Reactions of Gallium Hydrides with 1,4-Di-t-butyl-1,4-diazabutadiene: Subvalent and Hydrometallation Products

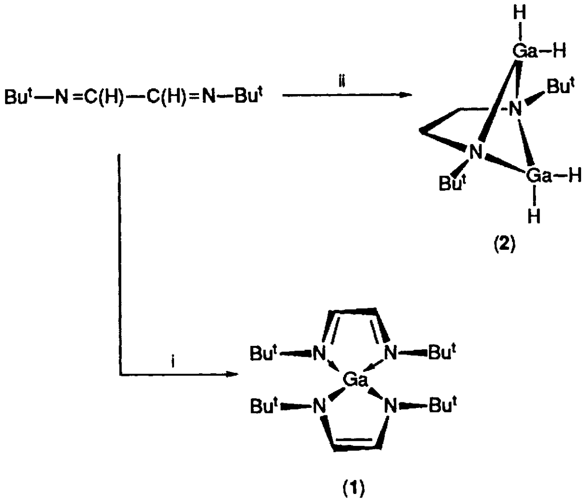
Mark J. Henderson,[a] Colin H. L. Kennard,[b] Colin L. Raston,*[a] and Graham Smith[c]

[a] *Division of Science and Technology, Griffith University, Nathan, Brisbane, 4111, Australia*
[b] *Department of Chemistry, University of Queensland, St. Lucia, Brisbane, Qld. 4067*
[c] *Department of Chemistry, Queensland University of Technology, P.O. Box 2434, Brisbane, Qld. 4001*

Reaction of $LiGaH_4$ and gallium metal with 1,4-di-t-butyl-1,4-diazabutadiene (dbdab) in diethyl ether at room temperature yields the monomeric, formally gallium(II) species [Ga(dbdab)$_2$], (**1**), previously prepared using metal vapours, and $GaH_3{\cdot}NMe_3$ with dbdab in hexane at −80 °C yields the novel hydrogallation product [{H_2Ga}$_2${μ-N(Bu^t)CH_2}$_2$], (**2**) which has magnetically distinct geminal hydrides ($^2J_{HH}$ 44 Hz) in agreement with the crystal structure (<Ga–N>2.01$_3$ Å, <Ga–H> 1.5$_6$ Å) and IR data (νGa–H 1920, 1870 cm^{-1}).

Gallium hydrides tend to be thermally unstable decomposing to gallium metal and hydrogen close to room temperature.[1] Such decompositions have exciting potential in delivering highly activated gallium metal in reactions with organic compounds, albeit in highly reducing hydrogen-containing environments and with the possibility of competing hydride attack at unsaturated moieties (hydrometallation). Herein, we show that (i) lithium gallium hydride, $LiGaH_4$,[2] in the presence of a catalytic amount of gallium indeed acts as a source of activated metal in the presence of 1,4-di-t-butyl-1,4-diazabutadiene (dbdab) yielding the formally subvalent gallium(II) compound [Ga(dbdab)$_2$], (**1**); and (ii) the trimethylamine adduct of gallane, $GaH_3{\cdot}NMe_3$,[2] yields a novel hydrometallation product, [{H_2Ga}$_2${μ-N(Bu^t)CH_2}$_2$], (**2**). It is noteworthy that there has been recent interest in the synthesis of gallane,[3] and that diazabutadienes are useful ligands in stabilizing low-valent homoleptic compounds, for example, of transition[4,5] and lanthanoid elements,[5] and main group elements.[6]

Details of the synthesis of compounds (**1**) and (**2**) are summarized in Scheme 1.† The yield of compound (**1**) is modest but better than that obtained using metal vapours (34% *versus* 20%). In the absence of $LiGaH_4$ only traces of compound (**1**) are formed after several days whereas, in the absence of gallium metal, intractable brown oils are obtained. A likely mechanism is that the gallium metal catalyses decomposition of $LiGaH_4$ to activated gallium which then undergoes electron transfer with dbdab; the alternative of complexation of dbdab to GaH_4^- as the primary process would tend to favour hydrometallation. For the reaction of $GaH_3{\cdot}NMe_3$ with dbdab, Lewis base *N*-centred ligand displacement is likely to take place prior to hydrometallation, as in many reactions of metal hydrides with unsaturated substrates.[7] Interestingly, the diazabutadiene condenses with two equivalents of the gallane adduct even with an excess of dbdab, possibly because replacing one hydride with an amido centre reduces the nucleophilic character of the remaining hydrides. A hexane solution of $GaH_3{\cdot}NMe_3$ and dbdab in the



Scheme 1: i, $LiGaH_4$, Ga, OEt_2, $-H_2$, LiH; ii, $GaH_3{\cdot}NMe_3$, Hexane, −80 °C, $-NMe_3$.

