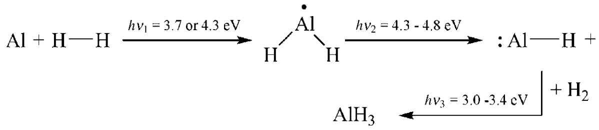
Gallium Chemistry (2)

DOI: 10.1002/anie.200805982

Addition of Hydrogen or Ammonia to a Low-Valent Group 13 Metal Species at 25 °C and 1 Atmosphere[**]

*Zhongliang Zhu, Xinping Wang, Yang Peng, Hao Lei, James C. Fettinger, Eric Rivard, and Philip P. Power**

In Group 13 metal chemistry, the direct reaction of metal atoms with small molecules such as H_2, CO, or NH_3 has enabled numerous simple derivatives with unusual bonding, coordination, or reactivity to be trapped and studied at low temperatures in frozen, inert matrixes.[1,2] The characterization of these species by spectroscopic and computational methods has provided much useful bonding and reactivity information. For example, it was reported that the direct reaction of H_2[3] or NH_3[4] with the metals under photolysis affords, among other things, compounds such as MH, MH_2, MH_3, M_2H_2, $HMNH_2$, MNH_2, or H_2MNH_2 (M = Al, Ga, or In). The pathway for the formation of AlH_3 involves the sequence shown in Scheme 1,[5–7] in which H_2 is added to monovalent :Al−H in the final step. A similar mechanism was also proposed for the photolysis of monovalent :Ga−H to afford GaH_3 in solid hydrogen.[8] To date, there are no examples of addition reactions of H_2 or NH_3 with heavier Group 13 metal compounds under ambient conditions. However, in the case of the lightest Group 13 element boron, it has been shown that H_2 reacts reversibly with a phosphonium borate species $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$.[9] Furthermore, work in the neighboring Group 14 elements has demonstrated that H_2 reacts with digermynes,[10] distannynes,[11] and stable carbenes[12] and that NH_3 reacts with stable carbenes[12] or a stannylene[13] under ambient conditions. Recent experimental results have shown that heavier Group 13 species MR (M = Ga, In, or Tl;[14,15] R = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$ (Ar′) or 2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$ (Ar*)) or MNR_2 (M = Ga[16] or Tl,[17] NR_2 = N(SiMe$_3$)(2,6-Mes$_2$C$_6$H$_3$) or N(Me)(2,6-Mes$_2$C$_6$H$_3$), Mes = 2,4,6-Me$_3$C$_6$H$_2$) exist as monomeric species either in solution or the solid state at room temperature (the alkyl species :GaC(SiMe$_3$)$_3$ is also known to be monomeric in solution and in the vapor phase, although it is tetrameric in the solid state[16]). The presence of a one-coordinate metal center in these compounds suggests that they could display a reactivity similar to that shown for the last step in Scheme 1. Furthermore, if the reaction could be carried out at room temperature, the greater than 200 K temperature difference might allow it to proceed without the necessity for photolysis. We describe herein the treatment of solutions of the gallium(I) aryl species GaAr (Ar = Ar′ or 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$-4-(Me$_3$Si)C$_6$H$_2$ (Ar″)) with H_2 and NH_3 and show that the reactions proceed readily at 25 °C and 1 atm pressure to give the products {Ar′Ga(μ-H)H}$_2$ (**1**) or {Ar″Ga(μ-NH$_2$)H}$_2$ (**5**) in good yield.



