HNGaH (as drawn) at the B3YLP level of theory.

Ga−N distances of 1.682 (R = H) and 1.701 Å (R = Ph), in good agreement with the experimental value, as well as very low barriers to linearization of ca. 1 kcal mol^{-1}. The softness of the trans-bending angles agrees with the essentially negligible strength of the "extra" N → Ga π-donor interaction (structure A), and this is in line with the AIM bond order of 1.574 calculated for trans-bent HGaNH (Ga−N = 1.682 Å, HNGa = 129.9°, HGaN = 166.1°), which points to a structural model between B and C.

MO calculations for HNMH (M = Ga or In) model species show that the HOMO has M−N π-character; HOMO-1 has lone pair/π-character which correlates with the M−H and N−H bonds. HOMO-2 has M−N σ-bond character, whereas HOMO-3 and -4 are associated with M−H and N−H bonding (Figure 2). These results are in agreement with data for HAlNH where a trans-bent structure (Al−N = 1.633 Å, HAlN = 165.2°, HNAl = 154.5°) and a low linearization barrier (0.2 kcal mol^{-1}) were calculated.[18] It was predicted that the isomer AlNH$_2$ is 40 kcal mol^{-1} more stable than HAlNH. Moreover, AlNH$_2$ should be isolable due to the high energy of the transition state (72.4 kcal mol^{-1} above AlNH$_2$) between them. The synthesis of MNR$_2$ (M = Al−In) species isomeric to **1** and **2** is in hand.

Supporting Information Available: CIF data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Blackie-Chapman & Hall: London, 1993.

(2) For the reviews of various precursors to III-V compounds, see: Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. Jegier, J. A.; Gladfelter, W. L. *Coord. Chem. Rev.* **2000**, *206−207*, 631.

(3) Gardiner, M. G.; Raston, C. L. *Coord. Chem. Rev.* **1997**, *166*, 1.

(4) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood-Wiley: Chichester, 1979. Brothers, P. J.; Power, P. P. *Adv. Organomet. Chem.* **1996**, *39*, 1. Carmalt, C. J. *Coord. Chem. Rev.* **2001**, *223*, 217.

(5) Cesari, M.; Cucinella, S. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, B. D., Eds.; Academic: London, 1987; Vol. 1, Chapter 6.

(6) Schulz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 969. Fischer, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 271. Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 791. Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. *Organometallics* **1999**, *18*, 2037.

(7) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

(8) Paetzold, P. *Prog. Inorg. Chem.* **1987**, *31*, 123.

(9) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2842. Wright, R. J.; Phillips, A. D.; Hardman, N. J.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 8538.