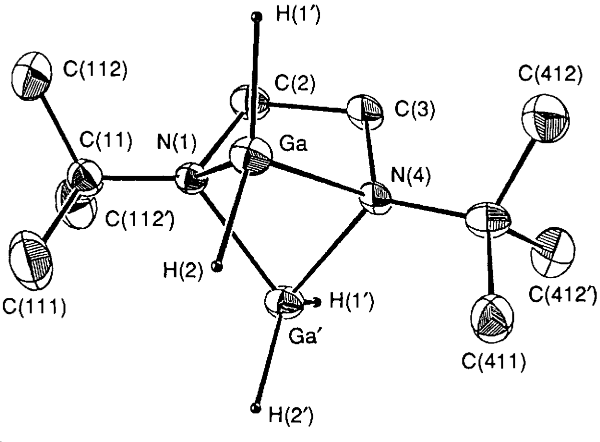


Figure 1. Molecular projection of [{H_2Ga}$_2${μ-N(Bu^t)CH_2}$_2$] (**2**), with 20% thermal ellipsoids for non-hydrogen atoms and arbitrary radii hydrogen atoms shown. Selected bond distances (Å) and angles (°): Ga–N(1) 2.022(9), Ga–N(4) 1.999(8), Ga···Ga 2.823(2), Ga–H(1) 1.57(8), Ga–H(2) 1.54(12), N(1)–C(2) 1.48(2), N(4)–C(3) 1.50(2), C(2)–C(3) 1.58(2), N(1)–C(11) 1.47(2), N(4)–C(41) 1.53(2), N(1)–Ga–N(4) 74.4(7), Ga–N(1)–Ga′ 88.6(5), Ga–N(4)–Ga′ 89.8(5), N(1)–Ga–H(1) 109(3), N(1)–Ga–H(2) 105(5), N(4)–Ga–H(1) 108(3), N(4)–Ga–H(2) 106(5), H(1)–Ga–H(2) 137(3), Ga–N(1)–C(2) 99.9(7), Ga–N(1)–C(11) 123.6(6), Ga–N(4)–C(3) 101.7(7), Ga–N(4)–C(41) 123.7(5).

---

† *Synthesis and characterization:* (**1**): A solution of $LiGaH_4$ (3.46 mmol from 0.61 g $GaCl_3$)[2] in OEt_2 (60 ml) was added over 10 min to a stirred mixture of 1,4-di-t-butyl-1,4-diazabutadiene (1.65 g, 9.48 mmol) and one drop of gallium metal in OEt_2 (10 ml) at room temperature. After 2 h, solvent and excess diazabutadiene were removed *in vacuo* yielding a brown solid which was taken up in toluene. The resulting solution was filtered and cooled to −30 °C affording a green precipitate of (**1**) (0.45 g, 34%).[6]

(**2**): To a stirred slurry of $GaH_3{\cdot}NMe_3$ (0.72 g, 5.47 mmol)[2] in hexane (30 ml) at −80 °C was added sublimed 1,4-di-t-butyl-1,4-diazabutadiene (0.46 g, 2.73 mmol) in hexane (10 ml) over 10 min. After one day at room temperature the hexane was removed *in vacuo* yielding a white powder of (**2**) (0.78 g, 91% yield). m.p. 107 °C (decomp.); ^{1}H NMR (250 MHz, C_6D_6), δ (rel. $SiMe_4$) 1.05 (18 H, s, CMe_3) 4.92, 5.28 (2 × 2 H, d, GaH, $^2J_{HH}$ 44 Hz) 2.90 (4 H, s, CH_2); ^{13}C NMR, δ 28.9 (s, CMe_3) 44.0 (s, CH_2) 53.4 (s, CMe); IR: $\nu_{Ga\text{-}H}$ 1920, 1870 cm^{-1}.

presence of gallium metal also yields (**2**), but it then slowly decomposes over several hours, depositing finely divided gallium. Compound (**2**) has remarkable thermal stability for a gallium hydride, being sublimable *in vacuo* at 95 °C, decomposing to gallium metal at 107 °C. The hydride centres constitute an AB spin system, $^2J_{HH}$ 44 Hz, in agreement with the solid state structure (*X*-ray crystallography and IR spectroscopy), with the coupling through quadrupole gallium (^{69}Ga, 60%, ^{71}Ga, 40% $I = 3/2$) resulting in broad lines.