Scheme 1. Low-temperature reactions of atomic aluminum and hydrogen.[5–7]

Although experimental observations in solid hydrogen matrix and corresponding theoretical calculations showed that hydrogenation of the simple monovalent gallium(I) species GaH to GaH_3 is not spontaneous and requires a considerable activation energy of 43.1 kcal mol^{-1},[8,18] the reaction between (GaAr′)$_2$ (**3**, monomeric in solution) and H_2 gas proceeded smoothly, and the toluene solution of **3** faded from a deep green color to light brown within 3 h. Cooling of the resulting solution to 8 °C produced pale yellow crystals of {Ar′Ga(μ-H)H}$_2$ (**1**).[19] Various attempts to synthesize **1** through an alternative route involving the reaction of an organogallium(III) halide Ar′GaX$_2$ (X = Cl and I) with hydride sources such as (iBu$_2$AlH)$_2$, NaH, LiBH$_4$, and LiBHEt$_3$ resulted in mixtures of products, and ^{1}H NMR spectroscopy of the reaction mixtures indicated the absence of the target compound **1**. However, the reaction of the β-diketiminate gallium halide LGaI$_2$ (L = {N(C$_3$H$_3$-2,6-iPr$_2$)C(Me)}$_2$CH) with LiH·BEt$_3$ has been reported to give monomeric LGaH$_2$ in high yield.[20] Compound **1** (Figure 1) crystallizes as a centrosymmetric dimer with gallium atoms bound to both terminal and bridging hydrogen atoms, which were located on an electron difference map. The Ga-H-Ga and H-Ga-H angles are 93.4(8) and 86.6(8)°, respectively. A close Ga···Ga separation of 2.5275(3) Å is observed, mainly as a result of the relative shortness of the Ga−H bonds. The bridging Ga−H bond lengths are 1.69(2) and 1.78(2) Å, and the terminal Ga−H bond length is 1.46(2) Å. There is a dihedral angle of 56.3° between the Ga$_2$H$_2$ plane and the plane of the central ring of the Ar′ group. The terminal Ga−H bond length is similar to those of published examples with bulky aryl ligands, such as monomeric Mes*$_2$GaH (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$),[21] Ar$^{\#}_2$GaH (Ar$^{\#}$ = C$_6$H$_3$-2,6-Mes$_2$),[21] and

---

[*] Z. L. Zhu, Dr. X. Wang, Y. Peng, H. Lei, Dr. J. C. Fettinger,
Dr. E. Rivard, Prof. P. P. Power
Department of Chemistry, University of California
One Shields Avenue, Davis, CA 95616 (USA)
Fax: (+1) 530-752-8995
E-mail: pppower@ucdavis.edu

[**] We thank the Department of Energy Office of Basic Energy Sciences DE-FG-02-07ER4675 for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200805982.

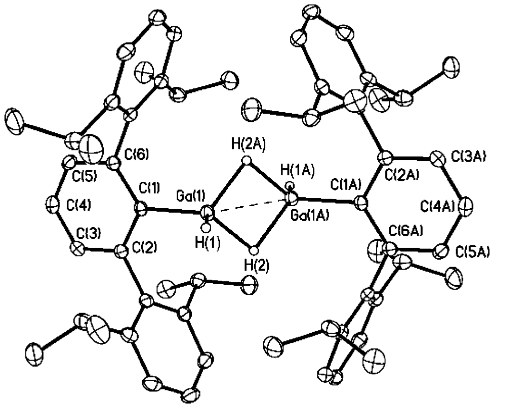


Figure 1. Thermal ellipsoid (50%) plot of **1**. Carbon-bound hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga(1)–H(1) 1.46(2), Ga(1)–H(2) 1.69(2), Ga(1)–H(2A) 1.78(2), Ga(1)–Ga(1A) 2.5275(3), Ga(1)–C(1) 1.9862(13); C(1)-Ga(1)-H(1) 116.2(8), C(1)-Ga(1)-H(2) 119.8(8), C(1)-Ga(1)-H(2A) 109.7(7), H(1)-Ga(1)-H(2) 103.8(11), Ga(1A)-Ga(1)-H(1) 119.0(8), Ga(1)-H(2)-Ga(1A) 93.4(8), C(1)-Ga(1)-Ga(1A) 124.77(4); the dihedral angle between the Ga_2H_2 ring and the central aryl planes is 56.3°.