(10) The azide Ar″N$_3$ was synthesized in a manner similar to that described for 2,6-Trip$_2$H$_3$C$_6$N$_3$.[10a] Yield 63%; mp 124−127 °C (dec 145 °C). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 1.34 (s, 18H, *p*-C(CH$_3$)$_3$), 2.09 (s, 12H, *o*-CH$_3$), 7.07 (d, 2H, *m*-C$_6$H$_3$) $^3J_{HH}$ = 7.5 Hz, 7.13 (s, 4H, *m*-(4-Bu^t-Xyl)), 7.23 (t, 1H, *p*-C$_6$H$_3$) $^3J_{HH}$ = 7.5 Hz. ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz, 25 °C): δ = 21.02 (*o*-CH$_3$) 31.63 *p*-(CH$_3$)$_3$, 34.61 (*p*-C(CH$_3$)$_3$), 124.22 (*m*-(4-Bu^t-Xyl)), 125.28 (*p*-C$_6$H$_3$), 129.99 (*m*-C$_6$H$_3$), 134.57 (*i*-(4-Bu^t-Xyl)), 134.90 (*o*-C$_6$H$_3$), 136.07 (*o*-(4-Bu^t-Xyl)), 137.05 (*i*-C$_6$H$_3$), 150.69 (*p*-(4-Bu^t-Xyl)). IR: $\nu_{(N-N)}$ 2060 cm^{-1}, 2140 cm^{-1}. **1** and **2**: Under anaerobic and anhydrous conditions, Ar″N$_3$ (0.366 g, 0.835 mmol) in hexane (30 mL) was added dropwise to a solution of Ar′GaGaAr′ (0.390 g, 0.418 mmol) in hexane (40 mL) with cooling to ca. 0 °C. Gas (N$_2$) was evolved, and the solution changed from a green to a deep red color. Stirring was continued overnight, and the solution was warmed to room temperature. Upon reducing the volume to ca. 10 mL, the product **1** precipitated as a red solid. Yield: 0.33 g, 45%; mp 215−216 °C. A saturated solution of **1** in hexane afforded crystals suitable for X-ray crystallography at ca. −20 °C. The indium imide was synthesized in an analogous manner and recrystallized from −20 °C toluene to give **2** as dark green crystals. Yield: 0.330 g, 45%; mp 184−185 °C. **1**, ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 0.97 (d, 12H, *o*-CH(CH$_3$)$_2$) $^3J_{HH}$ = 6.4 Hz, 0.98 (d, 12H, *o*-CH(CH$_3$)$_2$) $^3J_{HH}$ = 6.4 Hz, 1.42 (s, 18H, *p*-C(CH$_3$)$_3$), 2.03 (s, 12H, *o*-CH$_3$), 2.54 (sept, 4H, CH(CH$_3$)$_2$) $^3J_{HH}$ = 6.4 Hz, 6.67 (t, 1H, *p*-C$_6$H$_3$, Ar′) $^3J_{HH}$ = 7.2 Hz, 6.75 (d, 2H, *m*-C$_6$H$_3$, Ar″) $^3J_{HH}$ = 7.6 Hz, 7.03 (m, 3H, Ar−H), 7.118 (s, 4H, *m*-(4-Bu^t-Xyl)), 7.15 (d, 4H, *m*-Dipp) $^3J_{HH}$ = 7.6 Hz, 7.25 (t, 2H, *p*-Dipp) $^3J_{HH}$ = 7.6 Hz. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 25 °C): δ = 21.33 (*o*-CH$_3$), 24.85 (*o*-CH-(CH$_3$)$_2$), 25.45 (*o*-CH(CH$_3$)$_2$), 31.29 (*o*-CH(CH$_3$)$_2$), 32.05 (*p*-C(CH$_3$)$_3$), 34.57 (*p*-C(CH$_3$)$_3$), 117.42 (*p*-C$_6$H$_3$, Ar′), 123.91 (*m*-Dipp), 124.87 (*m*-(4-Bu^t-Xyl)), 128.82, 129.94 (*m*-C$_6$H$_3$ unassigned), 130.40 (*p*-C$_6$H$_3$ unassigned), 134.54, 136.57 (*o*-(4-Bu^t-Xyl)), 140.52, 140.75, 145.44, 147.06 (*o*-C$_6$H$_3$, Ar′), 147.60, 148.17, 150.52 (*p*-(4-Bu^t-Xyl)), 152.76 (*i*-C$_6$H$_3$, Ar′). UV/vis (hexanes): λ_{max} nm (ϵ, mol L^{-1} cm^{-1}): 303 (26 500), 366 (3900). **2**, ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 0.97 (d, 12H, *o*-CH(CH$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz, 1.04 (d, 12H, *o*-CH(CH$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz, 1.40 (s, 18H, *p*-C(CH$_3$)$_3$), 2.09 (s, 12H, *o*-CH$_3$), 2.58 (sept, 4H, CH(CH$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz, 6.60 (t, 1H, *p*-C$_6$H$_3$, Ar′) $^3J_{HH}$ = 7.6 Hz, 6.83 (d, 2H, *m*-C$_6$H$_3$, Ar″) $^3J_{HH}$ = 7.2 Hz, 7.0−7.10 (m, 3H, Ar−H unassigned), 7.13 (d, 4H, *m*-Dipp) $^3J_{HH}$ = 7.5 Hz, 7.15 (s, 4H, *m*-(4-Bu^t-Xyl)), 7.24 (t, 2H, *p*-Dipp) $^3J_{HH}$ = 7.2 Hz. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz, 25 °C): δ = 20.82 (*o*-CH$_3$) 24.28 (*o*-CH(CH$_3$)$_2$), 25.37 (*o*-CH(CH$_3$)$_2$), 30.93 (*o*-CH(CH$_3$)$_2$), 31.78 (*p*-C(CH$_3$)$_3$), 34.40 (*p*-C(CH$_3$)$_3$), 114.40 (*p*-C$_6$H$_3$, Ar′), 123.92 (*m*-Dipp), 124.85 (*m*-(4-Bu^t-Xyl)), 129.39 (*p*-Ar unassigned), 129.73 (*m*-Ar unassigned), 130.50 (*p*-Ar unassigned), 136.86 (*o*-(4-Bu^t-Xyl)), 140.62, 141.61, 146.76 (*o*-Dipp), 146.83 (*o*-C$_6$H$_3$, Ar′), 147.93, 155.30 (*p*-(4-Bu^t-Xyl)), 162.15 (*i*-C$_6$H$_3$, Ar′). UV/vis (hexanes): λ_{max} nm (ϵ, mol L^{-1} cm^{-1}): 291 (11 100), 359 (6940). (a) Twamley, B.; Hwang, C. S.; Hardman, N. J.; Power, P. P. J. *Organomet. Chem.* **2000**, *609*, 152.