Results of the *X*-ray structure determination of (**2**)‡ are presented in Figure 1. Molecules lie on mirror planes with the nitrogen and adjacent carbon atoms restricted to the planes. Despite this, the overall symmetry is C_{2v} to within 3σ of bond distances and angles. Each amido centre spans two metal centres forming a butterfly-shaped four-membered Ga_2N_2 ring system, the dihedral angle between each GaN_2 section being 123.7°. In the related compound, $[\{H_2GaN(CH_3)_2\}_2]$, the *N*-centres also bridge forming a planar Ga_2N_2 ring (gas phase),[8] and in trimeric $[\{H_2GaN(CH_2)_2\}_3]$ such bridging is part of a six-membered Ga_3N_3 ring in a chair conformation.[9] The Ga–N distances in (**2**), 2.01$_3$ Å (mean), are within the established range for bridging amides, *viz*. 2.027(4) Å, $[\{H_2GaN(CH_3)_2\}_2]$,[8] 1.97 Å $[\{H_2GaN(CH_2)_2\}]$,[9] and 2.00 Å (mean), $[\{Br_2Ga(\mu\text{-}NHSiMe_3)\}_2]$,[10] which also has a planar four-membered ring system. The N–Ga–N angles, 74.4(7), 90.6(8), 100, and 90.4(7)° respectively, reflect the difference in association and planar *versus* butterfly-shaped Ga_2N_2 cores. Diffraction data were of sufficient accuracy to allow the location of the hydrido atoms and refine them positionally and with isotropic thermal parameters. One pair is directed parallel to the symmetry axis, the others almost at right angles to it, with both Ga–H distances comparable with those in $[\{H_2GaN(CH_3)_2\}_2]$,[8] and the terminal Ga–H bond in $[Ga(BH_4)_2H]$.[11]

We thank the Australian Research Council for support of this work, and Griffith University and the University of Queensland for equipment.

Received, 10th April 1990; Com. 0/01621G

---

‡ *Crystal data* for (**2**): (T = 296 K; Enraf-Nonius CAD4 diffractometer, crystal mounted in a capillary): $C_{10}H_{26}Ga_2N_2$, M = 313.8, orthorhombic, space group *Pnma*, a = 12.819(3), b = 10.634(2), c = 10.864(4) Å, U = 1481.0(7) Å^3, $F(000)$ = 648; Z = 4, D_c = 1.41 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 38.0 cm^{-1}, specimen 0.38 × 0.25 × 0.26 mm, 1530 unique reflections, 1380 with $I > 2.5\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°; R = 0.054, R' = 0.058, s = 0.80. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

References

1 'Chemistry of the Elements,' N. N. Greenwood and A. Earnshaw, Pergamon Press, 1984, p. 257.

2 D. F. Shriver and A. E. Shirk, *Inorg. Synth.*, 1977, **17**, 42, 45.

3 A. J. Downs, M. J. Goode, and C. R. Pulham, *J. Am. Chem. Soc.*, 1989, **111**, 1936.

4 V. Rosenberger and H. tom Dieck, *Chem. Ber.*, 1920, **123**, 83, and references therein.

5 F. G. N. Cloke, H. C. de Lemos, and A. A. Sameh, *J. Chem. Soc., Chem. Commun.*, 1986, 1344.

6 F. G. N. Cloke, G. R. Hanson, M. J. Henderson, P. B. Hitchcock, and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1989, 1002.

7 E. Kaufmann, P. v. R. Schleyer, K. N. Houk, and Y-D. Wu, *J. Am. Chem. Soc.*, 1985, **107**, 5560.

8 P. L. Baxter, A. J. Downs, D. W. H. Rankin, and H. E. Robertson, *J. Chem. Soc., Dalton Trans.*, 1985, 807.

9 W. Harrison, A. Storr, and J. Trotter, *Chem. Commun.*, 1971, 1101; M. F. Lappert, P. P. Power, A. R. Sanger, and R. C. Srivastava, 'Metal and Metalloid Amides,' Ellis Horwood, 1980, p. 114.

10 D. J. Hodgson, B. J. Schwatz, and T. N. Sorrell, *Inorg. Chem.*, 1989, **28**, 2228.

11 M. T. Barlow, C. J. Dain, A. J. Downs, G. S. Laurenson, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1982, 597.