dimeric $(Trip_2GaH)_2$ (Trip = 2,4,6-$i$$Pr_3C_6H_2$).[21] Examination of the ^{1}H NMR spectrum for **1** in C_6D_6, however, revealed only one signal corresponding to the gallium hydride at $\delta =$ 7.67 ppm that had a 1:1 intensity ratio with respect to the aryl ligand resonances. The IR spectrum of **1** in nujol displays one medium-intensity band at 1844 cm^{-1}, which is within the terminal Ga–H bond stretching range of 1720 to 2050 cm^{-1}.[21–23]

The same procedure as that employed for **1**, using D_2 instead of H_2, afforded the deuteride **2**. The ^{1}H NMR spectrum of **2** in C_6D_6 was identical to that of **1**, except that the assigned Ga–H signal at $\delta = 7.67$ ppm was not observed (Figure 2). However, a signal at $\delta = 7.70$ ppm was found in the deuterium (^{2}H) NMR spectrum of **2** in benzene and clearly shows the formation of a Ga–D bond instead of a Ga–H bond. Variable-temperature ^{2}H NMR experiments of **2** were also performed in toluene from room temperature to −30 °C. A similar Ga–D signal was found at $\delta = 7.67$ ppm, and this signal remained a sharp singlet during the temperature change. When **2** was dissolved in a donor solvent, diethyl ether, a significant upfield shift of the Ga–D signal was observed ($\delta = 4.86$ ppm). This shielded position of the Ga–D resonance is consistent with those of well-known amine gallane adducts in the range of $\delta = 4.5$ to 5.0 ppm,[24] indicating that base-free deuteride **2** readily formed a complex with diethyl ether. Both **1** and **2** are thermally stable at room temperature, and decomposition starts to occur at relatively high temperatures around 200 °C.

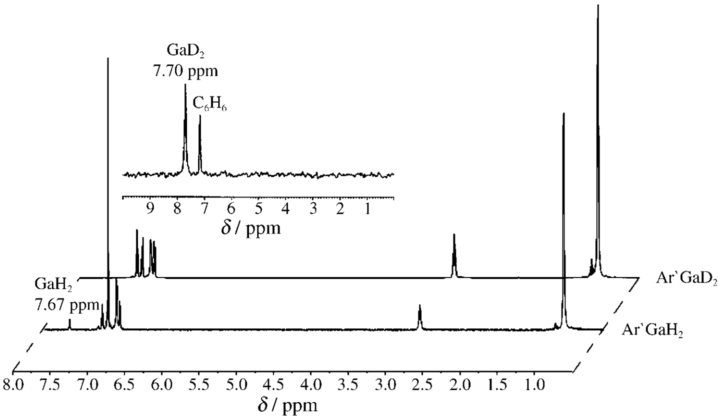


Figure 2. ^{1}H NMR spectra of **1** and **2**; the inset shows the ^{2}H NMR spectrum of **2**.

Ammonation of organogallium(III) species at high temperature is a well-known route for the preparation of gallium nitride.[25] However, to our knowledge, reaction of NH_3 with a low-valent Ga^I species is rare and has only been reported for the reaction of neopentylgallium(I) $\{Ga(CH_2CMe_3)\}_n$ with NH_3 at temperatures above 460 °C,[25a] which gives $C(CH_3)_4$, H_2, and GaN. The $(GaAr)_2$ compounds (Ar = Ar′ (**3**) and Ar″ (**4**)) react readily with NH_3 at room temperature to yield colorless crystals of $\{Ar''Ga(\mu\text{-}NH_2)H\}_2$ (**5**) suitable for X-ray diffraction[19] or $\{Ar'Ga(\mu\text{-}NH_2)H\}_2$ (**6**) as a colorless, amorphous solid. Compound **5** has a centrosymmetric dimeric structure (Figure 3) in which the gallium atoms are symmetrically bridged by the NH_2 ligands, the hydrogen atoms of which were located in the electron density map. The rhombohedral Ga_2N_2 core is planar with N-Ga-N and Ga-N-Ga angles of 85.19(7) and 91.81(7)°, respectively, and subtends a dihedral angle of 42.8° with respect to the central aryl plane of the terphenyl ligand. The Ga–N bridging bond length of 1.986(2) Å is within the reported 1.928–2.053 Å range observed in the trimers $(Me_2GaNH_2)_3$[25a] and $(tBu_2GaNH_2)_3$.[25e] However, it is longer than the 1.847–1.857 Å observed in $LGa(NH_2)_2$ (L = HC{(CMe)(2,6-$i$$Pr_2C_6H_3N$)}$_2$), in which NH_2 is a terminal ligand.[25f] The gallium atoms are each bound to a terminal hydrogen atom, which can also be located in the electron density map, with a Ga–H bond of 1.54(2) Å and N-Ga-H angle of 109.4(6)°. The IR spectrum displayed two weak but