(11) Crystal data for compounds **1**·0.5C$_6$H$_{12}$, **2**·0.5C$_7$H$_8$, and N$_3$Ar″ at 90 K with Mo Kα (λ = 0.71073 Å) radiation: (**1**·0.5C$_6$H$_{12}$) a = 11.7036(6) Å, b = 24.8171(12) Å, c = 18.4566(9) Å, β = 91.4380(10)°, monoclinic, space group P2$_1$/n, Z = 4, R1 = 0.0517 for 5838 (I > 2σ(I)) data, wR2 = 0.1293 for all (7669) data; (**2**·0.5C$_7$H$_8$) a = 11.7845(16) Å, b = 24.639(3) Å, c = 18.441(2) Å, β = 90.402(4)°, monoclinic, space group P2$_1$/n, Z = 4, R1 = 0.0422 for 6980 (I > 2σ(I)) data; N$_3$Ar″ a = 24.9918(19) Å, b = 6.3325(5) Å, c = 32.709(2) Å, β = 95.868(4)°, monoclinic, space group P2$_1$/c, Z = 4, R1 = 0.0728 for 6897 (I > 2σ(I)) data.

(12) Hardman, N. J.; Cui, C.; Roesky, H. W.; Fink, W. H.; Power, P. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2172.

(13) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 5th ed.; Wiley: New York, 2001; pp 20−24.

(14) Baird, C.; Datta, R. K. *Inorg. Chem.* **1972**, *11*, 17.

(15) Drzaic, P. S.; Brauman, J. I. *J. Phys. Chem.* **1984**, *88*, 5285.

(16) Treboux, G.; Barthelat, J.-C. *J. Am. Chem. Soc.* **1993**, *115*, 4870.

(17) Calculations were performed using a hybrid method[17a] of Hartree−Fock and density functional theories (DFT) with Becke's exchange functional (B3)[17b] and the Lee−Yang−Parr nonlocal correlation function (LYP).[17c] A 6-31G basis set was employed for H; 6-31(d) and 6-311G(d) were used for C, N and Ga, respectively. Calculations were performed using the Gaussian 98 suite of programs.[17d] The molecule represents an energy minimum and is optimized as having C_s symmetry. (a) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (b) Becke, A. D. *Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Wang, Y.; Parr, R. G. *Phys. Rev.* **1998**, *B37*, 78. (d) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.

(18) Davy, R. D.; Jaffrey, K. L. *J. Phys. Chem.* **1994**, *98*, 8930.

JA029422U