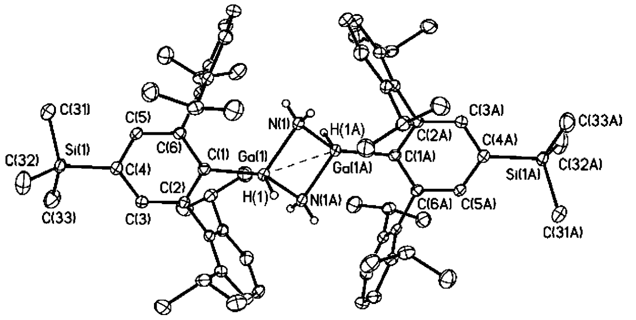


Figure 3. Thermal ellipsoid (30%) plot of **5**. Carbon-bound hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga(1)–H(1) 1.54(2), Ga(1)–N(1) 1.986(2), Ga(1)–N(1A) 1.988(2), Ga(1)–C(1) 1.991(2), Ga(1)–Ga(1A) 2.9257(5); C(1)-Ga(1)-N(1) 115.90(7), C(1)-Ga(1)-N(1A) 117.55(7), C(1)-Ga(1)-H(1) 118.3(6), N(1)-Ga(1)-H(1) 109.4(6), Ga(1)-N(1)-Ga(1A) 94.81(7), N(1)-Ga(1)-N(1A) 85.19(7), Ga(1)-C(1)-C(2) 120.80(13); the dihedral angle between Ga_2N_2 and central aryl planes is 42.8°.

sharp bands at 3365 and 3310 cm^{-1} arising from the two N–H stretching modes of the NH_2 groups and one sharp band of medium intensity at 1864 cm^{-1} arising from the Ga–H stretching mode. Examination of the ^{1}H NMR spectrum of **5** in C_7D_8 also confirmed the presence of the amido hydride gallium core, with signals corresponding to the gallium amide and gallium hydride units at $\delta = -0.55$ and 4.52 ppm, respectively, in the correct intensity ratio to the aryl ligand resonances (Figure 4).

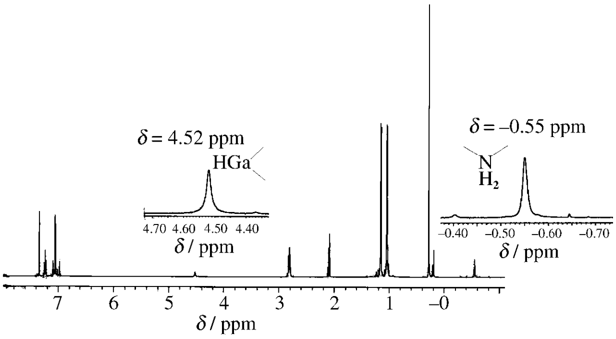


Figure 4. ^{1}H NMR spectrum of **5** in C_7D_8.

In summary, we have shown that a low-valent aryl gallium(I) species readily undergoes insertion into H–H or N–H bonds at room temperature and 1 atm pressure. These reactions represent rare instances of insertion of main-group centers into these bonds under ambient conditions.[9–13] Unlike the corresponding reactions of H_2 or NH_3 with $SnAr'_2$, which afford $\{Ar'Sn(\mu\text{-}H)\}_2$ or $\{Ar'Sn(\mu\text{-}NH_2)\}_2$ products and eliminate Ar′H,[13] the reactions of **:**GaAr do not result in arene (Ar′H) elimination. Instead, the reactions proceed by simple addition of these molecules to a heavier main-group-element center. The insertion into the N–H bond of NH_3 is particularly noteworthy because of the current interest in the involvement of such reactions in important catalytic cycles.[26]

Experimental Section

Standard Schlenk techniques were used for all syntheses, and all sample manipulations were carried out under anaerobic and anhydrous conditions. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 600 spectrometer and referenced to known standards. ^{2}H NMR spectra were recorded on a Bruker 500 spectrometer and referenced to known standards.

$\{ArGa(\mu\text{-}H)H\}_2$ (**1**) and $\{ArGa(\mu\text{-}D)D\}_2$ (**2**): A deep green solution of Ar′GaGaAr′ (**3**, 0.50 g, 0.53 mmol) in toluene (30 mL) was stirred at room temperature for 3 h under a H_2 atmosphere to give a light brown solution. Storage of the solution at approximately 8 °C afforded X-ray quality pale yellow crystals of **1**. More crystals of **1** were obtained by continued concentration and cooling of the mother liquor. Yield: 0.31 g, 62 %; decomposed into dark brown solid upon heating to 220 °C, then melted at 235 °C. ^{1}H NMR (600 MHz, C_6D_6, 25 °C): $\delta = 1.04$ (d, 48 H, $o\text{-CH}(CH_3)_2$, $^3J_{HH} = 6.6$ Hz), 2.97 (sept, 8 H, $CH(CH_3)_2$, $^3J_{HH} = 7.2$ Hz), 6.99 (d, 4 H, $m\text{-}C_6H_3$, $^3J_{HH} = 7.2$ Hz), 7.04 (d, 8 H, $m\text{-}C_6H_3\text{-}i\text{Pr}_2$, $^3J_{HH} = 7.8$ Hz), 7.16 (t, 2 H, $p\text{-}C_6H_3$, $^3J_{HH} = 7.8$ Hz), 7.23 (t, 4 H, $p\text{-}C_6H_3\text{-}i\text{Pr}_2$, $^3J_{HH} = 7.8$ Hz) 7.67 ppm (s, 2 H, GaH_2); $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz, 25 °C): $\delta = 24.1$ ($o\text{-CH}(CH_3)_2$), 25.5 ($o\text{-CH}(CH_3)_2$), 30.7 ($o\text{-}CH(CH_3)_2$), 123.8, 127.9, 128.1, 129.2, 139.3, 145.4, and 147.1 ppm (Ar*C*), the signal of *ipso*-C_6H_3 was not found; IR (Nujol): $\tilde{\nu} = 1844$ cm^{-1} (ν_{GaH_2}, medium). Compound **2** was prepared in a similar way to that described for **1** under a D_2 atmosphere. ^{1}H NMR (600 MHz, C_6D_6, 25 °C): essentially the same as **1** except that the GaH_2 peak was absent; $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz, 25 °C): essentially the same as **1**. $^2H\{^1H\}$ NMR (C_6H_6, 76.8 MHz, 25 °C): $\delta = 7.70$ ppm (GaD_2).

$(Ar''Ga)_2$ (**4**): A rapidly stirred slurry of “GaI” (2.60 g, 10.5 mmol) in toluene (20 mL) at ca. −78 °C in a dry ice/acetone bath was treated dropwise with Ar″Li (2.50 g, 5.24 mmol) in toluene (60 mL) over a period of 1 h. The solution was then warmed to room temperature and stirred for 12 h, after which the slurry was allowed to settle and the mother liquor was separated from the precipitate (LiI and some Ga metal). The solvent was removed under dynamic vacuum, and pale brown $(Ar''GaI)_2$ was recovered. $(Ar''GaI)_2$ in THF (70 mL) was added to a Schlenk tube containing finely cut sodium (120 mg, 5.24 mmol) at ambient temperature. After stirring for 2 days, the solution was filtered, and the solvent was removed under dynamic vacuum. The residue was extracted with hexane (50 mL), and the slurry was allowed to settle. The supernatant solution was separated from the precipitate (NaI), and its volume was concentrated to ca. 10 mL. Storage for 2 days in a freezer (ca. −18 °C) afforded dichroic red/green solid **5**. Yield: 1.38 g, 44 %; m.p. 192–194 °C. ^{1}H NMR (600 MHz, C_6D_6, 25 °C): $\delta = 0.25$ (s, 18 H, $Si(CH_3)_3$), 1.08 (d, 48 H, $o\text{-CH}(CH_3)_2$, $^3J_{HH} = 7.2$ Hz), 2.98 (sept, 8 H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 7.2$ Hz), 7.07 (d, 8 H, $m\text{-}C_6H_3\text{-}i\text{Pr}_2$, $^3J_{HH} = 6.8$ Hz), 7.21 (t, 4 H, $p\text{-}C_6H_3\text{-}i\text{Pr}_2$, $^3J_{HH} = 6.8$ Hz), 7.33 ppm (s, 4 H, $m\text{-}C_6H_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz, 25 °C): $\delta = -0.75$ ($(CH_3)_3Si$), 25.1 ($o\text{-CH}(CH_3)_2$), 25.6 ($o\text{-CH}(CH_3)_2$), 31.2 ($o\text{-}CH(CH_3)_2$), 123.8, 129.2, 133.0, 139.5, 144.1, 147.3, 147.7, and 205.5 ppm (Ar*C*); $^{29}Si\{^1H\}$ NMR (C_6D_6, 119.2 MHz, 25 °C): $\delta = -4.72$ ppm.

$\{Ar''Ga(\mu\text{-}NH_2)H\}_2$ (**5**) and $\{Ar'Ga(\mu\text{-}NH_2)H\}_2$ (**6**): Several drops of liquid ammonia were added to a deep green solution of **4** (0.15 g, 0.14 mmol) in toluene (30 mL) at −78°. The color of the solution changed to light yellow upon warming to room temperature. Storage of this solution at −18 °C afforded X-ray quality colorless crystals of **5**. Yield: 0.11 g, 73 %; m.p. 293 °C. ^{1}H NMR (600 MHz, C_7D_8, 25 °C): $\delta = -0.55$ (s, 4 H, NH_2), 0.27 (s, 18 H, $Si(CH_3)_3$), 1.05 (d, 24 H, $o\text{-CH}(CH_3)_2$, $^3J_{HH} = 7.2$ Hz), 1.16 (d, 24 H, $o\text{-CH}(CH_3)_2$, $^3J_{HH} = 7.2$ Hz), 2.82 (sept, 8 H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 7.2$ Hz), 4.52 (s, 2 H, GaH), 7.06 (d, 8 H, $m\text{-}C_6H_3\text{-}i\text{Pr}_2$, $^3J_{HH} = 7.8$ Hz), 7.24 (t, 4 H, $p\text{-}C_6H_3\text{-}i\text{Pr}_2$, $^3J_{HH} = 7.8$ Hz), 7.35 ppm (s, 4 H, $m\text{-}C_6H_2$); $^{13}C\{^1H\}$ NMR (C_7D_8, 150.9 MHz, 25 °C): $\delta = 0.80$ ($(CH_3)_3Si$), 23.3 ($o\text{-CH}(CH_3)_2$), 26.2 ($o\text{-CH}(CH_3)_2$), 31.1 ($o\text{-}CH(CH_3)_2$), 123.3, 129.1, 133.2, 138.2, 142.6, 147.1, 147.2, and 148.4 ppm (Ar*C*); $^{29}Si\{^1H\}$ NMR (C_7D_8, 119.2 MHz, 25 °C): $\delta = -4.59$; IR (Nujol): $\tilde{\nu} = 3365, 3310$ (ν_{NH_2}, weak), 1864 cm^{-1} (ν_{Ga-H}, medium). **6** was prepared in a similar way to that described for **5**, but using **3** rather than **4**. ^{1}H NMR (600 MHz, C_7D_8, 25 °C): $\delta = -0.62$ (s, 4 H, NH_2), 1.03 (d, 24 H, $o\text{-CH}(CH_3)_2$, $^3J_{HH} = 7.2$ Hz), 1.15 (d, 24 H, $o\text{-CH}(CH_3)_2$, $^3J_{HH} = 7.2$ Hz), 2.81 (sept, 8 H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 7.2$ Hz), 4.47 (s, 2 H, GaH), 7.04 (d, 8 H, $m\text{-}C_6H_3\text{-}i\text{Pr}_2$, $^3J_{HH} = 7.8$ Hz), 7.06 (d, 4 H, $m\text{-}C_6H_3$, $^3J_{HH} = 7.2$ Hz), 7.19–7.25 ppm (m, 6 H, $p\text{-}C_6H_3\text{-}i\text{Pr}_2$ and $p\text{-}C_6H_3$); $^{13}C\{^1H\}$ NMR (C_7D_8, 150.9 MHz, 25 °C): $\delta = 23.5$ ($o\text{-CH}(CH_3)_2$), 26.3 ($o\text{-CH}(CH_3)_2$), 31.0 ($o\text{-}CH(CH_3)_2$), 123.3, 127.2, 128.8, 129.4, 142.3, 147.2, 147.9, and 220.2 ppm (Ar*C*).

Received: December 8, 2008
Published online: January 29, 2009

Keywords: gallium · Group 13 elements · insertion · low-valent species

---

[1] A. J. Downs, H.-J. Himmel, L. Manceron, *Polyhedron* **2002**, *21*, 473.

[2] H.-J. Himmel, A. J. Downs, T. M. Greene, *Chem. Rev.* **2002**, *102*, 4191.

[3] H.-J. Himmel, L. Manceron, A. J. Downs, P. Pullumbi, *J. Am. Chem. Soc.* **2002**, *124*, 4448.

[4] H.-J. Himmel, A. J. Downs, T. M. Greene, *J. Am. Chem. Soc.* **2000**, *122*, 9793.

[5] G. V. Chertihin, L. Andrews, *J. Phys. Chem.* **1993**, *97*, 10295.

[6] F. A. Kurth, R. A. Eberlein, H. Schnöckel, A. J. Downs, C. R. Pulham, *J. Chem. Soc. Chem. Commun.* **1993**, 1302.

[7] P. Pullumbi, Y. Bouteiller, L. Manceron, C. Mijoule, *Chem. Phys.* **1994**, *185*, 25.

[8] X.-F. Wang, L. Andrews, *J. Phys. Chem. A* **2003**, *107*, 11371.

[9] a) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124; b) G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880; c) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 8196; *Angew. Chem. Int. Ed.* **2007**, *46*, 8050.

[10] G. H. Spikes, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 12232 – 12233.

[11] Y. Peng, M. Brynda, B. D. Ellis, J. C. Fettinger, E. Rivard, P. P. Power, *Chem. Commun.* **2008**, 6042 – 6044.

[12] G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2007**, *316*, 439.

[13] Y. Peng, B. D. Ellis, X. Wang, P. P. Power, *J. Am. Chem. Soc.* **2008**, *130*, 12268.

[14] N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 2667.

[15] R. J. Wright, M. Brynda, J. C. Fettinger, A. R. Betzer, P. P. Power, *J. Am. Chem. Soc.* **2006**, *128*, 12498.

[16] A. Haaland, K.-G. Martinsen, H. V. Volden, W. Kaim, E. Waldhör, W. Uhl, U. Schütz, *Organometallics* **1996**, *15*, 1146.

[17] R. J. Wright, M. Brynda, P. P. Power, *Inorg. Chem.* **2005**, *44*, 3368.

[18] a) J. Moc, *Chem. Phys. Lett.* **2004**, *395*, 38; b) J. Moc, *Chem. Phys.* **2005**, *313*, 93.

[19] Crystallographic data for **1** and **5**: Recorded at 90 K with $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å): **1**: triclinic, space group $P\bar{1}$, $a = 9.2539(5)$, $b = 12.6999(7)$, $c = 13.0183(8)$ Å, $\alpha = 63.3940(8)$, $\beta = 96.178(3)$, $\gamma = 69.0339(8)°$, $Z = 1$, $R1 = 0.0244$ for 5468 ($I > 2\sigma(I)$) data, $wR2$ (all data) $= 0.0612$; **5**: monoclinic, space group $P2_1/n$, $a = 13.388(3)$, $b = 15.214(3)$, $c = 15.665(3)$ Å, $\beta = 96.178(3)°$, $Z = 2$, $R1 = 0.0366$ for 5996 ($I > 2\sigma(I)$) data, $wR2$ (all data) $= 0.0929$. CCDC 710888 (**1**) and 710887 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

[20] S. Singh, H.-J. Ahn, A. Stasch, V. Jancik, H. W. Roesky, A. Pal, M. Biadene, R. Herbst-Irmer, M. Noltemeyer, H.-G. Schmidt, *Inorg. Chem.* **2006**, *45*, 1853.

[21] R. J. Wehmschulte, J. J. Ellison, K. Ruhlandt-Senge, P. P. Power, *Inorg. Chem.* **1994**, *33*, 6300.

[22] R. J. Wehmschulte, J. M. Steele, M. A. Khan, *Organometallics* **2003**, *22*, 4678.

[23] a) *Comprehensive Organometallic Chemistry*, *Vols. 1 and 2* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**; *Comprehensive Organometallic Chemistry II*, *Vols. 1 and 2* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**; b) A. J. Downs, *Coord. Chem. Rev.* **1999**, *189*, 59; c) S. Aldridge, A. J. Downs, *Chem. Rev.* **2001**, *101*, 3305, and references therein.

[24] C. Jones, G. A. Koutsantonis, C. L. Raston, *Polyhedron* **1993**, *12*, 1829.

[25] a) O. T. Beachley, Jr., J. C. Pazik, M. J. Noble, *Organometallics* **1998**, *17*, 2121; b) J.-W. Hwang, S. A. Hanson, D. Britton, J. F. Evans, K. F. Jensen, W. L. Gladfelter, *Chem. Mater.* **1990**, *2*, 342; c) M. J. Almond, M. G. B. Drew, C. E. Jenkins, D. A. J. Rice, *Chem. Soc. Dalton Trans.* **1992**, 5; d) H. S. Park, S. D. Waezsada, A. H. Cowley, H. W. Roesky, *Chem. Mater.* **1998**, *10*, 2251; e) D. A. Atwood, A. H. Cowley, P. R. Harris, R. A. Jones, S. U. Koschmieder, C. M. Nunn, J. L. Atwood, S. G. Bott, *Organometallics* **1993**, *12*, 24; f) V. Jancik, L. W. Pineda, A. C. Stückl, H. W. Roesky, R. Herbst-Irmer, *Organometallics* **2005**, *24*, 1511.

[26] a) A. L. Casalnuovo, J. C. Calabrese, D. Milstein, *Inorg. Chem.* **1987**, *26*, 971; b) J. Zhao, A. S. Goldman, J. S. Hartwig, *Science* **2005**, *307*, 1080.